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University of Southampton

Faculty of Natural & Environmental Sciences

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**Oxidative Cyclisation of 1,5-dienes by Metal Oxo Agents: Synthetic and
Computational Investigations**

by

AQEEL ALAA HUSSEIN

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Abstract

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Oxidative Cyclisation of 1,5-dienes by Metal Oxo Agents: Synthetic and Computational Investigations

by

Aqeel Alaa Hussein

2,5-dihydroxyalkyl substituted tetrahydrofurans (THF-diols) are present in many natural and synthetic products. An efficient approach to THF-diols involves oxidative cyclisation of 1,5-dienes mediated by permanganate ion. The permanganate-promoted oxidative cyclisation of 2-methylenehex-5-enoic acid bearing different aromatic esters was investigated with chiral phase transfer catalyst (**CPTC**), realising excellent ee's and yields for the first time as a direct approach. No asymmetric induction was obtained in the absence of aromatic ester group in substrates. Two functional groups, α -naphthyl and 2,3-dichlorophenyl, displayed ee's in the range of 90%-97%, indicating that the high ee's can be achieved through a combination of steric and electronic effects where the optimised aryl ester group may achieve a π -stacking interaction with the CPTC. Moderate ee's were achieved for the majority of aromatic ester substitutions with electron-withdrawing or electron-donating groups, with the exception of the 2,3-dichlorophenyl ester. Enantioinduction was decreased when the electron-rich alkene was substituted with a *trans*-phenyl group. The **CPTC** oxidative cyclisation of a 1,5,9-trienoate containing the α -naphthyl group showed a moderate ee and yield.

The reaction mechanism of THF-diol formation from permanganate-mediated and osmium-promoted oxidative cyclisation of 1,5-dienes was studied using high-level DFT simulations ((SMD)-M062X/aug-cc-pVDZ/ECP), showing good agreement with experimental observations, and led to an understanding the key role of acid in promoting the cyclisation step. Ligand exchange with sigma donors such as water and NMO was shown for the FRS intermediate Os(VI) and Mn(V) glycolates. Cyclisation of the protonated Os(VI) dioxoglycolate and Mn(V) glycolate was found to be kinetically and thermodynamically favoured in comparison to other pathways such as reoxidation (Os(VI)→Os(VIII) or Mn(V)→Mn(VI)). Although reoxidation of Mn(V)→Mn(VI) was calculated to be disfavoured, decomposition to carbonyl compounds and Mn(IV) was found to be the favoured pathway rather than cyclisation if reoxidation takes place. However, in the absence of acid,

reoxidation of Os(VI)→Os(VIII) was found to be favoured and stimulated a second cycle pathway over cyclisation, as observed experimentally.

Additional insight into the contributory factors was provided by FMO and distortion/interaction energy analysis, in which increasing electrophilicity of the protonated intermediates Os(VI) and Mn(V) glycolates leads to favorable TS interaction energy and attenuated distortion of the tetrahedral Os(VI) and Mn(V) glycolates to deliver the favoured TS's. An asynchronous (3+2) addition of the O—M—O species, M = Os or Mn, across the alkene double bond with faster development of the C—O[M] bonds compared to C—O[THF] bonds, was obtained by molecular dynamics simulations performed on the SRS. Releasing THF-diol from Mn(III) THF-diolate was found to be accessed via acidic disproportionation, whereas for the Os-catalysed reaction, reoxidation of Os(IV) THF-diolate was required to release THF-diol and an Os(VIII) species to complete the catalytic cycle.

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Research Thesis: Declaration of Authorship

Print name: Aqeel Alaa Hussein

Title of thesis: **Oxidative Cyclisation of 1,5-dienes by Metal Oxo Agents: Synthetic and Computational Investigations**

I declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

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Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
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Definitions and Abbreviations

δ	Chemical shift
AD	Asymmetric dihydroxylation
ADMP	Atom-centered density matrix propagation
aq.	Aqueous
Ar	Aromatic
APT	Atomic polar tensor
ANO	Amine <i>N</i> -oxides
aug-cc-pVDZ	Augmented correlation-consistent polarized valence double zeta
Å	Angstrom
br	Broad
CSA	10-Camphorsulfonic acid
CPTC	Chiral phase transfer catalyst
CASSCF	Complete-active space self-consistent field
CAS	Complete-active space
CFT	Crystal field theory
calc	Calculated
cat.	Catalytic
°C	Celsius
d	Doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	Dicyclohexylcarbodiimide
DHQ	Dihydroquinine

DHQD	Dihydroquinidine
DFT	Density functional theory
DMAP	4-(Dimethylamino)-pyridine
DMF	Dimethylformamide
DME	Dimethoxyethane
DIEA	N, N-diisopropylethylamine
dr	Diastereoisomeric ratio
DZ	Double zeta
dis	Distortion
ee	Enantiomeric excess
E	Energy (total electronic energy)
ECP	Effective core potential
exp	Experimental
equiv	Equivalent(s)
Et	Ethyl
Et ₂ O	Diethyl ether
EtOAc	Ethyl acetate
EDG	Electron donating group
EWG	Electron withdrawing group
e	Electron unit
eV	Electron volt
<i>F</i>	Faraday
FRS	First reaction step
FMO	Frontier molecular orbital
fs	Femtosecond

Definitions and Abbreviations

G	Free energy
H	Enthalpy
h	Hour(s)
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
HOMO	Highest occupied molecular orbital
IR	Infrared
IRC	Intrinsic reaction coordinate
int	Interaction
<i>i</i> Pr	Isopropyl
<i>J</i>	Coupling constant
K	Kelven
kcal	Kilocalorie
LUMO	Lowest unoccupied molecular orbital
m	Multiplet
MD	Molecular dynamics
Me	Methyl
min	Minute(s)
mmol	Millimole(s)
mol	Mole
MS	Mass spectrometry
MEP	Minimum energy path
Mp	Melting point
NaHMDS	Sodium hexamethyldisilazide
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide

NMR	Nuclear magnetic resonance
NOESY	Nuclear overhauser effect spectroscopy
<i>n</i> -Bu	<i>n</i> -Butyl
ox	Oxidation
<i>n</i> -BuLi	<i>n</i> -Butyllithium
PE	Petroleum ether
Ph	Phenyl
PHAL	Phthalazine
PES	Potential energy surface
ppm	Parts per million
PTC	Phase transfer catalyst
PCM	Polarizable continuum model
PNO	Pyridine-N-oxide
quant.	Quantitative
q	Quartet for NMR or quintet spin multiplicity
qr	Quartet for spin multiplicity
RDS	Rate determining step
rt	Room temperature
red	Reduction
<i>S</i>	Spin quantum number
SRS	Second reaction step
s	Singlet
SiO ₂	Silica gel
SMD	Solvation model based on density
SCF	Self-consistent field

Definitions and Abbreviations

SOA	Secondary oxidising agent
t	Triplet for NMR and spin multiplicity
<i>t</i>	Tertiary
TBAB	Tetra-N-Butylammonium bromide
TPAP	Tetrapropylammonium perruthenate
TBME	<i>t</i> -Butyl methyl ether
TEA	Tetraethyl ammonium
TMA	Tetramethyl ammonium
<i>t</i> -BuOK	Potassium <i>tert</i> -butoxide
TS	Transition state
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMEDA	<i>N,N,N', N'</i> -Tetramethylethylenediamine
TMSCl	Trimethylsilyl chloride
TMO	Trimethylamine <i>N</i> -oxide
LDA	Lithium diisopropylamide
V	Volt
VDZ	Valence double zeta
$\Delta G^\ddagger$	Free energy of activation
ΔG	Free energy of reaction
ΔH	Enthalpy of reaction
λ	Reorganisation energy

Chapter 1 Oxidative cyclisation of 1,5-dienes

This chapter summarises the synthesis of THF-diols from permanganate-mediated and osmium-promoted oxidative cyclisation of 1,5-dienes, and provides selected recent literature examples. Experimental and theoretical mechanistic studies on oxidative cyclisation and relationship to dihydroxylation will be discussed.

1.1 General introduction

2,5-disubstituted tetrahydrofuran diols (THF-diols) are important structural units present in many bioactive natural and synthetic products, including polyether ionophore antibiotics and *Annonaceous* acetogenins.^{1–9} *Annonaceous* Acetogenins have been used in treating cancer but this potential is tempered with concerns of their neurotoxicity. Uvaricin (**1.1**), Panatellin (**1.2**), Goniocin (**1.3**), and Mucocin (**1.4**) are examples of *Annonaceous* acetogenins (**Figure 1.1**). Acetogenins have been shown to exhibit a variety of biological activities including: insecticidal,^{10,11} pesticidal,^{12–14} antifeedant,¹⁵ antiparasitic and antimicrobial.¹⁶ Most importantly, many acetogenins exhibit highly selective cytotoxicity against tumour cell lines.^{17–21}

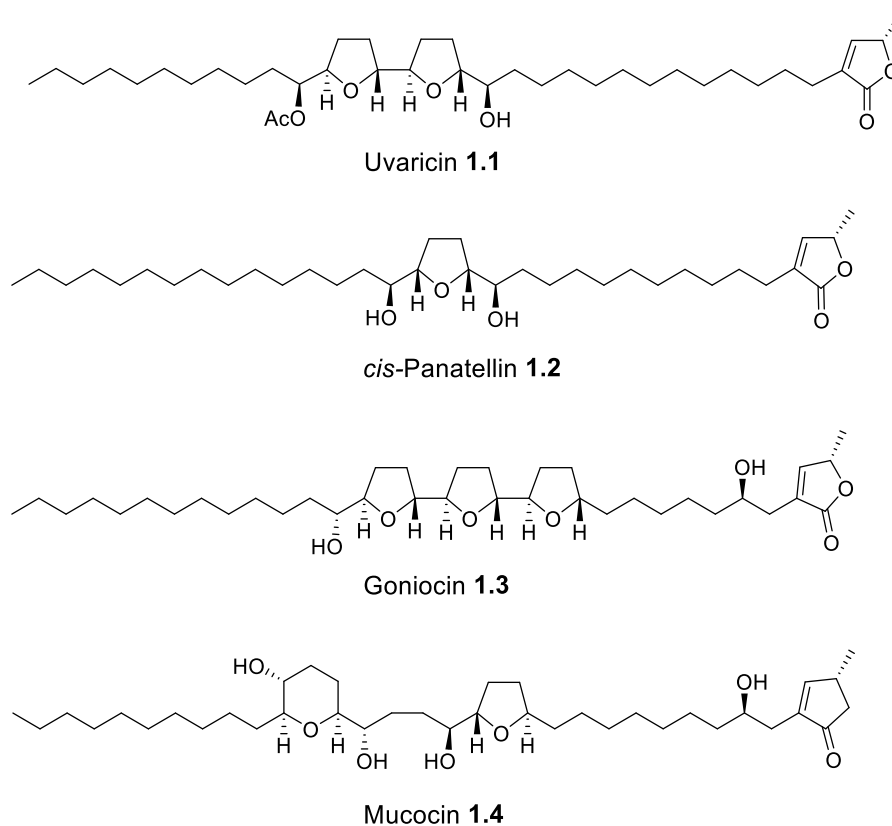


Figure 1.1: Examples of *Annonaceous* acetogenins

Polyether ionophores are ion carriers.²² They reversibly bind ions, which they transport across a cell membrane. Examples of ionophore are Ionomycin (**1.5**), Monensin (**1.6**), and Nonactin (**1.7**) (**Figure 1.2**). In the absence of a protein pore, they are able to disrupt the membrane potential by conducting ions via lipid membrane, and thus they could exhibit cytotoxic properties. They exhibit high affinities for ions such as Li^+ , Na^+ , K^+ , Rb^+ , Ag^+ , and Ti^+ .^{23–25}

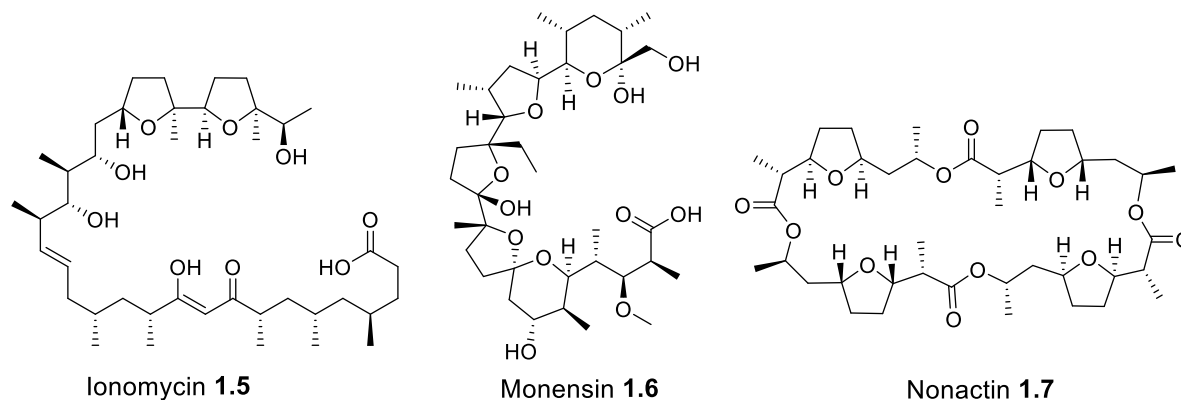
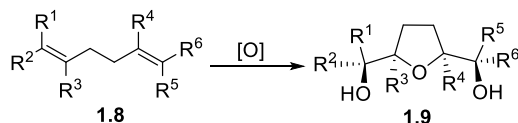


Figure 1.2: Examples of polyether ionophores.

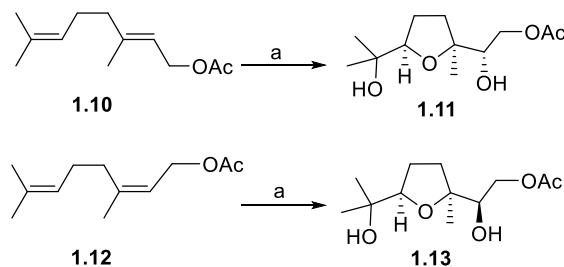
One of the most important ways to synthesise THF rings is by oxidative cyclisation of 1,5-dienes mediated by transition-metal-oxo species such as MnO_4^- , OsO_4 , and RuO_4 (**Scheme 1.1**).^{4,26–38} This reaction is particularly powerful because it involves the stereospecific suprafacial addition of two oxygen atoms across each of the two alkenes, combined with the stereoselective formation of a 2,5-disubstituted tetrahydrofuran ring, leading to control of relative stereochemistry of up to four stereogenic centres in the product.



Scheme 1.1: Diastereoselective oxidative cyclisation of 1,5-dienes **1.8** by metal oxo species to afford *cis*-THF-diols **1.9**. **Reagents:** $[\text{O}] = \text{MnO}_4^-$, OsO_4 , or RuO_4 .

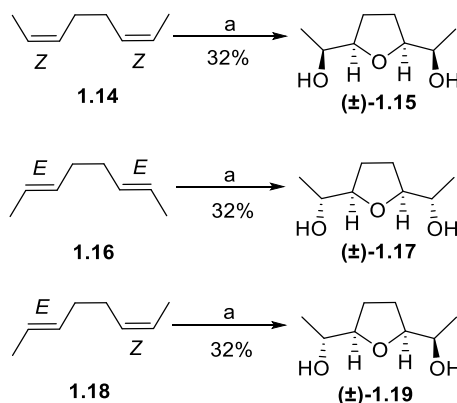
1.1.1 Permanganate-mediated oxidative oxidative cyclisation

In 1924, Kötze and Steche attempted to oxidise geranyl acetate (**1.10**) and neryl acetate (**1.12**) using potassium permanganate under slightly acidic conditions. They could not identify the product formed from this reaction but they described it as “oxidodioxygeraniolmonoacetate”.³⁹ The product was later identified as a 2,5-disubstituted THF-diol **1.11** by Klein and Rojahn (**Scheme 1.2**).⁴⁰



Scheme 1.2: Permanganate-promoted oxidative cyclisation of 1,5-dienes **1.10** and **1.12**. **Reagents & conditions:** (a) KMnO_4 , acetone/ H_2O (5:1), CO_2 bubbling, pH 7.5, $0\text{ }^\circ\text{C}$, 30 min.

Later, Walba *et al.*⁴¹ studied the permanganate-mediated oxidative cyclisation of several 1,5-dienes **1.14**, **1.16** and **1.18**. In their work, weakly acidic conditions (pH 6.3) were used due to the formation of carbonic acid from bubbling a CO_2 gas in water (**Scheme 1.3**). By using gas chromatography analysis, they found that the THF-diol products **1.15**, **1.17** and **1.19** were obtained in at least 97% stereoselectivity with 32% yield. They also highlighted the stereospecificity of the reaction (the diene geometry influences diastereoselectivity).



Scheme 1.3: Permanganate-mediated oxidative cyclisation of 1,5-dienes **1.14**, **1.16** and **1.18**. **Reagents & conditions:** (a) KMnO_4 , acetone/water (5:1), pH 7.5, CO_2 bubbling, $-20\text{ }^\circ\text{C}$, 30 min.

Walba *et al.* suggested a reaction mechanism based on Sharpless' proposal for the oxidation mechanism of olefins by different oxo transition metal species.⁴² They proposed that after the initial formation of a π -complex **1.21** between diene **1.20** and MnO_4^- , an octahedral Mn(VII) intermediate **1.22** is produced *via* two [2+2] cycloaddition reactions (**Figure 1.3**). Then, alkyl migration from Mn to one of the oxygen atoms with retention of stereochemistry affords **1.23** after reductive elimination. The resulting Mn(III) diolate **1.24** then undergoes oxidation and hydrolysis to yield the *cis*-THF **1.25** and MnO_2 as a by-product.

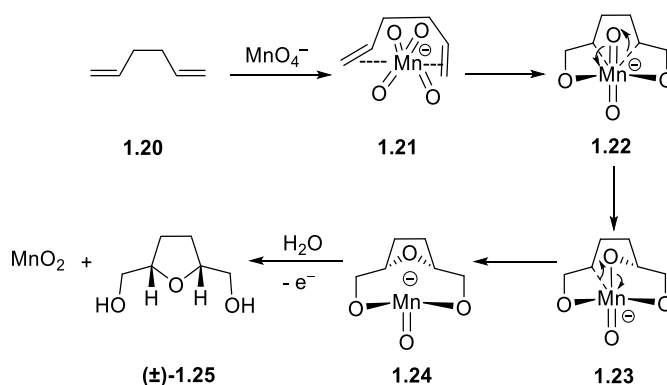
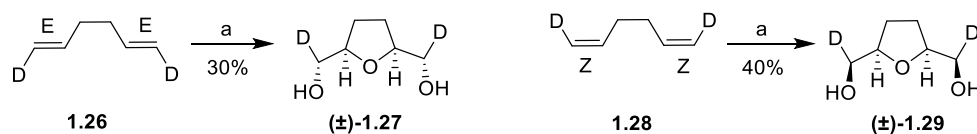


Figure 1.3: Walba's proposed mechanism for the permanganate-mediated oxidative cyclisation of 1,5-diene **1.20**.

In 1979, Baldwin *et al.*⁴³ explored the permanganate ion oxidative cyclisation of labelled 1,5-dienes **1.26** and **1.28** (Scheme 1.4). They also reported comparable yields to those obtained by Walba. Thus, the THF-diols **1.27** and **1.29** were isolated with 30% and 40% yields from *E,E*-diene **1.26** and *Z,Z*-diene **1.28** respectively. The stereochemistry was proved by NMR studies.



Scheme 1.4: Permanganate ion oxidative cyclisation of labelled 1,5-dienes **1.26** and **1.28**. **Reagents & conditions:** (a) KMnO_4 , acetone/water (5:1), CO_2 bubbling, 0°C , 30 min.

Although reaction mechanisms for THF-diol formation have been proposed by both Walba⁴¹ and Baldwin,⁴³ the mechanism proposed by Baldwin has become more widely accepted (Figure 1.4). Baldwin's proposed mechanism involves initial (3+2) cycloaddition of MnO_4^- to one of the diene double bonds yielding the intermediate Mn(V) glycolate **1.31**, which is then oxidised into Mn(VI) glycolate **1.32** by another MnO_4^- before undergoing a second (3+2) cycloaddition with the other double bond producing Mn(IV) diolate **1.33**. Finally, basic hydrolysis of the Mn(IV) diolate **1.33** affords *cis*-THF **1.34**.

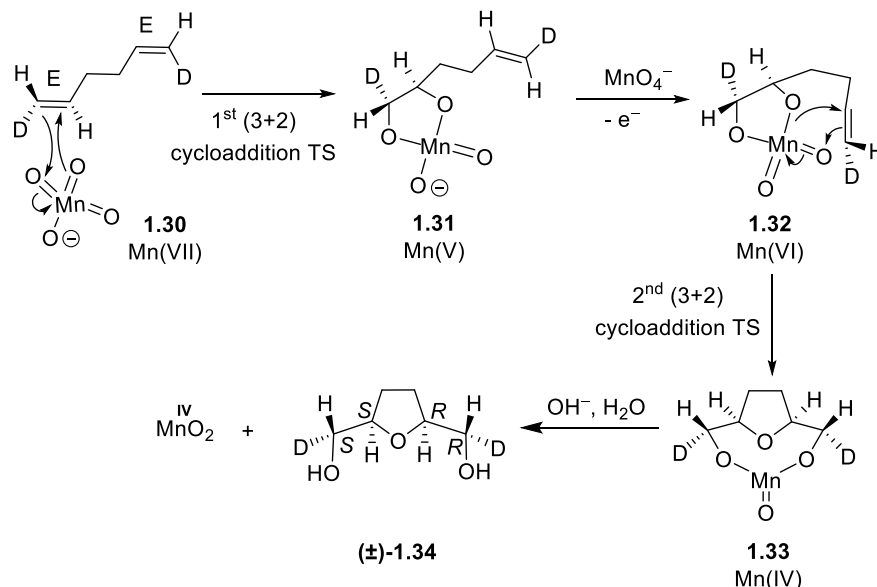


Figure 1.4: Baldwin's proposed mechanism for the permanganate ion oxidative cyclisation of 1,5-diene **1.30**.

A few important points in Baldwin's proposed mechanism are worthy of mention. Baldwin used weakly acidic conditions based on the Klein and Rojahn procedure.⁴⁰ The evidence cited for the reoxidation of Mn(V) to Mn(VI) came from a paper by Pode and Waters, who stated that hypomanganate (MnO_4^{3-}) is not a suitable oxidant for alkenes.⁴⁴ They also reported oxidation of hypomanganate to manganate instantaneously by permanganate. However, this earlier work was carried out under strongly alkaline conditions (10 N KOH). They found that olefinic acids are slowly oxidised by manganate but not by hypomanganate, although alkaline manganate oxidation is impractical for *cis*-diol preparation due to the low yields. However, no yields were reported in their study. Furthermore, manganate and hypomanganate are doubly and triply negatively charged species whereas Mn(V) glycolate is singly negatively charged species and, therefore, direct comparison is not reasonable.

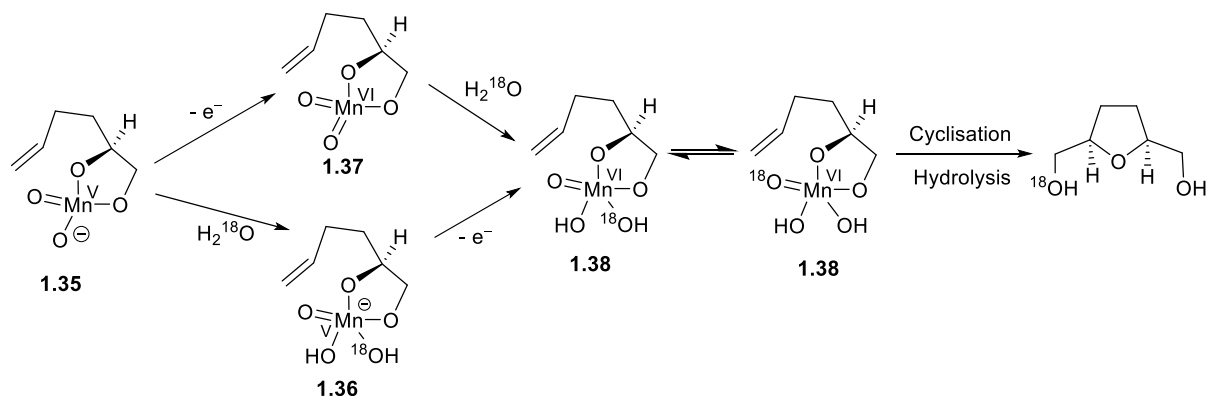
So, there are several questions to answer relating to the proposed mechanism:

- Does Mn(V) reoxidise into Mn(VI) under neutral or weakly acidic conditions?
- Does cyclisation proceed by way of Mn(VI) glycolate?
- Another relevant question relating to Baldwin's proposal is that if Mn(VI) glycolate does react with alkenes, would Mn(VI) glycolate **1.32** undergo an intermolecular reaction with another alkene to give a Mn(VI) bisglycolate rather than the intramolecular reaction (cyclisation)?

Baldwin's mechanism was also investigated by Wolf and Ingold⁴⁵ by using 92% H_2^{18}O as solvent. According to Wolfe's study, mass spectrometry analysis showed the presence of only one labelled

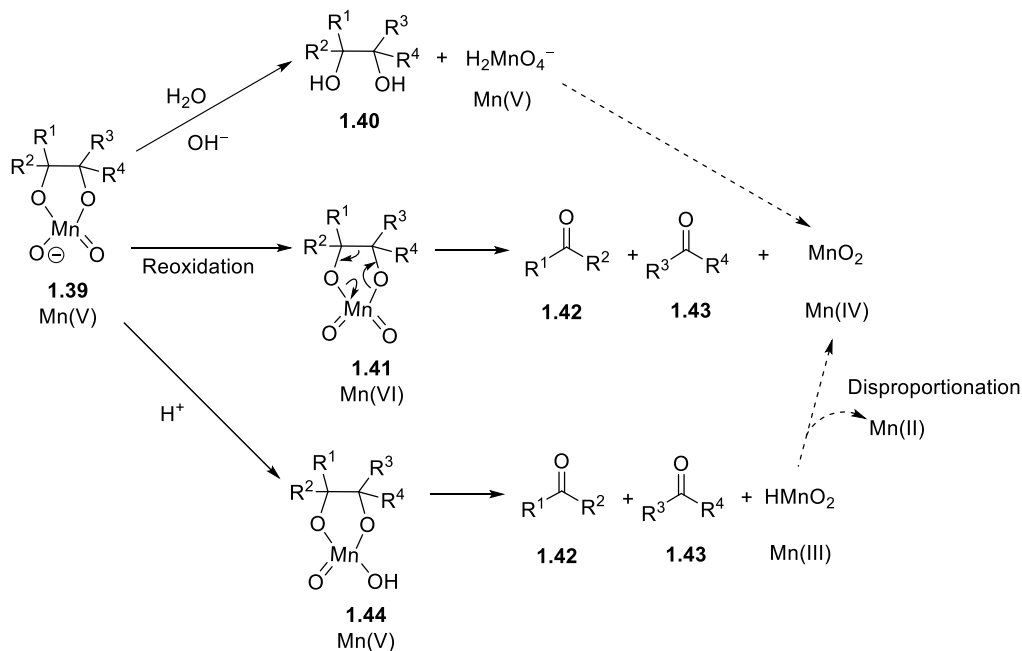
Chapter 1

oxygen in the THF adduct which infers that one of the oxygen atoms derived from the solvent. This is incompatible with Walba's mechanism as well as Klein and Rojahn, in which all three oxygen atoms are derived from a single molecule of permanganate. Here too, a symmetrical substrate is converted into a symmetrical product in an asymmetrical manner which confirms sequential oxidation of the two double bonds *via* an intermediate Mn glycolates (**1.32**), in agreement with Baldwin's mechanism. The key finding is that there is some oxygen exchange at Mn, likely through a more highly coordinated intermediate. However, this intermediate could be Mn(V) or Mn(VI) (Scheme 1.5).



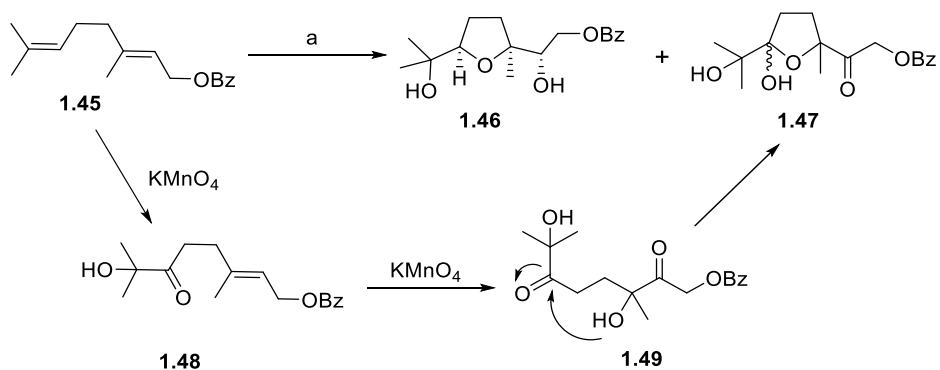
Scheme 1.5: Incorporation of labelled water (H_2^{18}O) into Mn(V) or Mn(VI) glycolates from Wolf and Ingold.⁴⁵

The yield of the oxidative cyclisation of 1,5-dienes at this early stage was often low due to a number of competing side reactions. For example, the Mn(V) species can enter different reaction manifolds such as hydrolysis to give the dihydroxylation product; decomposition to give two carbonyl compounds, or reoxidation into a Mn(VI) species followed by decomposition into carbonyl compounds (Scheme 1.6).^{46,47}



Scheme 1.6: Possible reaction manifolds for Mn(V) glycolate **1.39** species competing with cyclisation.

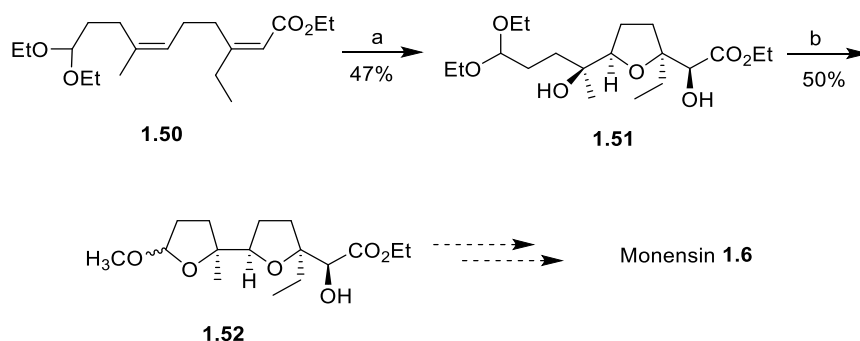
In the case of geranyl benzoate (**1.45**), the permanganate-mediated oxidative cyclisation in the presence of phase transfer catalyst led to lactol **1.47**, which has been isolated (**Scheme 1.7**).⁴⁸ A plausible mechanism for its formation involves sequential oxidation of the double bonds to give α -hydroxy ketone **1.48**, then α -hydroxy ketone **1.49**, which cyclises to give lactol **1.47**.



Scheme 1.7: By-products of the permanganate oxidative cyclisation of geranyl benzoate **1.45**.
Reagents & conditions: (a) 0.4 M KMnO_4 (2 equiv), AcOH (4 equiv), Adogen 464 (0.4 equiv)/ Et_2O or TBAB/ CH_2Cl_2 or TBAB (0.4 equiv)/ Et_2O .

Walba continued on the permanganate-promoted oxidative cyclisation of 1,5-dienes through the synthesis of some key intermediates in natural product synthesis.^{49,50} For example, he synthesised

the B/C ring fragment of monensin (**1.52**) in which he was able to introduce the four stereocentres with correct relative stereochemistry in a single step (**Scheme 1.8**). Although the oxidative cyclisation of diene **1.50** was achieved in a yield of only 20%, generating four new stereocentres with control of relative stereochemistry was considered a success due to the level of molecular complexity introduced. Treatment of THF-diols **1.51** with trimethyl orthoformate in the presence of acid closes the B ring to give the fragment **1.52** of the natural product monensin (**1.6**).



Scheme 1.8: Walba's synthetic approach to monensin (**1.6**) using the permanganate-promoted oxidative cyclisation of 1,5-diene **1.50**. **Reagents & Conditions:** a) KMnO_4 , H_2O , acetone, pH 7.5, CO_2 ebullition; b) $\text{HC}(\text{OMe})_3$, TsOH , benzene.

Since then the oxidative cyclisation has become an extremely powerful reaction for the synthesis of bioactive natural products. However, the development of methods to control absolute stereochemistry has been a key requirement in achieving this.

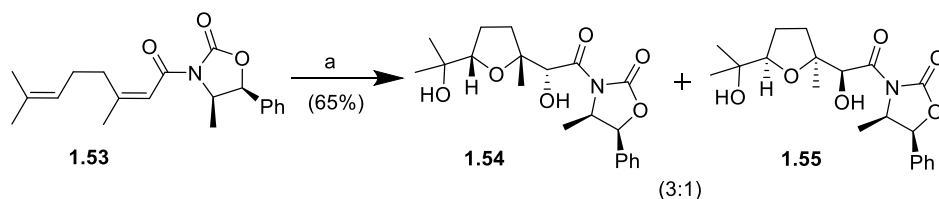
1.1.1.1 Stereoselective approaches in permanganate oxidative cyclisation

This section will describe the stereoselective methods for THF-diol formation using permanganate-mediated oxidative cyclisation. Firstly, we will introduce the application of chiral auxiliaries in THF ring formation. Secondly, the use of chiral phase transfer catalysis in the oxidation of olefins and oxidative cyclisation of 1,5-dienes will be described.

1.1.1.1.1 Applications of chiral auxiliaries in stereoselective oxidative cyclisation

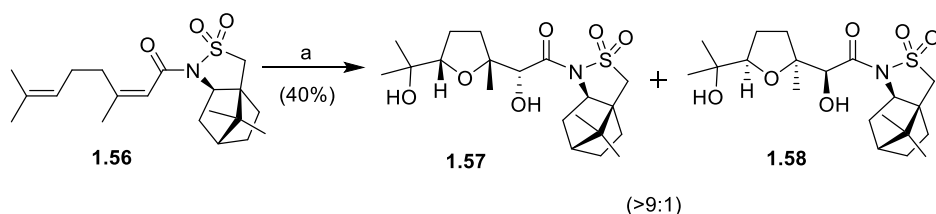
Different chiral auxiliaries were reported to achieve diastereoselective oxidative cyclisation of 1,5-dienoic acid derivatives by permanganate ion (**Scheme 1.9**).⁵¹ Oxidative cyclisation of oxazolidinone dienoate **1.53** afforded non-racemic THF-diols **1.54** and **1.55** in a 3:1 ratio and in a good yield of

65%. The major diastereoisomer **1.43** results from an attack on the *Re* face of the conjugated double bond.



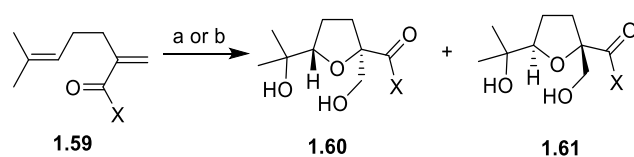
Scheme 1.9: Permanganate-promoted oxidative cyclisation of dienoate **1.53**. **Reagents & conditions:** a) KMnO_4 , acetone/water (10:1), pH 7.5, CO_2 bubbling, -30°C .

Improved stereoselectivity was achieved by changing the auxiliary from the Evans' oxazolidinone to Oppolzer's camphorsultam (**Scheme 1.10**).^{52,53} Oxidative cyclisation of diene **1.56** yielded the corresponding THF-diol adducts **1.57** and **1.58** in ratio of >9:1 respectively with a moderate yield of 40%.



Scheme 1.10: Permanganate-promoted oxidative cyclisation of dienoate **1.56**. **Reagents & conditions:** a) KMnO_4 , acetone/water (10:1), pH = 7.5, CO_2 bubbling, -30°C , 30 min.

Kocienski and Brown applied the sultam auxiliary approach in a synthesis of the complex polyether ionophore antibiotic salinomycin.⁵⁴ Subsequently, the Brown group have exploited chiral auxiliary mediated oxidative cyclisation of dienoates and trienoates with the total synthesis of acetogenins,⁵⁵ and terpenoids.⁵⁶ (2*R*)-10,2-Camphorsultam and a range of cyclohexyl chiral auxiliaries were used in these studies (entries 1-6, **Table 1.1**). A single isomeric THF-diol system **1.49** was obtained by the oxidative cyclisation of dienoate **1.48a** when (2*R*)-10,2-camphorsultam was used, although only moderate yield (38%) was achieved (entry 1, **Table 1.1**). Whereas the other dienoates **1.48b–e** bearing different auxiliaries had afforded diastereoisomeric THF diols **1.49b–e** and **1.50b–e** with yields of 57–99 (entries 2-5). No diastereoselectivity (dr 1:1) was obtained when tolylcyclohexyl dienoate was applied with 57% yield (entry 6). However, more bulky TTC-dienoate **1.48** afforded excellent selectivity (dr 32.3:1) and good yield (62%, entry 3). An excellent yield of 92% was obtained for the oxidation of **1.48g** (entry 7).

Table 1.1: Investigation of stereocontrolled permanganate-mediated oxidative cyclisation of 1,5-dienes by Brown and co-workers using different chiral auxiliaries.⁵⁶

Entry	X	Diene	Condition	Reaction Yield (%)	dr (1.60:1.61)
1		(-)- 1.59a	a	38	Only 1.60
2		(-)- 1.59b	b	94	4.2:1 ⁱⁱ
3		(±)- 1.59c	b	62 ⁱ	32.3:1 ⁱⁱⁱ
4		(±)- 1.59d	b	99 ⁱ	1.8:1 ⁱⁱⁱ
5		(±)- 1.59e	b	82 ⁱ	1.3:1 ⁱⁱⁱ
6		(±)- 1.59f	b	57 ⁱ	1:1 ^b
7		1.59g	b	92	1:1 (er)

Reagents & conditions: a) KMnO_4 , AcOH, Adogen 464, $\text{Et}_2\text{O}/\text{H}_2\text{O}$, rt, 30 min; b) NaMnO_4 , AcOH, acetone–water, -35 to -5 °C, 1 h. ⁱRacemic products were obtained. ⁱⁱRatio of diastereoisomers estimated from the ^1H NMR spectrum. ⁱⁱⁱRatio of diastereoisomers determined using HPLC.

NOESY data carried out by the Brown group for TTC dienoate **1.59c** showed an interesting cross peak between the β proton H_a signal and the aromatic ring protons (**Figure 1.5**).⁵⁷ This through space interaction indicated there was a stacked conformation of the phenyl ring and enoate moiety. This conformation was consistent with the high diastereoselectivity observed by permanganate oxidative cyclisation of the TTC dienoate **1.59c** (dr 32.3:1).

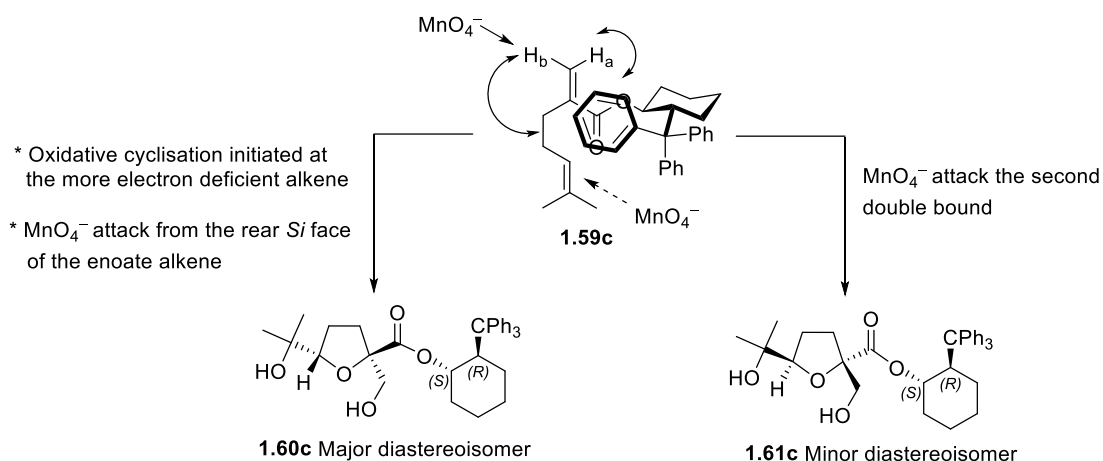
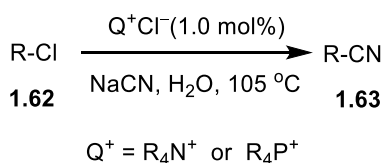


Figure 1.5: Through space interactions of vinylic β proton signals (H_a , H_b) of the TTC dienoate **1.59c** during the diastereoselective permanganate-mediated oxidative cyclisation.

1.1.1.1.2 Permanganate phase-transfer oxidation of olefines and dienes

1.1.1.1.2.1 Phase-transfer catalysis

The term “phase-transfer catalysis (PTC)” was first introduced by Starks in 1971 to explain the critical role of tetraalkylammonium or phosphonium salts (Q^+X^-) in a reaction where two substances are located in different immiscible phases. This process is often inhibited because of the inability of reagents to come together.⁵⁸ The tremendous rate enhancement achieved with phase transfer catalysis is due to the generation of a neutral complex consisting of quaternary onium and anion, in which the anion is solubilised in organic solvents and sufficiently reactive. An illustrative example is the use of PTC in the cyanation of alkyl halides (**Scheme 1.11**).



Scheme 1.11: Phase transfer catalysis process in the cyanation of alkyl halides.

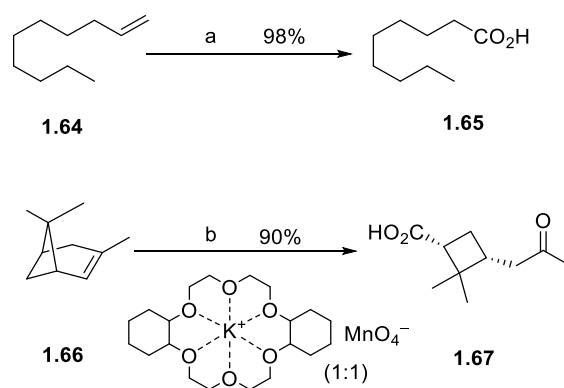
In the case of a nucleophilic substitution under PTC, the high rate of displacement is mainly due to the high lipophilicity and the large ionic radius; where the more dissociated ion pairing results in higher reactivity. Although the catalytic activity of quaternary onium salts was known by Stark the foundations were laid by contribution from Starks, Makosza, and Brändström in the mid of 1960s.^{59–61} Since then, PTC has dramatically growing as a practical methodology for organic synthesis. The exponential growth in PTC use is due to simple experimental procedures, mild reaction conditions,

and the use of relatively inexpensive and environmentally friendly reagents and solvents and the possibility of easy transfer of these laboratory procedures to large-scale synthesis.^{62–67} The use of chiral PTC has proven to be a unique and reliable technique for catalytic synthesis in numerous valuable chemical reactions for preparation of chiral organic compounds from prochiral substrates. The approach has been successfully used in many organic reactions such as alkylation, conjugate addition, Mannich reaction, aldol reactions, cyclisation, ring-opening reactions, and hydrolysis.^{62,68–}

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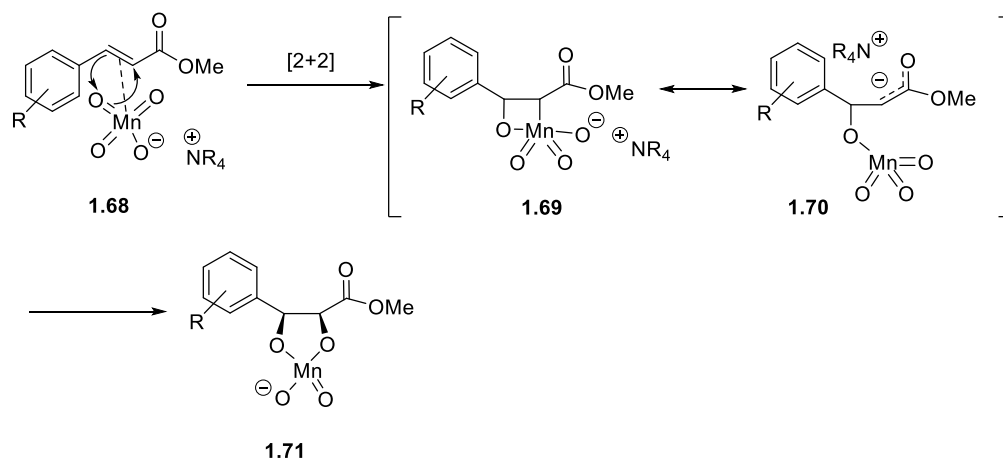
1.1.1.1.2.2 Permanganate oxidation of olefines under PTC

Applications of PTC in permanganate oxidation emerged after 1971.⁵⁸ Prior to this, permanganate oxidations were carried out in water with the addition of a miscible organic solvent to aid the solubility of the organic substrate. Organic chemists started to use PTC with permanganate ion to improve the efficiency of oxidation by increasing the solubility in organic solvents. Generally, permanganate oxidation under PTC can be carried out in two ways: aqueous permanganate (liquid-liquid PTC) or solid permanganate (solid-liquid PTC). Two important factors control this method; the ability of the PTC to transfer the permanganate ion into the organic phase, and to what extent they will exist as an ion pair in the organic phase.⁷⁶ The ability of permanganate to be carried into the organic phase depends on the polarity of the solvent and PTC as well as the catalyst structure. The first use of PTC with permanganate ion was in 1971, where Starks used catalytic tetrabutylammonium bromide as PTC with a mixture of water and benzene to oxidatively cleave lipophilic alkene **1.64** to nonanoic acid (**1.65**) in 98% yield (**Scheme 1.12**).⁷⁷ In the following year, Sam and Simmons had published the oxidative cleavage of alkene **1.66** into carboxylic acid **1.67** (90%) using equimolar of crown ethers as PTC and KMnO_4 .⁷⁸



Scheme 1.12: Early use of PTC in the permanganate oxidative cleavages of alkenes. **Reagents and Conditions:** a) KMnO_4 , TBAB (5 mol %), benzene, H_2O ; b) KMnO_4 , 18-crown ether, benzene, H_2O .

Between 1982-1987, Lee *et al.* investigated permanganate-mediated oxidations of alkenes under phase transfer catalysis.⁷⁹⁻⁸¹ The reaction rate was investigated by using different substituted (electron withdrawing and donating groups) methyl cinamates as a model.⁷⁹ They found that the rate of reaction increased with electron withdrawing groups on the aromatic ring. They also studied a range of alkyl ammonium PTCs. They indicated that the reaction rate was decreased with PTC and surprisingly was affected by the identity of the quaternary ammonium. Here, they pointed out that, specifically for the symmetrical tetraalkylammonium ions, the longer the four alkyl chains became, the slower the rate of reaction. However, the reaction rate dramatically increased if one of the alkyl chains was replaced with a methyl group (similar to the structure of adogen 464). They stated that the presence of the smaller group on the ammonium ion allows the permanganate ion to get closer to form a tighter ion pair so, the rate of reaction increases. In terms of mechanism, they concluded that the reaction proceeded through either an electron-rich or electron-deficient transition state depending on the substituents following a [2+2] cycloaddition pathway (**Scheme 1.13**). They proposed that [2+2] TS **1.68** gave a four membered ring intermediate **1.69** and subsequent rearrangement lead to an enolate-like structure **1.59**. The latter is stabilised by the interaction with the ammonium ion. They mentioned that the electron rich enolate intermediate is stabilised by the presence of electron withdrawing groups on the aryl ring. Further rearrangement gives the cyclic manganese(V) glycolate **1.71**, which can then enter different pathways, such as hydrolysis, cleavage etc.

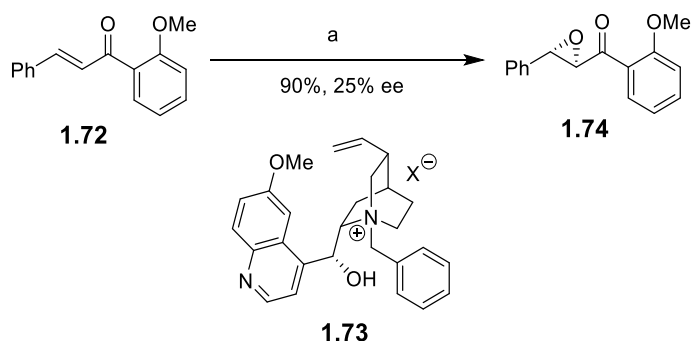


Scheme 1.13: Lee's proposed mechanism for PTC oxidations of substituted methyl cinamates by permanganate ion.

1.1.1.1.2.3 Chiral phase-transfer catalysis of olefin oxidation

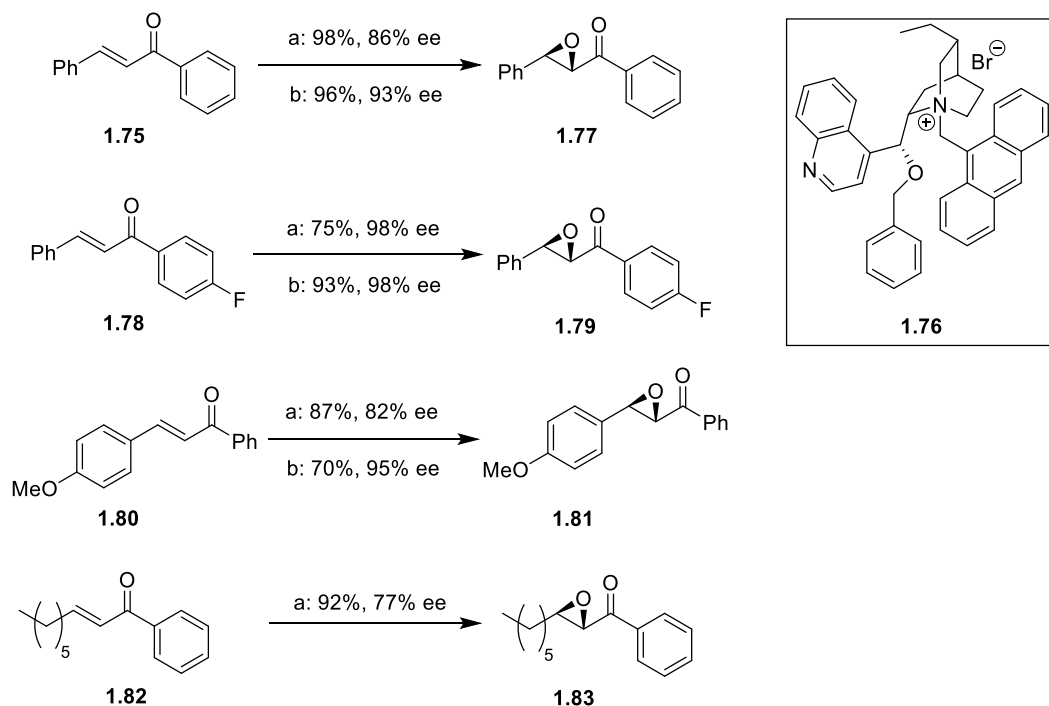
Chiral PTC (CPTC) was firstly introduced in the 1970's for the purpose of asymmetric alkylations and Michael additions. In 1976, Wynberg *et al.* described the asymmetric epoxidation of chalcone

derivatives with hydrogen peroxide using alkaloid based ammonium salt **1.73** as CPTC (**Scheme 1.14**).⁸² They achieved a reasonable enantiomeric excess of 25%. In 1978, they pointed out that the stereochemical outcome was reversed when the oxidant was changed to *t*-BuOOH or sodium hypochlorite.⁸³ Later, and in 1998, Lygo and Wainwright suggested that this was due to hydrogen bonding between hydrogen peroxide and the hydroxyl group of the catalyst.⁸⁴ Then, many studies were done on the asymmetric epoxidation of chalcones with a variety of catalysts to improve the selectivity but without great success.^{85–88}



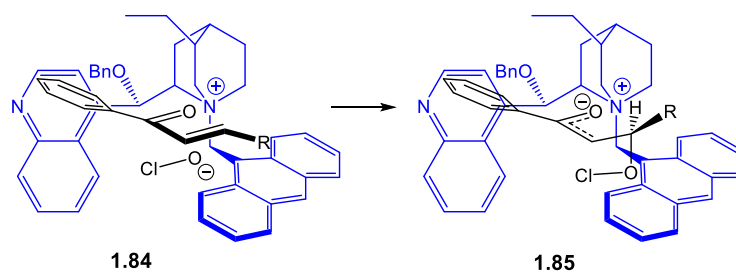
Scheme 1.14: Early use of CPTC in the epoxidation of chalcone. **Reagents and Conditions:** a) H₂O₂ (aq), **1.73** (5 mol %), toluene.

In the late of 1990's a breakthrough in the asymmetric epoxidation of α,β -unsaturated phenones was made by Lygo *et al.* when they used Cinchona alkaloids as CPTC.^{84,89–92} They reported a remarkable improvement in the enantiomeric excess, 70–98% ee, could be achieved through benzylation of the secondary alcohol present in the catalyst **1.73** and replace the benzyl group in **1.73** with an anthracyl group in **1.76** (**Scheme 1.15**). Their methodology showed that both enantiomers can be prepared by starting with either cinchonidine or its pseudo-enantiomer cinchonine, both showing equal inducement of chirality. In 1999, Corey *et al.* published broadly similar results to those achieved by Lygo *et al.* using the same catalyst but Corey *et al.* achieved higher yields and selectivities when they carried out the reactions at $-40\text{ }^{\circ}\text{C}$ (**Scheme 1.14**).⁹³



Scheme 1.15: Lygo's and Corey's asymmetric nucleophilic epoxidation using hypochlorite in the presence of cinchonidinium salt. **Reagents and Conditions:** a) Lygo's conditions: **1.76** (1 mol %), 15% aq NaOCl (2 equiv), toluene, 12–24 h, rt; b) Corey's conditions: **1.76** (10 mol %), KOCl aq, toluene, $-40\text{ }^{\circ}\text{C}$, 12 h.

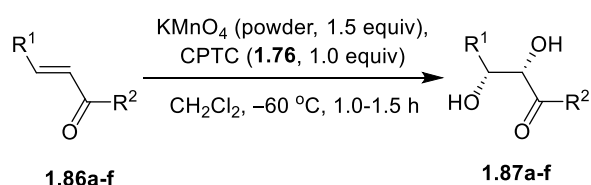
To understand the selectivity of epoxidation, Lygo proposed that the transition state **1.73** forms in a similar arrangement of Michael-type addition leading to an enolate-like structure **1.74** (**Scheme 1.16**). This enolate-like intermediate is stabilised through ionic interaction with the proximate ammonium cation. If the substrate is sterically restricted by the quinoline, benzyl and anthracene groups, high inducement of chirality is achieved.



Scheme 1.16: Lygo's proposed intermediate in the phase-transfer catalysed nucleophilic epoxidation of olefins.

The similarity between Lee's transition state shown in **Scheme 1.13** and those formed in the phase-transfer catalysed nucleophilic epoxidation of enones led the Brown group to suggest that CPTC developed for the epoxidation reaction might also be applied to the phase-transfer oxidative cyclisation of dienes by permanganate. In 2002, the Brown group published the first use of CPTC in the permanganate-promoted dihydroxylation of enones (**Table 1.2**).⁹⁴ The dihydroxylation product was achieved by using powdered KMnO_4 under phase conditions but with a stoichiometric amount of the catalyst and without any additives. They achieved really promising selectivities (65%-80% ee) with moderate yields (19%-52%).

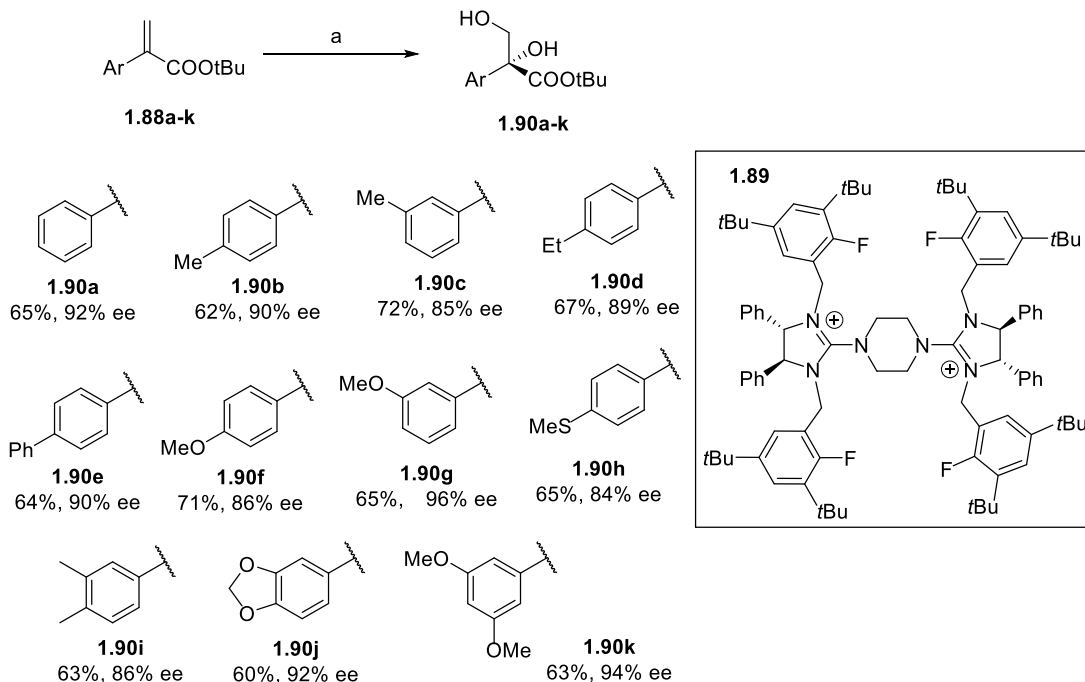
Table 1.2: Asymmetric permanganate-promoted dihydroxylation of enones with CPTC by Brown and co-workers.



Entry	R ¹	R ²	Alkene	Yield (%) [BRSM (%)]	ee (%)
1	<i>n</i> Bu	(<i>p</i> -Br)C ₆ H ₄	1.86a	52 [59]	77
2	<i>n</i> Bu	(<i>p</i> -Cl)C ₆ H ₄	1.86b	32 [64]	77
3	<i>n</i> Bu	(<i>p</i> -OMe)C ₆ H ₄	1.86c	34 [61]	80
4	<i>n</i> Bu	(<i>p</i> -me)C ₆ H ₄	1.86d	40 [93]	75
5	Et	Ph	1.86e	19 [37]	65
6	<i>i</i> Pr	Ph	1.86f	28 [59]	67

BRSM is the yield calculated based on recovered starting material.

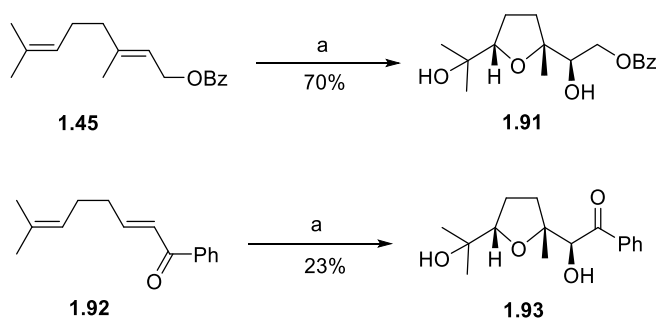
More recently, Tan *et al.* reported a chiral dicationic bisguanidinium-catalyzed asymmetric oxidation reaction of alkenes with potassium permanganate (**Scheme 1.17**).⁹⁵ They obtained very good yields (60% – 70%) and very high enantiomeric excesses (84% – 96%) with a catalytic amount of the catalyst and in the presence of 20% aq. potassium iodide as an additive. It is very surprising to achieve such high yields and selectivities using an aqueous solution at low temperature (–60 °C).



Scheme 1.17: Asymmetric permanganate-mediated dihydroxylation using a chiral bisguanidinium catalyst (**1.89**) by Tan *et al.*⁹⁵ **Reagents and conditions:** KMnO_4 , **1.89** (2 mol%), TBME, 20 wt% aq. KI, -60°C .

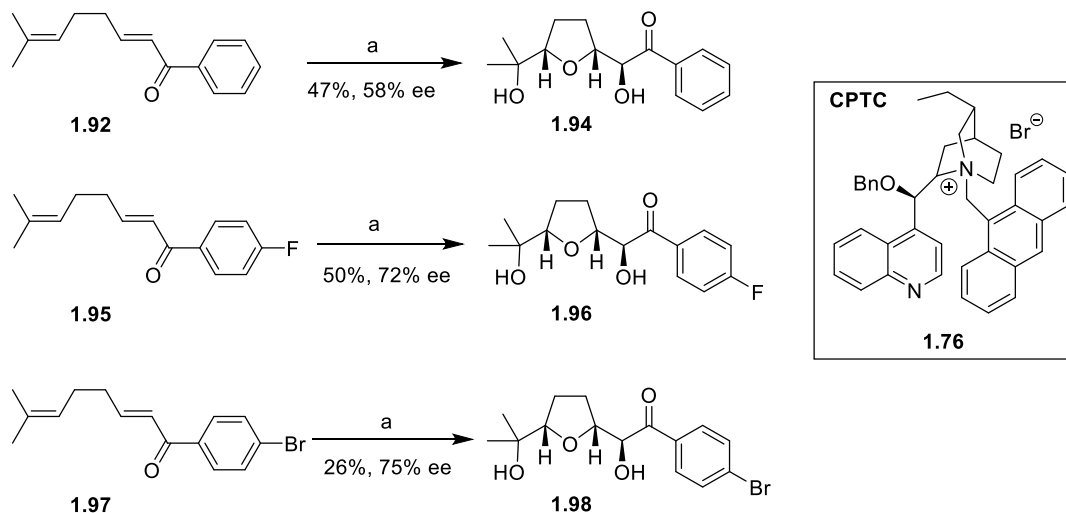
1.1.1.1.2.4 Permanganate-promoted chiral phase-transfer catalysed oxidative cyclisation of 1,5-dienes

The first permanganate-mediated oxidative cyclisations of 1,5-dienes catalysed using PTC was carried out in the Brown group using a liquid-liquid system.^{96,97} They used aqueous permanganate ion along with PTC (adogen 464) and acetic acid to promote the cyclisation (**Scheme 1.18**). Dienes **1.45** and **1.92** were oxidatively cyclised to the corresponding racemic THF's **1.91** and **1.93** respectively, with varying success. Thus, the oxidative cyclisation of much more lipophilic substrates was allowed. These promising results enabled the development of an asymmetric oxidative cyclisation using a chiral ammonium salt.



Scheme 1.18: Permanganate mediated phase-transfer catalysed oxidative cyclisations. **Reagents and Conditions:** a) 0.4 M KMnO_4 (2 eq), AcOH (4 eq), adogen 464 (0.4 eq), Et_2O .

In 2001, the Brown group published the first use of CPTC in permanganate-promoted oxidative cyclisation of aromatic 1,5-dienones (**Scheme 1.19**).⁴⁸ Oxidative cyclisation of the unsubstituted 1,5-dienone **1.92** afforded the corresponding THF-diols **1.94** with a moderate yield of 47% and good ee of 58%. Substitution on the phenyl ring **1.97** and **1.95** increased the enantiomeric excess up to 75% for *p*-bromo derivative **1.98**.⁹⁶



Scheme 1.19: KMnO_4 oxidative cyclisation under phase transfer conditions. **Reagents & conditions:**

a) KMnO_4 (powdered, 1.6 equiv), AcOH (6.5 equiv), **1.76** (0.1 equiv), CH_2Cl_2 , $-30\text{ }^\circ\text{C}$.

This work provides the foundation for the experimental investigations described here.

1.1.2 DFT studies on the permanganate oxidative cyclisation of 1,5-dienes

Modern computational chemistry can play an important role in understanding the mechanistic pathways for the oxidative cyclisation of 1,5-dienes to THF-diols. However, little theoretical work has been carried out on the mechanism of this reaction. Understanding of the mechanism needs to consider two main steps; the alkene oxidation step (as a first reaction step) and cyclisation step (as a second reaction step). The next sections will describe the previous computational studies performed on permanganate alkene oxidation of and permanganate-mediated oxidative cyclisation of 1,5-dienes.

1.1.2.1 Computational studies on alkene oxidation by permanganate ion

Permanganate ion has been applied extensively in organic reactions involving oxidation of double bonds. The application of this reagent in chemical synthesis has spurred considerable interests in the underlying reaction mechanism (**Figure 1.5**).^{98–101} Olefin dihydroxylation catalysed by MnO_4^- has

been the subject of extensive theoretical studies over the last 20 years.^{102–109} The mechanism of the oxidation of alkenes by MnO_4^- is believed to be similar to that of OsO_4 , although the reaction rates are influenced differently by the donor and acceptor substituents around the double bond. The initial step of alkene oxidation was believed to involve either a direct (3 + 2) cycloaddition TS **1.100** to form a five-membered Mn(V) glycolate **1.101** or [2+2] cycloaddition TS **1.103** between double bond and the O=Mn group of MnO_4^- to form a metalladioxatane **1.104**. The latter rearranges into Mn(V) glycolate **1.101**. Many theoretical studies on the alkene oxidation by permanganate ion have been highlighted in **Table 1.3**. The energy barrier and reaction were calculated depending on the type of cycloaddition either (3+2) or [2+2] cycloaddition using different levels of theory

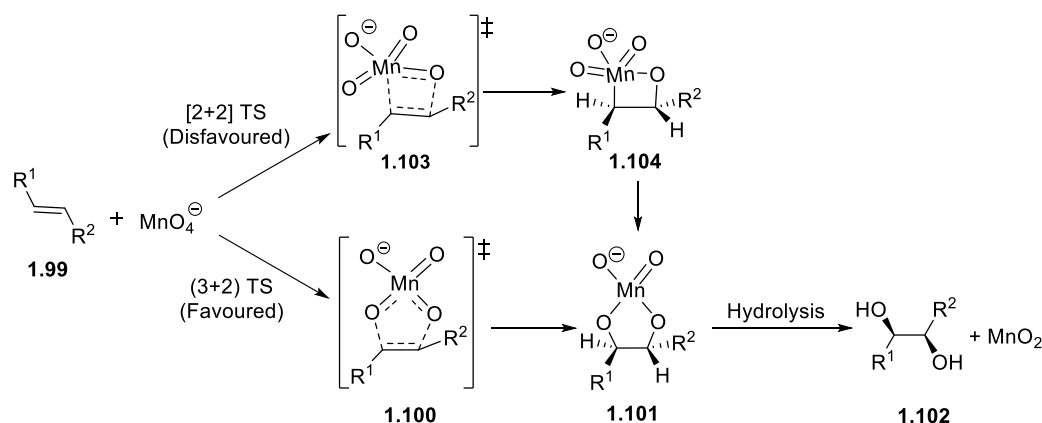
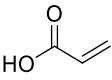
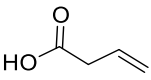
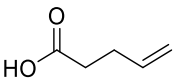
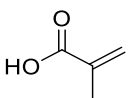
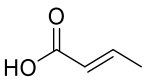
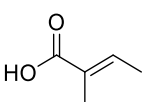
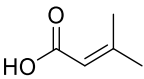
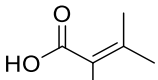
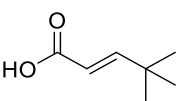


Figure 1.6: Proposed reaction mechanism of olefin dihydroxylation by MnO_4^- .

All computational studies have shown that (3+2) cycloaddition pathway is favoured by at least 45 kcal/mol in activation energy over a [2+2] cycloaddition pathway. The (3+2) addition is an exergonic process from the point view of thermodynamics whereas [2+2] is endergonic. All these calculations were performed on a singlet spin multiplicity surface within the density functional theory (DFT). Strassner and Busold¹¹⁰ had used the B3LYP/6-311+G(d,p) level of theory to calculate the reaction barrier and energies of addition for different unsaturated carboxylic acids (**Table 1.3**). They showed good agreement with the experimental results reported by Freeman and Kappos,¹¹¹ concluding that the alkene oxidation proceeds by (3+2) cycloaddition; all [2+2] cycloadditions have significantly higher energy barriers and are thermodynamically unfavourable.

Table 1.3: Strassner and Busold's study on alkene oxidation by MnO_4^- investigated by computational simulations, and comparison with experimental data.

Alkene	Addition pthway	ΔG_{calc}^+ ^a	ΔG_r^a	ΔG_{exp}^+ ^b
	[3+2]	15.7	-35.3	17.1
	[2+2]	61.5	26.8	
	[3+2]	22.0	-37.8	17.8
	[2+2]	63.4	25.0	
	[3+2]	21.3	-38.1	17.6
	[2+2]	62.0	24.7	
	[3+2]	18.3	-34.5	17.1
	[2+2]	63.7	27.7	
	[3+2]	18.3	-32.9	17.4
	[2+2]	64.8	29.8	
	[3+2]	19.6	-32.6	17.0
	[2+2]	65.9	29.7	
	[3+2]	21.8	-30.0	18.3
	[2+2]	66.7	33.6	
	[3+2]	21.4	-35.7	18.6
	[2+2]	67.2	32.5	
	[3+2]	20.3	-33.9	18.0
	[2+2]	67.3	30.8	

^a Calculated in gas phase using the B3LYP/6-311+G(d,p) level of theory at 298.15 K and taken from Ref 110.¹¹⁰ ^b Activation energies measured in water at 298 K and taken from Ref 111.¹¹¹

Houk and Strassner¹⁰⁸ found that the enthalpy of activation for the oxidation of ethene by MnO_4^- needs enthalpy of activation 9.3 kcal/mol to proceed through (3+2) cycloaddition TS with $\Delta H_r = -47.2$ kcal/mol and 50.5 kcal/mol through [2+2] TS as an endothermic step ($\Delta H_r = 18.6$ kcal/mol), both calculated by the B3LYP/6-31G*/6-311+G(d,p) level of theory. Aniahyei *et al.*¹¹² confirmed these results using the B3LYP/6-31G*/LANL2DZ level of theory. Aniahyei *et al.* found that the triplet ground state of reactants $\text{MnO}_4^- + \text{alkene}$ is less stable than the singlet by 22.4 kcal/mol whereas the triplet Mn(V) glycolate is more stable than the singlet by 2.1 kcal/mol.

Wiberg *et al.*¹¹³ investigated the permanganate oxidation of different monosubstituted alkenes using both experimental and theoretical approaches (**Table 1.4**). Their DFT study was performed with the B3LYP/6-311++G** level of theory in water. The calculated free energy of activation was not in

a good agreement with the measured one for allyl alcohol and acrylonitrile. They used a coupled cluster with singles and doubles model (CCSD) to calculate the overall energy changes for the permanganate oxidation of acrylonitrile. They found a significant difference in energy of reaction between CCSD and B3LYP; -45 kcal/mol for B3LYP and -73 kcal/mol for CCSD, both calculated in the gas phase. Experimentally, they calculated the heat of reaction for permanganate ion with a large excess of allyl alcohol in aqueous solution, $\Delta H_r = -87 \pm 2$ kcal/mol. In spite of a difference of 15.0 kcal/mol between the calculated and measured energy, they stated that this result is in accord with CCSD calculations.

Table 1.4: Wiberg *et al.* study of alkene oxidation by MnO_4^- investigated by computational simulations and compared with experimental data.

Alkene	$\Delta G_{\text{calc}}^\ddagger$ ^a	$\Delta H_{\text{calc}}^\ddagger$ ^a	ΔG_r ^a	ΔH_r ^a	$\Delta G_{\text{exp}}^\ddagger$ ^b
$\text{CH}_2=\text{CH}_2$	20.1	9.9	-31.3	-47.6	
$\text{CH}_2=\text{CHCH}_3$	22.0	10.8	-30.9	-42.8	
$\text{CH}_2=\text{CHF}$	21.2	10.1	-39.6	-51.0	
$\text{CH}_2=\text{CHCH}_2\text{OH}$	21.9	10.7	-29.8	-41.9	14.6
$\text{CH}_2=\text{CHCF}_3$	21.4	9.9	-31.2	-43.0	
$\text{CH}_2=\text{CHCCl}_3$	22.9	11.5	-31.3	-43.2	
$\text{CH}_2=\text{CHCN}$	17.7	8.5	-29.2	-39.0	14.2

^a Calculated in gas phase using the (PCM)-B3LYP/6-311++G(d,p) level of theory at 298.15 K and taken from Ref 95.¹¹³ ^b Activation energies measured in water at 298 K and taken from Ref 113.¹¹³

Adamczyk *et al.* performed a DFT study on reaction of trichloroethene ($\text{ClCH}=\text{CCl}_2$) with permanganate in aqueous solution using a modern DFT functional, PCM/M05-2X/aug-cc-pVDZ level of theory.¹¹⁴ They found that (3+2) cycloaddition needs a barrier of 12.2 kcal/mol which is comparably in agreement with experimental result (10.3 kcal/mol).

Javan *et al.*¹¹⁵ studied the effect of hydrogen bonding between ethylene glycol and permanganate ion and its influence on oxidation of olefins in both gas and solution phase by means of B3LYP/6-311++G** level of theory (**Figure 1.7**). They found that the interaction energy of MnO_4^- with EG is -12.4 kcal/mol as a thermodynamically favourable influence due to the strong hydrogen bonding, leading to kinetically and thermodynamically favourable alkene oxidation. That was reasoned that the HOMO-LUMO gap in MnO_4^- decreases which will then affect the electrophilicity and reactivity of permanganate.

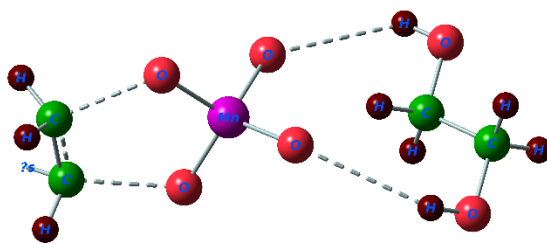


Figure 1.7: MnO_4^- is hydrogen bonded to ethylene glycol during (3+2) cycloaddition TS.

More importantly, Ogino *et al.*¹¹⁶ performed an experimental and computational kinetic study for reaction of MnO_4^- with a series of styrene derivatives in dichloromethane solution and in the presence of the tetraethylammonium ion as a phase transfer catalyst (**Figure 1.8**). The B3LYP/6-311G(d,p)//B3LYP/LanL2DZ level of theory was used in their study. They found broadly good agreement between their experimental and calculated results for the substituent effects on the permanganate oxidation of styrene derivatives. They have optimised the (3+2) transition states in the form of an ion pair with a quaternary ammonium ion. However, a disagreement between the theoretical and experimental free energy of activation values was found in the absence of phase transfer catalyst. This was attributed to the electrostatic effect of the quaternary ammonium ion. However, when they incorporated the quaternary ammonium ion, the activation barriers of permanganate oxidation have been lowered consequently, and the increased reaction rates are in reasonable agreement with their experimental results.

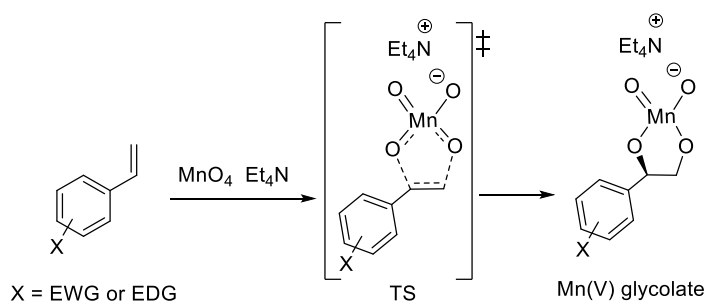


Figure 1.8: Quaternary ammonium ion interaction with MnO_4^- during alkene oxidation step.

Prior to the work of Ogino *et al.*, experimental work on quaternary ammonium permanganate oxidation of methyl cinnamate was carried out by Lee and Brown.⁴⁷ On the rate constant effect, Lee and Brown⁴⁷ stated that the quaternary ammonium ion has a surprisingly large effect on the rates of reactions due to the increased solubility of permanganate ion, and the excess addition of it did not change the rates. Therefore, the presence of PTC is consistent with lower activation barrier for the (3+2) reaction.^{116 47}

In summary, all computational studies confirmed that first reaction step of alkene oxidation follows a (3+2) cycloaddition pathway. Hydrogen bonding and PTC are important factors for the alkene oxidation with MnO_4^- , and it has been proposed that these effects lead to lowering of the activation barriers.

1.1.2.2 DFT Calculations on oxidative cyclisation of 1,5-dienes

In 2007, Poethig and Strassner reported a gas phase DFT study on permanganate-promoted oxidative cyclisation of 1,5-dienes using the B3LYP/6-311+G(d) level of theory as shown in **Figure 1.9**.¹¹⁷ They explained the stereospecificity of this reaction by confirming a mechanism with one permanganate ion adding successively across the two double bonds. They calculated the activation barrier for the first reaction step (alkene oxidation step) to be 25.1 kcal/mol on singlet ground state which is higher than any alkene oxidation mentioned above (**Table 1.3**). According to Baldwin's proposed mechanism, the intermediate Mn(V) ester on singlet ground state can undergo a comproportionation into Mn(VI) by another MnO_4^- . Poethig and Strassner checked the possibility of reoxidation from Mn(V) into Mn(VI) using different oxidising agents either in the gas phase or in solution (PCM model) but this led to a thermodynamically unfavourable process and, therefore, they rejected the possibility of reoxidation. According to the reported results by Wolf and Ingold showing labelled oxygen incorporation into THF-diols, they proposed adding a water molecule to the intermediate Mn(V) **1.106**. They found that the addition of water into Mn(V) intermediate **1.106** giving Mn(V) **1.109** raised the energy by 4.3 kcal/mol, considering this as a thermoneutral process. They mentioned that water plays an important role in the reaction mechanism by significantly lowering the activation energies. Depending on the oxidation state of manganese, they also referred to different spin states. Their DFT calculations referred to that with or without water Mn(V) and Mn(III) intermediates preferred to be in a triplet and quintet spin multiplicity, respectively. They concluded that the reaction proceeds to the Mn(V) in the triplet state **1.06**, followed by the addition of a water molecule **1.109**, and cyclisation on quintet surface **1.110** to form the quintet product **1.111**.

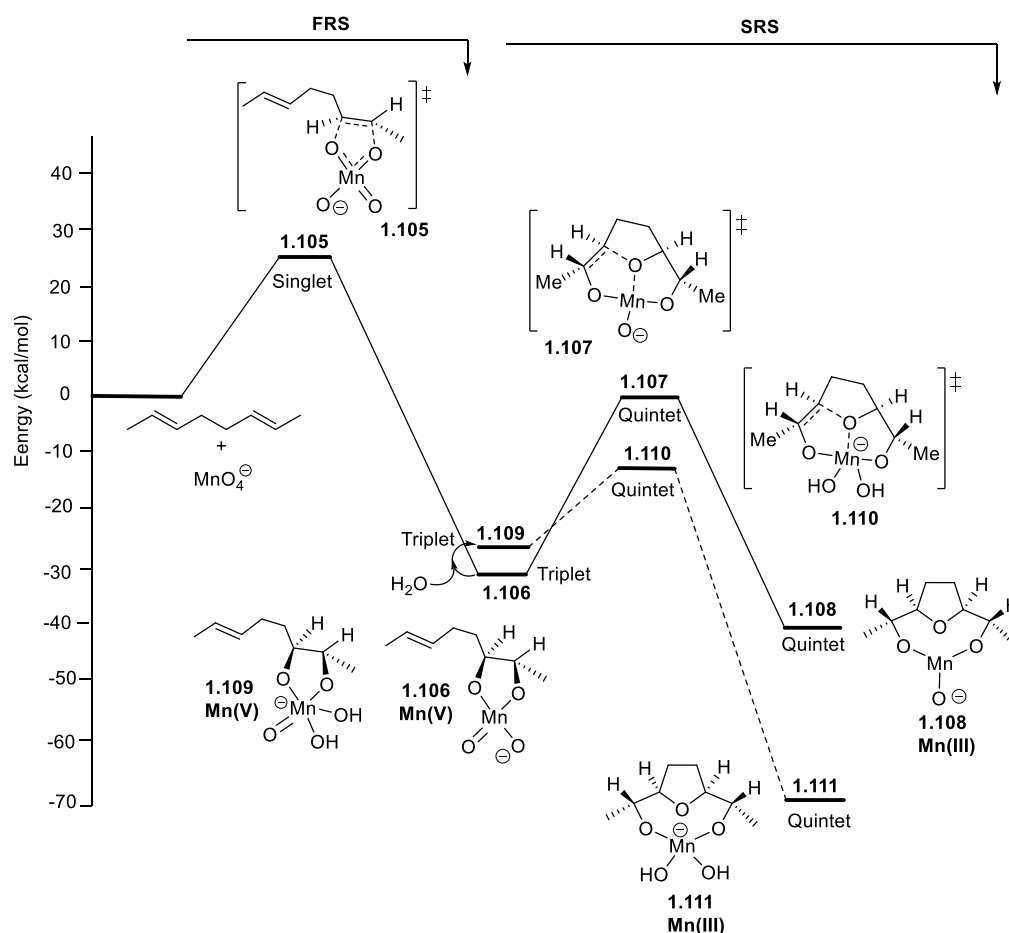


Figure 1.9: Suggested minimum energy pathway (MEP) for the oxidative cyclisation of 1,5-diene by permanganate ion from Poethig and Strassner study.¹¹⁷

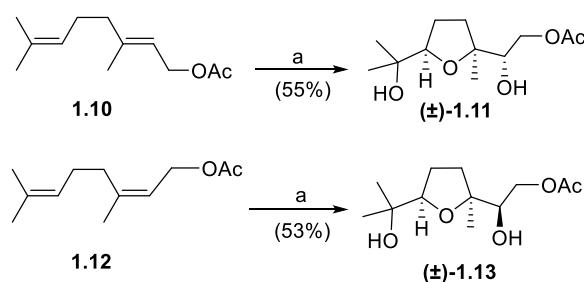
Overall, Poethig and Strassner's study showed the basic mechanistic proposal for the oxidative cyclisation of 1,5-dienes promoted by MnO_4^- . However, important considerations derived from experimental observations were not taken into account. Firstly, we believe that the level of theory both function and basis set are not suitable for the permanganate ion reactions, due to the treatment of the Mn atom. Secondly, it is very well-known that Mn(V) species are diamagnetic with low spin ($S = 0$) and that means intermediate Mn(V) glycolate is likely to be singlet spin rather than triplet spin state.^{118–122} This then suggests that cyclisation proceeds via a low spin transition state giving a singlet Mn(III) product rather than quintet. Thirdly, their calculated cyclisation step was not a (3+2) cycloaddition because the TS shows only THF ring formation due to the behaviour of function B3LYP. Furthermore, and most significantly, the role of acid is not considered because most of the reported literature describes oxidative cyclisation under moderately to weakly acidic conditions such as acetic acid or carbonic acid. Finally, their study did not explain the other pathways that can cause lower yields due to the comproportionation or disproportionation of Mn(V).

In summary, this study is in agreement with the basic mechanistic proposal for the oxidative cyclisation of 1,5-dienes by permanganate ion. However, the calculations did not fully consider experimental conditions. Therefore, we believe that it is important to re-evaluate the reaction mechanism computationally using a suitable level of theory.

1.1.3 Osmium-promoted oxidative cyclisation of 1,5-dienes

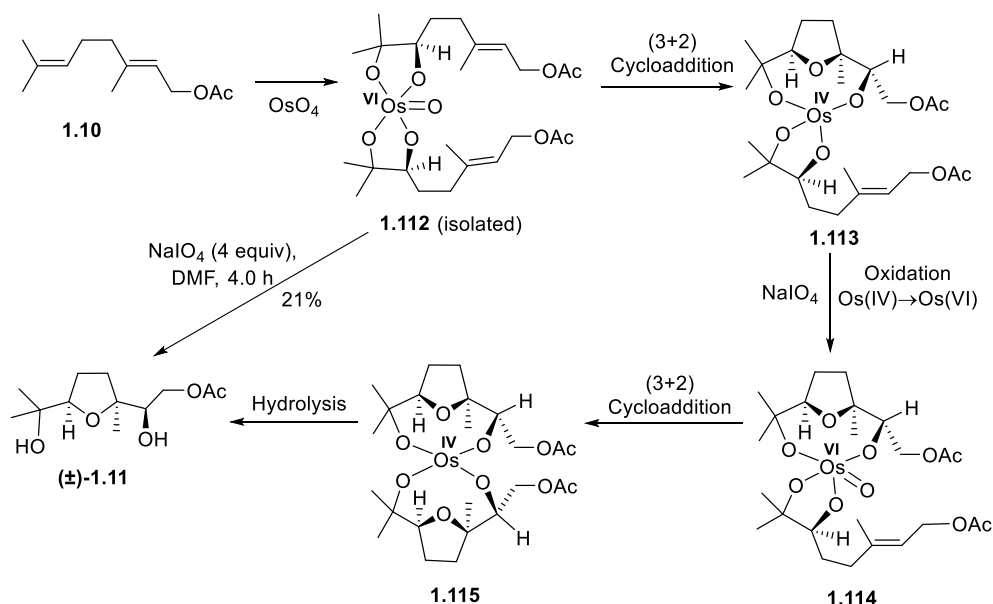
This section summarises the synthesis of THF-diols from the osmium-catalysed oxidative cyclisation of 1,5-dienes. Experimental and theoretical mechanistic studies on Os-promoted oxidative cyclisation and dihydroxylation will also be discussed.

Oxidative cyclisation of 1,5-dienes by osmium tetroxide (OsO_4) was first reported in 1998 by Piccialli *et al.* in DMF using sodium periodate as a co-oxidant.¹²³ Their oxidation led to moderate yields of the *cis*-THF-diol systems **1.11** and **1.13** either starting from *trans* geranyl acetate (**1.10**) or *cis* neryl acetate (**1.12**) respectively (**Scheme 1.20**).



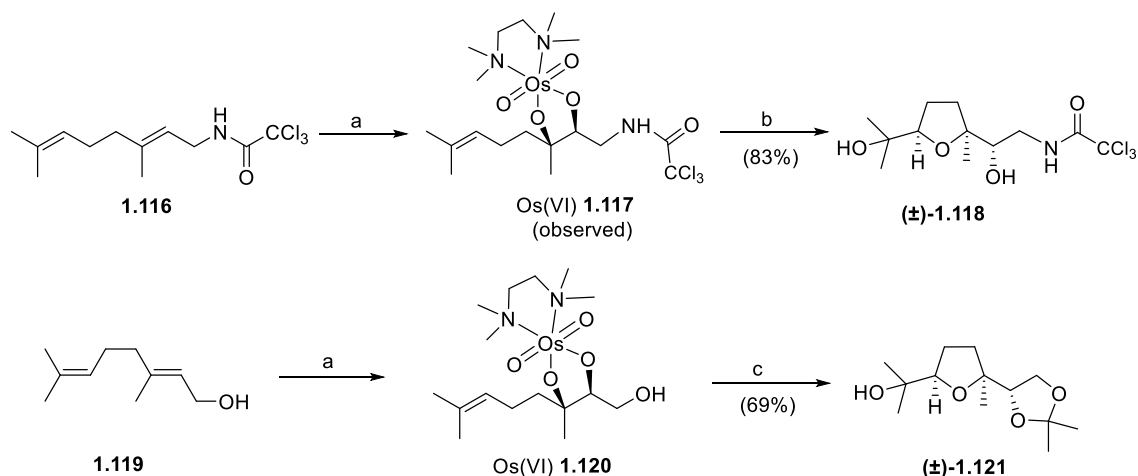
Scheme 1.20: Osmium-catalysed oxidative cyclisations of geranyl acetate (**1.10**) and neryl acetate (**1.12**) by OsO_4 . **Reagents and conditions:** a) OsO_4 (5.0 mol %), NaIO_4 (4.0 equiv), DMF, 16 h.

Under these reaction conditions geranyl acetate (**1.1**) also afforded the second cycle intermediate Os(VI) bisglycolate (**1.112**) (stereochemistry not determined) (**Scheme 1.21**). It was possible to obtain a low yield of THF diol (**1.11**) (21%) by subjecting an impure sample of **1.112** to $\text{OsO}_4/\text{NaIO}_4$ in DMF. The low yield could be explained by competition of other pathways from Os(VI) bisglycolate (**1.112**). Piccialli suggested that these results provide evidence for the bisglycolate as an intermediate in oxidative cyclisation. Replacing the co-oxidant NaIO_4 with *N*-methylmorpholine-*N*-oxide (NMO), the oxidation of 1,5-diene led to conventional dihydroxylation product, and none of the oxidative cyclisation product was obtained. In the case of reaction using NMO, the second cycle bisglycolate Os(VI) complex (**1.112**) was observed. Indeed, dihydroxylation is the observed outcome when typical Os-catalysed dihydroxylation, or asymmetric dihydroxylation conditions are applied to dienes and polyenes.^{124–126} Additionally, it is not known whether the Os-catalysed oxidative cyclisation reaction proceeds via complex **1.112** or not.



Scheme 1.21: Piccialli's proposed mechanism for the Os-catalysed oxidative cyclisation of 1,5-diene **1.10**.

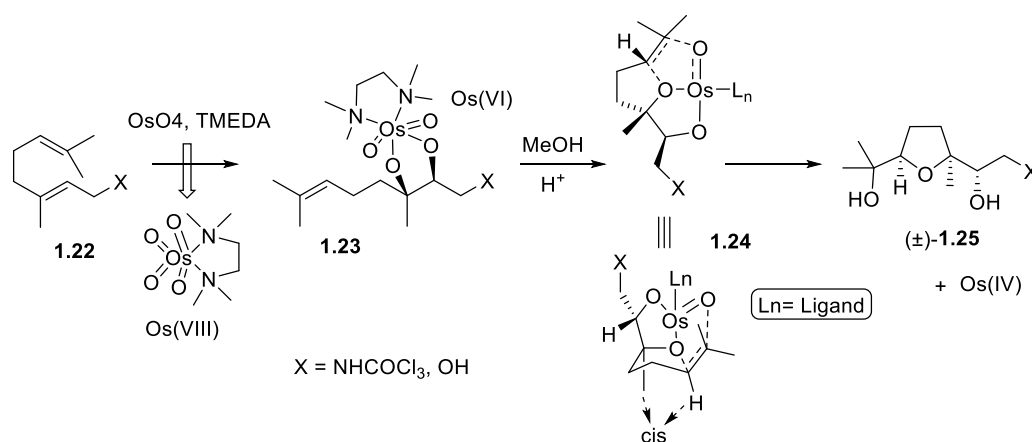
A combination of OsO₄ and tetramethylethylenediamine (TMEDA) was used for the oxidative cyclisation of 1,5-functionalised dienes by Donohoe *et al.* leading to the *cis*-THF diols **1.118** and **1.121** in good yields (**Scheme 1.22**).¹²⁷ It was thought that the OsO₄/TMEDA combination provides a hydrogen bond acceptor which can direct the regioselectivity of the initial osmylation, leading to isolation of glycolates **1.117** and **1.120** which provided further strong evidence to support the initial step of the Baldwin mechanism. Exposure of the intermediate Os(VI) glycolate esters to acidic conditions promoted the cyclisation to form THF-diols.



Scheme 1.22: Synthesis of THF-diols using OsO₄/TMEDA complex followed by acidic treatment.

Reagents and conditions: a) OsO₄ (1.0 equiv), TMEDA (1.0 equiv), CH₂Cl₂, -78 °C; b) MeOH, HCl, rt; c) (MeO)₂CMe₂, TFA.

Donohoe *et al.* suggested a mechanism for the oxidative cyclisation by OsO_4 /TMEDA based on the (3+2) cycloadditions proposed by Baldwin *et al.*⁴³ for permanganate-promoted oxidative cyclisation (**Scheme 1.23**). Here, the oxidation number of the osmium reduces from Os(VIII) into Os(VI) and then acidic exposure affords the THF system **1.125**. It was thought that the acid can serve either to promote the rapid ligand exchange to allow the cyclisation or protonate the oxo–ligand species. The protonation of the oxo–ligand species will make the osmium–oxo species a better electrophile and more reactive towards cyclisation. The mechanism shows that the stereoselectivity of the THF ring can be explained by the transition state structure **1.124**, in which the intact glycol osmium bonds provide the stereochemistry across the incipient THF ring.¹²⁸ Significantly, the reaction shows cyclisation of an Os(VI) intermediate.



Scheme 1.23: Donohoe's proposed mechanism of OsO_4 /TMEDA oxidative cyclisation under acid conditions.

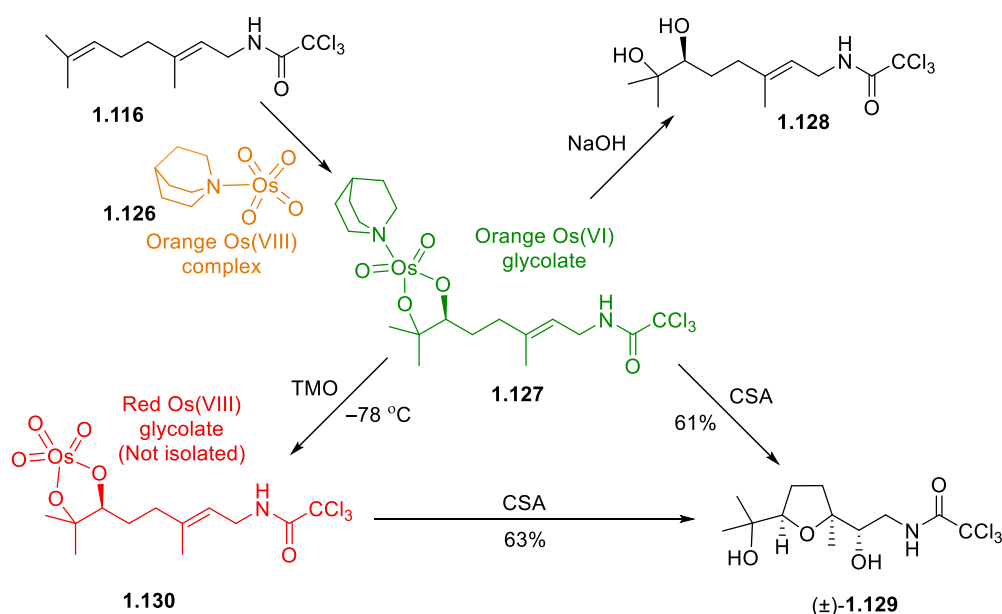
1.1.3.1 Donohoe's developments of the catalytic oxidative cyclisation reactions using OsO_4

Piccialli's discovery of the osmium tetroxide catalysed oxidative cyclisation represented an important development. However, some of the drawbacks in Piccialli's procedure are worth consideration. Using a strong reoxidant such as NaIO_4 led to the formation of overoxidised side products and resulted in lower reaction yields. In Piccialli's work only two dienes were shown to be amenable to the reaction conditions, and the full scope of the conditions was not explored. Since the dihydroxylation of alkenes by OsO_4 can proceed by a second cycle, the possibility of entering a second cycle could affect the yield of the oxidative cyclisation.

Donohoe and co-workers have conducted extensive studies on the catalytic OsO_4 oxidative cyclisation of 1,5-dienes leading to reliable and efficient catalytic version of the reaction.³⁴ They first examined the requirement for an appropriate acid that allows for efficient cyclisation (**Scheme 1.22**). They found that the use of strong acid was necessary for cyclisation, and camphorsulfonic

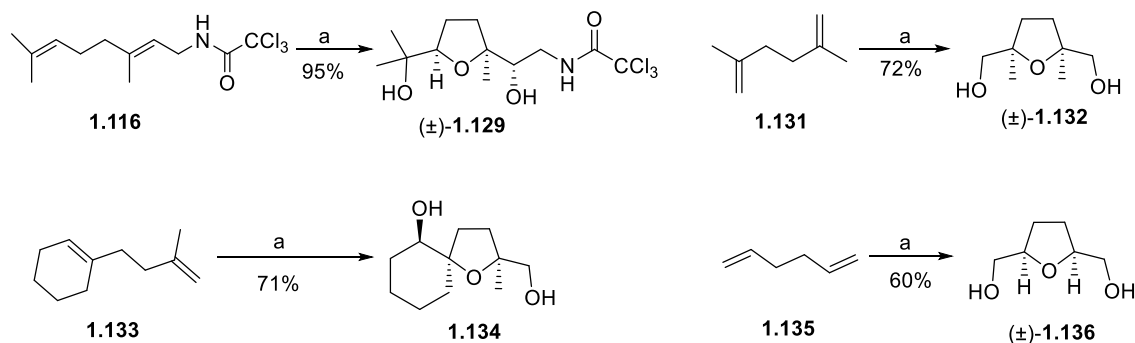
acid (CSA) was identified to deliver excellent results. Mildly acidic, neutral, or basic conditions failed to promote cyclisation or cleaved the glycolate ester (**Scheme 1.24**). In early work they noted that it was not known whether strongly acidic conditions were needed to promote the cyclisation step itself, or simply to first cleave the TMEDA ligand from the osmium prior to cyclisation. Using such a strong acid can presumably cleave the TMEDA ligand due to the driving force of ammonium salt formation. Therefore, the role of acid will firstly promote and facilitate the cyclisation step and secondly promote release of THF-diol.

Donohoe's team probed the reaction mechanism using stoichiometric experiments in which they visibly checked the colour of the solution at each addition (**Scheme 1.24**). When geranyl trichloroacetate (**1.116**) was subjected to quinuclidine and osmium tetroxide at $-78\text{ }^{\circ}\text{C}$, an orange-red complex **1.126** between quinuclidine and osmium tetroxide was initially obtained, and as this warmed to $-50\text{ }^{\circ}\text{C}$, a green Os(VI) glycolate complex **1.127** formed (not isolated). The formation of Os(VI) glycolate **1.127** is pivotal, and represents the key intermediate for formation of vicinal diol or THF-diol. Addition of NaOH to **1.127** resulted in Os–O bond cleavage furnishing diol **1.128**. Correspondingly, the addition of trimethylamine *N*-oxide (TMO) to **1.127** led to a colour change to red. The authors interpreted this colour change to be oxidation of the Os(VI) dioxoglycolate to Os(VIII) trioxoglycolate **1.130**. Subsequently, cyclisation occurred with CSA to give THF-diol **1.129** in 63% yield. Furthermore, treating **1.127** with CSA also afforded THF-diol **1.129** in 61% yield. In this case, cyclisation of an Os(VI) intermediate into THF-diol can be carried out in the absence of TMO. From this study, they have concluded that; firstly, TMEDA or other tertiary amines were not necessary for oxidative cyclisation; secondly, both Os(VI) and Os(VIII) glycolates can cyclise onto a pendant alkene to give THF-diol product.



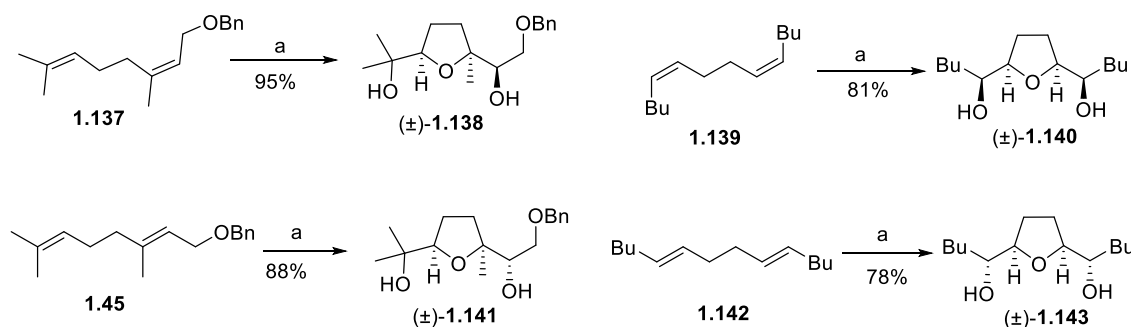
Scheme 1.24: Donohoe and co-workers investigations on the oxidative cyclisation of diene **1.116** using stoichiometric osmium.

At this point, Donohoe and co-workers started to look for a suitable reoxidant mild enough to avoid overoxidation of the THF-diol products, and still allow osmium tetroxide to be used catalytically. They found that TMO, a well-known reoxidant in osmium catalysed dihydroxylation of olefines,¹²⁹ was effective under acidic conditions, giving a yield of 95% of the THF-diol ($\pm$)-**1.129** from for geranyl geranyl trichloroacetate (**1.116**, **Scheme 1.25**).¹³⁰



Scheme 1.25: Catalytic use of OsO_4 as oxidising agent under acidic conditions. **Reagents and conditions:** a) OsO_4 (5.0 mol %), Me_3NO (4.0 equiv), CSA (6.0 equiv), CH_2Cl_2 .

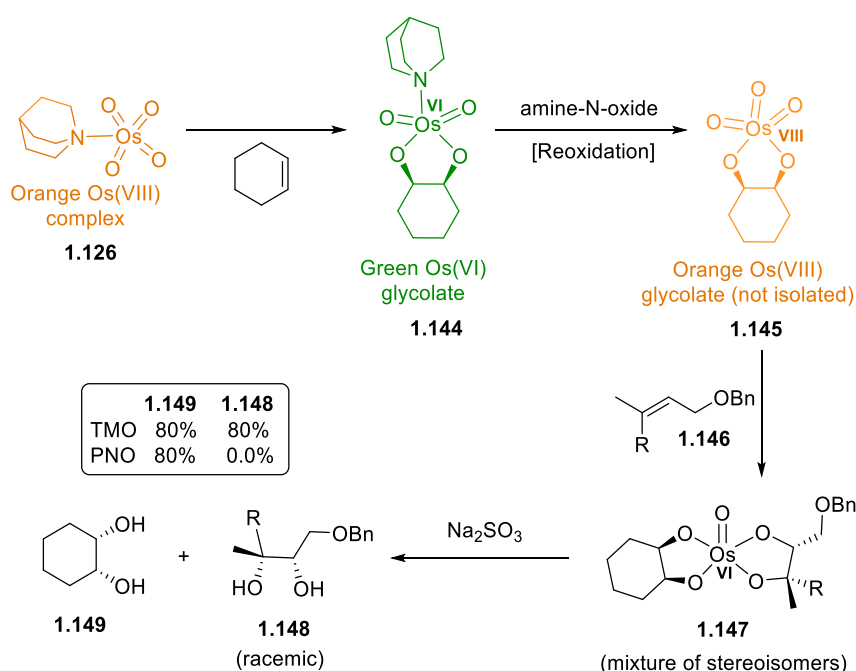
The oxidative cyclisation of dienes **1.131**, **1.133** and **1.135** under acidic conditions furnished THF-diols **1.132**, **1.134** and **1.136** with 72%, 71% and 60% yields respectively without over oxidised products (**Scheme 1.25**). However, dienes **1.137**, **1.139**, **1.45** and **1.142** were unreactive toward cyclisation and instead returned diols (**Scheme 1.26**). Therefore, Donohoe's group screened different solvents to cyclise nerol benzyl ether (**1.137**). It was found that using an excess of trifluoroacetic acid (TFA) in a 9:1 mixture of acetone/water promoted cyclisation in 95% yield in the case of diene **1.137** and 81%, 88% and 78% yields for dienes **1.139**, **1.45**, and **1.142** respectively. This was a notable success for the cyclisation of di and trisubstituted alkenes with such high yields.



Scheme 1.26: OsO_4 catalysed oxidative cyclisation under aqueous acidic conditions. **Reagents and conditions:** a) OsO_4 (5.0 mol %), Me_3NO (4.0 equiv), TFA (excess), acetone: H_2O (9:1).

Furthermore, comparisons between the reoxidants pyridine-N-oxide (PNO) and TMO were undertaken by Donohoe's group to confirm the milder oxidising properties of PNO to avoid

Reoxidation of Os(VI)→Os(VIII) and restrict the reaction to an Os(VI)/Os(IV) cycle rather than Os(VIII)/Os(VI) cycle (**Scheme 1.27**).^{34,131} The addition of cyclohexene to the orange complex **1.126** gave green Os(VI) glycolate **1.144** which was followed by addition of TMO to result in formation of putative orange Os(VIII) glycolate **1.145**.¹³² To investigate the formation of Os(VIII) glycolate, alkene **1.146** was added and the Os(VI) bisglycolate **1.147** was believed to be formed. The latter underwent reductive hydrolysis to furnish two diols **1.148** and **1.149** in a 1:1 ratio and 80% yield. In contrast, when Os(VI) glycolate **1.145** was treated with PNO no color change was observed and subsequently no Os(VI) bisglycolate (**1.40**) was formed because the Os(VI) glycolate (**1.37**) was unable to oxidise the second alkene **1.146** and, therefore, only diol **1.142** was obtained upon hydrolysis.



Scheme 1.27: Donohoe's stoichiometric experiment comparison between TMO and PNO.

The oxidative cyclisation of 1,5-dienes using catalytic amounts of OsO₄ (5 mol %) under acidic conditions led to remarkably high yields of THF-diols.^{130,133,134} The precise role of the acid in Donohoe's oxidative cyclisation is not known, but they suggested a mechanism in which the cyclisation step proceeds via protonation of one of the oxo ligands of Os(VI) glycolate intermediate (**Figure 1.7**). One of the possible reason is that 2nd (3+2) cycloaddition is an inverse electron demand process with the alkene site being the electron-rich 2e⁻ component (HOMO) and the :O–Os=O moiety is the electron-poor 4e⁻ component (LUMO). Thus, protonation of an oxo ligand will lower the energy of the LUMO orbitals, and leads to a reduced energy gap resulting in a more favourable cyclisation. Donohoe and co-workers stated that this suggestion is analogous to the Lewis acid catalysed 1,3-dipolar cycloaddition (3+2) cyclisation of vinyl ethers with nitrones, where

coordination of oxygen of the nitron to a Lewis acid lowers the LUMO energy and facilitates an inverse electron demand cyclisation.¹³⁵

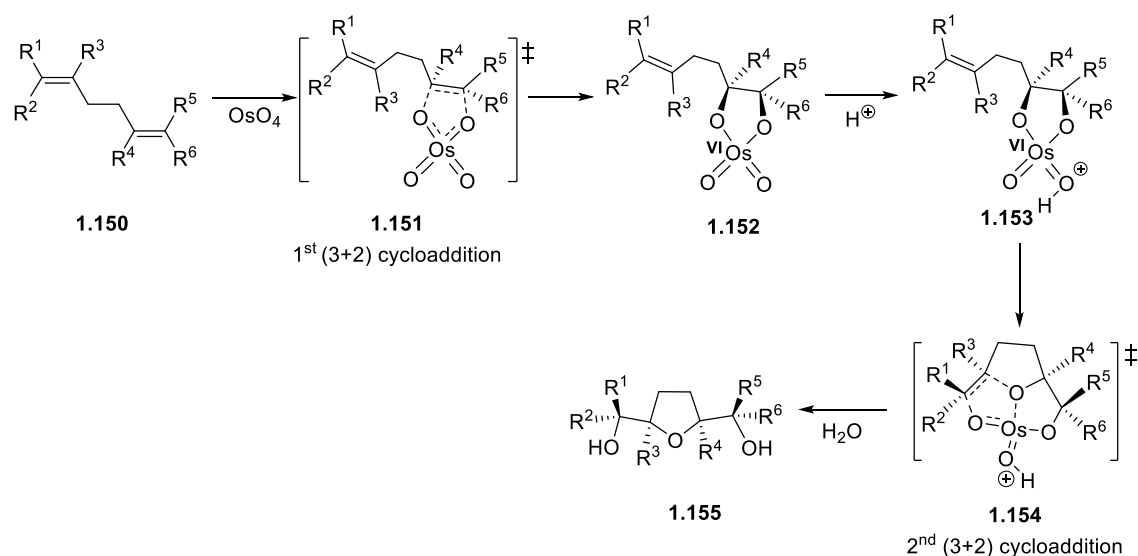


Figure 1.10: Donohoe's proposed mechanism for the oxidative cyclisation of 1,5-diene under acidic conditions.

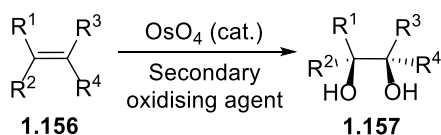
1.1.4 DFT studies on the Os-catalysed oxidative cyclisation of 1,5-dienes

DFT simulations for the OsO₄ oxidative cyclisation of 1,5-diene are important tools in understanding the mechanistic pathways. Very little computational work has been carried out on this mechanism. Since the reaction has two main steps; the alkene oxidation step (first reaction step) and the cyclisation step (as a second reaction step), the next sections will describe the most important computational and experimental studies that have been performed on OsO₄ dihydroxylation of alkenes and computational studies on OsO₄ oxidative cyclisation of 1,5-dienes.

1.1.4.1 General overview of OsO₄ dihydroxylation of alkenes

The use of osmium tetroxide in selective dihydroxylation of alkenes has been known for more than 110 years (**Scheme 1.28**).¹³⁶ It has become one of the most efficient catalytic reactions developed in the laboratory,¹³⁷ which utilises a secondary oxidizing agent (SOA).^{138–144} The most commonly use of the SOA's are the amine *N*-oxides (ANO) such as *N*-methylmorpholine *N*-oxide (NMO), trimethylamine *N*-oxide (TMO), and pyridine *N*-oxide (PNO) in addition to potassium hexacyanoferrate(III) (K₃Fe(CN)₆).^{140,145–158} As it is an extremely reliable and powerful reaction, numerous synthetic approaches to *syn*-diols have been developed and published over the last 100 years. In fact, the *cis*-dihydroxylation is one of the cornerstone reactions of organic synthesis, especially the asymmetric

version of the reaction.^{159,160} The diol moiety is a common motif in many biologically active natural products and important intermediates in many syntheses.^{161–163} The total synthesis of alkaloids,^{164–171} lactones,^{172–180} amino acids,¹⁸¹ lipids,^{182–186} polyketides,^{187–190} terpenes,^{191–195} macrolides,^{196–205} cyclic ethers,^{6,206–212} flavonoids,^{213–215} pyrans,^{216–221} and many others^{222–232} rely on the use of OsO₄ in dihydroxylation.



Scheme 1.28: Dihydroxylation of alkenes by OsO₄.

Two well-known methods of catalytic dihydroxylation using OsO₄ with a SOA are the Upjohn¹⁴⁹ and Sharpless^{193,233} dihydroxylations. The latter is an asymmetric dihydroxylation (AD) of alkenes using cinchona alkaloid-derived ligands to achieve enantioselectivity.^{154,233–238} The OsO₄-chiral alkaloid ligand complex (DHQD) (**Figure 1.8**) was reported soon after the discovery of the NMO based version of the AD.²³⁹

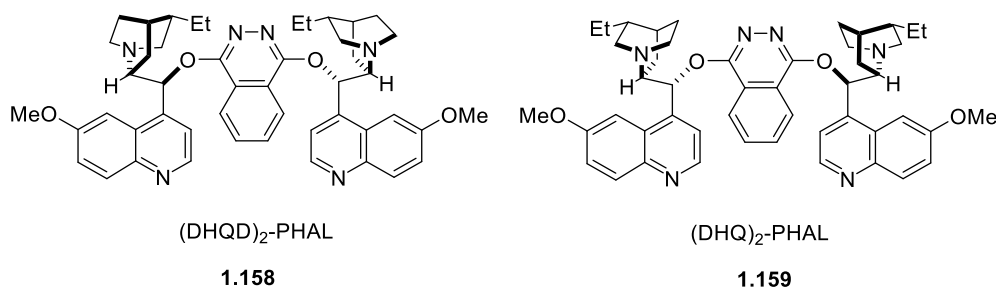


Figure 1.11: The catalysts used in asymmetric dihydroxylation approach. DHQD₂ (left) is used in AD-mix-β whilst DHQ₂ (right) is used in the AD-mix-α. Both comprise of two cinchona alkaloid derivatives coupled by a central phthalazine linker.

Several mechanistic studies have been published for both traditional stoichiometric (without SOA) and catalytic (with SOA) OsO₄ oxidation of alkenes.^{155–158} Sharpless stated that *syn*-diol formation is first order in alkene and also first order in OsO₄ in both stoichiometric and catalytic process using NMO as a SAO in aqueous *t*-butanol. He also indicated that the rate-determining step (RDS) is the initial addition of OsO₄ to the double bond in a (3+2) cycloaddition manner giving a dioxomonoglycolatoosmium(VI) adduct.^{154,233–235} Debates about the differences between (3+2) and [2+2] cycloaddition pathways will be described later, although we will assume a (3+2) process for the following discussions.

Few reports related to the electronic and stereoelectronic effects on turnover or product distribution in the osmium-catalysed dihydroxylations have appeared in the literature.^{240–242} Most mechanistic interpretations are mainly based on product distributions and are speculative because the catalytic cycle comprises of several poorly defined steps. These steps include reoxidation of Os(VI) into Os(VIII) glycolate prior to hydrolysis, the competition between the hydrolysis of Os(VI) or Os(VIII) glycolates, and the possibility for a second cycle. Little is known about these steps in the proposed “second cycle” (see **Figure 1.12**).^{234,243}

The Sharpless or Upjohn dihydroxylation process are complicated by a potential secondary catalytic cycle, meaning that there are at least two diol-producing cycles (**Figure 1.12**).^{153,234} The second cycle may have a negative effect on the efficiency of the reaction, particularly relating to enantioselectivity. It is believed that the second cycle is responsible for lowering the selectivity of the AD in a dramatic way. If the Os(VI) glycolate intermediate **1.160** is oxidised to Os(VIII) glycolate before it dissociates, then the resulting Os(VIII) glycolate may dihydroxylate another alkene with lower enantioselectivity.

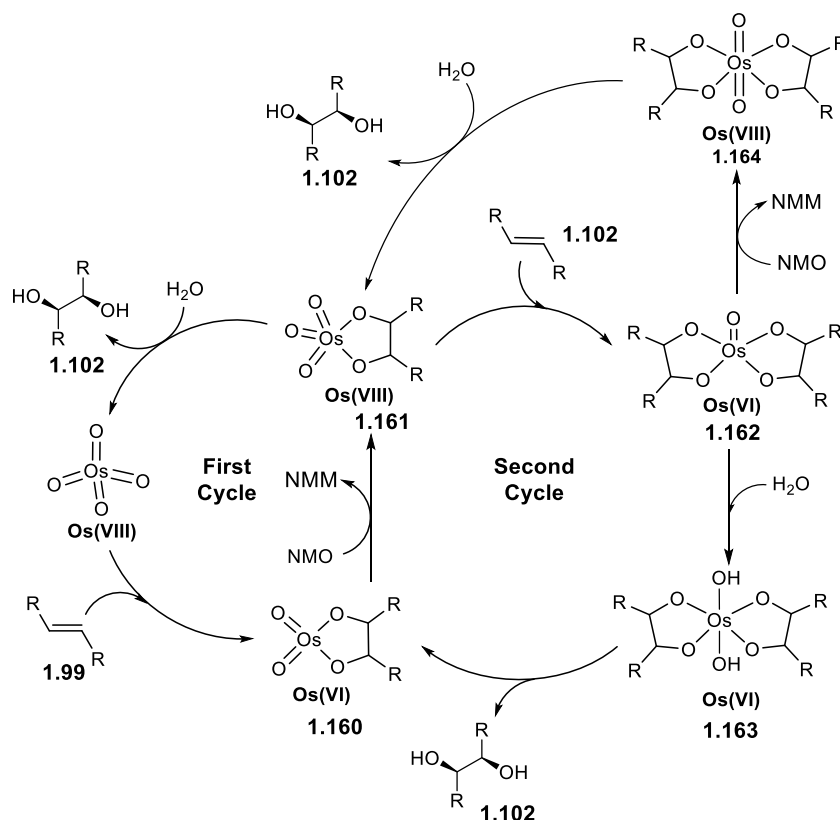


Figure 1.12: Dihydroxylation of alkenes by OsO_4 using NMO as SOA, showing the two proposed catalytic cycles.

The key problem is that the putative Os(VIII) trioxoglycolate **1.161** occupies the pivotal position at the junction between the two cycles (**Figure 1.12**). Sharpless and co-workers proved the existence

of the second cycle.¹¹¹ They performed dihydroxylation experiment under anhydrous conditions in toluene. When one equivalent of OsO_4 was allowed to react with an olefin, an emerald green Os(VI) glycolate **1.160** was formed.²⁴⁴ When a different olefin was added and followed by an equivalent of anhydrous NMO, a rapid formation of bisglycolate Os(VI) **1.162** was observed and then a 1:1 ratio of each diol was liberated after reductive hydrolysis.²⁴⁵ The second cycle works as efficiently as the first cycle in producing diols from olefines. In the context of AD, they indicated that achieving high enantioselectivities require the second cycle to be minimised. It was found that if alkene was added slowly, high selectivities were observed because Os(VIII) **1.161** needs a sufficient time to undergo hydrolysis rather than get trapped into the second cycle by reacting with another olefin. It is worth pointing out that the trioxoglycolate **1.161** and dioxobisglycolate **1.162** have not been isolated from the reaction mixtures, or characterised by other means.

Additional support for the proposed second cycle, came from adding sodium citrate to the AD reaction. The level of enantioselectivity achieved in asymmetric dihydroxylations of styrene reduced to almost zero even in the presence of small amount of added citrate (**Figure 1.10**).²⁴³ It is proposed that citrate shunts the dihydroxylation process almost exclusively into second cycle, which is a non-enantioselective catalytic cycle.

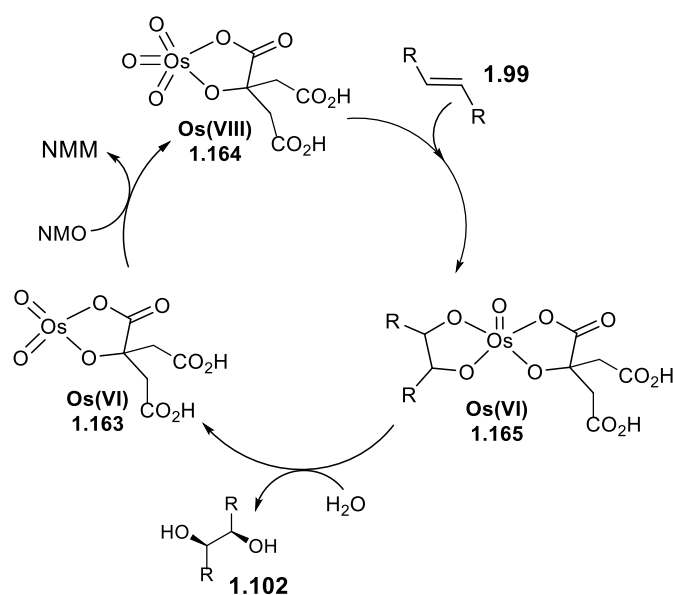


Figure 1.13: Prevailing catalytic cycle in dihydroxylations with added citric acid.

1.1.4.2 Computational simulations on alkene oxidation by OsO_4

This first reaction step of alkene oxidation has been studied in detail over the last 20 years using computational chemistry approaches, where the energy barrier and reaction energy were

calculated depending on the type of cycloaddition; either (3+2) or [2+2] cycloaddition (**Figure 1.11**).^{47,102–105,108,110–113,116,246–255} For the formation of Os(VI) esters, the scientific debate about the (3+2) cycloaddition (forming a five-membered transition state) and [2+2] cycloaddition (forming osmaoxetane via an alkene complex) has been resolved in favour of the (3+2) cycloaddition mechanism. The proposed [2+2] pathway is highly energetic in terms of kinetic and thermodynamic aspects. DelMonte *et al.*¹⁰⁵ studied the osmium tetroxide mediated dihydroxylation of alkenes with and without an amine within the B3LYP/6-31G(d) level of theory. They found the $\text{OsO}_4 \cdot \text{NH}_3$ has a lower activation barrier and is more exergonic compared to oxidation without ammonia. They also confirmed that (3+2) pathway is significantly favoured over the [2+2] pathway.

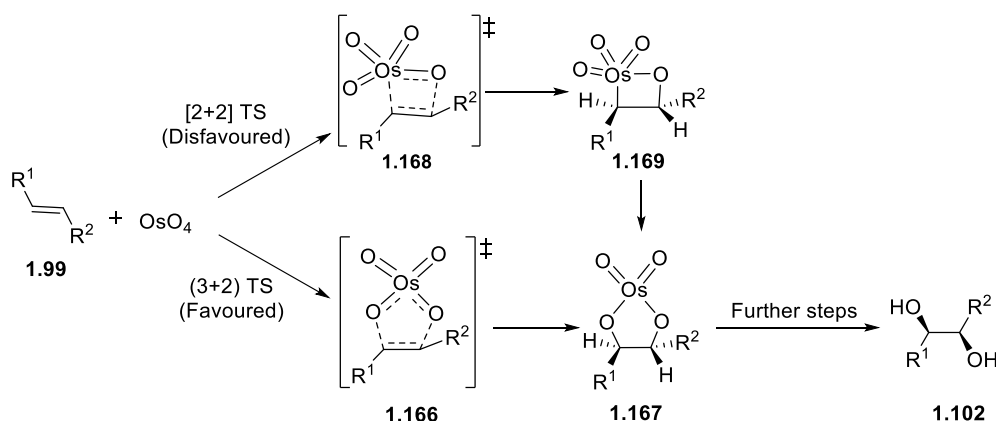


Figure 1.14: Proposed reaction mechanism of alkene osmylation.

1.1.4.3 DFT Calculations for oxidative cyclisation of 1,5-dienes

In 2010, Poethig and Strassner²⁵⁶ studied the reaction mechanism of the oxidative cyclisation of 1,5-dienes by osmium tetroxide using the same level of theory that had been used for permanganate ion oxidative cyclisation (B3LYP with the basis set 6-311+G(d) for C, H, O atoms and Hay-Wadt VDZ (n+1) ECP for Os atom) (**Figure 1.15**). Different pathways were proposed to understand the reaction mechanism. Here, the addition of a water molecule to the intermediate produced from the FRS did not show a comparable stabilisation in energy which was in contrast to their findings for the permanganate oxidative cyclisation.¹¹⁷ They found that increasing the spin multiplicity from singlet into quintet led to an increase in the energy of reaction. They reported that the energy barrier for the first reaction step was significantly lower compared to that for permanganate, which they suggested might be a reason for the advantage of using osmium tetroxide in some reactions where the transformation with permanganate fails. This seems unlikely to us because the permanganate oxidative cyclisation is rapid, even at temperatures as low as -78°C , whereas the osmium-promoted or catalysed reactions are much slower. Another point

mentioned in their work is that reoxidation of Os(VI) into Os(VIII), based purely on thermodynamic data, led to noticeable decrease in the activation barrier for the cyclisation step (**Figure 1.13**).

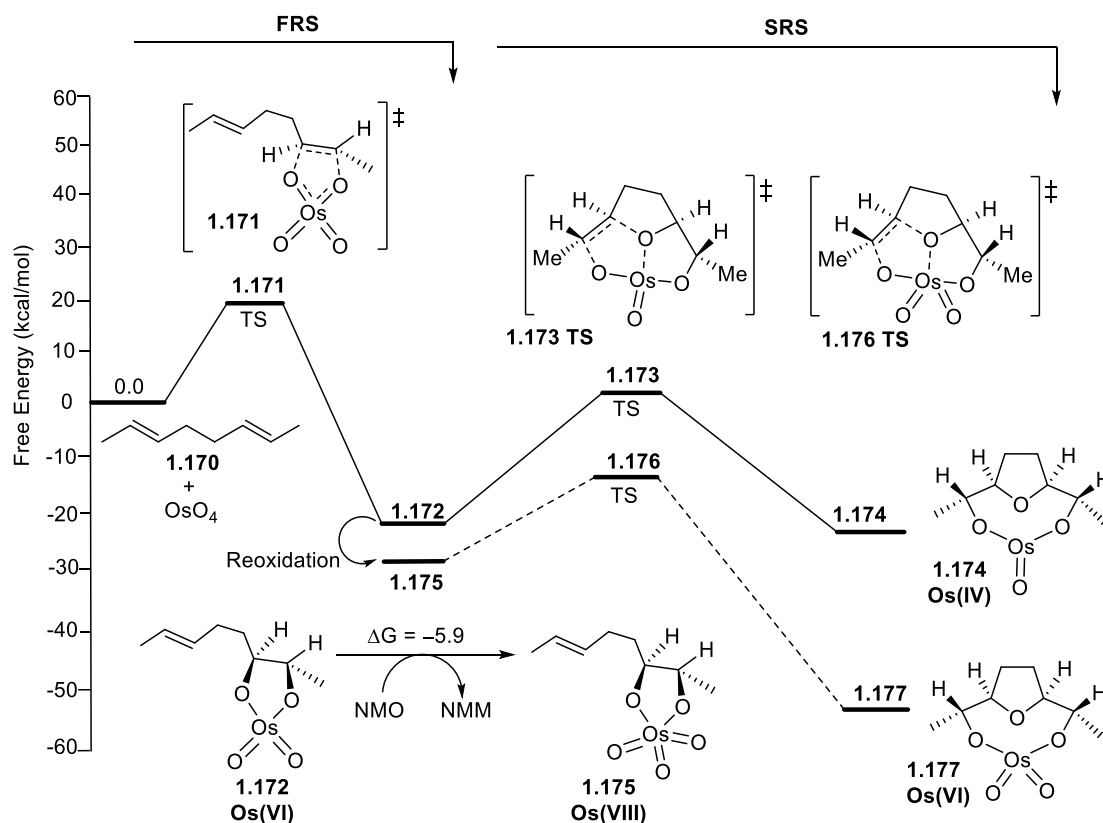


Figure 1.15: Energetic profile for the oxidative cyclisation of 1,5-diene **1.170** by OsO₄ calculated by Poethig and Strassner using the B3LYP/6-311+G(d)/ECP level of theory in gas phase.²⁵⁶

Overall, their DFT studies supported the basic mechanistic proposal for the oxidative cyclisation of 1,5-dienes catalysed by OsO₄. However, there are many important considerations, derived from experimental observations that were not taken into account. Most significantly, the role of acid (Bronsted or Lewis) was not considered at all; the SRS is known to be viable through an Os(VI) intermediate (see Scheme **1.10** and **1.22**) under acidic conditions.³⁴ Additionally, examples of oxidation of 1,5-dienes (and polyenes) catalysed by OsO₄ using NMO as the terminal oxidant, where reoxidation to form an Os(VIII) trioxoglycolate intermediate occurs, do not result in oxidative cyclisation and instead yield dihydroxylated products.^{123,257} This is to say, when acid is not present, normal dihydroxylation is the preferred/only observed pathway. Where Os(VIII) trioxoglycolate intermediates are present, an alternative reaction manifold, namely intermolecular osmylation (the so-called second cycle),^{193,234} competes with cyclisation. This pathway was not considered in the 2010 study. Therefore, the conclusion that the reaction proceeds through direct cyclisation of an Os(VIII) intermediate seemed doubtful to us, or at least, incomplete.

1.1.5 Conclusions

Oxidative cyclisations of 1,5-dienes using transition-metal-oxo species stand out as one of the most direct methods for stereoselective formation of THF diols, transforming simple starting materials into structurally complex products in a single reaction. It is a powerful reaction used in THF-diol natural product synthesis due to the stereospecific manner, and ability to control absolute stereochemistry.

Permanganate-mediated oxidative cyclisation has been shown to be an efficient method in THF-diol synthesis and for the dihydroxylation of alkenes. Key reaction features include the ability to employ chiral auxiliaries and chiral phase transfer catalyst to obtain enantiomerically enriched products. In comparison to other metal oxo agents such as OsO_4 or Ru oxo, oxidative cyclisation of 1,5-dienes by MnO_4^- is the only process that can directly transform 1,5-dienes to enantiomerically enriched products. Asymmetric oxidative cyclisation reactions using OsO_4 and Ru oxo species are typically performed on an enantioenriched dihydroxyalkene in order to achieve enantioenriched THF diols. In addition, permanganate ion is a cheap, and safe oxidising agent compared to others oxo agents, which allows it to be suitable for research laboratory scale and industrial applications. However, oxidative cyclisation using MnO_4^- does typically proceed with yields lower than the analogous reaction of Ru and Os.

The reaction mechanism for the permanganate-mediated oxidative cyclisation of 1,5-dienes has been presented according to currently accepted proposal by Baldwin, and similarly the osmium-promoted oxidative cyclisation mechanism has been proposed. However, for the permanganate-mediated reaction, it is still not clear whether cyclisation proceeds via a Mn(VI) or Mn(V) glycolate intermediate. Also, for the osmium-promoted reaction, it is not clear whether cyclisation occurs via Os(VI) or Os(VIII) glycolate intermediates. DFT studies investigated only the basic mechanistic proposal for the oxidative cyclisation of 1,5-dienes by MnO_4^- or OsO_4 , in which important considerations derived from experimental observations were not taken into account. Most significantly, the role of acid was not considered in these DFT studies, in which different reaction manifolds would be then encountered.

1.2 Aims and objectives

The objectives of this thesis can be considered in two parts. The first part concerns an experimental investigation of the asymmetric oxidative cyclisation of 1,5-dienoates in the presence of chiral phase transfer catalyst. The second part involves an in-depth theoretical study of the mechanisms of oxidative cyclisation by MnO_4^- and OsO_4 leading to the THF-diol product. The key aims and plan of this thesis research are summarised below:

- 1) Experimental studies involves permanganate-mediated oxidative cyclisation of 1,5-dienoates with **CPTC**, determining enantioselectivity and the absolute stereochemistry of the major product (**Figure 1.16**).

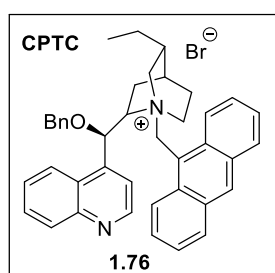
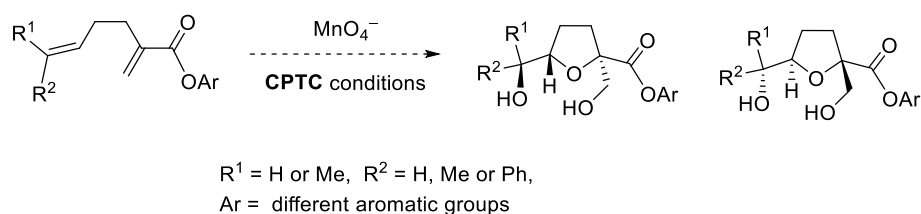


Figure 1.16: Permanganate-mediated oxidative cyclisation of 1,5-dienoates using **CPTC** conditions.

Extend the results to oxidative cyclisation of 1,5-dienes to 1,5,9-trienoate for the purpose of synthesising natural products such as eurylene (**Figure 1.17**).

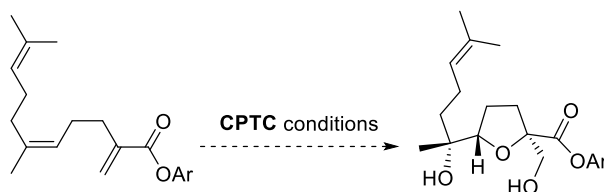


Figure 1.17: Permanganate-mediated oxidative cyclisation of 1,5,9-trienoate using **CPTC** conditions.

- 2) Theoretical studies using DFT calculations to realise an improved understanding of the reaction mechanism for the oxidative cyclisation of 1,5-dienes by MnO_4^- and OsO_4 , and relating the findings to experimental observations. The oxidative cyclisation reactions will be considered as two reaction steps, namely manganation/osmylation and cyclisation. Understanding the role of acid in the permanganate-mediated and osmium oxidative cyclisations will be a key part of these studies. Since both MnO_4^- and OsO_4 oxidative cyclisations have been reported to involve possible reoxidation of Mn(V) glycolate and Os(VI) glycolate into Mn(VI) and Os(VIII) respectively, exploration of these steps is crucial. The proposals to be investigated are summarised in **Figure 1.18**.

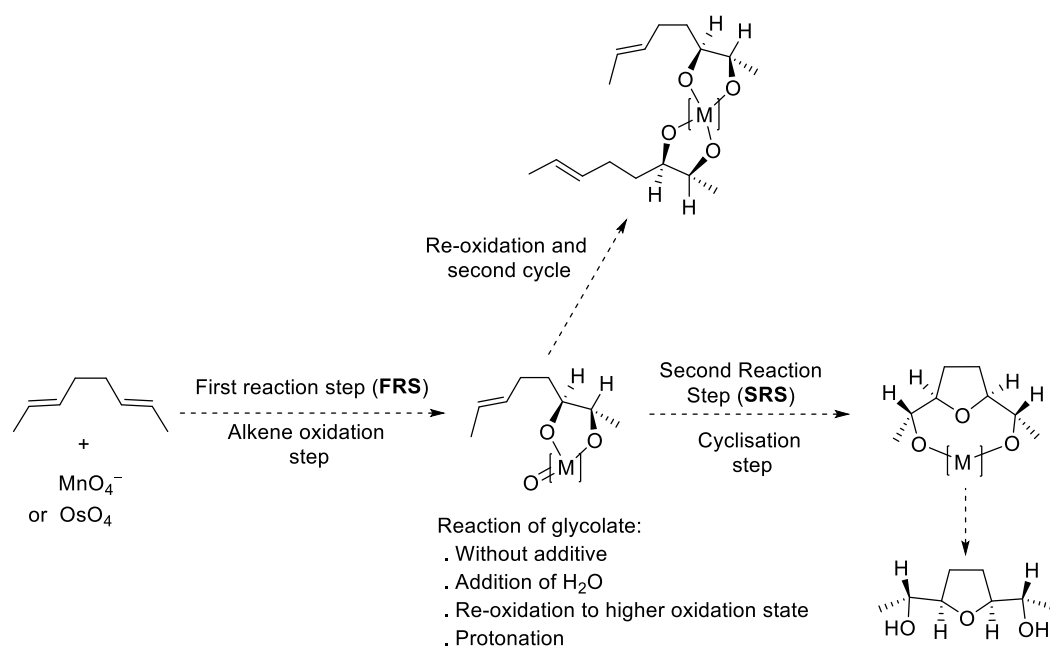


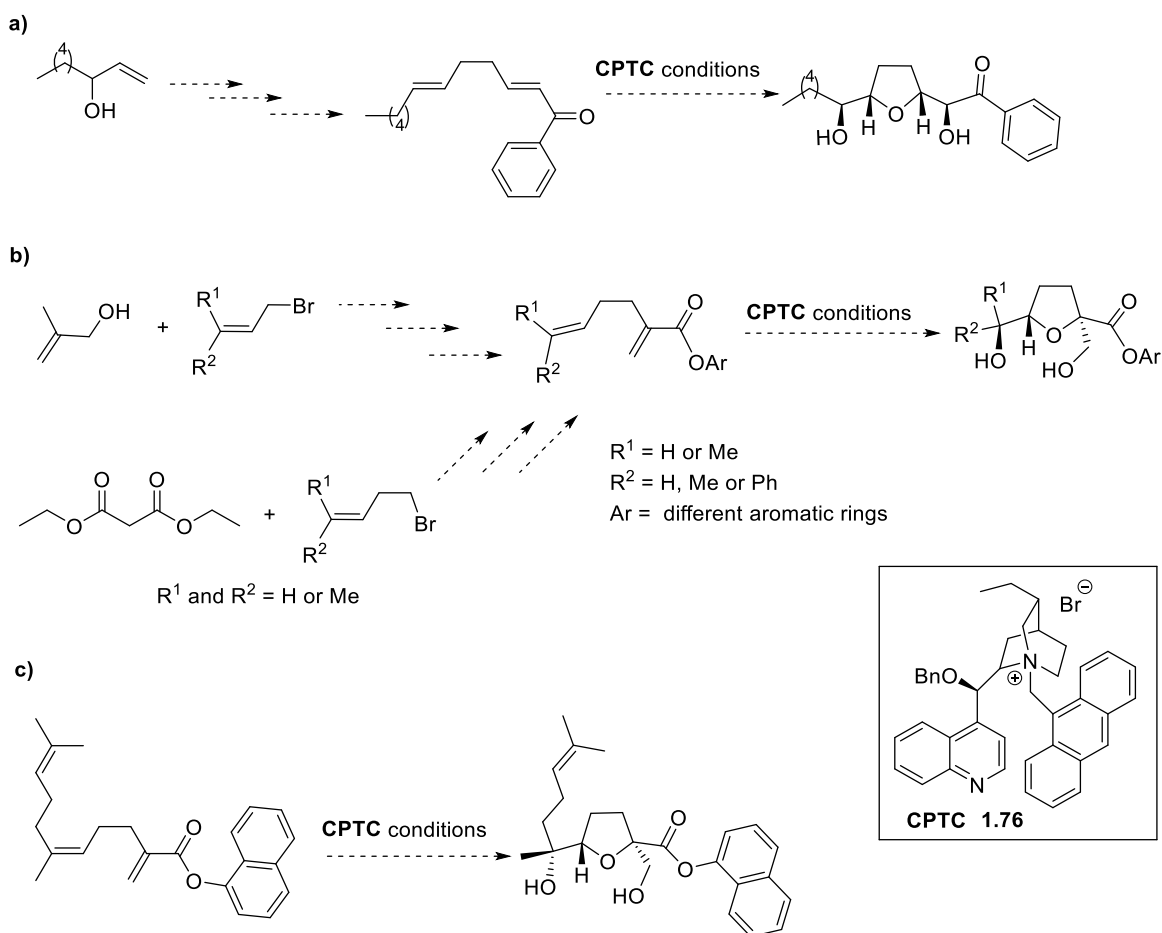
Figure 1.18: Summary of the mechanistic study considered for MnO_4^- and OsO_4 oxidative cyclisation of 1,5-diene.

Considerations of different spin multiplicities, frontier molecular orbital (FMO), distortion/interaction analysis, and classical molecular dynamics (MD) will also be included for both MnO_4^- and OsO_4 oxidative cyclisations.

Chapter 2 Results and Discussions

2.1 Asymmetric oxidative cyclisation of 1,5-dienes and a 1,5,9-triene by MnO_4^- using CPTC

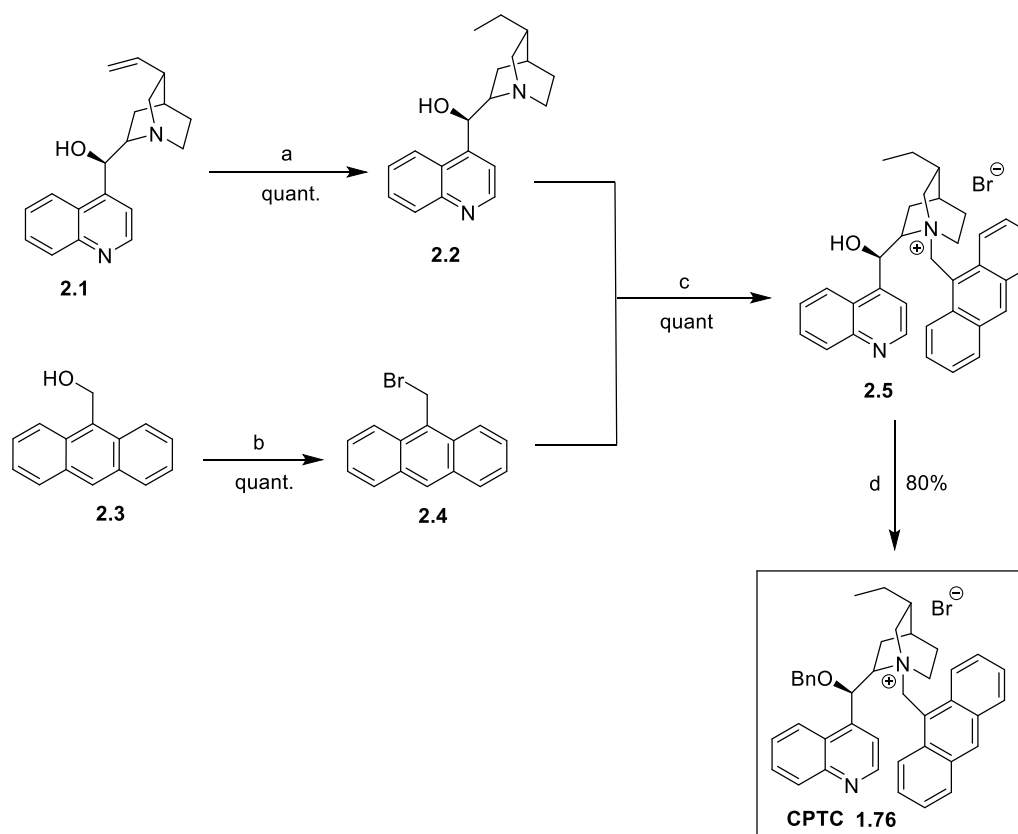
This chapter focuses on permanganate-mediated oxidative cyclisation of 1,5-dienes and a 1,5,9-triene under **CPTC** conditions (**Scheme 2.1**). Firstly, 1,2-disubstituted 1,5-dienone will be synthesised followed by its oxidative cyclisation under **CPTC** conditions in order to assess the asymmetric induction for the **CPTC** (**Scheme 2.1-a**). Different 1,1-disubstituted aromatic dienoates will be synthesised to explore the **CPTC** oxidative cyclisation (**Scheme 2.1-b**). Finally, we will extend the **CPTC** oxidative cyclisation conditions to a 1,5,9-trienoate (**Scheme 2.1-c**), which is a potential intermediate in the synthesis of eurylene. The initial task was to synthesise the **CPTC 1.76**.



Scheme 2.1: Overview of the permanganate-mediated oxidative cyclisation, showing synthesis and oxidations of a) 1,2-disubstituted 1,5-dienone; b) 1,1-disubstituted 1,5-dienoates; c) 1,1-disubstituted 1,5,9-trienoate.

2.2 Preparation CPTC (1.35)

CPTC salt **1.76** was synthesised in four steps starting from cinchonidine (**2.1**) in 94% overall yield (**Scheme 2.2**).^{258–261} Firstly, reduction of the vinyl group in cinchonidine (**2.1**) was achieved using H₂ over activated palladium on carbon to give dihydrocinchonidine (**2.2**) in quantitative yield. After bromination of 9-anthracyl methanol (**2.3**), the tertiary amine **2.2** was converted into quaternary ammonium salt **2.5** by reaction with 9-anthracyl bromide (**2.4**) in quantitative yield. Finally, protection of the secondary alcohol of the quaternary ammonium salt **2.5** gave the title catalyst **1.76** in 80% yield as a yellow powder. An important point is that the catalyst has to be of high purity in order to be used in the permanganate ion oxidative cyclisation, and the **CPTC** should be stored away from light. Therefore, the product was recrystallised two-THree times and purity was confirmed by ¹HNMR analysis.

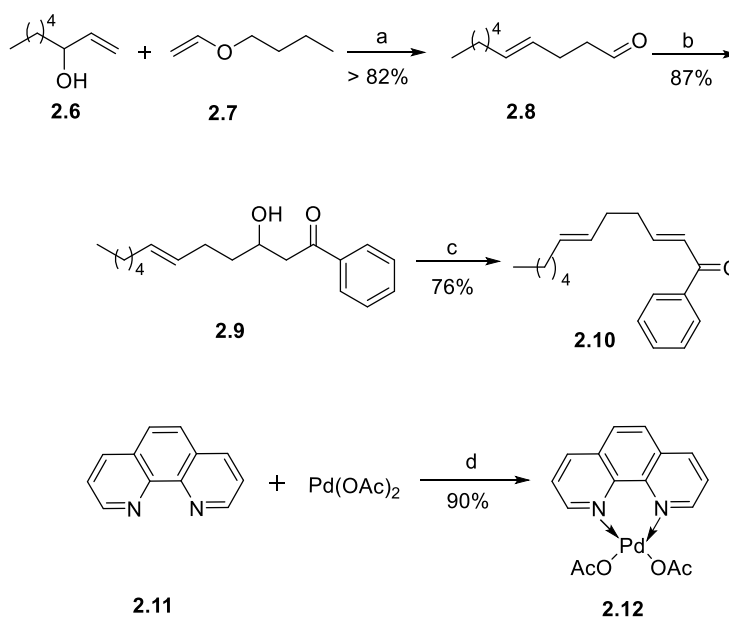


Scheme 2.2: Synthesis of **CPTC 1.76**. **Reagents and conditions:** a) Pd/C, H₂, MeOH, rt, 6 h; b) PBr₃, toluene, 0 °C to rt, 2 h; c) toluene, 90 °C, 3 h; d) BnBr, KOH (50% aq.), CH₂Cl₂, rt, 4 h.

2.3 Synthesis and oxidative cyclisation of 1,2-disubstituted 1,5-dienone

2.3.1 Synthesis of 1,2-disubstituted 1,5-dienone 2.10

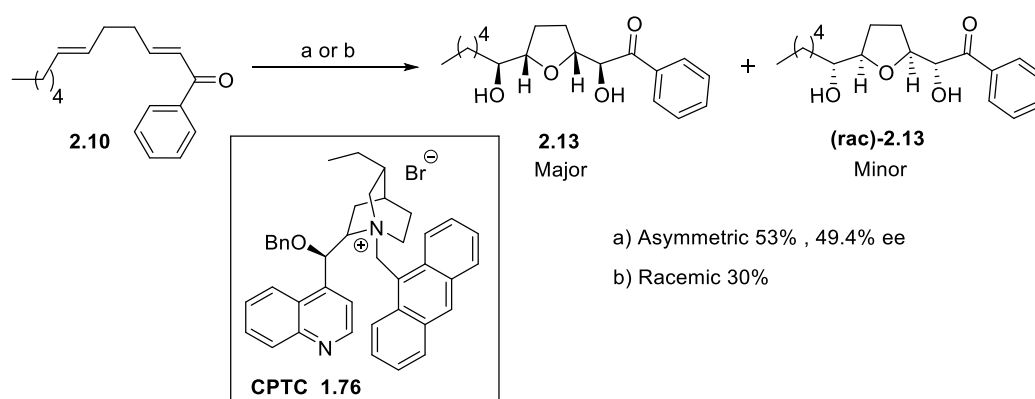
Achieving the stereocontrolled synthesis of the *trans*-diene **2.10** is required to allow investigation of the oxidative cyclisation and, therefore, highly selective methods were investigated (**Scheme 2.3**). To prepare the *trans*-diene, the first step was reaction of the allylic alcohol **2.6** with vinyl butyl ether (**2.7**) by means of a sequential vinyl ether exchange-Claisen rearrangement process catalysed by a palladium(II)-phenanthroline complex **2.12**. This led to formation of γ,δ -unsaturated aldehyde **2.8** under mild conditions.²⁶² Without using an excess of the vinyl ether the reaction did not take place. Many Claisen rearrangements require high temperature to proceed, and so a vinyllating agent with a high boiling point is desirable. The vinyllating agent used in this case has a boiling point quite close to the reaction temperature, so an excess of vinyl ether was employed to avoid loss by evaporation and achieve high efficiency.²⁶² This method is a convenient and better approach to γ,δ -unsaturated aldehydes compared to using Hg(II) catalysts, in terms of toxicity and yield.²⁶³ The aldol reaction of a modest excess of acetophenone with aldehyde **2.8** resulted in formation of β -hydroxy phenone **2.9** with an excellent yield (87%).²⁶⁴ Dehydration of β -hydroxy ketone **2.9** was accomplished by mesylation then treatment with DBU giving *trans*-diene **2.10** in good yield.



Scheme 2.3: Synthesis of *trans* dienone **2.10**. **Reagents and conditions:** a) Pd catalyst **2.12**, 93 °C, 48 h; b) acetophenone (1.3 equiv), LDA (1.3 equiv), THF, −78 °C; c) (i) MsCl, Et₃N, CH₂Cl₂; (ii) DBU, CH₂Cl₂; d) DME, rt.

2.3.2 Oxidative cyclisation of aromatic 1,5-dienone **2.10** under CPTC

Oxidative cyclisation of *trans*-diene **2.10** was conducted under **CPTC** conditions (**Scheme 2.4**). The oxidation reaction using **CPTC** was carried out using previously optimised conditions to give THF-diol **2.13** as an enantiomerically enriched mixture.⁴⁸ An improved yield (53%) and reasonable selectivity of 49.4% ee was achieved.²⁶⁴ The diene was also cyclised under racemic conditions. The racemic sample was used to develop the chiral HPLC method. A low yield for the racemic reaction was observed, at least in part due to the absence of a phase transfer catalyst, e.g. adogen 464. For convenience, the terminology “racemic conditions” is used to describe permanganate oxidation in the absence of the enantiomerically enriched chiral phase-transfer catalyst (**CPTC**). The terminology “**CPTC** conditions” refers to oxidative cyclisation in the presence of **CPTC**.



Scheme 2.4: Permanganate-mediated oxidative cyclisation of diene **2.10**. **Reagents and conditions:** a) **CPTC** conditions: KMnO₄, **1.76**, AcOH, CH₂Cl₂, -60 °C, 4 h; b) Racemic conditions: KMnO₄, acetone/AcOH (3:2), -60 °C, 4 h.

2.4 Synthesis and oxidative cyclisation of 1,1-disubstituted aromatic 1,5-dienoates

The oxidative cyclisation of 1,1-disubstituted 1,5-dienes was carried out on three different groups of aromatic dienoates based on the substitution of the electron-rich alkene side of the molecule (**Figure 2.1**). When R¹ and R² on the distal alkene are both methyl groups, this will be classified as group one. In group two R¹ and R² are hydrogens, whereas in group three R¹ and R² are H and phenyl group respectively. Within the three groups different aromatic esters will be prepared. The next sections will describe the synthesis and oxidative cyclisation of these groups separately.

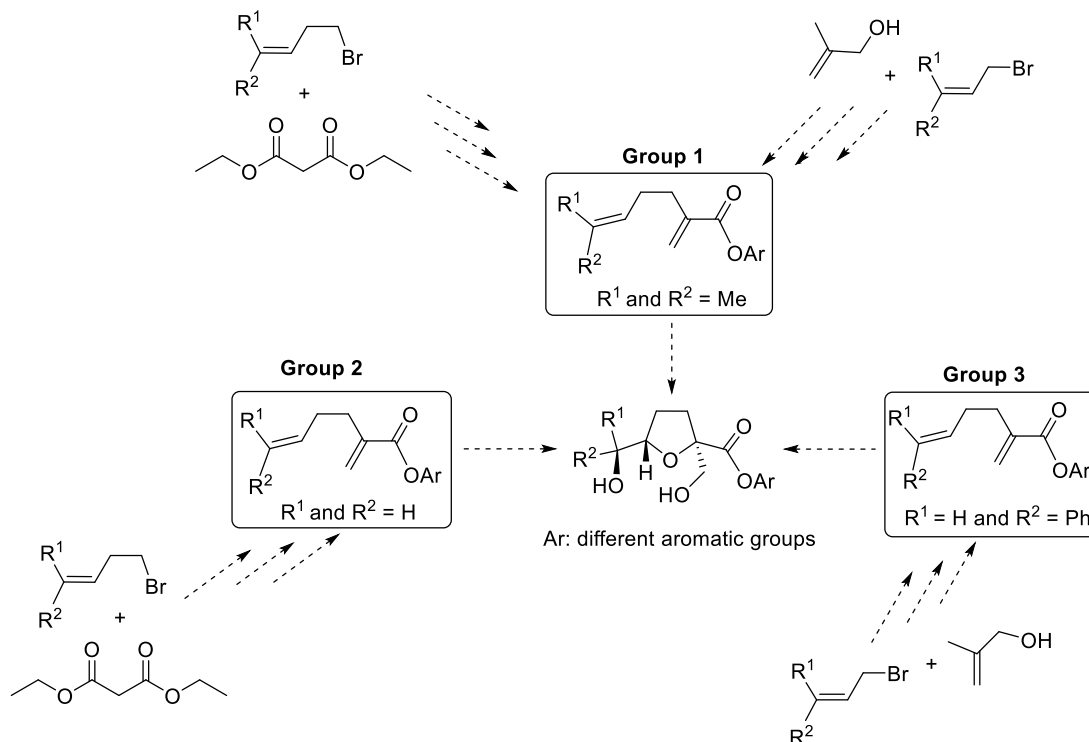
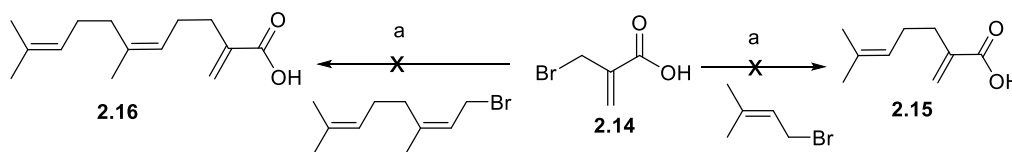


Figure 2.1: Overview of aromatic 1,5-dienoate.

2.4.1 Toward the synthesis and oxidative cyclisation of group one dienoate substrates

2.4.1.1 Synthesis of 6-methyl-2-methylenehept-5-enoic acid (**2.15**)

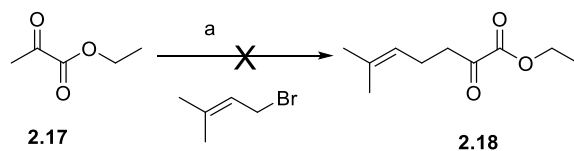
Several different approaches were considered for the preparation of 1,5-dienoic acid **2.15**. Our lab investigations began using the direct cross-coupling reaction of two different alkyl halides reported by Ma and Chan (**Scheme 2.5**).²⁶⁵ We applied two different halides to couplings with 2-(bromomethyl) acrylic acid (**2.13**), but without success. In addition to the unsuccessful trials the acrylic acid **2.14** is relatively expensive and so this method was not investigated further.



Scheme 2.5: Attempted preparation 1,5-dienoic acid **2.15** using a direct cross-coupling approach.

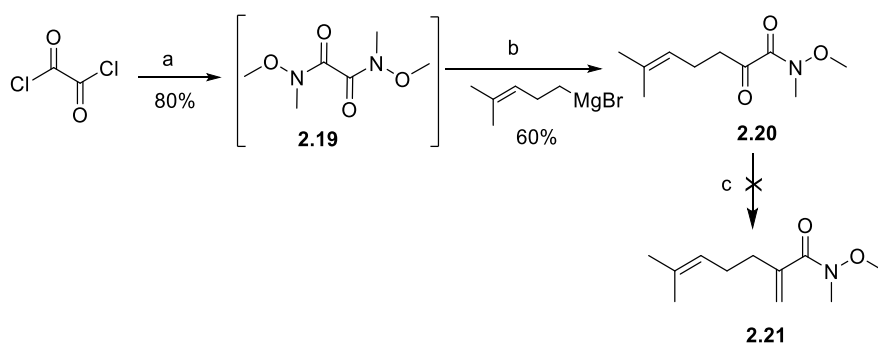
Reagents & conditions: a) Mn, CuCl₂, H₂O, 10 h, rt.

Ethyl pyruvate (**2.17**) was investigated as a precursor to prepare diketone **2.18** which could then undergo Wittig reaction to make the 1,5-dienoate (**Scheme 2.6**). This was also unsuccessful using different equivalents of LDA to deprotonate ethyl pyruvate. It is possible that ethyl pyruvate reacts with itself or decomposes during the deprotonation before reaction with prenyl bromide.



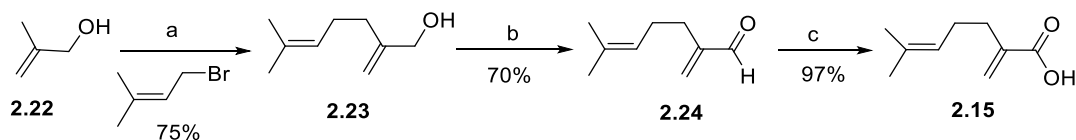
Scheme 2.6: Synthesis of diketones **2.18**. **Reagents & conditions:** a) LDA, THF, -78°C , 30 min then allyl bromide, -78°C , 1 h.

Next, the formation of Weinreb amide **2.21** was attempted (**Scheme 2.7**). The addition of Weinreb amine to oxalyl chloride gave the double Weinreb amide **2.19** in good yield (80%) and this was followed by addition of the Grignard reagent to give the ketoamide **2.20** in acceptable yield (60%).²⁶⁶ When ketoamide **2.20** was submitted to Wittig conditions, 1,5-diene **2.21** was not obtained. Although there was a reaction, it did not lead to the desired compound **2.21** and we were not able to identify the products formed.



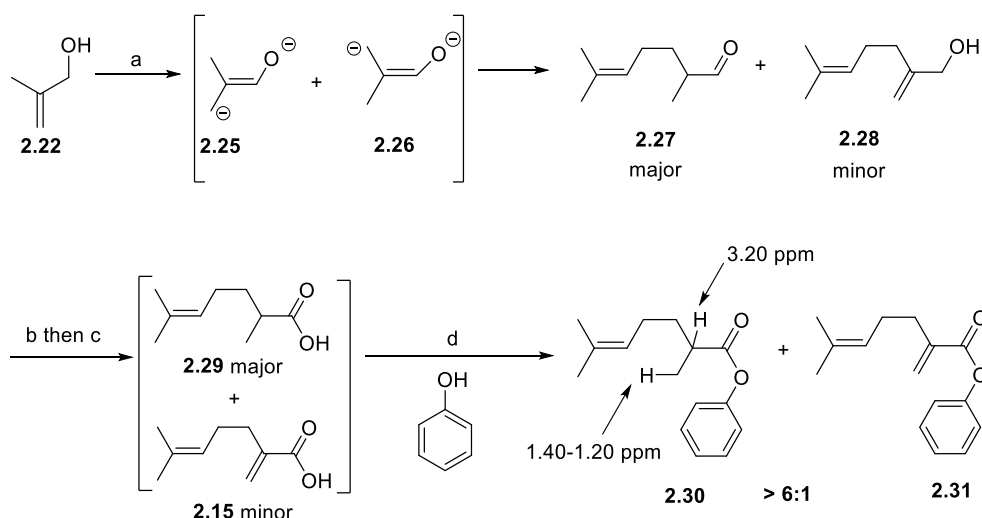
Scheme 2.7: Attempted Weirneb amide pathway to prepare 1,5-diene **2.21**. **Reagents & conditions:**
a) HCl.HNCH₃(OCH₃), Et₃N, CH₂Cl₂, 0 °C, 30 min; b) Grignard reagent, THF, 0 °C, 30 min; c) Ph₃PMeBr, DBU or *t*-BuOK, CH₂Cl₂, 10 h, 45 °C.

In view of the failure of the above three approaches to afford the desired 1,5-dienoic acid, attention turned back to a route previously developed in the Brown group, involving coupling of prenyl bromide with the dianion of methallyl alcohol (**2.22**) (**Scheme 2.8**). Deprotonation of methallyl alcohol (**2.22**) by an excess of *n*-BuLi in Et₂O led to the formation of dark red gum attributed to the dianion of **2.22**. This was followed by the dropwise addition of allyl bromide to give dienol **2.23** in 75% yield.²⁶⁷ This alcohol was oxidised to aldehyde **2.24** using activated MnO₂ in *n*-hexane with an acceptable yield of 70%. The aldehyde was efficiently converted to carboxylic acid **2.15** in excellent yield (97%) using silver oxide (Ag₂O), freshly prepared from reacting AgNO₃ and NaOH in water. The acid was used without further purification for the esterification.



Scheme 2.8: Synthesis of 1,5-dienoic acid **2.15**. **Reagents & conditions:** a) *n*-BuLi (6.0 equiv) in Et₂O, TMEDA, THF, –5 °C to rt, 38 h then allyl bromide in THF, –78 °C to rt 8 h; b) MnO₂, *n*-hexane, 0 °C to rt, 15 h; c) AgNO₃, NaOH, H₂O, rt, 14 h.

Although the methallyl alcohol dianion method is a very useful procedure, care is required to avoid formation of an aldehyde byproduct, which is observed when *n*-BuLi in hexane is used (**Scheme 2.9**). By using *n*-BuLi in Et₂O the undesired byproduct is minimised. However, where the undesired aldehyde was formed, the double oxidation by MnO₂ and Ag₂O gave two inseparable carboxylic acids **2.29** and **2.15**. After esterification with phenol, two esters were formed **2.30** (major) and **2.31** (minor) with more than 6:1 ratio according to ¹H NMR analysis.

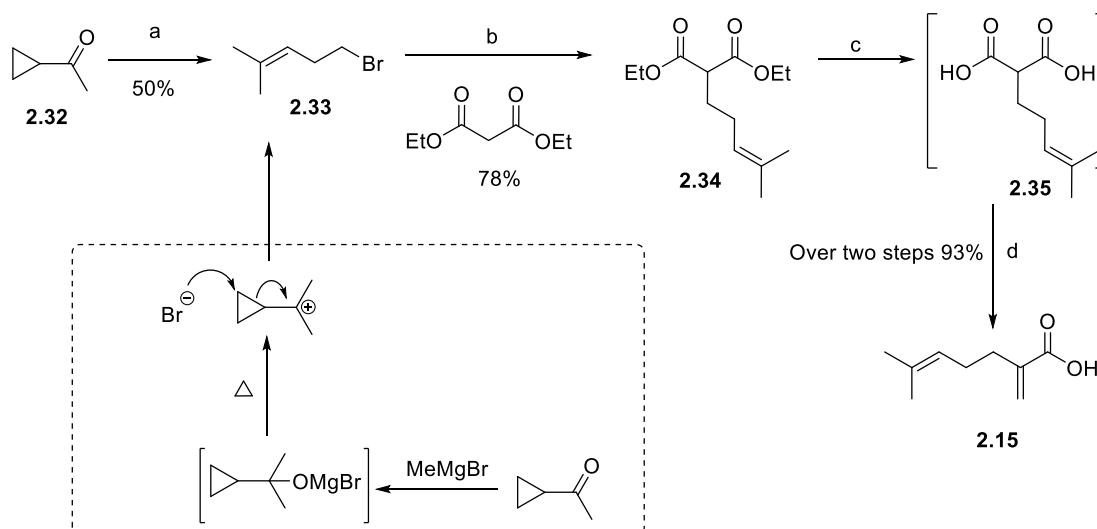


Scheme 2.9: Formation of by-product **2.30** when *n*-BuLi in *n*-hexane was used. **Reagents & conditions:** a) *n*-BuLi in *n*-hexane, TMEDA, THF, –5 °C to rt, 38 h then allyl bromide in THF, –78 °C to rt 8 h; b) MnO₂, *n*-hexane, 0 °C to rt, 15 h; c) AgNO₃, NaOH, H₂O, 14 h, d) DCC, CH₂Cl₂, rt, 15 h.

A safer more practical approach to the synthesis of 1,5-dienoic acid **2.15** was sought which avoided the technically demanding conditions shown in **Scheme 2.8**. This approach was established through alkylation of diethyl malonate with alkyl bromide **2.33** (**Scheme 2.10**). The alkyl halide **2.33** is expensive and therefore it was synthesised by reacting cyclopropyl methyl ketone with methylmagnesium bromide in THF according to the procedure reported by Schwartz and co-workers.²⁶⁸ The mechanism is shown within **Scheme 2.10**. Mono alkylation of diethyl malonate

Chapter 2

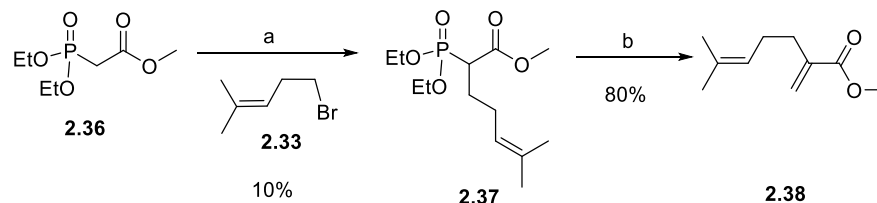
using K_2CO_3 in acetone afforded the mono substituted diester **2.34** with 78% yield. Double alkylation was not observed when K_2CO_3 was used. However, if a stronger base such as NaOEt was used the double alkylation product was observed, leading to a difficult separation. The hydrolysis of diester **2.34** at room temperature gave the diacid intermediate **2.35**, which was used directly in the next step. Doebner modification of the Knoevenagel condensation was used to prepare the required dienoic acid **2.15** by treating the diacid with formaldehyde in the presence of diethyl amine. This pathway is more robust than the dianion pathway in terms of safety, cost and accessibility, and is preferred for practical access to dienoic acid **2.15**.



Scheme 2.10: Alternative synthesis pathway of 1,5-diene acid **2.15**. **Reagents & conditions:** a) MeMgBr , Et_2O , THF, 20 min; b) Alkyl halide, K_2CO_3 , acetone, rt, 48 h; c) KOH , H_2O , EtOH , 24 h, rt; d) CH_2O (40%), Et_2NH , reflux, overnight.

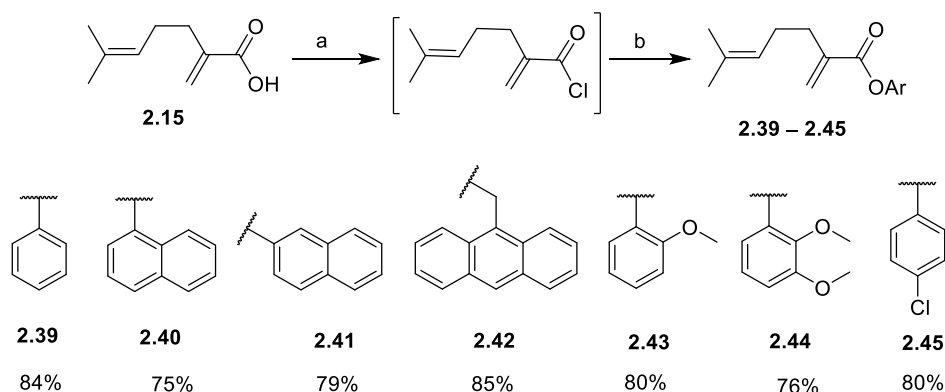
2.4.1.2 Preparation of group one 1,5-dienoate esters

With the alkyl halide **2.33** already in hand, methyl 1,5-dienoate **2.38** was firstly synthesised through alkylation with methyl diethylphosphonoacetate (**2.36**) (**Scheme 2.11**). The deprotonation of diethyl phosphonoacetate with NaH followed by the addition of alkyl halide **2.33** afforded the alkylated product **2.37** with a very low yield of only 10% and recovery of the rest of the alkyl halide. This low yield is probably due to elimination of the homoprenyl bromide system. Refluxing the alkylated intermediate **2.37** with 40% formaldehyde and in the presence of diethyl amine as a base gave the desired methyl 1,5-dienoate **2.38**. Because of the low yield of first step, we did not hydrolyse the diene to the corresponding acid **2.15**. However, the route did provide a small quantity of methyl ester to investigate the **CPTC** oxidative cyclisation.



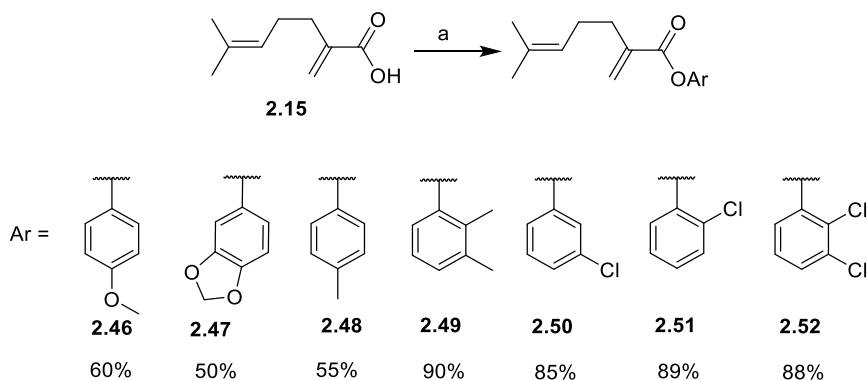
Scheme 2.11: Alternative synthesis of 1,5-diene **2.38**. **Reagents & conditions:** a) **2.36**, NaH, THF, 0 °C, 10 min, then alkyl halide **2.33**, rt, 24 h; b) CH₂O (40%), Et₂NH, reflux, 15 h.

Following the formation of carboxylic acid (**2.15**), the next task was to prepare the corresponding 1,5-dienoate esters. We have investigated two esterification methods; direct esterification using DCC, DMAP, with DIEA and the indirect esterification through formation of the acid chloride intermediate. Esters **2.39–22.45** were prepared by formation of the acid chloride of 1,5-dienoic acid **2.15** followed by coupling with the alcohol in the presence of Et₃N (**Scheme 2.12**). These aromatic dienoates were obtained in good yields 76%-85%.



Scheme 2.12: Synthesis of aromatic 1,5-dienoate esters **2.39–2.45** through the acid chloride intermediate. **Reagents & conditions:** a) (COCl)₂, DMF, CH₂Cl₂, 0 °C to rt, 2 h; b) ArOH, Et₃N, CH₂Cl₂, 0 °C to rt, 1 h.

Esters **2.46–2.52** were prepared using direct esterification (**Scheme 2.13**). The yields of esters **2.49–2.52** are excellent whereas lower yields of 50%-60% were obtained for aromatic dienoates **2.46–2.48**. None of these yields represent optimised processes.



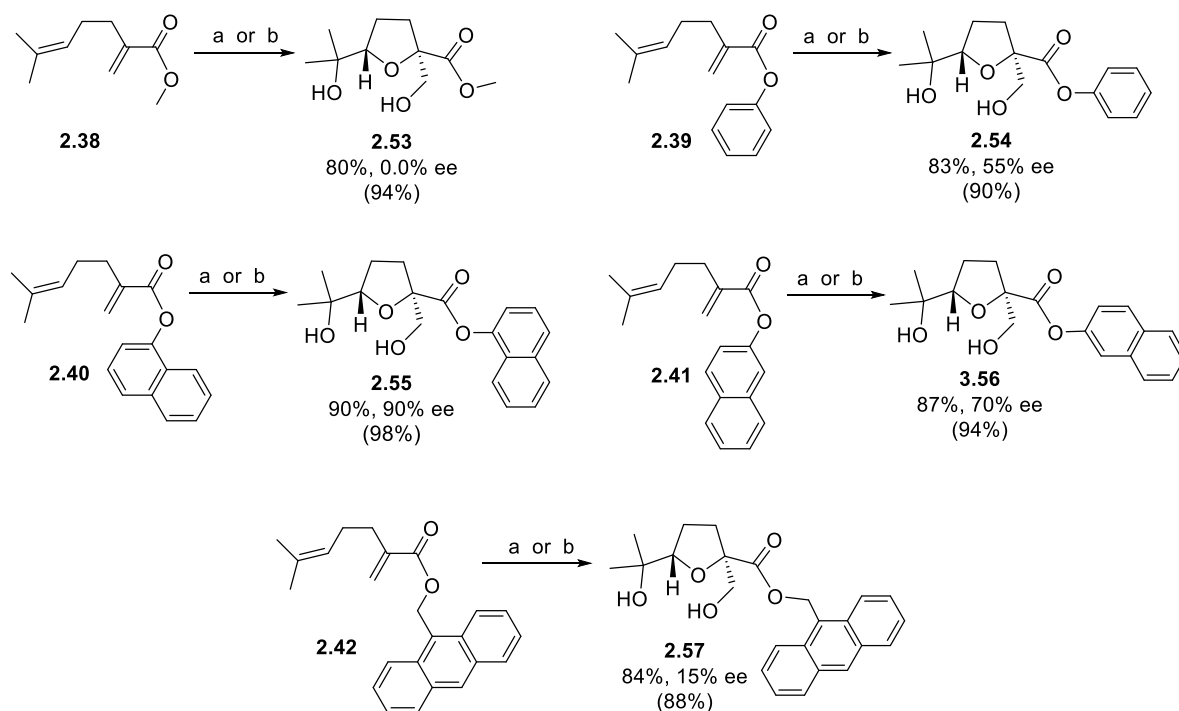
Scheme 2.13: Synthesis aromatic 1,5-diene esters **2.46–2.52** using coupling agent. **Reagents & conditions:** a) alcohol, DMAP, DCC, DIEA, CH₂Cl₂, rt, 15 h.

2.4.1.3 Permanganate-mediated oxidative cyclisation of group one dienoates

The aromatic dienoates **2.39–2.52** were investigated in the asymmetric permanganate-mediated oxidative cyclisation using the previously optimised conditions (see **Schemes 2.13, 2.15, and 2.16**).⁴⁸ The aromatic dienoates were also cyclised under racemic conditions using the optimised AcOH:acetone (2:3) system in the presence of phase transfer catalyst adogen 464 to give the corresponding racemic THF-diols. Although our methodology is based on the earlier work in the group, three important observations were made concerning the effect of water, and the use of acid, and purity of the **CPTC** catalyst. The important influence of acetic acid was seen when we carried out the reaction in the absence of acid for 8–9 hours. In the absence of AcOH, there was no reaction until acetic acid was added, whereupon the reaction commenced. All the reactions investigated using **CPTC** were carried out using dry dichloromethane. However, many side products were seen by TLC if the solvent was wet, leading to reduced yield. Finally, the need for pure **CPTC** is crucial for efficient reaction. If the catalyst was not pure, very low conversions and low yields were achieved and starting material was recovered. The use of impure catalyst and long reaction times (7–8 hours) resulted in the a formation of black-brown suspension, which is MnO₂ formed as a result of disproportionation of the permanganate ion in acidic conditions. Therefore, we recrystallised the **CPTC** regularly in order to ensure consistently good results.

We have divided the group one substrates into three subgroups shown in **Schemes 2.14, 2.16, and 2.17**. **Scheme 2.14** shows the oxidative cyclisation of dienoates **2.38–2.42**. Methyl 1,5-dienoate **2.38** gave THF-diol **2.53** gave with no observed enantioselectivity in 80% yield under **CPTC** conditions. The racemic oxidative cyclisation conditions gave 94% yield. The selectivity for formation of simple methyl THF-diol adduct (**2.53**) was measured by HPLC after derivatisation of the primary alcohol with benzoate group (**Scheme 3.15**). However, once we introduced any aryl

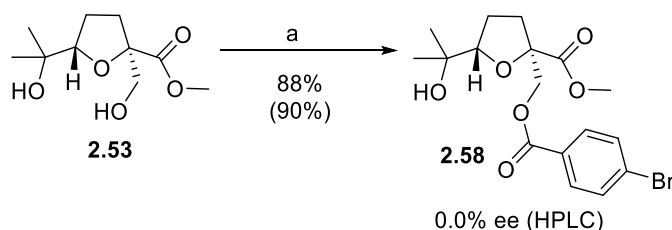
containing ester group instead of the methyl group, asymmetric induction was observed demonstrating the need for the stacking between the catalyst and substrate.



Scheme 2.14: Permanganate-mediated oxidative cyclisation of 1,5-dienoates **2.38–2.42**. **Reagents and conditions:** a) **CPTC** conditions: KMnO_4 , **1.76**, AcOH (6.5 equiv), CH_2Cl_2 , -60°C , 3–4 h; b) Racemic conditions: KMnO_4 , adogen 464 (10 mol %), acetone/AcOH (3:2), -20°C , 30 min. Yields for reactions performed under racemic conditions are in brackets.

Starting from simple phenyl dienoate **2.39**, the corresponding THF-diol **2.54** was formed with moderate selectivity (55% ee) and with a very good yield of 85% (**Scheme 2.14**). Increasing the size of the aromatic ring in the substrate from phenyl (diene **2.39**) into α -naphthyl (diene **2.40**) resulted in an excellent asymmetric induction of 90% ee with an excellent yield (90%). The importance of shape was highlighted with β -naphthol dienoate **2.41**, where a lower ee of 70% was obtained instead of 90% ee for α -naphthol dienoate **2.40**. This is proposed to be due to a steric interaction with the **CPTC** aromatic pocket. These results indicate that stacking is not the only important factor to reach high ee's but the size and shape of aromatic ring is effective too in producing a good “fit” with the catalyst. In other words, it can be seen that α -naphthyl group has good fit parameters with the aromatic pocket of the catalyst. That means that when the substrate is not restricted within the aromatic pocket between quinoline and anthracyl groups, both sides of the enoate double bond will be more accessible to the permanganate ion (see computational model in **Figure 2.2**). The cyclisation of 9-anthracyl dienoate **2.42** gave a low ee of 15% but with a very good yield of 84%. The

low induction for **2.42** might be attributed to either that the anthracyl group being too large for the aromatic pocket of the **CPTC**, or the extra benzylic CH₂ on the anthracene group.



Scheme 2.15: Selective benzoylation of THF-diol **2.53** for chiral HPLC analysis. **Reagents & conditions:** a) 4-Bromobenzoyl chloride, DMAP, CH₂Cl₂, rt, 0 °C, 30 min. Yield in parenthesis refers to derivatisation of the racemic product.

Based on Lygo's proposed model for phase-transfer catalysed nucleophilic epoxidation of olefines (shown in **Scheme 1.16**), we have built a computational model for **CPTC** and substrate **2.40** to attempt understand the asymmetric induction in the permanganate-mediated oxidative cyclisation under **CPTC** condition (**Figure 2.2**). This model was initially produced using a quantum mechanic/molecular mechanic (QM/MM) approach to find the lowest energy conformation. The lowest energy conformation was then subjected to full DFT optimisations using the wb97xd/6-311+G(d,p)//wb97xd/6-31G(d) level of theory and the optimised complex is shown in **Figure 2.2**. The calculations show that the aromatic ring in the substrate sits between the anthracene and quinoline rings in the catalyst, whereas the substrate carbonyl interacts with the quaternary centre. It can be seen that four important effects have to be taken in account. These effects are hydrogen bonding, stacking (including CH- π , π - π , and cation- π stacking), aromatic ring shape/size, and electronic effects. Firstly, stacking interactions between the aromatic ring of the catalyst, especially the anthracyl group, and aromatic ring of the substrate shown in zone A are an important requirement to give selectivity; the aliphatic ester **2.38** gave no selectivity (**Scheme 2.14**). Secondly, most hydrogen bonding interaction between **CPTC** and substrate shown in zone B is localised between the carbonyl group of the substrate and the positively polarised hydrogen atoms of the methylene groups around the nitrogen of the **CPTC**. This is important for the **CPTC** + substrate **2.40** to maintain a stable complex during the induction event.²⁶⁹ Zone C shows an interaction between the substituents (hydrogens, methyl, or phenyl groups) on the electron-rich alkene and **CPTC** groups (either benzyl group's phenyl, ethyl or CH₂ around N). According to **Figure 2.2**, MnO₄⁻ approaches either from the top (*Re*) face to give the minor enantiomer or from the lower (*Si*) face of the double bond to give the major enantiomer. This proposed model is consistent with the observed experimental outcome for the enantioselective oxidative cyclisation of dienoate **2.40** in the presence of the **CPTC**. However, this analysis is based on the ground state complex of the

interacting substrate and CPTC, and other conformations of diene and CPTC complex may be possible leading to lower energy TS structures.

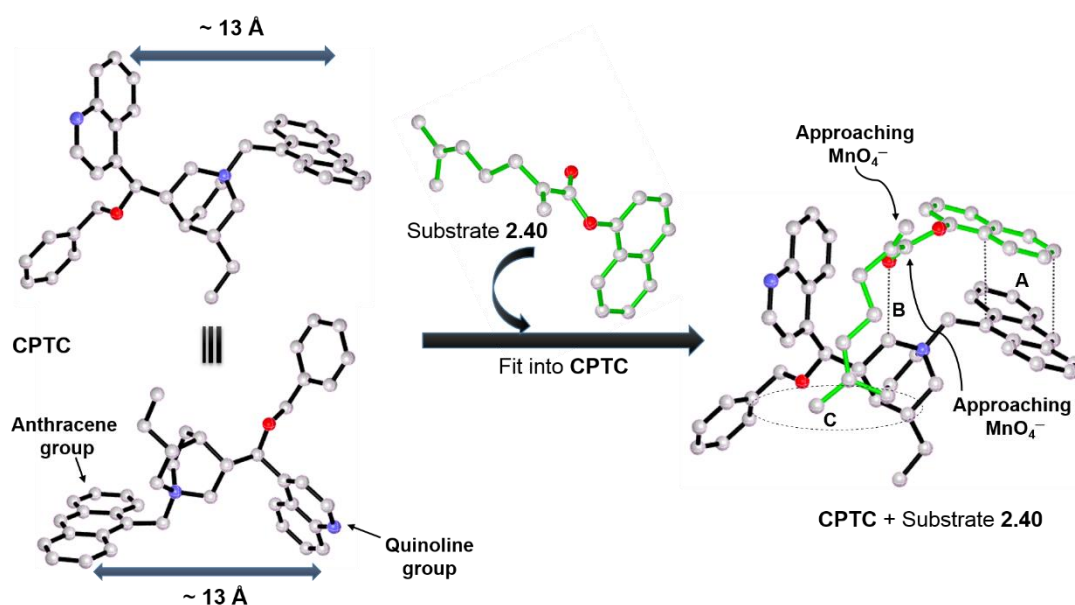
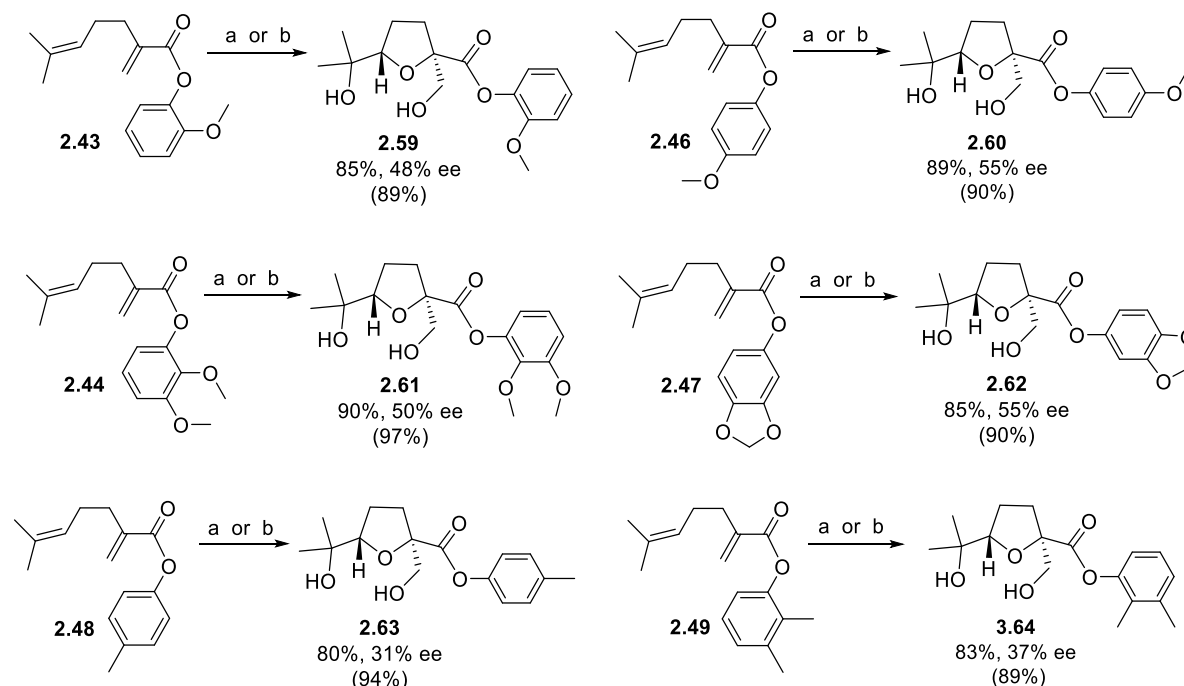


Figure 2.2: General representation for Interaction of CPTC and substrate **2.40**, showing different zones of interaction A, B, and C. Hydrogen atoms are omitted for clarity.

Next, we explored the effect of substituents on the aromatic ring; both electron-donating and electron-withdrawing groups. **Scheme 3.16** shows the effect of electron-donating groups on the asymmetric oxidative cyclisation for dienoates **2.43**, **2.44** and **2.46–2.49**. In general, donating groups have shown no improvement on selectivity in comparison to the simple phenyl dienoate **2.39**. Starting with the methoxy group, *o*-methoxy phenyl dienoate **2.43** cyclises to give THF-diols **2.59** in 85% yield and moderate *ee* of 48%, whereas the *para* substituted **2.46** shows slightly higher selectivity of 55% *ee* and 89% yield. 2,3-dimethoxy phenyl dienoate **2.44** shows the highest yield for both asymmetric (90%) and racemic (97%) conditions, but with a moderate *ee* of 50%. Despite the fact that 2,3-dimethoxy phenyl dienoate **2.44** appears to have a similar shape to α -naphthyl dienoate **2.40**, its selectivity was lower (50% *ee*). This can be explained by rotation of the methyl groups leading to destabilisation the transition state due to the steric repulsion with the aromatic pocket of catalyst.

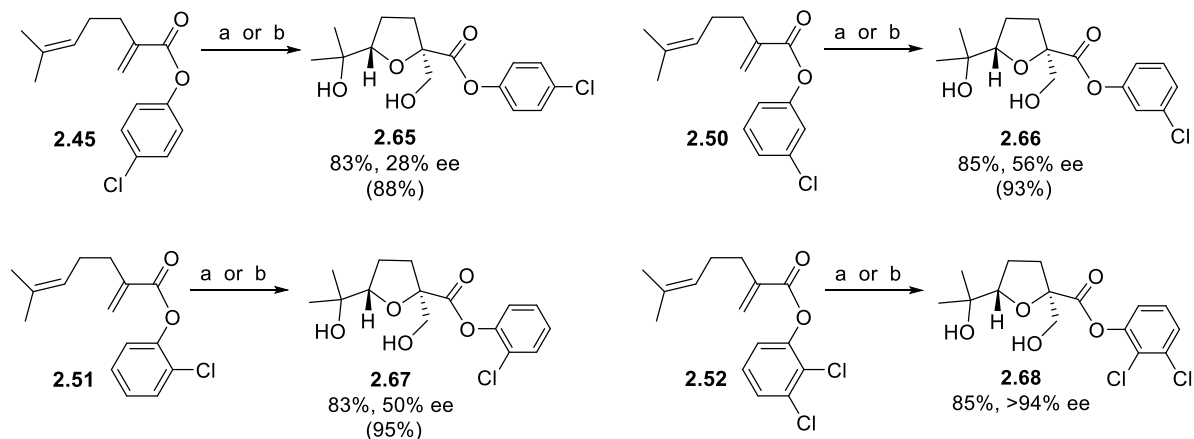
The oxidative cyclisation of 5-benzodioxolyl dienoate **2.47** gave 55% *ee* with 85% yield. Dienoate **2.47** appears to have a similar shape to β -naphthyl dienoate **2.41**, however the oxidative cyclisation of the latter gave a higher induction of 70% *ee* due to reduced π -stacking interactions in 5-benzodioxolyl group in **2.47**. The effect of methyl-substitution in phenyl dienoates **2.48** and **2.49** was not positive either in terms of enantioselectivity. *p*-Methyl phenyl dienoate **2.48** gave the lowest selectivity of 31% *ee* with 80% yield compared to 55% *ee* for *p*-methoxy diene **2.46**. The

oxidative cyclisation of *o,m*-dimethyl phenyl dienolate **2.49** to THF-diol **2.64** gave the second lowest *ee* of 37% compared to 50% *ee* for *o,m*-dimethoxy diene **2.44**.



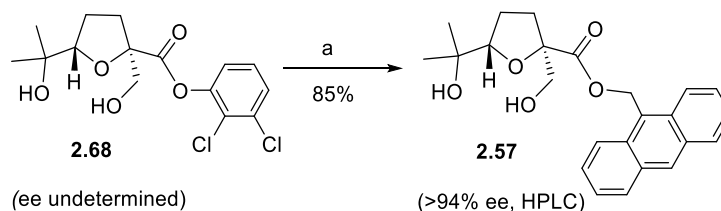
Scheme 2.16: Permanganate-mediated oxidative cyclisation of aromatic 1,5-dienolates **2.43**, **2.44** and **2.46–2.49**. **Reagents and conditions:** a) CPTC conditions: KMnO_4 , **1.76**, AcOH (6.5 equiv), CH_2Cl_2 , -60°C , 3–4 h; b) Racemic conditions: KMnO_4 , adogen 464 (10 mol %), acetone/AcOH (3:2), -20°C , 30 min. Yields for reactions performed under racemic conditions are in brackets.

The effect of electron-withdrawing substituents on the asymmetric oxidative cyclisation shown in **Scheme 3.17** is similar to the effects of electron-donating groups, with the exception of 2,3-dichlorophenyl. The asymmetric induction of *p*-chlorophenyl dienolate **2.45** shows the lowest selectivity of 28% *ee*. This is comparable to 31% *ee* for *p*-methyl dienolate **2.48**, indicating that the methyl group or chlorine atom in the *para* position show a similar effect. However, the enantiomeric excess achieved for *m*-chlorophenyl dienolate **2.50** was 56% which is double the selectivity for *para*-substitution. Correspondingly, the *ee* was decreased slightly to 50% for *o*-chlorophenyl dienolate **2.52**. When the phenyl ring was substituted at the *ortho* and *meta* positions, diene **2.52**, the asymmetric induction jumped to more than 94% *ee*. The structural similarity between 2,4-dichloro **2.52** and α -naphthyl **2.40** is apparent, where both rings are substituted in the 2- and 3-positions resulting in a very good fit with the pocket in the CPTC, leading to high *ee*. At this point, we can conclude that high enantiomeric excess for the oxidative cyclisation can be achieved when an α -naphthyl-like shape was present, for example dienolates **2.40** (**Scheme 2.14**) and **2.52** (**Scheme 2.17**).



Scheme 2.17: Permanganate-mediated oxidative cyclisation of aromatic 1,5-dienoate **2.45** and **2.50–2.53**. **Reagents and conditions:** a) CPTC conditions: KMnO_4 , **1.76** (10 mol %), AcOH (6.5 equiv), CH_2Cl_2 , $-60\text{ }^\circ\text{C}$, 3–4 h; b) Racemic conditions: KMnO_4 , adogen 464, acetone/AcOH (3:2), $-20\text{ }^\circ\text{C}$, 30 min. Yields for reactions performed under racemic conditions are in brackets.

The enantiomeric excess for the asymmetric induction of diene **2.52** was measured indirectly because THF-diol **2.68** was found to be unstable during purification by column chromatography (**Scheme 2.18**). Transesterification of **2.68** with anthracyl alcohol afforded THF-diol **2.57** with 85% yield. A crude sample of THF-diol **2.57** was used to measure its ee by chiral HPLC, comparing against the racemic THF-diol obtained from the oxidative cyclisation of dienoate **2.42**.



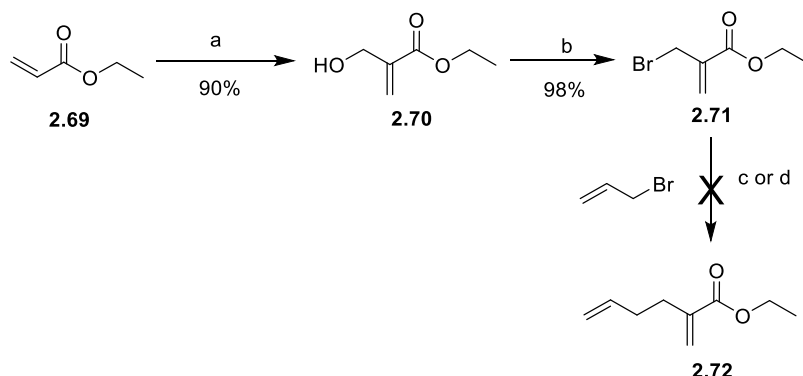
Scheme 2.18: Transesterification of enantiomerically enriched THF-diol **2.68** to allow ee determination using chiral HPLC. **Reagents & conditions:** a) 9-anthracyl alcohol, NaHMDS, THF, -78 to $-25\text{ }^\circ\text{C}$, 1.5 h, then **2.68**, THF, rt, 40 min.

2.4.2 The synthesis and oxidative cyclisation of group two dienoates

2.4.2.1 Synthesis of 2-methylenehex-5-enoic acid (**2.76**)

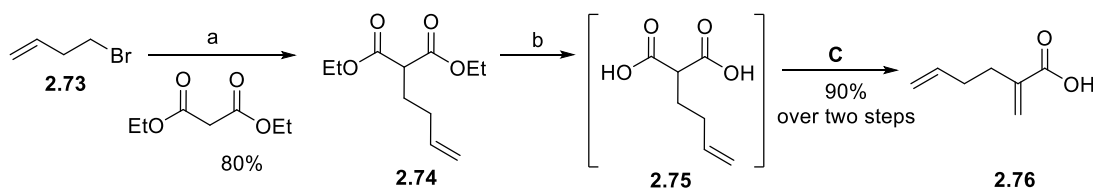
In this part we describe preparation of 1,5-dienoic acid where R^1 and R^2 are hydrogens. The preparation of 1,5-dienoic acid **2.76** began with the direct coupling of two alkyl halides: allyl bromide and halide **2.71** (**Scheme 2.19**). Initially, the Baylis-Hillman reaction was used to prepare

the alcohol **2.70** in 90% yield, through the coupling of an activated alkene derivative **2.69** with formaldehyde in the presence of DABCO. The alcohol **2.70** was brominated using PBr_3 under dry conditions to give the alkyl halide **2.71** in an excellent yield. Unfortunately, direct coupling of ester **2.71** with allyl bromide did not afford the 1,5-diene ester **2.72** by using either Mn/CuCl_2 in water or Grignard coupling and, therefore, this pathway was not investigated further.



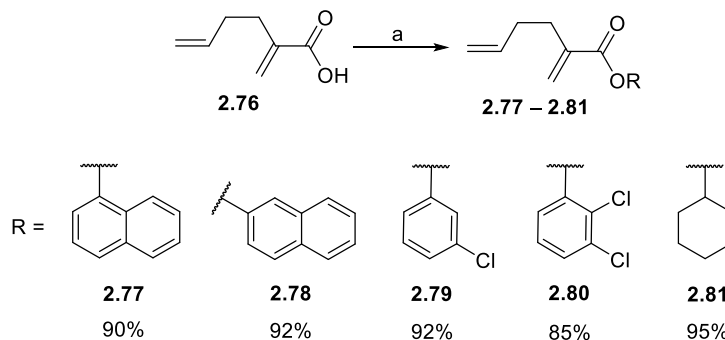
Scheme 2.19: Attempted synthesis of 1,5-dienoate ester **2.72**. **Reagents & conditions:** a) CH_2O (40% wt), DABCO, $\text{H}_2\text{O}/1,4\text{-dioxane}$ (1:1), 50°C , 2 h; b) PBr_3 , Et_2O , rt 2 h; c) Mn , CuCl_2 , H_2O , rt, 20 h; d) Allyl bromide, Mg , THF, reflux then ester **2.71**, LiBr , CuBr , -78°C 1 h.

The alkylation of diethyl malonate with commercially available 4-bromobut-1-ene (**2.73**) provided a successful pathway to the 1,5-dienoic acid **2.76** (**Scheme 2.20**). The mono alkylation of diethyl malonate with bromide (**2.73**) in the presence of K_2CO_3 and acetone afforded ester **2.74** with 80% yield. Here, the double alkylation side reaction was not detected. The hydrolysis of ester **2.74** at room temperature gave the intermediate diacid **2.75** which was refluxed directly with formaldehyde in the presence of diethyl amine in order to furnish the dienoic acid **2.76**.



Scheme 2.20: Synthesis of 1,5-dienoic acid **2.76**. **Reagents & conditions:** a) **2.73**, K_2CO_3 , acetone, rt, 48 h; b) KOH , H_2O , EtOH , 24 h, rt; c) CH_2O (40%), Et_2NH , reflux, 16 h.

Four aromatic esters as well as one aliphatic were obtained by reaction of dienoic acid **2.76** with different alcohols (**Scheme 2.21**). The aromatic esters **2.77–2.80** were obtained in very good yields between 92%–85%. The cyclohexyl dienoate **2.81** was obtained in 95% yield.

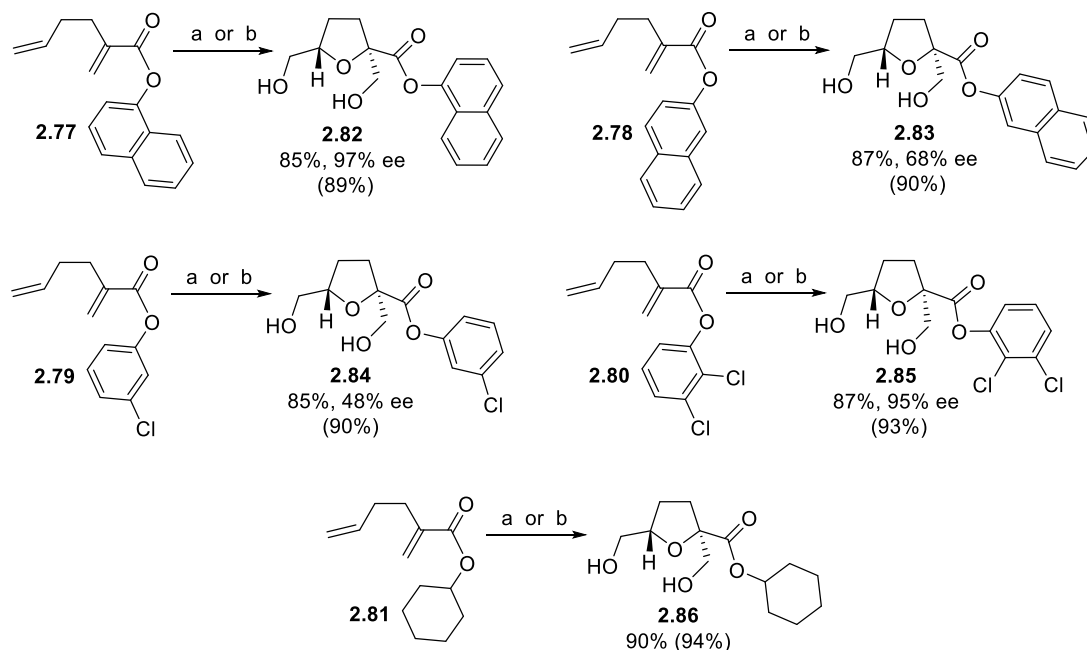


Scheme 2.21: Esterification of 1,5-diene **2.76**. **Reagents & conditions:** a) Alcohol, DMAP, DCC, DIEA, CH_2Cl_2 , rt, 15 h.

2.4.2.2 Permanganate-mediated oxidative cyclisation of group two dienoates ester

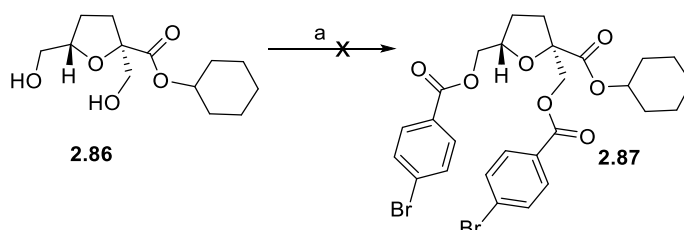
The **CPTC** oxidative cyclisations were carried out on the aforementioned dienoates **2.77–2.81** to give the corresponding enantiomerically enriched THF-diols (**Scheme 2.22**). The dienes were also cyclised under racemic conditions to confirm the separation of enantiomers by chiral HPLC. Pleasingly, improved *ee*'s were obtained for the substrates that stacked well with the aromatic pocket in **CPTC**. The α -Naphthyl dienoate **2.77** cyclised to THF-diol **2.82** in a high yield of 85% and an excellent selectivity of 97% *ee*, which is higher than α -Naphthyl dienoate analogue **2.40** (see **Scheme 2.14**). However, β -Naphthyl dienoate **2.78** was not affected by removing the two methyl groups from the electron rich-alkene site, giving THF-diol **2.83** with 68% *ee* and 87% yield. The asymmetric oxidative cyclisation of *m*-chlorophenyl dienoate **2.79** into its THF-diol **2.84** was achieved with 48% *ee* and 85% yield, correspondingly 56% *ee* was obtained for the similarly substituted diene **2.50** with (**Scheme 2.17**). Pleasingly, the oxidation of 2,3-dichlorophenyl dienoate **2.80** into THF-diol **2.85** showed excellent enantioselectivity of 95%, which is in accord with the selectivity of >94% *ee* observed for the corresponding diene **2.52** (**Scheme 2.17**). Again, 2,3-dichlorophenyl dienoate **2.80** is believed to provide similar structural properties to α -Naphthyl dienoate **2.77**.

The aliphatic ester **2.81** was used to confirm that aromatic properties are required for selectivity (**Scheme 2.22**). Although it gave high yields in both asymmetric and racemic conditions, we were not able to measure enantioselectivity for this reaction. Protection both of primary alcohol groups in cyclohexyl THF-diol **2.86** with benzoic acid did not afford the protected product **2.87**, which unexpectedly decomposed during purification. However, the crude TLC indicated the formation of the doubly protected THF adduct through the disappearance of THF-diol (**Scheme 2.23**). Due to time constraints, we have left this substrate without being able to measure the selectivity.



Scheme 2.22: Permanganate-mediated oxidative cyclisation of group two 1,5-dienoates **2.77–2.81**.

Reagents and conditions: a) CPTC conditions: KMnO_4 , **1.76** (10 mol %), AcOH (6.5 equiv), CH_2Cl_2 , -60°C , 3–4 h; b) Racemic conditions: KMnO_4 , adogen 464 (10 mol %), acetone/AcOH (3:2), -20°C , 30 min. Yields for reactions performed under racemic conditions are in brackets.

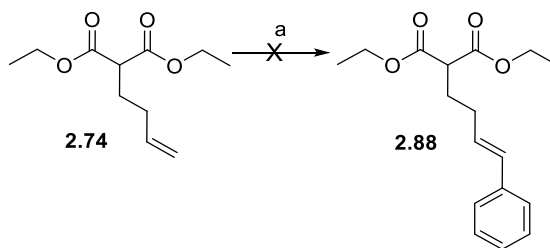


Scheme 2.23: Attempted derivatisation of THF-diol **2.86**. **Reagents & conditions:** a) 4-Bromo benzoic acid, DMAP, DCC, DIEA, CH_2Cl_2 , rt, 15 h.

2.4.3 Synthesis and oxidative cyclisation of group three dienates

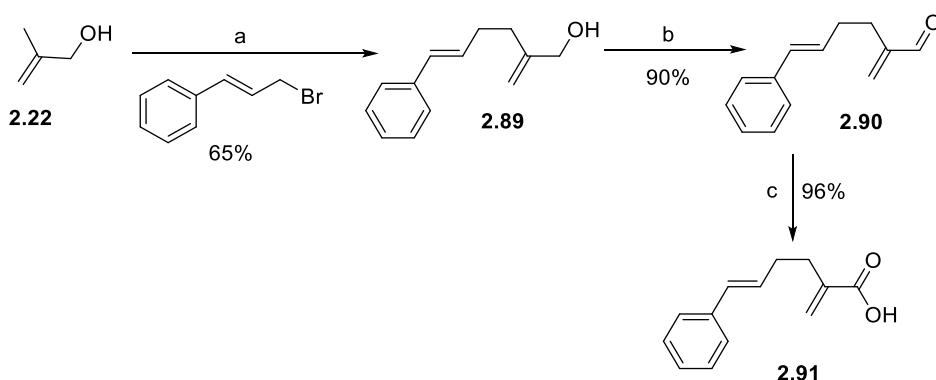
2.4.3.1 Synthesis of (*E*)-2-methylene-6-phenylhex-5-enoic acid (**2.91**)

In this section we describe oxidative cyclisation of 1,5-dienoates containing a phenyl substituent on the distal alkene to gain better understanding of the selectivity. Initially, we tried to develop a general synthesis of different 1,5-diene esters by cross-metathesis of **2.74** with styrenes (**Scheme 2.24**). Unfortunately, this approach failed using Grubbs I catalyst. Due to the poor initial results and high cost of the Grubbs catalyst this route was not explored further.



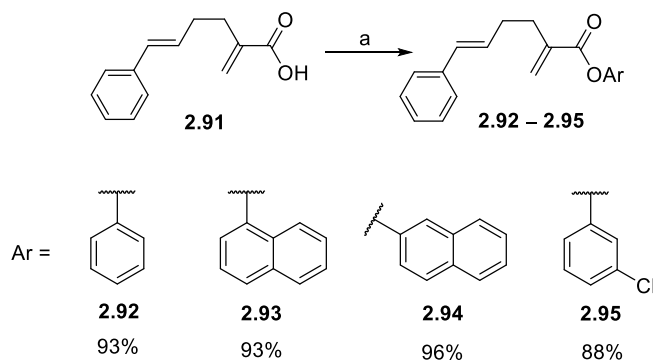
Scheme 2.24: Cross-metathesis of diethyl malonate **2.74** with styrene. **Reagents & Conditions:** a) Grubbs I (5 mol %), styrene, CH₂Cl₂, rt or reflux, 16 h.

Based on dianion chemistry, aromatic 1,5-dienoic acid **2.91** was successfully synthesised (**Scheme 2.25**). Deprotonation of methallyl alcohol (**2.22**) with *n*-BuLi, then reaction with cinnamyl bromide afforded diene **2.89** in good yield (75%). In this step, we have used a high concentration of *n*-BuLi (11.0 M in *n*-hexane) to improve the safety of the process by avoiding replacing the *n*-hexane by Et₂O. The alcohol **2.89** was then oxidised to aldehyde **2.90** in very good yield (90%) using activated manganese dioxide in *n*-hexane. The aldehyde **2.90** was efficiently converted into the desired carboxylic acid **2.91** in excellent yield (97%) using freshly prepared a silver oxide. The acid was used directly for the esterification reaction.



Scheme 2.25: Synthesis of 1,5-dienoic acid **2.91**. **Reagents & conditions:** a) (i) *n*-BuLi (6.0 equiv) in Et₂O, TMEDA, THF, -5 °C to rt, 38 h, (ii) cinnamyl bromide in THF, -78 °C to rt, 8 h; b) MnO₂, *n*-hexane, 0 °C to rt, 15 h; c) AgNO₃, NaOH, H₂O, 14 h.

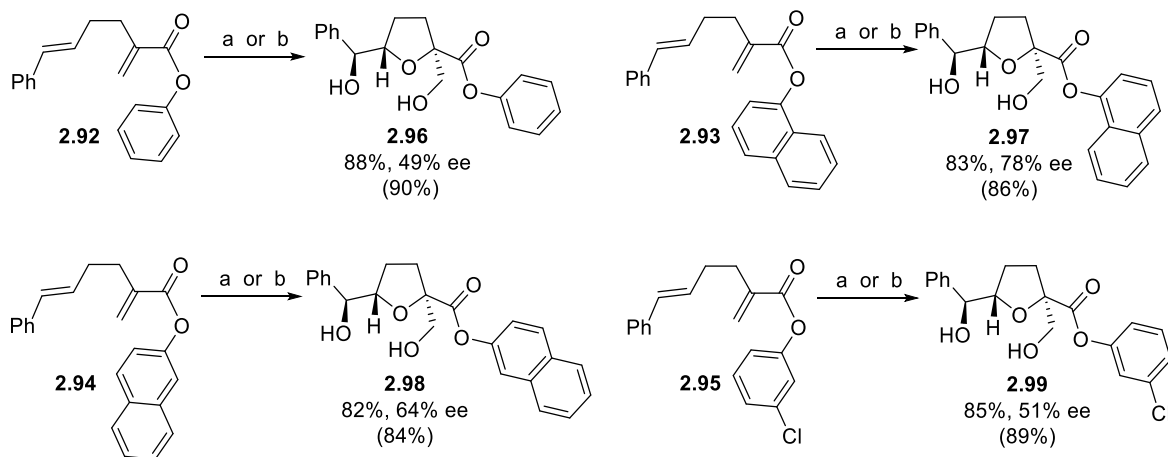
Using the previously described esterification methodology, four different aromatic esters were synthesised (**Scheme 2.26**). Excellent yields of 88%-96% were obtained for dienoates **2.92–2.95**. Now, the 1,5-dienes **2.92–2.95** have two different aromatic sites: an electron-deficient aromatic site located on the ester group and an electron-rich aromatic side located on the distal alkene.



Scheme 2.26: Synthesis of aryl dienoate esters **2.91–2.95**. **Reagents & conditions:** a) ArOH, DMAP, DCC, DIEA, CH₂Cl₂, rt, 16 h.

2.4.3.2 Permanganate-mediated oxidative cyclisation of group three dienoates

The enantioselective oxidative cyclisations were carried out on the aromatic dienoates **2.92–2.95** to give their corresponding THF-diols (**Scheme 2.27**). With two different aromatic substituents on the 1,5-diene, the asymmetric induction showed a moderate decrease compared to the corresponding dienoates shown in **Scheme 2.13** and **Scheme 2.16**. In the case of phenyl dienoate **2.92**, the selectivity of THF-diol **2.96** formation was decreased by 6%; this means 56% *ee* in the case of diene **2.39** and 49% *ee* for the current diene **2.92**. The same trend was obtained in the case of β -Naphthyl dienoate **2.94**, where a reduced *ee* of 64% was obtained for the THF-diol **2.96** formation. However, in comparison to the diene **2.40** (90% *ee*) (see **Scheme 2.14**) there was a decrease of 12% *ee* in the oxidative cyclisation of α -Naphthyl dienoate **2.93** (78% *ee*) (**Scheme 2.27**), and a greater decrease of 19% in comparison to the diene **2.77** (97% *ee*) (see **Scheme 2.22**). In the same manner, the asymmetric induction for *m*-chlorophenyl dienoate **2.95** into THF-diol **2.99** was 51% *ee*, only 5% decrease in *ee* in comparison to the diene **2.50** (see **Scheme 2.17**). We believe that there could be two possible reasons for the decrease in *ee*. The first one is that in the enantiocontrolled step, the disfavoured transition state that gives the minor enantiomer becomes more stable in dienes **2.92–2.95** due to the interaction between the phenyl ring on electron-rich alkene and the phenyl ring on CPTC (see zone C in **Figure 2.2**). The second reason could be the competition between electron-rich and electron-deficient alkene sites in the initial permanganation: i.e. the reaction is potentially initiated at both alkenes.

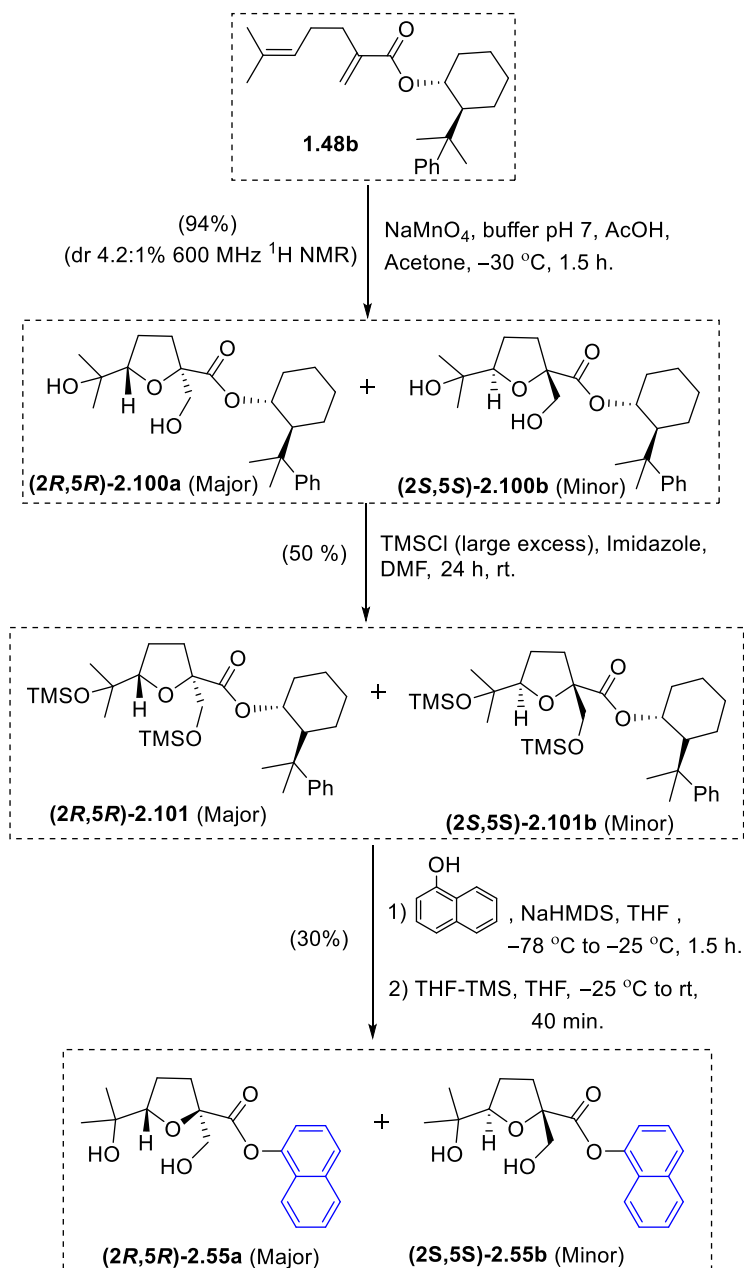


Scheme 2.27: Permanganate-mediated oxidative cyclisation of aromatic 1,5-dienoates **2.92–2.95**.

Reagents and conditions: a) **CPTC** conditions: KMnO_4 , **1.76** (10 mol %), AcOH (6.5 equiv), CH_2Cl_2 , -60°C , 3–4 h; b) Racemic conditions: KMnO_4 , adogen 464 (10 mol %), acetone/AcOH (3:2), -20°C , 30 min. Yields for reactions performed under racemic conditions are in brackets.

2.4.4 Determination of absolute configuration for the oxidative cyclisation product from α -naphthol dienoate **2.40**

The stereochemistry of the α -naphthol THF-diol ester **2.55** was determined by correlation with a THF-diol of known absolute stereochemistry (**Scheme 2.28**).⁵⁶ A sample of TCC dienoate **1.48b** was available from previous studies in the Brown group. The TCC oxidative cyclisation product **2.100**, which was known to be a mixture of **(2R,5R)-2.100a** and **(2S,5S)-2.100b** with a ratio of $\sim 4.2:1$ dr, was converted to the α -naphthol THF-diol ester **2.55**. HPLC comparison (**Figure 2.3**) with the sample from the **CPTC** oxidative cyclisation pathway showed that the major enantiomer to be **(2R,5R)-2.55a**.



Scheme 2.28: Conversion of the TCC-dienoate **1.48b** into α -naphthol THF-diols ester **(2R,5R)-2.55a** and **(2S,5S)-2.55b** for stereochemical correlation using chiral HPLC.

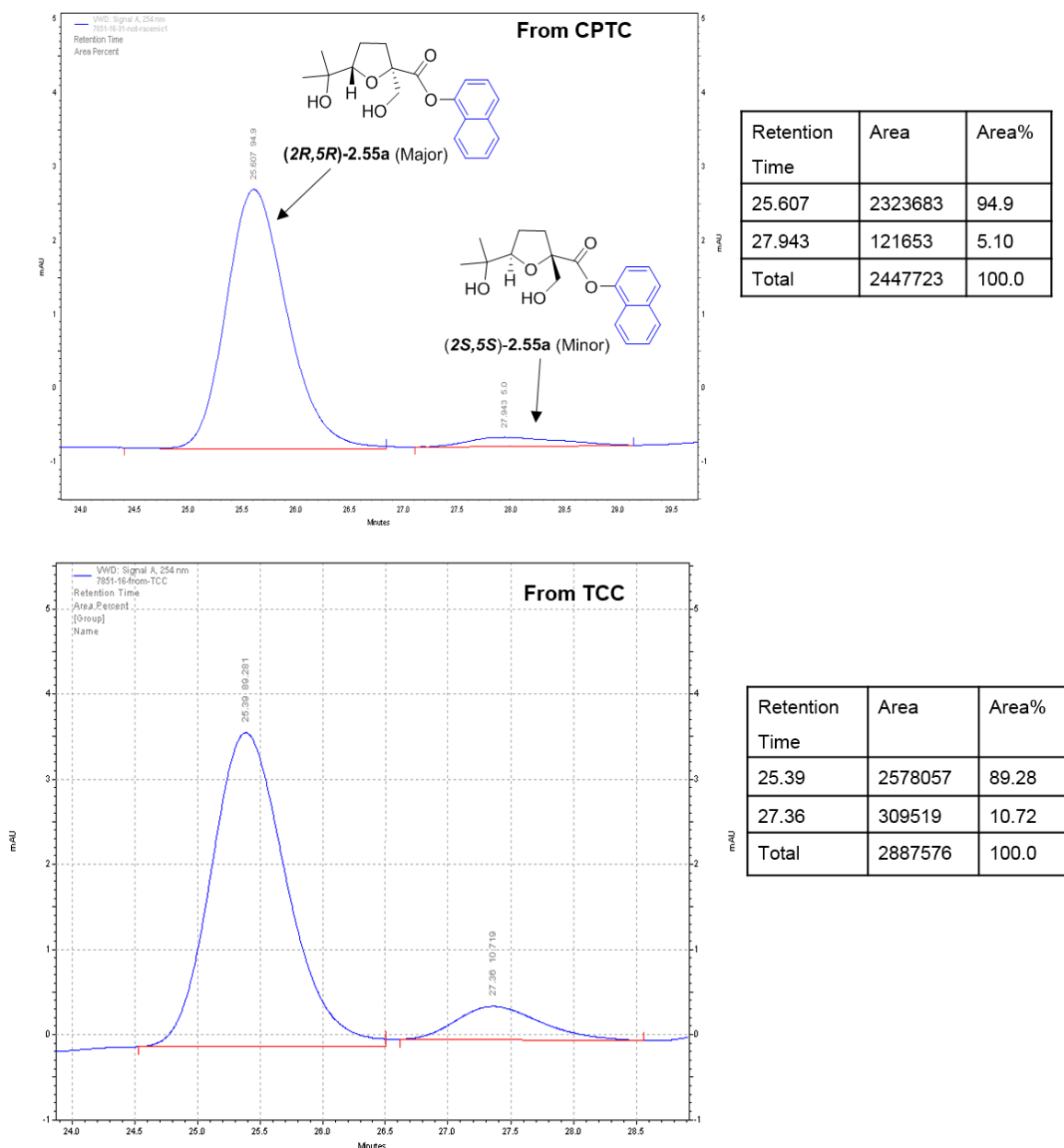


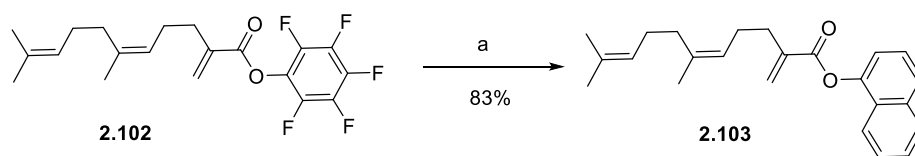
Figure 2.3: HPLC trace for the α -naphthol THF-diols ester **(2R,5R)-2.55a** and **(2S,5S)-2.55b**, 1 mL/min, 254 nm, OD-H, eluent: 2.5% isopropanol/hexane.

2.5 Permanganate-mediated oxidative cyclisation of trienoate **2.103** using CPTC conditions

The oxidative cyclisation of 1,5,9-triene is key step in the synthesis of the natural product eurylene developed in the Brown laboratory.^{32,270} Following the success of the oxidative cyclisation of aromatic 1,5-dienoates under chiral phase transfer conditions, specifically oxidation of α -naphthyl dienoate **2.40**, we decided to apply the **CPTC** transformation to the 1,5,9-triene system through attachment of α -naphthyl. The synthesis of α -naphthyl 1,5,9-trienoate **2.103** was accessed from

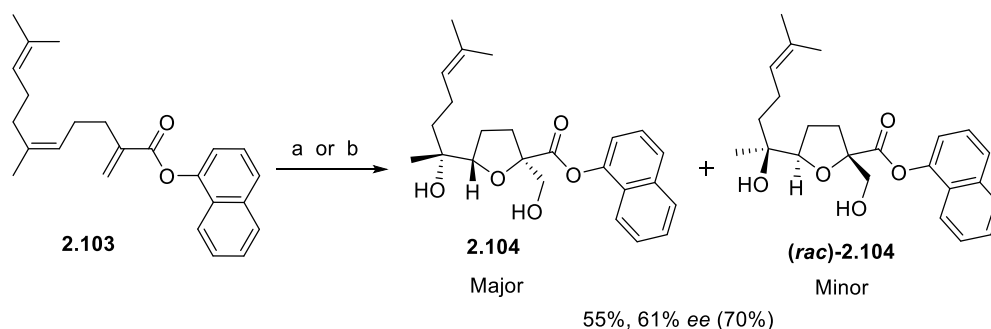
transesterification of PFP ester **2.102** with α -naphthol using NaHMDS in 83% yield (**Scheme 3.29**).

Fortunately, PFP ester **2.102** was available from previous studies in our laboratory.⁵⁷



Scheme 2.29: Synthesis of α -naphthol 1,5,9-trienoate **2.103**. **Reagents and conditions:** a) (i) NaHMDS, α -naphthol, THF, $-75\text{ }^{\circ}\text{C}$ to $-5\text{ }^{\circ}\text{C}$ over 1.5 h; (ii) PFP ester (**2.103**), THF, rt, 1 h.

The same oxidative cyclisation conditions used for the diene system was applied to the triene system but with 1.3 eq. of the permanganate ion to avoid over oxidation (**Scheme 2.30**). Unexpectedly, the reaction proceeded with lower yield (55%) and selectivity (61%) than the 1,5-diene system (90% yield and 90% ee). In addition we did not recover any starting material.²⁷¹ The lower yield for the triene system may be explained by competing reaction of permanganate ion at the three alkene sites. In terms of enantioselectivity, it is clearly evident that the triene system is longer than the diene system and, therefore, it is possible that triene is not a good “fit” within the catalyst due to the longer tail which may introduce steric interactions with the benzyl group on the CPTC (look zone C in **Figure 2.2**). This could also allow the permanganate ion to attack the remote double bond resulting in a lower yield.



Scheme 2.31: Permanganate-mediated oxidative cyclisation of trienoate **2.103** under CPTC conditions. **Reagents and conditions:** a) CPTC conditions: KMnO_4 , **1.76** (10 mol %), AcOH (6.5 equiv), CH_2Cl_2 , $-60\text{ }^{\circ}\text{C}$, 3–4 h; b) Racemic conditions: KMnO_4 , adogen 464 (10 mol %), acetone/AcOH (3:2), $-20\text{ }^{\circ}\text{C}$, 30 min. Yields for reaction performed under racemic condition are in brackets.

The use of different equivalents of the catalyst were investigated for the oxidative cyclisation of the trienoate **2.103**. Increasing the amount of the chiral catalyst did not show a noticeable effect on the selectivity although 0.3 equiv. of catalyst gives a slightly better ee of 64 % (**Figure 2.4**).

Unexpectedly, using more than 0.3 equiv. apparently decreases the enantioselectivity to 53% *ee*. At present, we do not have any good explanation for these results.

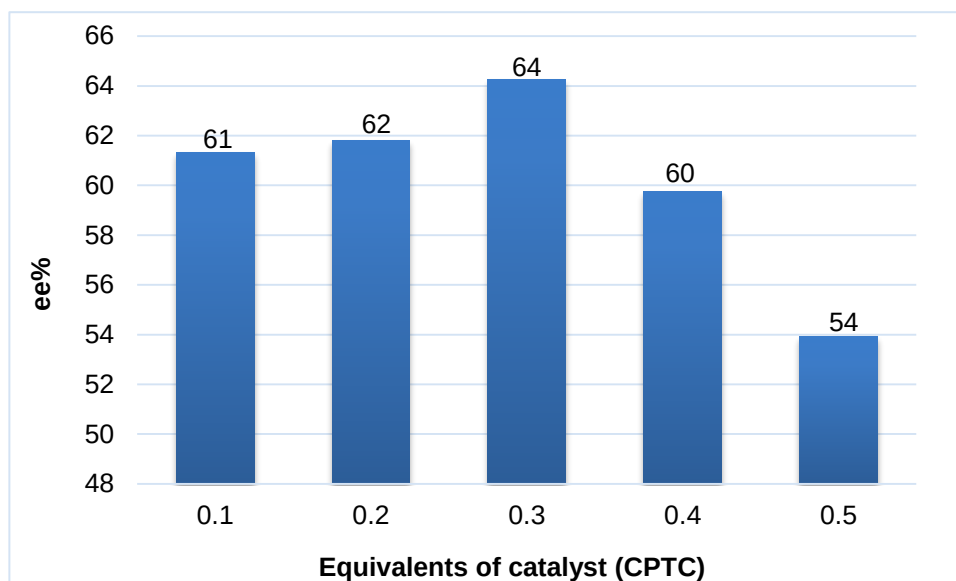
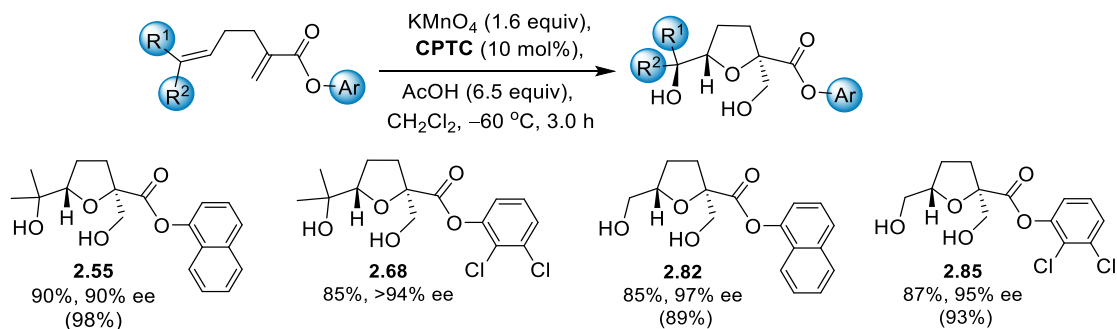


Figure 2.4: Enantiomeric excess investigation against the number of equivalent of **CPTC** in the permanganate-mediated oxidative cyclisation of α -naphthol 1,5,9-trieneoate **2.103**.

2.6 Conclusions

The permanganate promoted **CPTC** oxidative cyclisation of 1,5-dienoates bearing different aromatic esters have been investigated, realising excellent *ee*'s and yields for the first time as a direct oxidative cyclisation of 1,5-dienes. The oxidative cyclisation of 1,5-dienoates were carried out on three different groups of aryl dienates based on the substituents on the distal alkene.

Replacement of aromatic ester groups in the substrates with a simple methyl ester led to no asymmetric induction, which is believed to be due to the absence of CH- π , π - π , and cation- π interaction between substrate and **CPTC**. Two aryl ester groups, α -naphthyl and 2,3-dichlorophenyl, display *ee*'s in the range of 90%-97%, indicating that the high *ee*'s can be achieved π -stacking interactions combined with suitable shape and electronic properties (**Scheme 2.31**).



Scheme 2.31: Summary of the highest ee's achieved in the permanganate promoted **CPTC** oxidative cyclisation.

With the exception of 2,3-dichlorophenyl, the effect of substituents in the aromatic ring has not led to an improvement in the level of asymmetric induction. In general, electron-withdrawing and electron-donating groups present in phenyl esters display moderate ee's.

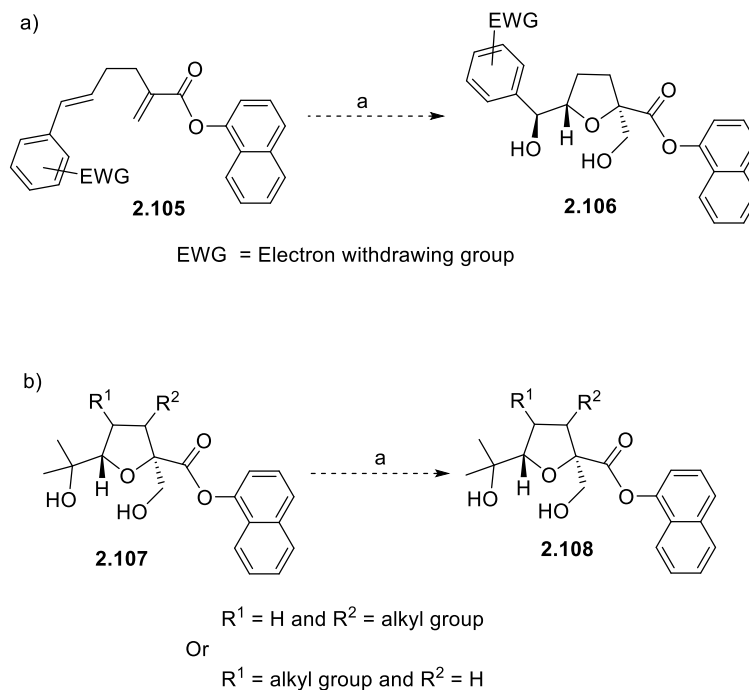
When the electron-rich alkene was substituted with a phenyl group, the enantioinduction is found to be decreased. This may suggest either an unfavourable steric interaction with the **CPTC**, or a competing reaction initiated at the styrene olefin.

The stereochemistry of **CPTC** oxidative cyclisation product was determined by correlation with a THF-diol obtained from diastereoselective oxidative cyclisation of a dienoate ester with a cyclohexyl chiral auxiliary. The absolute stereochemistry was shown to be (**2R,5R**) for THF diol **2.55a**.

The **CPTC** oxidative cyclisation of α -naphthyl 1,5,9-trienoate shows a moderate ee (61%) and yield (55%) in comparison to α -naphthyl 1,5-dienoate (90% yield and 90% ee). It is believed that the longer chain present in the trienoate interferes with the substrate binding.

2.7 Future work

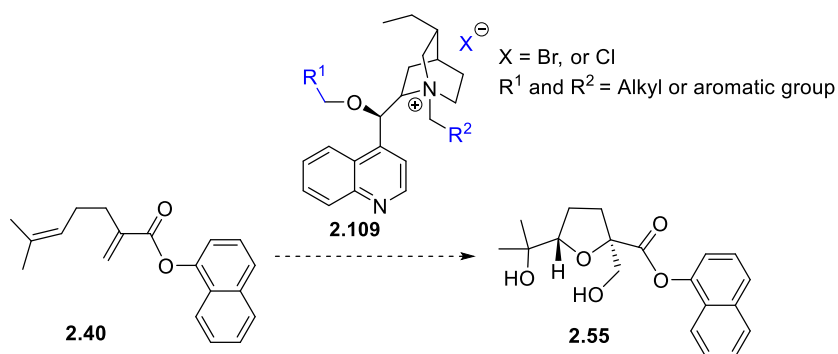
An elegant approach to the THF-diol synthesis has been demonstrated utilising an asymmetric permanganate-mediated oxidative cyclisation with high yields and ee's. Since α -naphthyl 1,5-dienoate has shown excellent selectivity, it would be interesting to explore α -naphthyl 1,5-dienoate but using different EWG substituted aromatic ring of the electron-rich alkene side to gain better understanding of the selectivity (**Scheme 3.32-a**). It would be also desirable to attach substituents on the ethylene linking group (CH_2 groups of incipient THF ring) to see how yield and selectivity will be affected (**Scheme 3.32-b**).



Scheme 2.32: Interesting substrates for the **CPTC 1.76** oxidative cyclisation. **Reagents and Conditions:** a) KMnO_4 (1.6 equiv), AcOH (6.5 equiv), **1.76** (10 mol%), CH_2Cl_2 .

Since the enantioselectivity of the permanganate-mediated oxidative cyclisation of 1,5-dienes is not fully understood, it would be highly desirable to investigate it computationally using DFT simulations to develop a model for the asymmetric induction. This would involve a comparison between the calculated and experimental selectivities.

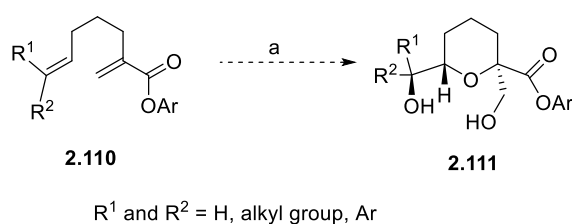
Furthermore, investigation of the effect of catalyst structure on enantioselectivity to develop fundamental understanding of catalyst design would be highly desirable in order to achieve high asymmetric induction. This would be achieved through a combination of computational and synthetic approaches to tailor the catalyst structure. Initial work will target the aryl ether (CH_2R^1) and quaternary ammonium (CH_2R^2) substituents (**Scheme 2.33**).



Scheme 2.33: Oxidative cyclisation of α -naphthyl 1,5-dienoate **2.40** using chiral PTC **2.109**.

Reagents and Conditions: a) $KMnO_4$ (1.6 eq), AcOH (6.5 equiv), **2.109** (10 mol %), CH_2Cl_2 .

Also, based on the optimised conditions of oxidative cyclisation of 1,5-dienoates, it would be interesting to extend the work into 1,6-dienoates (**Scheme 2.34**).



Scheme 2.34: Chiral phase-transfer catalysed synthesis of tetrahydropyranes through oxidative cyclisation of aromatic 1,6-dienoate ester. **Reagents and Conditions:** a) $KMnO_4$ (1.6 equiv), AcOH (6.5 equiv), **1.76** (10 mol %), CH_2Cl_2 .

Chapter 3 Results and Discussions

3.1 DFT examination of the permanganate-mediated oxidative cyclisation of 1,5-dienes

This chapter will describe the mechanism of permanganate-mediated oxidative cyclisation of 1,5-diene via high-level computational approaches. A DFT study of the permanganate-mediated oxidative cyclisation of (2*E*,6*E*)-octa-2,6-diene **3.1** to give (1*S**,1'*R**)-1,1'-((2*R**,5*S**)-tetrahydrofuran-2,5-diyl)diethanol (**3.2**) was performed using the M06-2X/aug-cc-pVDZ/Hay-Wadt (n+1) ECP level of theory (**Figure 3.1**). The reaction pathway of THF-diol formation was considered as two principle steps: first reaction step (FRS) represents the addition of MnO_4^- to one of the diene double bonds, and the second reaction step (SRS) represents the addition of an intermediate manganese glycolate across the remaining alkene. Although the FRS has been the subject of numerous DFT studies relating to olefin dihydroxylation reactions, the effect of counter ions (K^+ , Na^+ , or quaternary ammonium ion) are important terms which were not included in the literature studies. As for the SRS, possible secondary reactions that may occur prior to cyclisation under the experimental reaction conditions are of major interest to us. A number of possibilities were considered for the initially formed intermediate Mn(V) diester including reoxidation ($\text{Mn(V)} \rightarrow \text{Mn(VI)}$), addition of water, effect of counter ion, and effect of acid. Different spin multiplicities were considered due to the fact that manganese has different spin configurations depending on the oxidation state of Mn. For all pathways, frontier molecular orbital (FMO) analysis was used to understand the orbital interaction for the cyclisation step. Classical molecular dynamics (MD) and potential energy surface (PES) were used for three reasons; to confirm the validity of a TS, to dynamically understand the SRS at the atomic-level and to better understand the motion of atoms during the reaction event. Before we introduce the oxidative cyclisation mechanism, a comparison between experimental and theoretical free energies of activation for the FRS for different alkenes is provided in order to validate our computational method.

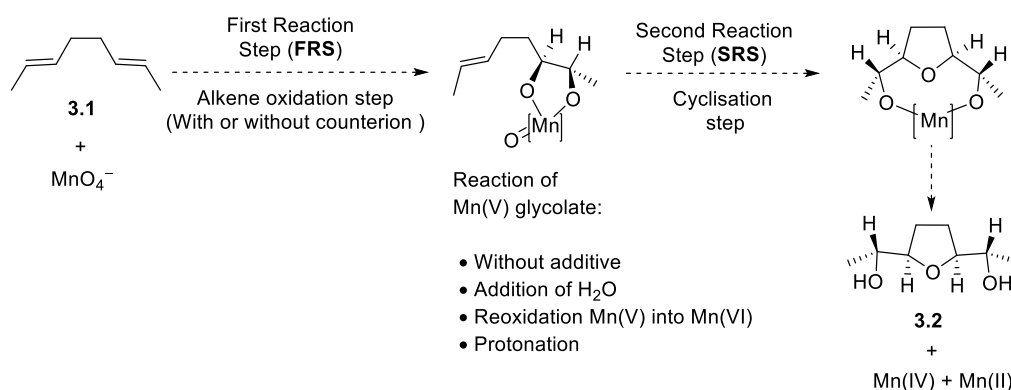


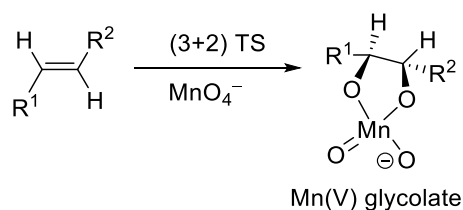
Figure 3.1: Summary of the different pathways considered for permanganate oxidative cyclisation of 1,5-diene **3.1**.

3.2 The validation of the level of theory ((SMD)-M06-2X/aug-cc-pVDZ/ECP) used in the present study

In order to validate the accuracy of the computational method, (SMD)-M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP, used in this investigation, free energies of activation were calculated for permanganation of various alkenes. **Table 3.1** shows a comparison between calculated and measured free energies of activation for permanganation of 8 different alkenes. The level of theory used throughout the current work gives calculated activation free energies that are in good agreement with the experimental values for the selected substrates. In the case of alkenoic acids, entries 3-7, we have calculated activation free energies for both the protonated and deprotonated forms (values for carboxylate ions shown in parentheses in **Table 3.1**). Optimised geometries of the free acids are shown in **Figure 3.2** whereas the carboxylate geometries are shown in **Figure 3.3**.

The calculated activation energy for the oxidation of allyl alcohol (**3.3**) is 14.8 kcal/mol and the experimental one is 14.6 kcal/mol (entry 1), only 0.2 kcal/mol difference. As for the energy of reaction, there is only one available experimental enthalpy of reaction for allyl alcohol oxidation found in the literature.¹¹³ The measured enthalpy of reaction, which was determined calorimetrically, was found to be $\Delta H_r = -87 \pm 2$ kcal/mol whereas the calculated one was $\Delta H_r = -99.6$ kcal/mol ($\Delta G_r = -85.8$ kcal/mol) in the absence of a counter ion, such as K^+ and Na^+ . In the presence of Na^+ , the calculated enthalpy of reaction becomes $\Delta H_r = -98.0$ kcal/mol ($\Delta G_r = -85.8$ kcal/mol) and the calculated activation energy decreased from 14.8 kcal/mol into 14.1 kcal/mol.

The deprotonated alkenoic acids have higher calculated activation energies, entries 3, 4 and 7. However, the calculated barriers for entries 5 and 6 are higher than the experimental results, both for the protonated and deprotonated forms. Because the double bond is not conjugated to the carboxylic group, we believe that the experimental results are less well accounted for by the calculations. Therefore, we have used (*E*)-hept-2-ene (**3.24**), entry 8, as an experimental model to validate the accuracy of our calculation. We have found an excellent agreement between the measured and calculated barriers of 17.7 and 17.3 kcal/mol respectively (see entry 8). Importantly, (*E*)-hept-2-ene is the most representative example for our substrate **3.1** used for oxidative cyclisation pathway.

Table 3.1: Comparison between calculated and experimental free energies of activation for the permanganation for different alkenes.^a

Entry	alkene	Measured energies	Calculated energies	
		$\Delta G_{\text{exp}}^{\ddagger}$	$\Delta G_{\text{calc}}^{\ddagger}$	ΔG_{r}
1	Allyl alcohol (3.3)	14.6 ^b	14.8	−85.8
2	Acrylonitrile (3.6)	14.2 ^b	15.5	−82.0
3	Acrylic acid (3.9)	14.1 ^c	14.9 (18.3)	−82.0 (−81.8)
4	Crotonic acid (3.12)	14.3 ^c	15.9 (19.5)	−80.7 (−83.0)
5	Vinylacetic acid (3.15)	14.8 ^c	18.1 (16.7)	−87.9 (−83.5)
6	4-Pentenoic acid (3.18)	14.5 ^c	18.7 (16.5)	−83.2 (−82.2)
7	Cinnamic acid (3.21)	13.9 ^c	14.82 (17.2)	−77.0 (−75.3)
8	(<i>E</i>)-hept-2-ene (3.24)	17.7 ^d	17.3	−83.9

^a The energies for entries 1–8 were calculated at the (SMD)-M06-2X/aug-cc-pVDZ/ECP level of theory in water at 298.15 K. ^b Taken from reference 113 and measured at 298 K in H₂O.¹¹³ ^c Taken from reference 272 measured at 298 K in H₂O.²⁷² ^d Taken from reference 273 and measured at 298 K in H₂O.²⁷³ Energies between brackets calculated for carboxylate form. Energies are in kcal/mol.

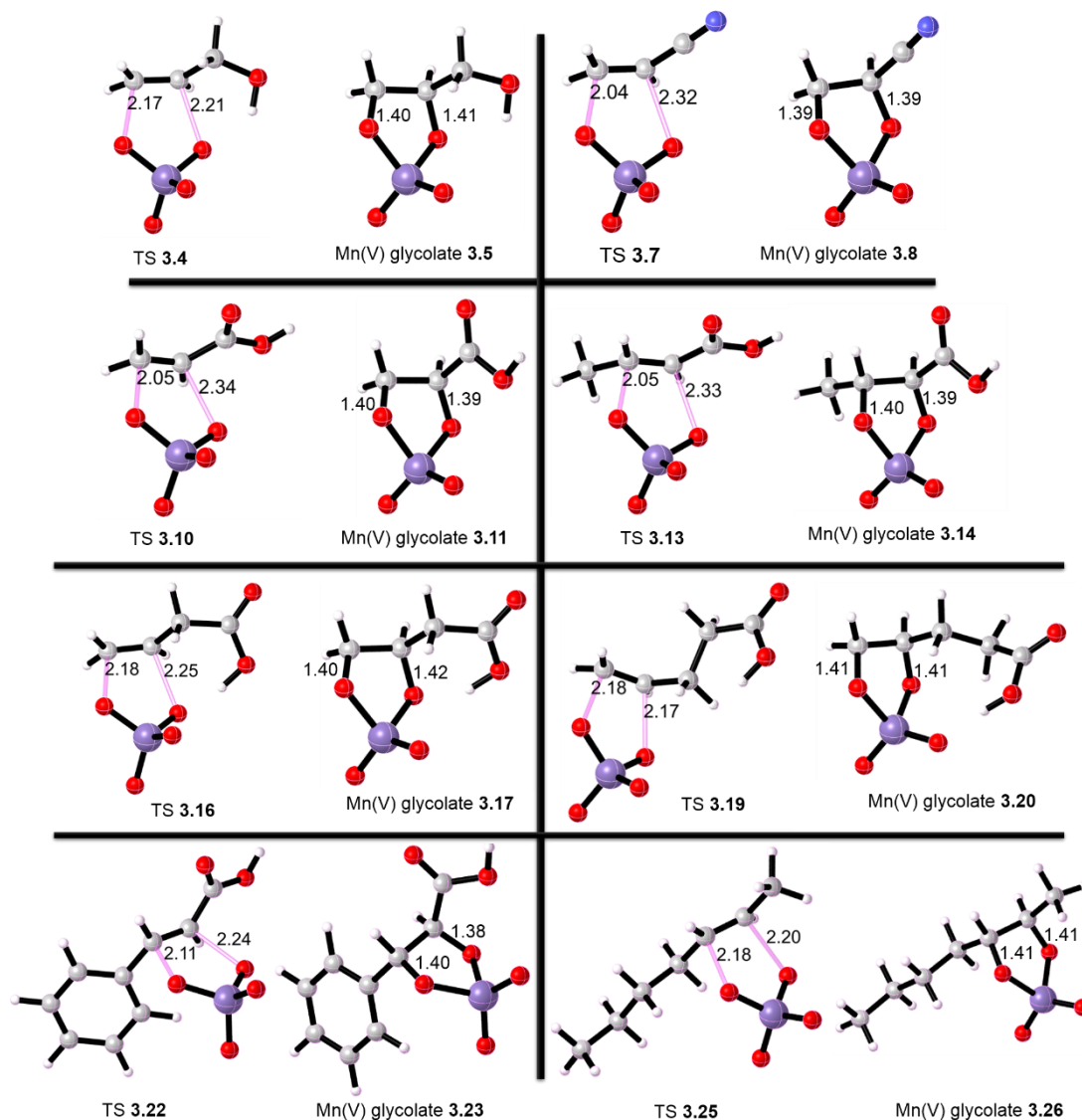


Figure 3.2: Optimised geometries for permanganation of different alkenes, showing TS's and Mn(V) glycolate.

We have also calculated the free energy of activation for the permanganate oxidation of styrene, *p*-methyl styrene, and *p*-Nitro styrene in the presence of tetraethyl ammonium (TEA) ion as a PTC (**Figure 3.4**). The level of theory used in the calculation shows a good agreement with the experimental results. Here, we have included the dispersion interactions to better account for interaction in the ionic pairing of the oxidising agent ($\text{MnO}_4^- \text{Et}_4\text{N}^+$).²⁷⁴

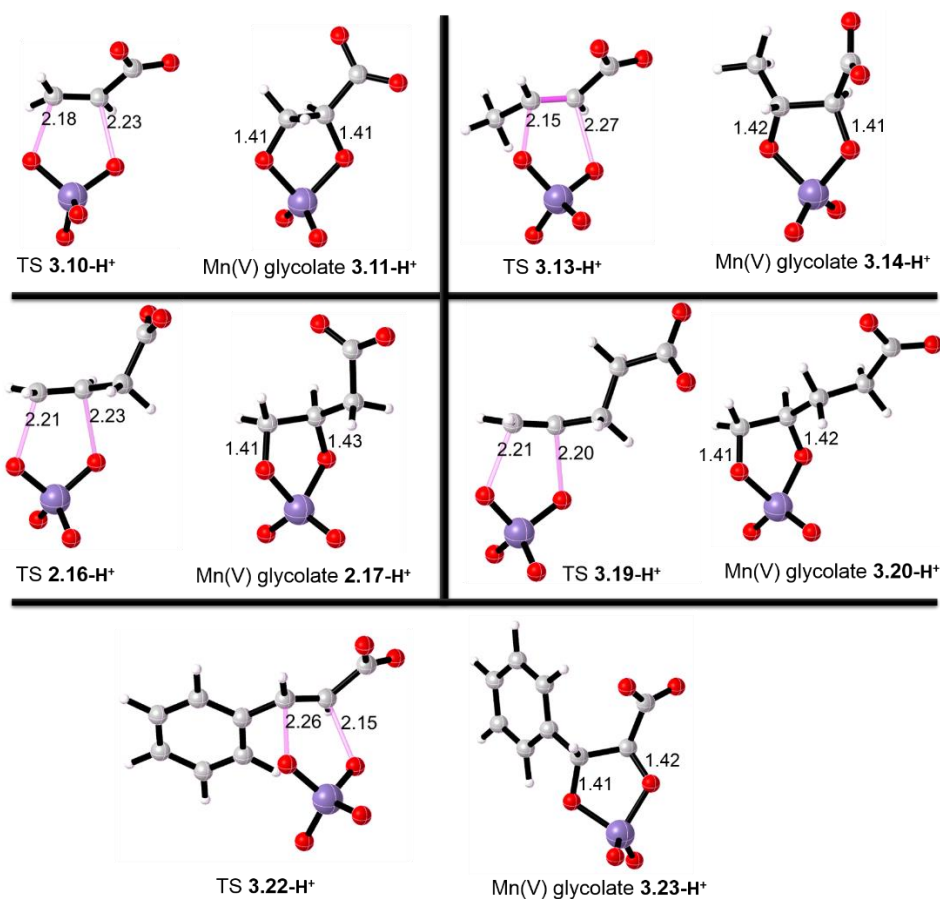


Figure 3.3: Optimised geometries for permanganation of alkenoic carboxylates, showing TS's and Mn(V) glycolate.

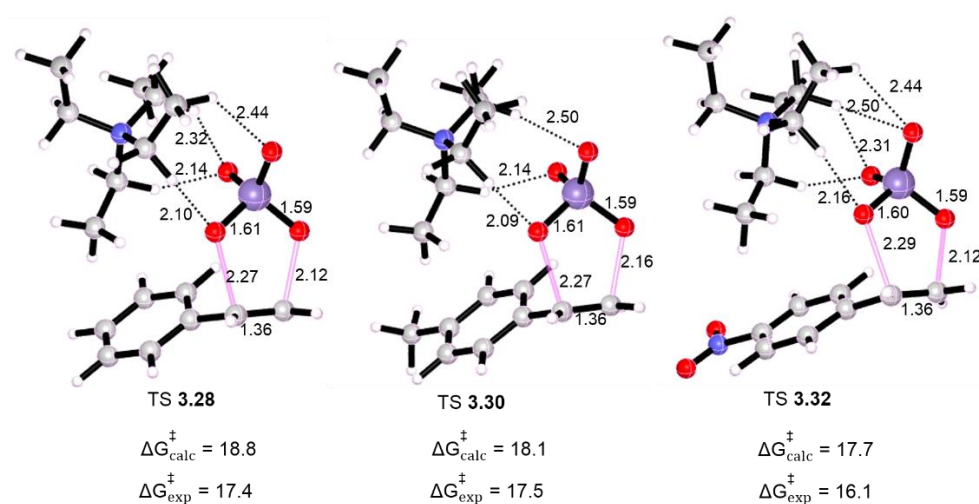


Figure 3.4: Comparison between the calculated and experimental free energies of activation for the permanganation of styrene (3.27), *p*-methyl styrene (3.28), and *p*-Nitro styrene (3.29) in the presence of TEA ion calculated by (SMD)-M06-2X-D3/aug-cc-pVDZ/Hay-Wadt (n+1) ECP level of theory in CH₂Cl₂ at 298.15 K. Experimental results taken from reference 116 and measured at 298 K in CH₂Cl₂.¹¹⁶ Energies are in kcal/mol.

Overall, the level of theory (SMD)-M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP used for calculations shows good agreement with the experimental measurements.

3.3 Proposed pathways for the permanganate-mediated oxidative cyclisation of 1,5-diene

The principle focus here will be on the cyclisation step (SRS). In addition, the effect of counter ion on the FRS will be studied. In order to investigate the cyclisation mechanism, five different pathways have been suggested according to the experimental reaction conditions calculated by the SMD-(acetone)-(U)M06-2X/aug-cc-pVDZ/Hay-Wadt (n+1) ECP level of theory at 253.15 K. The most representative experimental conditions seen in chapter one are either aqueous acidic condition (e.g. aqueous KMnO_4 or NaMnO_4 , AcOH/acetone-water, -20°C) or acidic phase transfer catalysis condition (e.g. powdered KMnO_4 , adogen 464, AcOH/acetone, -20°C). Four proposed pathways for the Mn(V) intermediate include:

- Oxidative cyclisation without any additives
- With addition of a water molecule
- In the presence of counter ions Na^+ and Me_4N^+
- Under acidic condition

Based on Baldwin's proposed mechanism, the Mn(V) reoxidises into Mn(VI) to facilitate cyclisation, so a fifth pathway to be considered is cyclisation from a reoxidised Mn(VI) intermediate.

Here, all discussions will be focused on singlet spin multiplicity. However, high spin state pathways are explained in **section 3.8** of this chapter.

3.3.1 Oxidative cyclisation without additives

The simplest pathways to consider for oxidative cyclisation of 1,5-dienes by permanganate ion is without any additives. We have excluded a triplet transition state for the FRS, but intermediate Mn(V) glycolate **3.34s** has additional potential energy hypersurfaces accessible; triplet and quintet in addition to singlet PES. High spin pathways are explained in **section 3.6**. According to our computational model, the formation of tetrahedral singlet Mn(V) glycolate **3.34s** ($\Delta G_r = -86.0$ kcal/mol, $\Delta H_r = -90.7$ kcal/mol) from the FRS is exergonic proceeding via a dynamically concerted (3+2) cycloaddition TS **3.33** with a free energy barrier of 17.1 kcal/mol (**Figure 3.5**). Interestingly, the calculated enthalpy of Mn(V) glycolate formation is in an excellent agreement with the experimental result for the oxidation of allyl alcohol (**3.3**) ($\Delta H_r = -87 \pm 2$ kcal/mol).¹¹³ Cyclisation via singlet TS **3.35s** ($\Delta G^\ddagger = 37.6$ kcal/mol) resulted in formation a tetrahedral THF-diolate intermediate **3.36s** as an exergonic step ($\Delta G_r = -26.1$ kcal/mol). The TS **3.35s** was found to be a

dynamically concerted (3+2) cycloaddition according to the C–O bond vibration with asynchronicity of 0.39 Å at the TS (**Figure 3.5**). This means that the C–O[Mn] bond formation precedes closure of the THF ring (see TS **3.35s**).

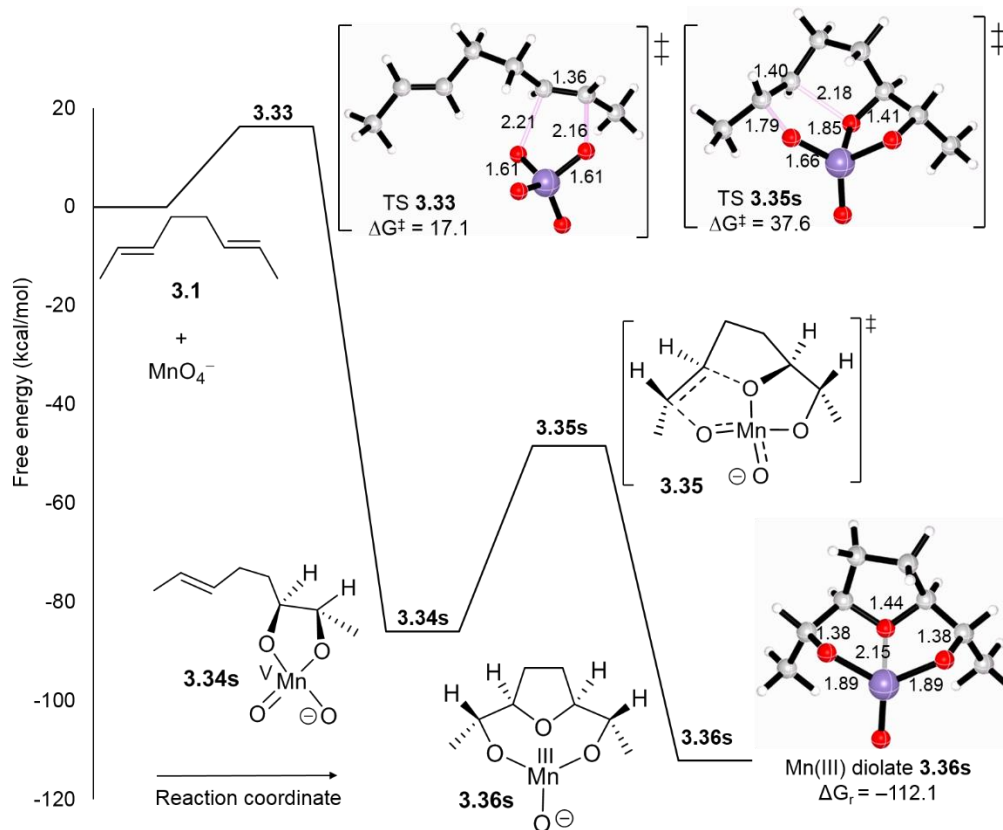


Figure 3.5: Reaction energy diagram for the permanganate oxidative cyclisation of 1,5-diene **3.1** without additives, showing TS's and intermediates for the FRS and SRS (singlet (s) spin multiplicities). Here, Mn(VII) $\rightarrow$ Mn(V) $\rightarrow$ Mn(III).

3.3.2 Oxidative cyclisation of Mn(V) glycolate: the effect of hydration on the SRS

The oxidative cyclisation step has been investigated in the presence of water (**Figure 3.6**). The optimisation of H_2O insertion into the Mn(V) glycolate has resulted in formation of square pyramidal geometry Mn(V) glycolate **3.34s_{H2O}**, where one oxygen is vertical on four planer oxygens producing penta-coordinated complex as a lowest local minimum.^{275,276} Simulation results showed an increase in energy for the singlet hydrated Mn(V) glycolate **3.34s_{H2O}** ($\Delta\Delta G_{\text{H}_2\text{O}} = +5.2$ kcal/mol). Although the singlet hydration was not an exergonic step, it is on the borderline of thermoneutral ligand exchange which might explain the results of Wolfe and Ingold who showed exchange of the oxygen atoms experimentally.⁴⁵ Moreover, a mechanistic study on the oxygen exchange between $\text{Mn}^{\text{V}}=^{16}\text{O}$ and H_2^{18}O has been done by Song *et. al.*¹¹⁹ indicating that the ligand exchange occurs at fast rate.

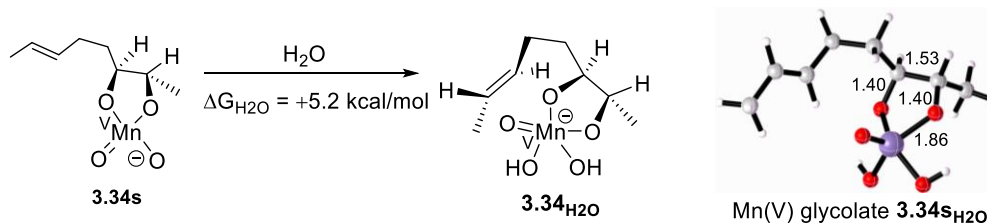


Figure 3.6: Addition of water to Mn(V) glycolate **3.34s**.

The singlet pathway led to the cyclisation product **3.36s_{H2O}** (**Figure 3.7**). Free energy of activation was found to decrease from 37.6 kcal/mol in the absence of water (see **Figure 3.5**) to 30.0 kcal/mol via TS **3.35s_{H2O}** (**Figure 3.7**), although it is still high compared to experimental observation. The singlet PES cyclisation is an exergonic reaction with $\Delta G_r = -47.9$ kcal/mol compared to $\Delta G_r = -26.1$ kcal/mol in the absence of water (**Figure 3.5**).

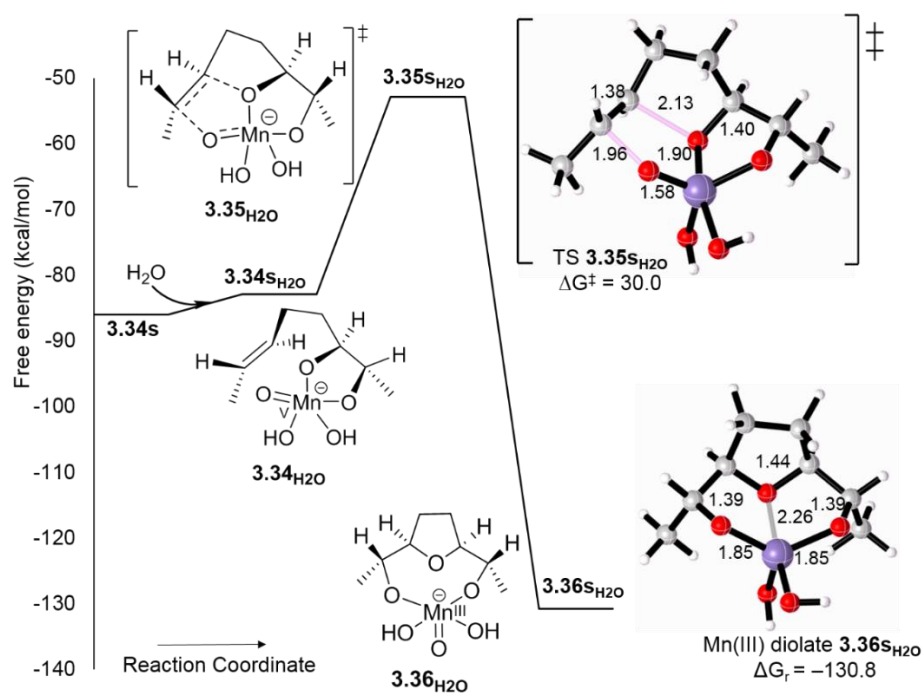


Figure 3.7: Reaction energy diagram showing the SRS for the permanganate oxidative cyclisation of 1,5-diene **3.1** with water addition.

3.3.3 Oxidative cyclisation of Mn(VI) glycolate: Reoxidation of Mn(V) → Mn(VI)

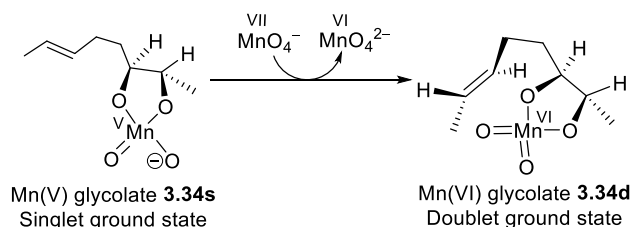
This section will describe the effect of reoxidation of Mn(V) into Mn(VI) via comproportionation with MnO_4^- to validate cyclisation of a Mn(VI) glycolate intermediate according Baldwin's proposed mechanism.⁴³ Intermediates and TS's for Mn(VI) pathways were calculated by single point energy

calculations using the (SMD)-(U)M06-2X/aug-cc-pVDZ/Hay-Wadt (n+1) ECP level of theory based on geometries optimised by the (U)M06-2X/aug-cc-pVDZ level of theory otherwise mentioned.

3.3.3.1 Cyclisation via non-hydrated Mn(VI) glycolate

Baldwin proposed a mechanism where reoxidation of Mn(V) glycolate to Mn(VI) occurs by MnO_4^- . In order to evaluate this redox reaction, we calculated the Gibbs free energy of Mn(VI) formation using both implicit solvation models such as polarisable continuum model (PCM) and solvation model based on density (SMD) and explicit solvent molecules. The spin multiplicity of Mn(VI) glycolate is doublet due to the single unpaired electron. The free energy of reoxidation **3.34s** $\rightarrow$ **3.34d** in solution was calculated from B3LYP and M06-2X functional with full electronic basis sets; (U)M06-2X/aug-cc-pVDZ and (U)B3LYP/6-311+G(d) (**Table 3.2**). Here, we have selected three solvents (acetone, water, and dichloromethane) which represent typical experimental conditions. Clearly, reoxidation of Mn(V) $\rightarrow$ Mn(VI) under solvent effect is not supported by calculations using either PCM and SMD with the selected solvents. This result is reasonable because Mn(VI) is known to be stable only under highly basic conditions whereas the reaction conditions are weakly acidic. Also, Mn(VI) species disproportionates rapidly under acidic conditions.^{44,277,278}

Table 3.2: Energies of reoxidation reaction for the Mn(V) glycolate **3.34s** into Mn(VI) glycolate **3.34d** in different solvents using a full electronic basis sets at 298.15 K in kcal/mol.



Solvation model/solvent	Free energy (ΔG_r) (U)B3LYP/6-311+G(d)	Free energy (ΔG_r) (U)M06-2X/aug-cc-pVDZ
PCM/water	20.4	33.8
PCM/ CH_2Cl_2	31.1	22.0
PCM/acetone	24.3	26.4
SMD/ CH_2Cl_2	34.8	27.2
SMD/acetone	29.2	20.0

In order to avoid using full electronic basis sets such as 6-311+G(d) and aug-cc-pVDZ on Mn atom in DFT calculations, we have run a single point energy calculation using (U)M06-2X/aug-cc-

pVDZ/Hay-Wadt (n+1) ECP, based on geometries optimised by the (U)M06-2X/aug-cc-pVDZ level of theory. **Figure 3.8** shows an energetic diagram for the comproportionation of Mn(V) into Mn(VI) glycolate in which the activation energy of electron transfer was calculated using Marcus theory approach. The most important part in Marcus theory is the reorganisation energy (λ) which is the energy required to reorganize nuclei without electron transfer occurring.²⁷⁹ In other word, reorganisation energy is the energy required to reorganise nuclei from coordinates of reactant state to coordinates of product state including reorganisation of relevant solvent molecules. One of the methods most often employed is the four-point method proposed by Nelsen,^{280–282} which has been extensively applied because of its simplicity and it has been successfully proven for many systems.^{283–288} The output of Nelsen calculations is the total reorganization energy which is then applied in the Marcus equation of electron transfer $\Delta G^\ddagger = (\lambda + \Delta G_r)^2/4\lambda$.

Nelsen's procedure to calculate λ for reoxidation reaction involves four steps:

1. Geometry optimisation of reactants (**3.34s** and **MnO₄⁻**) on a singlet spin state to give thier free energy; $G_1 = -1122.408646$ Ha (Ha = hartree)
2. Single point energy calcu7lations of the reactants but on a doublet spin state; $G_2 = -1122.357328$ Ha, this means that estimation of the energy of products is based on geometry of reactants.
3. Geometry optimisation of products (**3.34d** and **MnO₄²⁻**) on a doublet state; $G_3 = -112.366739$ Ha
4. Single point energy calclations of the products but on a singlet spin state; $G_4 = -1122.367208$ Ha, this means that estimation of the energy of reactants is based on geometry of products.

Computation of the reorganisation energy requires substraction of G_4 from G_1 to give λ_1 and G_2 from G_3 to give λ_2 . That means $\lambda_1 = G_4 - G_1 = 26.0$ kcal/mol, and $\lambda_2 = G_2 - G_3 = 5.9$ kcal/mol. Now, the average of both λ_1 and λ_2 will give the total reorganisation energy, $\lambda = \lambda_1 + \lambda_2/2 = 16.0$ kcal/mol.

By applying the free energy of reoxidation ($\Delta G_r = 26.3$ kcal/mol) and reorganisation energy ($\lambda = 16.0$ kcal/mol) in the Marcus equation of electron transfer, the activation energy of reoxidation was found to be 28.0 kcal/mol (**Figure 3.8**). It should be noted that the major energetic contribution in this activation energy is the driving force of reaction ($\Delta G_r = 26.3$ kcal/mol). Based on our high-level DFT simulations, the disproportionation is more favoured than comproportionation because it needs only 1.7 kcal/mol of free energy of activation to return to Mn(V) and Mn(VII) as a very exergonic step of $\Delta G_r = -26.3$ kcal/mol. This result explains the harsh conditions needed to form Mn(VI), experimentally under highly basic conditions of 10 N KOH.^{44,277,278} Therefore, this reoxidation is unlikely to happen under the conditions of oxidative cyclisation.

As seen in **Figure 3.8-b**, the two oxo ligands on Mn(VI) **3.34d** have different bond lengths. One of them has a radical character due to the longer bond 1.76 Å, specifically the unpaired electron on Mn(VI) is located on the O—Mn bond. However, prior to the electron transfer both of them have similar distances of 1.56 Å or 1.57 Å as shown in **3.34s**. The interaction energy required to bring both electron donor, Mn(V) glycolate **3.34s**, and the electron acceptor, MnO_4^- , into the equilibrium complex **3.34s** • MnO_4^- was found to be +8.2 kcal/mol (see complex in the box in **Figure 8-a**). Computationally, the complex **3.34s** • MnO_4^- was optimised under a cavity of solvent in order to keep the donor and acceptor under effect of solvent. The donor-acceptor distance at the equilibrium point was 44.8 Å and this means that the electron hops from **3.34s** to MnO_4^- at a very long distance.²⁸⁹ However, the electron hop appears to be disfavoured.

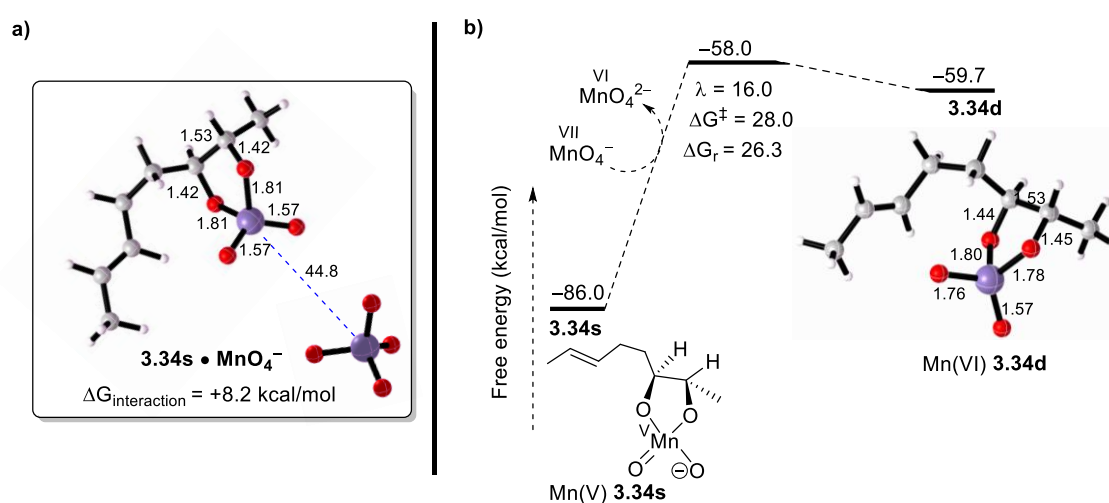


Figure 3.8: a) Precursor Complex **3.34s** • MnO_4^- and b) energetic profile of comproportionation of Mn(V) glycolate into Mn(VI) glycolate in acetone at 253.15 K, where the activation energy was calculated based on Marcus theory.

Although comproportionation seems unlikely to occur, we have also calculated the doublet cyclisation step from **3.34d** into **3.36d** in order to check the possibility of doublet cyclisation (**Figure 3.9**). We could not locate a doublet TS connecting the pathway from Mn(VI) glycolate **3.34d** to Mn(IV) diolate **3.36d**. However, the located one, which was found at a similar energetic level to the intermediate Mn(VI) glycolate due to the radical character of the O—Mn bond (length is 1.76 Å), is invalid because the desired vibration between alkene site and Mn site was found to be only partially achieved; only C2 and O6 atoms vibrate to each other whereas C1 and O5 atoms did not. This indicates that THF ring formation is disallowed due to the disallowed orbital symmetry between the LUMO site and HOMO site (see FMO analysis section). The atomic polar tensor (APT) charges show that the THF ring should be formed after the first C2—O6 bond formation. Here, the dynamical motion of atoms to make the first C—O bond shows an attacking order from oxygen into carbon, in

which the nucleophilicity of adjacent carbon C1 will be increased resulting in a forbidden THF ring formation due to repulsion between C1 and O5 atoms. In order to check this pathway in detail we have carried out PES and MD calculations on TS **3.35d** (see below).

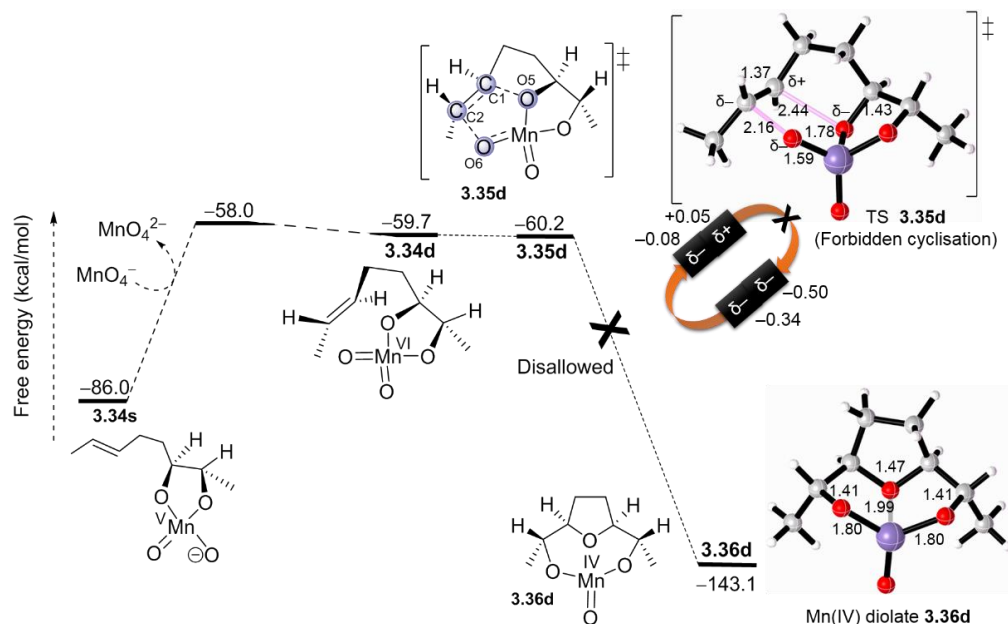


Figure 3.9: Energetic profile for the doublet cyclisation step **3.34d** → **3.36d** in acetone at 253.15 K, showing a forbidden cyclisation. APT charges in electron (e) units.

MEP calculation along the PES for the TS **3.35d** has been performed under acetone (**Figure 3.10**). The result show the O6—C2 bond formation on both sides of TS; **3.35d_a** and **3.35d_b** instead of giving the product **3.36d** or reactant **3.34d**.

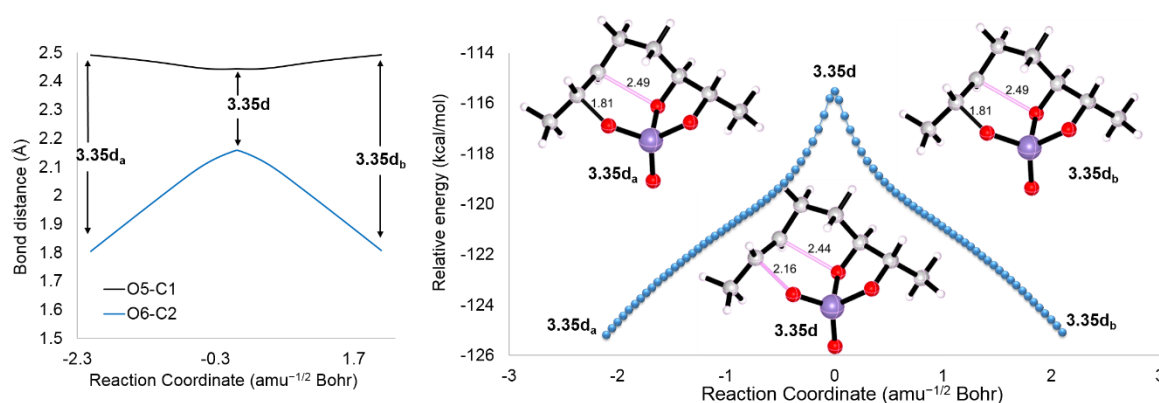


Figure 3.10: PES examination on doublet pathway Mn(VI) → Mn(IV), showing the formation and deformation of O5—C1 and O6—C2 bonds respectively as well as the relative energy along reaction coordinate in acetone/SMD model.

MD calculation for the forward propagation of TS **3.35d** considering the typical reactive bonds O5—C1 (C—O[THF]) and O6—C2 (C—O[Mn]) was carried out in acetone (**Figure 3.11**). Although results show formation of the C2—O6 bond and a deformation of C1—O5, glycolate decomposition is seen. Propagation after 250.0 fs showed a breaking of C19—C20. At 500.0 fs the Mn27—O8 and Mn27—O5 bonds are completely broken resulting in formation of two aldehydes. This supports well-known experimental observations which link formation of Mn(VI) with decomposition.^{46,47}

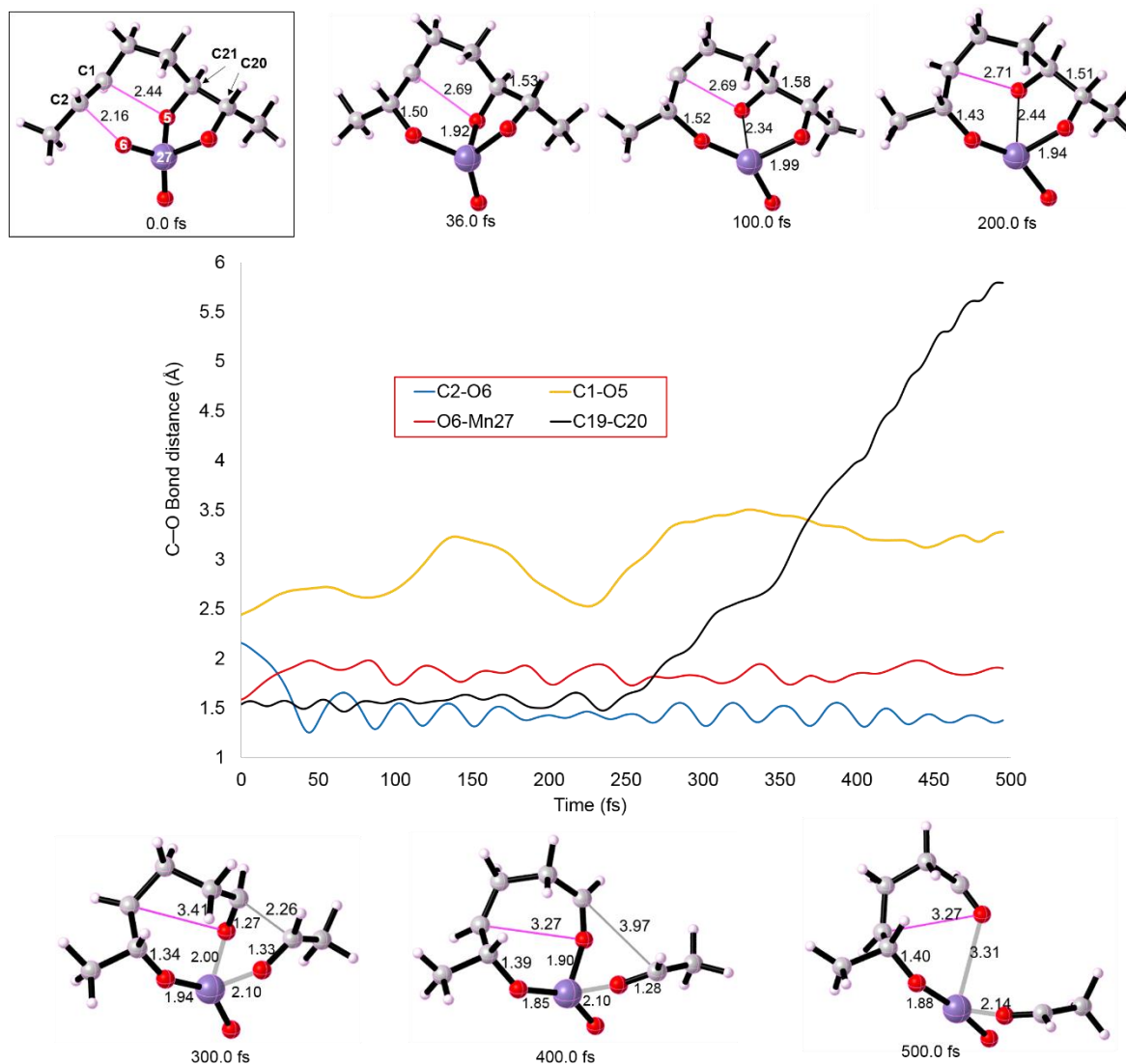
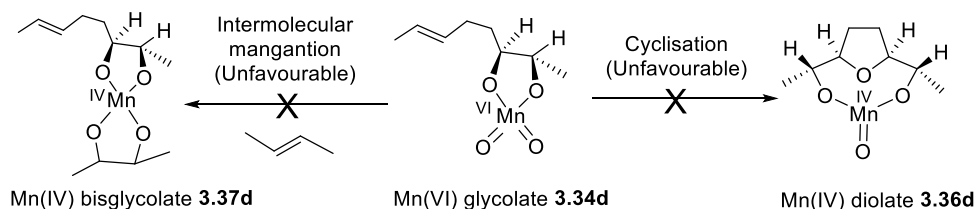


Figure 3.11: Molecular dynamics examination on TS **3.35d** in acetone, showing snapshots at different times for cleavage of the Mn(VI) glycolate.

Since our simulations showed that cyclisation on doublet pathway Mn(VI) $\rightarrow$ Mn(IV) was not possible, we also looked into the intermolecular reaction of Mn(VI) glycolate with another alkene (**Scheme 3.2**). All efforts failed to locate a transition state for the intermolecular manganation using different basis sets such as 6-31G, 6-311+G(d,p), cc-pVDZ and aug-cc-pVDZ with both DFT functionals B3LYP and M06-2X. Therefore, we concluded that intermolecular manganation using Mn(VI) glycolate is not likely to occur.



Scheme 3.2: Disfavoured intermolecular and intramolecular cyclisation manganation from Mn(VI) glycolate **3.34d**.

Since the cyclisation of Mn(VI) glycolate is disfavoured, decomposition pathways were considered (**Figure 3.12**). The decomposition pathway was calculated to be kinetically disfavoured over the backward disproportionation of Mn(VI) into Mn(V) glycolate. Cleavage of the C—C bond in **3.34d** was achieved through TS **3.38d** with a barrier of only 6.4 kcal/mol giving the initially decomposed doublet product **3.39d** ($\Delta G_r = -2.0$ kcal/mol) followed by a spin jump to quartet Mn(IV) **3.39qr**. The quartet product **3.39qr** is lower in energy than **3.39d** by -71.5 kcal/mol, giving rise to the thermodynamic driving force for the degradation of Mn(VI) glycolate. It has been reported that oxidation of Mn(V) into Mn(VI) leads to decomposition into aldehydes as the expected pathway.^{46,47} Therefore, formation of Mn(VI) leads to glycolate decomposition rather than cyclisation by a kinetically and thermodynamically favourable pathway. Interestingly, this decomposition pathway was supported by molecular dynamic simulations on TS **3.35d** (see **Figure 11**).

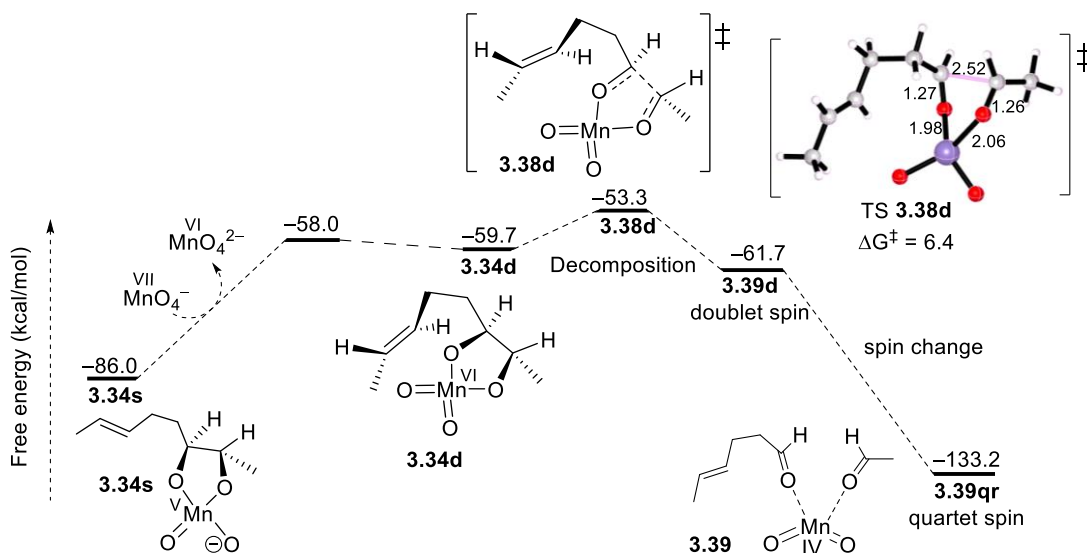


Figure 3.12: Decomposition pathway of Mn(VI) glycolate.

Although reoxidation of hydrated Mn(V) **3.34**_{sH2O} is energetically disfavoured, a doublet cyclisation pathway from Mn(VI) glycolate **3.34**_{dH2O} to the Mn(IV) diolate **3.36**_{dH2O} was calculated (**Figure 3.13-b**). The located TS **3.35**_{dH2O} was found to be more stable than the **3.34**_{dH2O}. However, this TS does

not connect reactant **3.34d**_{H2O} and product **3.36d**_{H2O} along the PES because of the disallowed orbital symmetry (see FMO analysis section).

3.3.3.3 Summary of Mn(VI) glycolate pathways

To summarise the computational investigation of oxidative cyclisation via Mn(VI) pathways, some important points may be highlighted:

- Reoxidation of non-hydrated Mn(V) glycolate into Mn(VI), **3.34s**→**3.34d**, is energetically disfavoured ($\Delta G_r = 26.3$ kcal/mol, $\Delta G^\ddagger = 28.0$ kcal/mol). We could not locate TS is either for cyclisation via pathway **3.34d**→**3.36d**, or for intermolecular manganation via pathway **3.34d**→**3.37d** due to the disallowed orbital symmetry. Furthermore, formation of Mn(VI) glycolate opens up a decomposition pathway giving aldehydes and MnO₂.
- Reoxidation of hydrated Mn(V) glycolate, **3.34s**_{H2O}→**3.34d**_{H2O}, is highly disfavoured energetically ($\Delta G_r = +35.2$ kcal/mol, $\Delta G^\ddagger = 84.7$ kcal/mol).
- Since it is known from the results of Wolfe and Ingold,⁴⁵ and Song¹¹⁹ that Mn(V) is able to undergo ligand exchange with water, hydration of Mn(V), **3.34s**→**3.34s**_{H2O}, outpaces reoxidation and also favours hydration energetically.
- The reoxidation of Mn(V) to Mn(VI) was explored via hydrated Mn(V) glycolate **3.34s**_{H2O}, which was also found to be highly disfavoured based on Marcus theory. This is in agreement with the stability of Mn(VI), which is only stable in strongly alkaline conditions (10 N KOH). The oxidative cyclisation conditions are weakly acidic conditions,⁴⁴ and therefore any reoxidation seems highly improbable.
- On the basis of the computational results and known stability of Mn(VI), cyclisation via Mn(VI) pathway seems unlikely and the SRS should proceed via a Mn(V) intermediate.

3.3.4 Oxidative cyclisation under acidic conditions: the effect of counter ion

Understanding the role of acid and, in general, the role of the counter ion is one of the most important aspects in this study. Counter ions such as Na⁺ (based on aqueous acidic conditions), quaternary ammonium ion (based on acidic PTC conditions), and H⁺ will be considered in order to stabilise the negative charge of Mn species. Potassium ion (K⁺) was excluded from our calculations because the basis set aug-cc-pVDZ is not suitable for potassium.

3.3.4.1 The effect of Na⁺ counter ion on oxidative cyclisation

The FRS and SRS proceed under effect of counter ions Na⁺. Including Na⁺ in the calculations stabilise the charge on permanganate ion and decreases the alkene oxidation step barrier from 17.1 kcal/mol into 15.6 kcal/mol through (3+2) TS **3.33**_{Na}, giving a neutral tetrahedral Mn(V) glycolate **3.34**_{sNa} with free energy of reaction of −81.8 kcal/mol (**Figure 3.14**). The calculated enthalpy of reaction was −93.8 kcal/mol compared to −90.7 kcal/mol in the absence of Na⁺, both results are relatively close to the experimental one obtained for allyl alcohol oxidation ($\Delta H_r = -87 \pm 2$ kcal/mol).¹¹³ Cyclisation of the sodium salt Mn(V) has shown a decreased energy barrier ($\Delta G^\ddagger = 26.9$ kcal/mol) via TS **3.35**_{sNa} compared to the addition of water ($\Delta G^\ddagger = 30.0$ kcal/mol) or without additive ($\Delta G^\ddagger = 37.6$ kcal/mol). The sodium ion shows kinetic and thermodynamic stabilisation of 10.7 and 14.4 kcal/mol respectively on the SRS, although the barrier of cyclisation is still relatively high.

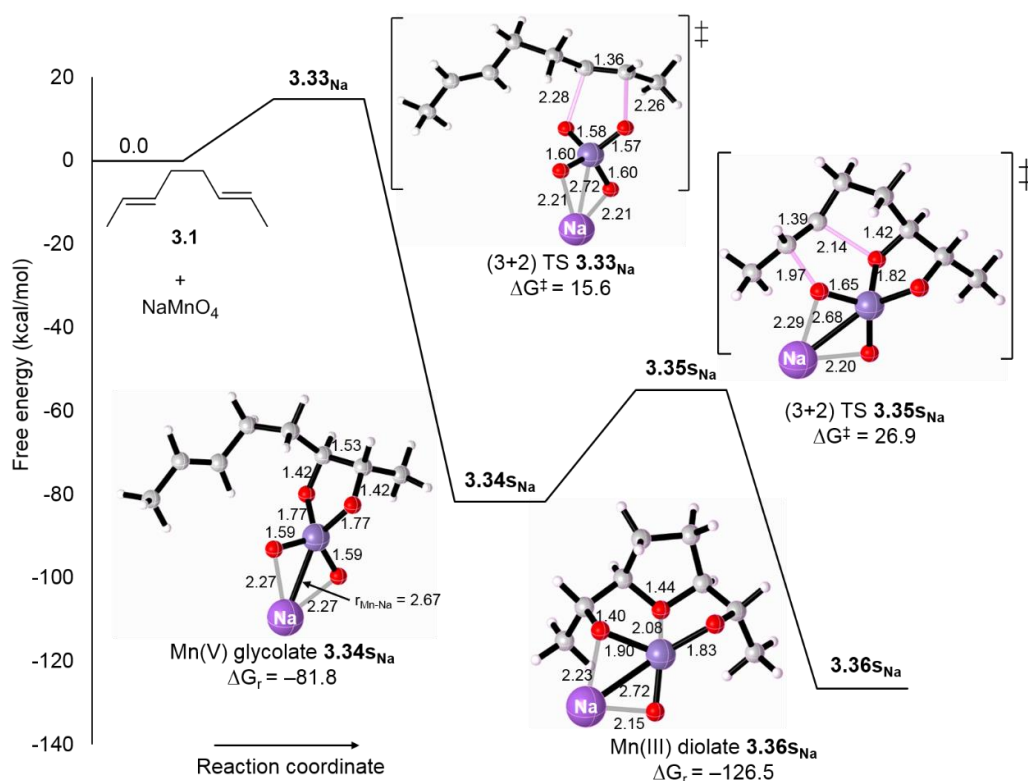


Figure 3.14: Energetic profile showing the effect of Na⁺ on oxidative cyclisation of 1,5-diene by permanganate ion.

3.3.4.2 The effect of quaternary ammonium ion on oxidative cyclisation

The effect of phase transfer catalysts, specifically quaternary ammonium ions such as tetramethyl ammonium (TMA) ion, have been studied on the FRS and SRS (**Figure 3.15**).^{116 79–81} A complex of oxidising agent (MnO₄[−] and TMA) reacts with the diene through TS **3.33** • TMA and leads to Mn(V) glycolate as an ion pair. This counter ion shows a decrease in the barrier of alkene oxidation via

(3+2) TS **3.33 • TMA** ($\Delta G^\ddagger = 15.4$ kcal/mol), similar to Na^+ . The main reason for decreasing the activation energy of permanganation is the ionic interaction between the positively charged area around N and the negatively charged oxo ligand on Mn. This could be also attributed to hydrogen bonding between hydrogen atoms of methyl groups around nitrogen and oxygen atoms as visualised by the APT charges on TS **3s • TMA**.²⁶⁹ The Mn(V) glycolate complex **3.34s • TMA** was formed with $\Delta G_r = -79.2$ kcal/mol as free energy of reaction. The neutral Mn(V) glycolate **3.34s • TMA** cyclises into Mn(III) diolate THF ring with a barrier of 29.6 kcal/mol via **3.35s • TMA** with reaction free energy of -37.4 kcal/mol. This barrier is lower by 8 kcal/mol than without TMA counter ion (see **Figure 3.5**) and higher by around 3.0 kcal/mol than with sodium ion (see **Figure 3.14**).

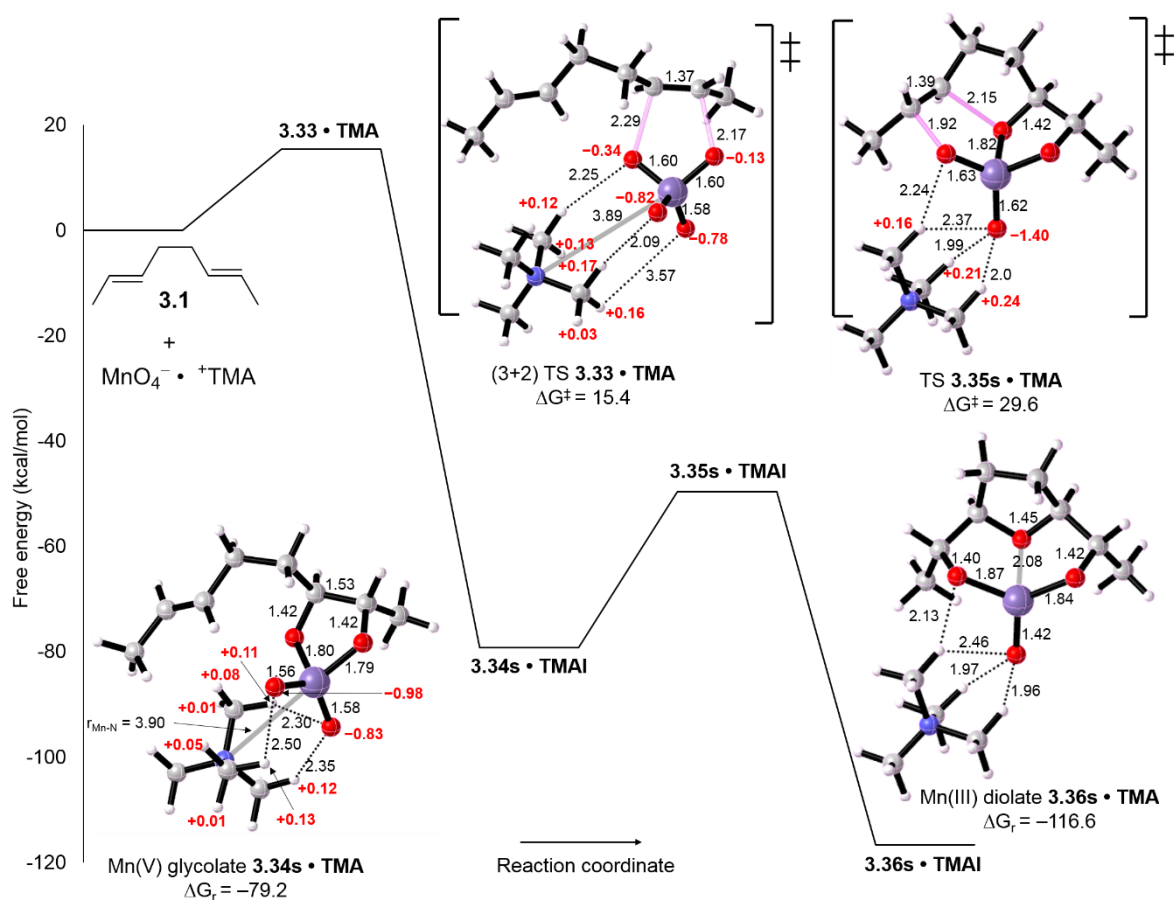


Figure 3.15: The effect of tetramethyl ammonium ion on the oxidative cyclisation of 1,5-diene **3.1**. APT charges of hydrogens and oxo ligands are shown in bold red in e units.

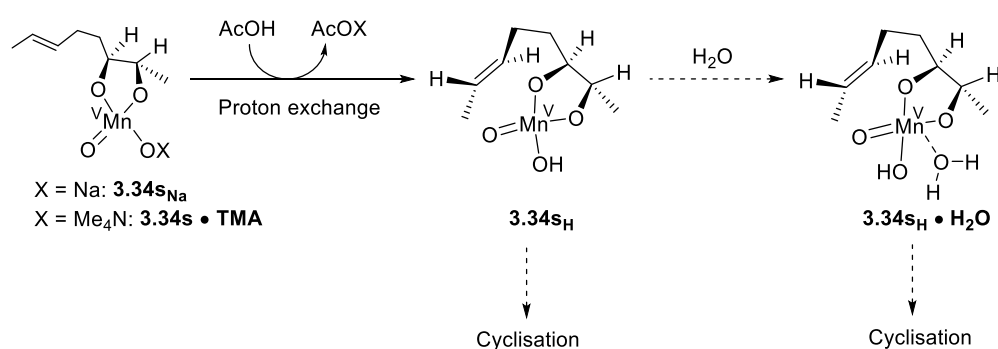
3.3.4.3 The effect of acid on oxidative cyclisation

The effect of acid on the oxidative cyclisation is one of the most important factors for our study to focus on. We have selected acetic acid as the acid source, as it is the one used experimentally. Acetic acid may have a role in stabilising the negative charge on Mn(V) glycolate through protonation. In the case of protonation, an important question is “does protonation happen before

the alkene oxidation step or at the stage of the first intermediate **3.34s**?" There is a big difference in pKa between acetic acid (pKa = 4.76) and permanganic acid HMnO₄ (pKa = -2.25)²⁹⁰ and, therefore, we have excluded the possibility of forming HMnO₄.

Protonation is often rapid due to the high mobility of proton in a solvent but their rates depend on acidity of the protonating species; the stronger acid the faster protonation. Generally, the rates of protonation and deprotonation are affected by the accompanied structural changes.²⁹¹ Marcus theory has been used to calculate the activation of proton transfer by acetic acid.²⁹² Since the protonation of Mn(V) glycolate showed no significant structural changes, we have decided not to calculate the barrier of protonation and use only their thermodynamic free energies instead.

It is known that FRS, formation of Mn(V) glycolate, proceeds under phase transfer catalysis conditions without the need for acid.^{47,79–81,116} Experimentally, and in our work, we have seen that oxidative cyclisation does not proceed without acid, although the phase transfer catalyst was involved. That implies that acid is needed for cyclisation step. At this point, counter ions such as Me₄N⁺ (acidic PTC conditions) and Na⁺ (aqueous acidic conditions) have to be involved in the protonation step. Therefore, a proton exchange between these counter ions and acetic acid is more likely to take place (**3.34s_H**, **Scheme 3.4**). Since it is known that Mn(V) accepts a water molecule, an additional reasonable pathway involves addition of water to the protonated Mn(V) to give **3.34s_H • H₂O** (**Scheme 3.4**).

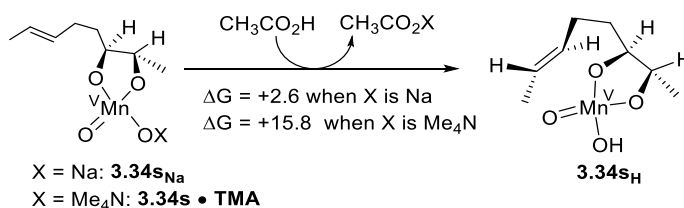


Scheme 3.4: Summary of the effect of acid on oxidative cyclisation of Mn(V) glycolate.

3.3.4.3.1 Protonation of tetrahedral Mn(V) **3.34s**

From Mn(V) glycolate two protonation reactions have been considered, using acetic acid as proton source (**Scheme 3.5**). The proton exchange with acetic acid was calculated to be endergonic ($\Delta G = 15.8$ kcal/mol) when exchange occurs with **3.34s • TMA** and thermoneutral ($\Delta G = 2.6$ kcal/mol) when exchange occurs with **3.34s_{Na}**. The high endergonicity for formation of **3.34s_H** from **3.34s • TMA** is believed due to either the hydrogen bonding arising from hydrogen atoms of methyl groups

around N and oxygen atoms on Mn(V) glycolate **3.34s • TMA** (see **Figure 3.17**) or formation of an unstable salts tetramethylammonium acetate.



Scheme 3.5: Protonation of intermediate Mn(V) glycolate calculated in acetone at 253.15 K. Energies are in kcal/mol.

DFT calculations show a high stabilisation on the SRS when Mn(V) glycolate is protonated (**Figure 3.16**) compared to with (**Figure 3.6**) and without (**Figure 3.5**) water. Cyclisation of protonated Mn(V) glycolate **3.34s_H** display a barrier of 12.2 kcal/mol via TS **3.35s_H** to give protonated Mn(III) THF-diolate **3.36s_H** as an exergonic step ($\Delta G_r = -66.3$ kcal/mol).

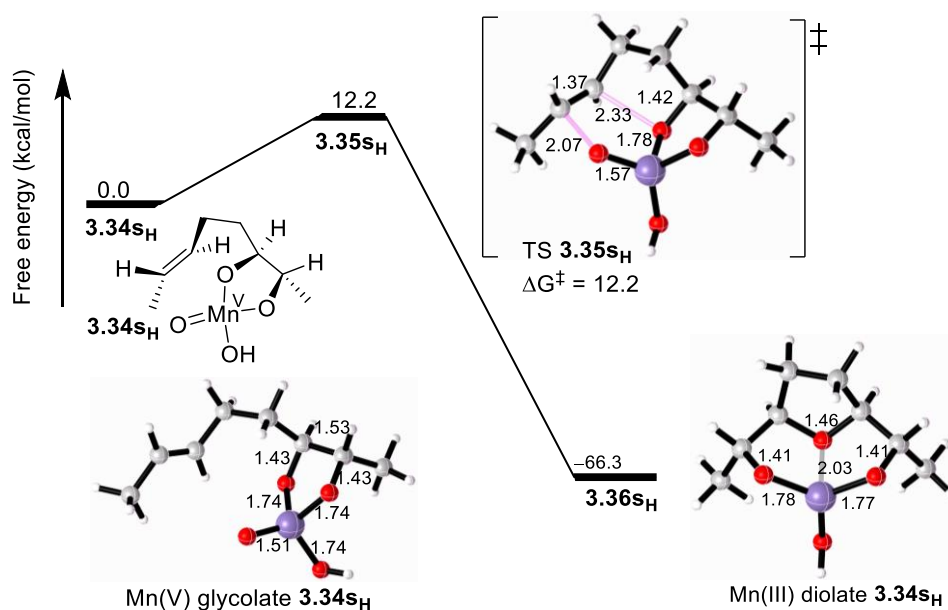


Figure 3.16: Energetic profile for the effect of protonation on oxidative cyclisation, showing intermediate and TS for protonated Mn(V) pathway.

A greater decrease in activation energy for cyclisation was achieved compared to other counter ions Na⁺ and TMA (**Figure 3.17**). This would suggest that the nature of the counter ion has an significant effect on cyclisation kinetically and thermodynamically. In this manner, proton is more highly favoured than sodium ion and the latter is favoured over a quaternary ammonium ion. This would be consistent with our experimental observations, where no THF-diol formation was observed without without acidic conditions.

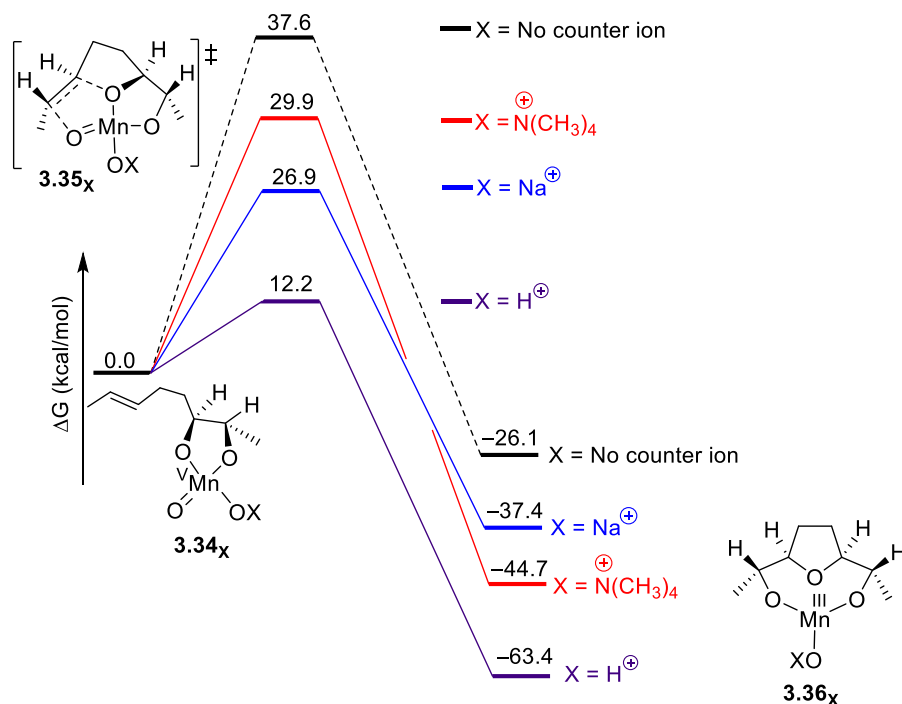


Figure 3.17: The effect of counter ions on cyclisation of Mn(V) glycolate.

3.3.4.3.1.1 Addition of water to protonated Mn(V) glycolate **3.34_{sH}**

Addition of water to protonated Mn(V) glycolate **3.34_{sH}** to give **3.34_{sH} • H₂O** has been examined (**Figure 3.18**). This pathway investigates cyclisation under acidic conditions in the presence of water. The hydrated protonated intermediate **3.34_{sH} • H₂O** is more stable than the protonated Mn(V) glycolate **3.34_{sH}** by 6.2 kcal/mol, indicating that a favourable insertion of a water molecule into the Mn(V) glycolate. Due to the stabilisation of **3.34_{sH}** by the addition of water ligand, the barrier of cyclisation for **3.34_{sH} • H₂O** becomes 15.2 kcal/mol via distorted square pyramidal (3+2) cycloaddition TS **3.35_{sH} • H₂O** ($\Delta G_r = -67.9$ kcal/mol, **Figure 3.18**) rather than 12.2 kcal/mol via TS **3.35_{sH}** ($\Delta G_r = -63.4$ kcal/mol, **Figure 3.16**).

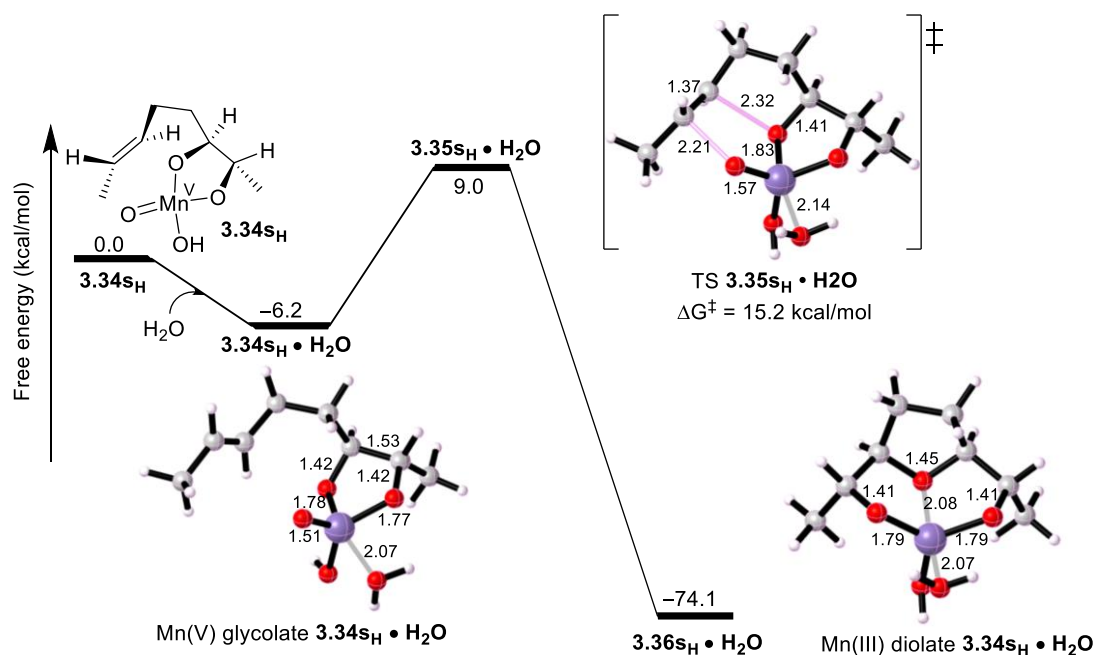


Figure 3.18: Energetic profile showing the effect of water addition to protonated Mn(V) glycolate pathway.

3.4 Decomposition of Mn(V) intermediates

We have calculated the decomposition pathways for the Mn(V) intermediates **3.34s** and **3.34s_{H2O}** (Figure 3.19) and **3.34s_H** (Figure 3.20). Based on our DFT calculations, and in addition to experimental observation, Mn(V) glycolate is more stable than Mn(VI), but it is surprising that the decomposition pathways for Mn(V) intermediates are thermodynamically and kinetically less favourable compared to that of Mn(VI) glycolate. However, that is not the case for the protonated Mn(V) glycolate. For instance, the activation free energy for decomposition for **3.34s_{H2O}** was calculated to be $\Delta G^\ddagger = 41.7$ kcal/mol as a slightly exergonic step of $\Delta G_r = -1.3$ kcal/mol whereas **3.34s** needs an additional 19.6 kcal/mol to overcome the barrier with high endergonicity of $\Delta G_r = 28.6$ kcal/mol (Figure 3.19). Cyclisation of both **3.39s_{H2O}** and **3.39s** are relatively favoured kinetically and thermodynamically (see Figure 3.5 and 3.7) over decomposition (Figure 3.19). However, The Mn(VI) glycolate **3.34d** needs only 6.4 kcal/mol to pass the decomposition barrier as a highly thermodynamically favourable step ($\Delta G_r = -73.5$ kcal/mol, see Figure 3.12).

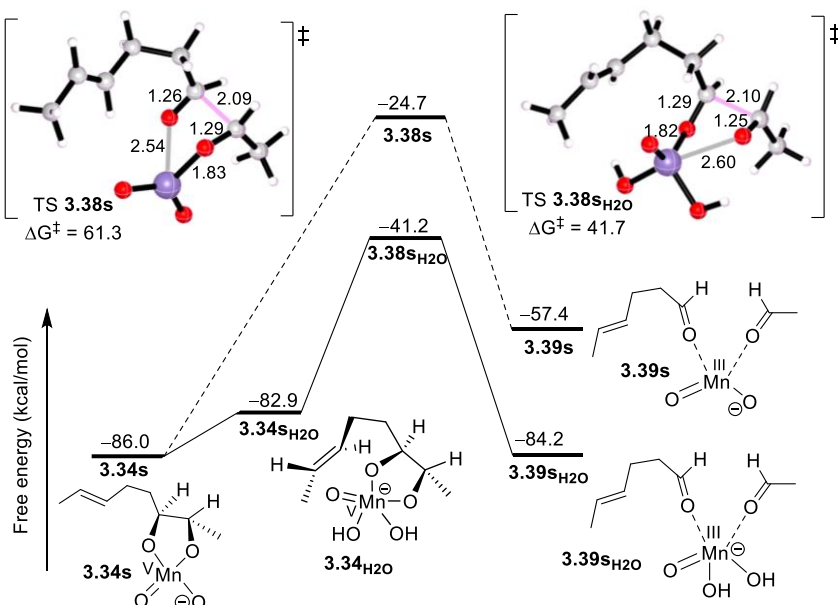


Figure 3.19: Decomposition pathway of hydrated **3.34s_{H2O}** and non-hydrated **3.34s** Mn(V) glycolate.

Moving to the protonated intermediate **3.34s_H**, our calculations showed a lower barrier of 19.8 kcal/mol for C–C bond breaking with substantial thermodynamic driving force compared to **3.34s** and **3.34s_{H2O}** (**Figure 3.20**). This results is in good agreement with the experimental observation; it has been seen that under acidic conditions Mn(V) glycolates decompose to give cleavage products; aldehydes and Mn(III).⁴⁶ The calculated decomposition barrier indicates the possibility of competition between cyclisation and decomposition for protonated Mn(V) glycolate. However, it is apparent that cyclisation is kinetically and thermodynamically favourable over decomposition.

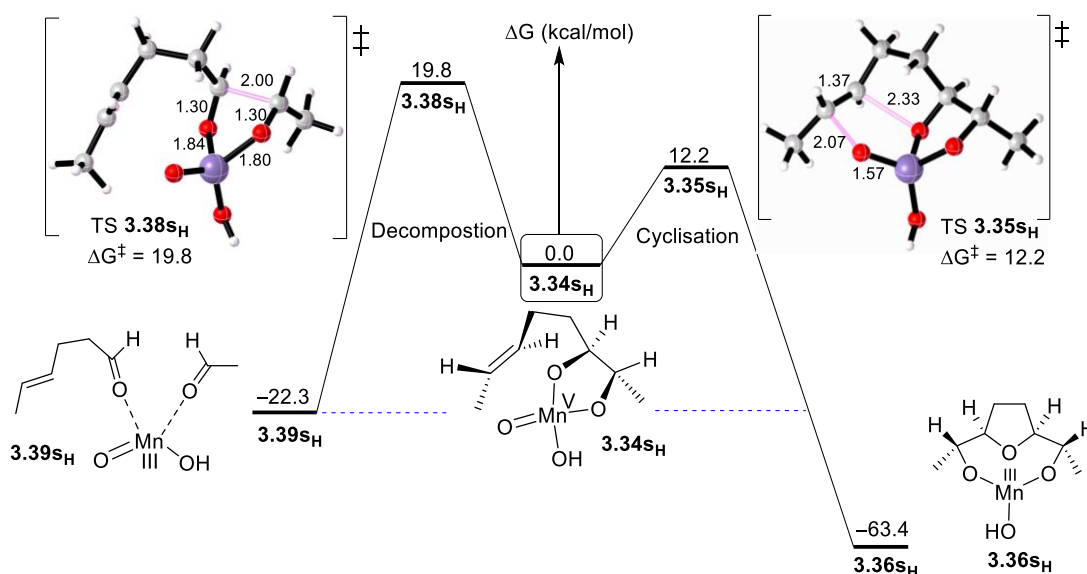


Figure 3.20: Competition between decomposition and cyclisation pathway of protonated Mn(V) glycolate **3.34s_H**.

3.5 Frontier molecular orbital analysis of the SRS

Frontier molecular orbital (FMO) analysis of FRS intermediate Mn(V) glycolates and their interactions are examined to understand the influence of additives on cyclisation (**Figure 3.21**). FMO analysis of the intermediate Mn(V) glycolates show that HOMO's are mainly localised on the electron-rich alkene groups (donor) while the LUMO's are predominantly located on the Mn(V) glycolate groups (acceptor). In general, decreasing the energy gap or increasing electrophilicity of the metal centre decreases the activation energy of cyclisation. In the case of negatively charged cyclisation, cyclisation with TS's **3.35s** and **3.35s_{H2O}**, the HOMO-LUMO energy gap for hydrated Mn(V) glycolate **3.34s_{H2O}** is 6.9 eV compared to 7.0 eV in the absence of water **3.34s**.

However, introducing the counter ion has shown a noticeable decrease in the activation energy of THF ring formation due to the uncharged cyclisation pathways except **3.34s • TMA**. For instance, comparison between ions Na⁺ and H⁺, the result shows superior orbital overlap for H⁺ over Na⁺. The HOMO–LUMO energy gap has decreased from 6.3 eV in **3.34s_{Na}** into 5.3 eV in **3.34s_H** in line with the decrease in the barrier of TS **3.35s_H** ($\Delta G^\ddagger = 12.2$ kcal/mol) over TS **3.35s_{Na}** ($\Delta G^\ddagger = 26.9$ kcal/mol) due to attenuation of the LUMO energy to -2.6 eV. A large counter ion like tetramethyl ammonium ion showed a relatively higher energy gap of 6.5 eV compared to Na⁺ (6.3 eV) and H⁺ (5.3 eV) due to the lower electrophilicity of the Mn oxo site (LUMO = -1.0 eV) as a result of hydrogen bonding between oxo ligands and TMA. When protonated Mn(V) is ligated with water to give **3.34_H • H₂O**, the energy gap increases into 5.7 eV which explain the higher barrier of cyclisation for TS **3.35_H • H₂O** over TS **3.35_H**.

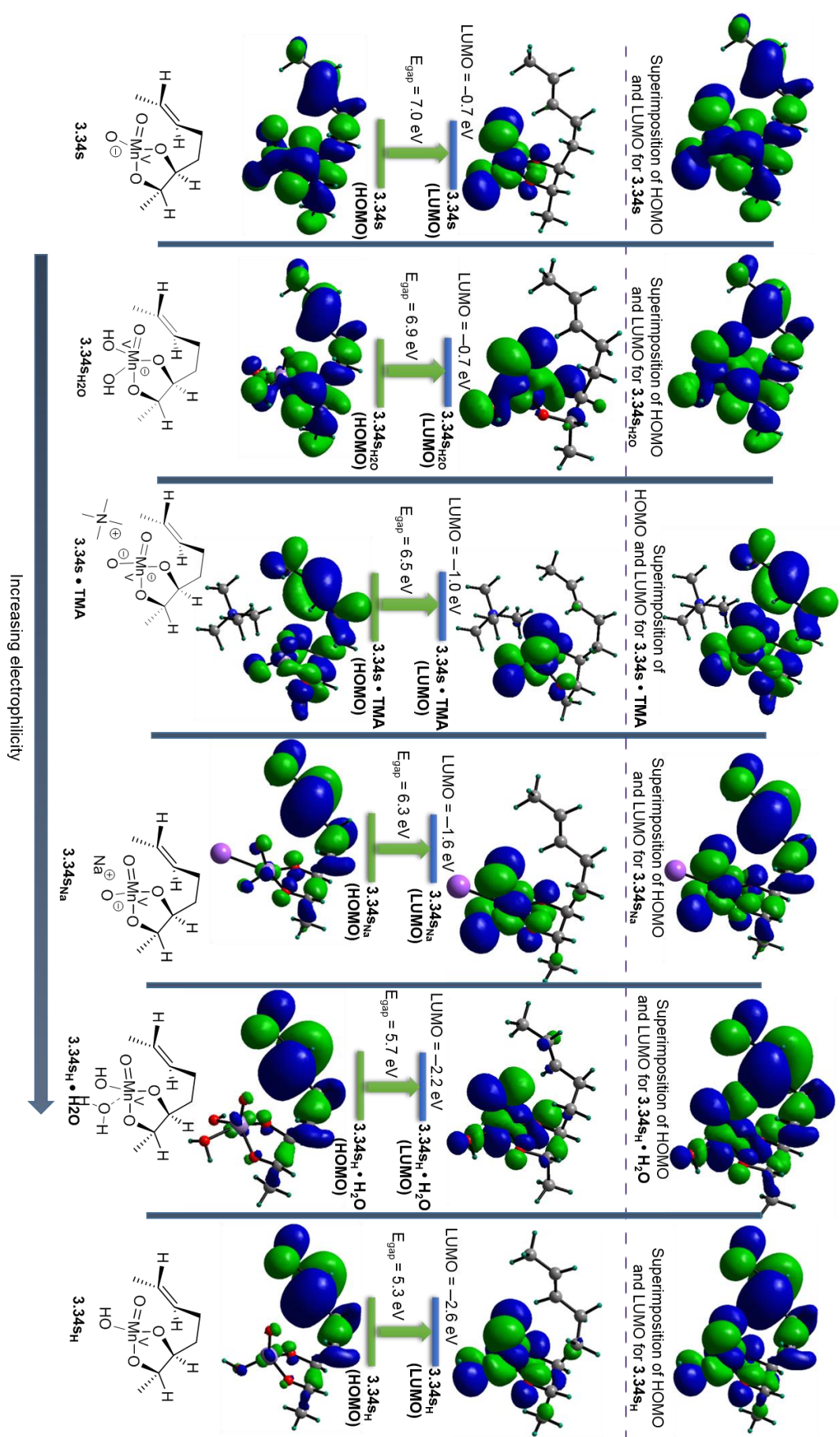


Figure 3.21: Visual representation (with a 0.02 isosurface) of the calculated HOMO and LUMO orbitals and their orbital overlap for Mn(V) glycolate.

Figure 3.22 shows the HOMO's, LUMO's, and their superimposition for the intermediate Mn(VI) glycolates **3.34d** and **3.34d_{H2O}**. The HOMO's and LUMO's are represented on alkene and Mn=O moieties respectively with a noticeable decrease in electrophilicity due to the radical character of Mn=O compared to the Mn(V) glycolate intermediates. The orbital overlapping of Mn(VI) intermediates are partially achieved resulting in only terminal C—O bond formation without realisation of the THF ring.

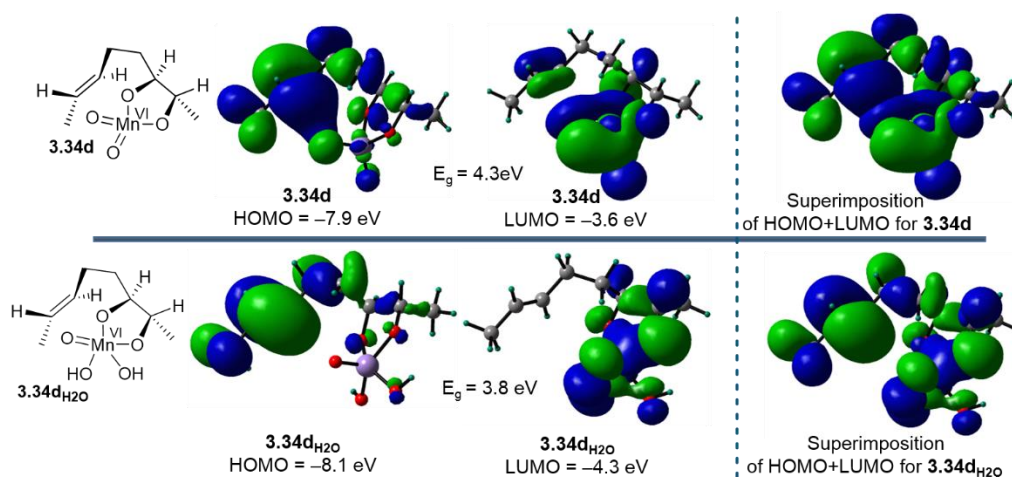


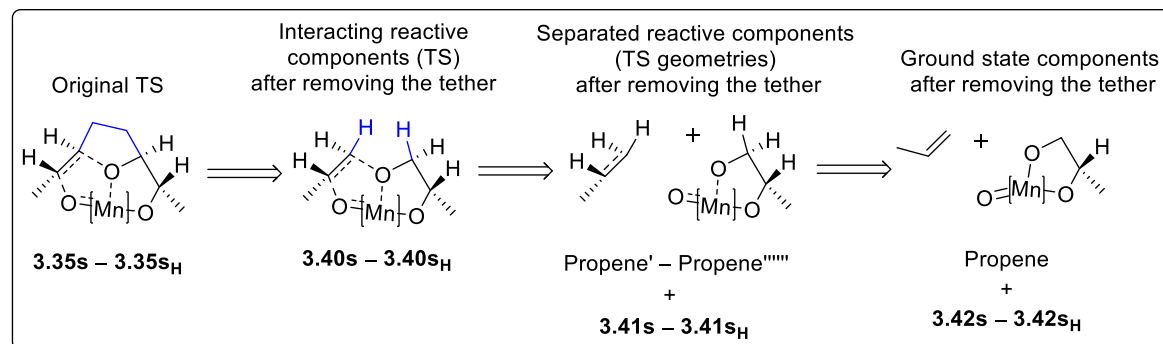
Figure 3.22: Visual representation (with a 0.02 isosurface) of the calculated HOMO and LUMO orbitals as well as their orbital overlap for the intermediate Mn(VI) glycolates **3.34d_{H2O}** and **3.34d**.

3.6 Distortion/interaction analysis of the SRS TS's

A model developed to analyse distortion/interaction was used to understand the effect of additives on the cyclisation step, in which we calculate the interaction and distortion energies for the SRS (**Table 3.3**). The model is based on one for (3+2) cyclisation with the tether removed from the reacting components described by Houk and co-workers.^{293–295} The approach involves replacing the ethylene linking group (CH₂ groups of incipient THF ring) by hydrogen atoms in the ground state reactant (intermediates **3.34s**, **3.34s_{H2O}**, **3.34s_{Na}**, **3.40s • TMA**, **3.34s_H • H₂O** and **3.34s_H**), and the corresponding TS structures. Single point energy calculations of the obtained interacting reactive components (**3.40s**, **3.40s_{H2O}**, **3.40s • TMA**, **3.40s_{Na}**, **3.40s_H • H₂O**, and **3.40s_H**) and the separated reactive components (**3.41s**, **3.41s_{H2O}**, **3.41s • TMA**, **3.41s_{Na}**, **3.41s_H • H₂O**, and **3.41s_H**), with their respective TS geometries preserved, provides an estimate of the interaction energies. Similarly, comparison of the separated reactive components in their TS geometries and ground state geometries (**3.42s**, **3.42s_{H2O}**, **3.42s • TMA**, **3.42s_{Na}**, **3.42s_H • H₂O**, and **3.42s_H**) gives distortion energies required to achieve the TS's. Based on the assumption that energies for distortion of the components and the tether are additive, distortion of the tether is obtained from the difference between the activation energies of the tethered systems and the tethered removed. $\Delta E_{app}^\ddagger$, or the

apparent activation energy, refers to the sum of the total distortion energies and interaction energies.

Table 3.3: Distortion/interaction analysis for the TS's **3.35s**, **3.35s_{H2O}**, **3.35s • TMA**, **3.35s_{Na}**, **3.35s_H • H_{2O}**, and **3.35s_H** during the SRS. Energies are in kcal/mol.



TS	$\Delta E^\ddagger$	$\Delta E_{\text{app}}^\ddagger$	$\Delta E_{\text{dis}}^\ddagger$ (total)	$\Delta E_{\text{dis}}^\ddagger$ (alkene)	$\Delta E_{\text{dis}}^\ddagger$ (Mn glycolate)	$\Delta E_{\text{dis}}^\ddagger$ (tether)	$\Delta E_{\text{int}}^\ddagger$
3.35s	31.6	29.3	15.7	6.1	9.6	2.3	+13.6
3.35s • TMA	30.9	32.3	17.3	9.0	8.3	-1.4	+15.0
3.35s_{H2O}	22.9	26.5	16.3	7.1	9.2	-3.6	+10.2
3.35s_{Na}	24.6	27.5	16.4	8.4	8.0	-2.9	+11.1
3.35s_H • H_{2O}	14.3	12.1	6.9	3.3	3.6	+2.2	+5.2
3.35s_H	10.5	14.2	8.9	4.0	4.9	-3.7	+5.3

Generally, increasing the interaction energy decreases the activation energy for cyclisation except for the TS **3.35s • TMAI**. Both liganded protonated TS **3.35s_H • H_{2O}** and protonated tetrahedral TS **3.35s_H** have the highest interaction energy (+5.3 kcal/mol and +5.2 kcal/mol, respectively) (**Figure 3.24**). This results in a lower barrier of cyclisation for TS **3.35s_H** ($\Delta E^\ddagger = 10.5$ kcal/mol) and **3.35s_H • H_{2O}** ($\Delta E^\ddagger = 14.3$ kcal/mol). However, TS **3.35s • TMA** has the lowest interaction energy of +15.0 kcal/mol whereas **3.35s** and **3.35s_{H2O}** have the second lowest interaction energies of +13.6 and +10.2 kcal/mol respectively. Increasing the total distortion energy substantially increases the overall barrier for the SRS. For instance, TS's **3.35s**, **3.35s_{H2O}**, **3.35s • TMAI**, and **3.35s_{Na}** have the highest total distortion energies of 13.6, 16.3, 17.3, and 16.4 kcal/mol respectively, compared to the lowest distortion energies of 8.9 and 6.9 kcal/mol for TS's **3.35s_H** and **3.35s_H • H_{2O}** respectively. The estimated distortion energies of the tethers varies in the range -3.7 to 2.3 kcal/mol. Overall, this study showed a good understanding on why activation energy changes with different additives on Mn(V) pathways due to the change in electrophilicity of the Mn(V) moieties. **Figure 3.23** shows showing interacting reactive, separated reactive, and ground state components from distortion/interaction analysis for the TS **3.35s_H** during the SRS.

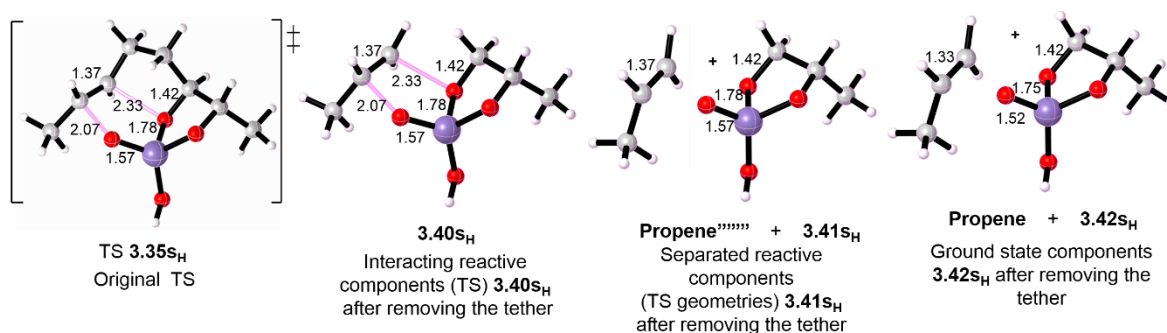


Figure 3.23: Distortion/interaction analysis for the TS **3.35_{sH}** during the SRS, showing interacting reactive, separated reactive, and ground state components.

3.7 Molecular dynamics simulation of the SRS TS's

Since significant differences between the progressions of the two C—O bond formations in the cyclisation step for the calculated TS structures **3.35** were seen, it would be valuable to have more insight towards the chronology of formation of these bonds from the point of molecular dynamic (MD) simulations, especially the asynchronous bond length and time. The time between the first and second C—O bond formations during the cyclisation pathway is the asynchronous time or the timing gap. The asynchronous length shows the difference in length between the same C—O bond formation. Classical MD calculations were carried out on one trajectory, where the forward and backward propagation of TS's are initiated in the region of the potential energy surface near the TS ($t = 0$ fs) showing the typical reactive bonds toward product (Mn(III)) and reactant (Mn(V)). **Figure 3.24** shows snapshots for the forward propagation of TS's **3.35** at the time of first and second C—O bond formation. In general, a greater development of the terminal C—O[Mn] bond relative to the C—O[THF] bond was noticed.

Direct MD calculations show the highest degree of timing gap of 15.25 and 11.0 fs for glycolate Mn(V) **3.35s** (without additives) with **TMA** Mn(V) pathways with highest asynchronous lengths of 0.63 and 0.5 Å respectively (**Figure 3.24-a** and **Figure 3.24-e** respectively). The shortest timing gap was 4.25 fs obtained for Mn(V) counter by Na⁺ pathways with an asynchronous length of 0.36 Å (**Figure 3.24-c**). The other pathways show timing gaps in the range 7.0 to 8.0 fs.

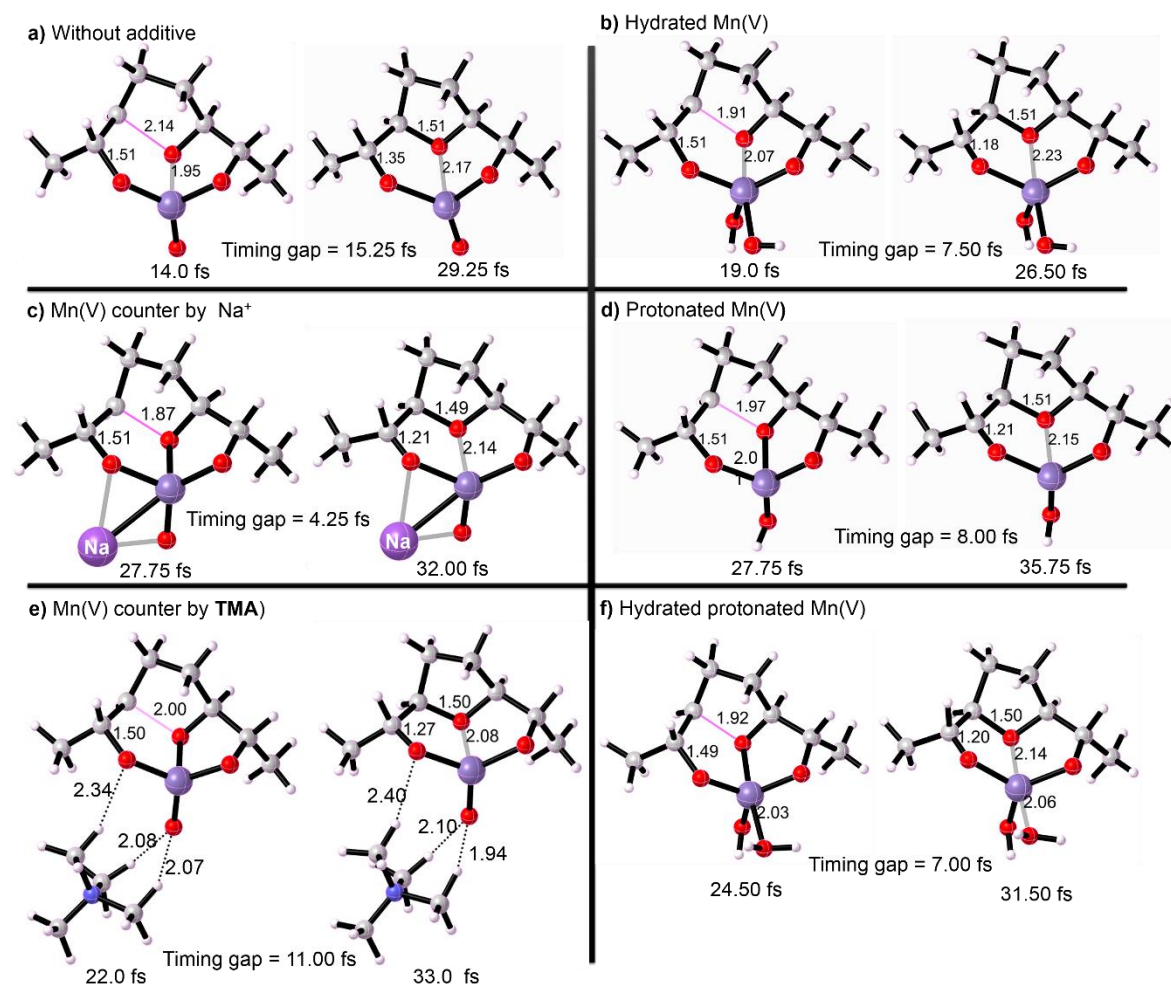


Figure 3.24: Snapshots for the forward propagation of TS's **3.35** at the time of first and second C—O bond formation. TS corresponds to $t = 0$. Timing gap represents time between the first and second C—O bond formations.

Since the protonated pathways are calculated to be the favoured pathways for cyclisation, **Figure 3.25** and **Figure 3.26** shows a typical forward and backward trajectory for the protonated and protonated hydrated Mn(V) pathways. Generally, both of protonated Mn(V) and protonated water-liganded Mn(V) show 8.00 and 7.00 fs timing gaps respectively with comparable asynchronous lengths of 0.46 and 0.41 Å respectively, where the C—O[THF] proceeds after the progression of terminal C—O[Mn] bond. In the case of protonated Mn(V) pathway (**Figure 3.25**), the forwards propagation of the transition state geometry ($t = 0$ fs) realises formation of the C2—O26[Mn] bond (C2—O26 = 1.51 Å) at 27.75 fs while the C—O[THF] bond (C1—O5 = 1.97 Å) is still in the transition zone, requiring a further 8.00 fs to form. Snapshots of the backward propagation of TS **3.35_{sH}** are shown at -50.0 and -100.0 fs (**Figure 3.25**).

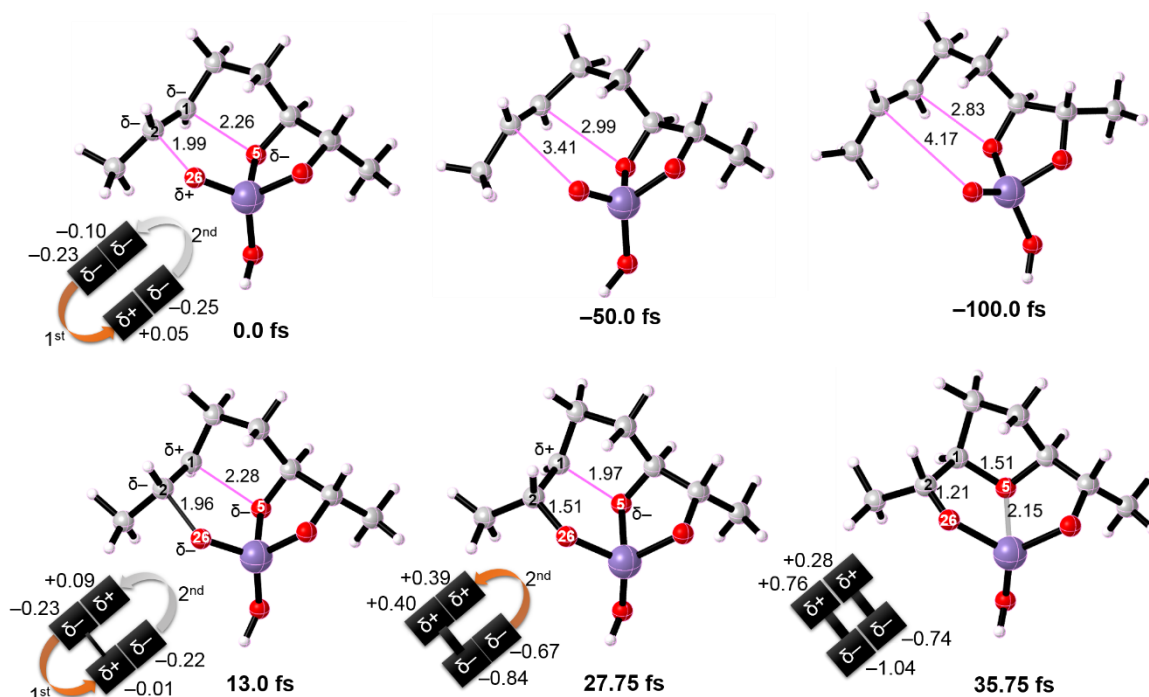


Figure 3.25: Snapshots from a typical SRS trajectory for protonated Mn(V) pathway leading to THF formation and to Mn(V) glycolate. APT charges are shown on the reacting carbon and oxygen atoms in e units. Trajectories initiated in the region of the potential energy surface near TS (time = 0 fs) showing reactive bonds.

In the protonated hydrated Mn(V) pathway (**Figure 3.26**), a similar behaviour in the progression of C—O bond formation was obtained. The terminal C2—O30[Mn] bond starts growing at 13.0 fs and then forms at 24.50 fs (C2—O30 = 1.49 Å) whereas C1—O5[THF] is in the transition zone at 1.92 Å needs further 7 fs to be fully formed at 31.50 fs (C1—O5 = 1.50 Å). Here, the length of H₂O—Mn bond decreases from 2.14 Å at t = 0 to 2.03 Å at t = 31.50 fs, however it increases into 2.28 Å at –100.0 fs in the backward propagation.

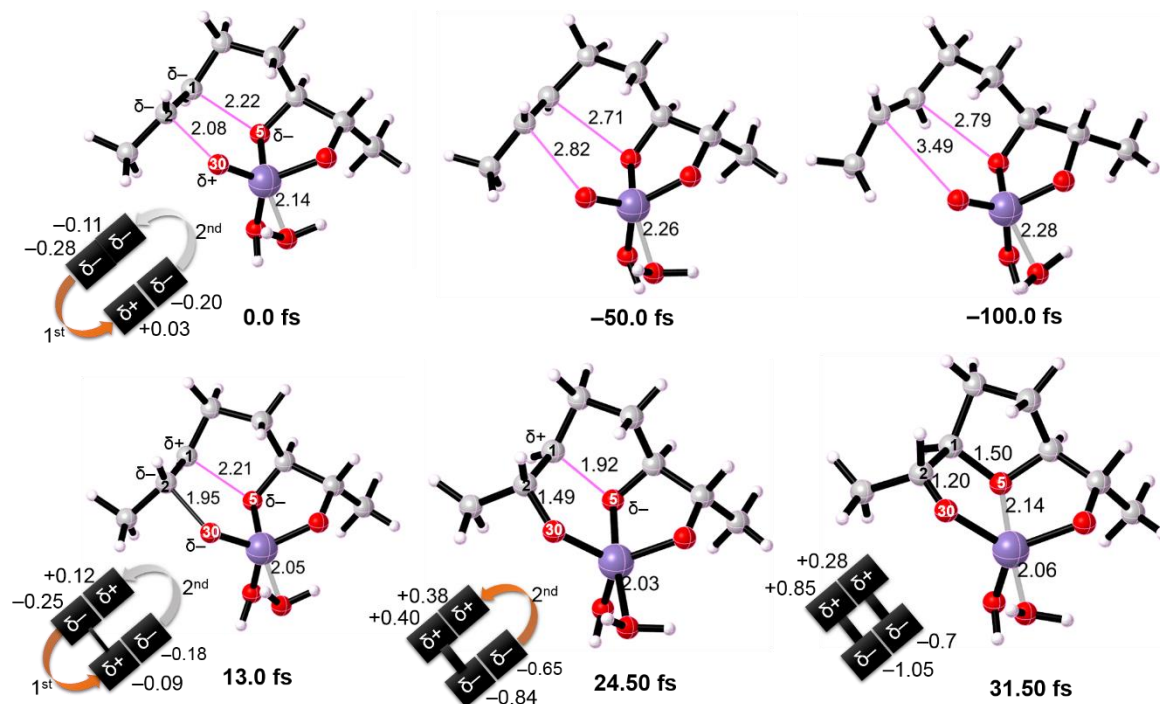


Figure 3.26: Snapshots from a typical SRS trajectory for protonated hydrated Mn(V) pathway leading to THF formation and to Mn(V) glycolate. APT charges are shown on the reacting carbon and oxygen atoms in e units. Trajectories initiated in the region of the potential energy surface near TS (time = 0 fs) showing reactive bonds.

The atomic polar tensor charges shown on the reacting oxygen atoms for both pathways (shown in **Figure 3.25** and **Figure 3.26**) at the TS (time = 0 fs) allow a visualisation of the electron-deficient and electron-rich sites, while both reacting olefinic carbons are electron-rich. The first C—O bond formation, involving the addition of electron-rich carbon into electron-deficient oxygen of O—Mn, starts to form by transferring the charge from carbon to oxygen at $t = 13.0$ fs in which both atoms becomes negative and the bond is not fully formed. This progresses to formation of C2—O26 or C2—O30 bonds at $t = 27.75$ fs and $t = 24.50$ fs respectively, while the nascent C1—O5[THF] is still in the transition zone. As the first C—O bond approaches formation, the carbon of the incipient THF ring becomes more electron poor, $C1 = +0.39$ e or $+0.38$ e, leading to union with the electron-rich O5—Mn ($O5 = -0.67$ e or -0.65 e) to realise the second C—O bond formation at $t = 35.75$ or 31.50 fs.

3.8 Effect of high spin multiplicity on the SRS

The effect of high spin multiplicities on the SRS has been examined, although it is known that Mn(V) oxo species have low spin configurations.^{118–121} The high spin pathways were calculated only in the absence of additive for Mn(V) and for the hydrated Mn(V) pathway.

3.8.1 Calculated energies for high spin multiplicity pathways for the SRS in the absence of additives for oxidative cyclisation of Mn(V) glycolate

Different spin multiplicities have been investigated for the SRS in the absence of additives (**Figure 3.28**). Computationally, the triplet Mn(V) glycolate **3.34t** ($\Delta G_r = -101.3$ kcal/mol) is lower energy than singlet **3.34s** by 15.3 kcal/mol. Experimentally, Mn(V) oxo compounds are diamagnetic with low spin ($S = 0$) (**Figure 3.27-a** and **Figure 3.27-b**).^{118–121} We believe that the main reason why the triplet is calculated to be more energetically stable than singlet configuration is that DFT approximations try to fill the non-bonding d -orbitals according to ligand field theory (LFT) or to stabilise d -orbitals according to crystal field theory (CFT). Recently, Yang *et al.*¹²² confirmed the favourability of singlet over triplet states using complete-active space self-consistent field method (CASSCF) to match the experimental evidence for Mn(V)-oxo complex (**Figure 3.27-c**).

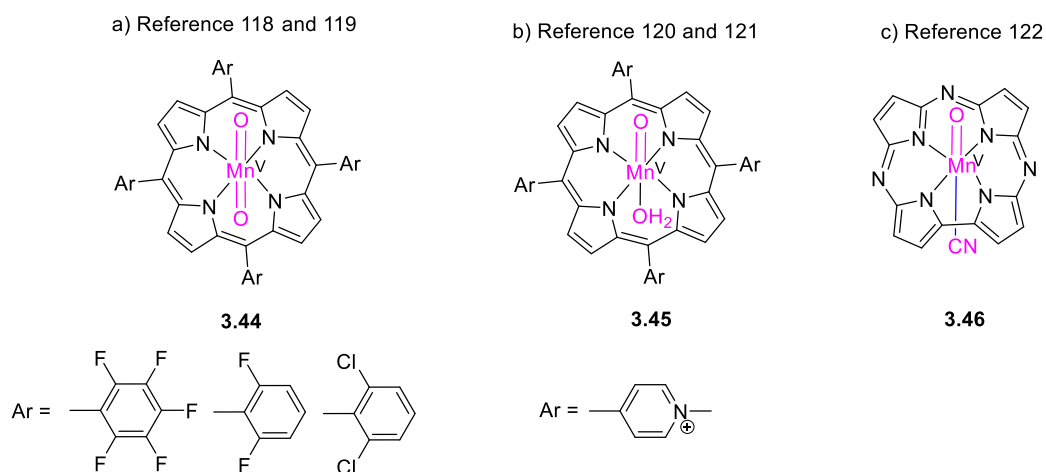


Figure 3.27: Structure of manganese(V) oxo complexes.

Using CASSCF in the calculation is challenging due to the memory and time required to converge the energy of the system. However, checking the spin state ordering of the Mn(V) glycolate is important. In order to assess the singlet-triplet spin state, all bonding and antibonding metal-ligand orbitals and electrons must be included in CAS space. That means 28 electrons and 16 orbitals have to be involved in the calculation; CAS(28,16). CAS calculation was carried out by a single point energy calculation based on geometry optimised by the M06-2X/aug-cc-pVDZ level of theory. We could not carry out CAS(28,16) because of the limited memory provided by our available supercomputer. However, we managed to converge the energy by using smaller CAS. A CAS of 4 electrons and 6 orbitals (CAS(4,6)) decreased the energy gap between the singlet and triplet into 5.5 kcal/mol, still favouring of triplet over singlet. When we increased the number of electrons and orbitals, we experienced a convergence problem. Using CAS(8,7), which was used by Yang *et al.*¹²², favoured singlet over triplet by 23.8 kcal/mol in acetone/SMD. Although singlet is the spin state of

Mn(V) glycolate according to CASSCF, it is worthwhile testing the cyclisation on high spin multiplicities; triplet and quintet.

It has been found that searching for high spin TS is very challenging within the M06-2X functional. The quintet TS **3.35q** was higher in energy than triplet **3.35t** but both of them did not lead to the second intermediate Mn(III) diolate (**Figure 3.28**). The TS's **3.35t** and **3.35q** are able only to form the terminal C2—O6 bond (C—O[Mn]) of **3.36t** and **3.36q** Mn(III) diolate without cyclisation, and this would explain why the located TS's **3.35t** and **3.35q** have lower energy barriers than **3.35s**. All efforts to cyclise **3.35t** and **3.35q** into **3.36t** and **3.36q** failed using either PES or MD simulations because of the forbidden dynamical charges between the reacting atoms shown (repulsion between oxygen and carbon atoms) resulting in mismatched orbital symmetry between Mn(V) and alkene moieties (see **Figure 3.29**).

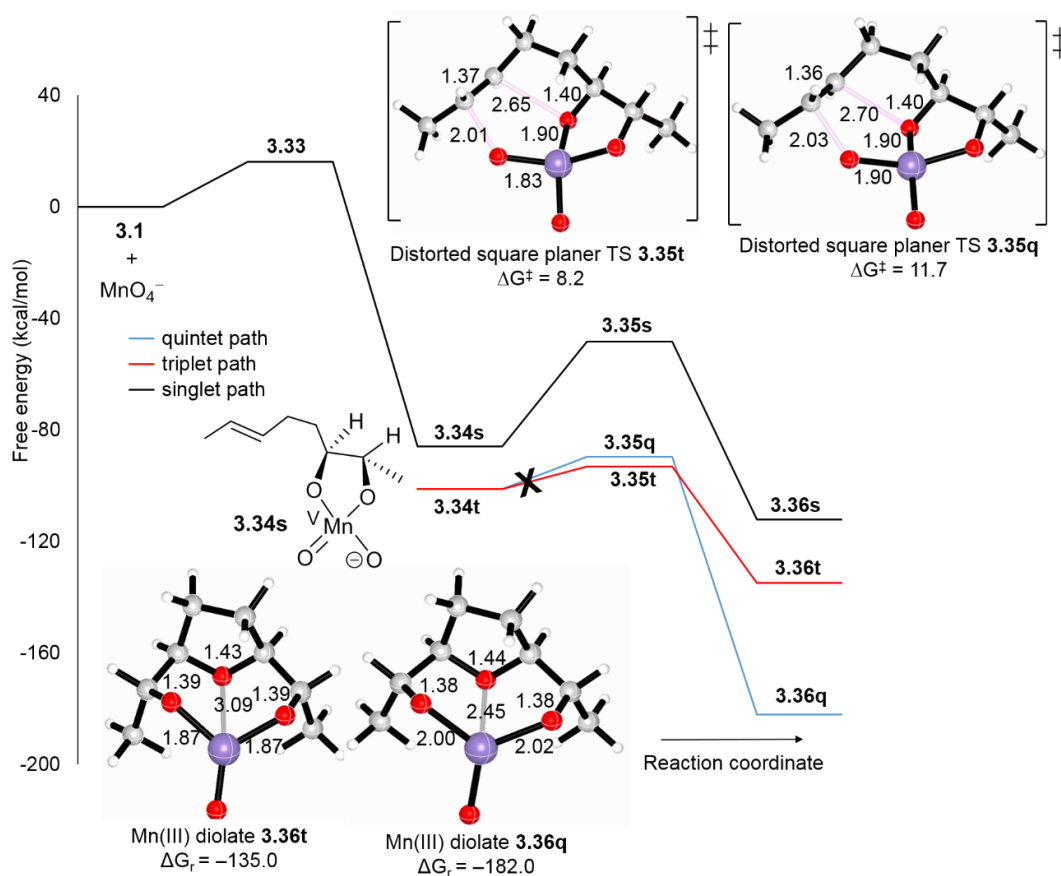


Figure 3.28: Reaction energy diagram for the permanganate oxidative cyclisation of 1,5-diene **3.1** under without additives, showing TS's and intermediates for the SRS triplet (t) and quartet (q) spin multiplicities.

The APT charges for the atoms forming the THF ring along the TS's are shown in **Figure 3.29**. In the case of TS **3.35s**, when C2 attacks O6 atom to form C2—O6 bond consequently C1 atom becomes positively charged atom leading to union with O5 to form C1—O5 bond of the THF ring. However,

in the case of triplet and quintet TS's, charge flux along the cyclisation path fails due to unfavourable atomic charges on atoms in which the only vibration in TS's **3.35t** and **3.35q** is between C2 and O6 atoms, so only C2—O6 bond formation is achieved without development of the C1—O5 bond. Interestingly, in the case of high spin TS's **3.35t** and **3.35q** the asynchronous bond length between the first and second C—O bond formation was found to be 0.64 Å and 0.67 Å for **3.35t** and **3.35q** respectively which clearly shows the unfavourable interaction between C1 and O5 due to their repulsion.

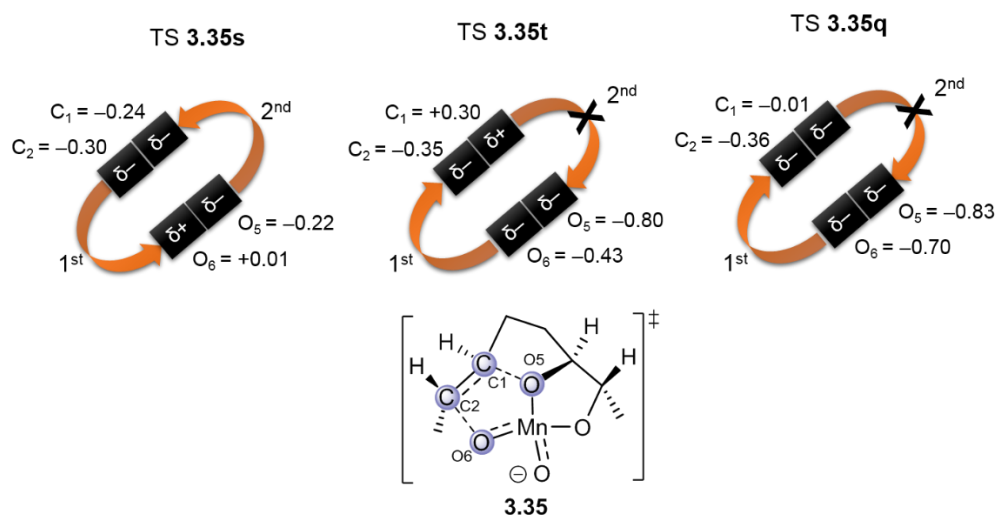


Figure 3.29: APT derived charges for the atoms forming the THF-diolate along TS's **3.35** in e units.

An additional understanding of disfavoured high spin state cyclisation ($S = 1$ and $S = 2$) may be obtained from crystal field theory (CFT) approximation in this case.²⁹⁶ According to CFT, it is possible to only have a singlet tetrahedral transition state despite having two electrons in d -orbital because of the repulsion between the d -electrons ($\text{Mn-}d^2$) and the neighbouring negative charge, and in addition to electronegativity arising from oxo ligands around Mn. Here, in order to find a triplet TS we have to break the symmetry of the tetrahedral geometry into the square planer (TS **3.35t**) to allow for more distribution of the static electric field produced by the surrounding charge. This results in a distorted triplet TS (distorted square planer TS, only 2 degeneracies in d -orbitals, 2 splitting). Further distortion would be required in the case of a quintet TS **3.35q** in order to have a symmetry breaking in both wave function and geometry (see triplet and quintet TS's in **Figure 3.28**). Having a quintet TS seems also unreasonable. This is because there are no more than 2 electrons in d -orbitals, and in order to have a quintet TS means that the negative charge should spread over the d -orbitals to allow for more degeneracies. In other words, there is a participation to the overall splitting arising from negative charge in order to provide four unpaired electrons. Within CFT manifestation, quintet spin multiplicity (4 d -orbitals degeneracies) exists in square pyramidal geometry which we do not have here. This problem was not found in the Poethig and Strassner

study because within the B3LYP approximation repulsions between the charge and unpaired electrons are ignored to facilitate a high spin cyclisation.¹¹⁷ In conclusion, there is no triplet and quintet TS's and the reaction must proceed via a singlet pathway. This is supported using CASSCF, indicating that Mn(V) adopts a low spin configuration rather than triplet.

3.8.2 Calculated energies for different spin pathways for the SRS from hydrated Mn(V) glycolate **3.34**_{H₂O}

The effect of high spin on hydrated Mn(V) pathway has been calculated (**Figure 3.29**). The addition of water into triplet Mn(V) glycolate **3.34t** is exergonic ($\Delta G_{H_2O} = -7.2$ kcal/mol) using M06-2X functional (**Figure 3.30**). The spin ordering using CASSCF/aug-cc-pVDZ was carried out with CAS(8,7) with application of condensed solvation model SMD in acetone. The splitting energy for preference of singlet over triplet was found to be 22.0 kcal/mol. Again, this means that singlet is the spin multiplicity of hydrated Mn(V) glycolate which is in agreement with the experimental observations. Again, although CASSCF calculation confirms the favourability of singlet over triplet, the cyclisation step was investigated under three different *d*-orbitals splitting (**Figure 3.30**). The high spin Mn(III) THF-diolate **3.36q**_{H₂O} is more stable than the corresponding low spin triplet **3.36t**_{H₂O} and singlet **3.36s**_{H₂O}. It has been reported that high spin of Mn(III) complexes are more stable than low spin.

297,298

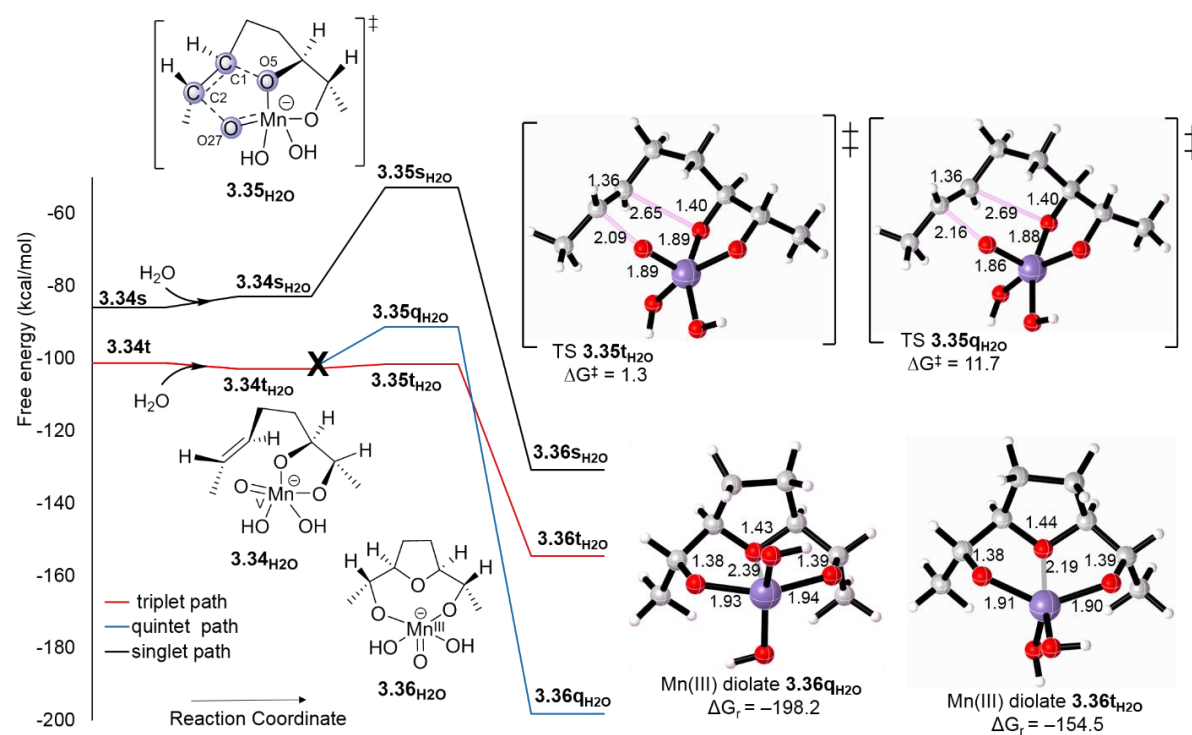


Figure 3.30: Reaction energy diagram for the SRS permanganate oxidative cyclisation of 1,5-diene **3.1** with water addition, showing TS's and intermediates for the SRS triplet (t) and quartet (q) spin multiplicities.

In order to understand the possibility of having a high spin transition states for the SRS despite d^2 configuration we have to take into account the effect of addition water into Mn. Since the negative charge is transferred onto the Mn atom due to the addition of water molecule into Mn(V) glycolate, so it would be easier to produce more than two degeneracies in order to give four splittings and result in formation of square pyramidal geometry. However, this is still an invalid degeneracy. Notwithstanding it is invalid splitting, it carries out without a symmetry breaking in wave function and geometry because the tetrahedral geometry was already broken due to the formation of square pyramidal. Low activation barriers of 1.3 and 11.7 kcal/mol are obtained for triplet **3.35t_{H2O}** and quintet **3.35q_{H2O}** respectively, but only realising C2–O27 (C–O[Mn]) bond formation due to unfavourable interaction between C1 and O5 (**Figure 3.31**). However, all trials to cyclise the high spin TS's within PES and MD calculations failed due to charge repulsion between carbon (C1) and oxygen (O5) atom.

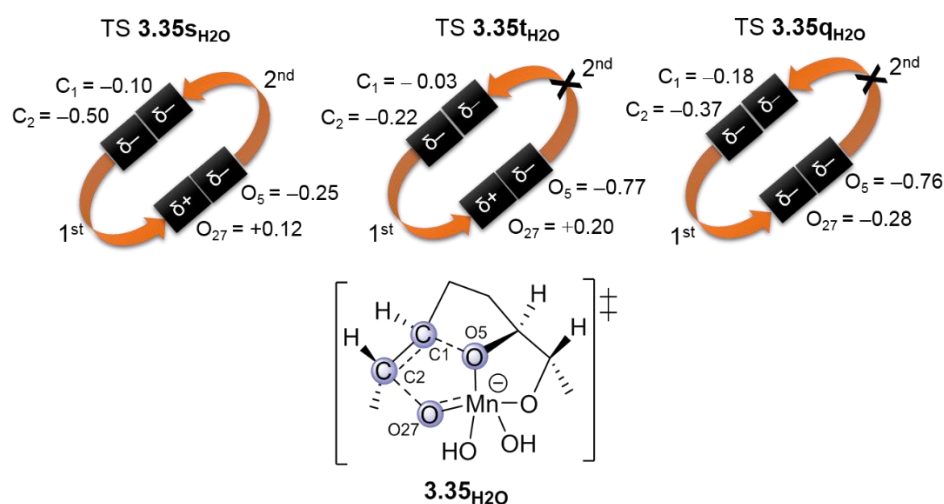


Figure 3.31: APT derived charges for the atoms forming the cycloadduct in e units for TS **3.35_{H2O}**.

3.9 Hydrolysis of Mn(III) THF ring intermediate **3.36_H**

Hydrolysis of Mn(III) diolate **3.36s_H** into THF-diols has been explored using DFT calculations (**Figure 3.32**). Since the reaction proceeds via protonated Mn(V) into Mn(III) on a singlet hypersurface, two possibilities of hydrolysis for singlet Mn(III) diolate **3.36s_H** to release THF-diol have been considered; either via a dissociative mechanism due to the addition of water molecule or disproportionation. According to our calculations, quintet Mn(III) is more stable than the singlet, and therefore hydrolysis will be studied in both spin configurations. In general, the addition of water to Mn(III) diolate gives THF-diols and HMnO₂, and the latter will disproportionate into Mn(IV) and Mn(II).

Hydrolysis via singlet pathway seems to be highly disfavoured (**Figure 3.32**). The addition of water to Mn(III) **3.36s_H** via TS **3.47s** has a barrier of 11.8 kcal/mol to give a thermodynamically unstable intermediate **3.48s** ($\Delta G_r = 9.7$ kcal/mol), in which one of the O–Mn bond is broken to form one of

the hydroxyl groups. Releasing the THF-diols and singlet Mn(III) (HMnO₂) from **3.48s** requires a very high activation energy of 62.6 kcal/mol via TS **3.49s** with a disfavoured endergonicity of $\Delta G_r = 56.8$ kcal/mol. Therefore, the reverse reaction is more likely from both TS's **3.47s** and **3.49s**. On the other hand, hydrolysis from high spin Mn(III) diolate **3.36q_H** is more favourable (**Figure 3.32**). The addition of water needs a barrier of 9.7 kcal/mol via TS **3.47q_H** to give intermediate **3.48q** ($\Delta G_r = 7.7$ kcal/mol). The release of THF-diol from high spin intermediate **3.48q** via TS **3.49q** has a lower activation energy of 20.0 kcal/mol compared to 62.6 kcal/mol in the case of the singlet pathway; however it is still thermodynamically disfavoured ($\Delta G_r = 17.1$ kcal/mol). Also, although the quintet hydrolysis seems possible, the reverse reaction from both TS's **3.47q_H** and **3.49q** seems more favourable.

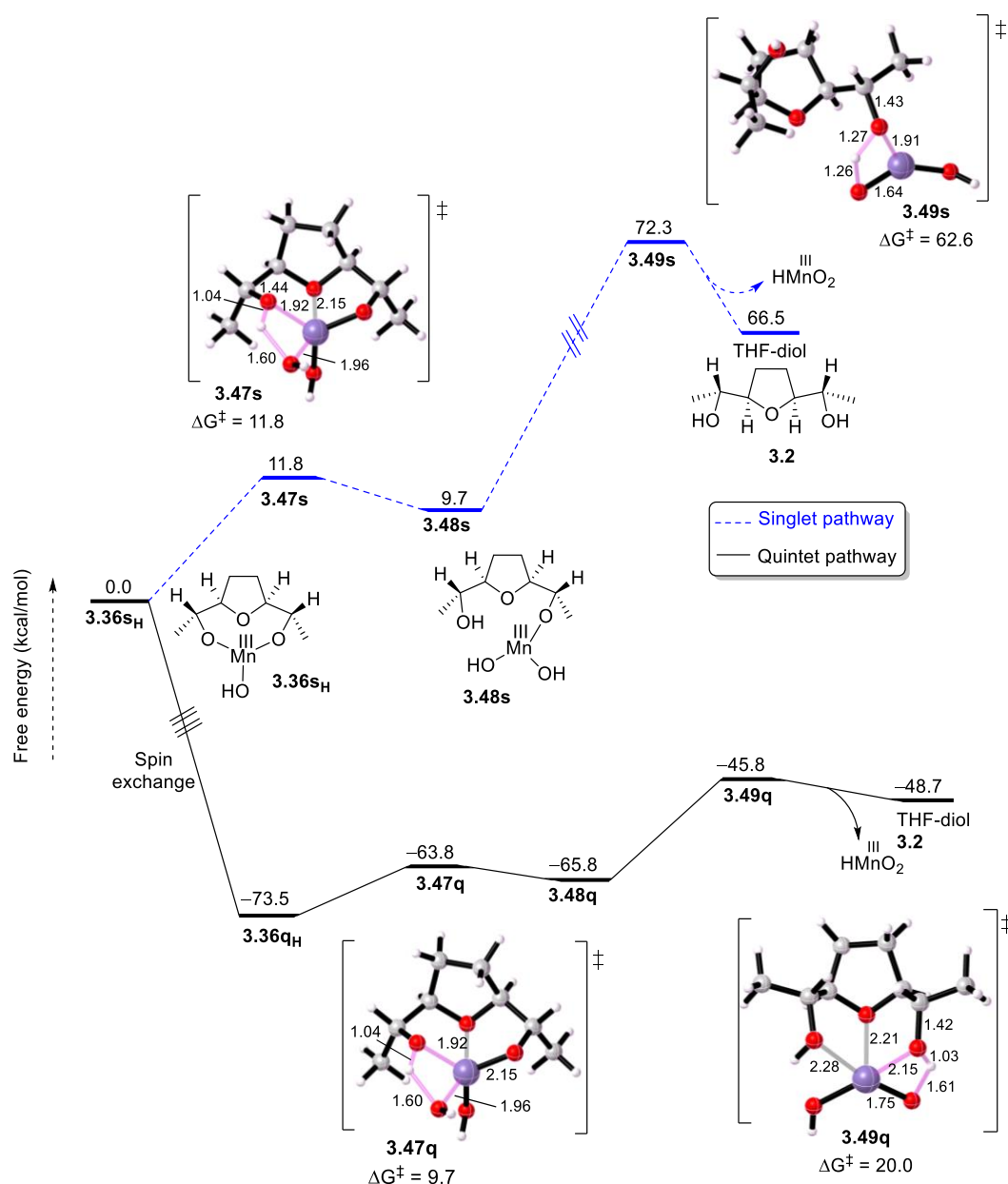


Figure 3.32: THF-diol release from hydrolysis of singlet **3.36s_H** and quintet **3.36q_H** via addition of water.

Disproportionation of Mn(III) into Mn(IV) and Mn(II) was considered in acidic condition but in the absence of water. It is well-known that Mn(III) disproportionates into Mn(IV) and Mn(II) under acidic conditions.²⁹⁷ Mn(III) aqua species tend to disproportionate to Mn(II) and Mn(IV) via multinuclear O-bridged structures such as Mn(III)-Mn(III) complexes.²⁷⁷ Disproportionation is a specific type of redox reaction in which a species is simultaneously reduced and oxidised to form two different species with lower and higher oxidation states based on a Latimer diagram.^{297,298} According to the Latimer diagram, Mn(III) has a tendency to disproportionate into Mn(IV) and Mn(II) species because the potential energy on the right of the species in the Latimer diagram is higher than that on the left (**Figure 3.33-a**). For instance, the free energy of disproportionation of Mn(III) into Mn(IV) and Mn(II) is -12.9 kcal/mol as a spontaneous process (**Figure 3.33-b**). Therefore, the disproportionation pathway for Mn(III) diolate should be favoured.

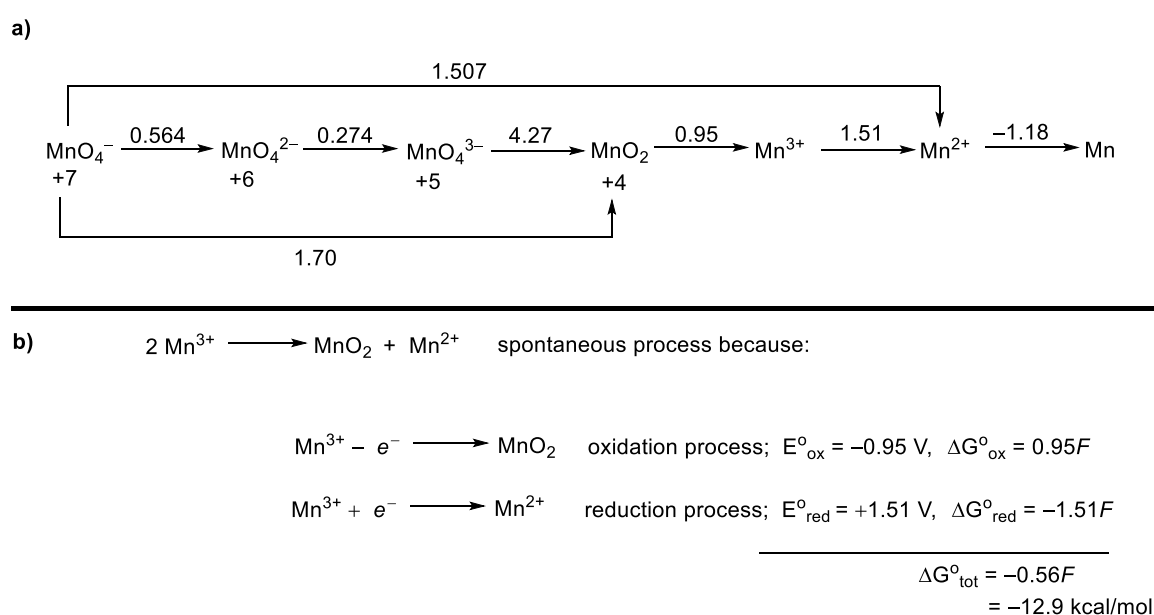


Figure 3.33: a) Latimer diagram for a series of Mn species in acidic solution and b) explanation of disproportionation for Mn(III) based on Latimer diagram. The symbol V is volt unit. The symbol F is Faraday unit; $1F = 23.061$ kcal per volt gram equivalent.

Disproportionation calculations are performed on singlet, triplet, and quintet spin states. According to the reaction conditions, and in the presence of acetic acid, two of Mn(III) species will disproportionate to give two THF-diols, MnO_2 , and $\text{Mn}(\text{OAc})_2$ in which two molecules of acetic acid are required to release the THF-diols and stabilise the Mn(II) species (**Figure 3.34**). Water molecules are also liganded to Mn(II) if aqueous conditions are applied. The spin states of MnO_2 and $\text{Mn}(\text{OAc})_2$ are quartet and sextet respectively. This means that the disproportionation of Mn(III) starts from either singlet, triplet or quintet and gives the product with quartet and sextet spins for MnO_2 and $\text{Mn}(\text{OAc})_2$ respectively. The disproportionation of quintet Mn(III) **3.36q_H** is highly disfavourable

($\Delta G_{\text{disp}} = 63.7$ kcal/mol) whereas the low spin singlet **3.36_{sH}** is highly exergonic ($\Delta G_{\text{disp}} = -82.9$ kcal/mol) compared to the moderate exergonicity ($\Delta G_{\text{disp}} = -26.7$ kcal/mol) for the low spin triplet **3.36_{tH}** disproportionation. It has been reported that the high spin Mn(III) is more stable than low spin,^{297,298} so the disproportionation via high spin would be less favourable. At this point, the triplet pathway is the most favourable from the Latimer diagram. The most important intermediate in disproportionation is the formation of complex **3.50s**, in which the OH group of **3.36_{sH}** inserted into the other Mn(III) diolate resulting in formation of four membered bridged complex as an exergonic step ($\Delta G_{\text{complexation}} = -13.8$ kcal/mol). One of the oxygen atoms in this complex **3.50s** behaves as a ligand. Inner-sphere electron transfer may then happen after complex formation followed by addition of acetic acid to release MnO₂ and Mn(OAc)₂ and two THF-diols (**Figure 3.34**).

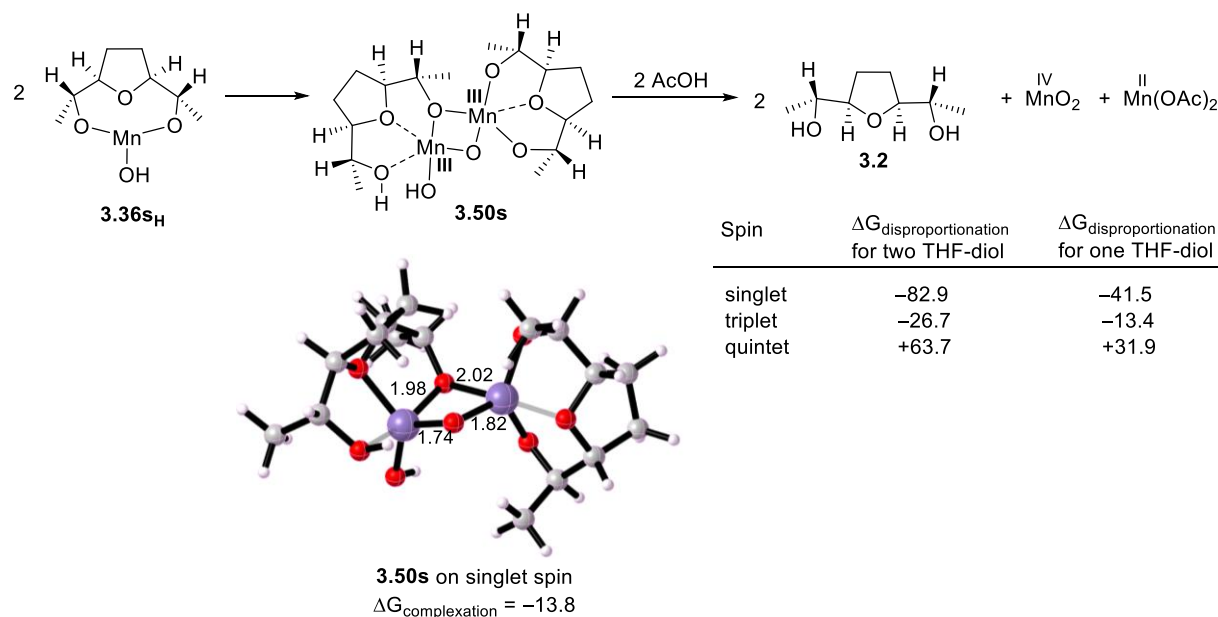
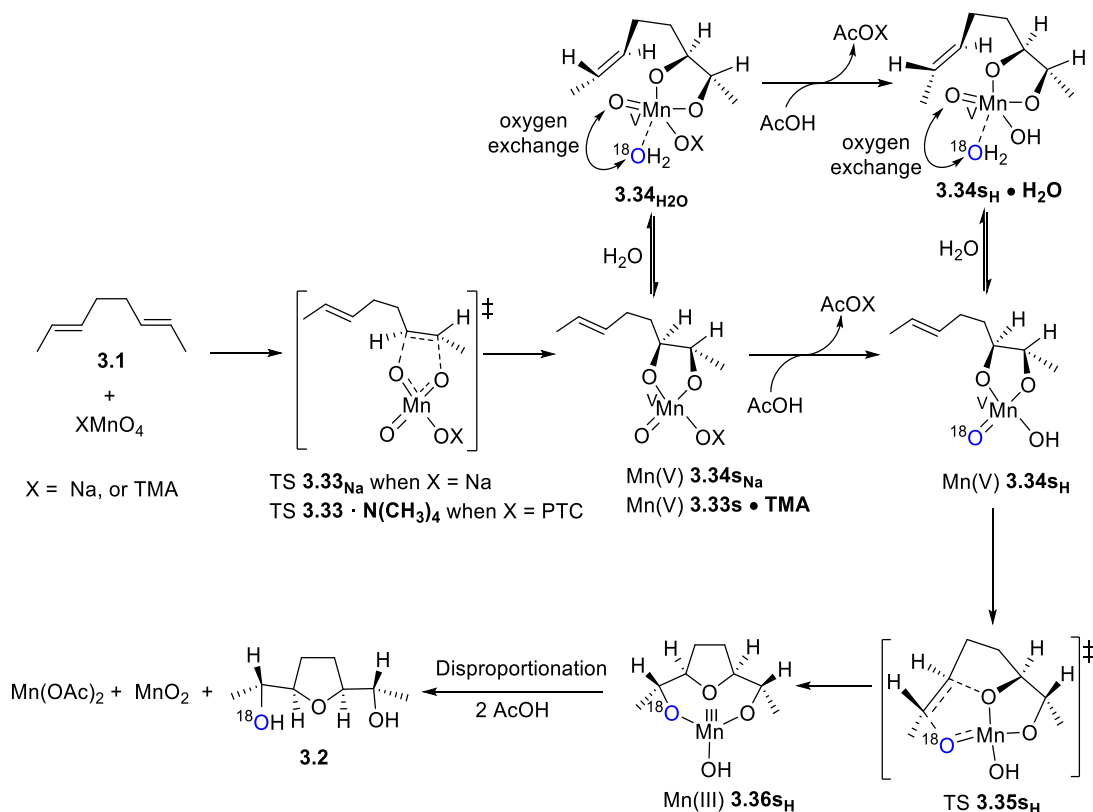


Figure 3.34: Disproportionation of protonated Mn(III) diolate **3.36_H** for different spins, showing a singlet complex **3.50s**. Energies are in kcal/mol.

3.10 Developing a plausible full mechanistic description for permanganate-mediated oxidative cyclisation of 1,5-dienes

The mechanism proposed for permanganate-mediated oxidative cyclisation of 1,5-dienes is shown in **Scheme 3.6**, where the reaction is generally carried out under acidic conditions: aqueous acidic conditions (e.g. aqueous KMnO₄ or NaMnO₄, AcOH/acetone-water) or acidic phase transfer catalysis conditions (e.g. powdered KMnO₄, adogen 464, AcOH/acetone). On the basis of DFT calculations, the effect of counter ion is crucial in order to facilitate the SRS in which a proton exchange occurs prior to cyclisation. This would then be followed by acidic disproportionation of Mn(III) THF-diolate to release THF-diol **3.2** and Mn(II) and Mn(IV).



Scheme 3.6: Proposed reaction mechanism of permanganate-mediated oxidative cyclisation of 1,5-diene **3.1**. Blue oxygen atom refers to the oxygen exchange with water according to Wolf and Ingold study.

3.11 Conclusions

The reaction mechanism of THF-diol formation from permanganate-mediated oxidative cyclisation of 1,5-dienes has been studied using high-level DFT simulation ((SMD)-M062X/aug-cc-pVDZ/ECP), showing an agreement with experimental observation, especially concerning the role of acid.

The simulations show that the FRS and SRS proceeds through singlet spin hypersurface pathways because Mn(V) is diamagnetic rather paramagnetic.^{118–122} This is in contradiction to the conclusions published in the DFT study from Poethig and Strassner.¹¹⁷

The simulation explains the results of Wolfe and Ingold⁴⁵ as an exchange of the oxygen atoms due to the addition of water to Mn(V) glycolate, which is also consistent with the ligand exchange showed by Song *et al.*¹¹⁹ However, DFT calculations do not support cyclisation via hydrated Mn(V) pathway, and cyclisation should proceed via protonated Mn(V) intermediate.

The reoxidation Mn(V)→Mn(VI) is found to be highly disfavoured. However, if oxidation occurs, cyclisation of Mn(VI) glycolate remains unfavourable due to disallowed orbital symmetry, and

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preferential decomposition into two aldehydes and Mn(IV) as the favoured pathway. This finding is also in agreement with experimental observations.^{46,47}

The calculations explain two different conditions for the reaction: aqueous acidic condition or acidic phase transfer catalyst conditions, where protonated Mn(V) glycolate forms prior to cyclisation. The two conditions show that the nature of counter ion has a noticeable effect on the barrier to cyclisation, where Mn(V) glycolate cyclises faster with H⁺ than Na⁺ and ⁺N(CH₃)₄. This is in agreement with our experimental observations, where there is no THF-diol formation without acid.

In acidic conditions, the Mn(V) glycolate enters a competition between cyclisation and decomposition but the cyclisation is calculated to be favoured.^{46,47}

MD simulations performed on the SRS, show an asynchronous (3+2) addition of the O—Mn—O species **3.34** across the alkene double bond with faster formation of the C—O[Mn] bond compared to C—O[THF] bond with 8.0 fs timing gap in the case of the protonated Mn(V) glycolate intermediate.

An additional insight into the contributory factors on cyclisation was provided by FMO calculations and distortion/interaction energy analysis, where increasing the electrophilicity of Mn(V) intermediate resulting in a favourable TS interaction energy.

Hydrolysis of SRS intermediate Mn(III) THF-diolate has been found to follow disproportionation pathway, where the acidic disproportionation of two Mn(III) THF-diolates **3.36s_H** releases two THF-diols **3.2** and Mn(II) and Mn(IV).

3.12 Future work

Because spin configurations of Mn(V) glycolate and Mn(III) diolate are critical to understanding the reaction mechanism of oxidative cyclisation, it is highly desirable to further investigate them using complete active space perturbation theory second order (CASPT2) to achieve a better description of the electronic states.

Since we have explored the permanganate-mediated oxidative cyclisation of a simple 1,5-diene (**Scheme 3.6**), it would be of great interest to understand regioselectivity of MnO₄[−] in the oxidative

cyclisation of 1,5-dienes using high-level DFT calculations when an electron-deficient alkene is present in the 1,5-diene structure (**Figure 3.35**). This is highly relevant to our experimental investigations using dienolate and dienone systems in the presence of chiral PTC or chiral auxiliaries.

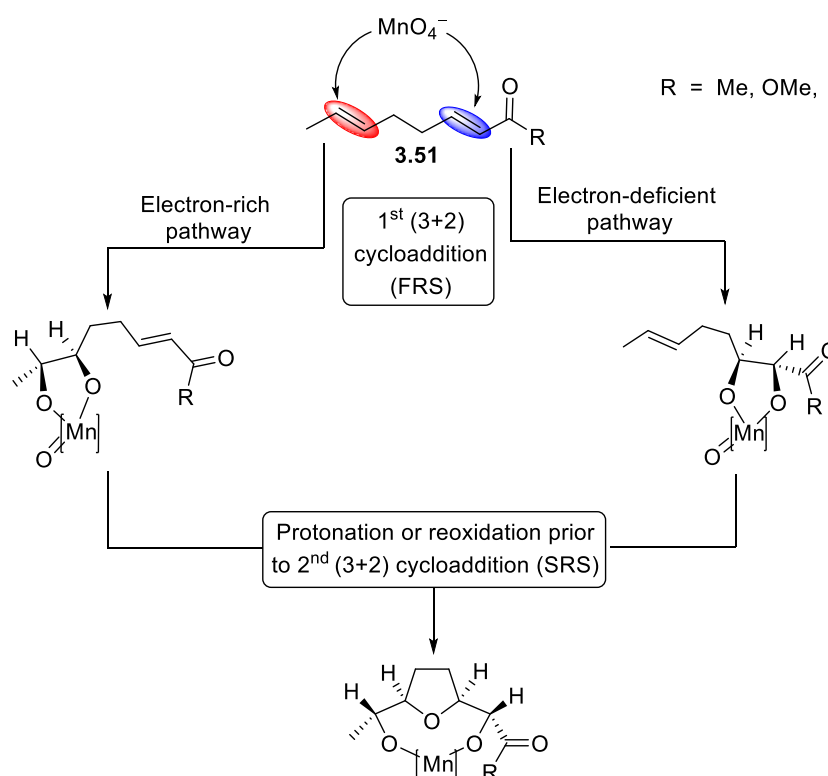


Figure 3.35: Regioselectivity of MnO_4^- in the oxidative cyclisation of asymmetrical 1,5-dienes containing electron-deficient group.

Furthermore, DFT simulations would also be used to understand the stereoselectivity of oxidative cyclisation by permanganate ion using chiral auxiliaries such as TTC, TCC, and Camphorsultam (**Figure 3.36**).

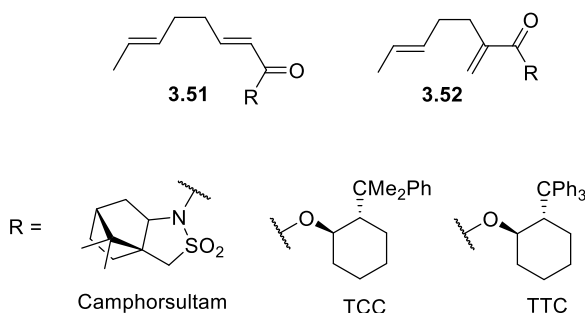


Figure 3.36: Structures of chiral auxiliaries used with two different 1,5-dienes.

Chapter 4 Results and Discussions

4.1 DFT examination of the osmium-promoted oxidative cyclisation of 1,5-dienes

This chapter will describe the mechanism of osmium-catalysed oxidative cyclisation of 1,5-diene studied using high-level DFT calculations, leading to a detailed description of the mechanism, which is consistent with experimental observations and highlights the important role of acid in the reaction. Oxidative cyclisation of (2*E*,6*E*)-octa-2,6-diene (**3.1**) to give (1*S**,1'*R**)-1,1'-((2*R**,5*S**)-tetrahydrofuran-2,5-diyl)diethanol (THF-diol **3.2**) was investigated using the M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of theory with acetone as a representative medium (SMD solvation model) at 298.15 K. In a similar way to the permanganate-mediated oxidative cyclisation, the reaction pathway is considered as two principal steps: FRS represents the (3+2) cycloaddition of OsO₄ with one of the diene double bonds whereas the SRS is the addition of an intermediate osmate glycolate across the remaining alkene (**Figure 4.1**). Since the FRS has been studied extensively in the context of olefin dihydroxylation,^{102,103,105,108,251,254} our principal focus here is the SRS. Different possible secondary reactions that may occur prior to cyclisation under conditions commensurate with experimental protocols have been proposed. The possible reaction manifolds considered for the initially formed intermediate Os(VI) dioxoglycolate include addition of water and NMO, reoxidation (Os(VI) → Os(VIII)), and protonation. In addition, the potential for a second cycle osmylation (intramolecular reaction of Os(VIII) glycolate with a different olefin) was also taken into account. All calculations are described for low spin pathways unless indicated. FMO analysis, MD simulations, PES calculations, and distortion/interaction analyses are also described, giving additional insight into, and chronology of, bond forming events. We also evaluate subsequent steps leading to release of THF-diol product and propagation of a catalytic cycle in the presence or absence of acid.

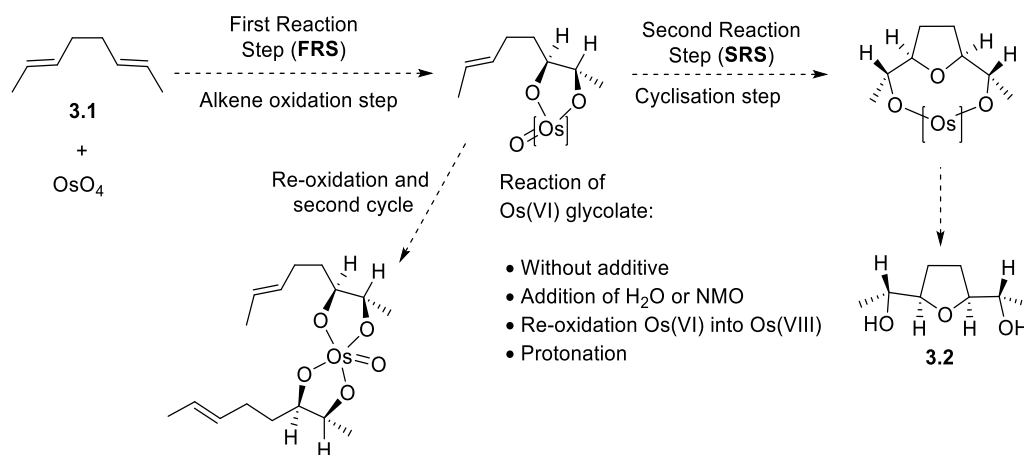


Figure 4.1: Summary of the different pathways considered for osmium-promoted oxidative cyclisation of 1,5-diene **3.1**.

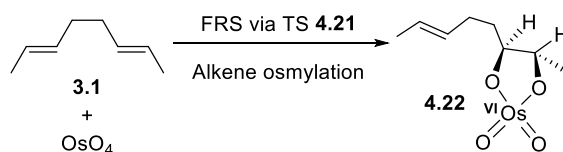
Initially, a validation of the level of theory used for calculations has been done through comparison between experimental and theoretical activation energies of osmylation for different alkenes.

4.2 The validation of the level of theory (SMD)-M06-2X/aug-cc-pVDZ/ECP

In order to validate the level of theory used in this work, two of DFT functionals (M06-2X and B3LYP) and basis sets (aug-cc-pVDZ/ECP and 6-311+G(d)/ECP) should be tested through comparison between experimental and calculated activation energies of osmylation. We could not validate the accuracy of the level of theory via reaction energies due to the absence of experimental data in the literature, and therefore only activation energies are presented for comparison. Basis set selection was validated for osmylation of 1,5-diene **3.1** (FRS, **Table 4.1**). Calculations were performed using the same functional M06-2X with Pople (entries 1–3) and Dunning type basis sets (entries 4–7), also taking into account the effect of diffuse function on the calculation. Experimental kinetic data for osmylation of (*E*)-but-2-ene in *t*-BuOH/H₂O (6:1) gives an activation energy of 17.9 kcal/mol (entry 8).²⁹⁹ In the present work, activation energies obtained from Pople and Dunning cc-pVDZ show substantial differences, and results from Pople basis sets with or without diffuse function deviate significantly from the experimental data. Dunning style basis sets without diffuse function also fail to provide free energies of activation that are consistent with experimental data for osmylation. Application of the augmented Dunning basis set, aug-cc-pVDZ, provides a calculated activation free energy of 17.6 kcal/mol in acetone, and 18.0 kcal/mol in *t*-BuOH, which are in good agreement with the experimental activation energy for osmylation of a representative disubstituted olefin, (*E*)-but-2-ene (17.9 kcal/mol).

In this work, (*E*)-2-butene is also used as a model for the 1,5-diene **3.1** in some calculations to reduce computational expense. Osmylation of (*E*)-2-butene was studied by DFT in order to confirm that the results are generally representative of the osmylation of 1,5-diene **3.1** (**Figure 4.2**). The (3+2) cycloaddition reaction of OsO₄ with (*E*)-2-butene is an exergonic reaction ($\Delta G_{\text{osm}} = -43.5$ kcal/mol, acetone SMD) with a barrier of 16.5 kcal/mol. The activation energy of osmylation calculated using M06-2X is in good agreement with experimental data (see **Tables 4.1** and **4.2**), and 1.6 kcal/mol lower than that calculated for osmylation of the more sterically demanding 1,5-diene **3.1** ($\Delta G_{\text{osm}}^{\ddagger} = 17.6$ kcal/mol).

Table 4.1: Effect of basis set on calculated activation energies for osmylation of 1,5-diene **3.1** calculated using the functional (SMD)-M06-2X.^a



entry	basis set	solvent (SMD)	$\Delta G^\ddagger$ (kcal/mol)
1	6-311G(d,p)/ECP	acetone	8.9
2	6-311++G(d,p)/ECP	acetone	8.7
3	6-311++G(2d,3pd)/ECP	acetone	13.7
4	cc-pVDZ/ECP	acetone	8.4
5	cc-pVTZ/ECP	acetone	15.9
6	aug-cc-pVDZ/ECP	acetone	17.6
7	aug-cc-pVDZ/ECP	<i>t</i> -BuOH	18.0 ^b (273.15 K)
8	$\Delta G^\ddagger$ for (<i>E</i>)-but-2-ene calculated from experimental data from ref 283	<i>t</i> -BuOH/H ₂ O (6:1)	17.9 ^c

^a Calculations performed on extended, lowest energy conformers for **3.1** and **4.21** in acetone or *t*-BuOH (SMD model) at 298.15 or 273.15 K. ^b Calculated at 273.15 K in *t*-BuOH. ^c Taken from ref 299, and the free energy of activation was obtained from the experimental rate constant ($k = 0.02499 \text{ M}^{-1} \text{ s}^{-1}$) for the osmylation of (*E*)-but-2-ene obtained in *t*-BuOH/H₂O (6:1) at 273 K.²⁹⁹

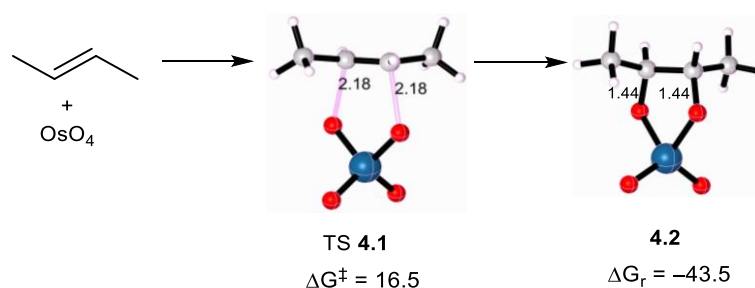


Figure 4.2: Osmylation of (*E*)-2-butene in acetone calculated at the (SMD)-M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of theory at 298.15 K. (Energies are in kcal/mol).

In order to gain further confidence in the computational method applied here, free energies of activation were calculated for osmylation of a variety of alkenes, for which experimental rate constant data are available. **Table 4.2** shows a comparison between calculated and measured energies for osmylation of five styrene derivatives, (*E*)-but-2-ene and 1-octene in *t*-BuOH or *t*-BuOH/H₂O mixtures. The level of theory used throughout the current work, M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP, gives calculated activation free energies that are in good agreement with the experimental values for the selected substrates. Osmylation is exergonic with

free energies of reaction in the range -35.9 to -40.5 kcal/mol. B3LYP using the augmented basis set overestimates activation energies for the osmylation step, while the basis set /6-311+G(d)/Hay-Wadt VDZ (n+1) ECP gives activation energies that are closer to the experimental values, although less sensitivity to electronic factors is evident within the series of styrene derivatives. The free energies of reaction are found to differ considerably between M06-2X and B3LYP.

Table 4.2: Comparison between calculated and experimental activation energies for the osmylation of alkenes in *t*-BuOH at 325.15 K. (Energies are in kcal/mol).^a

alkene	Experimental results		M06-2X		B3LYP	
	k ($\text{M}^{-1} \text{s}^{-1}$)	$\Delta G_{\text{exp}}^{\ddagger}$	$\Delta G_{\text{calc}}^{\ddagger}$	ΔG_{r}	$\Delta G_{\text{calc}}^{\ddagger \text{ b}}$	$\Delta G_{\text{r}}^{\text{ b}}$
styrene (4.3)	2.40 ^c	18.52	18.3 ^e	-36.5 ^e	24.1 (19.5) ^e	-5.1 (-13.4) ^e
4-methylstyrene (4.6)	2.77 ^c	18.43	17.9 ^e	-36.4 ^e	23.2 (19.2) ^e	-5.3 (-13.8) ^e
4-chloromethyl styrene (4.9)	3.08 ^c	18.36	17.5 ^e	-36.3 ^e	24.5 (19.8) ^e	-5.2 (-14.3) ^e
4-trifluoromethyl styrene (4.12)	0.86 ^c	19.19	19.4 ^e	-35.9 ^e	25.1 (19.8) ^e	-3.6 (-12.9) ^e
4-chlorostyrene (4.15)	3.30 ^c	18.32	18.5 ^e	-37.3 ^e	23.8 (19.8) ^e	-4.1 (-12.8) ^e
1-octene (4.18)	3.09 ^c	18.36	19.8 ^e	-40.5 ^e	24.8 (20.8) ^e	-9.6 (-18.5) ^e
(<i>E</i>)-but-2-ene (50)	0.02499 ^d	17.94	17.6 ^f	-44.0 ^f	22.3 (18.0) ^f	-12.2 (-21.5) ^f

^a Calculations performed using M06-2X and B3LYP functionals with aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP basis set. All results were calculated in *t*-BuOH (SMD model). ^b Results between brackets obtained using B3LYP/6-311+G(d)/Hay-Wadt VDZ (n+1) ECP level of theory. ^c Taken from ref 157 and 300.^{157,300} Rate constant measured at 323 K in *t*-BuOH. ^d Taken from ref 299.²⁹⁹ Rate constant measured at 273 K in *t*-BuOH/H₂O (6:1). ^e Calculated at 325.15 K. ^f Calculated in *t*-BuOH (SMD model) at 273.15 K.

Optimised geometries from the M06-2X calculations for the osmylated styrene derivatives, 1-octene and their corresponding transition states are shown in **Figure 4.3**. Greater development of the bond between an oxo group and the terminal methylene carbon is evident in all TS's, most notably for the styrenes.

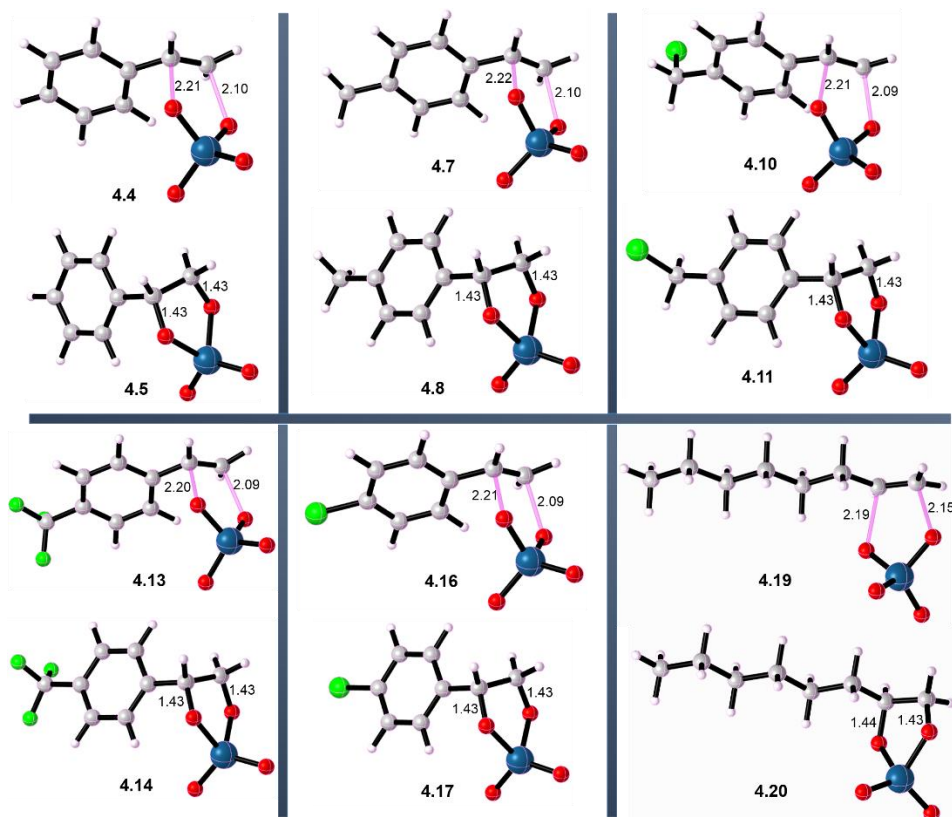


Figure 4.3: Optimized geometries for osmylation of styrene derivatives and 1-octene showing TS's and Os(VI) dioxoglycolate calculated at the (SMD)-M06-2X/aug-cc-pVDZ/ECP level of theory.

4.3 Osmium-promoted oxidative cyclisation suggested pathways

Since the osmylation step (FRS) is well-known in the literature, the main focus here will be on the cyclisation process leading to the THF ring formation. To evaluate the cyclisation mechanism, cyclisation is considered through either Os(VI) or Os(VIII) glycolate intermediates according to the reaction conditions and all the suggested pathways are calculated using the SMD-(acetone)-(U)M06-2X/aug-cc-pVDZ/Hay-Wadt (n+1) ECP level of theory at 298.15 K (**Figure 4.4**). Two pathways are considered for Os(VI) cyclisation. The first suggested pathway is without ligand coordination, and with or without protonation. The second suggested pathway is the oxidative cyclisation with a ligand, either a water molecule or NMO, again with and without protonation. Os(VIII) glycolates are also investigated with and without acid. In addition to the cyclisation pathways, the second cycle (intramolecular osmylation of another 1,5-diene) is also considered for relevant Os glycolate intermediates, specifically Os(VIII) and NMO • Os(VI) glycolate complexes. All protonation pathways consider the site of protonation, which can be on alkoxy or oxo groups.

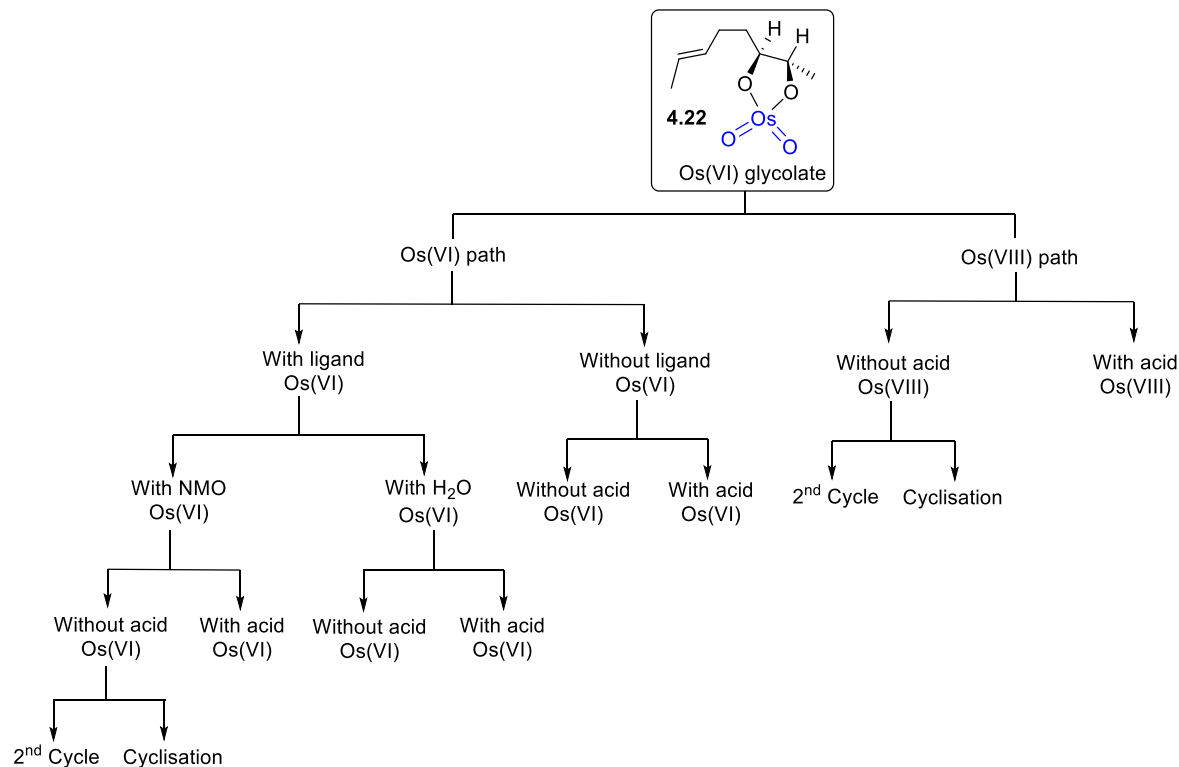


Figure 4.4: Flow diagram showing the mechanistic pathways considered for the osmium-catalysed oxidative cyclisation of 1,5-diene **3.1**.

4.3.1 Oxidative cyclisation via Os(VI) glycolate intermediate

4.3.1.1 Oxidative cyclisation via non-liganded Os(VI) glycolate intermediate

This section will describe the oxidative cyclisation of 1,5-dienes in the absence of ligands under both acidic and non-acidic conditions (**Figure 4.5**). Initially, the direct oxidative cyclisation of 1,5-diene **3.1** by OsO_4 was considered via Os(VI) dioxoglycolate intermediate **4.22** as the simplest pathway (**Figure 4.5**, black pathway). The FRS leads to tetrahedral Os(VI) dioxoglycolate **15** by way of (3+2) cycloaddition TS **4.21** with a free energy barrier of 17.6 kcal/mol as an exergonic reaction ($\Delta G_{\text{osm}} = -42.0$ kcal/mol). The calculated activation energy is in good agreement with experimental values (see **Table 4.1** and **4.2**).^{106,157,299,300} The SRS proceeds from tetrahedral Os(VI) dioxoglycolate **4.22** to Os(IV) diolate **4.24** by addition of $\text{O}=\text{Os}=\text{O}$ across the remaining alkene through TS **4.23** with a barrier of 25.2 kcal/mol as an exergonic step ($\Delta G_{\text{cyc}} = -24.4$ kcal/mol). Discussion here is confined to singlet spin configurations pathway as known Os(VIII) and Os(VI) oxoglycolates are diamagnetic.¹³⁸ Further details about the effect of spin multiplicity on oxidative cyclisation can be found in section **4.7**.

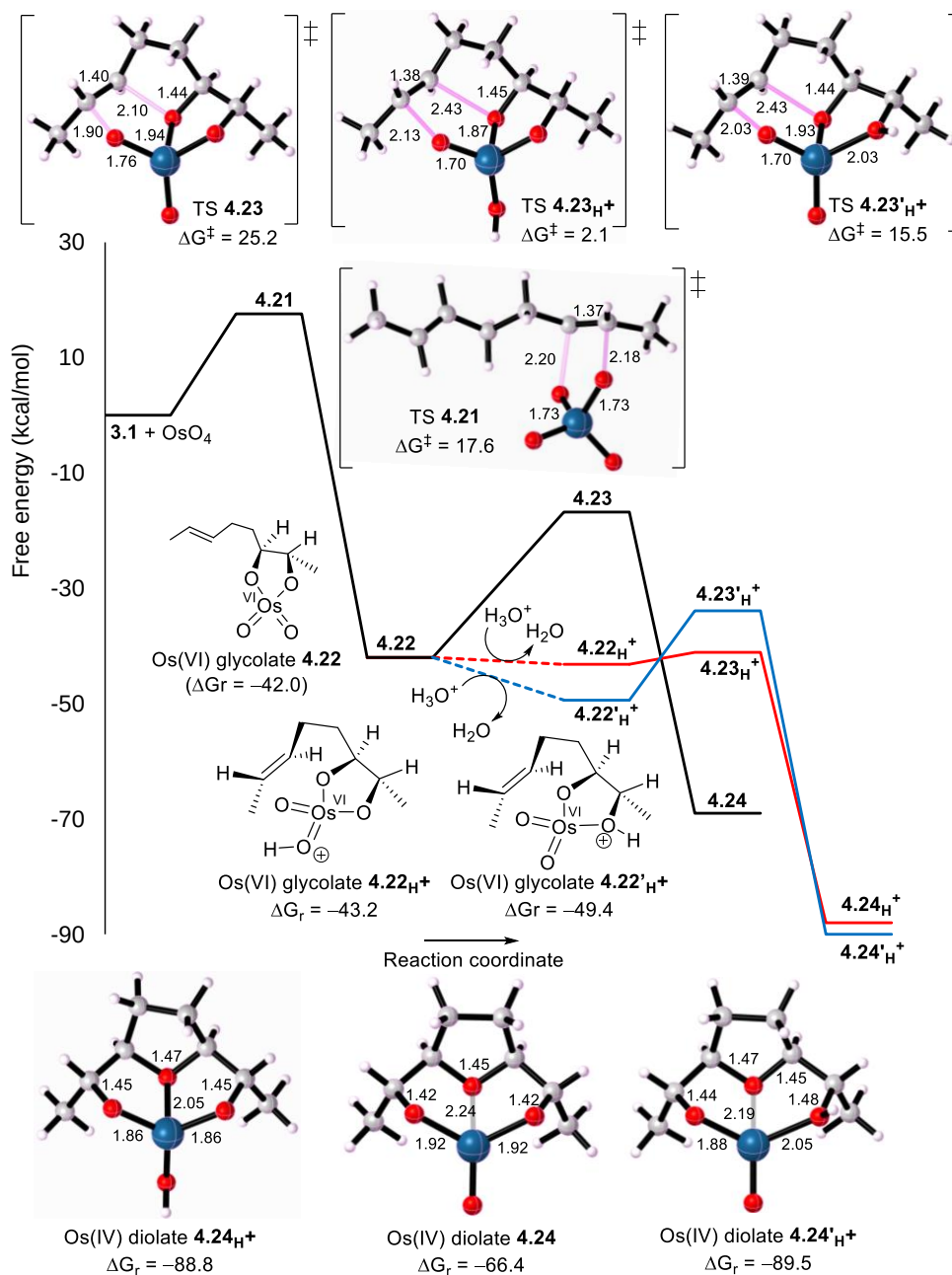


Figure 4.5: Reaction energy diagram for the direct (Os(VIII) → Os(VI) → Os(IV)) oxidative cyclisation of 1,5-diene **3.1** by OsO₄ (singlet spin multiplicity), showing the effect of acid on cyclisation and regioselectivity of protonation.

The influence of Bronsted acid was then investigated, exploring the proposal that protonation of the first intermediate Os(VI) dioxoglycolate (**4.22** → **4.22_H⁺** / **4.22'_H⁺**) offers a viable pathway for cyclisation (**Figure 4.5**, blue and red pathways). Indeed, calculations indicate that protonation of an oxo ligand using strong acid (H₃O⁺) to give **4.22_H⁺** is approximately thermoneutral ($\Delta G_{H^+} = -1.2$ kcal/mol), but the effect on the barrier to cyclisation is substantial. The protonated Os(VI) pathway displays a relative stabilisation of TS **4.23_H⁺** in comparison to **4.23**, proceeding with a lower energy barrier of 2.1 kcal/mol as an exergonic reaction ($\Delta G_{cyc} = -45.6$ kcal/mol). Isomer **4.22'_H⁺** protonated on the glycolate ligand is more stable by 6.2 kcal/mol relative to **4.22_H⁺**, but exhibits an increased

barrier for cyclisation of 15.5 kcal/mol. Based on Marcus theory,^{301–306} the alkoxy protonated Os(VI) **4.22'**_H⁺ can isomerise intramolecularly into oxo protonated Os(VI) **4.22**_H⁺ with an activation energy of 9.7 kcal/mol ($\Delta G_r = 6.2$ kcal/mol and $\Delta G_0^\ddagger = 6.2$). Here, it is worth noting that intrinsic barrier and free energy of proton transfer are equal in the case of intramolecular proton transfer reaction (see the computational details in the experimental chapter).

4.3.1.2 Oxidative cyclisation via liganded Os(VI) glycolate intermediate

Other pathways are possible for cyclisation including addition of water or NMO to the intermediate **4.22** with or without acid (**Figure 4.6**). In the absence of acid, the addition of a water or NMO molecule to Os(VI) dioxoglycolate **4.22** is calculated to be an exergonic process, leading to pentacoordinate intermediate **4.22**_{H2O} or **4.22** • NMO, which is 4.2 and 5.1 kcal/mol lower in energy than **4.22**. The overall reaction from **4.22**_{H2O} into THF–Os(IV) complex **4.24**_{H2O} remains thermodynamically favourable ($\Delta G_{cyc} = -18.3$ kcal/mol) but this requires a higher energy barrier of 29.5 kcal/mol to be overcome, via distorted trigonal bipyramidal (3+2) cycloaddition TS **4.23**_{H2O} compared to the pathway **4.22**→**4.24**. However, cyclisation of **4.22** • NMO is calculated to be kinetically ($\Delta G^\ddagger = 36.0$ kcal/mol, TS **4.23** • NMO) and thermodynamically ($\Delta G_{cyc} = -7.0$ kcal/mol) less favourable compared to with and without water.

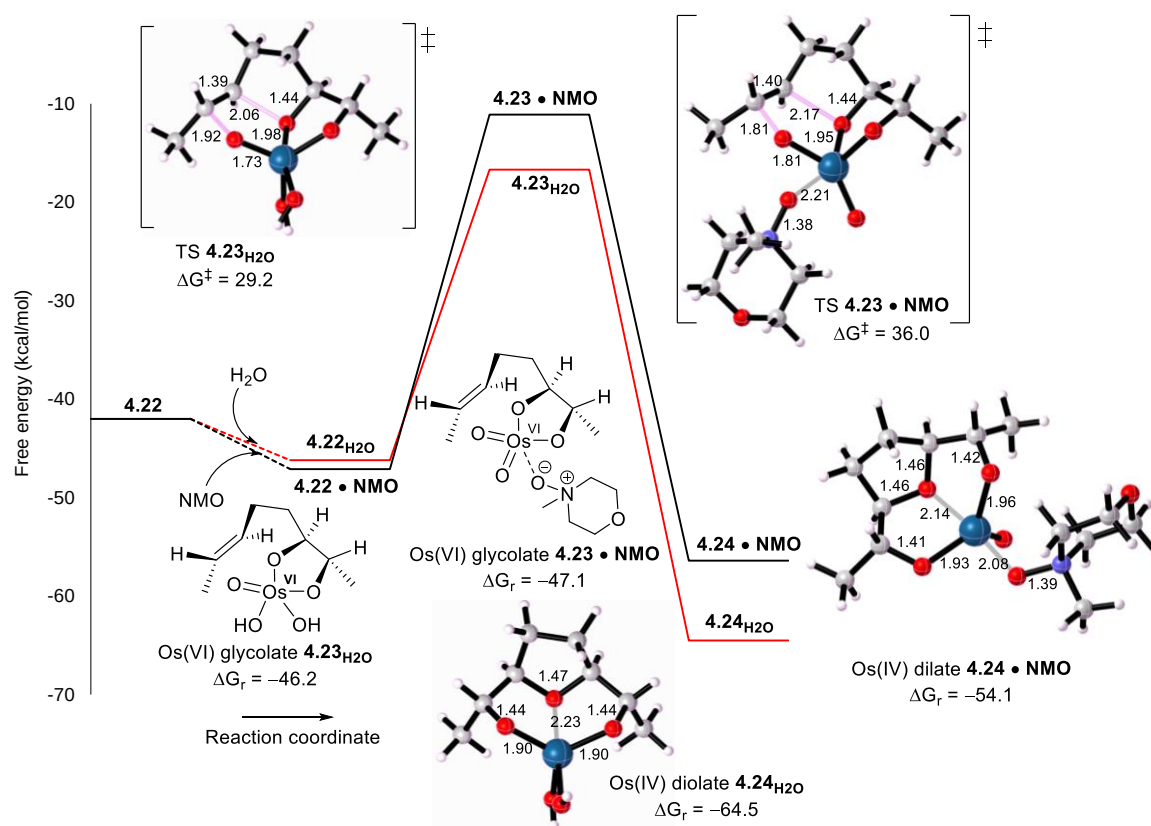


Figure 4.6: Reaction energy diagram for the liganded Os(VI) oxidative cyclisation (singlet spin multiplicity) in the absence of acid.

The protonation of liganded Os(VI) glycolate **4.22**_{H₂O} and **4.22** • **NMO** was considered in a similar way to the non-liganded intermediate Os(VI) **4.22**. DFT simulations show that protonation of intermediates **4.22**_{H₂O} and **4.22** • **NMO** is highly exergonic (**Figure 4.7**). Protonation of OH group in **4.22**_{H₂O} to give **4.22**_{H⁺} • **H₂O** displays a stabilisation of 19.8 kcal/mol and cyclisation proceeds with a reduced barrier of 11.7 kcal/mol via TS **4.23**_{H⁺} • **H₂O** as an exergonic reaction ($\Delta G_{\text{cyc}} = -38.2$ kcal/mol) in comparison to **4.23**_{H₂O}. Protonation of **4.22** • **NMO** is highly exergonic, with a significant preference for oxo protonation (**4.22** • **NMO** → **4.22**_{H⁺} • **NMO**, $\Delta G_{\text{H}^+} = -51.4$ kcal/mol). Cyclisation of **4.22**_{H⁺} • **NMO** to Os(IV) THF diolate complex **4.24**_{H⁺} • **NMO** displays a barrier of 26.4 kcal/mol via TS **4.23**_{H⁺} • **NMO** with a reaction free energy of $\Delta G_{\text{cyc}} = -19.3$ kcal/mol. This barrier is significantly higher than the non-liganded protonated pathway (**4.22**_{H⁺} → **4.24**_{H⁺}, $\Delta G^\ddagger = 2.1$ kcal/mol); however the overall free energy of Os(IV) formation via **4.22**_{H⁺} • **NMO** is more favourable ($\Delta G_{\text{tot}} = -117.6$ kcal/mol).

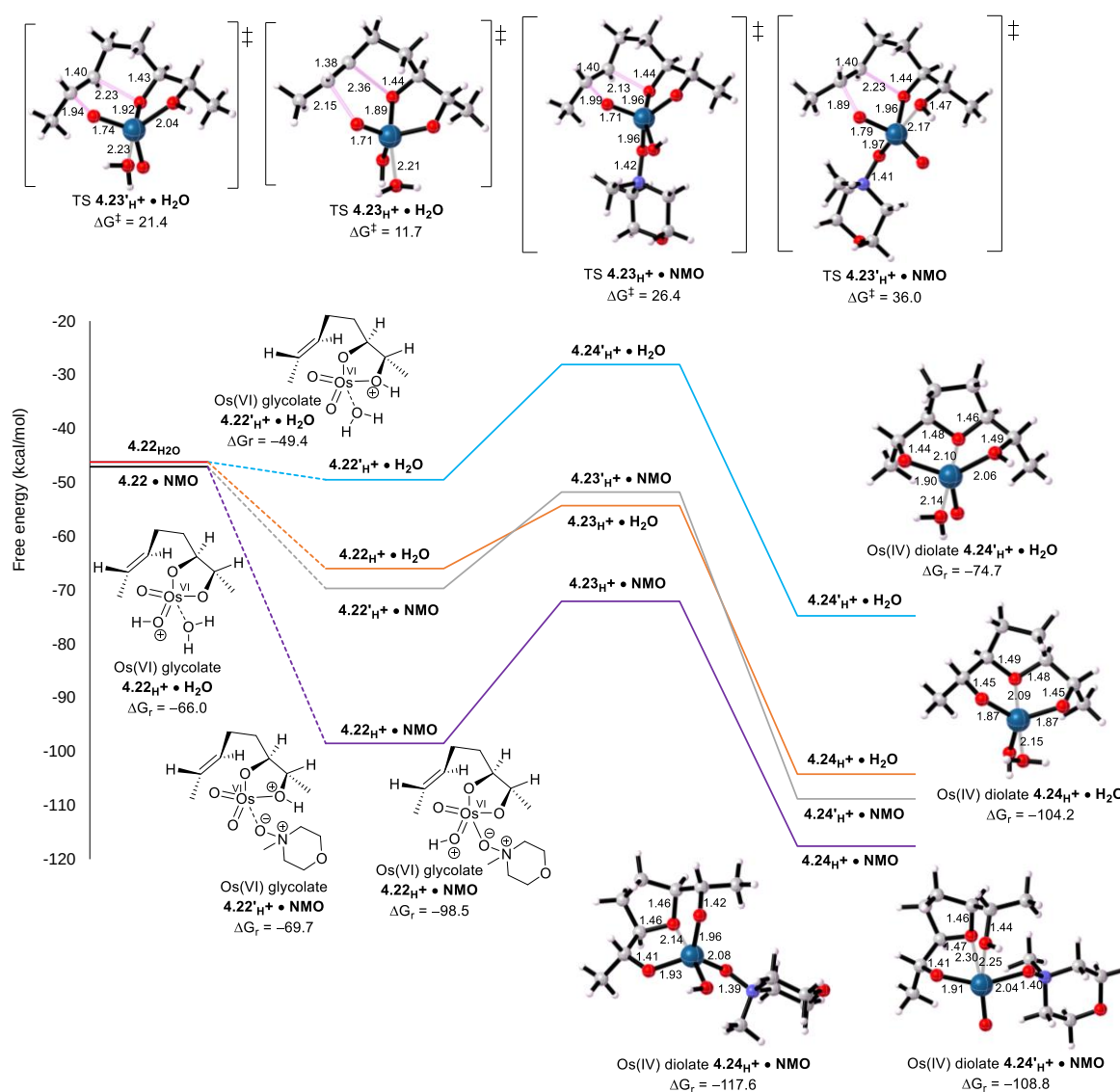


Figure 4.7: Reaction energy diagram for the liganded Os(VI) oxidative cyclisation (singlet spin multiplicity) in the presence of acid, showing regioselectivity of protonation.

The alkoxy protonated isomer **4.22'**_{H+} • NMO is noticeably less stable than **4.22**_{H+} • NMO by 28.8 kcal/mol although it exhibits a decreased barrier for cyclisation of 17.9 kcal/mol as a more exergonic step ($\Delta G_{\text{cyc}} = -39.1$ kcal/mol). Since the intramolecular proton transfer (**4.22'**_{H+} • NMO → **4.22**_{H+} • NMO) is highly exergonic ($\Delta G = -28.8$ kcal/mol), isomer **4.22**_{H+} • NMO would be dominant. Similarly, hydrated intermediate **4.22'**_{H+} • H₂O is more likely to interconvert into **4.22**_{H+} • H₂O.

Considering water and NMO liganded pathways, and in the presence of strong or weak acid, the reaction is likely to proceed through protonated NMO-complexed Os(VI) glycolate **4.22**_{H+} • NMO due to the significant stabilisation arising from strong interaction between oxo protonated Os(VI) and NMO (**Figure 4.7**).

4.3.2 Oxidative cyclisation of Os(VIII) glycolate intermediate

Although the DFT calculations above have identified kinetically and thermodynamically favourable cyclisation pathways of protonated Os(VI) intermediate **4.22**_{H+} in the presence and absence of NMO ligand, reoxidation of Os(VI) dioxoglycolates to Os(VIII) trioxoglycolates by NMO is well known and should also be evaluated.^{193,234} It should be noted, however, that typical catalytic dihydroxylation using NMO or TMO is not conducted under acidic conditions. Oxidation of Os(VI) dioxoglycolate **4.22** to trioxoglycolate **4.22**_[ox], by NMO, is calculated to be endergonic ($\Delta G_{\text{ox}} = 16.8$ kcal/mol) using the M06-2X functional (**Figure 4.8**). We were unable to find a transition state for this and other oxygen transfer reactions from NMO to Os using transition state search of quantum calculations. Also, scanning the bond between NMO and Os(VI) shows a decrease in energy with decreasing in distance between NMO and the Os(VI) species indicating a barrierless association leading to a stable complex Os(VI) • NMO. Therefore, the reoxidation was considered as two elementary steps.³⁰⁷ The first step is the formation of complex between Os(VI) and the good sigma donor ligand NMO, and the second step is dissociation of the N–O bond to release Os(VIII) and *N*-methylmorpholine (NMM). Thus, the formation of Os(VIII) glycolate will depend on the stability of the complex; the more stable complex the slower reoxidation proceeds.

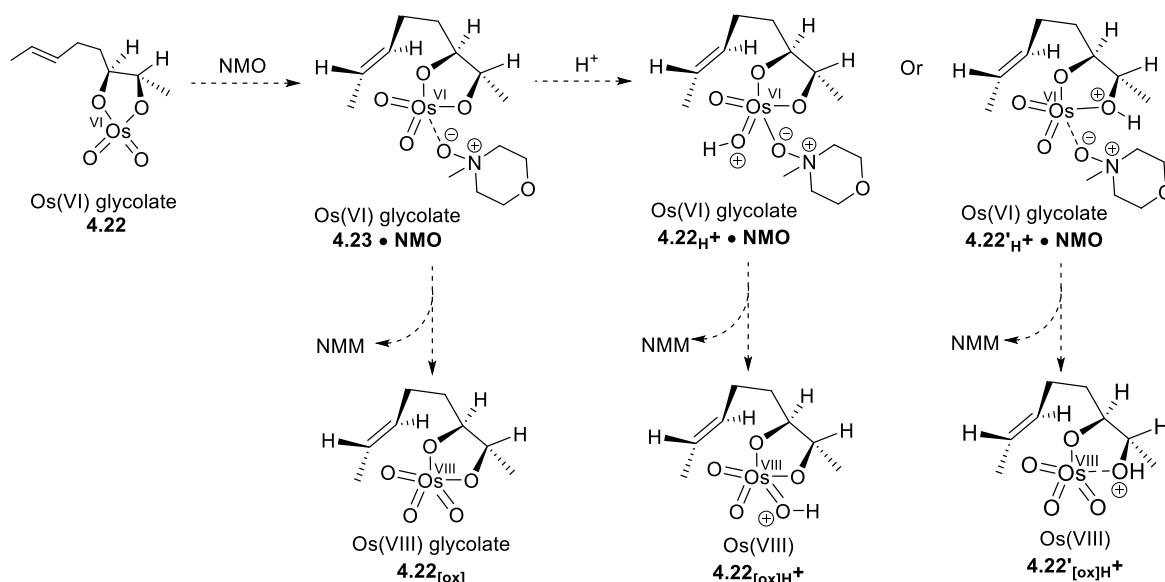


Figure 4.8: Reoxidation of Os(V) glycolate to Os(VIII) by NMO.

Since NMO stabilises **4.22** by 5.1 kcal/mol, more than 21.9 kcal/mol is required to release **4.22_[ox]** (**Figure 4.9**). However, the calculated energy indicates reoxidation by NMO to be a relatively slow step, and this is consistent with reported kinetic data.^{155–157} The ensuing cyclisation reaction of **4.22_[ox]** to **4.24_[ox]** via the distorted square pyramidal (3+2) cycloaddition TS **4.23_[ox]** has a comparatively lower activation energy barrier (11.8 kcal/mol) than without reoxidation (**4.22**→**4.24**, 25.2 kcal/mol).

According to our calculations, the presence of acid does not facilitate reoxidation of **4.22** due to the significant stabilisation arising from protonation of **4.22 • NMO** (**Figure 4.9**). Since protonation of **4.22 • NMO**→**4.22'H⁺ • NMO** is highly exergonic ($\Delta G_{H^+} = -51.4$ kcal/mol), the formation of protonated Os(VIII) glycolate **4.22_[ox]H⁺** becomes highly disfavoured ($\Delta G_{ox} = 67.6$ kcal/mol) and, therefore, cyclisation ($\Delta G^\ddagger = 26.4$ kcal/mol, see **Figure 4.7**) is favoured over reoxidation. However, if the reoxidation is able to proceed to Os(VIII) trioxoglycolate **4.22_[ox]H⁺**, only 5.0 kcal/mol is required to overcome TS **4.23_[ox]H⁺** to give THF diolate **4.24_[ox]H⁺** ($\Delta G_{cyc} = -68.0$ kcal/mol). Similarly, the formation of **4.22'_[ox]H⁺** from **4.22'H⁺ • NMO** is endergonic ($\Delta G = 22.1$ kcal/mol) and, so, cyclisation of **4.22'H⁺ • NMO** is also favoured ($\Delta G^\ddagger = 17.9$ kcal/mol) over reoxidation.

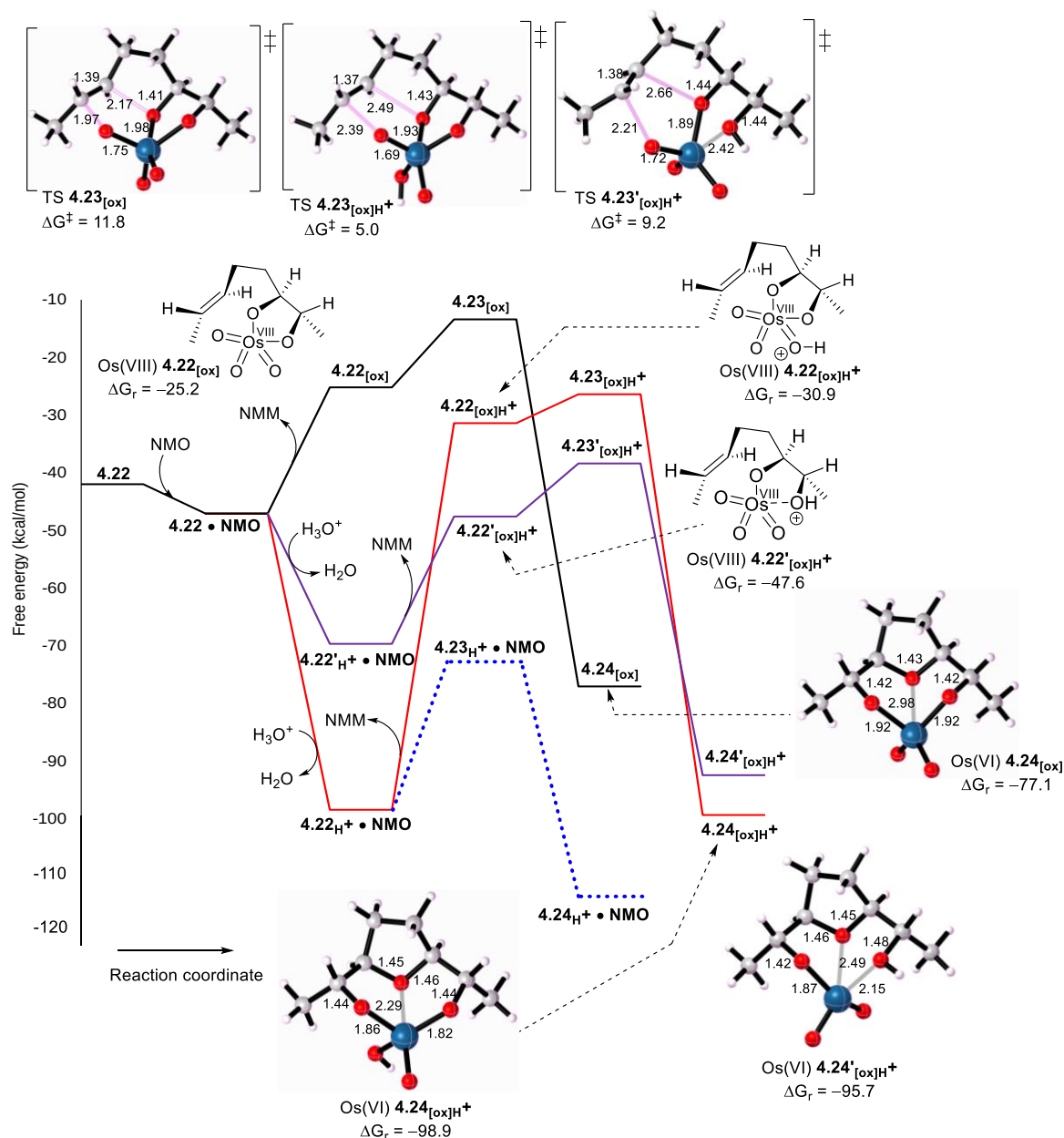


Figure 4.9: Reaction energy diagram of Os(VIII) intermediate cyclisation, showing the effect of acid on the on reoxidation Os(VI)→Os(VIII). Dotted blue line represents cyclisation of **4.22_H⁺ • NMO**.

It is important to recognise that the influence of protonation has been calculated using strong acid (H₃O⁺), which is commensurate with the conditions optimised for oxidative cyclisation by Donohoe and co-workers (e.g. 5 equiv CSA or TFA). When acid is absent, osmylation of a second molecule of substrate (represented here using *E*-but-2-ene as a model for diene **3.1**, **Figure 4.10**) by Os(VIII) trioxoglycolate **4.22_[ox]** leads to second cycle adduct **4.26** as an exergonic ($\Delta G_{\text{osm}} = -76.0$ kcal/mol) reaction with a barrier of 5.3 kcal/mol. Second cycle osmylation is therefore kinetically favoured in comparison to cyclisation of **4.22_[ox]**, as is indeed the experimental outcome in the absence of acid.

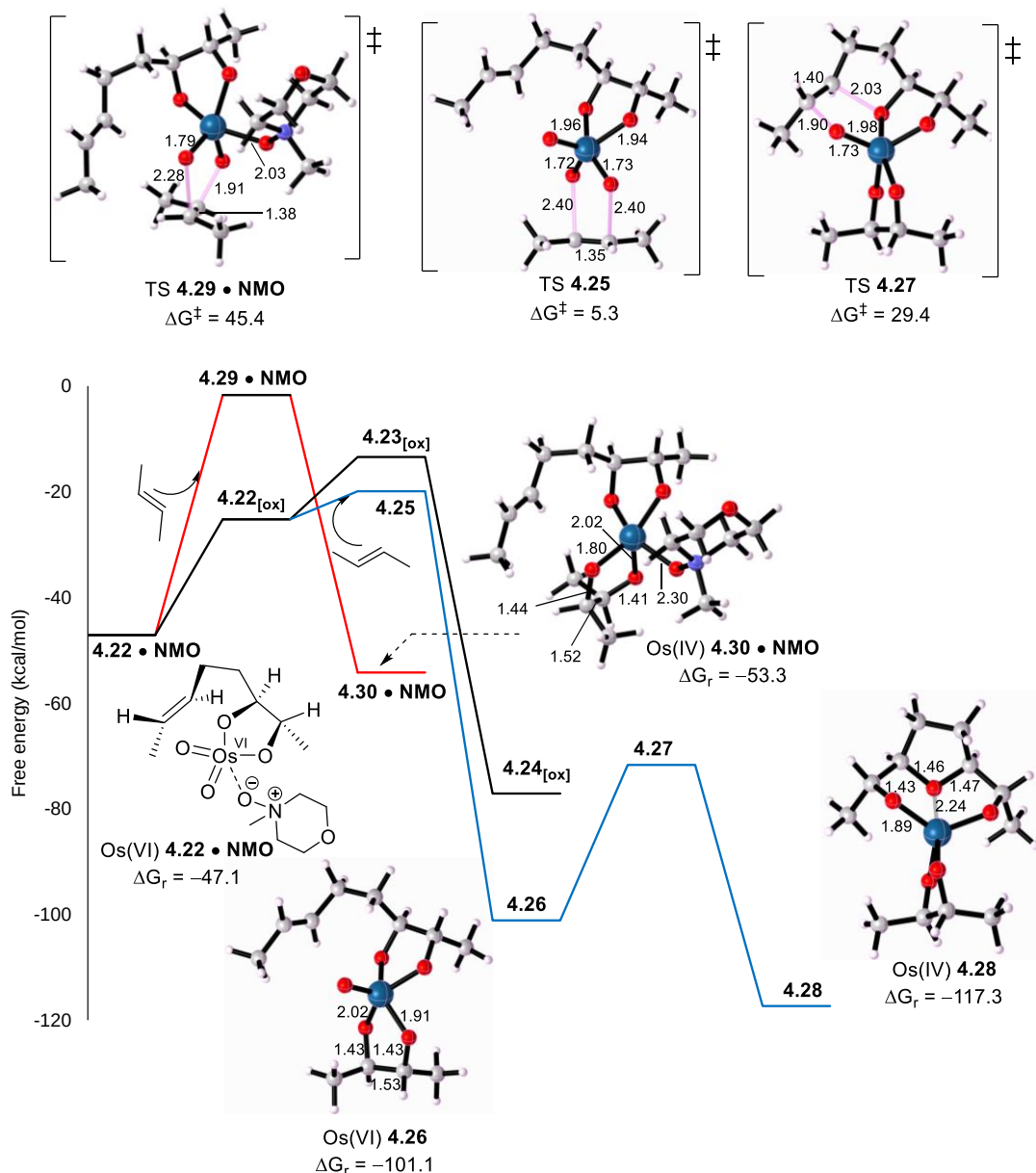


Figure 4.10: Energetic comparison between cyclisation of Os(VIII) trioxoglycolate **4.22_[ox]** (black pathway) and intermolecular osmylation of *E*-but-2-ene (blue pathway). Intermolecular osmylation of *E*-but-2-ene by complex **4.22 • NMO** is also shown (red pathway). Diene **3.1** is replaced by *E*-but-2-ene to reduce computational complexity.

For completion, the possibility for a second cycle adduct **1.112** (Scheme 1.21) to undergo the SRS to form THF-diol products was evaluated using model oxobisglycolate **4.26** (**4.26**→**4.27**→**4.28**, Figure 4.11). The pathway for cyclisation of **4.26**, shows a comparatively high activation barrier ($\Delta G^\ddagger = 29.4$ kcal/mol), and it seems more likely that if the second cycle adduct is an intermediate in THF-diol formation, **4.26** would undergo hydrolysis to return **4.22** and a molecule of diol. The resulting Os(VI) glycolate **4.22** could then cyclise through one of the protonation pathways described above (**4.22_{H+}**→**4.24_{H+}** or **4.22_{H+}**→**4.22_{H+} • NMO**→**4.24_{H+} • NMO**), if acid of sufficient strength is present.

Continuing investigation of the second cycle, reaction of **4.22** • **NMO** with *E-but-2-ene* was calculated and found to be kinetically and thermodynamically unfavourable via TS **4.29** • **NMO** ($\Delta G^\ddagger = 45.4$ kcal/mol, $\Delta G_{\text{osmy}} = -7.2$ kcal/mol, **Figure 4.10**, red pathway), indicating that any second cycle is likely to proceed through formation of trioxoglycolate **4.22**_[ox]. Furthermore, hydrolysis of Os(VIII) trioxoglycolate **4.22**_[ox] into 1,2-diol **4.34** has been calculated and compared with cyclisation and intermolecular osmylation (**Figure 4.11**). DFT calculations show that addition of water to **4.22**_[ox] is disfavoured and has a high activation energy ($\Delta G^\ddagger = 45.4$ kcal/mol, TS **4.31**) leading to formation of unstable intermediate ($\Delta G_r = 17.4$ kcal/mol). However, overall release of the diol **4.34** is exergonic ($\Delta G_{\text{hyd}} = -8.0$ kcal/mol). It is indicated that where **4.22**_[ox] formation can occur, it will enter the second cycle providing acid is not present.

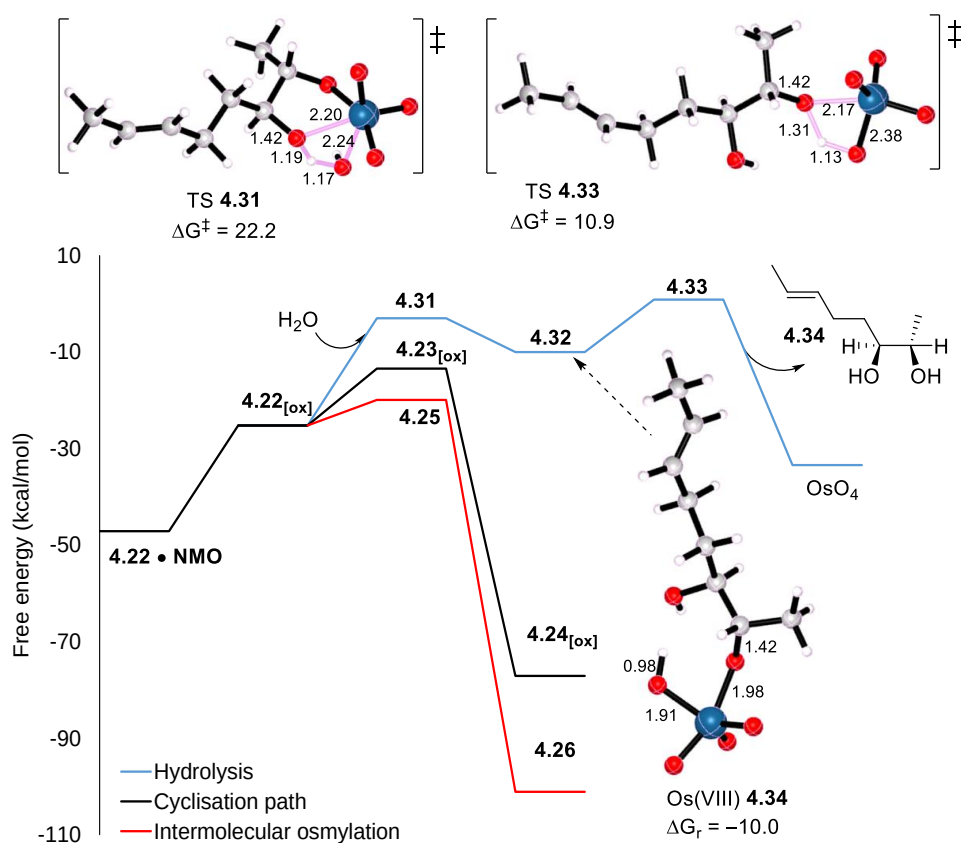


Figure 4.11: Energetic comparison between hydrolysis (blue pathway), cyclisation (black pathway), and intermolecular osmylation (red pathway) of oxidised intermediate Os(VIII) trioxoglycolate **4.22**_[ox]. Extended conformation for hydrolysis was used to reduce computational complexity.

4.3.3 Summary of Os(VI) and Os(VIII) pathways

Experimentally, most efficient oxidative cyclisation of 1,5-dienes is achieved under conditions developed by Donohoe's group, where a stoichiometric excess of strong acid is used. They also

showed that cyclisation of Os(VI) glycolates occurs in the presence of acid. Our calculations are consistent with these results where the Os(VI) dioxoglycolate **4.22** favours cyclisation by way of the protonated intermediate **4.22_H⁺** with a low calculated barrier of 2.1 kcal/mol. It is also shown that acid has a great effect on Os(VI) glycolate oxidation (Os(VI)→Os(VIII)), where cyclisation through liganded protonated Os(VI) glycolate **4.22_H⁺ • NMO** (**4.22_H⁺ • NMO**→**4.24_H⁺ • NMO**, $\Delta G^\ddagger = 26.4$ kcal/mol) outpaces reoxidation by NMO.

Oxidative cyclisation has been demonstrated where strong acid has not been deliberately added to the reaction medium (i.e. Piccialli's conditions: OsO₄/NaIO₄ in DMF, **Scheme 1.21**).¹²³ However, periodic acid may well be present under these reaction conditions, so acid-catalysed cyclisation of Os(VI) or Os(VIII) intermediates is still feasible, albeit at a slower rate or in competition with other pathways. Again, our calculations are in accord with the experimental observations, and under weakly acidic conditions and using a stronger oxidant, reoxidation of the first intermediate **4.22** to an Os(VIII) trioxoglycolate **4.22_[ox]** is possible, and cyclisation may then occur by protonated pathways via Os(VIII) trioxoglycolate **4.22'_[ox]^H⁺**. However, Os(VIII) trioxoglycolate **4.22_[ox]** may also enter alternative reaction manifolds including intermolecular osmylation ($\Delta G^\ddagger = 5.3$ kcal/mol, $\Delta G_r = -76.0$ kcal/mol), as evidenced by the isolation of second cycle products (Os(VI) bisglycolates **1.112** under Piccialli's reaction conditions (**Scheme 1.21**). Finally, in absence of acid (OsO₄/NMO), second cycle osmylation is preferred over cyclisation and direct hydrolysis (**Figure 4.11**), leading to normal dihydroxylation products only.

4.4 Frontier molecular orbital analysis of the SRS.

To understand the influence of additives and reoxidation on the SRS, FMO's were examined (**Table 4.3**). FMOs calculated for the intermediate Os(VI) and Os(VIII) glycolates show HOMO's mainly localised on the electron-rich alkenes (donor) and LUMO's predominantly located on Os oxo groups (acceptor). The HOMO-LUMO energy gap for hydrated Os(VI) glycolate **4.22_{H2O}** is 6.6 eV compared to 5.7 eV in the absence of water, contributing to a higher energy barrier for cyclisation attributed in part to decreased electrophilicity (LUMO = -1.5 eV) of **4.22_{H2O}**. The addition of NMO into **4.22** increases the activation energy of cyclisation from 25.2 kcal/mol in **4.23** into 36.0 kcal/mol in **4.23 • NMO** due to the decrease in electrophilicity from -2.3 eV into -1.5 eV.

Protonation of **4.23 • NMO** decreases the energy gap from 6.0 eV in **4.22 • NMO** into 5.5 eV or 5.4 eV in **4.22_H⁺ • NMO** or **4.22'_H⁺ • NMO** respectively, in line with the lowering of barrier to cyclisation. Although the oxidised first intermediate Os(VIII) glycolate **4.22_[ox]** has a decreased energy gap of 4.8 eV in comparison to Os(VI) glycolate **4.22**, consistent with increased electrophilicity of the Os(VIII)

site in **4.22**_[ox], it still requires 11.8 kcal/mol to overcome the cyclisation barrier. It is proposed that this is at least in part due to steric interactions of oxo ligands and less favourable TS geometry (see **Figure 4.12**).

Table 4.3: Comparison between calculated FMO's energies for Os(VI) and Os(VIII) glycolate intermediates and free energy of activations of their corresponding TS's.

Intermediate	LUMO (eV)	Energy gap (eV)	$\Delta G^\ddagger$ (kcal/mol)
4.22 _{H₂O}	-1.6	6.6	29.2
4.22 • NMO	-1.5	6.0	36.0
4.22	-2.3	5.7	25.2
4.22 _{H⁺} • NMO	-2.6	5.5	26.4
4.22' _{H⁺} • NMO	-2.6	5.4	19.9
4.22 _[ox]	-3.3	4.8	11.8
4.22' _{H⁺}	-3.6	4.6	15.5
4.22 _{H⁺} • H ₂ O	-3.5	4.6	11.7
4.22 _{H⁺}	-4.1	4.1	2.1
4.22' _{[ox]H⁺}	-4.9	3.6	9.2
4.22 _{[ox]H⁺}	-5.5	3.1	5.0

Protonation of an oxo ligand of the Os(VI) dioxoglycolate (**4.22**→**4.22**_{H⁺}) decreases the HOMO-LUMO gap to 4.1 eV due to attenuation of the LUMO energy to -4.1 eV. The calculated SRS cyclisation barrier shows a commensurate reduction from 11.8 kcal/mol for **4.22**_[ox] to 2.1 kcal/mol via **4.22**_{H⁺}, which can also be attributed to favourable orbital overlap arising from the tetrahedral TS geometry, and reduced steric interactions. It is clear that the addition of ligands such as water or NMO to **15**_{H⁺} decreases the electrophilicity of LUMO sites although water has lower energy gap (**4.22**_{H⁺} • H₂O, 4.6 eV) than NMO (**4.22**_{H⁺} • NMO, 5.5 eV). Again, this confirms that NMO is a strong sigma donor ligand, resulting in a less favorable interaction between metal oxo (LUMO) and alkene (HOMO) (see below). Protonated Os(VIII) trioxoglycolate isomers **4.22**_{[ox]H⁺} and **4.22'**_{[ox]H⁺} have the lowest HOMO-LUMO gap of 3.1 eV and 3.6 eV respectively, although the barrier to cyclisation remains higher than for the protonated Os(VI) dioxoglycolate **4.22**_{H⁺}. The higher barrier for **4.22'**_{[ox]H⁺} is believed to be due to increased distortion at the TS (see below). **Figure 4.12** show a visualisation of the HOMO's and LUMO's for the selected Os glycolates **4.22**_{H⁺}, **4.22**_{H⁺} • NMO, **4.22**_{H⁺} • H₂O, **4.22**_[ox], and **4.22'**_{[ox]H⁺} and **4.22**_{[ox]H⁺}.

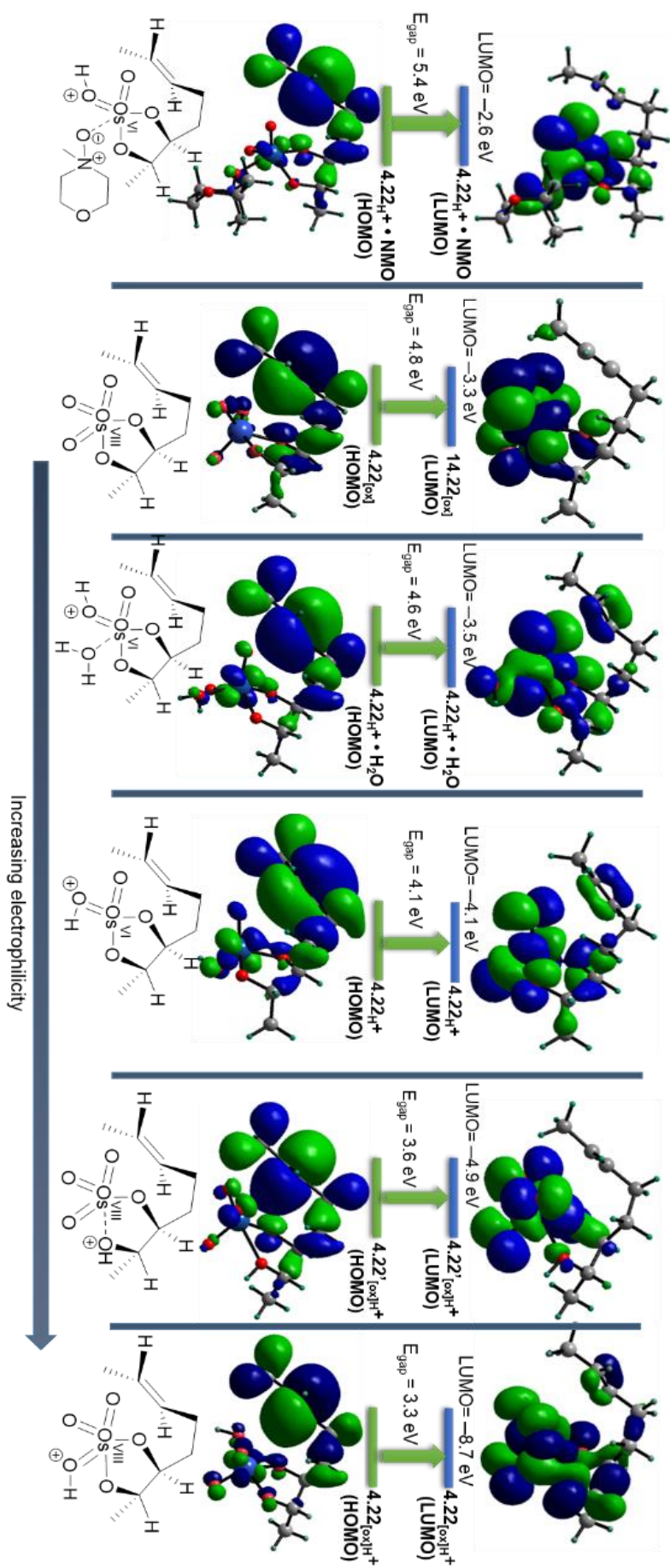


Figure 4.12: Visualization (0.02 isovalue surface) of the HOMO's and LUMO's for the Os glycolates $4,22_{\text{H}^+}$, $4,22_{\text{H}^+} \bullet \text{NMO}$, $4,22_{\text{H}^+} \bullet \text{H}_2\text{O}$, $4,22_{[\text{ox}]}$, and $4,22'_{[\text{ox}]\text{H}^+}$ and $4,22'_{[\text{ox}]\text{H}^+}$.

4.5 Distortion/interaction analysis of the SRS TS's.

Estimated contributions of interaction and distortion energies for the SRS were obtained using a model for (3+2) cyclisation with the tether removed from the reacting components by adaptation of an approach described by Houk and co-workers (see section 3.5).^{293–295} The interacting reactive components are **4.35_{H+}**, **4.35_{H+} • NMO**, and **4.35_{H+} • H₂O**, **4.35_[ox]**, **4.35_{[ox]H+}**, and **4.35'_{[ox]H+}** (Figure 4.12). The separated reactive components are **4.36_{H+}**, **4.36_{H+} • NMO**, and **4.36_{H+} • H₂O**, **4.36_[ox]**, **4.36_{[ox]H+}**, and **4.36'_{[ox]H+}**, and their corresponding ground state geometries are **4.37_{H+}**, **4.37_{H+} • NMO**, and **4.37_{H+} • H₂O**, **4.37_[ox]**, **4.37_{[ox]H+}**, and **4.37'_{[ox]H+}**. The differences in energies between these species can be used to estimate interaction and distortion energies at the TS.

A greater stabilising interaction energy is evident for protonated Os(VIII) TS's **4.35'_{[ox]H+}** (–8.7 kcal/mol) and **4.35_{[ox]H+}** (–5.8 kcal/mol) compared to protonated TS's Os(VI) **4.35_{H+}** (–3.0 kcal/mol) and **4.35_{H+} • H₂O** (–2.9 kcal/mol) whereas a destabilising one is obtained for Os(VIII) TS **4.35_[ox]** (+1.3 kcal/mol) and protonated NMO-chelated Os(VI) TS **4.35_{H+} • NMO** (+2.2 kcal/mol) (Figure 4.13). However, it is unfavourable distortion of the protonated Os(VIII) trioxoglycolate (+11.4 kcal/mol) that contributes substantially to the higher overall barrier for the SRS compared to the protonated Os(VI) TS (+3.2 kcal/mol). It is clear that addition of NMO to protonated Os(VI) TS results in a substantial increase of activation energy for cyclisation via **4.23_{H+} • NMO** ($\Delta G^\ddagger = 26.4$), and this is manifested from the highest distortion energy for protonated NMO-complexed Os(VI) glycolate (+16.1 kcal/mol) as well as its alkene fragment (+8.2 kcal/mol). The addition of water to protonated Os(VI) TS increases the activation energy by 5 times due to the increase in distortion energy from +3.2 kcal/mol in protonated Os(VI) glycolate to +6.0 kcal/mol in hydrated protonated Os(VI) glycolate. An intermediate distortion energy (+5.5 kcal/mol) is observed for Os(VIII) glycolate **4.35_[ox]**, but in this case distortion of the alkene (+7.1 kcal/mol) increases the overall distortion energy. According to this analysis, protonated Os(VI) pathway combines a favourable interaction energy (–3.0 kcal/mol) with minimal distortion of the reacting components, leading to the lowest barrier for the SRS. Estimated distortion of the tethers varies in the range –4.5 to 1.6 kcal/mol, and is greatest for the protonated Os(VIII) system. Overall, these findings give fascinating insight into factors contributing to SRS activation energies.

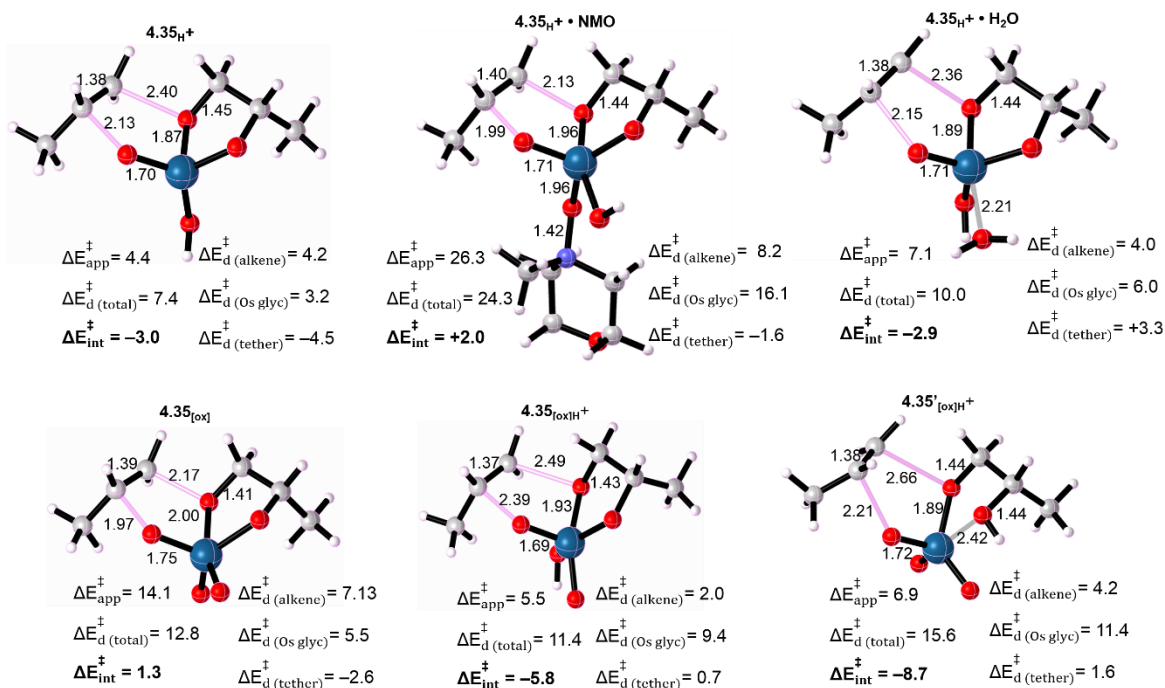


Figure 4.13: Distortion/interaction analysis for Os(VI) TS's **4.23_H⁺**, **4.23_H⁺ • NMO**, and **4.23_H⁺ • H₂O** and Os(VIII) TS's **4.23_[ox]**, **4.23_{[ox]H}⁺** and **4.23'_{[ox]H}⁺** during the SRS, showing interacting reactive components **4.35**. Energies are in kcal/mol.

4.6 Molecular dynamics simulation of the SRS.

Significant differences are seen (**Figure 4.14**) in the progression of the two C—O bond formations in the calculated TS structures **4.23**, with a greater development of C—O[Os] bond relative to the C—O[THF] bond, which is most pronounced in protonated TS's **4.23_H⁺** and **4.23'_{[ox]H}⁺**. To gain insight into the timings of bond formation and the changes in geometry for each of the four TS's **4.23** and their progression, molecular dynamics (MD) simulations were performed, propagating TS geometries **4.23** towards products **4.24** or backwards to intermediates **4.22**. **Figure 4.14** shows snapshots for propagation of transition states for the different pathways at the time of formation of the first C—O bond (C—O[Os]), with development of the C—O[THF] bond lagging behind to varying extents. Direct dynamic simulations show the highest degree of asynchronicity (timing gap between C—O bond formations) of 12 fs (average of 39 reactive trajectories) and 15.5 fs for the protonated Os(VI) and alkoxy protonated Os(VIII) pathways respectively (**Figure 4.14**). The hydrated protonated Os(VI) pathway shows an asynchronicity of 10.0 fs. The non-protonated Os(VIII) and NMO-complexed protonated Os(VI) pathways show shorter timing gap of 2.25 fs and 3.50 fs (average of 47 reactive trajectories). However, the oxo protonated Os(VIII) pathway shows the shortest timing gap of 0.50 fs.

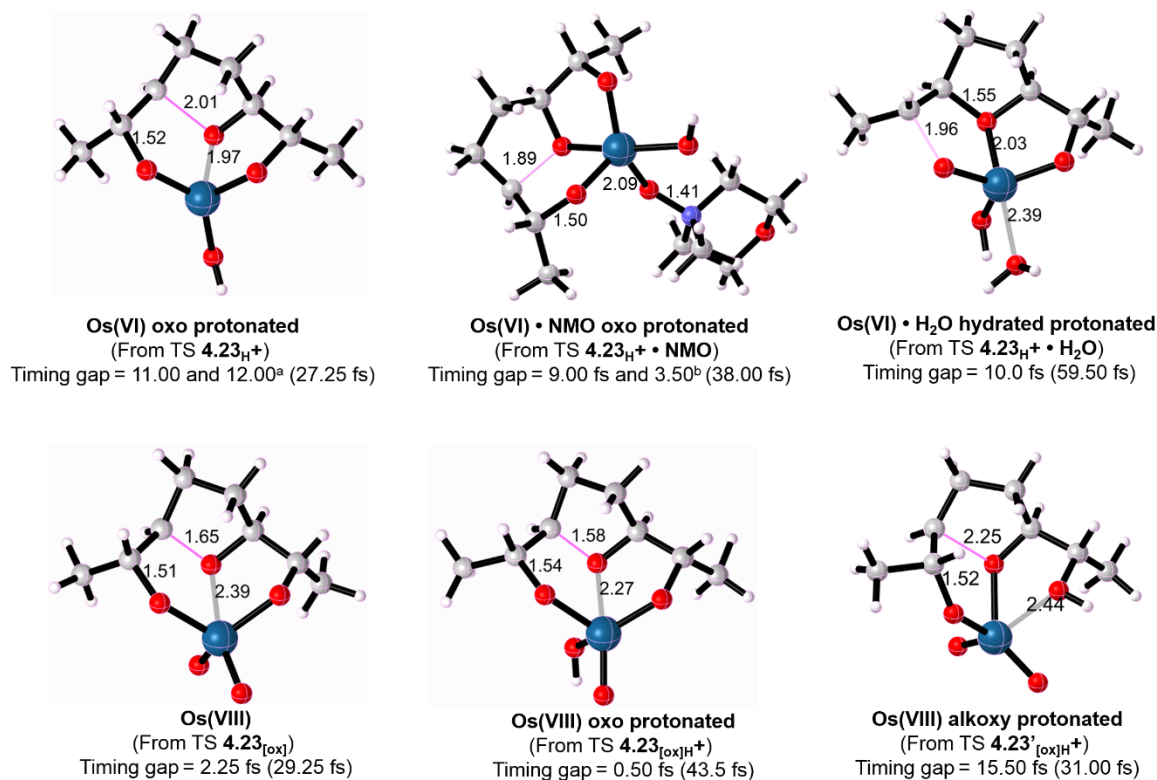


Figure 4.14: Snapshots for the forward propagation of TS's **4.23** at the time of first C—O bond formation. TS corresponds to time = 0. Timing gap represents time between the first and second C—O bond formations. ^a Average timing gap from 39 random reactive trajectories of TS **4.23_H⁺**; where the median time of C—O[Os] = 45.25 fs and C—O[THF] = 57.25 fs. ^b Average timing gap from 47 random reactive trajectories of TS **4.23_H⁺ • NMO**; where the median time of C—O[Os] = 35.00 fs and C—O[THF] = 38.50 fs.

To gain more details about TS's **4.23_H⁺** and **4.23_H⁺ • NMO**, 50 randomly chosen trajectories were initiated in acetone/SMD from TS structures (**Figure 4.14**). In the case of TS **4.23_H⁺**, 11 (22%) trajectories returned to reactant Os(VI) **4.23_H⁺** while 39 (78%) trajectories proceed into product Os(IV) THF-diolate. Out of the 39 reactive trajectories 5 of them (12%) show a fully concerted (3+2) cycloaddition for TS **4.23_H⁺** and the rest shows asynchronous (3+2) cycloaddition with formation of C—O[Os] as a first step and C—O[THF] as a second step. Fully concerted cycloaddition means that there is zero timing gap between C—O[Os] and C—O[THF] bonds formation. In the case of TS **4.23_H⁺ • NMO**, 47 (94%) of 50 trajectories gave Os(IV) THF diolate and only 3 (6%) trajectories returned into intermediate **4.23_H⁺ • NMO**, in which 7 reactive trajectories (14.9%) proceeds in a concerted fashion. In addition, only 4 trajectories show the opposite sequencing of bond formation TS **4.23_H⁺ • NMO**.

Focussing on the protonated Os(VI) pathway (**Figure 4.15**), and for a typical trajectory, forwards propagation of the transition state geometry (t = 0 fs) realizes formation of the C—O[Os] bond (C—O = 1.51 Å) at 27 fs, while the C—O[THF] bond (2.01 Å) is still in transition, requiring a further 11 fs

to form. Atomic polar tensor charges shown on the reacting oxygen atoms at the TS ($t = 0$ fs) allow visualisation of electron-deficient and electron-rich sites for the Os species, while both reacting olefinic carbons are electron-rich. When the first C—O bond, involving the electron-deficient Os—O oxygen, progresses to formation at $t = 27$ fs, the nascent C—O[THF] bond is still in transition. As the first C—O bond approaches formation, the carbon of the incipient THF ring becomes more electron poor leading to union with the electron-rich Os—O oxygen to realise the second C—O bond formation at $t = 38$ fs.

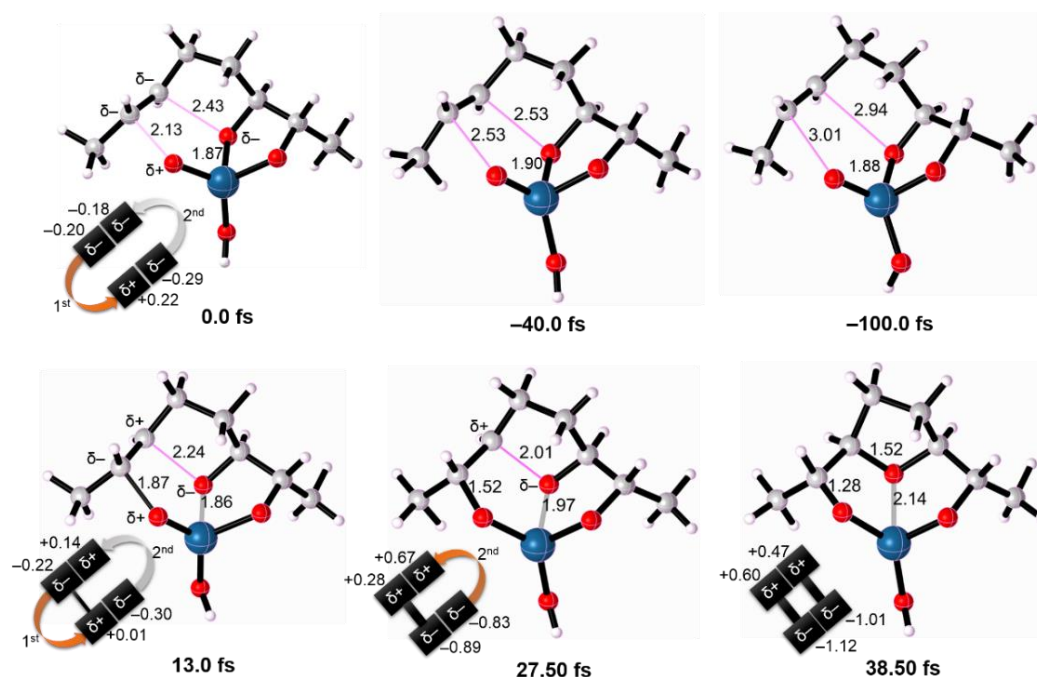
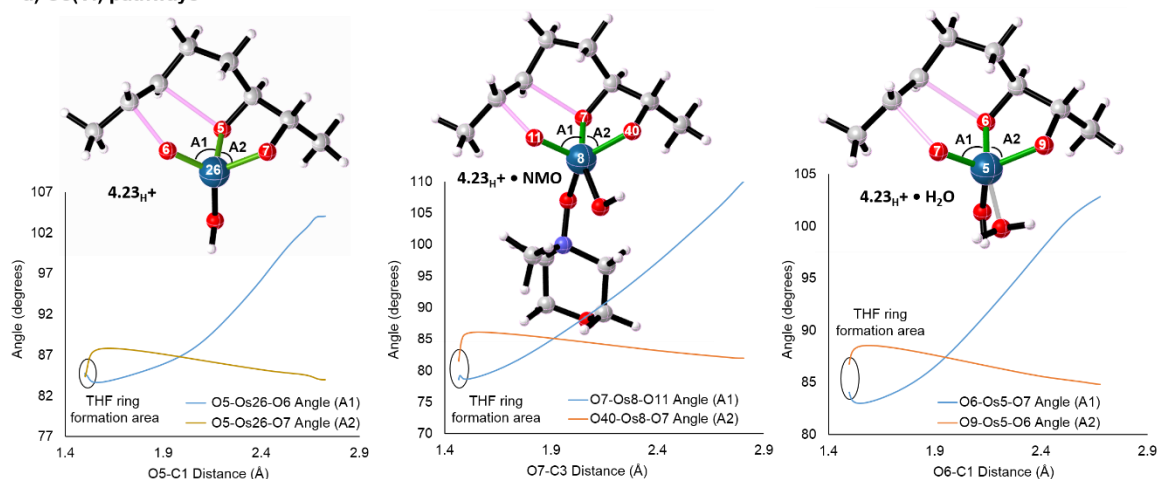


Figure 4.15: Snapshots from a typical SRS trajectory for the protonated Os(VI) pathway leading to THF formation. APT charges are shown on the reacting carbon and oxygen atoms in e units. Trajectories initiated in the region of the potential energy surface near TS (time = 0 fs) showing reactive bonds.

MD and PES simulations also facilitate visualisation of geometrical changes occurring around the osmium centre during the SRS for the protonated and oxidised pathways, where more substantial reorganisation is evident for the Os(VIII) species (**Figure 4.16**). Plotting the the O—Os—O bond angles (A1 and A2) against length of the forming C—O[THF] bond provides a convenient visualisation of geometrical changes, showing that bond angle A2 remains approximately the same in the protonated pathway during THF ring formation (**4.22_{H+}** → **4.24_{H+}**, **Figure 4.15-a**), while the angle A1 decreases from 104° (**4.22_{H+}**) to 85° (**4.24_{H+}**). Also, pathways **4.22_{H+}** • **NMO** → **4.24_{H+}** • **NMO** and **4.22_{H+}** • **H₂O** → **4.24_{H+}** • **H₂O** showed similar angle changes to the non-ligated protonated Os(VI) pathway.

a) Os(VI) pathways



b) Os(VIII) pathways

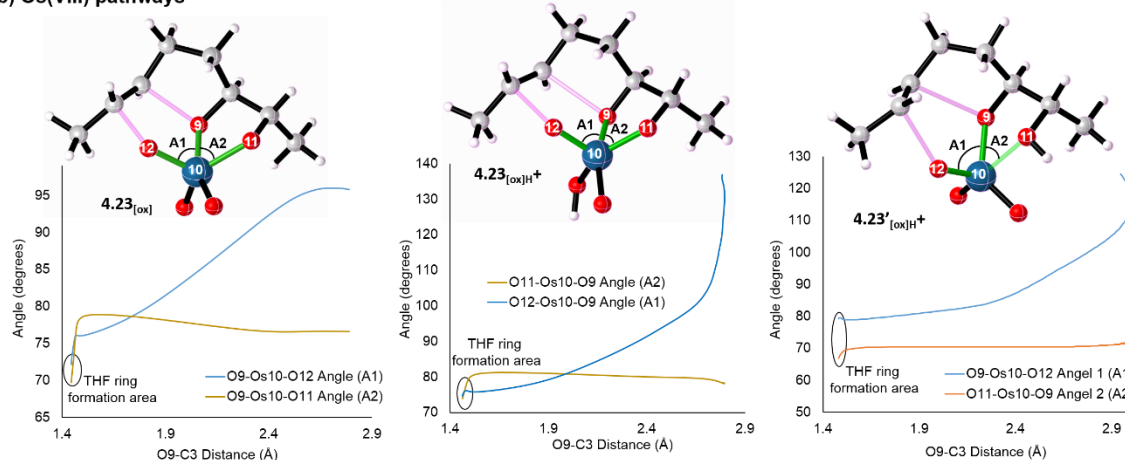


Figure 4.16: Graphical representation of geometrical changes around Os for the SRS showing plots of bond angles against C—O(THF) bond length during the THF ring formation. (a) Os(VI) pathways: protonated Os(VI) TS **4.23_H⁺**, **4.23_H⁺ • NMO**, and **4.23_H⁺ • H₂O**. (b) Os(VIII) pathways: Oxidised TS **4.23_[ox]**, and protonated oxidised TS's **4.23_{[ox]H}⁺** and **4.23'_{[ox]H}⁺**.

Backwards propagation of the protonated Os(VIII) trioxoglycolate TS's (square pyramidal) **4.23_[ox]**, **4.23_{[ox]H}⁺**, and **4.23'_{[ox]H}⁺** reveals significant changes in O—Os—O bond angles in the reacting moiety in comparison to the tetrahedral protonated Os(VI) pathway. The oxidised intermediate **4.22_[ox]** shows marginally increased geometrical changes, where A2 decreases from 77° in **4.22_[ox]** to 69° in **4.24_[ox]**, and A1 shows a reduction of 24° from 96° (**4.22_[ox]**) to 72° in **4.24_[ox]** (**Figure 4.16-b**). The bond angle change for A1 is far more striking for protonated Os(VIII) pathway where it is reduced from 140° in **4.22_{[ox]H}⁺** to 75° in **4.22_{[ox]H}⁺**, with the major deformation of the Os(VIII) trioxoglycolate occurring prior to the TS. It is proposed that additional geometrical reorganisation is required for the protonated Os(VIII) intermediate to achieve suitable orbital overlap, counteracting the energetic benefits of the lower HOMO-LUMO energy gap. It is believed that this is a significant contributor to the higher free energy of activation. The geometrical changes for the

alcoholate protonated Os(VIII) pathway are similar to those for the oxo protonated Os(VIII) pathway, in which the angel A1 reduces from 124° (**4.22'**_{[ox]H⁺}) into 79° in **4.24'**_{[ox]H⁺}. However, the THF ring formation through TS **4.23'**_{[ox]H⁺} requires more activation energy because of the disfavoured interaction energy.

4.7 Conformational analysis of Os glycolate intermediate

Conformational analysis of Os(VI) dioxoglycolate intermediate, focusing on “extended” and folded “wing” conformations, was performed using the (SMD)-M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of theory (Figure 3.17). Unsurprisingly, for diene **3.1** and the FRS TS **4.21** extended conformations are preferred over wing conformations. For example, the extended TS **4.21'** is favoured over wing conformations **4.21** and **4.21''** by 3.9 and 0.5 kcal/mol respectively.

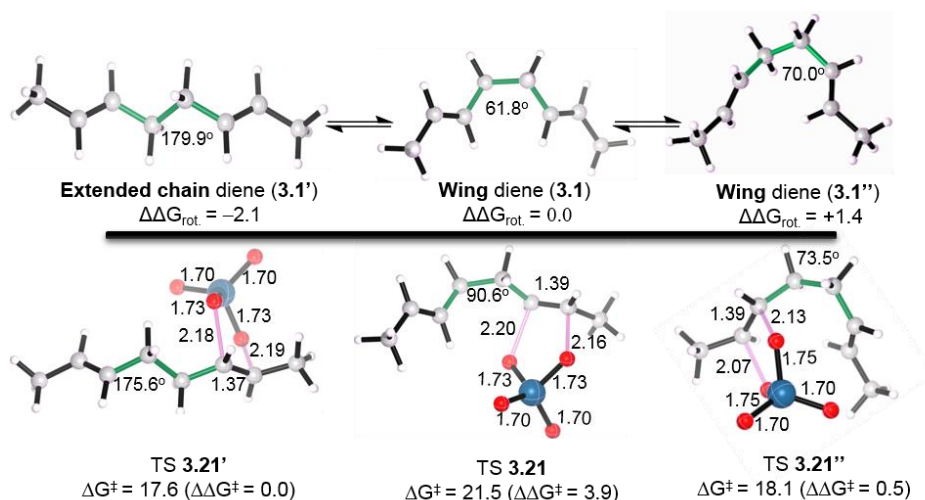
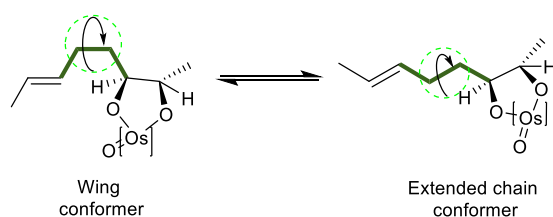


Figure 4.17: Conformational analysis for the initial (3+2) cycloaddition (FRS) TS between OsO₄ and the 1,5-diene. Dihedral angles (in degrees) are highlighted in green. (Energies are in kcal/mol).

More interesting conformational behaviour is noted for the Os(VI) and Os(VIII) glycolate intermediates **4.22** and **4.22**_[ox] (Table 4.4 and Figure 4.18). The neutral intermediates **4.22**, **4.22**_{H₂O} and **4.23**_[ox] show the anticipated preference for extended conformations in the gas phase, whereas folded conformations of protonated Os glycolates **4.22**_{H⁺}, **4.22**_{[ox]H⁺} and **4.23'**_{[ox]H⁺} are favoured. This may be attributed to a stabilising interaction between pendant alkene and positively charged Os glycolate in the absence of solvent. Application of the SMD solvent model (acetone) reduces the energy differences for the protonated conformers, with extended and wing conformations of the Os(VI) glycolate **4.22**_{H⁺} of approximately equal energy. Even under the solvent model, the wing conformation of the protonated Os(VIII) intermediate remains preferred. Water or NMO liganded protonated Os(VI) glycolate, **4.22**_{H⁺} • H₂O and **4.22**_{H⁺} • NMO, prefers

wing conformation under gas and solvent phase calculations. By contrast, hydrated Os(VI) glycolate **4.22**_{H₂O} and reoxidised Os(VIII) glycolates possessing increased steric bulk around the Os center show significant preferences for the extended conformations. These results indicate that the reactive conformations required for cyclisation in the SRS are accessible for all investigated intermediates, with the protonated intermediates apparently showing modest predisposition towards reactive conformations.

Table 4.4: Conformational analysis of Os glycolate intermediates **4.22** showing relative energies of rotation between wing and extended chain conformers in gas phase and in acetone. (Energies are in kcal/mol).



Intermediate	dihedral change	gas phase		solvent model (acetone)	
		ΔG_{rot}	K_{eq}	ΔG_{rot}	K_{eq}
4.22	67.7°→178.3°	−2.3	4.7x10 ¹	−1.0	5.4x10 ⁰
4.22 _{H₂O}	65.7°→178.5°	−1.3	8.9x10 ⁰	−3.2	2.2x10 ²
4.22 _[ox]	69.8°→179.3°	−1.1	6.3x10 ⁰	−2.2	4.1x10 ¹
4.22 _{[ox]H⁺}	69.2°→179.6°	+6.6	6.9x10 ^{−4}	+0.8	2.6x10 ^{−1}
4.22' _{[ox]H⁺}	72.1°→177.0°	+3.2	4.5x10 ^{−3}	+3.3	3.8x10 ^{−3}
4.22 _{H⁺}	63.8°→177.4°	+5.3	1.3x10 ^{−4}	−0.2	1.4x10 ⁰
4.22 _{H⁺} • H ₂ O	62.0°→179.6°	+2.5	1.5x10 ^{−2}	+0.6	3.6x10 ^{−1}
4.22 _{H⁺} • NMO	63.2°→179.9°	+1.4	9.4x10 ^{−2}	+0.4	5.0x10 ^{−1}

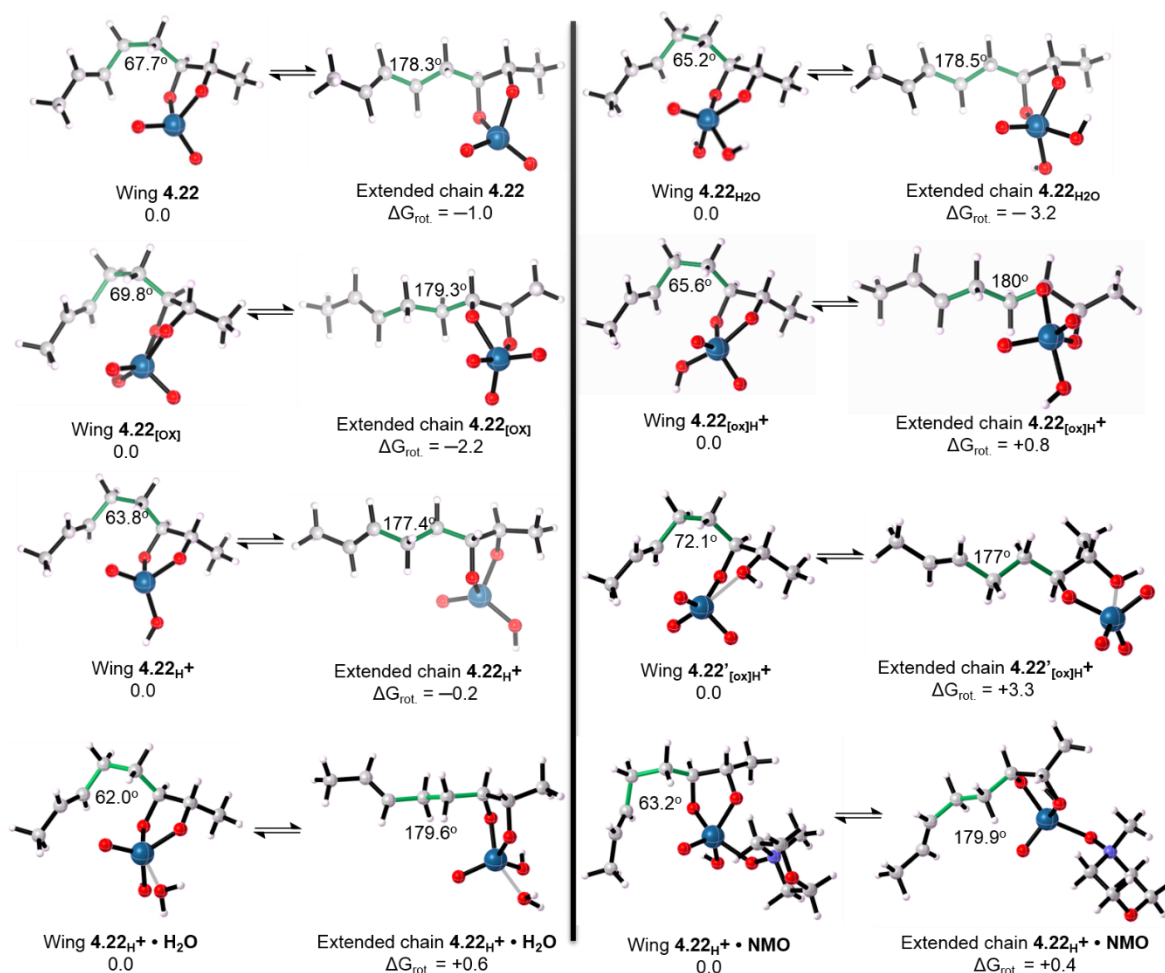


Figure 4.18: Optimised geometries of Os glycolate intermediates **4.22**, showing wing and extended conformers. Dihedral angles highlighted in green. (Energies are in kcal/mol).

4.8 Effect of high spin multiplicity on the SRS

Known Os(VI) oxo species, including Os(VI) glycolates,¹³⁸ have low spin configurations. Nevertheless, we decided to calculate high and low spin pathways for the FRS. Since there are two non-bonded electrons in Os(VI) glycolate (Os- d^2), singlet ($S = 0$) and triplet ($S = 2$) configurations are possible whereas Os(IV) diolate has four non-bonded electrons (Os- d^4); leading to the possibility of singlet, triplet, and quintet ($S = 2$) states. Here, high spin pathways were calculated only in the absence of additives for Os(VI), hydrated Os(VI), and non-ligated protonated intermediates and TS's.

4.8.1 Calculated energies for high spin multiplicity pathways for the SRS in the absence of additives or reoxidation (Os(VI)→Os(VIII))

Our calculated results are consistent with experimental observations, showing that high spin pathways are disfavored in comparison to singlet pathways. **Figure 4.19** shows optimised

geometries for the triplet and quintet transition states **4.23t** and **4.23q** and THF-diolate intermediates **4.24t** and **4.24q**, which are comparatively higher in energy than the corresponding low spin configurations. Os(IV) species **4.24** show small differences in energy between low and high spin configurations in our calculations. However, isolated Os(IV) oxo derivatives are less common, and known Os(IV) species (e.g. $[\text{Os}_2\text{OCl}_{10}]^{4-}$) favours octahedral coordination geometries and low spin configurations.³⁰⁸ Therefore, intermediates **4.24** are not representative of isolated Os(IV) compounds, and are likely to undergo rapid reoxidation by NMO (see below) or acquire ligands from solution.

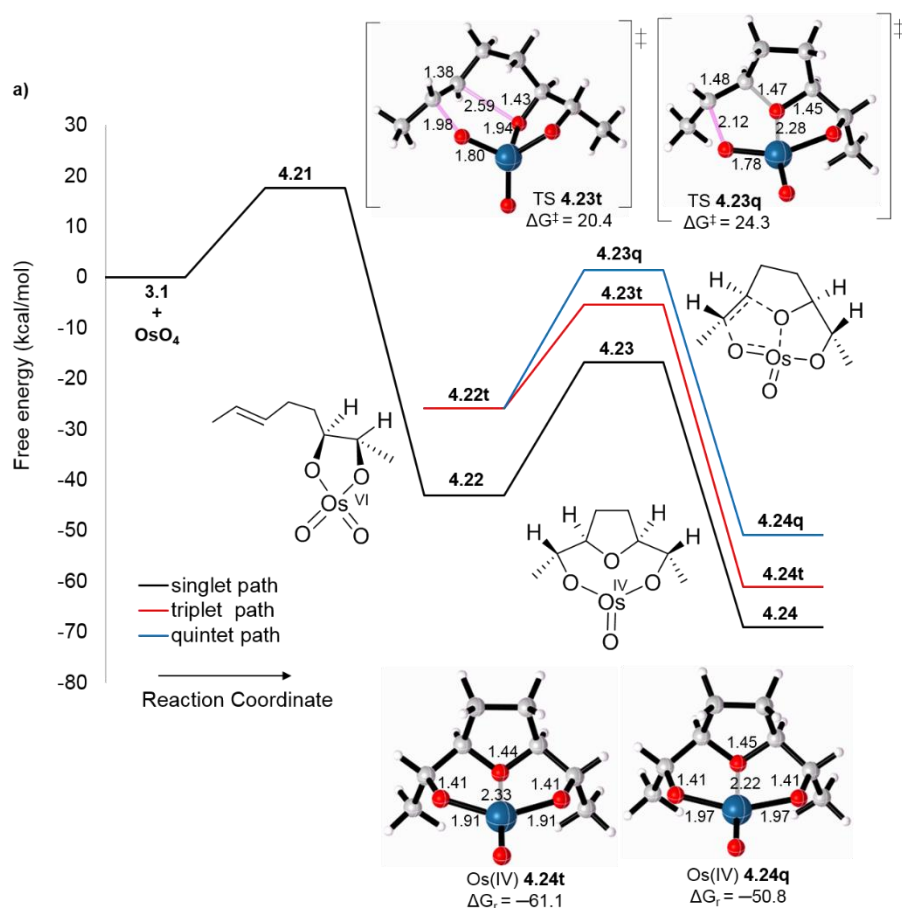


Figure 4.19: Oxidative cyclisation of 1,5-diene **3.1** by OsO_4 without additives, showing different spin configurations for Os(VI) and Os(IV). Here, t and q refer to triplet and quintet.

4.8.3 Calculated energies for different spin pathways for the SRS from hydrated Os(VI) glycolate **4.22_{H2O}**

Different spin pathways for the SRS have been calculated for the hydrated Os(VI) glycolate (**Figure 4.20**). **Figure 4.20** shows the low spin pathway is favoured over triplet and quintet pathways for hydrated Os(VI) glycolate **4.22_{H2O}**.

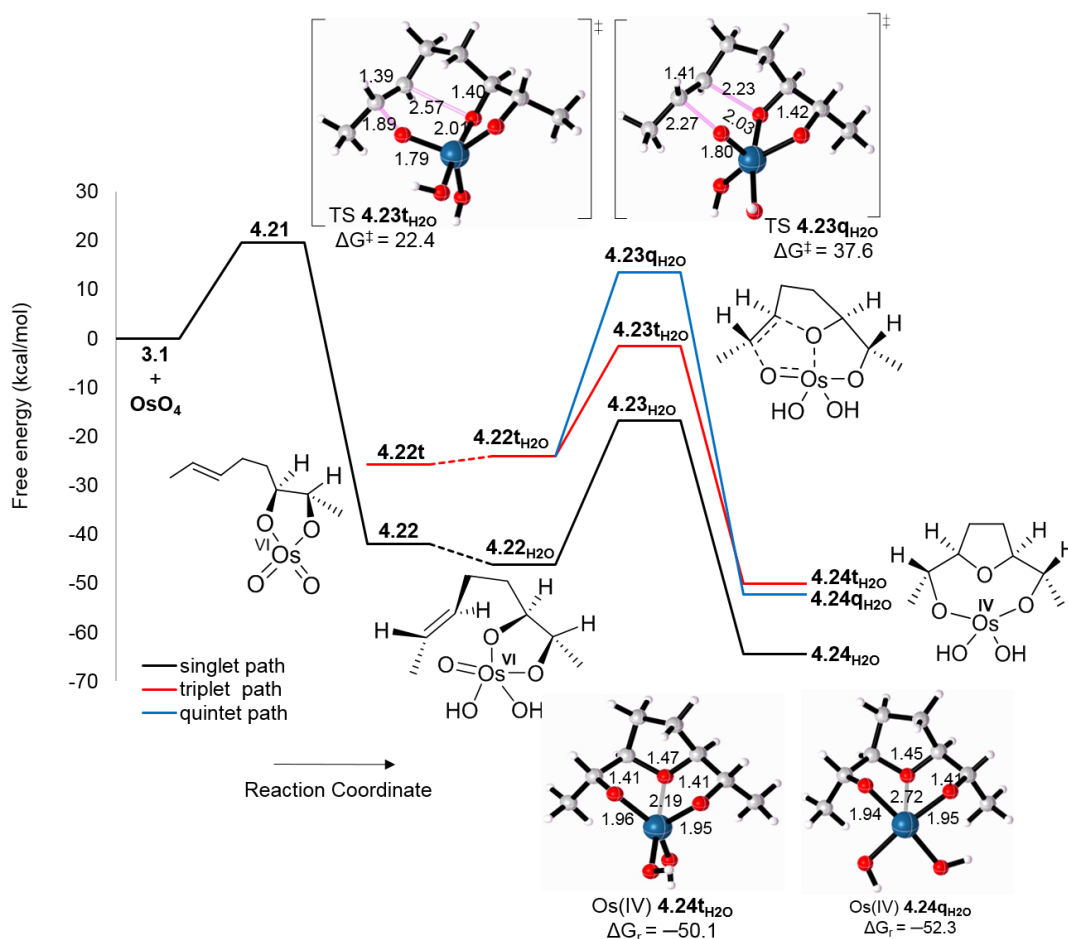


Figure 4.20: Oxidative cyclisation of 1,5-diene **3.1** by OsO₄, showing hydration of the first intermediate **4.22** with different spin configurations for Os(VI) and Os(IV).

4.8.4 Calculated energies for different spin pathways for the SRS from protonated Os(VI) glycolate 15_H⁺

Figure 4.21 shows the effect of protonation on the SRS with a notably decreased barrier to cyclisation. The Singlet MEP is favoured kinetically, presenting the lowest barrier to cyclisation, while the quintet TS **4.23q_H⁺** is highest in energy by around 18 kcal/mol. High spin Os(IV) THF-diolate intermediates **4.24t_H⁺** and **4.24q_H⁺** are calculated to be similar in energy to **4.24_H⁺**. As discussed above, such Os(IV) species are likely undergo rapid and energetically favourable reoxidation to Os(VI).

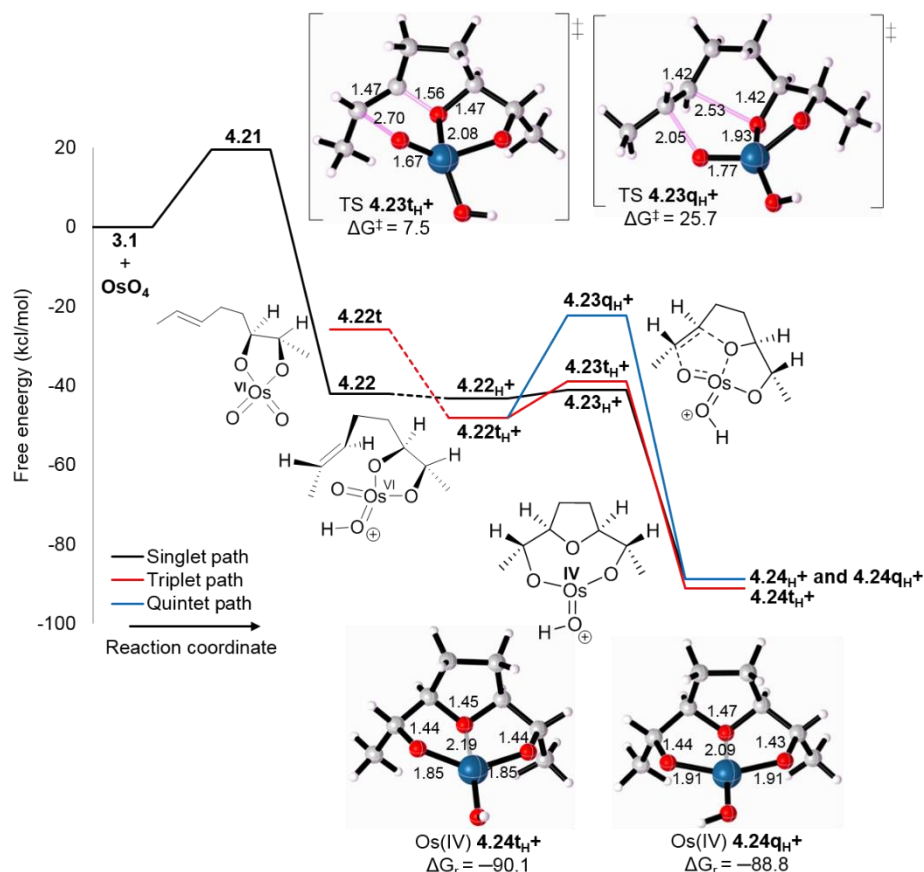


Figure 4.21: Oxidative cyclisation of 1,5-diene **3.1** by OsO_4 , showing protonation of the first intermediate **4.22** with high and low spin Os(VI) and Os(IV).

In summary, DFT calculations indicate that high spin pathways are less favourable compared to low spin pathways. This is consistent with reported Os(VI) and Os(VIII) compounds, which are known to have low spin configurations.

4.9 Reoxidation of Os(IV) monooxodiolate **4.24** to Os(VIII) trioxodiolate **4.24**_{[ox][ox]} in the presence and absence of acid

Since our simulation showed that reaction of NMO with **4.22**_H⁺ to form **4.22**_H⁺ • NMO is found to be highly favourable, the oxidative cyclisation, in the presence of amine-N-oxide under acidic conditions, is more likely to proceed via intermediate **4.22**_H⁺ • NMO. Thus, to more fully understand the overall reaction pathway, the fate of the initial product of the SRS, Os(IV) diolate **4.24**_H⁺ • NMO, needs consideration along with regeneration of an Os(VIII) species capable of turning over diene **3.1** in a catalytic process (**Figure 4.22**). Perhaps the simplest possibility is to consider oxidation of Os(IV) diolate **4.24**_H⁺ • NMO followed by hydrolysis to release THF-diol **3.1** and Os at a higher oxidation level. Alternatively, a higher oxidation state of Os THF-diolate may enter a “second cycle”

and osmylate another substrate molecule **3.1** to release THF-diol **3.2** and regenerate **4.22_{H+} • NMO**. Both of these possible cycles are evaluated below.

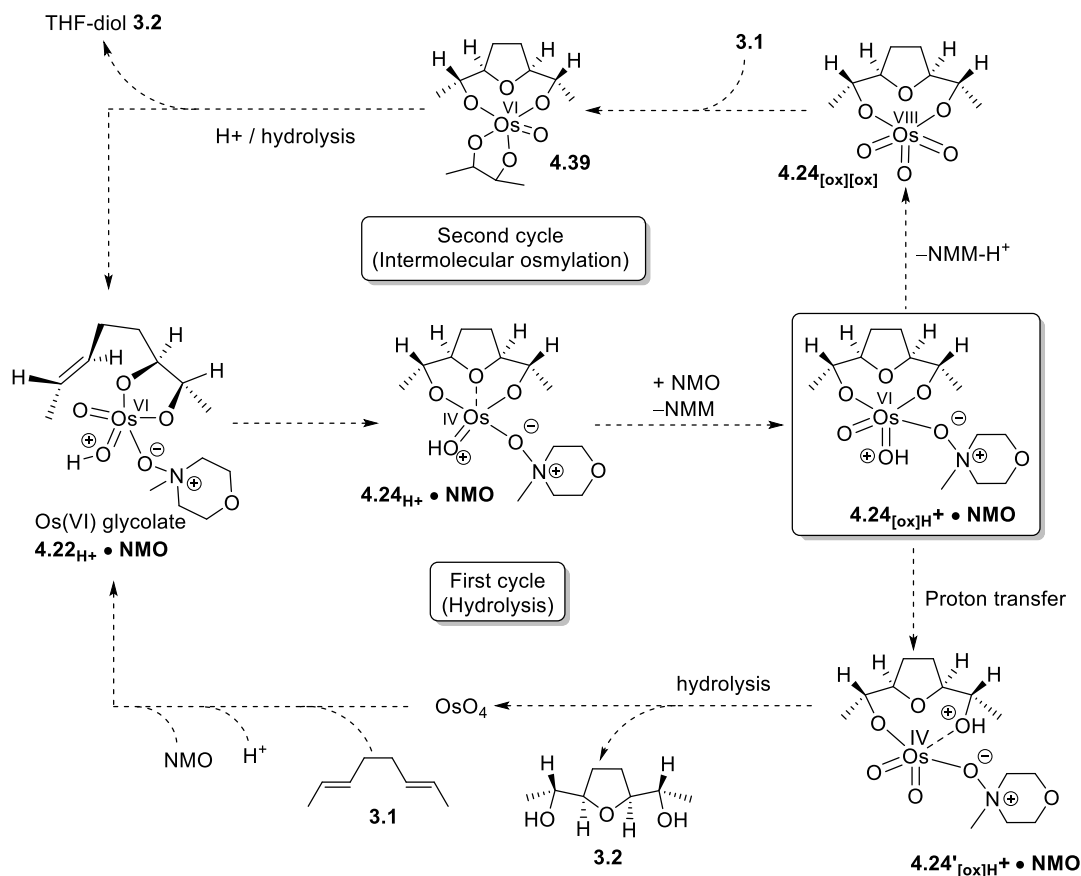


Figure 4.22: Overview of possible catalytic cycles for oxidative cyclization of 1,5-diene **3.1** under acidic conditions.

Protonated Os(IV) THF-diolate NMO complex **4.24_{H+} • NMO** is thermodynamically more stable than the protonated Os(IV) **4.24_{H+}** species by $\Delta G = -28.7$ kcal/mol (**Figure 4.23**). The intermediate **4.24_{H+} • NMO** is able to coordinate another NMO ligand to give an octahedral Os(IV) THF-diolate **4.24_{H+} • 2 NMO** ($\Delta G = -19.6$ kcal/mol), which undergoes oxo-transfer to afford octahedral Os(VI) species **4.24_{[ox]H+} • NMO** and release of NMM (**Figure 4.23**). DFT calculations show that oxidation of protonated Os(VI) THF-diolate **4.24_{[ox]H+} • NMO** to protonated Os(VIII) THF-diolate **4.24_{[ox][ox]H+}** is highly endergonic ($\Delta G = 44.5$ kcal/mol), so other possible pathways need to be considered. Calculations indicate two scenarios for intermediate **4.24_{[ox]H+} • NMO**; either hydrolysis to release THF-diol, OsO_4 and NMM (indicated as first cycle), or participation in a second cycle after reoxidation to Os(VIII) THF-diolate **4.24_{[ox][ox]}**. The key difference between entering both cycles is the proton transfer. On one hand, the first cycle is facilitated by intramolecular proton transfer from oxo (**4.24_{[ox]H+} • NMO**) to glycolate (**4.24'_{[ox]H+} • NMO**) ligand with an activation energy of 13.6 kcal/mol as a moderately endergonic step ($\Delta G = 8.7$ kcal/mol). On the other hand, the second cycle is encouraged by proton transfer and breaking of N—O bond in **4.24_{[ox]H+} • NMO** to give Os(VIII)

THF-diolate **4.24**_{[ox][ox]} and release NMM-H⁺ with higher barrier of 25.7 kcal/mol and less thermodynamically favourable step ($\Delta G = 10.9$ kcal/mol). The activation energies of proton transfer were obtained using Marcus theory, where intrinsic barrier (19.9 kcal/mol) is the energy difference between **4.24**_{[ox][ox]} • NMM-H⁺ (structure shown in box in **Figure 4.23**) and **4.24**_{[ox]H}⁺ • NMO.

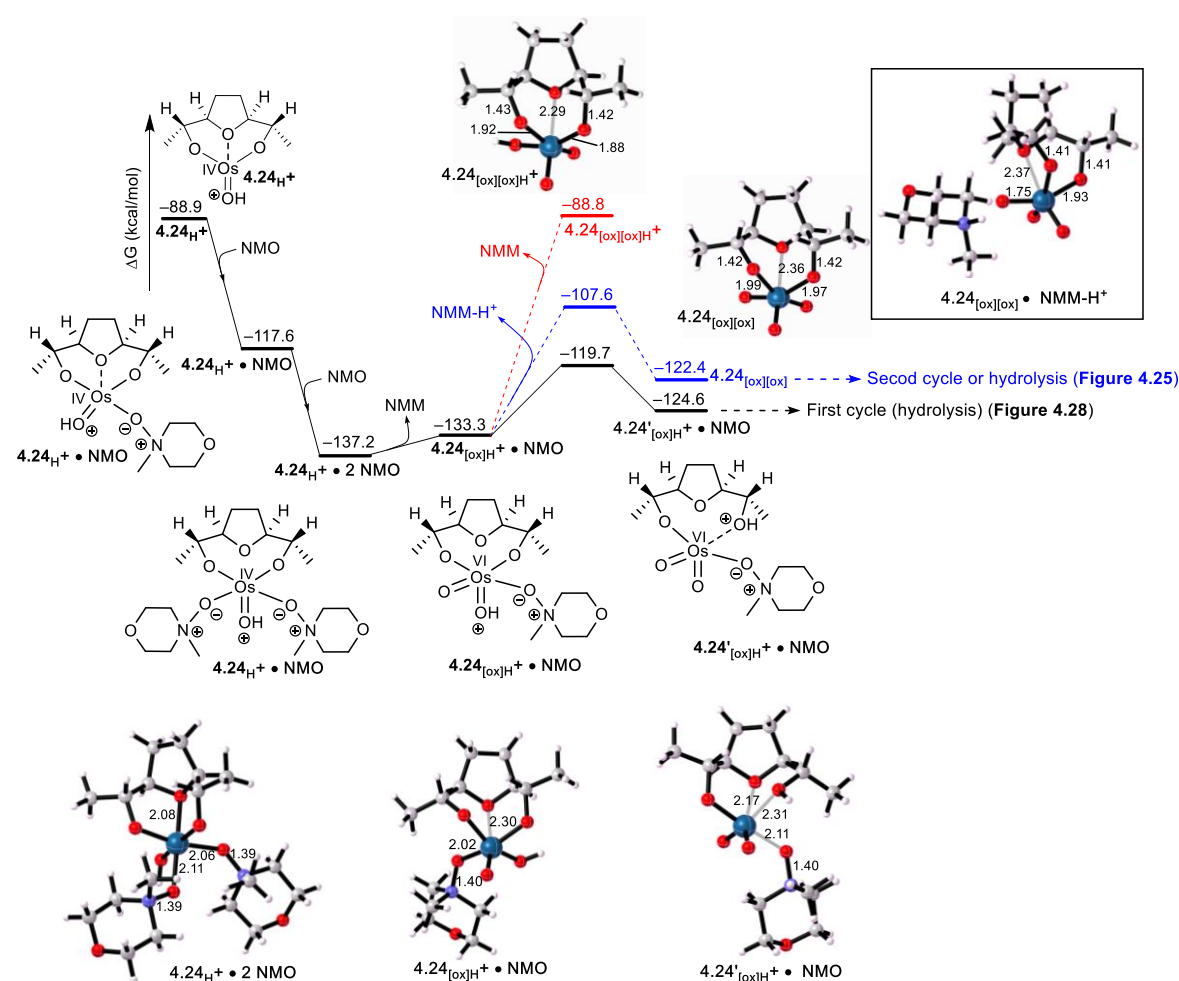


Figure 4.23: Computational evaluation of the oxidation of Os(IV) THF-diolate to liganded Os(VIII) THF-diolate in the presence of acid.

Interestingly, in the absence of acid (**Figure 4.24**), the corresponding oxidation of **4.24** to **4.24**_[ox] is an energetically favourable process ($\Delta G = -12.3$ kcal/mol) because an unstable complex **4.24** • NMO is formed before N—O bond dissociation to release Os(VI) THF-diolate **4.24**_[ox]. However, the oxidation of latter to Os(VIII) THF-diolate **4.24**_{[ox][ox]} is endergonic ($\Delta G = 12.3$ kcal/mol) due to a more favourable complex formation with NMO to give **4.24**_[ox] • NMO ($\Delta G = -8.3$ kcal/mol) leading to an endergonic process ($\Delta G = 4.1$ kcal/mol) for oxidation from Os(VI)→Os(VIII).

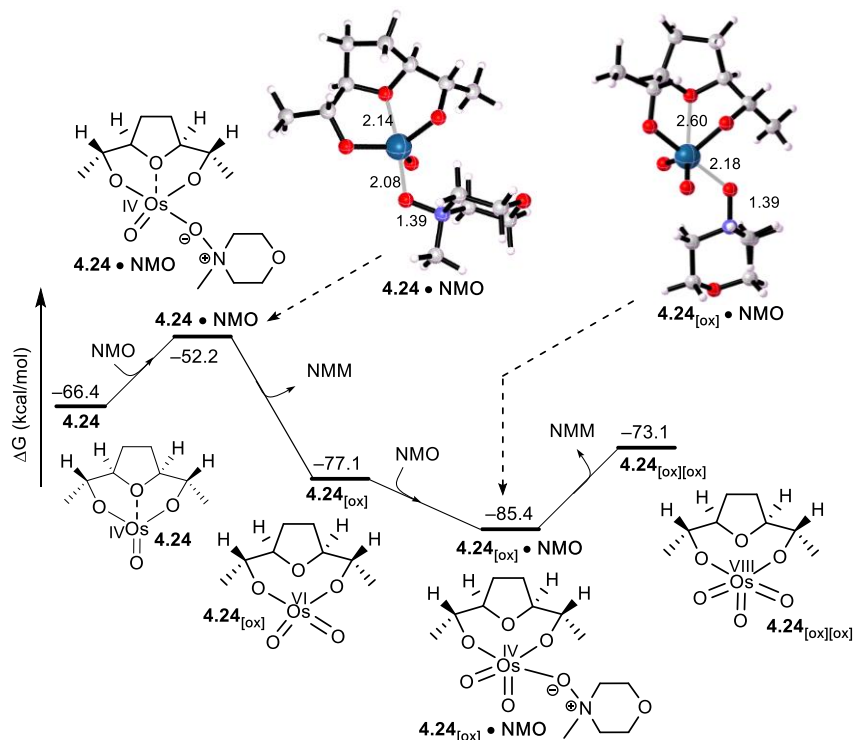


Figure 4.24: Computational evaluation of the oxidation of Os(IV) THF-diolate to Os(VIII) THF-diolate in the absence of acid.

In summary, in the presence of acid, reoxidation of protonated NMO-adduct Os(IV) THF-diolate **4.24_H⁺ • NMO** to its Os(VI) THF-diolate **4.24_{[ox]H⁺} • NMO** is favoured over reoxidation into Os(VIII) THF-diolate **4.24_{[ox][ox]}**. However, in the absence of acid, reoxidation of Os(IV) THF-diolate to Os(VIII) THF-diolate seems accessible. If Os(VIII) THF-diolate forms, a competition between hydrolysis (first cycle) and entering second cycle is possible (see next section).

4.9.1 Competition between hydrolysis of Os(VIII) trioxodiolate **4.24_{[ox][ox]}** and second cycle pathway

Bifurcation of Os(VIII) THF-diolate **4.24_{[ox][ox]}** into the first cycle (hydrolysis) and second cycle has been calculated (**Figure 4.25**). The capacity of **4.24_{[ox][ox]}** to osmylate another molecule of diene **3.1** in a second cycle was evaluated using *E*-but-2-ene. Indeed, osmylation can proceed to afford tetraester **4.39** with a modest barrier of 11.8 kcal/mol, as a thermodynamically (−63.2 kcal/mol) favoured pathway. However, access to this second cycle requires an unfavourable dissociation of **4.24_{[ox]H⁺} • NMO** to release **4.24_{[ox][ox]}** (see **Figure 4.23**). Also, when strong acid is present, protonation of **4.24_{[ox][ox]}** into **4.24'_{[ox][ox]H⁺}** is favoured over intermolecular osmylation (**Figure 4.25**). This means that, any formation for **4.24_{[ox][ox]}** will again enter the first cycle through protonation of its glycolate to give **4.24'_{[ox][ox]H⁺}**. At this point, and under strongly acidic conditions the formation of **4.24_{[ox][ox]}** is likely to be a minor pathway, and therefore first cycle is favoured over second cycle

as shown in **Figure 4.25**. However, in the absence of acid, entering the second cycle is favoured (blue pathway, **Figure 4.25**). This means that acid retards the second cycle and accelerates first cycle by catalysing hydrolysis of the osmate ester. Simulation also shows that reoxidation of Os(VI) tetraester **4.39** to Os(VIII) tetraester **4.40** is highly disfavoured ($\Delta G_{\text{ox}} = 48.0$ kcal/mol) (**Figure 4.25**), and so hydrolysis of **4.39** is investigated (see below).

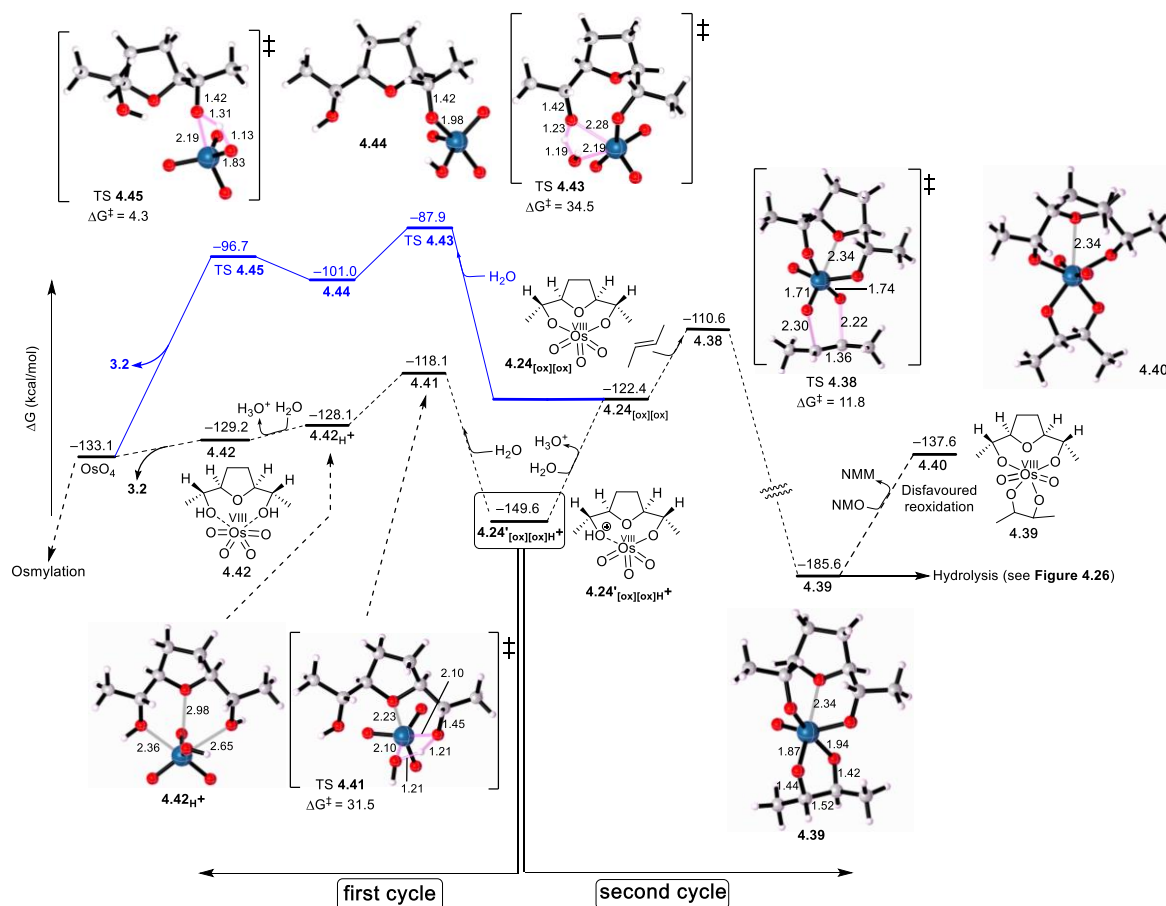


Figure 4.25: Computational evaluation of reaction manifolds from protonated Os(VIII) THF-diolate **4.24'**_{[ox][ox]H⁺}, corresponding to hydrolysis (first cycle) or osmylation and hydrolytic release of the THF diol (second cycle) in the presence of acid (black pathway) and absence of acid (blue pathway). To reduce the complexity of the calculation 1,5-diene **3.1** is replaced with *E*-but-2-ene in the second cycle.

Figure 4.26 shows the calculated pathway for the acid-catalysed hydrolysis of the second cycle product **4.39** from Os(VIII) trioxoglycolate **4.34'**_{[ox][ox]}. Hydrolysis of the Os(VI) tetraester **4.39** is catalysed by acid, liberating either the THF-diol (**4.39**→**3.2**+**4.2**_{H⁺} • NMO, **Figure 4.26–a**) or glycol (**4.39**→**4.58**+**4.24'**_{[ox]H⁺} • NMO, **Figure 4.26–b**). Release of the THF-diol product **3.1** is comparatively favoured by 13.0 kcal/mol, thus offering a viable pathway to regenerate an Os(VI) dioxoglycolate intermediate **4.2**_{H⁺} • NMO (model for **4.24**_{H⁺} • NMO) capable of propagating a catalytic cycle. Overall, formation of THF-diol from alkoxy protonated tetraester **4.46** is exergonic whereas release of glycol is thermoneutral from **4.52**.

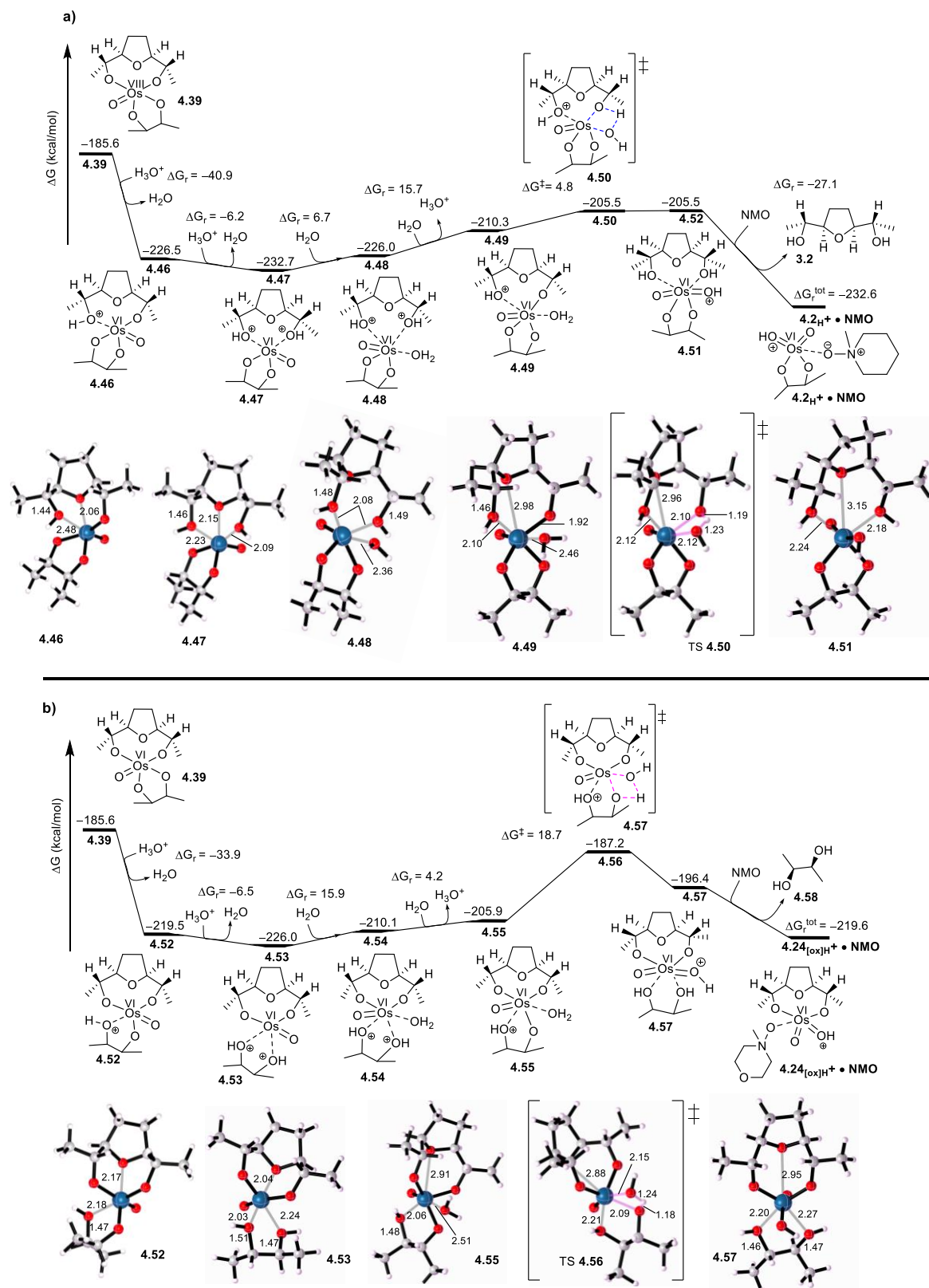


Figure 4.26: Calculated hydrolysis pathways leading to (a) THF-diol **3.1** release or (b) vicinal-diol **4.58** release from second cycle adduct **4.39** under acid catalysis.

Figure 4.27 shows an energetic comparison between the release of THF-diol **3.1** and vicinal diol **4.58** from the second cycle adduct **4.39** in the absence of acid. Again, release of the THF-diol is the

more favourable pathway kinetically and thermodynamically, although it is significantly higher in energy than the acid catalysed one.

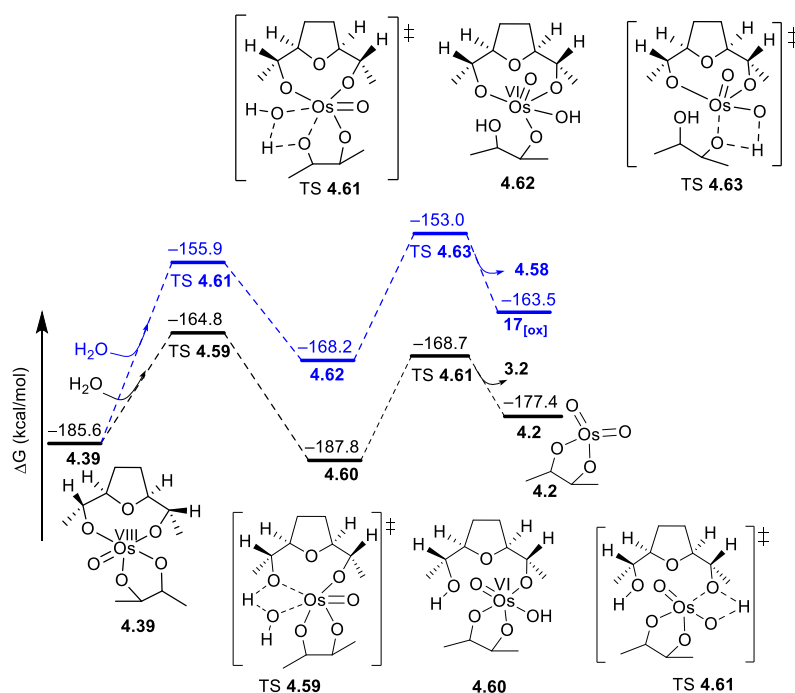


Figure 4.27: Hydrolysis of Os(VI) intermediate **4.39** in the absence of acid to release either THF-diol **3.2** and Os(VI) diolate **4.2** (black pathway) or release glycol **4.58** and Os(VI) THF diolate **4.24_[ox]** (blue pathway).

4.10 Completing the catalytic cycle

Figure 4.28 shows a bifurcation for Os(VI) THF-diolate **4.24_{[ox]H⁺}** • **NMO** corresponding to hydrolytic release (first cycle) of the THF diol via either Os(VI) or Os(VIII) pathways. Now, release of OsO₄ and THF-diol **3.1** from **4.24_{[ox]H⁺}** • **NMO** is an exergonic process ($\Delta G = -30.2$ kcal/mol) with a barrier of 21.6 kcal/mol for the addition of water (**Figure 4.28**, Os(VI) hydrolysis). However, if **4.24_{[ox]H⁺}** • **NMO** reoxidises into Os(VIII) trioxodiolate **4.24_{[ox][ox]}**, protonation of its alkoxy group to give **4.24_{[ox][ox]H⁺}** is thermodynamically favoured and the latter needs a barrier of 31.5 kcal/mol to release THF diol. Thus, from both pathways the Os(VI) and Os(VIII) hydrolysis are relatively slow processes and comparable, and therefore the oxidation/hydrolysis could occur in either order.

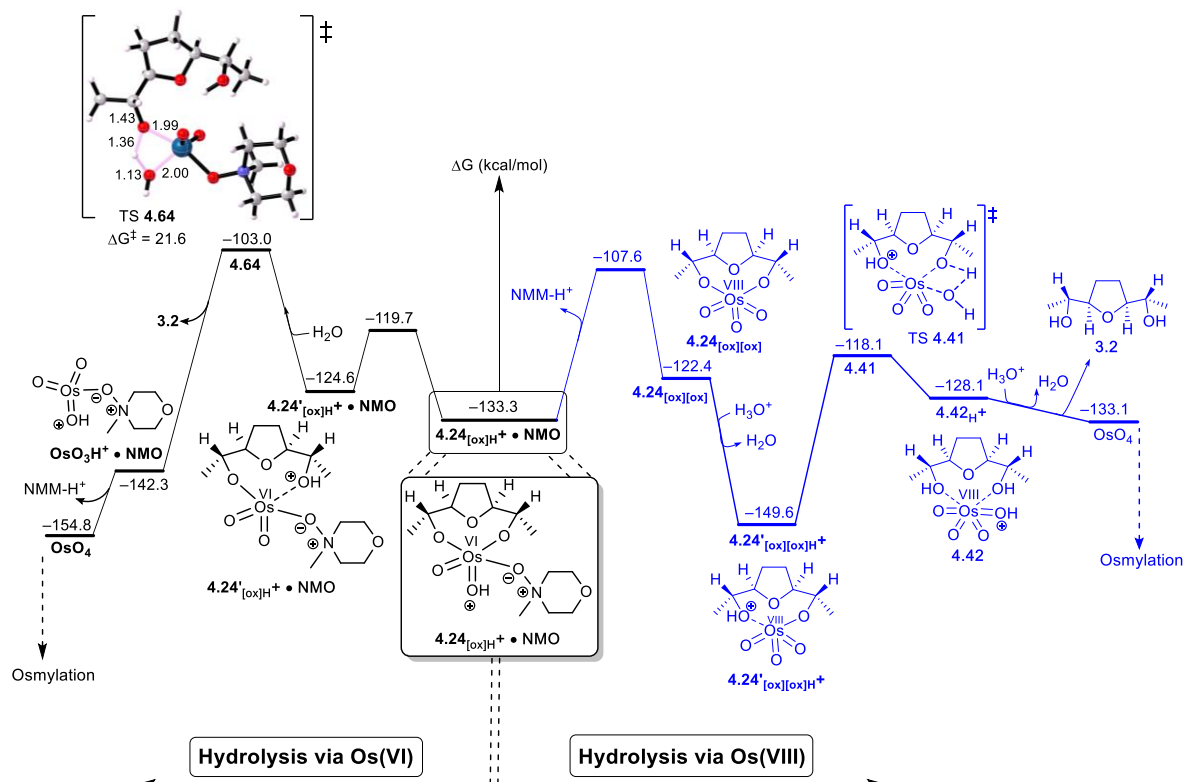


Figure 4.28: Computational evaluation of reaction manifolds from protonated Os(VI) THF-diolate **4.24** $[\text{ox}]\text{H}^+ \bullet \text{NMO}$ corresponding to first cycle hydrolytic release of the THF diol via Os(VI) and Os(VIII) hydrolysis pathways.

4.11 Conclusions

The reaction mechanism of the osmium-mediated oxidative cyclisation of 1,5-dienes to produce THF-diols has been explored using DFT calculations (SMD-M06-2X/aug-cc-pVDZ/ECP), leading to detailed description of catalytic cycle, and understanding of the key role of acid in promoting the cyclisation step (SRS). Calculations show that the oxidative cyclisation is kinetically and thermodynamically facilitated by acid in the absence (**4.22**→**4.22_H**→**4.24_H**) or presence of NMO (**4.22**→**4.22 • NMO**→**4.22_H • NMO**→**4.24_H • NMO**) for Os(VI) intermediates.

In the presence of acid, reoxidation of Os(VI) into Os(VIII) glycolate is highly disfavoured due to the significant stabilisation arising from protonation of oxo ligand in **4.22 • NMO** to give **4.24_H • NMO**. Calculations show that protonation of the Os(VI) dioxoglycolate (**4.22**→**4.22_H**→**4.24_H**) or NMO-adduct (**4.22**→**4.22 • NMO**→**4.22_H • NMO**→**4.24_H • NMO**) intermediates provides a kinetically favourable pathway compared to reoxidation (**4.22**→**4.22_[ox]**→**4.24_[ox]**) using NMO as the terminal oxidant. However, in the absence of acid, the well-known second cycle osmylation pathway

(**4.22**→**4.22**_[ox]→**4.26**_[ox]) is favoured over cyclisation (**4.22**→**4.22**_[ox]→**4.24**_[ox]) or hydrolysis to normal dihydroxylation product, and this is verified experimentally by the isolation of the second cycle (VI) adducts without added acid.

Significantly, our calculations are consistent with experimental data for osmium-mediated and catalysed reactions which proceed efficiently using an excess of TFA or CSA, but not using NMO alone. Furthermore, the DFT results for the SRS are also consistent with the related Os-catalysed oxidative cyclisation of dihydroxyalkenes which proceed through an Os(VI)/Os(IV) cycle.

Molecular dynamics simulations performed on the SRS, show asynchronous (3+2) addition of the O—Os—O species **4.22** across the alkene double bond with faster development of the C—O[Os] bonds compared to C—O[THF] bonds with 11.0 fs timing gap (39 random reactive trajectories) for the oxo protonated Os(VI) pathway and 3.50 fs timing gap (47 random reactive trajectories) from NMO-complexed oxo protonated Os(VI) pathway.

FMO calculations and distortion-interaction energy analysis provide additional insight into contributory factors, where increased electrophilicity of the protonated Os(VI) intermediate (favorable TS interaction energy), and attenuated distortion of the tetrahedral Os(VI) glycolate combine to deliver the favored TS.

DFT calculations show that osmium oxidative cyclisation is more likely to proceed through low spin multiplicity pathways.

Two catalytic cycles were evaluated for oxidative cyclisation of 1,5-dienes under acidic conditions, using osmium with NMO as the co-oxidant. Following the SRS (**4.22**→**4.22**_{H+}→**4.24**_{H+}), oxidation and hydrolysis steps are found to be catalysed by acid leading to the release of the THF-diol product **3.2** and OsO₄, which can continue the cycle. A more complex picture emerges when less strongly acidic conditions are present, where second cycles for osmylation involving Os(VIII) species, **4.22**_[ox] and **4.24**_{[ox][ox]}, may also compete.

Finally, on the basis of these results, and under strongly acidic conditions representative of those optimised by Donohoe and co-workers, osmium-catalysed oxidative cyclisation of 1,5-diene **3.1** is likely to involve OsO₄ as the catalytic species (**Figure 4.29**). Important features include promotion of the SRS by protonation of the Os(VI) glycolate **4.22** followed by complexation with NMO, which is favoured over reoxidation under strongly acidic conditions, and acid catalysis of reoxidation and hydrolysis steps.

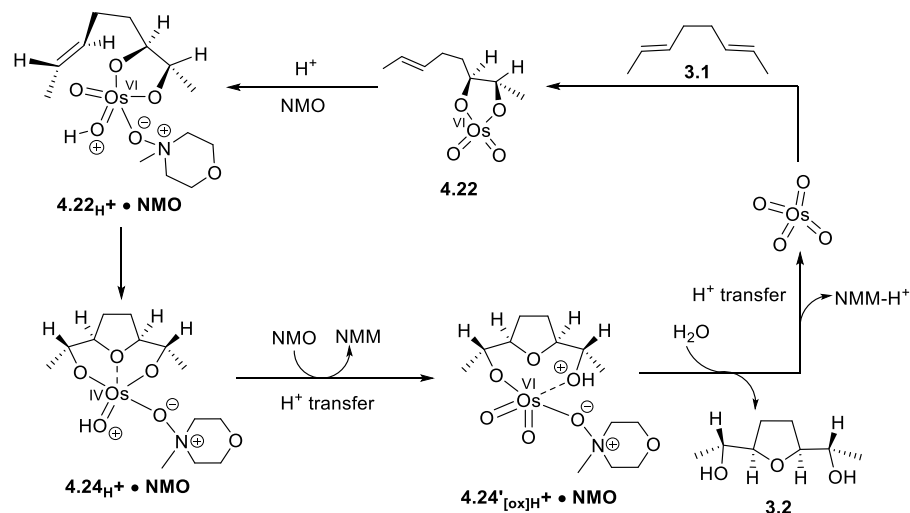


Figure 4.29: Proposed catalytic cycle for the Os-catalyzed oxidative cyclisation of 1,5-diene **3.1** in the presence of Bronsted acid.

4.12 Future work

Due to the insight gained into the osmium-promoted oxidative cyclisation of simple 1,5-diene (**Figure 4.30**), it will be attractive to explore regioselectivity of osmylation when an unsymmetrical diene bearing an electron-deficient group is present (**Figure 4.30**) and compared with the regioselectivity of MnO_4^- oxidation (**Figure 3.35**).

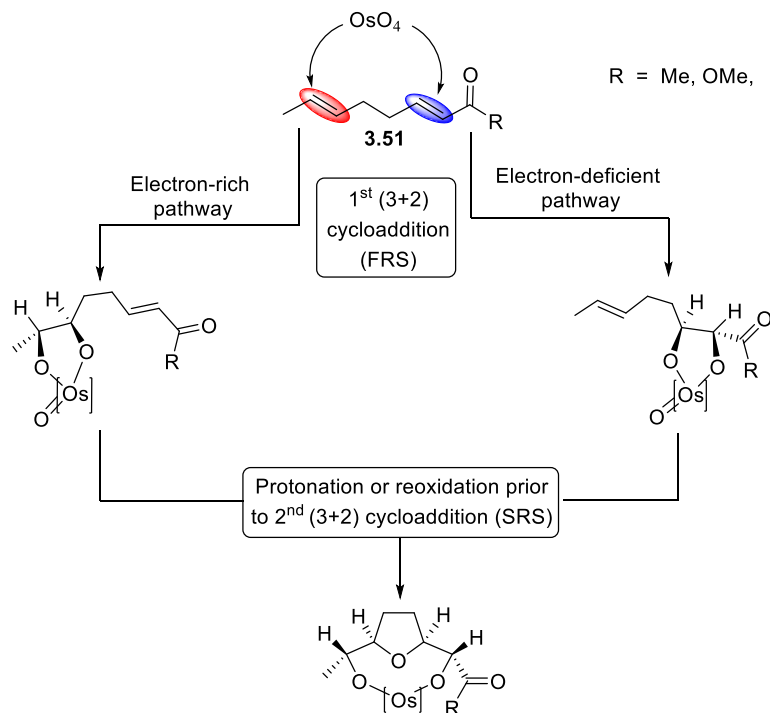


Figure 4.30: Regioselectivity of OsO_4 in the oxidative cyclisation of 1,5-diene in the presence of deficient group: ketone or ester group.

Since Os(VI) glycolate **4.64**, the intermediate in dihydroxylation and oxidative cyclisation reactions, has been isolated (see chapter one), it would be interesting to carry out mechanistic studies on NMO-adduct Os(VI) glycolate **4.66** using NMR and mass spectrometry techniques in order to verify the existence of such stable intermediate **4.66_H⁺ • NMO**, and gain an experimental evidence to support the DFT calculation results.

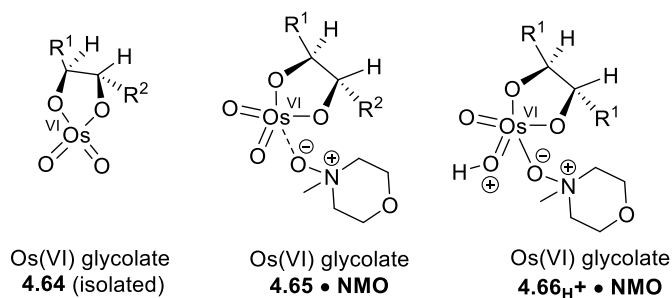


Figure 4.31: Structures of Os(VI) glycolate intermediates.

Chapter 5 Experimental and Computational

5.1 General procedure

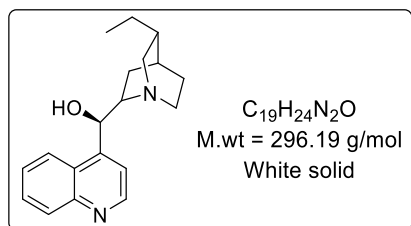
Chemicals were purchased from Sigma-Aldrich, Fisher Scientific. All air/moisture sensitive reactions were carried out under an inert atmosphere, in oven-dried or flame dried glassware. The solvents toluene, THF and Et₂O (from Na/benzophenone), MeOH and CH₂Cl₂ (from CaH₂) were distilled before use. TLC was performed on aluminium-precoated plates coated with silica gel 60 containing F₂₅₄ indicator; visualised under UV light (254 nm) and/or by staining with potassium permanganate. Flash column chromatography was performed using; high purity silica gel, Geduran®, pore size 60 Å, 230–400 mesh particle size, purchased from Merck. Fourier-transform infrared (FT-IR) spectra are reported in wavenumbers (cm⁻¹) and were collected as solids or neat liquids on a Nicolet 380 fitted with a Smart Orbit Goldengate attachment using OMNIC software package. Optical rotations were collected on an Optical Activity PolAAR 2001 machine. The solvent used for the measurement of the optical activity was normal chloroform.

¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ (purchased from Cambridge Isotope Laboratories, Inc.) at 298 K using Bruker DPX400, AVII400, AVIHD400 (400 and 100 MHz respectively) spectrometer. Chemical shifts values (δ) are reported in ppm relative to residual chloroform (δ 7.27 ppm for ¹H, δ 77.00 ppm for ¹³C). All spectra were reprocessed using ACD/Labs software version: 12.1. Coupling constants (*J*) were recorded in Hz. The following abbreviations for the multiplicity of the peaks are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), br (broad), and m (multiplet).

Melting points were obtained using a Gallenkamp Electrothermal apparatus and are uncorrected. Analytical HPLC was performed on an Agilent 1220 Infinity LC System utilising the Agilent EZChrom software package eluting with IPA/hexane mixtures (details in the experimental). Electrospray low resolution mass spectra were recorded on a Waters ZMD quadrupole spectrometer or Waters (Manchester, UK) TQD triple quadrupole analyser. High resolution mass spectra were obtained using Bruker APEX III FT-ICR mass spectrometer or MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight analyser. HRMS were recorded using positive ion electrospray ionisation (ESI⁺).

All calculations were initialised on localised S2 LINUX workstation supercomputer with 8 cores/16 GB memory, and then carried out on the University of Southampton supercomputer/iridis4.

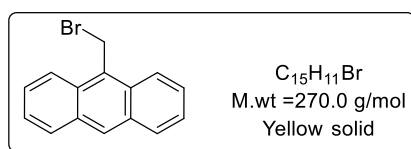
5.2 Experimental Details

(1*R*)-((4*S*)-5-Ethylquinuclidin-2-yl)(quinolin-4-yl)methanol (2.2)

A mixture of 10% Pd/C (650 mg, 2.21 mmol) and cinchonidine (**2.1**) (6.50 g, 22.1 mmol) in MeOH (230 mL) was stirred under an atmosphere of hydrogen. After 6 h the reaction mixture was purged with N_2 , then filtrated through celite and the filter cake was washed with MeOH (1.0 L). The filtrate was

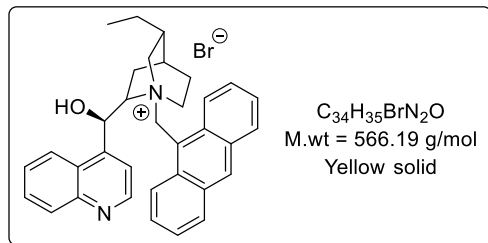
concentrated under reduced pressure to afford a white solid which was stirred in PE (200 mL) for 3 h. The precipitate was collected by filtration to afford the title compound **2.2** (6.55 g, 22.10 mmol, quant. yield) as a white solid. Physical and spectroscopic data are consistent with literature.²⁵⁸

^1H NMR (400 MHz, MeOD- d^4): δ 8.84 (1H, d, J = 4.5 Hz, CH-Ar), 8.25 (1H, d, J = 8.4 Hz, CH-Ar), 8.08 (1H, d, J = 8.5 Hz, CH-Ar), 7.76 (1H, t, J = 7.6 Hz, CH-Ar), 7.71 (1H, d, J = 4.5 Hz, CH-Ar), 7.64 (1H, t, J = 7.6 Hz, CH-Ar), 5.66 (1H, d, J = 3.8 Hz, CHOH), 3.60 (1H, dddd, J = 13.3, 10.7, 4.9, 2.5 Hz, CHOHCHNCH₂CH), 3.10 (2H, dd, J = 13.3, 10.1 Hz, 2 x CHN), 2.66 (1H, m, CHN), 2.34 (1H, br s, CHNCH₂CH), 1.83 (3H, m, CHCH₂CH), 1.52–1.37 (2H, m, NCH₂CH₂), 1.35–1.10 (2H, m, CH₂CH₃), 0.82 (3H, t, J = 7.3 Hz, CH₃) ppm. **^{13}C NMR (100 MHz, MeOD- d^4):** δ 152.7 (CH-Ar), 152.2 (C-Ar), 149.2 (C-Ar), 131.0 (C-Ar), 130.4 (CH-Ar), 128.5 (C-Ar), 127.5 (CH-Ar), 124.9 (CH-Ar), 120.3 (CH-Ar), 72.6 (CH), 61.9 (CH), 44.4 (CH₂), 38.9 (CH), 29.2 (CH), 28.9 (CH₂), 27.1 (CH₂), 22.3 (CH₂), 12.7 (CH₃) ppm. **LRMS:** (ES+) m/z 297.4 ([M+H]⁺).

9-(Bromomethyl)anthracene (2.4)

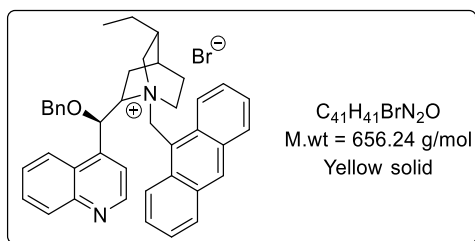
To a solution of anthracenemethanol (4.50 g, 21.6 mmol) in toluene (75 mL) at 0 °C was added dropwise PBr_3 (3.0 mL, 32.4 mmol). The reaction mixture was allowed to warm to rt, and stirred at this temperature for 2 h. Aqueous sat. NH_4Cl (250

mL) was added and the reaction mixture was extracted with EtOH (3 x 200 mL). The organic phases was combined, dried over $MgSO_4$, and concentrated under reduced pressure to afford a yellow solid (5.83 g, 21.6 mmol, quant. Yield). Physical and spectroscopic data are consistent with literature.²⁵⁹ **^1H NMR (400 MHz, $CDCl_3$):** δ 8.51 (1H, s, CH), 8.32 (2H, d, J = 8.8 Hz, CH), 8.05 (2H, d, J = 8.5 Hz, CH), 7.66 (2H, t, J = 7.7 Hz, CH), 7.52 (2H, d, J = 7.5 Hz, CH), 5.56 (2H, s, CH₂) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 131.9 (C), 130 (C), 129.6 (CH), 129.5 (C), 128.1 (CH), 127.1 (CH), 125.7 (CH), 123.8 (CH), 27.3 (CH₂) ppm. **LRMS:** (ES+) m/z 272 ([M+H]⁺).

(1*R*,4*R*,5*S*)-1-(Anthracen-9-ylmethyl)-5-ethyl-2-((*R*)-hydroxy(quinolin-4-yl)methyl)quinuclidin-1-ium bromide (2.5)

To a solution of 9-(bromomethyl)anthracene (**2.4**, 3.66 g, 13.5 mmol) in toluene (64 mL) was added dihydrocinchonidine (**2.2**, 4.00 g, 13.5 mmol). The reaction mixture was heated at 90 °C for 3 h, then the solution was concentrated under reduced pressure to

15 mL. PE (60 mL) was added and the mixture was stirred for 20 min. The resulting precipitate was filtrated and then triturated with hexane to afford the title compound as a light yellow solid (7.64 g, 13.5 mmol, quant. Yield). Physical and spectroscopic data are consistent with literature.²⁶⁰ **¹H NMR (400 MHz, EtOD-*d*⁶):** δ 8.92 (1H, br d, *J* = 9.3 Hz, CH-Ar), 8.87 (1H, d, *J* = 4.4 Hz, CH-Ar), 8.80 (1H, d, *J* = 7.7 Hz, CH-Ar), 8.07 (1H, d, *J* = 4.4 Hz, CH-Ar), 8.01 (1H, s, CH-Ar), 7.70 (1H, m, CH-Ar), 7.60 (1H, m, CH-Ar), 7.27–7.24 (4H, m, 4 x CH-Ar), 7.23–7.13 (6H, m, 6 x CH-Ar), 7.08 (1H, br s, NCHH-Ar), 6.43 (1H, br d, *J* = 13.7 Hz, CHOH), 6.02 (1H, br d, *J* = 13.9 Hz, NCHH-Ar), 4.83–4.56 (2H, m, CHOHCHNCH₂CH), 3.82 (1H, br d, *J* = 12.6 Hz, OHCHCHNCHHCH₂), 2.65 (1H, br dd, *J* = 12.3, 10.6 Hz, OHCHCHNCHHCH₂), 2.73–2.63 (1H, m, OHCHCHNCH₂CH), 2.27–2.15 (1H, m, OHCHCHCH₂CH), 1.56–1.15 (6H, m, CHOHCHNCH₂CH₂, OHCHCHCH₂CH, CH₂CH₃), 0.71 (3H, br t, *J* = 7.3 Hz, CH₃). **¹³C NMR (100 MHz, EtOD-*d*⁶):** δ 149.7 (CH-Ar), 147.5 (C-Ar), 145.7 (C-Ar), 138.1 (CH-Ar), 133.4 (CH-Ar), 132.8 (CH-Ar), 131.5 (C-Ar), 130.6 (C-Ar), 129.7 (CH-Ar), 129.3 (CH-Ar), 129.0 (CH-Ar), 128.8 (CH-Ar), 128.6 (CH-Ar), 128.5 (CH-Ar), 128.1 (CH-Ar), 127.6 (C-Ar), 126.2 (CH-Ar), 126.0 (CH-Ar), 125.5 (C-Ar), 125.1 (C-Ar), 124.4 (C-Ar), 120.5 (CH-Ar), 118.2 (CH-Ar), 67.3 (CH), 67.2 (CH₂), 64.0 (CH), 55.2 (CH₂), 51.0 (CH₂), 37.4 (CH), 26.7 (CH), 26.4 (CH₂), 23.5 (CH₂), 23.3 (CH₂), 11.7 (CH₃) ppm. **LRMS:** (ES+) *m/z* 487 (45% [M–Br]), 488 (18% [M+H]⁺).

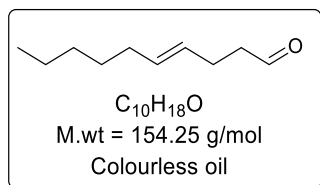
(1*R*,4*R*,5*S*)-1-(Anthracen-9-ylmethyl)-2-((*R*)-(benzyloxy)(quinolin-4-yl)methyl)-5-ethylquinuclidin-1-ium bromide (1.76)

To a suspension of *N*-9-anthracenylmethylcinchonidinium bromide (5.41 g, 10.4 mmol) in CH₂Cl₂ (30.0 mL) was added BnBr (3.70 mL, 31.1 mmol) and KOH (5.80 mL of 50% aq, 51.8 mmol). The resulting mixture was stirred vigorously at rt for 4 h,

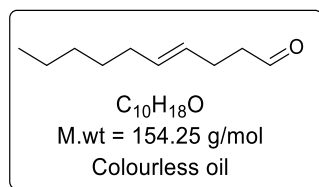
during which time all of the solids dissolved. The mixture was diluted with water (60 mL) and was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated to 20–30 mL. The mixture was then poured into PE (150 mL) and stirred for 1 h. The solution was filtered and washed with hexane to afford a yellow solid (95%). The precipitate then triturated with CH₂Cl₂:MeOH:Et₂O (1:2:3) to afford the benzyl ether **1.76** as a yellow solid (5.45 g,

8.3 mmol, 80%). Physical and spectroscopic data are consistent with literature data.²⁶¹ MP 143–144 °C (Lit.²⁶¹ 137–138 °C). **¹H NMR (400 MHz, EtOD-d⁶)**: δ 9.06 (1H, m, **CH**-Ar), 8.97 (1H, m, **CH**-Ar), 8.80 (1H, m, **CH**-Ar), 8.30–8.00 (4H, m, 4 x **CH**-Ar), 7.92 (1H, br s, **CH**-Ar), 7.80–7.65 (2H, m, 2 x **CH**-Ar), 7.60–7.40 (4H, m, 4 x **CH**-Ar), 7.15 (1H, m, **CH**-Ar), 6.32 (1H, br s, **NCHH**-Ar), 5.99 (1H, d, *J* = 12.8 Hz, **NCHH**-Ar), 5.11 (1H, br d, *J* = 11.3 Hz, **PhCHH**), 4.97 (1H, br d, *J* = 11.1 Hz, **PhCHH**), 4.82–4.59 (1H, m, **OCHCHN**), 4.41 (1H, m, **OCHCHNCHHCH₂**), 3.74 (1H, m, **OCHCHNCHHCH₂**), 3.34 (1H, s, **OCHCHNCHHCH**), 3.25–3.07 (1H, m, **OCHCHNCHHCH**), 2.70 (1H, m, **OCHCHNCH₂CH**), 2.49 (1H, m, **OCHCHCH₂CH**), 2.08 (1H, m, **OCHCHCHH**), 1.91 (1H, m, **OCHCHNCH₂CHH**), 1.60–1.45 (3H, m, **OCHCHCHH**, **CH₂CH₃**), 1.26 (1H, m, **OCHCHNCH₂CHH**), 0.66 (3H, m, **CH₃**) ppm. **¹³C NMR (100 MHz, EtOD-d⁶)**: δ 150.7 (**CH**-Ar), 149.3 (**C**-Ar), 142.5 (**C**-Ar), 138.0 (**C**-Ar), 134.7 (**CH**-Ar), 134.3 (**CH**-Ar), 133.6 (**C**-Ar), 132.7 (**C**-Ar), 132.6 (**CH**-Ar), 131.2 (**CH**-Ar), 131.0 (**CH**-Ar), 130.8 (**CH**-Ar), 130.5 (**CH**-Ar), 130.0 (**CH**-Ar), 129.5 (**CH**-Ar), 129.0 (**CH**-Ar), 128.7 (**CH**-Ar), 126.4 (**CH**-Ar), 126.1 (**CH**-Ar), 125.2 (**CH**-Ar), 124.7 (**C**-Ar), 118.9 (**C**-Ar), 72.5 (**CH₂**, **CH**), 69.5 (**CH**), 65.0 (**CH₂**), 57.5 (**CH₂**), 53.3 (**CH₂**), 37.1 (**CH**), 27.0 (**CH**), 26.6 (**CH₂**), 25.0 (**CH₂**), 23.3 (**CH₂**), 11.6 (**CH₃**). **LRMS**: (ES+) *m/z* 577 (85% [**M**-Br]), 578 (45% [**M**+H]⁺).

(*E*)-dec-4-enal (**2.8**)

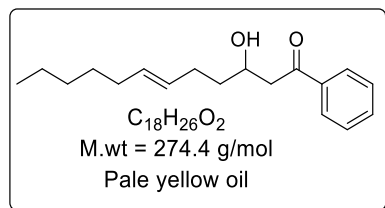


The procedure was carried out by adaptation of method described by Wei *et al.*²⁶² To a solution of the allylic alcohol **2.6** (14.5 mL, 93.6 mmol) in butyl vinyl ether (**2.7**) (73.0 mL, 562 mmol), was added the palladium catalyst **2.12** (190 mg, 0.468 mmol). The reaction mixture was heated at 93 °C for 48 h, during that period the reaction became black. The black mixture was allowed to cool to room temperature, filtered through celite, rinsed with Et₂O, and concentrated under reduced pressure to give a yellow oil. Purification by column chromatography on silica gel (Et₂O/hexane 1.5%) afforded the desired aldehyde **2.8** as a colourless oil (12.2 g, 79.1 mmol, 84%). Physical and spectroscopic data are consistent with literature.³⁰⁹ **FT-IR** *v*_{max} (**neat**): 2956 (s), 2924 (s), 2872 (s), 1725 (s), 1465 (w). **¹H NMR (400 MHz, CDCl₃)**: δ 9.77 (1H, t, *J* = 1.7 Hz, **CHO**), 5.52–5.35 (2H, m, **CH=CH**), 2.51 (2H, m, **CH₂CHO**), 2.34 (2H, q, *J* = 7.0 Hz, **CH₂**), 1.98 (2H, q, *J* = 6.8 Hz, **CH₂**), 1.39–1.20 (6H, m, 3 x **CH₂**), 0.89 (3H, t, *J* = 6.9 Hz, **CH₃**) ppm. **¹³C NMR (100 MHz, CDCl₃)**: δ 202.4 (**CHO**), 132.1 (**CH**), 127.6 (**CH**), 43.5 (**CH₂**), 32.5 (**CH₂**), 31.4 (**CH₂**), 29.1 (2 x **CH₂**), 25.2 (**CH₂**), 22.5 (**CH₂**), 14.0 (**CH₃**) ppm. **LRMS**: (ES+) *m/z* 155 ([**M**+H]⁺).

(E)-Dec-4-enal (2.8)

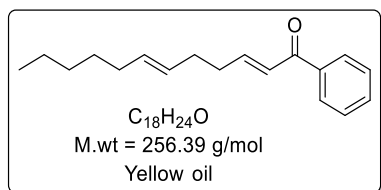
The procedure was carried out by adaptation of method described by Wei *et al.*²⁶² To a solution of the allylic alcohol **2.6** (14.5 mL, 93.6 mmol) in butyl vinyl ether (**2.7**, 73.0 mL, 562 mmol), was added the palladium catalyst **2.12** (190 mg, 0.468 mmol). The reaction mixture

was heated at 93 °C for 48 h, during that period the reaction became black. The black mixture was allowed to cool to rt, filtered through celite, rinsed with Et₂O, and concentrated under reduced pressure to give a yellow oil. Purification by column chromatography (SiO₂) eluting with Et₂O/Hex (1.5%) afforded the desired aldehyde **2.8** as a colourless oil (12.2 g, 79.1 mmol, 84%). Physical and spectroscopic data are consistent with literature values.³⁰⁹ **FT-IR** $\nu_{\max}$ (neat): 2956 (s), 2924 (s), 2872 (s), 1725 (s), 1465 (w). **¹H NMR (400 MHz, CDCl₃)**: δ 9.77 (1H, t, J = 1.7 Hz, CHO), 5.52–5.35 (2H, m, CH=CH), 2.51 (2H, m, CH₂CHO), 2.34 (2H, q, J = 7.0 Hz, CH₂), 1.98 (2H, q, J = 6.8 Hz, CH₂), 1.39–1.20 (6H, m, 3 x CH₂), 0.89 (3H, t, J = 6.9 Hz, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: δ 202.4 (CHO), 132.1 (CH), 127.6 (CH), 43.5 (CH₂), 32.5 (CH₂), 31.4 (CH₂), 29.1 (2 x CH₂), 25.2 (CH₂), 22.5 (CH₂), 14.0 (CH₃) ppm. **LRMS**: (ES+) m/z 155 ([M+H]⁺).

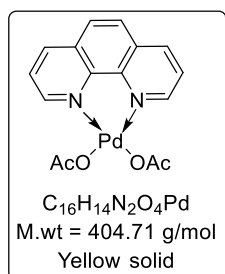
(E)-3-Hydroxy-1-Arenyldodec-6-en-1-one (2.9)

To a solution of LDA (8.50 mL of 1.0 M in THF, 8.50 mmol) at –78 °C under N₂ was added acetophenone (1.00 mL, 1.02 g, 8.34 mmol) in THF (3.3 mL) dropwise. The reaction was stirred for 45 min at –78 °C. Then, a solution of aldehyde **2.8** (1.00 g, 6.50

mmol) in THF (3.5 mL) was added dropwise. The reaction was stirred for 45 min then was quenched by addition of sat. aq. NH₄Cl (2.0 mL). The reaction was allowed to warm to rt over 1 h. The organic phases were separated and aqueous phase extracted with EtOAc (3 x 2.0 mL). The organic phases were combined, washed with brine (3 x 4.0 mL), dried (Na₂SO₄), and concentrated under reduced pressure to give a yellow oil. Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (5%→15%) gave β -hydroxy ketone **2.9** (1.55 g, 6.60 mmol, 87%) as a pale yellow oil. **FT-IR** $\nu_{\max}$ (neat): 3446 (br), 2955 (s), 2923 (s), 2853 (s), 1676 (s), 1597 (w), 1448 (w), 1211 (w), 1001 (s). **¹H NMR (400 MHz, CDCl₃)**: δ 7.95 (2H, dd, J = 7.7, 1.7 Hz, 2 x CH-Ar), 7.6 (1H, m, CH-Ar), 7.48 (2H, m, CH-Ar), 5.47 (1H, m, CH=CH), 5.44 (1H, m, CH=CH), 4.23 (1H, br m, CHOH), 3.20 (1H, d, J = 2.8 Hz, OH), 3.15 (1H, d, J = 2.8 Hz, CHHC=O), 3.07 (1H, m, CHHC=O), 2.10–2.27 (2H, m, CH₂), 1.99 (2H, br q, J = 7.2 Hz, CH₂), 1.64–1.76 (1H, m, CHHCHOH), 1.53–1.62 (1H, m, CHHCHOH), 1.22–1.40 (6H, m, 3 x CH₂), 0.89 (3H, t, J = 6.9 Hz, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: δ 200.5 (C=O), 136.4 (C-Ar), 133.1 (CH-Ar), 131.2 (CH), 129.2 (CH), 128.6 (2 x CH-Ar), 128.0 (2 x CH-Ar), 66.9 (CH), 44.6 (CH₂), 36.0 (CH₂), 32.2 (CH₂), 31.0 (CH₂), 28.9 (CH₂), 28.3 (CH₂), 22.2 (CH₂), 13.7 (CH₃) ppm. **LRMS**: (ES+) m/z 275 ([M+H]⁺). **HRMS** (ES+) m/z C₁₈H₂₆O₂Na Calculated: 297.1825, found: 297.1825.

(2E,6E)-1-Arenyldodeca-2,6-dien-1-one (2.10)

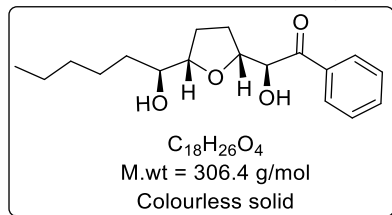
To a solution of β -hydroxy ketone **2.9** (1.02 g, 3.70 mmol) in CH_2Cl_2 (62 mL) at 0 °C was added dropwise methanesulfonyl chloride (0.600 mL, 630 mg, 5.43 mmol) and Et_3N (0.800 mL, 5.43 mmol). The mixture was allowed to warm to rt, and stirred for 2 h before addition of brine (13 mL) and H_2O (13 mL). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 x 15 mL). The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure before being redissolved in CH_2Cl_2 (40 mL). The solution was cooled to 0 °C whereupon DBU (1.10 mL, 7.40 mmol) was added dropwise. The reaction was allowed to warm to rt, then stirred at this temperature for 30 min. H_2O (13 mL), 2M HCl (7 mL) and brine (13 mL) were added. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 x 15 mL). The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure to give a pale yellow oil. Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (3%→6%) gave diene **2.10** (0.710 g, 2.80 mmol, 76%) as a yellow oil. **FT-IR** ν_{max} (neat): 2955 (s), 2923 (s), 2853 (s), 1670 (s), 1652 (s), 1520 (s), 1447 (w). **^1H NMR (400 MHz, $CDCl_3$)**: δ 7.93 (2H, d, J = 7.1 Hz, CH-Ar), 7.56 (1H, m, CH-Ar), 7.47 (2H, m, CH-Ar), 7.06 (1H, dt, J = 15.4, 6.7 Hz, CH=CHC=O), 6.89 (1H, dt, J = 15.4, 1.4 Hz, CH=CHC=O), 5.53–5.37 (2H, m, $CH_2CH=CHCH_2$), 2.40 (2H, q, J = 7.0 Hz, $CH_2CH=CHC=O$), 2.23 (2H, q, J = 6.9 Hz, $CH_2CH_2CH=CHC=O$), 1.99 (2H, q, J = 6.5 Hz, CH_2), 1.21–1.38 (6H, m, 3 x CH_2), 0.88 (3H, t, J = 6.9 Hz, CH_3) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 190.9 (C=O), 149.4 (CH), 138.0 (C-Ar), 132.5 (CH-Ar), 131.9 (CH), 128.5 (CH), 128.4 (2 x CH), 128.3 (2 x CH), 126.2 (CH), 32.4 (CH_2), 32.5 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 29.2 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. **LRMS**: (ES+) m/z 257 ($[M+H]^+$). **HRMS** (ES+) m/z $C_{18}H_{24}ONa$ Calculated: 257.19, found: 257.1899.

 $Pd(OAc)_2$ -Arenanthroline catalyst (2.12)

The procedure was carried out according to the method described by Wei *et al.*²⁶² To a flame dried RBF, under N_2 atmosphere at rt, was added $Pd(OAc)_2$ (100 mg, 0.450 mmol), 1,10-Arenanthroline (80 mg, 0.45 mmol) and anhydrous DME (2.0 mL). The reaction mixture was stirred at rt for 30 min resulting in formation of a yellowish precipitate. The solid was filtered, rinsed with Et_2O and dried under high-vacuum to obtain the desired catalyst **2.12** as a yellowish solid (160 mg, 0.400 mmol, 89%). **FT-IR** ν_{max} (neat): 3378 (br), 1593 (s), 1367 (m), 1317 (s), 1303 (s).

(S)-2-Hydroxy-2-((2R,5S)-5-((S)-1-hydroxyhexyl)tetrahydrofuran-2-yl)-1-Arenylethan-1-one**(2.13)**

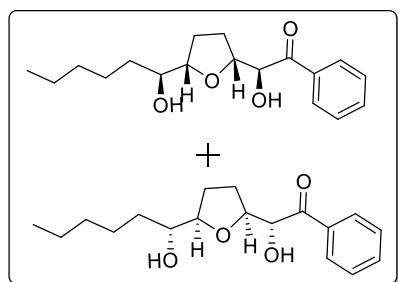
To a solution of diene **2.10** (200 mg, 0.780 mmol), chiral PT catalyst **1.76** (50 mg, 0.080 mmol) and



AcOH (0.170 mL, 2.97 mmol) in CH_2Cl_2 (12 mL) at $-60\text{ }^\circ\text{C}$, was added in one batch powdered $KMnO_4$ (200 mg, 1.25 mmol).

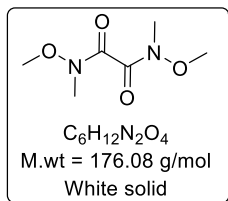
After 4 h vigorous stirring the reaction was quenched with sat. aq. $Na_2S_2O_5$ (15 mL), H_2O (3.5 mL) and CH_2Cl_2 (10 mL). The

organic phases were separated and the aqueous phase extracted with EtOAc (4 x 20.0 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure to give yellow oil. Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (15%) gave THF-diols **2.13** (128.7 mg, 0.42 mmol, 53%) as colourless solid. **MP** 58–59 $^\circ\text{C}$, **FT-IR** ν_{max} (neat): 3462(br), 2928 (s), 2858 (s), 1683 (s), 1598 (w), 1449 (w), 1264 (s) 1127 (s). **^1H NMR (400 MHz, $CDCl_3$)**: δ 7.91 (2H, d, $J = 7.5$ Hz, CH-Ar), 7.62 (1H, tt, $J = 7.5, 1.2$ Hz, CH-Ar), 7.51 (2H, t, $J = 7.5$ Hz, CH-Ar), 5.09 (1H, d, $J = 2.1$ Hz, CHOHC=O), 4.40 (1H, m, CHCHOHC=O), 4.12 (1H, m, CHCHOHC=O), 3.72 (1H, td, $J = 6.7, 5.3$ Hz, CHOHC=O), 3.33 (1H, dt, $J = 7.3, 4.9$ Hz, CHCHOH), 2.46–2.16 (2H, m, 2 x OH), 2.08–2.02 (2H, m, CH_2 -THF), 1.88 (2H, q, $J = 7.5$ Hz, CH_2 -THF), 1.17–1.53 (8H, m, 4 x CH_2), 0.88 (3H, t, $J = 6.9$ Hz, CH_3) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 205.0 (C=O), 134.5 (C-Ar), 134 (CH-Ar), 129.2 (2 x CH-Ar), 128.9 (2 x CH-Ar), 83.6 (CH), 80.3 (CH), 75.3 (CH), 74.2 (CH), 34.4 (CH_2), 32.2 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 25.7 (CH_2), 22.9 (CH_2), 14.3 (CH_3) ppm. **LRMS**: (ES+) m/z 307 (50%, $[M+H]^+$), 329 (100%, $[M+Na]^+$). **HRMS**: (ES+) m/z $C_{18}H_{26}O_4Na$ Calculated: 329.172, found: 329.1728. **HPLC**: Chiralpack® OD-H – (flow rate: 1.0 mL/min, 254 nm, eluent: 10% isopropanol/hexane, ee = 49.4%, Retention times = 7.92 (major), 9.54 (minor))

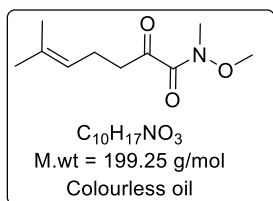
(rac)-(S)-2-Hydroxy-2-((2R,5S)-5-((S)-1-hydroxyhexyl)tetrahydrofuran-2-yl)-1-Arenylethan-1-one (rac)-2.13

To a solution of diene **2.10** (100 mg, 0.390 mmol), AcOH (0.090 mL, 1.50 mmol,) in CH_2Cl_2 (6.0 mL) at $-60\text{ }^\circ\text{C}$ was added in one batch powdered $KMnO_4$ (99 mg, 0.63 mmol). After 4 h vigorous stirring the reaction was quenched with sat. aq. $Na_2S_2O_5$ (8.0 mL), H_2O (2.0 mL) and CH_2Cl_2 (5.0 mL). The organic phase was

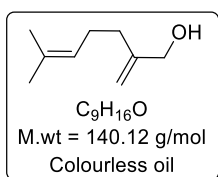
separated and the aqueous phase extracted with EtOAc (4 x 10 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure to colourless solid. Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (15%) gave THF-diols (**rac**)-**2.13** (30.6 mg, 0.10 mmol, 30%) as colourless solid: Characterisation data are in agreement with those reported above.

***N*¹,*N*²-dimethoxy-*N*¹,*N*²-dimethyloxalamide (2.19)**

To *N,O*-dimethylhydroxylamine hydrochloride (2.30 g, 23.6 mmol) in CH₂Cl₂ (23 mL) was added oxalyl chloride (1.02 mL, 11.82 mol) in one portion. The resulting mixture was cooled to 0 °C. A solution of Et₃N (6.3 mL, 47.3 mmol) in CH₂Cl₂ (17 mL) was added dropwise. The suspension was stirred 30 min at 0 °C and then washed twice with water (2 × 40 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 40 mL). The combined organic phases were concentrated under reduced pressure to ~6 mL, and cyclohexane (25 mL) was added dropwise and crystallisation occurred almost immediately. The resulting white solid was stirred for 30 min at rt and for 1.5 h at 0 °C, filtered, and dried under reduced pressure to obtain the title compound **2.19** as a white solid (1.66 g, 9.45 mmol, 80%). Physical and spectroscopic data are consistent with literature data.²⁶⁶ ¹H NMR (400 MHz, CDCl₃) δ 3.72 (6H, s, 2 × OCH₃), 3.15 (6H, s, 2 × NCH₃). ¹³C NMR (100 MHz, CDCl₃) 164.81 (2 × C=O), 62.0 (2 × OCH₃), 32.0 (2 × NCH₃) ppm.

***N*-methoxy-*N*,6-dimethyl-2-oxohept-5-enamide (2.20)**

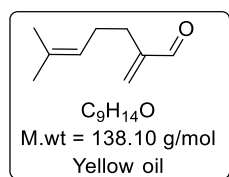
Step 1: To a stirred solution of Mg turnings (243 mg, 10.0 mmol) in THF (7 mL) was added dropwise alkyl halide **2.33** (0.650 mL, 4.80 mmol) with three drops of CH₂Br₂. The resulting mixture was stirred for 30 min at rt and then heated to reflux for 30 min. The mixture was cooled to rt and used directly in the next step. **Step 2:** Grignard solution prepared in step 1 was added to a solution of bis Weinreb amide **2.19** (0.70 g, 3.98 mmol) in THF (4 mL) at 0 °C. The solution was stirred for 2 h at 0 °C and then quenched with NH₄Cl (30 mL of sat. aq.). The aqueous layer was extracted with EtOAc (2 × 30 mL) and the combined organic phase was dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO₂) eluting with EtOAc/Hex (5% → 15%) to afford the title compound **2.20** as a colourless oil (0.480 g, 2.39 mmol, 60%). Physical and spectroscopic data are consistent with literature data.²⁶⁶ ¹H NMR (400 MHz, CDCl₃) δ 5.08 (1H, br t, *J* = 7.1 Hz, =CHCH₂), 3.76 (3H, s, OCH₃), 3.21 (3H, s, NCH₃), 2.71 (2H, t, *J* = 7.4 Hz, COCH₂), 2.33 (2H, q, *J* = 7.25 Hz, COCH₂CH₂), 1.68 (3H, s, CH₃), 1.62 (3H, s, CH₃). ¹³C NMR (100 MHz, CDCl₃) 200.3 (CH₂C=O), 168.10 (NC=O), 133.14 (C(CH₃)₂), 122.04 (=CHCH₂), 62.2 (OCH₃), 39.7 (CH₂C=O), 31.5 (NCH₃), 25.6 (CCH₃), 21.2 (=CHCH₂), 17.64 (CCH₃) ppm.

6-methyl-2-methylenehept-5-en-1-ol (2.23)

A solution of ⁿBuLi (97.7 mL of 2.5 M in hexane, 242 mmol) was added to an Ar purged flask. Using a double manifold the flask was placed under vacuum to remove the hexane. After 4 h the flask was refilled with Ar. To the concentrated ⁿBuLi was added Et₂O (84 mL) followed by TMEDA (42.5 mL, 282 mmol) at 0 °C. To this was added dropwise methallyl alcohol **2.22** (6.80 mL, 80.6 mmol) at 0 °C,

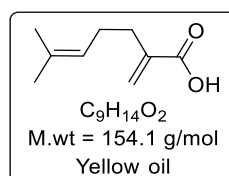
followed by THF (50 mL). The solution was stirred at 0 °C for 5 min, then the cooling bath was removed and the resultant yellow solution was stirred for 38 h at rt, during which time a dark red gum attributed to the corresponding dianion was observed in the reaction mixture. A solution of allyl bromide (6.00 g, 40.3 mmol) in Et₂O (12 mL) was added dropwise at –78 °C, and the mixture was stirred for 15 min. The cooling bath was removed and the reaction mixture was stirred for 8 h at rt. At 0 °C the reaction was carefully quenched with H₂O (40 mL), acidified to pH 3 with HCl (2.0 N), and re-extracted with Et₂O (8 x 70 mL), dried (MgSO₄), filtered and concentrated under reduced pressure to afford a crude product as a brownish yellow oil. The crude product was purified by column chromatography (SiO₂) eluting with EtOAc/Hex (5% → 35%) gave the title dienol **2.23** as a colourless oil (4.20 g, 30.0 mmol, 74%). Spectroscopic data are in agreement with the literature data.⁵⁶ **¹H NMR (400 MHz, CDCl₃)** δ 5.15–5.07 (1H, m, =CHCH₂), 5.04 (1H, m, =CHH), 4.90 (1H, d, *J* = 1.3 Hz, =CHH), 4.07 (2H, s, CH₂OH), 2.11 (2H, m, =CHCH₂) 1.80 (2H, m, CH₂CH₂) 1.69 (3H, m, CH₃), 1.61 (3H, s, CH₃), 1.27 (1H, br s, CH₂OH). **¹³C NMR (100 MHz, CDCl₃)** 148.9 (C) 132.0 (C), 123.8 (CH), 109.3 (=CH₂), 65.9 (CH₂OH), 33.0 (CH₂), 26.4 (CH₂), 25.6 (CH₃), 17.7 (CH₃) ppm. **LRMS:** (ES+) *m/z* 179 [M+K]⁺.

6-methyl-2-methylenehept-5-enal (**2.24**)



At 0 °C a mixture of alcohol **2.23** (3.00 g, 21.4 mmol) and activated MnO₂ (29.6 g, 342 mmol) in hexane (250 mL) was stirred for 30 min. Then, the ice bath was removed and stirring continued for 15 h. Filtration over through and concentration under reduced pressure afforded the title aldehyde **2.24** as a yellow oil. Purification by column chromatography (SiO₂) eluting with Et₂O/Hex (4%) gave the title compound as a yellow oil **2.24** (2.07 g, 15.0 mmol, 70%). Physical and spectroscopic data are consistent with literature data.⁵⁶ **¹H NMR (400 MHz, CDCl₃)**: δ 9.53 (1H, s, CHO), 6.23 (1H, s, =CHH), 5.99 (1H, s, =CHH), 5.11–5.03 (1H, m, =CHCH₂), 2.28 (2H, t, *J* = 6.6 Hz, CCH₂CH₂), 2.13 (2H, q, *J* = 7.5 Hz, CHCH₂), 1.68 (3H, d, *J* = 1.1 Hz, CH₃), 1.59 (3H, s, CH₃). **¹³C NMR (100 MHz, CDCl₃)**: 194.7 (CHO), 149.9 (CCHO), 134.1 (CH), 132.5 (C=CH), 123.5 (=CH₂), 28.0 (CH₂), 26.2 (CH₂), 25.6 (CH₃), 17.7 (CH₃) ppm. **LRMS:** (ES+) *m/z* 277 [2M+H]⁺.

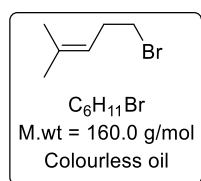
6-methyl-2-methylenehept-5-enoic acid (**2.15**)



Method 1: According to the procedure reported by Al-Hadedi,⁵⁷ silver oxide was prepared by adding a solution of silver nitrate (9.00 g, 53.2 mmol) in water (28 mL) to a solution of NaOH (4.20 g, 104 mmol) in water (77 mL) with rapid stirring at rt. Stirring was continued for 5 min, resulting in a brown semi-solid mixture. Aldehyde **2.24** (3.50 g, 25.3 mmol) was added at 0 °C, and after 1.5 h the ice bath was removed and the mixture was stirred at rt for 23 h. The silver suspension was removed by filtration, washing with several portions of hot water. EtOAc (70 mL) was added to the filtrate and washings,

then acidified with concentrated HCl to pH 1–2. The organic phase was separated, and the aqueous phase was re-extracted with EtOAc (4 x 100 mL). The combined organic phase was dried (MgSO₄), filtered and concentrated under reduced pressure to afford the title compound **2.15** as a dark yellow oil (3.74 g, 24.3 mmol, 97%). The crude product was used in subsequent reactions without further purification. Spectroscopic data are in agreement with the literature values.⁵⁶ **Method 2:** Following the procedure of Yip *et al.*,³¹⁰ to a mixture of EtOH/H₂O (1:1, 100 mL) at rt was added KOH (4.20 g, 74.8 mmol). After 5 min, the ester **2.34** (4.25 g, 17.6 mmol) was added to the vigorously stirring mixture. After 24 hr the mixture was diluted with water (70 mL), and EtOH was removed under vacuum. EtOAc (100 mL) was added and the mixture was acidified with 2N HCl (pH < 2.0). The combined organic phase was extracted EtOAc (4 x 10 mL), dried (MgSO₄), and concentrated under reduced pressure to afford the diacid intermediate as a white solid, which was directly taken into the next step. The diacid was dissolved in 40% formaldehyde solution (26.0 mL, 35.1 mmol) and Et₂NH (3.60 mL, 35.1 mmol) was added dropwise at rt. Then, the reaction mixture was heated to reflux. After 15 h, the mixture was cooled to rt, CH₂Cl₂ (70 mL) and sat. aq. NaHCO₃ (70 mL) were added. The organic layer was separated, washing with saturated NaHCO₃ solution (5 x 60 mL). The combined aqueous layers were acidified with 2.0 N HCl solution (pH < 2.0), extracted with Et₂O (6 x 100 mL), dried (MgSO₄), and concentrated under reduced pressure to afford the title acid **2.15** as a yellow oil (2.52 g, 16.3 mmol, 93% from ester). The crude product was used in subsequent reactions without further purification. Physical and spectroscopic data are consistent with literature values.⁵⁶ **¹H NMR (400 MHz, CDCl₃):** δ 6.30 (1H, s, =CHH), 5.65 (1H, d, *J* = 1.3 Hz, =CHH), 5.16–5.08 (1H, m, =CHCH₂), 2.33 (2H, t, *J* = 7.2 Hz, CH₂CH₂), 2.18 (2H, q, *J* = 7.5 Hz, CH₂CH₂), 1.69 (3H, s, CH₃), 1.61 (3H, s, CH₃), (OH signal not observed). **¹³C NMR (100 MHz, CDCl₃):** 172.7 (COOH), 139.7 (CCOOH), 132.5 (C(CH₃)₂), 127.2 (=CH₂), 123.1 (CH), 31.6 (CH₂), 26.9 (CH₂), 25.6 (CH₃), 17.7 (CH₃) ppm.

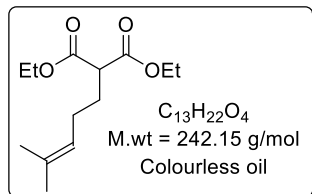
5-Bromo-2-methylpent-2-ene (**2.33**)



Following the procedure reported by Williams,²⁶⁸ to a stirred solution of MeMgBr (40.0 mL of 3.0 M in Et₂O, 120 mmol) in dry THF (40 mL), was added dropwise a solution of cyclopropyl methyl ketone **2.32** (10.0 mL, 100 mmol) in THF (15 mL). The mixture was heated to reflux for 20 min. On cooling to rt, the reaction mixture was slowly added to a cooled solution of conc. H₂SO₄ in water (1:2, 75 mL) at a rate that ensured that the temperature did not rise above 10 °C. Stirring was continued for 30 min. The organic layer was then separated, the aqueous solution was extracted with Et₂O (3 x 50 mL) and the combined organic phase was washed with sat. aq. NaHCO₃ (50 mL) and brine (30 mL). The organic layer was dried (Na₂SO₄), filtered and the solvent was removed *in vacuo*. The crude product was distilled under reduced pressure (60–65 °C/water aspirator) to afford the product **2.33** as a colourless oil (8.00 g, 50.0 mmol, 50%). Physical and spectroscopic data were consistent with reported values.³¹¹ **¹H NMR (400 MHz, CDCl₃):** δ 5.17–5.09 (1H, m, CHCH₂), 3.34 (2H, t, *J* = 7.2 Hz,

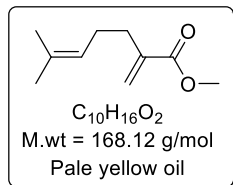
CH_2Br), 2.56 (2H, q, $J = 7.2$ Hz, CHCH_2), 1.72 (3H, m, CH_3), 1.64 (3H, s, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 135.0 (C), 120.9 (CH), 34.3 (CH_2Br), 31.8 (CH_2), 25.7 (CH_3), 17.9 (CH_3).

Diethyl 2-(4-methylpent-3-en-1-yl)malonate (2.34)



By adaption of a procedure by Klahn *et al.*,³¹² to suspension of oven dried (200 °C) K_2CO_3 (6.77 g, 49.0 mmol) in dry acetone (49 mL) under N_2 was added diethyl malonate (7.90 g, 7.5 mL, 49.0 mmol) and alkyl halide **2.33** (3.30 mL, 4.00 g, 24.5 mmol). The suspension was stirred at rt for 48 h. The reaction was quenched by sat. aq. NH_4Cl (40 mL) and the aqueous phase was extracted with EtOAc (3 x 60 mL), dried (MgSO_4), and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2) eluting with $\text{Et}_2\text{O}/\text{PE}$ (2%) to afford alkylated malonate **2.34** as a colourless oil (4.60 g, 19.1 mmol, 78%). Physical and spectroscopic data are consistent with literature values.³¹³ ^1H NMR (400 MHz, CDCl_3) δ 5.11–5.05 (1H, m, $=\text{CHCH}_2$), 4.27–4.12 (4H, m, 2 x OCH_2), 3.33 (1H, t, $J = 7.3$ Hz, $\text{O}=\text{CCHC}=\text{O}$), 2.03 (2H, q, $J = 7.3$ Hz, CH_2CH_2), 1.85–1.97 (2H, m, CH_2CH_2), 1.69 (3H, d, $J = 0.8$ Hz, CH_3), 1.58 (3H, s, CH_3), 1.27 (6H, t, $J = 7.1$ Hz, 2 x CH_2CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3): 169.6 (2 x $\text{C}=\text{O}$), 133.2 (C), 122.8 ($\text{CH}=\text{CH}_2$), 61.2 (2 x OCH_2), 51.4 ($\text{O}=\text{CCHC}=\text{O}$), 28.8 (CH_2CH_2), 25.7 (CH_2CH_2 and CCH_3), 17.6 (CCH_3), 14.0 (2 x CH_3) ppm.

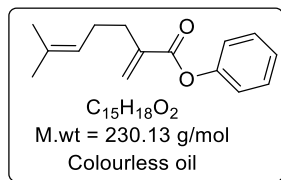
Methyl 6-methyl-2-methylenehept-5-enoate (2.38)



Step 1: At 0 °C to a solution of diethyl phosphonoacetate **2.36** (8.73 mL, 10.0 g, 47.6 mmol) in THF (105 mL) was added NaH (2.09 g of a 60% dispersion in mineral oil, 52.3 mmol) portionwise (CAUTION: evolution of H_2 gas). The resultant suspension was stirred for 10 min at 0 °C. Then alkyl halide **2.33** was added dropwise and the solution was stirred for 24 h at rt. The reaction was quenched with H_2O (100 mL), and the organic phases were extracted with Et_2O (4 x 100 mL), dried (MgSO_4) and concentrated under reduced pressure to give a yellow oil. Purification by column chromatography (SiO_2) eluting with $\text{Et}_2\text{O}/\text{PE}$ (10%) gave the intermediate phosphonate **2.37** as a colourless oil (1.39 g, 4.76 mmol, 10%), which was used directly in the next step. More than 5.0 g of alkyl halide was recovered. **Step 2:** The phosphonate **2.37** was taken up in 40% formaldehyde solution (6.80 mL, 9.34 mmol) and Et_2NH (1.00 mL, 9.34 mmol) was added dropwise at rt. Then, the reaction mixture was heated to reflux. After 15 h, the mixture was cooled to rt and water (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with Et_2O (4 x 10 mL). The combined organic layers were dried (MgSO_4), filtered and the solvents were removed under reduced pressure. Purification by column chromatography (SiO_2) eluting with $\text{Et}_2\text{O}/\text{PE}$ (5%) gave the titled dienoate **2.38** as a pale yellow oil (0.630 g, 3.74 mmol, 80% from **2.37**). ^1H NMR (400 MHz, CDCl_3) δ 6.14 (1H, m, $=\text{CHH}$), 5.53 (1H, q, $J = 1.3$ Hz, $=\text{CHH}$), 5.16–5.07 (1H, m, CHCH_2), 3.78 (3H, s,

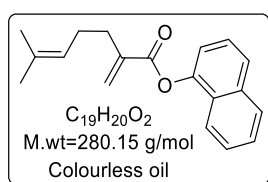
CH_3), 2.33 (2H, t, $J = 7.2$ Hz, CH_2), 2.16 (2H, q, $J = 7.6$ Hz, CH_2), 1.65–1.72 (3H, m, CH_3), 1.60 (3H, s, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3): 167.8 (C=O), 140.3 (C=CH₂), 133.8 (C-Ar), 132.3 (C(CH₃)₂), 124.8 (=CH₂), 123.3 (CH), 51.7 (OCH₃), 32.1 (CH₂), 26.9 (CH₂), 25.6 (CH₃), 17.7 (CH₃) ppm.

Phenyl 6-methyl-2-methylenehept-5-enoate (2.39)

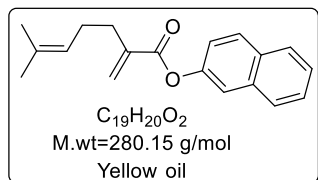


To a solution of the acid **3.25** (200 mg, 1.30 mmol) and DMF (0.130 mL, 1.70 mmol) in CH_2Cl_2 (2.3 mL) was added oxalyl chloride (0.200 mL, 1.7 mmol) dropwise at 0 °C. The mixture was stirred at rt for 2 h after which time gas evolution ceased. To a solution of phenol (183 mg, 1.90 mmol) in CH_2Cl_2 (6.0 mL) was added Et_3N (0.300 mL, 1.60 mmol) at 0 °C. The mixture stirred for 30 min at 0 °C before adding freshly prepared acid chloride dropwise. The reaction was allowed to warm to rt and stirred for 2 h. The mixture was concentrated under reduced pressure and purified by column chromatography (SiO_2) eluting with Et_2O /Hex (5%) to give the title compound **2.39** as colourless oil (251 mg, 1.10 mmol, 84%). **FT-IR** ν_{max} (neat): 2927(s), 2855 (s), 1733 (s), 1633 (s), 1592 (s), 1493 (w), 1455 (w), 1194 (s), 1162 (s) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.32 (2H, m, CH-Ar), 7.17 (1H, m, CH-Ar), 7.04 (2H, m, CH-Ar), 6.31 (1H, s, =CHH), 5.64 (1H, d, $J = 1.2$ Hz, =CHH), 5.12–5.05 (1H, m, =CHCH₂), 2.34 (2H, t, $J = 7.6$ Hz, CH_2CH_2), 2.18 (2H, q, $J = 7.6$ Hz, CH_2CH_2), 1.68 (3H, s, CH_3), 1.60 (3H, s, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3): 165.7 (C=O), 150.9 (C-Ar), 139.9 (C=CH₂), 132.6 (C(CH₃)₂), 129.4 (2 x CH-Ar), 126.6 (CH-Ar), 125.7 (=CH₂), 123.2 (CH), 121.6 (2 x CH-Ar), 32.2 (CH₂), 27.0 (CH₂), 25.7 (CH₃), 17.7 (CH₃) ppm. **LRMS**: (ES+) m/z 231 [M+H]⁺. **HRMS**: (ES+) m/z $\text{C}_{15}\text{H}_{19}\text{O}_2$ Calculated: 231.1372, found: 231.1380.

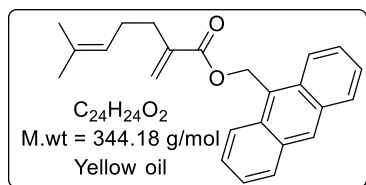
Naphthalen-1-yl 6-methyl-2-methylenehept-5-enoate (2.40)



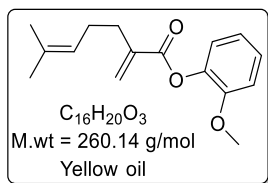
The title compound was prepared according to the method used for the synthesis of dienoate **2.39**, except using 1-Naphthol (281 mg, 1.60 mmol) and acid **2.15** (200 mg, 1.30 mmol). Purification by column chromatography (SiO_2) eluting with Et_2O /Hex (5%) gave the title dienoate **2.40** as colourless oil (273 mg, 1.00 mmol, 75%). **FT-IR** ν_{max} (neat): 3056 (br), 2926(s), 2854 (s), 1734 (s), 1632 (s), 1598 (s), 1508(w), 1257 (s), 1153 (s), 1112 (s) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.94–7.85 (2H, m, 2 x CH-Ar), 7.77 (1H, d, $J = 8.3$ Hz, CH-Ar), 7.55–7.48 (3H, m, 3 x CH-Ar), 7.30 (1H, m, CH-Ar), 6.59 (1H, s, =CHH), 5.85 (1H, d, $J = 1.2$ Hz, =CHH), 5.26–5.19 (1H, m, =CHCH₂), 2.56 (2H, t, $J = 7.3$ Hz, CH_2C), 2.34 (2H, q, $J = 7.4$ Hz, =CHCH₂), 1.75 (3H, s, CH_3), 1.68 (3H, s, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3): 166.0 (C=O), 147.1 (C-Ar), 140.1 (C=CH₂), 135.0 (C-Ar), 133.0 (C(CH₃)₂), 128.3 (CH-Ar), 127.3 (CH-Ar), 127.2 (C-Ar), 126.71 (CH-Ar), 127.7 (CH-Ar), 126.2 (CH-Ar), 125.7 (=CH₂), 123.5 (CH-Ar), 121.5 (2 x CH-Ar), 118.4 (CH-Ar), 32.5 (CH₂), 27.4 (CH₂), 26.0 (CH₃), 18.1 (CH₃) ppm. **LRMS**: (ES+) m/z 281 [M+H]⁺. **HRMS**: (ES+) m/z $\text{C}_{19}\text{H}_{21}\text{O}_2$ Calculated: 281.1533, found: 281.1536.

Naphthalen-2-yl 6-methyl-2-methylenehept-5-enoate (2.41)

The title compound was prepared according to the outlined method used for the synthesis of dienolate **2.39**, except using 2-Naphthol (280 mg, 1.60 mmol) with acid **2.15** (200 mg, 1.30 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/Hex (5%) gave the title dienolate **2.41** as yellow oil (287 mg, 1.03 mmol, 79%). **FT-IR** ν_{max} (neat): 3057 (s), 2966 (s), 2923 (s), 1731 (s), 1630 (s), 1511 (s), 1464 (s), 1264 (s), 1240 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 7.91–7.81 (m, 3H, 3 x CH-Ar), 7.62 (1H, d, *J* = 2.1 Hz, CH-Ar), 7.54–7.45 (2H, m, 2 x CH-Ar), 7.28–7.24 (1H, m, CH-Ar), 6.47 (1H, s, CHH), 5.77 (1H, d, *J* = 1.2 Hz, CHH), 5.22–5.15 (1H, m, CH), 2.50 (2H, t, *J* = 7.6 Hz, CH₂), 2.31 (2H, q, *J* = 7.3 Hz, CH₂), 1.74 (3H, s, CH₃), 1.67 (3H, s, CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 166.0 (C=O), 148.6 (C-Ar), 140.0 (C=CH₂), 133.8 (C-Ar), 132.6 (C(CH₃)₂), 131.5 (CH-Ar), 129.4 (C-Ar), 127.8 (CH-Ar), 127.7 (CH-Ar), 126.8 (CH-Ar), 126.5 (CH-Ar), 125.7 (=CH₂), 123.2 (CH), 121.2 (CH), 118.6 (CH-Ar), 32.2 (CH₂), 27.1 (CH₂), 25.7 (CH₃), 17.8 (CH₃) ppm. **LRMS**: (ES+) *m/z* 281 [M+H]⁺. **HRMS**: (ES+) *m/z* C₁₉H₂₀O₂Na Calculated:303.1356, found:303.1353 ([M+Na]⁺).

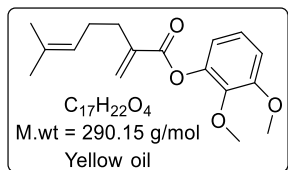
Anthracen-9-ylmethyl 7-methyl-3-methyleneoct-6-enoate (2.42)

The title compound was prepared according to the method used for the synthesis of dienolate **2.39**, except using anthracene methanol (405 mg, 1.95 mmol) with acid **2.15** (200 mg, 1.30 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/Hex (5%) gave the title dienolate **2.42** as yellow oil (380 mg, 1.10 mmol, 85%). **FT-IR** ν_{max} (neat): 3053 (s), 2916 (s), 2854 (s), 1709 (s), 1625 (s), 1527 (s), 1446(s), 1375 (s), 1281 (w), 1164 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.52 (1H, s, CH-Ar), 8.39 (2H, d, *J* = 8.7 Hz, 2 x CH-Ar), 8.05 (2H, d, *J* = 8.5 Hz, 2 x CH-Ar), 7.63–7.55 (2H, m, 2 x CH-Ar), 7.53–7.47 (2H, m, 2 x CH-Ar), 6.24 (2H, s, OCH₂), 6.12 (1H, d, *J* = 1.1 Hz, =CHH), 5.49 (1H, q, *J* = 1.3 Hz, CHH), 5.09–5.02 (1H, m, CHCH₂), 2.31 (2H, t, *J* = 7.6 Hz, CH₂C=), 2.12 (2H, br d, *J* = 7.6 Hz, CH₂), 1.63 (3H, s, CH₃), 1.45 (3H, m, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 167.8 (C=O), 140.5 (C=CH₂), 132.6 (C-Ar), 131.7 (CH-Ar), 131.4 (=C(CH₃)₂), 129.4 (C-Ar), 129.37 (CH), 126.9 (CH-Ar), 126.7 (CH-Ar), 125.8 (=CH₂), 125.4 (CH-Ar), 124.3 (CH), 123.6 (CH-Ar), 59.3 (CH₂-OAr), 32.3 (CH₂), 27.2 (CH₂), 25.7 (CH₃), 17.8 (CH₃) ppm. **LRMS**: (ES+) *m/z* 689 [2M+H]⁺. **HRMS**: (EI) *m/z* C₂₄H₂₄O₂⁺ Calculated:344.1768, found:344.1771.

2-methoxyphenyl 6-methyl-2-methylenehept-5-enoate (2.43)

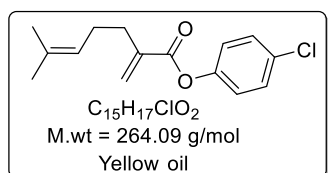
The title compound was prepared according to the method used for the synthesis of dienoate **2.39**, except using 2-methoxyphenol (214 mg, 1.73 mmol) with acid **2.15** (178 mg, 1.16 mmol). Purification by column chromatography (SiO_2) eluting with Et_2O/Hex (5%) gave the title dienoate

2.43 as yellow oil (241 mg, 0.930 mmol, 80%). **FT-IR** ν_{max} (neat): 2924 (s), 1736 (s), 1632 (s), 1500 (s), 1456 (s), 1376 (s), 1336 (s), 1256 (s), 1197 (s) cm^{-1} . **^1H NMR (400 MHz, $CDCl_3$)**: δ 7.22 (1H, ddd, J = 8.2, 7.4, 1.7 Hz, CH-Ar), 7.10 (1H, dd, J = 7.9, 1.7 Hz, CH-Ar), 7.02–6.94 (2H, m, 2 x CH-Ar), 6.41 (1H, s, =CHH), 5.72 (1H, d, J = 1.3 Hz, =CHH), 5.22–5.16 (1H, m, CHCH₂), 3.83 (3H, s, OCH₃), 2.47 (2H, t, J = 7.3 Hz, =CCH₂), 2.35–2.25 (2H, m, CH₂), 1.73 (3H, s, CH₃), 1.65 (3H, m, CH₃) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: 165.3 (C=O), 151.3 (COCH₃), 140.0 (C-Ar), 139.7 (C=CH₂), 132.4 (C(CH₃)₂), 126.6 (=CH₂), 126.5 (CH-Ar), 123.3 (=CH-CH₂), 122.8 (CH-Ar), 120.7 (CH-Ar), 112.5 (CH-Ar), 55.8 (OCH₃), 32.3 (CH₂), 26.9 (CH₂), 25.6 (CH₃), 17.7 (CH₃) ppm. **LRMS**: (ES+) m/z : 261 [M+H]⁺. **HRMS**: (ES+) m/z $C_{16}H_{21}O_3$ Calculated: 261.1485, found 261.1483.

2,3-dimethoxyphenyl 6-methyl-2-methylenehept-5-enoate (2.44)

The title compound was prepared according to the method used for the synthesis of dienoate **2.39**, except using 2,3-dimethoxyphenol (300 mg, 1.95 mmol) with acid **2.15** (200 mg, 1.30 mmol). Purification by column

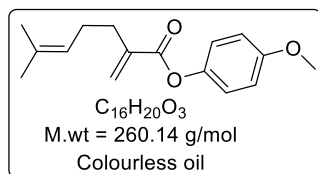
chromatography (SiO_2) eluting with Et_2O/Hex (5%) gave the title compound **2.44** as yellow oil (152 mg, 0.990 mmol, 76%). **FT-IR** ν_{max} (neat): 3936 (s), 1735 (s), 1632 (s), 1600 (s), 1492(s), 1473 (s), 1277 (s), 1243 (s), 1158 (w) cm^{-1} . **^1H NMR (400 MHz, $CDCl_3$)**: δ 7.04 (1H, t, J = 8.3 Hz, CH-Ar), 6.83 (1H, dd, J = 8.3, 1.4 Hz, CH-Ar), 6.72 (1H, dd, J = 8.3, 1.4 Hz, CH-Ar), 6.41 (s, 1H, =CHH), 5.73 (1H, d, J = 1.2 Hz, =CHH), 5.22–5.14 (1H, m, =CHCH₂), 3.88 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 2.47 (2H, t, J = 7.6 Hz, CCH₂), 2.28 (2H, q, J = 7.2 Hz, =CHCH₂), 1.72 (3H, s, CH₃), 1.64 (3H, s, CH₃) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: 165.4 (C=O), 153.8 (C-OCH₃), 144.5 (C-Ar), 141.2 (C-OCH₃), 139.7 (C=CH₂), 132.5 (=C(CH₃)₂), 126.6 (=CH₂), 123.4 (=CH-CH₂), 123.2 (CH-Ar), 115.2 (CH-Ar), 110.1 (CH-Ar), 60.7 (OCH₃), 56.0 (OCH₃), 32.2 (CH₂), 26.9 (CH₂), 25.6 (CH₃), 17.7 (CH₃) ppm. **LRMS**: (ES+) m/z : 291 [M+H]⁺. **HRMS**: (ES+) m/z $C_{17}H_{23}O_4$ Calculated: 291.1594, found 291.1591.

4-Chlorophenyl 6-methyl-2-methylenehept-5-enoate (2.45)

The title compound was prepared according to the method used for the synthesis of dienoate **2.39**, except using 4-chlorophenol (250 mg, 1.95 mmol) and acid **2.15** (200 mg, 1.30 mmol). Purification by column chromatography (SiO_2) eluting with Et_2O/Hex (5%) gave the title

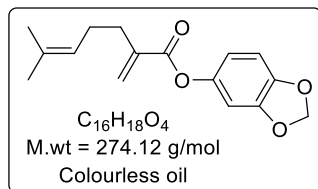
dienoate as yellow oil **2.45** (275 mg, 1.04 mmol, 80%). **FT-IR** $\nu_{\max}$ (neat): 2926 (s), 2856 (s), 1735 (s), 1632 (s), 1486 (s), 1439 (s), 1199 (s), 1084 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.40–7.34 (2H, m, 2 x CH-Ar), 7.11–7.05 (2H, m, 2 x CH-Ar), 6.39 (1H, s, =CHH), 5.75 (1H, d, J = 1.4 Hz, CH), 5.21–5.12 (1H, m, =CHCH₂), 2.44 (2H, t, J = 7.2 Hz, CH₂), 2.25 (2H, q, J = 7.2 Hz, CH₂), 1.72 (3H, s, CH₃), 1.64 (3H, s, CH₃) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 165.4 (C=O), 149.4 (C-Ar), 139.7 (C=CH₂), 132.6 (=C(CH₃)₂), 131.0 (C-Cl), 129.4 (2 x CH-Ar), 127.2 (=CH₂), 123.1 (2 x CH-Ar), 123.0 (=CH), 32.0 (CH₂), 26.9 (CH₂), 25.7 (CH₃), 17.7 (CH₃) ppm. **LRMS**: (ES+) m/z : 265 (100%, $\text{C}_{15}\text{H}_{18}^{35}\text{ClO}_2$) and 267 (30%, $\text{C}_{15}\text{H}_{18}^{37}\text{ClO}_2$). **HRMS**: (ES+) m/z $\text{C}_{15}\text{H}_{17}^{35}\text{ClO}_2\text{Na}$ Calculated: 287.0809, found: 287.0806.

4-methoxyphenyl 6-methyl-2-methylenehept-5-enoate (**2.46**)



To a solution of the acid **2.15** (108 mg, 0.700 mmol) in CH_2Cl_2 (2.3 mL) was added 4-methoxyphenol (110 mg, 0.700 mmol), $\text{Et}_2i\text{-PrN}$ (0.130 mL, 0.700 mmol), DMAP (17.0 mg, 0.140 mmol) followed by DCC (0.14 g, 0.700 mmol) at rt. The reaction was and stirred at rt for 15 h, then the volatiles were removed under reduced pressure. The crude product was purified by column (SiO_2) eluting with Et_2O /Hex (2%) to afford the title dienoate **2.46** as a colourless oil (0.109 g, 0.420 mmol, 60%). **FT-IR** $\nu_{\max}$ (neat): 2925 (s), 1731 (s), 1504 (s), 1376 (s), 1191 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.07–7.02 (2H, m, CH-Ar), 6.94–6.88 (2H, m, CH-Ar), 6.38 (s, 1H, C=CHH), 5.71 (1H, q, J = 1.2 Hz, =CHH), 5.20–5.13 (1H, m, =CHCH₂), 3.81 (3H, s, OCH_3), 2.41–2.48 (2H, m, CH₂), 2.26 (2H, q, J = 7.3 Hz, =CHCH₂), 1.72 (3H, s with unresolved coupling, CH₃), 1.64 (3H, s, CH₃) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 166.0 (C=O), 157.2 (C-Ar), 144.4 (C-Ar), 140.0 (C=CH₂), 132.5 (=C(CH₃)₂), 126.4 (C=CH₂), 123.2 (CH-CH₂), 122.3 (2 x CH-Ar), 114.4 (2 x CH-Ar), 55.6 (OCH_3), 32.1 (CH₂), 27.0 (CH₂), 25.7 (CH₃), 17.7 (CH₃) ppm. **LRMS**: (ES+) m/z : 261 $[\text{M}+\text{H}]^+$. **HRMS**: (ES+) m/z $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Na}$ Calculated: 283.1305, found: 283.1305.

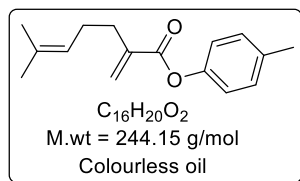
Benzo[d][1,3]dioxol-5-yl 6-methyl-2-methylenehept-5-enoate (**2.47**)



The title compound was prepared according to the method used for the synthesis of dienoate **2.46**, except using sesamol (110 mg, 0.800 mmol) and acid **2.15** (123 mg, 0.800 mmol). Purification by column chromatography (SiO_2) eluting with Et_2O /PE (2%) gave the title compound **2.47** as colourless oil (109 mg, 0.400 mmol, 50%). **FT-IR** $\nu_{\max}$ (neat): 2921 (s), 1733 (s), 1634 (s), 1502 (s), 1482 (s), 1376 (s), 1169 (s), 1124 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 6.79 (1H, d, J = 8.3 Hz, CH-Ar), 6.64 (1H, d, J = 2.2, Hz, CH-Ar), 6.56 (1H, dd, J = 8.3, 2.3 Hz, CH-Ar), 6.31 (s, 1H, =CHH), 5.99 (2H, s, OCH_2O), 5.71 (1H, s, C=CHH), 5.16 (1H, br t, J = 7.2 Hz, =CHCH₂), 2.43 (2H, t, J = 7.2 Hz, CH₂), 2.24 (2H, q, J = 7.2 Hz, CH₂), 1.71 (3H, s, CH₃), 1.63 (3H, s, CH₃) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 166.0 (C=O), 148.5 (C-Ar), 145.3 (C-Ar), 145.2 (C-Ar), 139.9 (C=CH₂), 132.6 (C(CH₃)₂), 126.6

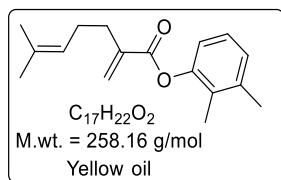
(C=CH₂), 123.2 (=CH-CH₂), 114.0 (CH-Ar), 108.0 (CH-Ar), 103.8 (CH-Ar), 101.7 (OCH₂O), 32.1 (CH₂), 27.0 (CH₂), 25.7 (CH₃), 17.7 (CH₃). **LRMS:** (ES+) *m/z* C₁₆H₁₉O₄: 275 [M+H]⁺. **HRMS:** (ES+) *m/z* C₁₆H₁₈O₄Na Calculated: 297.1098, found: 297.1097.

p-Tolyl 6-methyl-2-methylenehept-5-enoate (**2.48**)

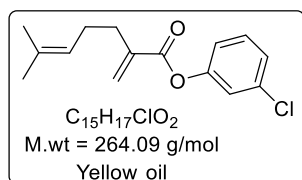


The title compound was prepared according to the method used for the synthesis of dienoate **2.46**, except using 4-methylphenol (70.3 mg, 0.650 mmol) and acid **2.15** (100 mg, 0.650 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound **2.48** as colourless oil (87.9 mg, 0.360 mmol, 55%). **FT-IR** *v*_{max} (neat): 2926 (s), 1733 (s), 1633 (s), 1507 (s), 1447 (s), 1197 (s), 1165 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.20 (2H, d, *J* = 7.7 Hz, CH-Ar), 7.04–6.98 (2H, m, CH-Ar), 6.39 (s, 1H, =CHH), 5.72 (1H, q, *J* = 1.2 Hz, =CHH), 5.22–5.14 (1H, m, =CHCH₂), 2.46 (2H, t, *J* = 7.2 Hz, CH₂), 2.37 (3H, s, Ar-CH₃), 2.27 (2H, q, *J* = 7.2 Hz, CH₂), 1.74–1.71 (3H, m, CH₃), 1.65 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.9 (C=O), 148.7 (C-Ar), 140.1 (C=CH₂), 135.3 (C-Ar), 132.6 (=C(CH₃)₂), 129.9 (CH-Ar), 126.4 (C=CH₂), 123.3 (=CH-CH₂), 121.3 (CH-Ar), 32.2 (CH₂), 27.0 (CH₂), 25.7 (CH₃), 20.9 (Ar-CH₃), 17.7 (CH₃) ppm. **LRMS:** (ES+) *m/z*: 245 [M+H]⁺. **HRMS:** (ES+) *m/z* C₁₆H₂₀O₂Na Calculated: 267.1354, found: 267.1356.

2,3-dimethylphenyl 6-methyl-2-methylenehept-5-enoate (**2.49**)

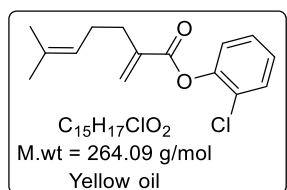


The title compound was prepared according to the method used for the synthesis of dienoate **2.46**, except using 2,3-dimethylphenol (0.240 g, 1.95 mmol) and acid **2.15** (0.300 g, 1.95 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound **2.49** as yellow oil (0.450 g, 1.76 mmol, 90%). **FT-IR** *v*_{max} (neat): 2924 (s), 1732 (s), 1633 (s), 1468 (s), 1157 (s), 1086 (w), 1115 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.03–7.15 (2H, m, CH-Ar), 6.90 (1 H, d, *J* = 8.0 Hz, CH-Ar), 6.43 (1H, s, C=CHH), 5.74 (1H, q, *J* = 1.2 Hz, C=CHH), 5.22–5.14 (1H, m, =CHCH₂), 2.47 (2H, t, *J* = 7.6 Hz, CH₂), 2.27–2.33 (5H, m, CH₂ and Ar-CH₃) 2.09 (3H, s, Ar-CH₃), 1.73 (3H, s with unresolved coupling, CH₃), 1.65 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.6 (C=O), 149.4 (OC-Ar), 140.0 (C=CH₂), 138.5 (C-CH₃), 132.5 (=C(CH₃)₂), 128.8 (C-CH₃), 127.4 (CH-Ar), 126.4 (CH-Ar), 126.0 (C=CH₂), 123.2 (CHCH₂), 119.4 (CH-Ar), 32.2 (CH₂), 27.1 (CH₂), 25.7 (CH₃), 20.0 (Ar-CH₃), 17.8 (CH₃), 12.4 (Ar-CH₃) ppm. **LRMS:** (ES+) *m/z*: 259 [M+H]⁺. **HRMS:** (ES+) *m/z* C₁₇H₂₃O₂ Calculated: 259.1685, found: 259.1693.

3-Chlorophenyl 6-methyl-2-methylenehept-5-enoate (2.50)

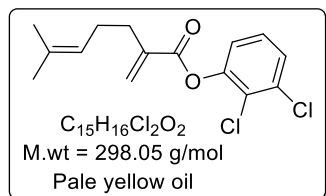
The title compound was prepared according to the method used for the synthesis of dienoate **2.46**, except using 3-chlorophenol (0.210 mL, 1.95 mmol) and acid **2.15** (0.300 g, 1.95 mmol). Purification by column

chromatography (SiO_2) eluting with Et_2O/PE (2%) gave the title dienoate **2.50** as a yellow oil (0.440 g, 1.66 mmol, 85%). **FT-IR ν_{max} (neat):** 2967 (s), 2952 (s), 1740 (s), 1632 (s), 1476 (s), 1447 (s), 1129 (s), 1157 (s), 1111 (w), 1090 (w) cm^{-1} . **^1H NMR (400 MHz, $CDCl_3$):** δ 7.33 (1H, t, J = 8.2 Hz, CH-Ar), 7.23 (1 H, ddd, J = 8.1, 2.0, 1.0 Hz, CH-Ar), 7.18 (1H, t, J = 2.0 Hz, CH-Ar), 7.04 (1H, ddd, J = 8.1, 2.0, 1.0 Hz, CH-Ar), 6.41–6.38 (1H, m, C=CHH), 5.75 (1H, q, J = 1.2 Hz, =CHH), 5.21–5.12 (1H, m, CHCH₂), 2.47–2.39 (2H, m, CH₂), 2.25 (2H, q, J = 7.2 Hz, CH₂), 1.72 (3H, d, J = 1.2 Hz, CH₃), 1.64 (3H, s, CH₃) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** 164.8 (C=O), 147.2 (OC-Ar), 139.3 (C=CH₂), 132.6 (C-Cl), 130.3 (=C(CH₃)₂), 127.7 (CH-Ar), 127.4 (CH-Ar), 127.0 (C=CH₂), 126.9 (CHCH₂), 123.8 (CH-Ar), 123.1 (CH-Ar), 32.1 (CH₂), 27.0 (CH₂), 25.7 (CH₃), 17.7 (CH₃) ppm. **LRMS:** (ES+) m/z : 265 (100%, $C_{15}H_{18}^{35}ClO_2$) and 267 (30%, $C_{15}H_{18}^{37}ClO_2$). **HRMS:** (ES+) m/z $C_{15}H_{17}^{35}ClO_2Na$ Calculated: 287.0804, found: 287.0809.

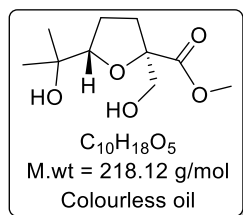
2-Chlorophenyl 6-methyl-2-methylenehept-5-enoate (2.51)

The title compound was prepared according to the method used for the synthesis of dienoate **2.46**, except using 2-chlorophenol (0.200 mL, 1.95 mmol) and acid **2.15** (0.300 g, 1.95 mmol). Purification by column chromatography (SiO_2) eluting with Et_2O/PE (2%) gave the title dienoate

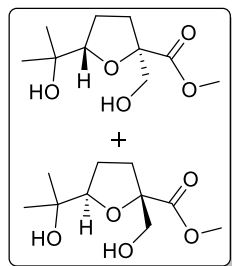
2.51 as yellow oil (0.460 g, 1.74 mmol, 89%). **FT-IR ν_{max} (neat):** 2967 (s), 2925 (s), 1740 (s), 1632 (s), 1476 (s), 1447 (s), 1129 (s), 1157 (s), 1111 (w), 1090 (w) cm^{-1} . **^1H NMR (400 MHz, $CDCl_3$):** δ 7.49–7.44 (1H, m, CH-Ar), 7.33–7.28 (1 H, m, CH-Ar), 7.24–7.17 (2 H, m, 2 x CH-Ar), 7.49–7.45 (1H, m, C=CHH), 5.78 (1H, q, J = 1.2 Hz, C=CHH), 5.21–5.13 (1H, m, =CHCH₂), 2.48 (2H, t, J = 7.6 Hz, CH₂), 2.29 (2H, q, J = 7.2 Hz, CH₂), 1.72 (3H, d, J = 1.1 Hz, CH₃), 1.64 (3H, s, CH₃) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** 164.8 (C=O), 147.2 (OC-Ar), 139.3 (C=CH₂), 132.6 (C(CH₃)₂), 130.3 (CH-Ar), 127.7 (CH-Ar), 127.4 (CH-Ar), 127.0 (C-Cl), 126.9 (C=CH₂), 123.8 (CHCH₂), 123.2 (CH-Ar), 32.1 (CH₂), 27.0 (CH₂), 25.7 (CH₃), 17.7 (CH₃) ppm. **LRMS:** (ES+) m/z : 265 (100%, $C_{15}H_{18}^{35}ClO_2$) and 267 (30%, $C_{15}H_{18}^{37}ClO_2$). **HRMS:** (ES+) m/z $C_{15}H_{17}^{35}ClO_2Na$ Calculated: 287.0804, found: 287.0809.

2,3-dichlorophenyl 6-methyl-2-methylenehept-5-enoate (2.52)

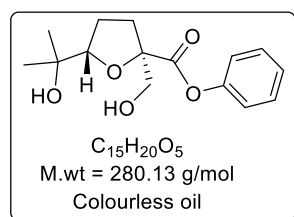
The title compound was prepared according to the method used for the synthesis of dienoate **2.46**, except using 2,3-dichlorophenol (0.210 g, 1.30 mmol) with acid **2.15** (0.200 g, 1.30 mmol). The crude product was purified by column chromatography (SiO₂) eluting with Et₂O/PE (2%) to afford the titled dienoate **2.52** as a pale yellow oil (0.340 g, 1.14 mmol, 88%). **FT-IR** $\nu_{\max}$ (neat): 2925 (s), 1741 (s), 1632 (s), 1576 (s), 1449 (s), 1238 (s), 1086 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.38 (1H, dd, J = 8.1, 1.5 Hz, CH-Ar), 7.25 (1H, t, J = 8.2 Hz, CH-Ar), 7.12 (1H, dd, J = 8.1, 1.5 Hz, CH-Ar), 6.48 (1H, s, =CHH), 5.80 (1H, d, J = 1.2 Hz, CH), 5.20–5.12 (1H, m, =CHCH₂), 2.47 (2H, t, J = 7.4 Hz, CH₂), 2.27 (2H, q, J = 7.4 Hz, CH₂), 1.72 (3H, s, CH₃), 1.64 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 165.4 (C=O), 148.5 (C-Ar), 139.0 (C=CH₂), 133.9 (C-Cl), 132.7 (C(CH₃)₂), 127.8 (CH-Ar), 127.7 (CH-Ar), 127.4 (C-Cl), 126.4 (C=CH₂), 123.0 (CHCH₂), 122.0 (=CH-Ar), 32.0 (CH₂), 26.9 (CH₂), 25.7 (CH₃), 17.8 (CH₃) ppm. **LRMS**: (ES+) m/z : 299 [M+H]⁺ (C₁₅H₁₇³⁵Cl₂O₂). **HRMS**: (ES+) m/z C₁₅H₁₆³⁵Cl₂O₂Na Calculated:321.0416, found:321.0420.

Methyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.53)

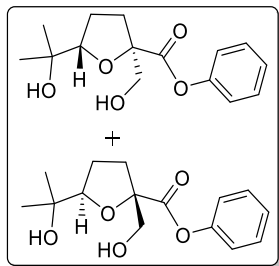
Following the procedure reported by Brown and co-worker,⁴⁸ at –60 °C to a solution of diene **2.38** (20.0 mg, 0.120 mmol), **CPTC** (8.0 mg, 0.012 mmol), and AcOH (0.080 mL, 0.75 mmol) in CH₂Cl₂ (1.4 mL), was added powdered KMnO₄ (30.0 mg, 0.19 mmol) in one batch. After 4 h of vigorous stirring, the reaction was quenched at –60 °C by addition of Na₂S₂O₅ (1.0 mL of sat. aq.), H₂O (1.0 mL) and CH₂Cl₂ (1.0 mL), then the mixture was allowed to warm to rt. The organic phases were separated and the aqueous phase extracted with EtOAc (4 x 5.0 mL). The combined organic phases were dried (Na₂SO₄) and concentrated under reduced pressure to give yellow oil. Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave racemic THF-diol **2.53** (16.8 mg, 0.0770 mmol, 80%) as a colourless oil. Physical and spectroscopic data are consistent with literature values.⁵⁶ **¹H NMR (400 MHz, CDCl₃)**: δ 4.06 (1H, t, J = 7.4 Hz, CH-THF), 3.87 (1H, m, CHHOH), 2.78–3.72 (4H, s, OCH₃ and CHHOH), 2.22–2.04 (2H, m, CH₂-THF), 2.01–1.87 (2H, m, CH₂-THF), 1.31 (3H, s, CH₃), 1.15 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 174.5 (C=O), 87.6 (CH-THF), 86.8 (C-THF), 71.5 ((CH₃)₂COH), 66.1 (CH₂OH), 52.3 (OCH₃), 32.0 (CH₂-THF), 27.5 (CH₂-THF), 26.0 (CH₃), 25.0 (CH₃) ppm.

(rac)-methyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.52)

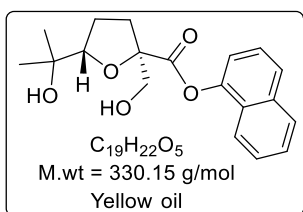
At $-30\text{ }^{\circ}\text{C}$, powdered KMnO_4 (26.9 mg, 0.17 mmol) was added in one batch to a rapidly stirred solution of diene **2.38** (22.0 mg, 0.13 mmol) and adogen 464 (0.02 mL, 0.02 mmol) in AcOH/acetone 2:3 (2.0 mL). The reaction was allowed to warm to $-10\text{ }^{\circ}\text{C}$ over 10 min and then stirred for 20 min at $-10\text{ }^{\circ}\text{C}$. The reaction was quenched by addition of iced $\text{Na}_2\text{S}_2\text{O}_5$ (1.0 mL of sat. aq.) at $-10\text{ }^{\circ}\text{C}$, H_2O (1.0 mL) and EtOAc (1.0 mL), then the mixture was allowed to warm to rt. The organic phases were separated and the aqueous phase extracted with EtOAc (4 x 2.0 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure to afford a yellow oil. Purification by column chromatography (SiO_2) eluting with EtOAc/PE (40%) gave racemic THF-diol **(rac)-2.52** (26.6 mg, 0.122 mmol, 94%) as colourless oil. Spectroscopic and physical data are consistent with that reported above.

Phenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.54)

The title compound was prepared according to the method used for the synthesis of THF-diol **2.38**, except using diene **2.39** (68.0 mg, 0.260 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (40%) gave enantiomerically enriched THF-diol **2.54** (70.0 mg, 0.25 mmol, 83%) as a colourless oil. Spectroscopic data are reported for a mixture of two enantiomers ($ee = 55\%$) determined by chiral HPLC analysis. $[\alpha]^{20.5}_{\text{D}} = +1.0$ (c 1.7, CHCl_3). **FT-IR** ν_{max} (neat): 3359 (br), 2975(s), 1748 (s), 1592 (s), 1492 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.39 (2H, t, $J = 7.3$ Hz, 2 x CH-Ar), 7.27–7.20 (1H, m, CH-Ar), 7.14–7.07 (2H, m, 2 x CH-Ar), 4.15 (1H, t, $J = 7.4$ Hz, CH-THF), 4.06 (1H, d, $J = 11.5$ Hz, CHHOH), 3.88 (1H, d, $J = 11.5$ Hz, CHHOH), 3.18 (2H, s, 2 x OH), 2.36–2.24 (2H, m, CH_2CH_2), 2.02 (2H, q, $J = 7.6$ Hz, CH_2CH_2), 1.34 (3H, s, CH_3), 1.18 (3H, s, CH_3) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 172.9(C=O), 150.8 (C), 129.8 (2 x CH), 126.3 (CH), 121.6 (2 x CH), 88.1 (C-THF), 87.2 (C-THF), 71.9 (C-OH), 66.4 (CH_2OH), 32.5 ($\text{CH}_2\text{-THF}$), 27.8($\text{CH}_2\text{-THF}$), 26.4 (CH_3), 25.3 (CH_3) ppm. **LRMS**: (ES+) m/z 303 [$\text{M}+\text{Na}$] $^+$. **HRMS**: (ES+) m/z $\text{C}_{15}\text{H}_{20}\text{O}_5\text{Na}$ Calculated: 303.11201, found: 303.1203. **HPLC**: Chiralpak[®] OD-H – (flow rate: 1.0 mL/min, eluent: 2.5% isopropanol/hexane, Retention times = 32.30 (minor), 34.52 (major)).

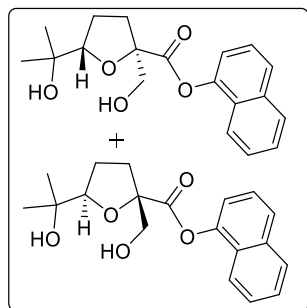
(rac)-Phenyl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.54)

Prepared using the method described for **(rac)-2.53** except using diene **2.39** (62.0 mg, 0.27 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave racemic THF-diol **(rac)-2.53** (67.9 mg, 0.24 mmol, 90%) as colourless solid as yellow oil. Spectroscopic and physical data are consistent with that reported above.

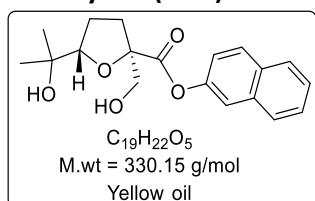
Naphthalen-1-yl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.55)

Method 1: The title compound was prepared according to the outlined method for **2.53**, except using diene **2.40** (71.0 mg, 0.25 mmol), KMnO₄ (64.5 mg, 0.40 mmol), CPTC (17.0 mg, 0.025 mmol), and AcOH (0.1 mL, 1.70 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **2.55** (75.2 mg, 0.23 mmol, 90%) as

yellow oil. Spectroscopic data are reported for a mixture of two enantiomers (ee = 90%) determined by HPLC analysis. **Method 2:** To a solution of 1-naphthol (231.0 mg, 1.60 mmol) in THF (5.0 mL) at -78 °C was added NaHMDS (1.6 mL, 1.0 M in THF). The solution was allowed to warm to -25 °C over 1.5 h whereupon a solution of **3.45a** and **3.45b** (110 mg, 0.20 mmol) in THF (2.0 mL) was added dropwise and stirred for 40 mins at rt. The reaction was quenched by NH₄Cl (10.0 mL) at -40 °C, extracted with CH₂Cl₂ (6 x 10.0 mL), dried (Na₂SO₄), and concentrated under reduced pressure. Purification by column chromatography eluting with EtOAc/Hex (40%) gave THF-diols **2.55a** and **2.55b** (20.0 mg, 0.06 mmol, 30%) as yellow oil. HPLC analysis was in agreement with those from CPTC oxidative cyclisation. $[\alpha]^{20.5}_D = +3.72$ (c 1.4, CHCl₃). **FT-IR** ν_{max} (neat): 3396 (br), 3054 (s), 2974(s), 1753(s), 1599 (s), 1462 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.98–7.84 (2H, m, 2 x CH-Ar), 7.77 (1H, d, *J* = 8.3 Hz, CH-Ar), 7.58–7.50 (2H, m, 2 x CH-Ar), 7.48 (1H, t, *J* = 7.8 Hz, CH-Ar), 7.26 (1H, s, CH-Ar), 4.24 (1H, t, *J* = 7.5 Hz, CH-THF), 4.18 (1H, d, *J* = 11.5 Hz, CHHOH), 4.0 (1H, d, *J* = 11.5 Hz, CHHOH), 2.76 (2H, br s, 2 x OH), 2.57–2.45 (1H, m, CHH-THF), 2.43–2.35 (1H, m, CHH-THF), 2.20–2.03 (2H, m, CH₂CH₂), 1.40 (3H, s, CH₃), 1.22 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 172.6(C=O), 146.3 (C-Ar), 134.7 (C-Ar), 128.0 (CH-Ar), 126.7 (CH-Ar), 126.68 (CH-Ar), 126.5 (C), 126.3 (CH-Ar), 125.5 (CH-Ar), 121.1 (CH-Ar), 117.9 (CH-Ar), 88.0 (C-THF), 87.1 (C-THF), 71.5 (C-OH), 66.5 (CH₂OH), 32.4 (CH₂-THF), 27.5 (CH₂-THF), 26.2 (CH₃), 25.2 (CH₃) ppm. **LRMS:** (ES+) *m/z* 348 [M+NH₄]⁺. **HRMS:** (ES+) *m/z* C₁₉H₂₆NO₅ Calculated: 348.1806, found: 348.1805 ([M+NH₄]⁺). **HPLC:** Chiralpak® OD-H – (flow rate: 1.0 mL/min, 254 nm, eluent: 2.5% isopropanol/hexane, Retention times = 25.607 (major), 27.943 (minor)).

(rac)-Naphthalen-1-yl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.55)

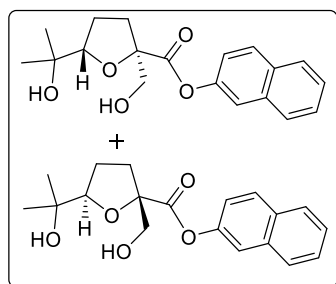
Using the outlined method for **(rac)-2.53** except using diene **2.40** (49.0 mg, 0.18 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.55** (57.0 mg, 0.17 mmol, 98%) as yellow oil. Spectroscopic and physical data are consistent with that reported above.

Naphthalen-2-yl (2S,5R)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.56)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.41** (71.0 mg, 0.25 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **2.56** (62.7 mg, 0.19 mmol, 87%) as yellow oil. Spectroscopic

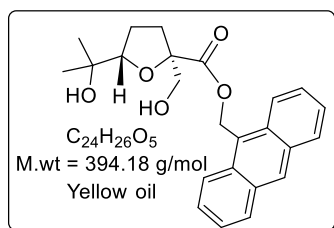
data are reported for a mixture of two enantiomers (ee = 69.5%) determined by HPLC analysis.

[α]^{20.5}_D = +1.1 (c 1.5, CHCl₃). FT-IR ν_{max} (neat): 3389 (br), 2925(s), 1736(s), 1631 (s), 1487 (w), 1240 (w) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.91–7.77 (3H, m, 3 x CH-Ar), 7.59 (1H, s, CH-Ar), 7.54–7.42 (2H, m, 2 x CH-Ar), 7.25 (1H, m, CH-Ar), 4.22 (1H, t, J = 7.4 Hz, CH-THF), 4.11 (1H, d, J = 11.5 Hz, CHHOH), 3.94 (1H, J = 11.4 Hz, CHHOH), 2.46–2.13 (4H, 2 x OH and CH₂-THF), 2.13–2.00 (2H, m, CH₂-THF), 1.37 (3H, s, CH₃), 1.21 (3H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): 172.7 (C=O), 148.1 (C-Ar), 133.7 (C-Ar), 131.5 (C-Ar), 129.5 (CH-Ar), 127.8 (CH-Ar), 127.6 (CH-Ar), 126.7 (CH-Ar), 125.8 (CH-Ar), 120.8 (CH-Ar), 118.4 (CH-Ar), 87.9 (C-THF), 86.9 (C-THF), 71.6 (C-OH), 66.4 (CH₂OH), 32.3 (CH₂-THF), 27.5 (CH₂-THF), 26.1 (CH₃), 25.2 (CH₃) ppm. LRMS: (ES+) m/z 353 [M+Na]⁺. HRMS: (ES+) m/z C₁₉H₂₆O₅Na Calculated: 353.1370, found: 353.1378. HPLC: Chiralpak® OZ-H – (flow rate: 1.0 mL/min, 270 nm, eluent: 2.5% isopropanol/hexane, Retention times = 83.316 (major), 91.51(minor)).

(rac)-Naphthalen-2-yl (2S,5R)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.56)

Using the outlined method for **(rac)-2.53** except using diene **2.41** (24 mg, 0.086 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.56** (26.7 mg, 0.08 mmol, 94%) as yellow oil. Spectroscopic and physical data are consistent with that reported above.

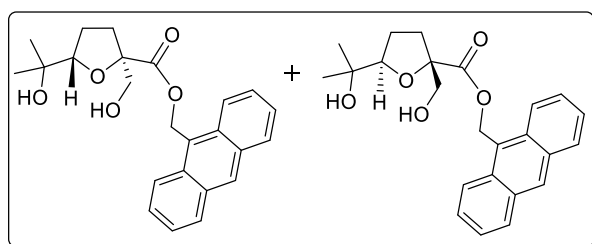
Anthracen-9-ylmethyl (2*S*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.57)



Method 1: The title compound was prepared according to the outlined method for **2.53**, except using diene **2.42** (54.0 mg, 0.156 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (40%) gave THF-diols **2.57** (50.2 mg, 0.132 mmol, 84%)

as gummy yellow oil. Spectroscopic data are reported for a mixture of two enantiomers ($ee = 15.3\%$) determined by HPLC analysis. **Method 2:** To a solution of anthracene methanol (70.0 g, 0.34 mmol) in THF (2.0 mL) at $-78^\circ C$ was added a solution of NaHMDS (0.330 mL of 1.0 M in THF, 0.330 mmol). The solution was allowed to warm to $-25^\circ C$ over 1.5 h whereupon a solution of crude THF-diol **2.67** in THF (2.0 mL) was added dropwise and stirred for 1.5 h at rt. The reaction was followed by TLC until transesterification completion. The reaction was quenched by NH_4Cl (5.0 mL) at $-40^\circ C$, extracted with CH_2Cl_2 (6 x 10.0 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Purification by column chromatography (SiO_2) eluting with EtOAc/hexane (40%) gave THF-diol **2.57** (56.4 mg, 0.143 mmol, 85%, $ee = 94.0\%$) as a gummy yellow oil. Yield was calculated over two steps starting from diene **2.52**. $[\alpha]^{22.5}_D = -0.37$ (c 2.7, $CHCl_3$). **FT-IR ν_{max} (neat):** 3388 (br), 2968(s), 1728(s), 1625 (s), 1447 (s), 1378 (s), 1262 (w) cm^{-1} . **^1H NMR (400 MHz, $CDCl_3$):** δ 8.49 (1H, s, CH-Ar), 8.32 (2H, d, $J = 8.7$ Hz, CH-Ar), 8.01 (2H, d, $J = 8.3$ Hz, 2 x CH-Ar), 7.62–7.53 (2H, m, 2 x CH-Ar), 7.53–7.46 (2H, m, 2 x CH-Ar), 6.24 (H, d, $J = 12.0$ Hz, OCHH), 6.18 (H, d, $J = 12.0$ Hz, OCHH), 3.96 (1H, t, $J = 7.4$ Hz, CH-THF), 3.82 (1H, d, $J = 11.5$ Hz, CHHOH), 3.67 (1H, d, $J = 11.5$ Hz, CHHOH), 2.72 (2H, br s, 2 x OH), 2.08–1.9 (2H, m, CH_2), 1.87–1.7 (2H, m, CH_2), 1.23 (3H, s, CH_3), 1.06 (3H, s, CH_3) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** 174.1 (C=O), 131.4 (2 x C-Ar), 131.0 (2 x C-Ar), 129.4 (2x CH-Ar), 129.1 (C-Ar), 126.7 (CH-Ar), 125.8 (2 x CH-Ar), 125.2 (2 x CH-Ar), 123.8 (2 x CH-Ar), 87.6 (C-THF), 86.9 (C-THF), 71.4 (C-OH), 66.0 (CH_2OH), 59.7 (CH_2), 32.0 (CH_2 -THF), 27.4 (CH_2 -THF), 25.9 (CH_3), 25.0 (CH_3) ppm. **LRMS:** (ES+) m/z 417 $[M+Na]^+$. **HRMS:** (ES+) m/z $C_{24}H_{26}O_5Na$ Calculated: 417.1683, found: 417.1686. **HPLC:** ChiralCell® AY-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 10% isopropanol/hexane, Retention times = 22.467 (major), 32.9 (minor)).

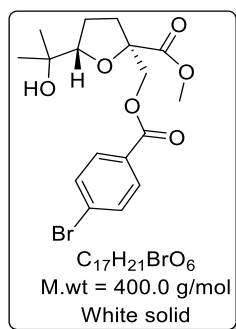
(rac)-Anthracen-9-ylmethyl (2*S*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.57)



Using the outlined method for **(rac)-2.53** except using diene **2.42** (20.0 mg, 0.06 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.57** (20.8 mg, 0.053 mmol, 88%) as

yellow oil. Spectroscopic and physical data are consistent with that reported above.

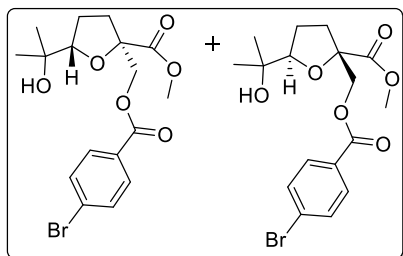
Methyl (2*R*,5*S*)-2-(((4-bromobenzoyl)oxy)methyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.58)



Under N_2 at 0 °C to a solution of THF-diol **2.53** (26.0 mg, 0.119 mmol) in CH_2Cl_2 (1.5 mL) was added pyridine (0.1 mL, 1.19 mmol), bromobenzoyl chloride (0.13 g, 0.595 mmol) and DMAP (36.0 mg, 0.30 mmol). After 30.0 min the reaction was quenched by addition of NH_4Cl (sat aq, 1.0 mL), citric acid (10% w/v aq, 0.5 mL), H_2O (1.0 mL) and CH_2Cl_2 (1.0 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3.0

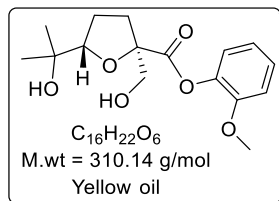
x 3.0 mL). The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure to give a yellow oil. Purification by column chromatography (SiO_2) eluting with Et_2O/PE (20%) gave the titled compound **2.58** as white solid (42.0 mg, 0.105 mmol, 88%). Spectroscopic data are reported for a mixture of two enantiomers (ee = 0.0%) determined by chiral HPLC analysis. **MP** 120–122 °C, **FT-IR** ν_{max} (neat): 3474 (br), 2979 (s), 1784 (s), 1734 (s), 1712 (s), 1586 (s), 1434 (s), 1399 (s), 1330 (s), 1297 (s), 1127 (w) cm^{-1} . **^1H NMR** (400 MHz, $CDCl_3$): δ 7.89 (2H, br d, J = 8.5 Hz, 2 x CH-Ar), 7.69 (2H, br d, J = 8.5 Hz, 2 x CH-Ar), 4.74 (1H, d, J = 11.4 Hz, CHH-O), 4.53 (1H, d, J = 11.4 Hz, CHH-O), 4.09 (1H, t, J = 7.5 Hz, CH-THF), 3.80 (3H, s, CH_3), 1.88–2.31 (5H, m, 2 x CH_2 -THF and OH), 1.26 (3H, s, CH_3), 1.13 (3H, s, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): 173.6 (C=O), 166.2 (C=O), 132.4 (C-Ar), 131.9 (C-Ar), 131.8 (2 x CH-Ar), 131.3 (2 x CH-Ar), 88.8 (C-THF), 85.4 (CH-THF), 70.9 (C-OH), 67.8 (CH_2OH), 52.9 (OCH_3), 33.4 (CH_2), 27.9 (CH_2), 26.0 (CH_3), 25.1 (CH_3) ppm. **LRMS**: (ES+) m/z 423 (100%, $C_{17}H_{21}^{79}BrO_6Na$) and 425 (85%, $C_{17}H_{21}^{81}BrO_6Na$). **HRMS**: (ES+) m/z $C_{17}H_{21}^{79}BrO_6Na$ Calculated: 423.0421, found: 423.0414. **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 1.0% isopropanol/hexane, Retention times = 18.567, 20.197).

(rac)-methyl (2*R*,5*S*)-2-(((4-bromobenzoyl)oxy)methyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.58)

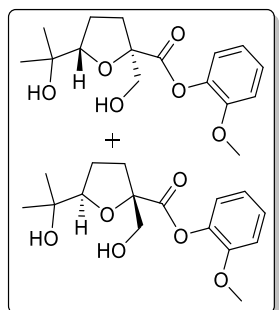


Using the outlined method for bromobenzoate **2.58** except using THF-diol **(rac)-2.53** (16.9 mg, 0.077 mmol) and bromobenzoyl chloride (85.0 mg, 0.387 mmol). Purification by column chromatography (SiO_2) eluting with Et_2O/PE (20%) gave bromobenzoate **(rac)-2.58** as white solid (28.0 mg, 0.07

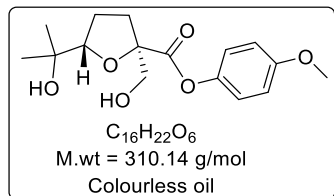
mmol, 90%). Spectroscopic and physical data are consistent with that reported above.

2-methoxyphenyl (2*S*,5*R*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.59)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.43** (26.2 mg, 0.1 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **2.59** (26.4 mg, 0.085 mmol, 85%) as yellow oil. Spectroscopic data are reported for a mixture of two enantiomers (ee = 48.0%) determined by HPLC analysis. $[\alpha]^{20.5}_D = -0.15$ (c 2.0, CHCl₃). **FT-IR** $\nu_{\max}$ (neat): 3382 (br), 2972(s), 1755(s), 1599 (s), 1607 (s), 1500 (s), 1465 (s), 1263 (s), 1172 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.22 (1H, d, *J* = 7.3 Hz, CH-Ar), 7.07 (1H, d, *J* = 8.2 Hz, CH-Ar), 6.96 (2H, m, 2 x CH-Ar), 4.17 (1H, t, *J* = 7.3 Hz, CH-THF), 4.05 (1H, d, *J* = 11.5 Hz, CHHOH), 3.9 (1H, d, *J* = 11.6 Hz, CHHOH), 3.83 (3H, s, OCH₃), 3.18 (1H, br s, CH₂OH), 2.62 (1H, br s, COH), 2.41 (1H, m, CHH-THF), 2.28 (1H, m, CHH-THF), 2.03 (2H, m, CH₂-THF), 1.34 (3H, s, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 172.0 (C=O), 150.8 (CH₃OC-Ar), 139.5 (O-C-Ar), 127.1 (CH), 122.8 (CH), 120.9 (CH), 112.4 (CH), 87.7 (C-THF), 87.1 (C-THF), 71.6 (C-OH), 66.2 (CH₂OH), 55.9 (OCH₃), 32.1 (CH₂-THF), 27.5 (CH₂-THF), 25.9 (CH₃), 25.1 (CH₃) ppm. **LRMS**: (ES+) *m/z* 333 [M+Na]⁺. **HRMS**: (ES+) *m/z* C₁₆H₂₂O₆Na Calculated: 333.1310, found: 333.1309. **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, eluent: 2.5% isopropanol/hexane, Retention times = 68.598 (minor), 74.965 (major)).

(rac)-2-methoxyphenyl (2*S*,5*R*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.59)

Using the outlined method for **(rac)-2.53** except using diene **2.43** (24.5 mg, 0.09 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.59** (24.8 mg, 0.08 mmol, 89%) as yellow oil. Spectroscopic and physical data are consistent with that reported above.

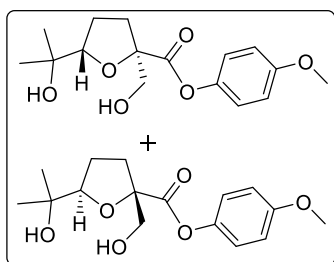
4-methoxyphenyl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.60)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.46** (25.0 mg, 0.096 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **2.60** (26.5 mg, 0.085 mmol, 89%) as colourless oil.

Spectroscopic data are reported for a mixture of two enantiomers (ee = 55.0%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +1.35$ (c 2.0, CHCl₃). **FT-IR** $\nu_{\max}$ (neat): 3374 (br), 2929 (s), 1749 (s), 1504 (s), 1464 (s), 1297 (s), 1189 (s), 1101 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 6.99–7.05 (2H, m, 2 x CH-Ar), 6.86–6.93 (2H, m, 2 x CH-Ar), 4.16 (1H, t, *J* = 7.4 Hz, CH-THF), 4.03 (1H, d, *J* = 11.5 Hz, CHHOH), 3.88

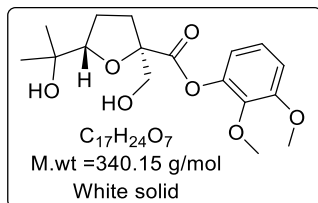
(1H, d, J = 11.5 Hz, CHHOH), 3.81 (3H, s, OCH₃), 3.09 (1H, br s, CH₂OH), 2.61 (1H, br s, COH), 2.18–2.36 (2H, m, CH₂-THF), 2.02 (2H, q, J = 7.54 Hz, CH₂-THF), 1.34 (3H, s, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 172.9 (C=O), 157.4 (C-Ar), 143.9 (C-Ar), 122.1 (2 x CH-Ar), 114.5 (2 x CH-Ar), 87.8 (CH-THF), 86.8 (C-THF), 71.5 (C-OH), 66.2 (CH₂OH), 55.6 (OCH₃), 32.2 (CH₂-THF), 27.5 (CH₂-THF), 26.1 (CH₃), 25.1 (CH₃) ppm. **LRMS:** (ES+) m/z 333 [M+Na]⁺. **HRMS:** (ES+) m/z C₁₆H₂₂O₆Na Calculated: 333.1317, found: 333.1309. **HPLC:** Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 1.0% isopropanol/hexane, Retention times = 80.087 (minor), 84.603 (major)).

(rac)-4-methoxyphenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.60)



Using the outlined method for **(rac)-2.53** except using diene **2.46** (12.0 mg, 0.046 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.60** (12.7 mg, 0.041 mmol, 90%) as colourless oil. Spectroscopic and physical data are consistent with that reported above.

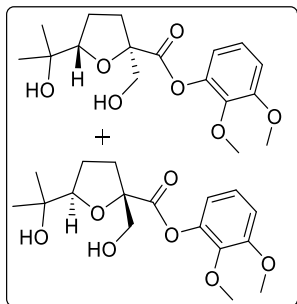
2,3-dimethoxyphenyl(2S,5R)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.61)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.47** (36.6 mg, 0.126 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **2.61** (38.6 mg, 0.113 mmol, 90%) as a white solid. **mp** 96–

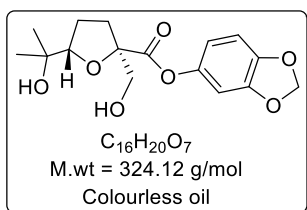
98 °C Spectroscopic data are reported for a mixture of two enantiomers (ee = 50.0%) determined by HPLC analysis. **[α]^{20.5}_D** = +4.84 (c 3.3, CHCl₃). **FT-IR $\nu_{\max}$ (neat):** 3277 (br), 2945(s), 2841 (s), 1762(s), 1599 (s), 1492 (s), 1473 (s), 1455 (s), 1277 (s), 1112 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.03 (1H, t, J = 7.7 Hz, CH-Ar), 6.83 (1H, dd, J = 8.3, 1.0 Hz, CH-Ar), 6.71 (1H, dd, J = 8.3, 1.2 Hz, CH-Ar), 4.16 (1H, t, J = 7.4 Hz, CH-THF), 4.05 (1H, d, J = 11.6 Hz, CHHOH), 3.92 (1H, s, CHHOH), 3.88 (3H, s, OCH₃), 3.83 (1H, s, OCH₃), 2.45–2.26 (2H, m, CH₂), 2.1–1.98 (2H, m, CH₂), 1.33 (3H, m, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 172.2 (C=O), 153.7 (CH₃OC-Ar), 143.9 (O-C-Ar), 140.8 (CH₃OC-Ar), 123.6 (CH), 115.0 (CH), 110.5 (CH), 87.7 (C-THF), 87.0 (C-THF), 71.5 (C-OH), 66.2 (CH₂OH), 60.6 (OCH₃), 56.1 (OCH₃), 32.1 (CH₂-THF), 27.5 (CH₂-THF), 26.0 (CH₃), 25.1 (CH₃) ppm. **LRMS:** (ES+) m/z 363 [M+Na]⁺. **HRMS:** (ES+) m/z C₁₇H₂₄O₇Na Calculated: 363.1409, found: 363.1411. **HPLC:** Chiralpak® AY-H – (flow rate: 1.0 mL/min, 210 nm, eluent: 10% isopropanol/hexane, Retention times = 22.708 (minor), 44.471 (major)).

(rac)-2,3-dimethoxyphenyl(2*S*,5*R*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.61)



Using the outlined method for **(rac)-2.53** except using diene **2.44** (50.0 mg, 0.172 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.61** (24.8 mg, 0.08 mmol, 89%) as a white solid. Spectroscopic and physical data are consistent with that reported above.

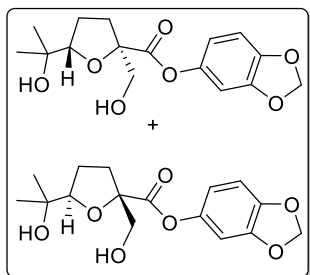
Benzo[d][1,3]dioxol-5-yl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.62)



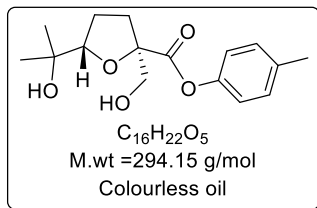
The title compound was prepared according to the outlined method for **2.53**, except using diene **2.47** (36.0 mg, 0.131 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diols **2.62** (36.0 mg, 0.111 mmol, 85%) as colourless oil. Spectroscopic

data are reported for a mixture of two enantiomers (ee = 55.0%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +1.3$ (c 1.5, CHCl₃). FT-IR $\nu_{\max}$ (neat): 3374 (br), 2923 (s), 1750 (s), 1502 (s), 1483 (s), 1245 (s), 1119 (w), 1056 (w) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 6.78 (1H, d, *J* = 7.3 Hz, CH-Ar), 6.62 (H, d, *J* = 2.3 Hz, CH-Ar), 6.54 (1H, dd, *J* = 8.31, 2.32 Hz, CH-Ar), 5.99 (2H, s, OCH₂O), 4.15 (1H, t, *J* = 7.4 Hz, CH-THF), 4.02 (1H, d, *J* = 11.4 Hz, CHHOH), 3.87 (1H, d, *J* = 11.5 Hz, CHHOH), 2.88 (1H, br s, CH₂OH), 2.35–2.57 (1H, m, COH), 2.25–2.35 (2H, m, CH₂-THF), 2.02 (2H, q, *J* = 7.5 Hz, CH₂-THF), 1.34 (3H, s, CH₃), 1.19 (3H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): 173.0 (C=O), 148.4 (C-Ar), 145.9 (C-Ar), 145.0 (2 x C-Ar), 114.0 (CH-Ar), 108.3 (CH-Ar), 103.8 (CH-Ar), 102.1 (OCH₂O), 88.1 (CH-THF), 87.1 (C-THF), 71.8 (C-OH), 66.6 (CH₂OH), 32.5 (CH₂-THF), 27.8 (CH₂-THF), 26.4 (CH₃), 25.5 (CH₃) ppm. LRMS: (ES+) *m/z* 347 [M+Na]⁺. HRMS: (ES+) *m/z* C₁₆H₂₀O₇Na Calculated: 347.1099, found: 347.1101. HPLC: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 1.0% isopropanol/hexane, Retention times = 79.563 (minor), 84.487 (major)).

(rac)-Benzo[d][1,3]dioxol-5-yl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.62)

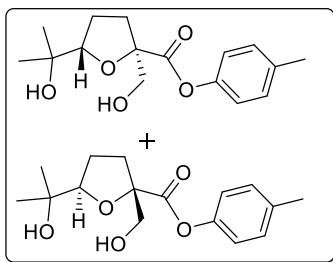


Using the outlined method for **(rac)-3.37** except using diene **2.47** (12.0 mg, 0.044 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diols **(rac)-2.62** (12.6 mg, 0.039 mmol, 90%) as colourless oil. Spectroscopic and physical data are consistent with that reported above.

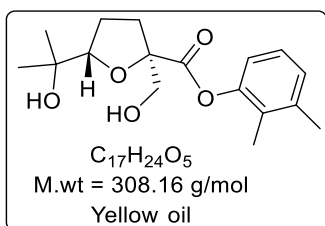
***p*-Polyl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.63)**

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.48** (44.0 mg, 0.18 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diols **2.63** (47.6 mg, 0.162 mmol, 90%) as colourless oil.

Spectroscopic data are reported for a mixture of two enantiomers (ee = 31.0%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +1.0$ (c 1.5, CHCl₃). **FT-IR** ν_{max} (neat): 3384 (br), 2975 (s), 1749 (s), 1507 (s), 1457 (s), 1380 (s), 1265 (s), 1193 (s), 1103 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 6.7.18 (2H, d, J = 8.1 Hz, 2 x CH-Ar), 6.98 (2H, d, J = 7.6 Hz, 2 x CH-Ar), 4.16 (1H, t, J = 7.4 Hz, CH-THF), 4.03 (1H, d, J = 11.5 Hz, CHHOH), 3.88 (1H, d, J = 11.4 Hz, CHHOH), 3.08 (1H, br s, CH₂OH), 2.52 (1H, br d, J = 10.03 Hz, COH), 2.35 (3H, s, CH₃-Ar), 2.34–2.24 (2H, m, CH₂-THF), 2.03 (2H, q, J = 7.4 Hz, CH₂-THF), 1.34 (3H, s, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 173.0 (C=O), 148.5 (C-Ar), 136.0 (C-Ar), 130.3 (2 x CH-Ar), 121.3 (2 x CH-Ar), 88.1 (CH-THF), 87.1 (C-THF), 71.9 (C-OH), 66.5 (CH₂OH), 32.5 (CH₂-THF), 27.8 (CH₂-THF), 26.4 (CH₃), 25.5 (CH₃), 21.2 (Ar-CH₃) ppm. **LRMS**: (ES+) m/z 317 [M+Na]⁺. **HRMS**: (ES+) m/z C₁₆H₂₂O₅Na Calculated: 317.1365, found: 317.1359. **HPLC**: Chiralpak® OZ-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 2.0% isopropanol/hexane, Retention times = 58.363 (major), 68.845 (minor)).

(rac)-*p*-Tolyl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.63)

Using the outlined method for **(rac)-2.53** except using diene **2.48** (36.0 mg, 0.147 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diols **(rac)-2.63** (40.6 mg, 0.138 mmol, 94%) as colourless oil. Spectroscopic and physical data are consistent with that reported above.

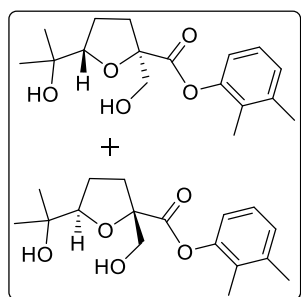
2,3-Dimethylphenyl (2*R*,5*S*)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.64)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.49** (80.0 mg, 0.31 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.64** (80.0 mg, 0.26 mmol, 83%) as a pale yellow oil. Spectroscopic data are reported for a mixture of two enantiomers

determined by HPLC analysis. $[\alpha]^{20.5}_D = +2.4$ (c 5.0, CHCl₃). **FT-IR** ν_{max} (neat): 3385 (br), 2976(s), 1749(s), 1467 (s), 1228 (s), 1055 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.13–7.03 (2H, m, 2 x CH-

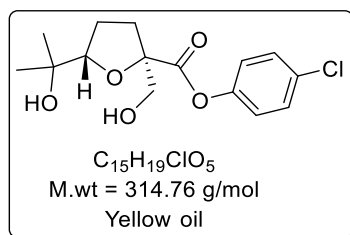
Ar), 6.86 (1H, d, $J = 7.7$ Hz, CH-Ar), 4.16 (1H, t, $J = 7.40$ Hz, CH-THF), 4.11–3.97 (1H, m, CHHOH), 3.90 (1H, br d, $J = 11.49$ Hz, CHHOH), 3.00 (1H, br s, CH₂OH) 3.53 (1H, br s, C–OH), 2.25–4.1 (5H, m, Ar–CH₃ and CH₂-THF), 2.09 (1H, m, Ar–CH₃), 2.03 (2H, q, $J = 7.62$ Hz, CH₂-THF) 1.34 (3H, s, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 172.5 (C=O), 148.9 (C-Ar), 138.6 (C-CH₃), 128.5 (C-CH₃), 127.6 (CH-Ar), 126.0 (CH-Ar), 119.1 (CH-Ar), 87.7 (CH-THF), 86.9 (C-THF), 71.5 (C(CH₃)₂), 66.2 (CH₂OH), 32.2 (CH₂-THF), 27.4 (CH₂-THF), 26.1 (CH₃), 25.0 (CH₃), 20.0 (Ar-CH₃), 12.2 (Ar-CH₃) ppm. **LRMS:** (ES+) m/z 331 [M+Na]⁺. **HRMS:** (ES+) m/z C₁₇H₂₄O₅Na Calculated:331.1517, found:331.1516. **HPLC:** Chiralpak® AY-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 5% isopropanol/hexane, $ee = 37.0.0\%$, Retention times = 16.417 (minor), 27.913 (major)).

(rac)-2,3-Dimethylphenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.64)



Using the outlined method for **(rac)-2.53** except using diene **2.49** (20.0 mg, 0.08 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.64** (21.9 mg, 0.071 mmol, 89%) as a pale yellow oil. Spectroscopic and physical data are consistent with that reported above.

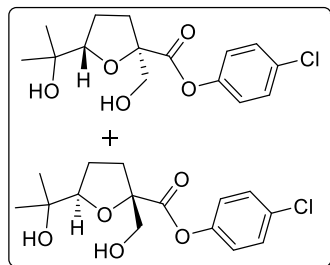
4-Chlorophenyl (2S,5R)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.65)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.45** (37.0 mg, 0.14 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **2.65** (36.5 mg, 0.116 mmol, 83%) as a yellow oil. Spectroscopic data are reported for a mixture of two enantiomers ($ee = 28.36\%$) determined by HPLC analysis. $[\alpha]^{20.5}_D = +0.68$ (c 2.5, CHCl₃). **FT-IR ν_{max} (neat):** 3396 (br), 2978(s), 1751(s), 1486 (s), 1264 (s), 1197 (s), 1073 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** 7.35 (2H, d, $J = 8.8$ Hz, 2 x CH-Ar), 7.05 (2H, d, $J = 8.8$ Hz, 2 x CH-Ar), 4.14 (1H, t, $J = 7.4$ Hz, CH-THF), 4.04 (1H, br d, $J = 11.0$ Hz, CHHOH), 3.86 (1H, br d, $J = 11.5$ Hz, CHHOH), 3.36 (1H, br s, CH₂OH), 2.78 (1H, br s, C–OH), 2.28 (2H, m, CH₂-THF), 2.01 (2H, q, $J = 7.6$ Hz, CH₂-THF), 1.34 (3H, s, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** 172.3 (C=O), 148.9 (C-Ar), 131.5 (C-Ar), 129.5 (2 x CH-Ar), 122.7 (2 x CH-Ar), 87.8 (C-THF), 86.9 (C-THF), 71.5 (C-OH), 66.2 (CH₂OH), 32.2 (CH₂-THF), 27.4 (CH₂-THF), 26.1 (CH₃), 25.0 (CH₃) ppm. **LRMS:** (ES+) m/z 337 (100%, C₁₅H₁₉³⁵ClO₅Na) and 339 (30%, C₁₅H₁₉³⁷ClO₅Na). **HRMS:** (ES+) m/z C₁₅H₁₉³⁵ClO₅Na Calculated: 337.0814, found: 337.0813. **HPLC:** Chiralpak® OD-H –

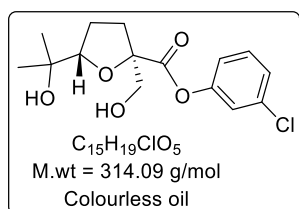
(flow rate: 1.0 mL/min, 220 nm, eluent: 2.5% isopropanol/hexane, Retention times = 25.958 (minor), 29.300 (major)).

(rac)-4-Chlorophenyl (2S,5R)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.65)



Using the outlined method for **(rac)-2.53** except using diene **2.45** (17.8 mg, 0.07 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.65** (19.3 mg, 0.062 mmol, 88%) as a yellow oil. Spectroscopic and physical data are consistent with that reported above.

3-Chlorophenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.66)

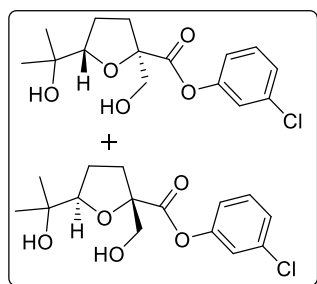


The title compound was prepared according to the outlined method for **2.53**, except using diene **2.50** (50.0 mg, 0.19 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.66** (53.4 mg, 0.17 mmol, 88%) as a colourless oil. Spectroscopic

data are reported for a mixture of two enantiomers (*ee* = 56.0%) determined by HPLC analysis.

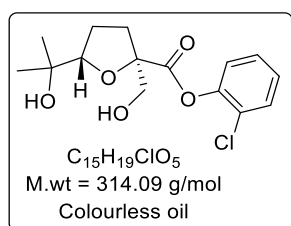
[α]_D^{20.5} = +5.8 (*c* 2.5, CHCl₃). **FT-IR** ν_{max} (neat): 3365 (br), 2975(s), 1753 (s), 1589 (s), 1472 (s), 1198 (s), 1104 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.32 (1H, t, *J* = 7.6 Hz, CH-Ar), 7.26–7.21 (1H, m, CH-Ar), 7.15 (1H, t, *J* = 2.1 Hz, CH-Ar) 7.03 (1H, d, *J* = 8.3 Hz, CH-Ar), 4.14 (1H, t, *J* = 7.4 Hz, CH-THF), 4.05 (1H, d, *J* = 11.5 Hz, CHHOH), 3.87 (1H, d, *J* = 11.5 Hz, CHHOH), 2.20–3.35(2H, m, CH₂-THF), 2.02 (1H, q, *J* = 7.58 Hz, CH₂-THF), 1.34 (3H, s, CH₃), 1.18 (3H, s, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 172.2 (C=O), 150.9 (C-Ar), 134.8 (C-Cl), 130.2 (CH-Ar), 126.4 (CH-Ar), 122.1 (CH-Ar), 119.8 (CH-Ar), 87.9 (CH-THF), 86.9 (C-THF), 71.6 (C(CH₃)₂), 66.3 (CH₂OH), 32.3 (CH₂-THF), 27.5 (CH₂-THF), 26.1 (CH₃), 25.1 (CH₃) ppm. **LRMS**: (ES+) *m/z* 332 (92%, C₁₅H₂₃³⁵ClNO₅) and 334 (38%, C₁₅H₂₃³⁷ClNO₅). **HRMS**: (ES+) *m/z* C₁₅H₁₉³⁵ClO₅Na Calculated:337.0812, found:337.0813. **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 2.5% isopropanol/hexane, Retention times = 28.167 (minor), 29.167 (major)).

(rac)-3-Chlorophenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.66)



Using the outlined method for **(rac)-2.53** except using diene **2.50** (20.0 mg, 0.08 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.66** (23.6 mg, 0.075 mmol, 93%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

2-Chlorophenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.67)

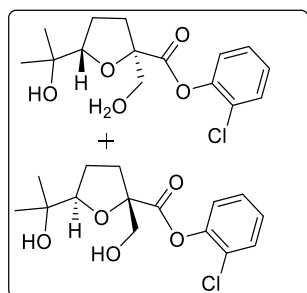


The title compound was prepared according to the outlined method for **2.53**, except using diene **2.51** (50.0 mg, 0.19 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.67** (49.6 mg, 0.158 mmol, 83%) as a colourless oil. Spectroscopic

data are reported for a mixture of two enantiomers (*ee* = 50.0%) determined by HPLC analysis.

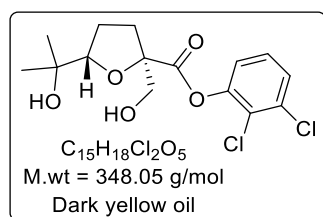
[α]_D^{20.5} = +4.7 (*c* 2.5, CHCl₃). **FT-IR** ν_{max} (neat): 3366 (br), 2974 (s), 1757 (s), 1584 (s), 1475 (s), 1212 (s), 1104 (w) cm⁻¹. **¹H NMR** (400 MHz, CDCl₃): δ 7.45 (1H, dd, *J* = 7.95, 1.59 Hz, CH-Ar), 7.33–7.28 (1H, m, CH-Ar), 7.25–7.16 (2H, m, 2 x CH-Ar), 4.19 (1H, d, *J* = 7.34 Hz, CH-THF), 4.10 (1H, d, *J* = 11.49 Hz, CHHOH), 3.92 (1H, d, *J* = 11.6 Hz, CHHOH), 3.18 (1H, br s, OH), 2.62 (1H, br d, *J* = 13.82 Hz, OH), 2.41–3.50 (1H, m, CHH-THF), 2.27–3.36 (1H, m, CHH-THF), 1.96–2.16 (2H, , CH₂-THF), 1.35 (3H, s, CH₃), 1.19 (3H, s, CH₃) ppm. **¹³C NMR** (100 MHz, CDCl₃): 171.5 (C=O), 146.5 (C-Ar), 130.3 (CH-Ar), 127.8 (CH-Ar), 127.3 (CH-Ar), 126.7 (C-Cl), 87.8 (CH-THF), 87.0 (C-THF), 71.6 (C(CH₃)₂), 66.1 (CH₂OH), 32.1 (CH₂-THF), 27.5 (CH₂-THF), 26.0 (CH₃), 25.1 (CH₃) ppm. **LRMS**: (ES⁺) *m/z* 332 (100%, C₁₅H₂₃³⁵ClNO₅) and 334 (45%, C₁₅H₂₃³⁷ClNO₅). **HRMS**: (ES⁺) *m/z* C₁₅H₁₉³⁵ClO₅Na Calculated:337.0812, found:337.0813. **HPLC**: Chiralpak® OZ-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 2.5% isopropanol/hexane, Retention times = 40.597 (major), 45.29 (minor)).

(rac)-2-Chlorophenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate ((rac)-2.67)



Using the outlined method for **(rac)-2.53** except using diene **2.52** (20.0 mg, 0.08 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.67** (23.9 mg, 0.076 mmol, 95%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

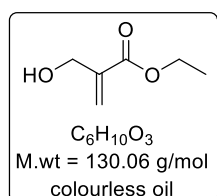
2,3-Dichlorophenyl (2R,5S)-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)tetrahydrofuran-2-carboxylate (2.67)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.52** (50.0 mg, 0.167 mmol). THF-diols **2.67** (90% conversion based on NMR) was reported as crude dark yellow oil, which was used directly into the next step to make

compound **2.57**. Spectroscopic data are reported as a crude. **FT-IR** $\nu_{\max}$ (neat): 3400 (br), 2926 (s), 1760 (s), 1576 (s), 1448 (s), 1264 (s), 1155 (w), 1050 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.47–7.33 (1H, m, CH-Ar), 7.29–7.21 (1H, m, CH-Ar), 7.11 (1H, dd, J = 8.13, 1.28 Hz, CH-Ar), 4.19 (1H, t, J = 7.40 Hz, CH-THF), 4.09 (1H, d, J = 11.5 Hz, CHHOH), 3.91 (1H, d, J = 11.6 Hz, CHHOH), 2.45 (1H, dt, J = 12.96, 7.95 Hz, CHH-THF), 2.35–2.20 (1H, m, CHH-THF), 2.13–1.98 (1H, m, CH_2 -THF), 1.40–1.28 (3H, m, CH_3), 1.19 (3H, m, CH_3) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 172.2 (C=O), 147.8 (C-Ar), 134.6 (C-Cl), 128.1 (CH-Ar), 127.0 (CH-Ar), 122.0 (C-Cl), 121.9 (CH-Ar), 87.8 (CH-THF), 87.0 (C-THF), 71.6 (C(CH_3)₂), 66.2 (CH_2OH), 29.7 (CH_2 -THF), 27.5 (CH_2 -THF), 26.0 (CH_3), 25.2 (CH_3) ppm. **LRMS**: (ES+) m/z 371 (61%, $C_{15}H_{18}^{35}\text{Cl}_2\text{O}_5\text{Na}$) and 373 (37%, $C_{15}H_{18}^{37}\text{Cl}_2\text{O}_5\text{Na}$). **HRMS**: (ES+) m/z $C_{15}H_{18}^{35}\text{Cl}_2\text{O}_5\text{Na}$ Calculated: 371.0431, found: 371.0424.

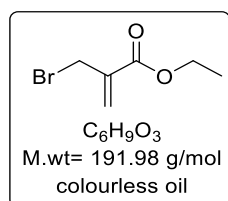
Ethyl 2-(hydroxymethyl)acrylate (2.70)



To a solution of formaldehyde (90.2 mL, 119.9 mmol) and ethylacrylate **2.69** (13.08 mL, 119.9 mmol) in 200.0 mL dioxane/ H_2O (1:1) was added DABCO (13.45 g, 119.9 mmol). At 50 °C the reaction progress was monitored by TLC until completion. The reaction mixture was partitioned with EtOAc (100 mL)

and water (100 mL). The organic layer was separated, dried (Na_2SO_4), and concentrated under reduced pressure to give the crude colourless oil. Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (10%) gave the titled alcohol (**2.70**) as a colourless oil (107.9 mmol, 90% yield). Physical and spectroscopic data are consistent with literature.³¹⁴ **^1H NMR (400 MHz, CDCl_3)** δ 6.24 (1H, s, =CHH), 5.88 (1H, s, =CHH), 4.32 (2H, s, CH_2OH), 4.23 (2H, q, J = 7.0 Hz, CH_2CH_3), 1.31 (3H, t, J = 7.15 Hz, CH_3) ppm.

Ethyl 2-(bromomethyl)acrylate (2.71)

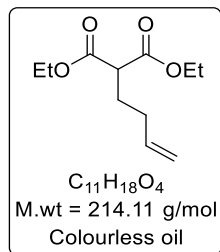


To a solution of alcohol **2.70** (10.5 gm, 80.7 mmol) in dry Et_2O (60.0 mL) was added PBr_3 (80.7 mmol, 7.7 mL) at –10 °C. Then, the temperature was allowed to rt and stirred for 2 h. Water (70.0 mL) was added and extracted with Et_2O (3 x 50.0 mL), dried (Na_2SO_4), and concentrated under reduced pressure to

give a colourless oil **2.71** (15.183 g, 79.09 mmol, 98%). Physical and spectroscopic data are

consistent with literature.³¹⁴ **¹H NMR (400 MHz, CDCl₃)** δ 6.35 (1H, s, =CHH), 5.83 (1H, d, J = 0.8 Hz =CHH), 4.8 (2H, s, CH₂Br), 4.24 (2H, q, J = 7.2 Hz, CH₂CH₃), 1.3 (3H, m, CH₃) ppm.

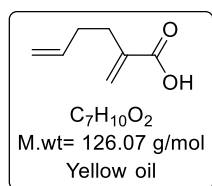
Diethyl 2-(but-3-en-1-yl)malonate (2.74)



The title compound was prepared according to the outlined method for diester **2.34**, except using alkyl halide **2.73** (10.0 gm, 7.5 mL, 74.6 mmol). The crude product was purified by column chromatography (SiO₂) eluting with Et₂O/PE (2%) afforded the title compound as a colourless oil **2.74** (12.8 g, 59.7 mmol, 80% yield). Physical and spectroscopic data are consistent with literature.³¹⁰

¹H NMR (400 MHz, CDCl₃) δ 5.75 (1H, ddt, J = 17.0, 10.3, 6.6, 6.6 Hz, CH₂=CH), 5.05 (1H, q, J = 1.5 Hz, CH=CHH), 5.02–1.94 (1H, m, CH=CHH), 4.18 (4H, q, J = 7.3 Hz, 2 x OCH₂CH₃), 3.34 (1H, t, J = 7.3 Hz, O=CCHC=O), 2.12–2.05 (2H, m, CH₂CH₂), 2.03–1.94 (2H, m, CH₂CH₂), 1.25 (6H, t, J = 7.2 Hz, 2 x CH₂CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 169.3 (C=O), 136.8 (CH=CH₂), 115.9 (CH=CH₂), 61.2 (2 x OCH₂), 51.3 (O=CCHC=O), 31.2 (CH₂CH₂), 27.8 (CH₂CH₂), 14.0 (2 x CH₃) ppm.

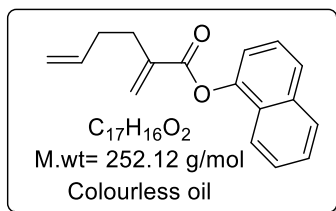
2-Methylenehex-5-enoic acid (2.76)



The title compound was prepared according to the outlined **method 2** for acid **2.15**, except using diester **2.74** (8.0 g, 37.4 mmol). The crude acid **2.76** was yellow oil (4.243 g, 33.66 mmol, 90%) which was used in the next step without further purification. Physical and spectroscopic data are consistent with

literature.³¹⁰ **¹H NMR (400 MHz, CDCl₃)**: δ 10.9 (1H, br s, COOH), 6.33 (1H, s, CHH=C), 5.82 (1H, ddt, J = 17.0, 10.3, 6.5, 6.5 Hz, CH₂=CH), 5.67 (1H, d, J = 1.2 Hz, CHH=C), 5.1–4.98 (2H, m, CH=CH₂), 2.42 (2H, t, J = 7.5 Hz, CH₂CH₂), 2.27 (2H, q, J = 7.2 Hz, CH₂CH₂). **¹³C NMR (100 MHz, CDCl₃)**: δ 172.6 (CO₂H), 139.3 (C=CH₂), 137.5 (CH=CH₂), 127.5 (C=CH₂), 115.3 (CH=CH₂), 32.4 (CH₂CH₂), 30.8 (CH₂CH₂) ppm.

Naphthalen-1-yl 2-methylenehex-5-enoate (2.77)

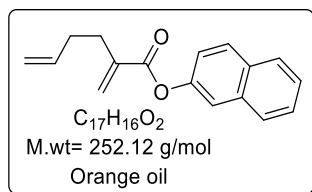


The title compound was prepared according to the outlined method for **2.46** except using 1-Naphthol (343.0 mg, 2.38 mmol) and acid **2.76** (0.3 g, 2.38 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound **2.77** as a

colourless oil (0.54 g, 2.14 mmol, 90% yield). **FT-IR ν_{max} (neat)**: 3927 (s), 1732 (s), 1635 (s), 1508 (s), 1389(s), 1223 (s), 1119 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.89 (2H, ddd, J = 9.2, 5.8, 3.4 Hz, 2 x CH-Ar), 7.77 (1H, d, J = 8.3 Hz, CH-Ar), 7.57–7.47 (3H, m, 3 x CH-Ar), 7.29 (1H, d, J = 0.7 Hz, CH-Ar),

6.62 (1H, s, C=CHH), 5.97–5.84 (2H, m, =CHH and CH=CH₂), 5.19–5.01 (2H, m, CH=CH₂), 2.63 (2H, t, *J* = 7.3 Hz, CH₂CH₂), 2.42 (2H, q, *J* = 7.6 Hz, CH₂CH₂), ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.6 (C=O), 146.8 (C-Ar), 139.5 (C=CH₂), 137.5 (CH=CH₂), 134.7 (C-Ar), 128.0 (CH-Ar), 127.1 (CH-Ar), 127.0 (C-Ar), 126.4 (2 x CH-Ar), 125.9 (C=CH₂), 125.4 (CH-Ar), 121.2 (CH-Ar), 118.1 (CH-Ar), 115.5 (CH=CH₂), 32.6 (CH₂), 31.4 (CH₂) ppm. **LRMS:** (ES+) *m/z* 253 [M+H]⁺. **HRMS:** (ES+) *m/z* C₁₇H₁₇O₂ Calculated:253.1219, found:253.1223.

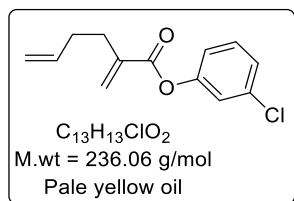
Naphthalen-2-yl 2-methylenehex-5-enoate (2.77)



The title compound was prepared according to the outlined method for **2.46**, except using 2-Naphthol (343.0 mg, 2.38 mmol) with acid **2.76** (0.3 g, 2.38 mmol). Purification by column chromatography (SiO₂) eluting with 2% Et₂O/PE gave the title compound as orange oil **2.78**

(0.55 g, 2.20 mmol, 92%). **FT-IR v_{max} (neat):** 3060 (s), 2923(s), 2853 (s), 1730 (s), 1630 (s), 1511 (s), 1464(s), 1206 (s), 1127 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃) δ** 7.93–7.79 (3H, m, 3 x CH-Ar), 7.61 (1H, d, *J* = 2.2 Hz, CH-Ar), 7.54–7.45 (2H, m, 2 x CH-Ar), 7.28 (1H, d, *J* = 9.0 Hz, CH-Ar), 6.5 (1H, s, C=CHH), 5.89 (1H, ddt, *J* = 17.0, 10.2, 6.6, 6.6 Hz, CH=CH₂), 5.79 (1H, m, C=CHH), 5.16–5.03 (2H, m, CH=CH₂), 2.58 (2H, t, *J* = 7.3 Hz, CH₂CH₂), 2.43–2.34 (2H, q, *J* = 7.5 Hz, CH₂CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.8 (C=O), 148.6 (C-Ar), 139.6 (C=CH₂), 137.5 (CH=CH₂), 133.8 (C-Ar), 131.5 (C-Ar), 129.4 (C-Ar), 127.8 (C-Ar), 127.6 (CH-Ar), 127.0 (CH-Ar), 126.6 (CH-Ar), 125.7 (C=CH₂), 121.2 (CH-Ar), 118.6 (CH-Ar), 115.4 (CH=CH₂), 32.6 (CH₂), 31.4 (CH₂) ppm. **LRMS:** (ES+) *m/z* 253 [M+H]⁺. **HRMS:** (ES+) *m/z* C₁₇H₁₆O₂Na Calculated:275.1045, found:275.1043.

3-Chlorophenyl 2-methylenehex-5-enoate (2.79)

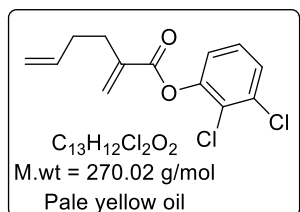


The title compound was prepared according to the outlined method for **2.46** except using 3-dichloro phenol (0.205 g, 1.59 mmol, 0.17 ml) and acid **2.76** (0.20 g, 1.59 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound **2.79** as pale

yellow oil (0.345 g, 1.46 mmol, 92% yield). **FT-IR v_{max} (neat):** 2928 (s), 1735 (s), 1633 (s), 1590 (s), 1470 (s), 1298 (s), 1199 (s), 1119 (w), 1089 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃): δ** 7.33 (1H, m, CH-Ar), 7.25 (1H, dd, *J* = 2.0, 1.0 Hz, CH-Ar), 7.18 (1H, t, *J* = 2.1 Hz, CH-Ar), 7.05 (1H, ddd, *J* = 8.10, 2.23, 1.04 Hz, CH-Ar), 6.43 (1H, s, C=CHH), 5.85 (1H, ddt, *J* = 17.1, 1.3, 6.6, 6.6 Hz, CH₂=CHCH₂), 5.77 (1H, q, *J* = 1.2 Hz, C=CHH), 5.13–5.00 (2H, m, CH=CH₂), 2.53 (2H, t, *J* = 7.5 Hz, CH₂CH₂), 2.37–2.30 (2H, m, CH₂CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.1 (C=O), 151.4 (C-Ar), 139.2 (C=CH₂), 137.2 (CH₂=CH), 134.7 (C-Cl), 30.0 (CH-Ar), 127.3 (CH-Ar), 126.0 (C=CH₂), 122.3 (CH-Ar), 120.0 (CH-Ar), 115.5

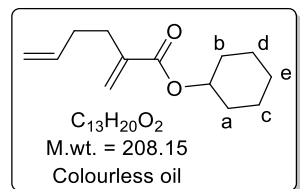
(CH₂=CH), 32.5 (CH₂), 31.2 (CH₂) ppm. **LRMS:** (ES+) *m/z*: 237 (100%, C₁₃H₁₄³⁵ClO₂) and 239 (39%, C₁₃H₁₄³⁷ClO₂). **HRMS:** (ES+) *m/z* C₁₃H₁₄³⁵ClO₂ Calculated: 237.0682, found: 237.067 ([M+H]⁺).

2,3-Dichlorophenyl 2-methylenehex-5-enoate (2.80)

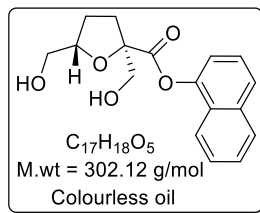


The title compound was prepared according to the outlined method for **2.46** except using 2,3-dichloro phenol (0.257 g, 1.59 mmol) and acid **2.76** (0.20 g, 1.59 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound **2.80** as pale yellow oil (0.36 g, 1.35 mmol, 85% yield). **FT-IR** *v*_{max} (neat): 2929(s), 2854 (s), 1741 (s), 1639 (s), 1449 (s), 1239 (s), 1157 (s), 1113 (w), 1089 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.38 (1H, dd, *J* = 8.1, 1.5 Hz, CH-Ar), 7.27 (1 H, t, *J* = 8.1 Hz, CH-Ar), 7.13 (1H, dd, *J* = 8.2, 1.5 Hz, CH-Ar), 6.53 (1H, s, C=CHH), 5.92–5.79 (2H, m, CH₂CH=CH₂ and C=CHH), 5.13–5.02 (2H, m, CH=CH₂), 2.55 (2H, t, *J* = 7.5 Hz, CH₂CH₂), 2.41–2.32 (2H, m, CH₂CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃):** 164.3 (C=O), 147.5 (C-Ar), 138.6 (C=CH₂), 137.3 (CH₂=CH), 133.9 (C-Cl), 128.02 (CH-Ar), 127.7 (CH-Ar), 127.4 (C-Cl), 126.4 (C=CH₂), 122.0 (CH-Ar), 115.5 (CH₂=CH), 32.4 (CH₂), 31.3 (CH₂) ppm. **LRMS:** (ES+) *m/z*: 271 (60%, C₁₃H₁₃³⁵Cl₂O₂) and 273 (30%, C₁₃H₁₃³⁷Cl₂O₂). **HRMS:** (ES+) *m/z* C₁₃H₁₃³⁵Cl₂O₂ Calculated: 271.0289, found: 287.0287.

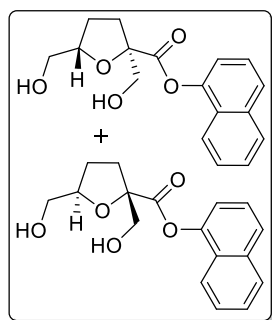
Cyclohexyl 2-methylenehex-5-enoate (2.81)



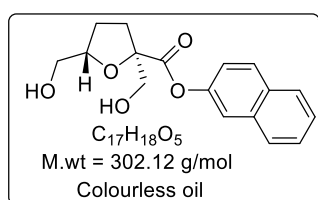
The title compound was prepared according to the outlined method for **2.46**, except using cyclohexanol (0.24 g, 2.38 mmol) with acid **2.76** (0.3 g, 2.38 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound as colourless oil **2.81** (0.47 g, 2.26 mmol, 95%). **¹H NMR (400 MHz, CDCl₃)** δ 6.15 (1H, s, C=CHH), 5.82 (1H, ddt, *J* = 17.0, 10.3, 6.7, 6.7 Hz, CH=CH₂), 5.51 (1H, q, *J* = 1.3 Hz, C=CHH), 5.08–4.95 (2H, m, CH=CH₂), 4.82–4.89 (1H, m, OCH), 2.41 (2H, t, *J* = 7.3 Hz, CH₂CH₂), 2.29–2.21 (2H, m, CH₂CH₂), 1.97–1.81 (2H, m, CHH_a and CHH_b), 1.72–1.69 (2H, m, CHH_a and CHH_b), 1.19–1.62 (6H, m, 3 x CH_{2,c}, CH_{2,d} and CH_{2,e}) ppm. **¹³C NMR (100 MHz, CDCl₃):** 166.6 (C=O), 140.7 (C=CH₂), 137.8 (CH₂=CH), 124.5 (CH₂=C), 115.0 (CH₂=CH), 72.61 (OCH), 32.6(^aCH₂ and ^bCH₂), 31.5 (CHCH₂), 31.3 (CH₂C=CH₂), 24.7 (^eCH₂), 23.6 (^cCH₂ and ^dCH₂) ppm. **LRMS:** (ES+) *m/z* 247 [M+K]⁺.

Naphthalen-1-yl (2*S*,5*R*)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.82)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.77** (55.0 mg, 0.22 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diols **2.82** (56.5 mg, 0.187 mmol, 85%) as a colourless oil. Spectroscopic data are reported for a mixture of two enantiomers (*ee* = 97.1%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +5.9$ (*c* 3.0, CHCl₃). **FT-IR** $\nu_{\max}$ (**neat**): 3420 (br), 1751 (s), 1599 (s), 1508 (s), 1389 (s), 1223 (s), 1092 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.98–7.83 (2H, m, 2 x CH-Ar), 7.76 (1H, d, *J* = 8.3 Hz, CH-Ar), 7.56–7.42 (3H, m, 3 x CH-Ar), 7.26 (1H, d, *J* = 7.6 Hz, CH-Ar), 4.53 (1H, tdd, *J* = 7.2, 7.2, 4.4, 2.8 Hz, CH-THF), 4.23 (1H, br d, *J* = 11.5 Hz, CCHHOH), 4.05–3.87 (2H, m, CHCHHOH and CCHHOH), 3.79 (1H, br s, CHCH₂OH), 3.63 (1H, br dd, *J* = 11.9, 4.3 Hz, CHCHHOH), 3.37 (1H, br s, CCH₂OH), 2.56–2.43 (1H, m, CHH-THF), 2.41–2.29 (1H, m, CHH-THF), 2.23–1.98 (2H, m, CHCH₂-THF) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 172.5 (C=O), 146.3 (C-Ar), 134.6 (C-Ar), 128.0 (CH-Ar), 126.7 (CH-Ar), 126.5 (CH-Ar and C-Ar), 126.3 (CH-Ar), 125.3 (CH-Ar), 121.0 (CH-Ar), 117.8 (CH-Ar), 87.8 (C-THF), 81.9 (CH-THF), 66.6 (CCH₂OH), 64.3 (CHCH₂OH), 32.3 (CH₂-THF), 26.9 (CH₂-THF) ppm. **LRMS**: (ES+) *m/z* 325 [M+Na]⁺. **HRMS** (ES+) *m/z* C₁₇H₁₈O₅Na Calculated: 325.1043, found: 325.1046. **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 254 nm, eluent: 2.5% isopropanol/hexane, Retention times = 6.970 (minor), 8.727 (major)).

(rac)-Naphthalen-2-yl (E)-2-methylene-6-Arenylhex-5-enoate ((rac)-2.82)

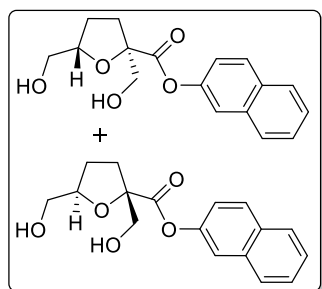
Using the outlined method for **(rac)-2.53** except using diene **2.77** (14.0 mg, 0.055 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diols **(rac)-2.82** (14.8 mg, 0.049 mmol, 89%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

Naphthalen-2-yl (2*S*,5*R*)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.83)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.78** (55.0 mg, 0.22 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.83** (59.8 mg, 0.198 mmol, 87%) as a colourless oil. Spectroscopic data are reported for a mixture of two enantiomers (*ee* = 68.6%) determined by HPLC analysis.

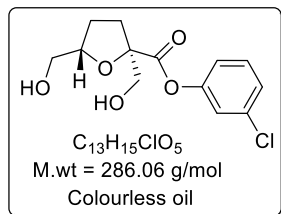
$[\alpha]^{20.5}_D = -0.55$ (c 2.0, CHCl_3). **FT-IR** ν_{max} (neat): 3388 (br), 2926 (s), 1749 (s), 1630 (s), 1510 (s), 1463 (s), 1265 (s), 1120 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.90–7.78 (3H, m, 3 x CH-Ar), 7.59 (1H, d, $J = 2.1$ Hz, CH-Ar), 7.54–7.45 (2H, m, 2 x CH-Ar), 7.24 (1H, dd, $J = 8.9, 2.3$ Hz, CH-Ar), 4.54–4.47 (1H, m, CH-THF), 4.14 (1H, d, $J = 11.6$ Hz, CCHHOH), 3.98–3.87 (2H, m, CHCHHOH and CCHHOH), 3.63 (1H, dd, $J = 11.9, 4.4$ Hz, CHCHHOH), 3.49 (1H, br d, $J = 7.1$ Hz, CHCH_2OH), 3.07 (1H, br s, CCH_2OH), 2.46–2.27 (2H, m, $\text{CH}_2\text{-THF}$), 2.21–1.95 (2H, m, CHH-THF), ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 172.6 (C=O), 148.1 (C-Ar), 133.7 (C-Ar), 131.6 (CH-Ar), 129.5 (C-Ar), 127.8 (CH-Ar), 126.7 (CH-Ar), 125.8 (CH-Ar), 120.7 (CH-Ar), 118.4 (CH-Ar), 87.9 (C-THF), 81.9 (CH-THF), 66.5 (CCH_2OH), 64.4 (CHCH_2OH), 32.2 ($\text{CH}_2\text{-THF}$), 26.9 ($\text{CH}_2\text{-THF}$) ppm. **LRMS**: (ES+) m/z 325 $[\text{M}+\text{Na}]^+$. **HRMS**: (ES+) m/z $\text{C}_{17}\text{H}_{18}\text{O}_5\text{Na}$ Calculated: 325.1053, found: 325.1046. **HPLC**: Chiralpak® OZ-H – (flow rate: 3.0 mL/min, 254 nm, eluent: 5% isopropanol/hexane, Retention times = 28.920 (major), 44.327 (minor)).

(rac)-Naphthalen-2-yl (2S,5R)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.83)



Using the outlined method for **(rac)-2.53** except using diene **2.78** (16.0 mg, 0.063 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.83** (17.2 mg, 0.057 mmol, 90%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

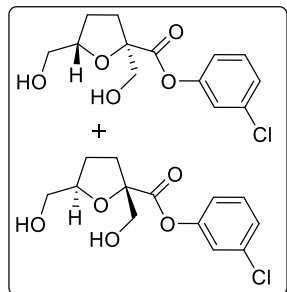
3-Chlorophenyl (2R,5S)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.84)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.79** (0.1 g, 0.424 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/PE (40%) gave THF-diol **2.84** (97.3 mg, 0.34 mmol, 80%) as a colourless oil. Spectroscopic data are reported for a mixture of two enantiomers ($ee = 48.0\%$) determined by HPLC analysis. $[\alpha]^{20.5}_D = +2.5$ (c 2.0, CHCl_3). **FT-IR** ν_{max} (neat): 3385 (br), 2927 (s), 1753 (s), 1589 (s), 1471 (s), 1197 (s), 1087 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.30 (H, m, CH-Ar), 7.25–7.20 (1H, m, CH-Ar), 7.15 (1H, t, $J = 2.0$ Hz, CH-Ar), 7.02 (1H, dt, $J = 8.1, 1.1$ Hz, CH-Ar), 4.48–4.37 (1H, m, CH-THF), 4.07 (1H, d, $J = 11.4$ Hz, CCHHOH), 3.92–3.78 (2H, m, CHCHHOH and CCHHOH), 3.74 (1H, s, CHCH_2OH), 3.58 (1H, dd, $J = 11.8, 4.5$ Hz, CHCHHOH), 2.37–2.16 (2H, m, $\text{CH}_2\text{-THF}$), 2.141.89 (2H, m, $\text{CH}_2\text{-THF}$) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 172.0 (C=O), 150.9 (C-Ar), 134.7 (C-Cl), 130.2 (CH-Ar), 128.4 (CH-Ar), 122.0 (C-Cl), 119.8 (CH-Ar), 87.6 (C-THF), 81.8 (CH-THF), 66.3 (CHCH_2OH), 64.1 (CCH_2OH), 32.0 ($\text{CH}_2\text{-THF}$), 26.7 ($\text{CH}_2\text{-THF}$) ppm. **LRMS**: (ES+) m/z 304 (100%, $\text{C}_{13}\text{H}_{19}^{35}\text{ClNO}_5$) and 306 (42%, $\text{C}_{13}\text{H}_{19}^{37}\text{ClNO}_5$). **HRMS**: (ES+) m/z $\text{C}_{13}\text{H}_{15}^{37}\text{ClO}_5\text{Na}$ Calculated: 309.0504, found: 309.0500 ($[\text{M}+\text{Na}]^+$). **HPLC**: Chiralpak® OZ-H –

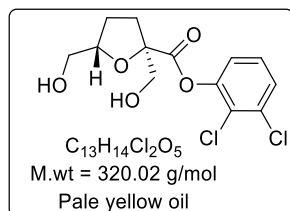
(flow rate: 1.0 mL/min, 250 nm, eluent: 2.5% isopropanol/hexane, Retention times = 75.420 (major), 106.877 (minor)).

(rac)-3-Chlorophenyl (2R,5S)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.84)



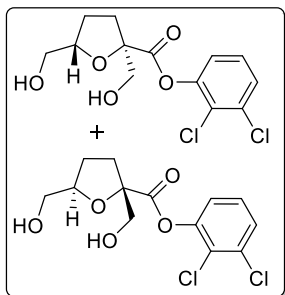
Using the outlined method for **(rac)-2.53** except using diene **2.79** (20.0 mg, 0.084 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.84** (21.7 mg, 0.076 mmol, 90%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

2,3-Dichlorophenyl (2R,5S)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.85)

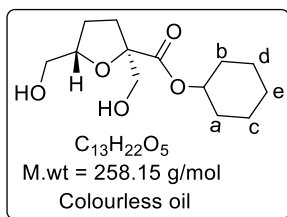


The title compound was prepared according to the outlined method for **2.53**, except using diene **2.80** (40.0 mg, 0.125 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (70%) gave THF-diol **2.85** (34.8 mg, 0.109 mmol, 87%) as a not very pure pale yellow oil.

Spectroscopic data are reported for a mixture of two enantiomers (*ee* = 95.4%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +2.3$ (*c* 2.0, CHCl₃). **FT-IR** $\nu_{\max}$ (**neat**): 3370 (br), 2925 (s), 2855 (s), 1733 (s), 1576 (s), 1477 (s), 1215 (s), 1197 (s), 1071 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.34 (1H, dd, *J* = 8.2, 1.2 Hz, CH-Ar), 7.20 (1H, t, *J* = 8.1 Hz, CH-Ar), 7.05–7.18 (1H, br d, *J* = 9.0 Hz, CH-Ar), 4.43–4.31 (1H, m, CH-THF), 4.07 (1H, d, *J* = 11.6 Hz, CCHHOH), 3.96–3.84 (2H, m, CHCHHOH and CCHHOH), 3.53 (1H, br dd, *J* = 11.9, 4.3 Hz, CHCHHOH), 2.45–2.19 (2H, m, CH₂-THF), 2.18–1.99 (2H, m, CH₂-THF), ppm. **¹³C NMR (100 MHz, CDCl₃)**: 171.5 (C=O), 148.1 (C-Ar), 133.8 (C-Ar), 127.8 (CH-Ar), 127.4 (CH-Ar), 126.1 (C-Ar), 122.0 (CH-Ar), 88.0 (C-THF), 82.0 (CH-THF), 65.7 (CHCH₂OH)₂, 63.9 (CCH₂OH), 31.9 (CH₂-THF), 29.4 (CH₂-THF) ppm. **LRMS**: (ES+) *m/z* 343 (100%, C₁₃H₁₄³⁵Cl₂O₅Na) and 345 (45%, C₁₃H₁₄³⁷Cl₂O₅Na). **HRMS**: (ES+) *m/z* C₁₃H₁₄³⁵Cl₂O₅Na Calculated:343.0114, found:343.0111 ([M+Na]⁺). **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 2.5% isopropanol/hexane, Retention times = 11.503 (minor), 12.297 (major)).

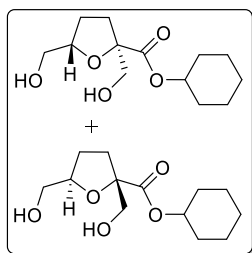
(rac)-2,3-Dichlorophenyl (2R,5S)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.85 (rac)-2.85)

Using the outlined method for **(rac)-2.53** except using diene **2.80** (29.0 mg, 0.084 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (70%) gave THF-diol **(rac)-2.85** (25.0 mg, 0.078 mmol, 93%) as a pale yellow oil. Spectroscopic and physical data are consistent with that reported above.

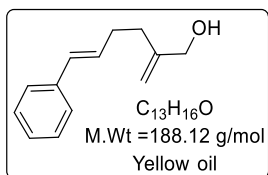
Cyclohexyl (2R,5S)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.86)

The title compound was prepared according to the outlined method for **2.53**, except using diene **2.81** (73.0 mg, 0.35 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.86** (82.6 mg, 0.32 mmol, 90%) as a colourless oil. Spectroscopic

data are reported for a mixture of two enantiomers. $[\alpha]^{20.5}_D = -2.0$ (c 1.3, CHCl₃). **FT-IR** ν_{max} (neat): 3400 (br & weak), 2924 (s), 2855 (s), 1719 (s), 1559 (s), 1455 (s), 1252 (s), 1103 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 4.90–4.81 (1H, m, OCH), 4.42–4.35 (1H, m, CH-THF), 3.92–3.82 (2H, m, CHCHHOH and CCHHOH), 3.75 (1H, br d, $J = 11.5$ Hz, CCHHOH), 3.57 (1H, br dd, $J = 11.8, 3.9$ Hz, CHCHHOH), 2.82 (1H, br s, CHCH₂OH), 2.52 (1H, br s, CCH₂OH), 2.25–2.08 (2H, m, CH₂-THF), 2.08–1.88 (2H, m, CH₂-THF), 1.87–1.78 (2H, m, CH_{2a}), 1.76–1.63 (2H, m, CH_{2b}), 1.57–1.25 (6H, m, CH_{2c}, CH_{2d}, CH_{2e}) ppm. **¹³C NMR (100 MHz, CDCl₃)**: δ 173.2 (C=O), 87.1 (C-THF), 81.4 (CH-THF), 73.5 (OCH), 66.2 (CCH₂OH), 64.6 (CHCH₂OH), 32.0 (^eCH₂ and ^dCH₂), 31.3 (CH₂-THF), 31.1 (CH₂-THF), 25.3 (^eCH₂), 23.5 (^cCH₂ and ^dCH₂) ppm. **LRMS**: (ES+) m/z 259 [M+H]⁺.

(rac)-Cyclohexyl (2R,5S)-2,5-bis(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.86)

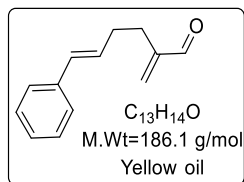
Using the outlined method for **(rac)-2.53** except using diene **2.81** (27.0 mg, 0.13 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.86** (25.0 mg, 0.078 mmol, 94%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

(E)-2-methylene-6-Arenylhex-5-en-1-ol (2.89)

To a solution of ⁿBuLi (14.0 mL, 11.0 M in hexane, 149.20 mmol) and Et₂O (70.0 mL) was added TMEDA (26.1 mL, 174.02 mmol) at 0 °C. To this was added dropwise methallyl alcohol (**2.22**) (4.2 mL, 49.72 mmol) at 0 °C,

followed by THF (40.0 mL). The solution was stirred at 0 °C for 5 min, then the cooling bath was removed and the resultant yellow solution was stirred for 38 h at rt, during which time a dark red gum attributed to the corresponding dianion was observed in the reaction mixture. A solution of cinnamyl bromide (4.9 g, 24.86 mmol) in Et₂O (10.0 mL) was added dropwise at -78 °C, and the mixture was stirred for 15 min. The cooling bath was removed and the reaction mixture was stirred for 8.0 h at rt. At 0 °C the reaction was carefully quenched with H₂O (30.0 mL), acidified to pH 3 with HCl (2.0 N), and re-extracted with Et₂O (8.0 x 60.0 mL), dried (MgSO₄), filtered and concentrated under reduced pressure to afford a crude product as a brownish yellow oil. The crude product was purified by column chromatography (SiO₂) eluting with Et₂O/Hex (5% to 20%) gave the title compound as a yellow oil **2.89** (3.04 g, 16.16 mmol, 65.0%). Spectroscopic data are in agreement with the literature.³¹⁵ **¹H NMR (400 MHz, CDCl₃)** δ 7.4–7.28 (4H, m, 4 x CH-Ar), 7.23 (1H, m, CH-Ar), 6.44 (1H, d, *J* = 16.0 Hz, Ph-CH=CH), 6.27 (1H, m, Ph-CH=CH), 5.1 (1H, d, *J* = 1.1 Hz, C=CHH), 4.95 (1H, d, *J* = 1.2 Hz, C=CHH), 4.12 (2H, s, CH₂OH), 2.41 (2H, q, *J* = 7.6 Hz, CHCH₂CH₂), 2.26 (2H, q, *J* = 7.5 Hz, CHCH₂CH₂), 2.18 (1H, s, OH). **¹³C NMR (100 MHz, CDCl₃)** 148.2 (C=CH₂), 137.6 (C-Ar), 130.1 (Ph-CH=CH), 129.9 (Ph-CH=CH), 128.4 (2 x CH-Ar), 126.9 (CH-Ar), 125.9 (2 x CH-Ar), 109.7 (CH₂=C), 65.8 (CH₂OH), 32.5 (CH₂), 31.2 (CH₂) ppm. **LRMS:** (ES+) *m/z* 227 [M+K]⁺.

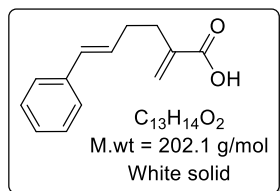
(*E*)-2-methylene-6-Arenylhex-5-enal (**2.90**)



The title compound was prepared according to the outlined method for diester **2.24**, except using alcohol **2.89** (10.0 gm, 7.5 mL, 74.6 mmol). Filtration over celite and concentration under reduced pressure afforded the

title aldehyde as a crude yellow oil **2.90** (2.68 g, 14.4 mmol, 90%) which was used without purification in the next step. Physical and spectroscopic data are consistent with literature.³¹⁶ **¹H NMR (400 MHz, CDCl₃)**: δ 9.57 (1H, s, CHO), 7.38–7.28 (4H, m, 4 x CH-Ar), 7.25–7.19 (1H, m, CH-Ar), 6.43 (1H, d, *J* = 15.9 Hz, Ph-CH=CH), 6.31 (1H, s, C=CHH), 6.25–6.15 (1H, m, Ph-CH=CH), 6.05 (1H, s, C=CHH), 2.50–2.36 (4H, m, 2 x CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 194.5 (CHO), 149.3 (C=CH₂), 137.5 (C-Ar), 134.5 (C=CH), 130.7 (Ph-CH=CH), 129.2 (Ph-CH=CH), 128.5 (CH-Ar), 127.0 (CH-Ar), 125.9 (2 x CH-Ar), 31.0 (CH₂), 27.6 (CH₂) ppm. **LRMS:** (ES+) *m/z* 187 [M+H]⁺.

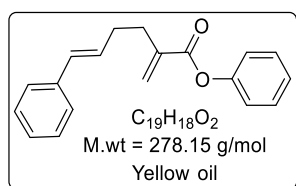
(*E*)-2-methylene-6-Arenylhex-5-enoic acid (**2.91**)



The title compound was prepared according to the outlined method for acid **2.15**, except using aldehyde **2.90** (3.5 g, 25.30 mmol). The crude product was purified by column chromatography (SiO₂) eluting with Et₂O/Hex (40%) gave the title compound as a white solid **2.91** (3.74 g,

24.30 mmol, 97%). Physical and spectroscopic data are in agreement with the literature.³¹⁰ **¹H NMR (400 MHz, CDCl₃)**: δ 11.9 (1H, br s, COOH), 7.39–7.28 (4H, m, 4 x CH-Ar), 7.25–7.19 (1H, m, CH-Ar), 6.44 (1H, d, J = 15.8 Hz, Ph-CH=CH), 6.37 (1H, s, C=CHH), 6.23 (1H, dt, J = 15.8, 6.6 Hz, Ph-CH=CH), 5.73 (1H, d, J = 1.1 Hz, C=CHH), 2.56–2.4 (4H, m, 2 x CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 172.6 (COOH), 139.2 (C=CH₂), 137.6 (C-Ar), 130.7 (Ph-CH=CH), 129.3 (Ph-CH=CH), 129.2 (Ph-CH=CH), 128.5 (2 x CH-Ar), 127.8 (CH-Ar), 127.0 (2 x CH-Ar), 126.0 (C=CH₂), 31.8 (CH₂), 31.4 (CH₂) ppm. **LRMS**: (ES+) m/z 203 [M+H]⁺.

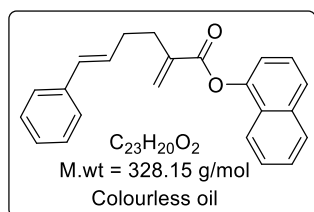
Phenyl (*E*)-2-methylene-6-Arenylhex-5-enoate (**2.92**)



The title compound was prepared according to the outlined method for compound **2.46**, except using phenol (139.7 mg, 1.48 mmol) with acid **2.91** (0.3 g, 1.48 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title compound **2.92** as yellow oil

(0.383 g, 1.38 mmol, 93%). **FT-IR $\nu_{\max}$ (neat)**: 3025 (s), 2928 (s), 1730 (s), 1631 (s), 1591 (s), 1492 (s), 1193 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.40–7.32 (4H, m, 4 x CH-Ar), 7.32–7.27 (2H, m, 2 x CH-Ar), 7.26–7.16 (2H, m, 2 x CH-Ar), 7.13–7.06 (2H, m, 2 x CH-Ar), 6.47–7.40 (2H, m, C=CHH and Ph-CH=CH), 6.29–6.19 (1H, m, Ph-CH=CH), 5.77 (1H, q, J = 1.2 Hz, C=CHH), 2.64–2.57 (2H, m, CH₂), 2.53–2.44 (2H, m, CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 165.6 (C=O), 150.9 (C-Ar), 139.5 (C=CH₂), 137.5 (C-Ar), 130.8 (Ph-CH=CH), 129.4 (Ph-CH=CH), 129.3 (2 x CH-Ar), 128.5 (2 x CH-Ar), 127.0 (2 x CH-Ar), 126.0 (2 x CH-Ar), 125.0 (C=CH₂), 121.6 (2 x CH-Ar), 32.0 (CH₂), 31.8 (CH₂) ppm. **LRMS**: (ES+) m/z 279 [M+H]⁺. **HRMS**: (ES+) m/z C₁₉H₁₉O₂ Calculated: 279.1377, found: 279.1380.

Naphthalen-1-yl (*E*)-2-methylene-6-Arenylhex-5-enoate (**2.93**)



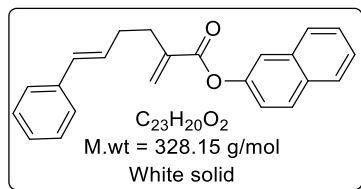
The title compound was prepared according to the outlined method for compound **2.46**, except using 1-Naphthol (143.0 mg, 0.99 mmol) with acid **2.91** (0.2 g, 0.99 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/Hex (2%) gave the title compound **2.93** as colourless oil (0.302 g, 0.92 mmol, 93%).

FT-IR $\nu_{\max}$ (neat): 3055 (s), 1733 (s), 1632 (s), 1597 (s), 1446 (s), 1154 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.79 (1H, br d, J = 7.8 Hz, CH-Ar), 7.76 (1H, br d, J = 8.3 Hz, CH-Ar), 7.66 (1H, d, J = 8.3 Hz, CH-Ar), 7.45–7.35 (3H, m, 3 x CH-Ar), 7.28 (2H, m, 2 x CH-Ar), 7.25–7.10 (4H, m, 4 x CH-Ar), 6.54 (s, 1H, C=CHH), 6.40 (1H, d, J = 15.8 Hz, Ph-CH=CH), 6.19 (1H, dt, J = 15.8, 6.9 Hz, Ph-CH=CH), 5.80 (1H, d, J = 1.1 Hz, C=CHH), 2.62 (2H, t, J = 7.4 Hz, CH₂), 2.54–2.43 (2H, m, CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 165.6 (C=O), 146.8 (C-Ar), 139.4 (C=CH₂), 137.5 (C-Ar), 134.7 (Ph-CH=CH), 130.9 (Ph-CH=CH), 129.3 (2 x CH-Ar), 128.5 (CH-Ar), 128.0 (CH-Ar), 127.4 (C-Ar), 127.0 (C-Ar), 126.9 (CH-Ar), 126.5 (2 x CH-Ar), 126.4 (CH-Ar), 126.0

(CH-Ar), 125.9 (C=CH₂), 125.4 (CH-Ar), 121.2 (CH-Ar), 118.1 (CH-Ar), 32.0 (CH₂), 31.9 (CH₂) ppm.

LRMS: (ES+) *m/z* 329 [M+H]⁺. **HRMS:** (ES+) *m/z* C₂₃H₂₀O₂Na Calculated:351.1360, found:351.1356.

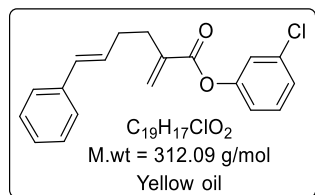
Naphthalen-2-yl (*E*)-2-methylene-6-Arenylhex-5-enoate (**2.94**)



The title compound was prepared according to the outlined method for **2.46**, except using 2-Naphthol (143.0 mg, 0.99 mmol) with acid **2.91** (0.2 g, 0.99 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/Hex (2%) gave the title

compound **2.94** as white solid (0.308 g, 0.94 mmol, 95%). **mp** 53–55 °C, **FT-IR** ν_{max} (neat): 3025 (s), 2926 (s), 1733 (s), 1629 (s), 1599 (s), 1511 (s), 1464 (s), 1207 (s), 1125 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.76 (2H, d, *J* = 8.6 Hz, 2 x CH-Ar), 7.69 (1H, m, CH-Ar), 7.47 (1H, d, *J* = 2.1 Hz, CH-Ar), 7.44–7.36 (2H, m, 2 x CH-Ar), 7.28 (2H, m, 2 x CH-Ar), 7.25–7.19 (2H, m, 2 x CH-Ar), 7.19–7.07 (2H, m, 4 x CH-Ar), 6.44–6.35 (2H, m, Ph-CH=CH and C=CHH), 6.19 (1H, td, *J* = 15.8, 6.8 Hz, Ph-CH=CH), 5.73 (1H, d, *J* = 1.0 Hz, C=CHH), 2.57 (2H, t, *J* = 7.5 Hz, CH₂), 2.45 (2H, q, *J* = 7.0 Hz CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.7 (C=O), 148.5 (C-Ar), 139.6 (C=CH₂), 137.6 (C-Ar), 133.8 (Ph-CH=CH), 131.4 (Ph-CH=CH), 130.8 (CH-Ar), 129.4 (C-Ar), 129.3 (Ph-CH=CH), 128.5 (2 x CH-Ar), 127.7 (CH-Ar), 127.6 (CH-Ar), 127.2 (CH-Ar), 127.0 (2 x CH-Ar), 126.5 (CH-Ar), 126.0 (CH-Ar), 125.7 (C=CH₂), 121.2 (CH-Ar), 118.6 (CH-Ar), 32.1 (CH₂), 31.8 (CH₂) ppm. **LRMS:** (ES+) *m/z* 329 [M+H]⁺. **HRMS:** (ES+) *m/z* C₂₃H₂₀O₂Na Calculated:351.1356, found:351.1356.

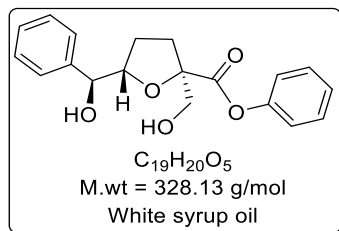
3-Chlorophenyl (*E*)-2-methylene-6-Arenylhex-5-enoate (**2.95**)



The title compound was prepared according to the outlined method for compound **2.46**, except using 3-chloro phenol (139.7 mg, 1.48 mmol) with acid **2.91** (0.3 g, 1.48 mmol). Purification by column chromatography (SiO₂) eluting with Et₂O/PE (2%) gave the title

compound **2.95** as yellow oil (0.383 g, 1.38 mmol, 93%). **FT-IR** ν_{max} (neat): 3024 (s), 2928 (s), 1734 (s), 1633 (s), 1590 (s), 1472 (s), 1200 (w), 1107 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃):** δ 7.39–7.29 (5H, m, 5 x CH-Ar), 7.26–7.20 (2H, m, 2 x CH-Ar), 7.16 (1H, t, *J* = 2.1, CH-Ar), 7.02 (1H, ddd, *J* = 8.1, 2.2, 1.0 Hz, CH-Ar), 6.49–6.42 (2H, m, Ph-CH=CH and C=CHH), 6.30–6.20 (1H, m, Ph-CH=CH), 5.82 (1H, q, *J* = 1.10 Hz, C=CHH), 2.66–2.57 (2H, m, CH₂), 2.55–2.47 (2H, m, CH₂) ppm. **¹³C NMR (100 MHz, CDCl₃):** 165.2 (C=O), 151.3 (C-Ar), 139.2 (C=CH₂), 137.5 (C-CH=CH), 134.7 (C-Cl), 130.9 (Ph-CH=CH), 130.1 (CH-Ar), 129.1 (Ph-CH=CH), 128.5 (2 x CH-Ar), 127.5 (CH-Ar), 121.1 (2 x CH-Ar), 126.1 (CH-Ar), 126.0 (C=CH₂), 122.3 (CH-Ar), 120.0 (CH-Ar), 32.0 (CH₂), 31.7 (CH₂) ppm. **LRMS:** (ES+) *m/z* 313 (50%, C₁₉H₁₈³⁵ClO₂) and 315 (10%, C₁₉H₁₈³⁷ClO₂). **HRMS:** (ES+) *m/z* C₁₉H₁₇³⁵ClO₂Na Calculated:335.0805, found:335.0809.

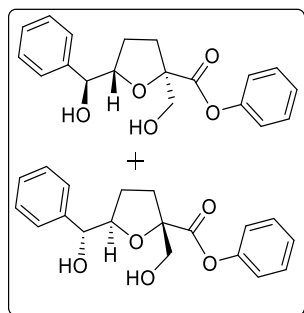
Phenyl (2*R*,5*S*)-5-((*S*)-hydroxy(phenyl)methyl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.96)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.92** (97.0 mg, 0.35 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.96** (0.101 g, 0.308 mmol, 88%) as a white syrup oil. Spectroscopic data are reported for a mixture of two enantiomers

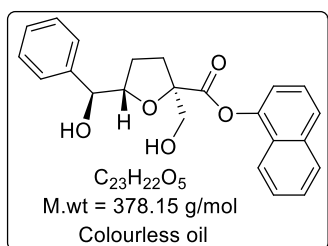
(ee = 49.0%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +9.5$ (c 5.0, CHCl₃). **FT-IR** ν_{max} (neat): 3450 (br), 2873 (s), 1749 (s), 1592 (s), 1493 (s), 1455 (s), 1188 (w) cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.46–7.28 (7H, m, 7 x CH-Ph), 7.27–7.21 (1H, m, CH-Ar), 7.14–7.06 (2H, m, 2 x CH-Ph), 4.63 (1H, d, J = 6.9 Hz, CHOH), 4.38–4.58 (1H, m, CH-THF), 4.07 (1H, br d, J = 11.5 Hz, CHHOH), 3.87 (1H, br d, J = 11.4 Hz, CHHOH), 3.60 (1H, br s, CHOH), 3.27 (1H, br s, CH₂OH), 2.36–2.18 (2H, m, CH₂-THF), 1.99–1.78 (2H, m, CH₂-THF) ppm. **¹³C NMR (100 MHz, CDCl₃)**: 172.3 (C=O), 150.5 (C-Ph), 140.3 (C-Ph), 129.5 (2 x CH-Ph), 128.5 (2 x CH-Ph), 128.1 (CH-Ph), 127.0 (2 x CH-Ph), 126.1 (CH-Ph), 121.3 (2 x CH-Ph), 85.2 (CH-THF), 85.1 (C-THF), 77.1 (CHOH), 66.2 (CHOH), 31.7 (CH₂-THF), 27.8 (CH₂-THF) ppm. **LRMS**: (ES+) m/z 351 [M+Na]⁺. **HRMS**: (ES+) m/z C₁₉H₂₀O₅Na Calculated: 351.1210, found: 351.1203. **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 1.0% isopropanol/hexane, Retention times = 149.16 (minor), 160.72 (major)).

(rac)-Phenyl (2*R*,5*S*)-5-((*S*)-hydroxy(phenyl)methyl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.96)



Using the outlined method for **(rac)-2.53** except using diene **2.92** (18.0 mg, 0.065 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.96** (19.2 mg, 0.056 mmol, 90%) as a white thick oil. Spectroscopic and physical data are consistent with that reported above.

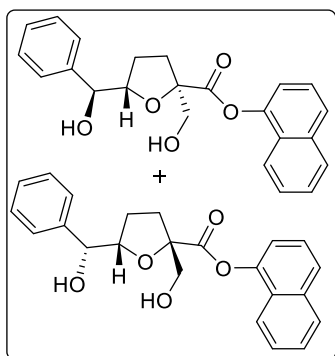
Naphthalen-1-yl (2*S*,5*R*)-5-((*R*)-hydroxy(phenyl)methyl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.97)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.93** (49.0 mg, 0.15 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.97** (46.9 mg, 0.124 mmol, 83%) as a colourless oil. Spectroscopic data are reported for a mixture of two enantiomers (ee

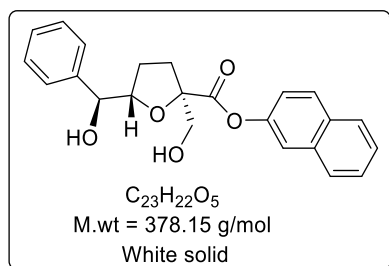
= 78.0%) determined by HPLC analysis. $[\alpha]^{20.5}_D = +5.4$ (c 2.5, CHCl_3). **FT-IR** ν_{max} (neat): 3460 (br), 2928 (s), 1749 (s), 1598 (s), 1454 (s), 1223 (s), 1090 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.95–7.82 (2H, m, 2 x CH-Ar), 7.76 (1H, d, $J = 8.2$ Hz, CH-Ar), 7.57–7.40 (5H, m, 5 x CH-Ar), 7.40–7.29 (3H, m, 3 x CH-Ar), 7.27–7.22 (1H, m, CH-Ar), 4.68 (1H, d, $J = 6.9$ Hz, CHOH), 4.61 (1H, q, $J = 6.9$ Hz, CH-THF), 4.20 (1H, br d, $J = 11.4$ Hz, CHHOH), 3.98 (1H, br d, $J = 11.6$ Hz, CHHOH), 3.48 (1H, br s, CHOH), 3.24 (1H, br s, CH_2OH), 2.53–2.40 (1H, m, CHH-THF), 2.40–2.28 (1H, m, CHH-THF), 2.23–1.88 (2H, m, CH_2 -THF) ppm. **^{13}C NMR (100 MHz, CDCl_3)**: 172.3 (C=O), 146.3 (C-Ar), 140.5 (C-Ar), 134.6 (C-Ar), 128.5 (CH-Ar), 128.2 (2 x CH-Ar), 128.0 (CH-Ar), 127.0 (2 x CH-Ar), 126.7 (2 x CH-Ar), 126.5 (C-Ar), 126.3 (C-Ar), 125.3 (CH-Ar), 121.0 (CH-Ar), 117.8 (CH-Ar), 87.9 (CH-THF), 85.3 (C-THF), 77.2 (CHOH), 66.5 (CH_2OH), 32.0 (CH_2 -THF), 28.0 (CH_2 -THF) ppm. **LRMS**: (ES+) m/z 401 $[\text{M}+\text{Na}]^+$. **HRMS**: (ES+) m/z $\text{C}_{23}\text{H}_{22}\text{O}_5\text{Na}$ Calculated: 401.1356, found: 401.1359. **HPLC**: Chiralpak® OD-H – (flow rate: 1.0 mL/min, 230 nm, eluent: 0.5% isopropanol/hexane, Retention times = 4.334 (minor), 5.236 (major)):

(rac)-Naphthalen-1-yl (2S,5R)-5-((R)-hydroxy(phenyl)methyl)-2(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.97)



Using the outlined method for **(rac)-2.53** except using diene **2.94** (25.0 mg, 0.076 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.97** (24.6 mg, 0.065 mmol, 86%) as a colourless oil. Spectroscopic and physical data are consistent with that reported above.

Naphthalen-2-yl (2S,5R)-5-((R)-hydroxy(phenyl)methyl)-2(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.98)

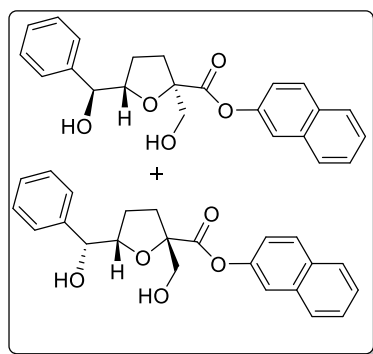


The title compound was prepared according to the outlined method for **2.53**, except using diene **2.94** (58.0 mg, 0.177 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/PE (40%) gave THF-diol **2.98** (54.8 mg, 0.145 mmol, 82%) as a white solid. Spectroscopic data are reported for a mixture of two enantiomers (ee = 64.0%) determined by HPLC

analysis. **mp** 106–108 °C, $[\alpha]^{20.5}_D = +7.7$ (c 2.5, CHCl_3). **FT-IR** ν_{max} (neat): 3447 (br), 2924 (s), 1746 (s), 1630 (s), 1511 (s), 1453 (s), 1264 (s), 1120 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3)**: δ 7.85 (2H, d, J

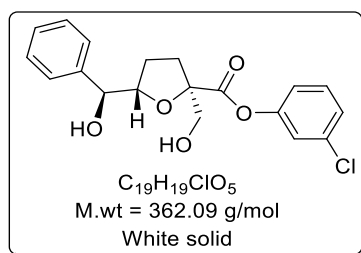
= 9.0 Hz, 2 x CH-Ar), 7.82–7.75 (1H, m, CH-Ar), 7.58 (1H, m, CH-Ar), 7.53–7.40 (4H, m, 4 x CH-Ar), 7.40–7.30 (3H, m, 3 x CH-Ar), 7.23 (1H, d, J = 9.0 Hz, CH-Ar), 4.66 (1H, d, J = 6.9 Hz, CHOH), 4.60–4.53 (1H, m, CH-THF), 4.17–4.08 (1H, m, CHHOH), 3.92 (1H, br d, J = 11.6 Hz, CHHOH), 3.48 (1H, br s, CHOH), 3.24 (1H, br s, CH₂OH), 2.41–2.25 (1H, m, CH₂-THF), 2.04–1.83 (2H, m, CH₂-THF) ppm. ¹³C NMR (100 MHz, CDCl₃): 172.4 (C=O), 148.0 (C-Ar), 140.4 (C-Ar), 133.7 (C-Ar), 131.5 (CH-Ar), 129.5 (C-Ar), 128.5 (2 x CH-Ar), 128.2 (CH-Ar), 127.8 (CH-Ar), 127.6 (2 x CH-Ar), 127.0 (CH-Ar), 126.7 (CH-Ar), 125.8 (CH-Ar), 120.7 (CH-Ar), 118.4 (CH-Ar), 87.7 (CH-THF), 85.2 (C-THF), 77.2 (CHOH), 66.4 (CH₂OH), 31.8 (CH₂-THF), 27.9 (CH₂-THF) ppm. LRMS: (ES+) m/z 401 [M+Na]⁺. HRMS: (ES+) m/z C₂₃H₂₂O₅Na Calculated: 401.1356, found: 401.1359 ([M+Na]⁺). HPLC: Chiralpak® AY-H – (flow rate: 1.0 mL/min, 230 nm, eluent: 0.2% isopropanol/hexane, Retention times = 79.803 (minor), 43.167 (major)).

(rac)-Naphthalen-2-yl (2S,5R)-5-((R)-hydroxy(phenyl)methyl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.98)



Using the outlined method for **(rac)-2.53** except using diene **2.94** (18.0 mg, 0.055 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.98** (17.4 mg, 0.046 mmol, 84%) as a white solid. Spectroscopic and physical data are consistent with that reported above.

3-Chlorophenyl (2R,5S)-5-((S)-hydroxy(phenyl)methyl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.99)

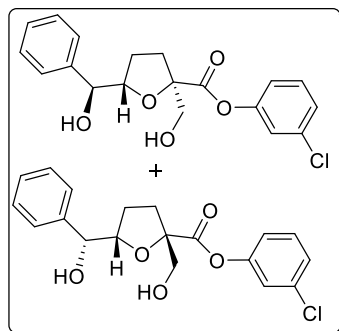


The title compound was prepared according to the outlined method for **2.53**, except using diene **2.95** (61.0 mg, 0.195 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **2.99** (60.0 mg, 0.166 mmol, 85%) as a white solid. Spectroscopic data are reported for a mixture of two

enantiomers (ee = 51.0%) determined by HPLC analysis. mp 116–118 °C, $[\alpha]^{20.5}_D$ = +12.0 (c 5.0, CHCl₃). FT-IR ν_{max} (neat): 3457, 3062 (s), 2865 (s), 1746 (s), 1591 (s), 1430 (s), 1234 (s), 1194 (w) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.46–7.28 (6H, m, 6x CH-Ar), 7.26–7.21 (1H, m, CH-Ar), 7.17–7.13 (1H, m, CH-Ar), 7.01 (1H, ddd, J = 8.1, 2.2, 1.1 Hz, CH-Ar), 4.62 (1H, d, J = 6.9 Hz, CHOH), 4.66–4.54 (1H, m, CH-THF), 4.07 (1H, d, J = 11.6 Hz, CHHOH), 3.85 (1H, br d, J = 11.6 Hz, CHHOH), 3.65 (1H, br d, J = 18.7 Hz, CHOH), 3.38 (1H, br s, CH₂OH), 2.36–2.07 (1H, m, CH₂-THF), 1.97–1.76 (2H, m, CH₂-THF) ppm. ¹³C NMR (100 MHz, CDCl₃): 171.9 (C=O), 150.9 (C-Ar), 140.3 (C-Ar), 134.7 (C-Cl), 130.2

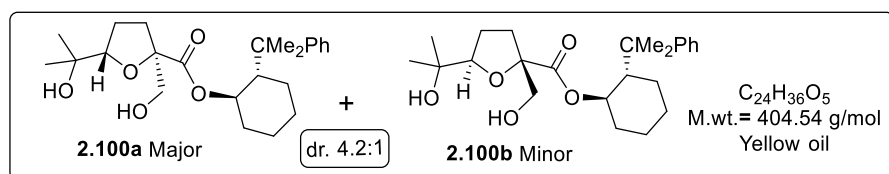
(CH-Ar), 128.5 (2 x CH-Ar), 128.2 (CH-Ar), 127.0 (2 x CH-Ar), 126.4 (CH-Ar), 122.1 (CH-Ar), 119.8 (CH-Ar), 85.3 (CH-THF), 85.2 (C-THF), 77.1 (CHOH), 66.3 (CHOH), 31.7 (CH₂-THF), 27.7 (CH₂-THF) ppm. **LRMS:** (ES+) *m/z* 385 (100%, C₁₉H₁₉³⁵ClO₅Na) and 387 (36%, C₁₉H₁₉³⁷ClO₅Na). **HRMS:** (ES+) *m/z* C₁₉H₁₉³⁵ClO₅Na Calculated: 385.818, found: 385.0813. **HPLC:** Chiralpak® OD-H – (flow rate: 1.0 mL/min, 250 nm, eluent: 1% isopropanol/hexane, Retention times = 103.567 (minor), 114.133 (major)).

(rac)-3-Chlorophenyl (2R,5S)-5-((S)-hydroxy(phenyl)methyl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate (rac)-2.99



Using the outlined method for **(rac)-2.53** except using diene **3.95** (22.0 mg, 0.060 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/PE (40%) gave THF-diol **(rac)-2.99** (19.2 mg, 0.053 mmol, 89%) as a white solid. Spectroscopic and physical data are consistent with that reported above.

(1R,2S)-2-(2-Arenylpropan-2-yl)cyclohexyl(2S,5R)-tetrahydro-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)furan-2-carboxylate (3.42a) and (1R,2S)-2-(2-Arenylpropan-2-yl)(2R,5S)-cyclohexyltetrahydro-2-(hydroxymethyl)-5-(2-hydroxypropan-2-yl)furan-2-carboxylate (2.100)

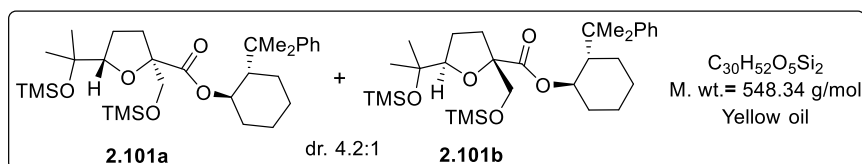


Following the method from Brown *et al.*,⁵⁶ to a vigorously stirred

mixture of TCC dieneoate (**1.59**) (56.0 mg, 0.158 mmol) and phosphate buffer (KH₂PO₄/Na₂HPO₄, pH 7) (0.3 mL) in acetone (0.4 mL) at –35 °C was added a solution of NaMnO₄ (0.6 mL, 0.4M aq., 0.237 mmol) containing AcOH (0.05 mL, 0.474 mmol). The purple mixture was stirred rapidly for 1.5 h, during which time the temperature of the acetone cooling bath had raised to –2 °C and the reaction mixture had turned dark brown. At this stage, the reaction was quenched with sat. aq. Na₂S₂O₅ (5.0 mL) to dissolve all of the precipitated manganese salt and brine (10 mL) was added. The mixture was then repeatedly extracted using CH₂Cl₂ (6 x 20.0 mL). The organic extracts were combined, dried (MgSO₄), filtered and concentrated under reduced pressure to afford the crude product as a yellow oil. The crude was purified by column chromatography (SiO₂) eluting with EtOAc/Hex (50%) to afford inseparable diastereoisomers **2.100a/2.100b** as a yellow oil (60 mg, 0.148 mmol, 94%). The dr. for **2.100a** and **2.100b** was 4.2:1 by 600 MHz ¹H NMR.⁵⁶ **¹H NMR (600**

¹H NMR (400 MHz, CDCl₃): δ 7.29–7.23 (4H, m, 4 x CH-Ar), 7.14 (1H, m, CH-Ar), 4.86_{min} and 4.76_{maj} (1H, td, *J* = 10.7, 4.3 Hz, OCH), 4.01_{maj} and 3.90_{min} (1H, t, *J* = 7.1 Hz, CH, THF), 3.68_{maj} and 3.60_{min} (1H, d, *J* = 11.0 Hz, CHHOH), 3.53_{maj} and 3.49_{min} (1H, d, *J* = 11.0 Hz, CHHOH), 3.03 (1H, br, OH), 2.82 (1H, br, OH), 2.05–1.78 (6H, m, 3 x CH₂, THF), 1.64 (1H, m, CH), 1.56 (1H, m, CH), 1.44 (1H, m, CH), 1.34_{maj} (3H, s, CH₃), 1.25–1.20 (2H, m, 2 x CH), 1.26_{maj} (3H, s, CH₃), 1.25_{maj} (3H, s, CH₃), 1.11_{maj} (3H, s, CH₃), 1.08 (1H, m, CH), 0.94 (1H, m, CH) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 173.5_{maj} and 173.1_{min} (C=O), 150.6_{min} and 150.4_{maj} (CCH-Ar), 128.2_{min} and 128.0_{maj} (2 x CH-Ar), 125.7_{maj} and 125.3_{min} (2 x CH-Ar), 125.34 (CH-Ar), 87.6_{maj} and 87.3_{min} (CH, THF), 86.6_{min} and 86.2_{maj} (CCH₂OH, THF), 76.5_{maj} and 76.4_{min} (OCH), 71.4_{min} and 71.30_{mij} (COH), 65.9_{maj} and 65.4_{min} (CH₂OH), 50.7_{maj} and 50.4_{min} (CHCPh), 40.3_{maj} and min (CPh), 31.9_{maj} and 31.3_{min} (CH₂CH(CH₃)), 30.3_{min} and 29.7_{maj} (CH₂CH₂CH), 28.7_{maj} and 28.4_{min} (CH₂, THF), 27.5_{maj} and min (CH₂, THF), 27.4_{maj} and min, (CH₃), 26.1_{maj} and min (CH₃), 25.8_{maj} and 25.7_{min} (CH₂C), 25.4_{maj} and min (CH₃), 25.1_{maj} and min (CH₃), 24.5_{maj} and min (CH₃) ppm. **LRMS: (ES⁺)** *m/z* 427 [M+Na]⁺.

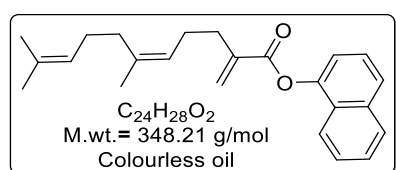
(1*R*,2*S*)-2-(2-Arenylpropan-2-yl)cyclohexyl (2*S*,5*R*)-2-(((trimethylsilyl)oxy)methyl)-5-(2-(((trimethylsilyl)oxy)propan-2-yl)tetrahydrofuran-2-carboxylate (2.100a) and (1*R*,2*S*)-2-(2-Arenylpropan-2-yl)cyclohexyl (2*R*,5*S*)-2-(((trimethylsilyl)oxy)methyl)-5-(2-(((trimethylsilyl)oxy)propan-2-yl)tetrahydrofuran-2-carboxylate (2.101b))



To a solution of THF-TCC **2.100a** and **2.100b** (170 mg, 0.42 mmol) in DMF (3.5 ml) was added

imidazol (350.0 mg, 5.13 mmol) followed by the addition of TMSCl (0.55 mL, 4.2 mmol) at $-5\text{ }^{\circ}\text{C}$. The reaction was stirred for 1 hr at $-5\text{ }^{\circ}\text{C}$ and then 24 hr at rt. The reaction was quenched with Sat. NH_4Cl (1.5 mL), then H_2O (2.0 mL), and extracted with Et_2O (5 x 10.0 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the crude yellow oil **2.100a** and **2.100b** (115 mg, 0.21 mmol, 50%) which was used in the next step without purification. The dr. for **2.101a** and **2.101b** was 4.2:1 by 400 MHz ^1H NMR.

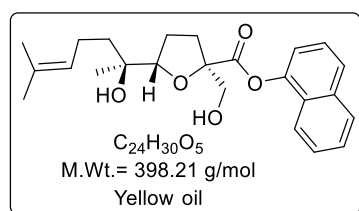
Naphthalen-1-yl (E)-6,10-dimethyl-2-methyleneundeca-5,9-dienoate (2.103)



To a solution of 1-Naphthol (0.597 g, 4.14 mmol) in THF (19 mL) was added NaHMDS (1M in THF, 3.030 mL) at $-75\text{ }^{\circ}\text{C}$. The mixture was allowed to warm to $-5\text{ }^{\circ}\text{C}$ over 1.5 h, then a solution of PFP ester **2.101** (1.072 g, 2.76 mmol) in THF (6 mL) was added dropwise at $-5\text{ }^{\circ}\text{C}$. The cooling bath was removed and the mixture was stirred for 1.5 h at rt. Et_2O (20 mL) and sat. aq. (12 mL) were

added to the mixture. The organic layer was separated, washed with sat. aq. (2 x 15 mL), dried (MgSO_4), filtered and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification with column chromatography (SiO_2) eluting with $\text{Et}_2\text{O}/\text{Hex}$ (5%) gave the title compound **2.103** as a colourless oil (0.8 g, 2.29 mmol, 83%). **FT-IR ν_{max} (neat):** 2963 (s), 2916 (s), 2855 (s), 1735(s), 1632 (s), 1598 (s), 1508 (s), 1443 (s), 1389 (s), 1223 (s), 1105 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3):** δ 7.88–7.81 (2H, m, 2 x CH-Ar), 7.72 (1H, d, J = 8.2 Hz, CH-Ar), 7.52–7.42 (3H, m, 3 x CH-Ar), 7.29–7.23 (1H, m, CH-Ar), 6.57–6.53 (1H, m, =CHH), 5.80 (1H, d, J = 1.3 Hz, =CHH), 5.20 (1H, td, J = 7.2, 1.2 Hz, CH_2CCH), 5.14–5.07 (1H, m, CH_3CCH), 2.52 (2H, t, J = 7.6 Hz, CH_2), 2.32 (2H, q, J = 7.3 Hz, CH_2), 2.13–2.02 (4H, m, 2 x CH_2), 1.72 (3H, d, J = 1.2 Hz, CH_3), 1.66 (3H, s, CH_3), 1.58 (3H, s, CH_3) ppm. **^{13}C NMR (100 MHz, CDCl_3):** 165.6 (C=O), 146.8 (C-Ar), 139.8 (C-Ar), 136.4 (=CH₂), 134.7 (C-CH), 131.6 (C-(CH₃)₂), 128.0 (C-Ar), 127.0 (CH-Ar), 126.8 (CH-Ar), 126.4 (CH-Ar), 126.3 (CH-Ar), 125.9 (CH-Ar), 125.4 (CH-Ar), 124.2 (=CH₂), 123.9 (CH-CH₂), 121.2 (CH-CH₂), 118.1 (CH-Ar), 32.4 (CH₂), 32.0 (CH₂), 26.9 (CH₂), 26.6 (CH₂), 25.7 (CH₃), 23.4 (CH₃), 17.6 (CH₃) ppm. **LRMS:** (ES+) m/z 349 [M+H]⁺. **HRMS:** (ES+) m/z $\text{C}_{24}\text{H}_{28}\text{O}_5\text{Na}$ Calculated: 371.1976, found: 371.1979.

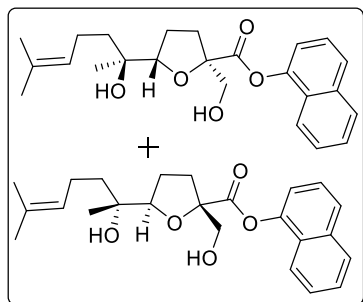
Naphthalen-1-yl ((2S,5R)-5-((S)-2-hydroxy-6-methylhept-5-en-2-yl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate (2.104)



The title compound was prepared according to the outlined method for **2.53**, except using diene **2.103** (37.0 mg, 0.14 mmol). Purification by column chromatography (SiO_2) eluting with EtOAc/Hex (40%) gave THF-diols **2.104** (36.5 mg, 0.116 mmol, 55%)

as a yellow oil. Spectroscopic data are reported for a mixture of two enantiomers (ee = 61.32%) determined by HPLC analysis. **$[\alpha]^{20.5}_{\text{D}}$** = +17.32 (c 2.5, CHCl_3). **FT-IR ν_{max} (neat):** 3413 (br), 3055(s), 2928 (s), 1753(s), 1599 (s), 1461 (s), 1264 (s), 1091 (w) cm^{-1} . **^1H NMR (400 MHz, CDCl_3):** δ 7.97–7.86 (2H, m, 2 x CH-Ar), 7.77 (1H, d, J = 8.3 Hz, CH-Ar), 7.56–7.45 (3H, m, 3 x CH-Ar), 7.28–7.24 (1H, m, CH-Ar), 5.13 (1H, br t, J = 7.1 Hz, $\text{CH}=(\text{CH}_3)_2$), 4.27 (1H, t, J = 7.5 Hz, CH-THF), 4.16 (1H, d, J = 11.5 Hz, CHHOH), 3.99 (1H, d, J = 11.5 Hz, CHHOH), 3.26 (1H, br s, CH_2OH), 2.59–2.35 (3H, m, OH and CH_2), 2.24–1.98 (4H, m, 2 x CH_2), 1.7 (3H, s, CH_3), 1.63 (3H, s, CH_3), 1.58–1.44 (2H, m, CH_2), 1.39 (3H, s, CH_3) ppm. **^{13}C NMR (100 MHz, CDCl_3):** 172.5 (C=O), 146.3 (C-Ar), 134.6 (C-Ar), 132.0 (C(CH₃)₂), 128.0 (CH-Ar), 126.8 (CH-Ar), 126.6 (CH-Ar), 126.5 (C-Ar), 126.2 (=CH), 125.3 (CH-Ar), 124.1 (CH-Ar), 121 (CH-Ar), 117.6 (CH-Ar), 87.4 (C-THF), 86.7 (C-THF), 73.4 (C-OH), 66.6 (CH_2OH), 38.2 (CH_2), 32.5 (CH_2 -THF), 25.8 (CH_2 -THF), 25.7 (CH_3), 24.0 (CH_2), 17.7 (CH_3) ppm. **LRMS:** (ES+) m/z 421 [M+Na]⁺. **HRMS:** (ES+) m/z $\text{C}_{24}\text{H}_{30}\text{O}_5\text{Na}$ Calculated: 421.1988, found: 421.1985. **HPLC:** Chiralpak® OZ-H – (flow rate: 1.0 mL/min, 270 nm, eluent: 5% isopropanol/hexane, Retention times = 20.233 (major), 25.183 (minor)).

(rac)-Naphthalen-1-yl (2*S*,5*R*)-5-((*S*)-2-hydroxy-6-methylhept-5-en-2-yl)-2-(hydroxymethyl)tetrahydrofuran-2-carboxylate ((rac)-2.104)



Using the outlined method for **(rac)-2.53** except using diene **2.103** (52.0 mg, 0.15 mmol). Purification by column chromatography (SiO₂) eluting with EtOAc/Hex (40%) gave THF-diols **(rac)-2.104** (41.8 mg, 0.105 mmol, 70%) as a yellow oil. Spectroscopic and physical data are consistent with that reported above.

5.3 Computational methods

All calculations were performed using Gaussian 09 using two DFT functionals. The hybrid functional B3LYP^{317–320} was used with the split valence triple- ζ (TZ) basis set 6-311+G(d)^{321–324} for C, H, O and N otherwise mentioned. The hybrid meta-generalized gradient approximation functional M06-2X^{325,326} was used with the augmented correlation-consistent polarized valence double- ζ (DZ) basis set (aug-cc-pVDZ)^{327–329} for C, H, O, and N atoms. Hay-Wadt VDZ (n+1) ECP was used for Mn and Os atoms.³³⁰ All minima intermediates were verified by the absence of negative eigenvalues in the vibrational frequency analysis. Transition state structures were found using the Berny algorithm,^{331,332} and verified by vibrational analysis. The transition states were visualised by animating the negative eigenvector coordinate. In order to determine the minimum energy path (MEP) on the potential energy surface (PES), intrinsic reaction coordinate (IRC) calculations, by defining the phase for the transition vector motion along the path, were performed for the identified transition states using the Hessian-based Predictor-Corrector integrator to confirm the reaction path proceeding in both directions (reactant and product), in which the Hessian was recomputed every 3 predictor steps with a step size along the reaction path of 0.05 Bohr.^{333–335} Free energies (ΔG) and enthalpies (ΔH) were obtained through thermochemical analysis based on vibrational frequencies. Atomic polar tensor changes (APT) are computed by during vibrational frequency calculations.³³⁶ All energies reported in this paper are Gibbs free energies or enthalpies at 253.15 and 298.15 K for Mn and Os oxidative cyclisation, respectively (otherwise mentioned) using unscaled frequencies. The effect of solvent was included via the solvation model based on density (SMD).³³⁷ The solvation model was used with acetone as a representative solvent medium otherwise mentioned. All energies are in kcal/mol. All activation free energies are quoted relative to infinitely separated reagents.

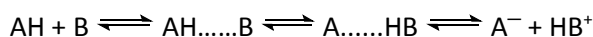
Direct molecular dynamics trajectory calculations using the atom-centered density matrix propagation (ADMP),^{338,339} where the electronic structures and the density matrix are propagated classically by using Lagrangian approach,^{340–342} were used to understand dynamics of the **SRS** at the atomic-level. ADMP was selected due to its suitability for application to organometallic systems, and reduced computational cost.³⁴³ The same level of theory (M06-2X/aug-cc-pVDZ for C, H, N and O, and Hay-Wadt VDZ (n+1) ECP for Mn and Os) was employed for calculations. The classical calculations were initialized in the region of the potential energy surface near to the transition state (TS), and performed using Gaussian 09. The TS was initiated into forward and backward propagations showing only one product and reactant. Products are defined as having C–O bonds between 1.4 and 1.5 Å whereas more than 3.0 Å was considered to represent separated species. A time step of 0.25 fs was used for all of the trajectories in this study over periods of 150.0 fs. The initial nuclear kinetic energy was set to 0.1 Hartree with a default density kinetic energy. The default

fictitious electron mass for the electronic degrees of freedom was 0.1 amu. To ensure that the DMDT simulations remain on the ground-state electronic surface, the supplied kinetic energy (0.1 hartrees) was less than the HOMO-LUMO gap (>4.5 eV / 0.17 hartrees). All dynamics were performed with fully converged SCF results without reporting the band gap at each step. A thermostat was employed to maintain a constant temperature either at 253.15 K or 298.15 K.^{344,345}

Also, the free energy of activation for all (3+2) cycloaddition TSs (osmylation and permanganation steps) were corrected using Truhlar's quasiharmonic correction, by raising vibrational frequencies that are below 100 cm^{-1} to 100 cm^{-1} .³⁴⁶

Computational details of the proton transfer calculations are summarised:

1. In the case of intermolecular proton transfer (PT) between two molecules $\text{AH} + \text{B} \rightarrow \text{A}^- + \text{BH}^+$, when we have a proton donor (AH) and proton acceptor (B):



Here, the energy difference between the separately optimised products ($\text{A}^- + \text{HB}^+$) and reactants ($\text{AH} + \text{B}$) gives the free energy of protonation (ΔG_r), whereas the energy difference between the encounter-complex optimised product ($\text{A} \cdots \cdots \text{HB}$) and reactant ($\text{AH} \cdots \cdots \text{B}$) gives the intrinsic barrier ($\Delta G_0^\ddagger$).

2. In the case of intramolecular PT, the encounter-complex will not be involved in the PT since the transfer occurs between two atoms within the same molecule which appears in **4.22_{H+}** and **4.22'_{H+}**. Therefore, $\Delta G_r = \Delta G_0^\ddagger$.
3. The activation energy of proton transfer is then calculated based on the following equation:

$$\Delta G^\ddagger = (\Delta G_r)^2 / 16\Delta G_0^\ddagger + \Delta G_0^\ddagger + \frac{1}{2} \Delta G_r$$

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Appendix A

All computational details involve cartesian coordinates and absolute energies are attached on CD driver.

Appendix A Computational details

Cartesian coordinates, total electronic energies (E), enthalpies (H), and free energies (G) of all stationary points during the reaction pathways. All provided geometries were optimised at the specified level of theory. All energies are in Hartree. Here, s, t, q, and qr refers to singlet, triplet, quintet, and quartet spin multiplicity, respectively.

5.3.1.1 Permanganate-mediated oxidative cyclisation computational and cartesian coordinates data accounted from (SMD)-M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of theory

MnO_4^-

Mn	-0.0002880	0.0001012	-0.0000458
O	1.0865250	0.5320782	-1.0139948
O	-1.0779050	-0.8502998	-0.7794868
O	0.6969800	-0.9058638	1.0885852
O	-0.7053120	1.2239842	0.7049422

E = -404.651852595
H = -404.634027, G = -404.661553

MnO_4^- (calculated in water at 298.15)

E = -404.670554893, H = -404.651444
G = -404.685111

MnO_4^- (optimisation by M062X/aug-cc-pVDZ)

E = -404.651704215, H = -404.633769
G = -404.660418

$\text{MnO}_4^- \bullet \text{TEAI}$

Mn	-3.5444651	-0.0296145	-0.3461509
O	-2.6539011	-0.1131815	-1.6514119
O	-5.0566681	-0.0554165	-0.7067009
O	-3.1750011	1.3087245	0.4169671
O	-3.1718061	-1.2583465	0.5844851
N	0.6015309	0.0032505	0.0726631
C	-0.1286311	-1.2433015	-0.3912779
H	-1.1552191	-1.1600365	-0.0280889
H	-0.1801721	-1.1728975	-1.4799729
C	-0.1224831	1.1846015	-0.5454039
H	-0.1683301	0.9844325	-1.6180419
H	-1.1510791	1.1462495	-0.1792199
C	0.4971859	2.5383785	-0.2563689
H	1.4925379	2.6669995	-0.6970609
H	-0.1635351	3.2858835	-0.7086069
H	0.5414919	2.7610905	0.8155701
C	0.4876689	-2.5555295	0.0539301
H	-0.1676871	-3.3480145	-0.3233769
H	1.4890159	-2.7305635	-0.3560069
H	0.5153649	-2.6607185	1.1439811
C	2.0463999	-0.0304265	-0.3435829
H	2.4986149	0.8865565	0.0445211
H	2.5000329	-0.8699425	0.1915211
C	2.2832229	-0.1550775	-1.8379899

H	1.8553519	0.6828545	-2.3977939
H	3.3658589	-0.1471625	-2.0051399
H	1.8916489	-1.0933395	-2.2438049
C	-0.7809351	0.2011965	2.2212761
H	-0.6302341	0.2059605	3.3067711
H	-1.3080631	1.1197225	1.9454601
H	-1.4347251	-0.6414685	1.9701051
C	0.5921119	0.1000835	1.5825851
H	1.2045809	0.9732025	1.8288141
H	1.1303159	-0.7841495	1.9373511

E = -776.018841587, H = -775.293123

G = -775.768260

MnO₄⁻ • 8H₂O

Mn	0.1175409	-0.3889253	-0.4244427
O	0.1937149	1.1838847	-0.2785477
O	-0.5290211	-0.7434733	-1.8100667
O	1.5609199	-0.9957513	-0.3436517
O	-0.7759861	-0.9876633	0.7051433
O	-2.1300811	0.9574447	2.7383613
H	-2.2364211	1.5889437	2.0137363
H	-1.7091491	0.1941747	2.3232023
O	-1.9141451	-3.6258213	1.6621143
H	-1.4002981	-2.8102613	1.7025413
H	-2.2899101	-3.5899103	0.7702713
O	4.1205569	-2.6701603	-0.2399457
H	3.2215069	-2.3612393	-0.0664187
H	4.6495639	-1.8713853	-0.1163047
O	4.1252209	0.2710527	0.3845903
H	4.0579169	1.1737577	0.0663283
H	3.2821129	-0.1327933	0.1272403
O	2.0448569	3.4078327	0.3769973
H	2.8998259	3.1109407	0.0575573
H	1.4404869	2.6816547	0.1630523
O	-2.0869831	2.7439787	0.3433393
H	-1.9013431	3.6880497	0.3341133
H	-1.2203781	2.3195907	0.2131493
O	-2.4309231	-2.9252013	-1.1986947
H	-1.7945161	-2.1988993	-1.2753887
H	-3.1011331	-2.7220093	-1.8563577
O	-2.2177641	1.7041907	-2.4646167
H	-2.3624051	2.0379387	-1.5679807
H	-1.6137671	0.9600587	-2.3393217

E = -1016.03327633, H = -1015.804746

G = -1015.873830

MnO₄⁻ • 8H₂O (in gas phase)

E = -1015.95313239, H = -1015.724602

G = -1015.793686

MnO₄²⁻ • 8H₂O

Mn	-0.0957412	-0.2993787	-0.5309842
O	-0.6878162	1.2550003	-0.5020592
O	-1.0635402	-1.3263937	-1.3823892
O	1.5083688	-0.4022887	-0.9016392
O	-0.3371262	-0.8968527	1.1500148
O	-1.2784672	0.6926553	3.3341608
H	-1.7461602	1.2586813	2.6916438
H	-0.9493542	-0.0197237	2.7685968
O	1.6967608	-2.3580777	2.4740388
H	0.9812518	-1.8466567	2.0438358

H	2.3791238	-2.3827397	1.7810528
O	3.7720958	-1.7646747	-0.4631962
H	2.8610648	-1.3841877	-0.5060802
H	4.3093988	-1.0187567	-0.7662222
O	3.3771658	1.5612423	-1.0342692
H	2.8761428	2.2979053	-1.3698072
H	2.6966648	0.8462453	-0.9859732
O	0.6140858	3.6251513	-0.6241652
H	1.3620058	3.4229603	-1.1735732
H	0.1341318	2.7603263	-0.5797292
O	-2.3730262	2.1370263	1.2439588
H	-2.3202972	3.0692773	1.0087038
H	-1.7290722	1.7141303	0.5938958
O	-2.0846592	-3.6969917	-0.6614472
H	-1.6084572	-2.8315417	-0.7404812
H	-2.6377022	-3.6695407	-1.4481032
O	-3.4627982	-0.2957037	-2.1382622
H	-3.6417872	0.1902713	-1.3213632
H	-2.5522562	-0.6373657	-1.9601582

E = -1016.24188165, H = -1016.020220
G = -1016.084929

MnO₄²⁻

Mn	0.1058476	-0.0031050	-0.1038200
O	0.8288126	1.4957590	-0.0948270
O	1.1393156	-1.2828130	0.1155410
O	-1.0596134	-0.2163300	-1.2957260
O	-1.0143624	0.0064890	1.3788320

E = -404.787710499, H = -404.773703
G = -404.806740

MnO₄²⁻ • 8H₂O (in gas phase)

E = -1016.01006754, H = -1015.788407
G = -1015.853114

MnO₄³⁻

Mn	-0.0001124	-0.0000242	-0.0001184
O	0.8851726	-0.9537352	-1.1628154
O	-0.7413694	1.3593248	-0.8051084
O	1.0944546	0.5786818	1.2300146
O	-1.2381454	-0.9842472	0.7380276

E = -404.920304199, H = -404.906335 G = -404.936153

MnO₄⁴⁻

Mn	-0.0001334	0.0000150	0.0000850
O	1.0363476	1.4323580	-0.1066400
O	-0.9581034	0.0358690	1.4895410
O	1.0573046	-1.4207010	-0.0245010
O	-1.1354154	-0.0475410	-1.3584850

E = -404.939043776, H = -404.927730
G = -404.957687

NaMnO₄

Mn	-0.4896148	0.0000012	-0.0000038
O	-1.3769848	0.0124712	1.2698972
O	-1.3776118	-0.0125648	-1.2694578
O	0.4834222	1.2786252	-0.0126508
O	0.4835602	-1.2785308	0.0122112
Na	2.2772292	-0.0000018	0.0000042

E = -566.850947354, H = -566.830190
G = -566.861952

NaMnO₄ (ln water at 298.15 K)
H = -566.842643, G = -566.879100

MnO₄⁻ • TMAI

Mn	-2.9988127	0.0645218	0.1247794
O	-2.4963297	0.0066238	-1.3769886
O	-4.5495497	0.1032708	0.1938674
O	-2.3652517	1.3515238	0.7981794
O	-2.4265787	-1.2069382	0.8772324
N	0.8658633	-0.0182982	-0.0362446
C	2.3507773	-0.0474162	-0.0949606
H	2.7061783	-0.9490242	0.4122874
H	2.6629563	-0.0583552	-1.1432806
H	2.7416543	0.8437878	0.4045484
C	0.3223033	-1.2596122	-0.6770436
H	0.7075933	-1.3064952	-1.6998216
H	0.6699363	-2.1187122	-0.0959436
H	-0.7699787	-1.2107612	-0.6771446
C	0.4312733	0.0430488	1.3973014
H	-0.6606437	0.0104128	1.4405514
H	0.8649043	-0.8168962	1.9163394
H	0.8068683	0.9777718	1.8234314
C	0.3664733	1.1896128	-0.7700776
H	0.8228413	2.0731218	-0.3139806
H	0.6703203	1.0975098	-1.8168806
H	-0.7227987	1.2313028	-0.6861506

E = -618.824583487, H = -618.635950
G = -618.676115

3.1

C	1.4909188	0.0650195	0.3644589
C	2.7732038	0.1359535	0.0013759
H	3.2073458	1.1217875	-0.1946501
H	1.0598958	-0.9199975	0.5695649
C	3.6860528	-1.0433785	-0.1560851
C	0.5794538	1.2495125	0.5083079
H	0.1479008	1.2652615	1.5203599
H	1.1646648	2.1708345	0.3833299
C	-0.5794582	1.2495175	-0.5082981
H	4.5479498	-0.9668855	0.5208929
H	3.1572278	-1.9789965	0.0612519
H	4.0840638	-1.0990555	-1.1785421
H	-1.1646702	2.1708445	-0.3833551
H	-0.1478792	1.2652215	-1.5203441
C	-1.4909392	0.0650495	-0.3644041
C	-2.7732792	0.1359855	-0.0015051
H	-1.0598112	-0.9199965	-0.5691291
C	-3.6860532	-1.0434085	0.1560249
H	-3.2074372	1.1218095	0.1944899
H	-4.5480302	-0.9669745	-0.5208591
H	-3.1571772	-1.9789765	-0.0614021
H	-4.0839432	-1.0991265	1.1785169

E = -313.128808619, H = -312.921500
G = -312.957248

3.1-extended

C	-4.3363515	0.1742613	0.1323367
H	-5.0447225	-0.3700087	-0.5073223
H	-4.7207155	0.1163643	1.1598857
H	-4.3286165	1.2263723	-0.1764263

C	-2.9634975	-0.4221407	0.0384177
H	-2.8639745	-1.4718067	0.3331757
C	-1.8755935	0.2281403	-0.3783053
H	-1.9709735	1.2791703	-0.6728853
C	-0.4986835	-0.3625477	-0.4590753
H	-0.5384295	-1.4278077	-0.1907043
H	-0.1222815	-0.3014097	-1.4913083
C	0.4987485	0.3624293	0.4599517
H	0.5384075	1.4276793	0.1915727
H	0.1225945	0.3012043	1.4922257
C	1.8757395	-0.2282507	0.3787647
H	1.9713325	-1.2792687	0.6733027
C	2.9634005	0.4221823	-0.0383583
H	2.8635675	1.4717713	-0.3333273
C	4.3362815	-0.1740977	-0.1330043
H	4.7197345	-0.1168827	-1.1609503
H	5.0451455	0.3706743	0.5056397
H	4.3288865	-1.2260277	0.1763937

E = -313.129564983, H = -312.921210
G = -312.959740

3.2

C	1.1283404	-0.1279243	0.3710792
H	1.2597614	-0.2414563	1.4632922
O	0.0000074	-0.8803603	-0.0389858
C	0.7715614	1.3287407	0.0210962
H	1.2004334	2.0358437	0.7383252
H	1.1593184	1.5784597	-0.9743628
C	-0.7716146	1.3286617	0.0208082
H	-1.2008546	2.0359587	0.7376232
H	-1.1590516	1.5778887	-0.9749018
C	-1.1283286	-0.1279373	0.3710662
H	-1.2596896	-0.2412783	1.4633102
C	2.3747484	-0.6548213	-0.3092238
H	2.1737144	-0.6734343	-1.3943208
C	-2.3747466	-0.6549023	-0.3091558
H	-2.1736986	-0.6736773	-1.3942528
C	-3.5852186	0.2214217	-0.0074748
H	-3.7330596	0.2916227	1.0779892
H	-3.4660646	1.2299487	-0.4212718
H	-4.4886286	-0.2184783	-0.4490618
C	3.5852514	0.2213627	-0.0073378
H	3.4663004	1.2299017	-0.4211598
H	3.7329334	0.2915697	1.0781472
H	4.4886964	-0.2186423	-0.4487508
O	-2.5743616	-1.9758083	0.1731002
H	-3.3406816	-2.3534223	-0.2690858
O	2.5742744	-1.9758443	0.1728382
H	3.3406564	-2.3533943	-0.2693288

E = -540.015159387, H = -539.790157
G = -539.832441

3.3

C	-0.1194238	-1.6615352	0.2116446
H	0.4126122	-2.6099542	0.1586086
H	-1.1341718	-1.6794532	0.6117856
C	0.4431602	-0.5252852	-0.1947614
H	1.4661082	-0.5191612	-0.5785014
C	-0.2477768	0.8031718	-0.1822274
H	-1.2155868	0.7162758	0.3366666
H	-0.4372568	1.1245688	-1.2202514

O	0.6061042	1.7359378	0.4704546
H	0.2262312	2.6154348	0.3865816

E = -193.062865497, H = -192.971250
G = -193.004373

3.4

C	-0.3146365	1.6177880	-0.0711491
H	0.0595385	2.4282040	0.5488689
H	-0.3735375	1.8005840	-1.1421971
C	-0.8976625	0.5190290	0.4805239
H	-1.0162395	0.4370510	1.5605719
C	-1.6387275	-0.4919540	-0.3551001
H	-1.1903325	-0.5011310	-1.3642911
H	-2.6967005	-0.2026820	-0.4548661
O	-1.6394135	-1.7880730	0.2110709
H	-0.7114145	-1.9335060	0.4617149
Mn	2.1376715	-0.4046630	0.0172539
O	0.8012095	-0.8625710	0.8096849
O	2.4285895	-1.3974260	-1.1626041
O	3.3336235	-0.2527170	1.0227569
O	1.7180315	1.0320670	-0.5622381

E = -597.731296921, G = -597.665849

3.4_{Na}

C	0.9097628	1.6018274	0.1167332
H	0.6716268	2.4684364	-0.4945828
H	0.9618668	1.7522414	1.1936742
C	1.3178918	0.4339944	-0.4428378
H	1.4177708	0.3455614	-1.5249328
C	1.8584048	-0.7083256	0.3737222
H	1.3805948	-0.6960266	1.3680812
H	2.9396218	-0.5735876	0.5195752
O	1.7094888	-1.9640286	-0.2554028
H	0.7781068	-2.0398246	-0.4981828
Mn	-1.9054012	0.0402504	-0.0810198
O	-0.6863852	-0.6478716	-0.8169118
O	-2.5129272	-0.9204166	1.0486752
O	-3.0732182	0.4102144	-1.1134668
O	-1.2778132	1.3341254	0.5536002
Na	-4.4893912	-0.8365706	0.0532762

E = -759.926438197, G = -759.860840

3.5

C	-0.3844855	-1.1638061	-0.8705970
H	0.2666895	-1.7839911	-1.5152990
H	-1.4008815	-1.1625361	-1.3100370
C	0.1884095	0.2434329	-0.7843900
H	0.5717955	0.5939679	-1.7608210
C	-0.8468855	1.2424849	-0.2657800
H	-1.3685275	0.7904719	0.5939220
H	-1.5793855	1.4862749	-1.0488830
O	-0.2095735	2.4501419	0.1176720
H	0.5899515	2.1444969	0.5744390
Mn	0.9211815	-1.0217551	1.4585750
O	1.2633945	0.1949959	0.1266020
O	0.3449655	-0.2635731	2.6962960
O	2.0783445	-2.0643521	1.5570400
O	-0.4349925	-1.6862531	0.4312610

E = -597.896478252, H = -597.781356
G = -597.825684

3.5_{Na}

C	-0.0359332	1.6197063	-0.0743728
H	0.3921598	2.3297313	0.6502152
H	-0.7257122	2.1634163	-0.7388148
C	-0.7190703	0.4702823	0.6487072
H	-1.2187043	0.7927443	1.5748492
C	-1.7155953	-0.2615157	-0.2443468
H	-1.2404942	-0.4572328	-1.2211268
H	-2.6071422	0.3586253	-0.4035888
O	-2.1429443	-1.4643678	0.3616602
H	-1.3407333	-1.8898048	0.6921652
Mn	1.6510588	-0.4250478	-0.1519718
O	0.3115278	-0.4410677	1.0156782
O	1.5720568	-1.6637788	-1.1412518
O	3.0625287	-0.1872767	0.5322952
O	1.0000878	1.0577553	-0.8618898
Na	3.7569098	-2.0021688	-0.6382068

E = -760.089831396, H = -759.970132
G = -760.019194

3.6

C	-0.9822146	-0.3853100	0.0000234
H	-2.0134946	-0.0383810	0.0001434
H	-0.8007926	-1.4585270	-0.0001446
C	0.0253894	0.4905620	-0.0000106
H	-0.1465106	1.5659720	0.0000414
C	1.4022354	0.0715280	-0.0001286
N	2.5153874	-0.2458440	0.0000754

E = -170.785992877, G = -170.760750

3.7

C	-0.6103585	1.2861566	-0.1459114
H	-0.2109275	2.0838736	0.4730346
H	-0.7566615	1.4959556	-1.2015944
C	-1.2451575	0.2309346	0.4443726
H	-1.2624675	0.1005026	1.5213626
Mn	1.8246905	-0.6550034	0.0270866
O	0.5097545	-1.2736284	0.6796686
O	2.3260685	-1.5593364	-1.1496864
O	2.9196465	-0.4296684	1.1278996
O	1.3193895	0.7721946	-0.5470234
C	-2.0542985	-0.6743754	-0.3162464
N	-2.7596785	-1.3776054	-0.9129624

E = -575.452436850, G = -575.421142

3.8

C	0.2479441	-1.0432623	-0.5191847
H	-0.1726409	-1.9594503	-0.0610767
H	1.0599401	-1.3325083	-1.2085247
C	0.7542971	-0.1622203	0.6268413
H	1.2922451	-0.7646403	1.3806843
Mn	-1.7084919	0.6867037	-0.0216907
O	-0.3447749	0.4626247	1.2024853
O	-1.7621569	2.1671477	-0.4967217
O	-2.9714339	-0.1104323	0.4259393
O	-0.7340589	-0.3234353	-1.1978647
C	1.7574431	0.8279457	0.1197983
N	2.5816881	1.5515277	-0.2506857

E = -575.611946535, G = -575.576483

3.9

C	-0.1949917	-1.5735417	0.0110191
H	0.3037583	-2.5406077	-0.0183069
H	-1.2828027	-1.5476177	0.0743531
C	0.4952983	-0.4346027	-0.0289259
H	1.5816393	-0.4022267	-0.0922619
O	0.6364893	1.9076723	-0.0367529
H	0.1010473	2.7141603	-0.0053669
C	-0.2224337	0.8659713	0.0132181
O	-1.4180047	1.0107923	0.0830241

E = -267.110197640, G = -267.070319

3.9-H⁺

C	-0.1771681	-1.2410109	0.0706166
H	0.3226999	-2.2123949	0.0877556
H	-1.2659711	-1.2035779	0.1337906
C	0.4990569	-0.0939559	-0.0252164
H	1.5915339	-0.0887339	-0.0906794
O	0.6281849	2.2497041	-0.1460974
C	-0.1740861	1.2882551	-0.0519184
O	-1.4242501	1.3017141	0.0217486

E = -266.651504846, G = -266.625514

3.10

C	-0.6947042	-0.8293945	-1.1584084
H	-0.3234582	-1.6008075	-1.8266424
H	-1.7072942	-0.9282365	-0.7747354
C	-0.0715522	0.3792715	-1.0795274
H	0.8816718	0.5807605	-1.5583684
O	0.0132958	2.6417915	-0.4506334
H	-0.4813902	3.2836105	0.0757066
Mn	1.0031628	-1.3155055	1.4382196
O	1.1712078	0.1695115	0.8866946
O	0.3565768	-1.2935925	2.8659346
O	2.3837898	-2.0624765	1.4114406
O	-0.0129162	-1.9997315	0.3836616
C	-0.7199252	1.4929555	-0.3852944
O	-1.7984642	1.4818435	0.1719516

E = -671.778229328, G = -671.731710

3.10-H⁺

C	-0.7356390	-0.4949795	-1.0711765
H	-0.3251170	-1.3097435	-1.6636685
H	-1.7799430	-0.5410605	-0.7660115
C	-0.0690650	0.6883205	-0.9220075
H	0.9182880	0.8201235	-1.3640465
O	-0.1516910	3.0416615	-0.8097345
Mn	0.9991440	-1.2345585	1.4760155
O	1.1273950	0.2534455	0.9076085
O	0.4929900	-1.2175465	2.9772135
O	2.3728580	-2.0129805	1.2930115
O	-0.1256220	-1.8681025	0.5148465
C	-0.7853370	1.9881065	-0.5287935
O	-1.9382610	1.8873135	-0.0432565

E = -671.314001571, G = -671.281543

3.11

C	-0.0641106	1.3235684	0.4213241
H	-0.5390036	2.1945134	-0.0691049

H	0.7509494	1.6801964	1.0724961
C	0.4543934	0.3956884	-0.6827189
H	0.9715244	0.9784994	-1.4668529
O	1.1974504	-1.8103546	-0.0515749
H	1.9386484	-2.2578086	0.3805941
Mn	-1.9688156	-0.4921666	0.0466701
O	-0.6348586	-0.2854786	-1.2056089
O	-1.9848166	-1.9491256	0.5992941
O	-3.2608636	0.2550064	-0.4086209
O	-1.0003696	0.5932894	1.1605971
C	1.5316274	-0.5125856	-0.0969789
O	2.6082444	-0.1132426	0.3004851

E = -671.936788247, G = -671.886050

3.11-H⁺

C	-0.7997185	-0.6389858	-0.4232262
H	-1.1955345	-0.8413168	-1.4312572
H	-1.6476645	-0.4281988	0.2584988
C	0.1308325	0.5657362	-0.4224092
H	0.8366235	0.4495022	-1.2681542
O	-0.8311095	2.6889992	0.2610068
Mn	1.1829415	-1.2224378	1.2530118
O	0.8440295	0.4897732	0.7940768
O	0.6664515	-1.5378698	2.7077408
O	2.6287585	-1.6321878	0.7740438
O	-0.0654475	-1.7538188	0.0435908
C	-0.6615225	1.8848322	-0.6794152
O	-1.0886405	1.9759732	-1.8675072

E = -671.478145815, G = -671.441047

3.12

C	-0.2976511	-0.7272920	0.1501264
H	-1.3345741	-0.6778750	0.4933544
C	0.3100549	0.4280300	-0.1337266
H	1.3412909	0.4783140	-0.4817086
O	0.3558669	2.7648850	-0.3116916
H	-0.1872911	3.5564710	-0.1856856
C	-0.4196981	1.7067180	0.0207274
O	-1.5618361	1.8365330	0.3925264
C	0.3353989	-2.0742460	0.0331104
H	-0.2348011	-2.7026630	-0.6643506
H	1.3706219	-2.0028960	-0.3176346
H	0.3226179	-2.5859790	1.0049524

E = -306.415002213, G = -306.349671

3.12-H⁺

C	-0.3153903	-0.3998778	0.1526800
H	-1.3509103	-0.3368028	0.5004630
C	0.2729327	0.7514662	-0.1773830
H	1.3090227	0.7665882	-0.5339170
O	0.2916727	3.0859982	-0.4445100
C	-0.4247113	2.1168412	-0.0908360
O	-1.6103623	2.1158162	0.3155300
C	0.3314357	-1.7545408	0.0823020
H	-0.2190123	-2.4279058	-0.5932070
H	1.3649347	-1.6751418	-0.2805030
H	0.3503877	-2.2424408	1.0693810

E = -305.954165501, G = -305.902525

3.13

C	-0.6836453	-0.3950754	-0.7657775

H	-1.7052273	-0.4823154	-0.3979975
C	-0.0599123	0.8078726	-0.5921785
H	0.8913517	1.0405036	-1.0621815
O	0.0156717	3.0267196	0.1728435
H	-0.4771183	3.6278426	0.7467795
Mn	1.0189367	-1.0139464	1.8181815
O	1.2761507	0.4643916	1.2826715
O	0.4843227	-0.9764594	3.2908865
O	2.3214497	-1.8778714	1.6633245
O	-0.1267443	-1.5707014	0.8237855
C	-0.7100653	1.8700316	0.1705695
O	-1.7844463	1.8185596	0.7354995
C	-0.2074283	-1.3955494	-1.7791165
H	-0.4823723	-2.4100444	-1.4735185
H	-0.6552433	-1.1874834	-2.7625245
H	0.8843197	-1.3464744	-1.8712475

E = -711.081631843, G = -711.00949

3.13-H⁺

C	-0.7312213	-0.0637926	-0.6481987
H	-1.7911133	-0.1164566	-0.4005997
C	-0.0989433	1.1274234	-0.4150377
H	0.8808647	1.3142654	-0.8550827
O	-0.2231003	3.4604304	-0.1126267
Mn	0.9949937	-1.0361406	1.7771073
O	1.3394897	0.4143554	1.1960923
O	0.7885137	-0.9784656	3.3466733
O	2.0993087	-2.0832816	1.3191293
O	-0.3950843	-1.3625706	1.0342793
C	-0.8434963	2.3770864	0.0679043
O	-2.0043203	2.2204924	0.5211403
C	-0.1270873	-1.1157476	-1.5408487
H	-0.5428473	-2.1069506	-1.3196887
H	-0.3023153	-0.8860106	-2.6062157
H	0.9563578	-1.1646366	-1.3640277

E = -710.614778135, G = -710.556512

3.14

C	0.0893984	0.7826026	0.5275821
H	0.9147324	1.0522116	1.2085271
C	0.6155734	-0.0899924	-0.6279159
H	1.1196744	0.5375706	-1.3857039
O	1.3863594	-2.3084544	-0.0889749
H	2.1361944	-2.7649254	0.3179951
Mn	-1.7885366	-1.0621784	0.0576701
O	-0.4630126	-0.7621804	-1.1831049
O	-1.7745766	-2.5438734	0.5381511
O	-3.0964986	-0.3226654	-0.3660149
O	-0.8381326	-0.0119714	1.2189841
C	1.7077424	-1.0067414	-0.0891309
O	2.7842194	-0.6113594	0.3126391
C	-0.5702176	2.0484656	-0.0149689
H	-1.3382616	1.7708876	-0.7488469
H	-1.0565066	2.5837006	0.8097411
H	0.1718494	2.7089036	-0.4866289

E = -711.240350559, G = -711.163427

3.14-H⁺

C	-0.0137154	0.4904240	0.4635735
H	0.1697966	0.1447040	1.5007645

C	0.2928466	-0.6884460	-0.4603465
H	0.3395956	-0.3036970	-1.4981305
O	1.7434006	-2.2848610	0.6406795
Mn	-2.3519344	-0.6925160	-0.0790425
O	-0.7999634	-1.5707740	-0.3310175
O	-3.0881174	-1.1988890	1.2175895
O	-3.1072494	-0.5247940	-1.4530445
O	-1.3876494	0.7964530	0.3107545
C	1.6898346	-1.3105330	-0.1386065
O	2.6543756	-0.7015090	-0.6873655
C	0.8181466	1.7340470	0.1876045
H	0.6006866	2.0905540	-0.8294255
H	0.5539856	2.5290780	0.9018645
H	1.8859606	1.4907590	0.2541485

E = -710.780826006, G = -710.718371

3.15

C	-0.2156882	-2.0474229	0.3331873
H	0.3243058	-2.9699179	0.1270443
H	-0.9545242	-2.0667929	1.1350893
C	0.0185208	-0.9398349	-0.3678317
H	0.7674898	-0.9406839	-1.1614927
C	0.2413978	1.4822701	0.2429053
C	-0.7004102	0.3611151	-0.1305887
H	-1.2139462	0.6751171	-1.0522847
H	-1.4368812	0.2714081	0.6728243
O	0.1377808	2.1926921	1.2088633
O	1.2404468	1.6234881	-0.6572687
H	1.7915078	2.3585621	-0.3504477

E = -306.407067879, G = -306.342065

3.15-H⁺

C	-0.0363226	-1.8933915	0.2517788
H	0.5947414	-2.7703695	0.1027868
H	-0.9041066	-2.0075435	0.9050178
C	0.2496764	-0.7192915	-0.3234282
H	1.1406314	-0.6225215	-0.9494482
C	0.3939144	1.7862755	0.1576038
C	-0.5202326	0.5467805	-0.1535362
H	-1.0163496	0.7980545	-1.1059442
H	-1.2927836	0.4512345	0.6196848
O	-0.1113566	2.6371435	0.9214308
O	1.5021884	1.7936295	-0.4259462

E = -305.947363592, G = -305.896114

3.16

C	-0.4239106	1.8805848	-0.1560064
H	-0.9694066	2.4302888	-0.9195424
H	-0.4844046	2.2502958	0.8645986
C	0.4680844	0.9138958	-0.4984914
H	0.6991504	0.7249678	-1.5445434
Mn	-2.1703146	-0.7888432	0.0727996
O	-0.8495236	-0.8636102	-0.8868824
O	-1.9898756	-1.7610272	1.2833466
O	-3.4619736	-1.0415382	-0.7721154
O	-2.1282896	0.7307288	0.5806676
C	1.2975694	0.2278568	0.5628976
H	0.6067764	-0.1517412	1.3335446
H	1.9951094	0.9269728	1.0378596
C	2.1268774	-0.9456112	0.0653646

O	1.4672974	-1.8804492	-0.6075054
H	0.4987554	-1.6143532	-0.6950154
O	3.3180794	-1.0384182	0.2790236

E = -711.076523588, G = -711.003140

3.16-H⁺

C	-0.1444472	1.2665786	0.7387821
H	-0.5616152	2.2475886	0.5250421
H	-0.0402732	0.9877446	1.7864061
C	0.4463058	0.5185416	-0.2403339
H	0.5160238	0.9238956	-1.2480749
Mn	-2.7129692	-0.3479914	-0.2168189
O	-1.3440342	-0.5518604	-1.0251119
O	-3.1801092	-1.7174174	0.4279171
O	-3.8117042	0.3144596	-1.1491379
O	-2.2639842	0.6818856	0.9335621
C	1.3156038	-0.6685414	0.0349681
H	1.0000188	-1.5012614	-0.6115339
H	1.2097598	-0.9944414	1.0774421
C	2.8328378	-0.4289874	-0.2687289
O	3.1018918	0.2953246	-1.2578999
O	3.6366948	-1.0255184	0.4935211

E = -710.61209694, G = -710.554678

3.17

C	-0.5915311	-1.4985136	-0.8017594
H	-0.0116901	-2.1894806	-1.4422344
H	-1.6208941	-1.4383166	-1.1986514
C	0.0892889	-0.1377676	-0.8077404
H	0.4247789	0.1364254	-1.8234074
Mn	0.8588279	-1.4153366	1.4378016
O	1.2318179	-0.2711146	0.0231466
O	0.4401019	-0.5556286	2.6668916
O	1.9047469	-2.5657356	1.5053776
O	-0.6218311	-1.9568846	0.5234616
C	-0.8357261	0.9578894	-0.2564674
H	-1.1828841	0.6279634	0.7350736
H	-1.7056061	1.1092964	-0.9049594
C	-0.1520251	2.3034454	-0.0842254
O	1.1078289	2.2516434	0.3435596
H	1.3700549	1.2815134	0.3892926
O	-0.7052591	3.3606014	-0.3051604

E = -711.245235114, G = -711.167313

3.17-H⁺

C	-0.1345389	-0.9641153	-0.9329246
H	0.5517121	-1.5186983	-1.6044246
H	-0.9488239	-0.5388003	-1.5395896
C	0.6372141	0.1362527	-0.2129736
H	1.4045601	0.5555897	-0.8827816
Mn	0.4389411	-1.9733933	1.4701864
O	1.2964191	-0.4982983	0.8807694
O	-0.3408909	-1.6604753	2.7987254
O	1.3597601	-3.2444843	1.3241194
O	-0.6617179	-1.8478213	0.0364654
C	-0.2614399	1.2790818	0.2520924
H	0.2704321	1.8554647	1.0228394
H	-1.1570489	0.8660067	0.7402064
C	-0.7098439	2.2734757	-0.8560526
O	-0.3266319	2.0412658	-2.0331696
O	-1.4181019	3.2389488	-0.4634886

E = -710.777800501, G = -710.714322

3.18

C	-1.2139915	-2.4378206	0.2624095
H	-1.2610795	-3.3813086	0.8035715
H	-2.0967235	-2.1406296	-0.3054375
C	-0.1213375	-1.6757416	0.2867225
H	0.7454355	-2.0022936	0.8688915
C	0.3995475	2.0986484	-0.1432765
C	0.0170775	-0.3611766	-0.4235845
H	0.8725565	-0.3950376	-1.1124605
H	-0.8854575	-0.1602686	-1.0157725
O	-0.4235935	2.9764734	-0.2050905
O	1.5952255	2.1857084	-0.7722765
H	1.6064535	3.0361464	-1.2358175
C	0.2393615	0.7874124	0.5776325
H	1.1456955	0.5921484	1.1650965
H	-0.6191705	0.8777394	1.2493915

E = -345.705694232, G = -345.614367

3.18-H⁺

C	-1.1099777	-2.2767207	0.0084794
H	-1.2226887	-3.2037167	0.5711944
H	-1.8837377	-2.0362827	-0.7231686
C	-0.0716847	-1.4569867	0.2030074
H	0.6736773	-1.7368207	0.9571804
C	0.7160473	2.3568813	-0.1785326
C	0.1701703	-0.1550597	-0.4928116
H	1.1274353	-0.1742887	-1.0322176
H	-0.6107977	0.0215083	-1.2458096
O	0.4659963	3.3887153	0.4855604
O	1.3163733	2.2466713	-1.2739646
C	0.2324493	1.0251783	0.4781144
H	0.9401743	0.7998673	1.2926964
H	-0.7434367	1.2010543	0.9502714

E = -345.245180385, G = -345.167475

3.19

C	0.9475891	1.6333940	-0.6134991
H	1.5646761	2.5262270	-0.5500371
H	0.6215461	1.3305100	-1.6061282
C	0.4367481	1.0479240	0.5030689
H	0.5808911	1.5034570	1.4802928
Mn	2.9712011	-0.7412300	-0.0020251
O	1.9702161	-0.3230220	1.1879358
O	2.6340552	-2.2015330	-0.4788351
O	4.4626151	-0.5438990	0.4453759
O	2.5907751	0.3092960	-1.1587822
C	-0.5346169	-0.0986990	0.3955058
H	-0.5256039	-0.6643530	1.3358929
H	-0.1332139	-0.7655540	-0.3867522
C	-3.0029148	-0.7436970	-0.0427231
O	-2.5550029	-2.0058390	-0.2288022
H	-1.5876989	-2.0189000	-0.2244732
O	-4.1895759	-0.5402060	0.0140259
C	-1.9573319	0.3519800	0.0542539
H	-1.9612999	0.8718250	-0.9146022
H	-2.3330548	1.0723190	0.7903079

E = -750.367704993, G = -750.269609

3.19-H⁺

C	1.0484893	-1.3783561	0.2623170
H	1.6303763	-1.9210381	1.0021350
H	1.1612343	-1.6776171	-0.7791000
C	0.3794393	-0.2321741	0.5812940
H	0.4399583	0.1236399	1.6118280
Mn	-1.7353677	-2.6223361	1.1683810
O	-1.5644257	-1.0290481	1.2420600
O	-2.9045707	-3.0056301	0.1769960
O	-1.9259157	-3.2230241	2.6208560
O	-0.3204407	-3.0819421	0.5601660
C	-0.1062587	0.7694899	-0.4311040
H	-1.0835287	1.1667419	-0.1307770
H	-0.2478177	0.2870299	-1.4065960
C	0.5389503	3.0524099	-1.5800560
O	-0.4453987	2.8657409	-2.3325520
O	1.3105253	4.0491759	-1.5448430
C	0.8943193	1.9251219	-0.5668110
H	1.0535623	2.4050239	0.4113420
H	1.8768693	1.5267919	-0.8655360

E = -749.909703243, G = -749.826245

3.20

C	0.4004511	-2.2553781	-0.0836401
H	0.6603811	-3.0810791	0.6030119
H	0.8499801	-2.4618281	-1.0717551
C	0.8813951	-0.9334281	0.5020460
H	1.9069571	-1.0040021	0.9068009
Mn	-1.6952279	-1.0392802	1.0387760
O	0.0018201	-0.6593231	1.5693620
O	-2.2944389	0.2751869	0.3865930
O	-2.4312759	-1.8718802	2.1211750
O	-0.9970239	-2.1431431	-0.2215840
C	0.8023781	0.1676769	-0.5718851
H	-0.1067229	-0.0243241	-1.1563051
H	1.6573861	0.0810319	-1.2573861
C	0.0337091	2.5463719	-0.8974150
O	-1.2698869	2.3193019	-1.0967160
H	-1.5982729	1.5514759	-0.5635941
O	0.5869811	3.4724808	-1.4510591
C	0.7312701	1.5777259	0.0308819
H	0.1534331	1.5055899	0.9620490
H	1.7267071	1.9768248	0.2506439

E = -750.539053663, G = -750.432048

3.20-H⁺

C	0.2944995	-2.0627937	-0.2263675
H	1.0503665	-2.7466367	0.2131965
H	0.3777895	-2.1196687	-1.3275375
C	0.5504935	-0.6419747	0.2778775
H	1.6417985	-0.4889857	0.4056575
Mn	-1.4124445	-1.7348367	1.7829855
O	-0.0439465	-0.5702407	1.5612175
O	-2.7907885	-0.9945377	1.6976865
O	-1.0830625	-2.7636007	2.9263485
O	-0.9931625	-2.4650737	0.1687135
C	0.0444595	0.4411793	-0.6756785
H	-1.0434085	0.3190593	-0.7908275
H	0.4998205	0.2862393	-1.6647515
C	0.4433485	2.9370193	-1.3636795
O	0.5917725	2.5312083	-2.5445595
O	0.3771725	4.1319013	-0.9703305

C	0.3887485	1.8624673	-0.2354715
H	-0.2900715	2.2162913	0.5488805
H	1.3966155	1.8629843	0.2166405

E = -750.072684852, G = -749.983597

3.21

C	-0.7590538	0.8264244	0.0195692
H	-1.8500028	0.8326654	0.0865712
C	-0.1555508	2.0214474	-0.0560948
H	0.9218712	2.1533664	-0.1264908
O	-0.2141538	4.3619594	-0.1275748
H	-0.8207278	5.1164644	-0.1146578
C	-0.9797908	3.2489104	-0.0451008
O	-2.1851498	3.2997904	0.0269382
C	-0.1135818	-0.4919976	0.0227782
C	-0.9227088	-1.6328856	0.1089942
C	1.2783232	-0.6574426	-0.0568108
C	-0.3618348	-2.9083056	0.1159772
H	-2.0044488	-1.5135716	0.1711422
C	1.8387752	-1.9290426	-0.0499408
H	1.9287802	0.2129054	-0.1246378
C	1.0208742	-3.0590816	0.0364742
H	-1.0055168	-3.7839096	0.1835302
H	2.9198292	-2.0438526	-0.1122168
H	1.4640682	-4.0538436	0.0415512

E = -498.114587671, G = -497.999967

3.21-H⁺

C	-1.2931152	-0.4934247	-0.0000008
H	-1.5977532	-1.5437867	0.0000022
C	-2.2875252	0.4037873	-0.0000038
H	-2.1001222	1.4809533	-0.0000058
O	-4.5626202	0.9729763	0.0000022
C	-3.7717072	-0.0003487	-0.0000048
O	-4.0130652	-1.2281507	0.0000052
C	0.1529158	-0.2160987	0.0000002
C	1.0593488	-1.2888947	-0.0000008
C	0.6895548	1.0844303	0.0000012
C	2.4379368	-1.0805277	-0.0000008
H	0.6634018	-2.3050047	-0.0000028
C	2.0641968	1.2960123	0.0000022
H	0.0140568	1.9383143	0.0000012
C	2.9514818	0.2155223	0.0000012
H	3.1139988	-1.9359907	-0.0000008
H	2.4511368	2.3154093	0.0000032
H	4.0278798	0.3848223	0.0000022

E = -497.654066836, G = -497.553630

3.22

C	0.4331575	0.7200847	0.5931537
H	0.6496545	1.0560257	1.6057767
C	1.2874425	1.0931567	-0.4062093
H	1.0244925	1.0083787	-1.4557513
O	3.1932455	2.2163197	-1.1916413
H	4.0025695	2.6303827	-0.8638003
Mn	2.1638245	-1.8898193	0.2180627
O	2.5142505	-0.7326513	-0.8323103
O	3.4452825	-2.3169642	1.0102377
O	1.4662495	-3.0836033	-0.5256993
O	1.1077685	-1.1799393	1.2037347
C	2.5199805	1.8163897	-0.0775953

O	2.9333445	2.0874627	1.0298617
C	-0.9263525	0.2288277	0.2998377
C	-2.0130175	0.6271097	1.0860817
C	-1.1485255	-0.6541233	-0.7672823
C	-3.3034205	0.1868407	0.7923747
H	-1.8406975	1.2928547	1.9323237
C	-2.4355065	-1.0959603	-1.0569633
H	-0.2933625	-1.0285463	-1.3314343
C	-3.5201795	-0.6720833	-0.2844033
H	-4.1416245	0.5091187	1.4106037
H	-2.5920965	-1.7946973	-1.8784293
H	-4.5264805	-1.0245653	-0.5105293

E = -902.781313011, G = -902.661467

3.22-H⁺

C	0.6933843	0.8534199	0.5474377
H	0.9137113	1.2198329	1.5496467
C	1.6040343	1.1388399	-0.4372593
H	1.3211323	1.0413919	-1.4846113
O	3.3237753	2.5452799	-1.2185503
Mn	2.0958963	-1.9778561	0.1681487
O	2.5097923	-0.7792581	-0.8150773
O	3.3714113	-2.6021651	0.8607577
O	1.2304753	-3.0410941	-0.6274713
O	1.1741853	-1.2379511	1.2471007
C	2.8059813	2.0647499	-0.1776563
O	3.0978083	2.2942899	1.0193507
C	-0.6640637	0.3808069	0.2602437
C	-1.7403807	0.7325659	1.0925357
C	-0.9352747	-0.4460921	-0.8478473
C	-3.0414657	0.3167479	0.8120757
H	-1.5398757	1.3494509	1.9697927
C	-2.2325377	-0.8628241	-1.1252093
H	-0.0995507	-0.7946431	-1.4547493
C	-3.3002137	-0.4785481	-0.3057973
H	-3.8599427	0.6121189	1.4719407
H	-2.4125057	-1.5172941	-1.9795963
H	-4.3157777	-0.8117681	-0.5252043

E = -902.318660475, G = -902.211346

3.23

C	-0.9123282	0.3331084	0.0628784
H	-1.6677192	0.6791834	-0.6625976
C	-0.0791042	1.5463704	0.5488394
H	0.7304358	1.7649564	-0.1706516
O	-1.0834572	3.4129274	1.7018394
H	-1.6807032	4.1588134	1.5492514
Mn	-0.6701552	0.1523994	2.7554334
O	0.4434728	1.2535324	1.7955174
O	-1.5658562	0.9915034	3.7097104
O	0.0897258	-1.1310106	3.2221744
O	-1.5497862	-0.1937066	1.1877784
C	-0.9608252	2.7940864	0.5193034
O	-1.4941462	3.2166414	-0.4862186
C	-0.0225632	-0.6747076	-0.6475506
C	0.3961058	-1.8468606	-0.0156556
C	0.3984228	-0.4191686	-1.9576326
C	1.2273568	-2.7449006	-0.6889026
H	0.0726818	-2.0363836	1.0064194
C	1.2263988	-1.3151216	-2.6303516
H	0.0668888	0.4964984	-2.4524816

C	1.6449778	-2.4859946	-1.9940326
H	1.5543508	-3.6551926	-0.1856126
H	1.5440508	-1.1047726	-3.6520976
H	2.2917748	-3.1922016	-2.5153596

E = -902.934765171, G = -902.807838

3.23-H⁺

C	-0.9057800	-0.0473697	0.5462861
H	-0.9726670	-0.5091157	1.5465401
C	-1.4096000	-1.0998007	-0.4484189
H	-1.1252610	-0.7891807	-1.4720359
O	-0.7625170	-3.2621987	-1.2393339
Mn	-3.4595970	0.5637953	0.0343811
O	-2.8196310	-1.0830587	-0.3310729
O	-4.3427840	0.5469253	1.3342831
O	-3.9340410	1.2723943	-1.2870389
O	-1.7617180	1.0693893	0.4480411
C	-0.8457200	-2.5444117	-0.2153729
O	-0.5160220	-2.8412527	0.9643691
C	0.5288160	0.3619053	0.2976801
C	0.8323520	1.6195263	-0.2356909
C	1.5817640	-0.5226077	0.5811871
C	2.1568800	1.9924803	-0.4770359
H	0.0026070	2.2918373	-0.4485269
C	2.9024880	-0.1487747	0.3372031
H	1.3289250	-1.5089587	0.9765911
C	3.2005490	1.1113933	-0.1905209
H	2.3751170	2.9780413	-0.8944099
H	3.7097090	-0.8508337	0.5545761
H	4.2361310	1.3998743	-0.3816799

E = -902.471539858, G = -902.358703

3.24

C	0.9844766	-0.1815358	-0.1554421
H	0.7809876	-0.9578358	0.5972449
H	1.0054036	-0.6911428	-1.1314471
C	-0.1567494	0.8389022	-0.1405201
H	-0.2046004	1.3231172	0.8455709
H	0.0683366	1.6276562	-0.8759281
C	-1.4869574	0.2214272	-0.4582211
H	-1.5875664	-0.2360778	-1.4486431
C	-2.5264564	0.1748792	0.3768969
H	-2.4209814	0.6311472	1.3664289
C	-3.8500674	-0.4575758	0.0651259
H	-4.0805354	-1.2602068	0.7790039
H	-4.6629494	0.2782292	0.1349759
H	-3.8527424	-0.8814128	-0.9462281
C	2.3462176	0.4517162	0.1140889
H	2.5387786	1.2236812	-0.6454141
H	2.3156216	0.9699172	1.0839619
C	3.4803226	-0.5686728	0.1111579
H	4.4497426	-0.0929288	0.3025979
H	3.3191266	-1.3325208	0.8833279
H	3.5405926	-1.0807628	-0.8585381

E = -275.042171578, G = -274.882183

3.25

C	-1.3862724	0.0942982	0.6610465
H	-0.9022204	-0.8153558	1.0384355
H	-1.4868174	0.7907202	1.5105455
C	-0.4720924	0.7065042	-0.3953005

H	-0.3905924	0.0104562	-1.2445555
H	-0.9279714	1.6358082	-0.7788835
C	0.9272806	0.9750152	0.0943105
H	1.0877416	1.0833442	1.1672675
C	1.9390146	1.2644902	-0.7718615
H	1.7054696	1.4325222	-1.8224605
C	3.3334536	1.5771512	-0.3169085
H	4.0478956	0.9285932	-0.8401335
H	3.6065406	2.6243942	-0.5190285
H	3.4321666	1.3884092	0.7595945
Mn	1.9195456	-1.9093998	-0.6399465
O	2.2601816	-0.7174758	-1.6678695
O	1.3677696	-1.0942958	0.6363345
O	0.7696236	-2.8124448	-1.2226105
O	3.2342806	-2.6873668	-0.2645535
C	-2.7702394	-0.2431048	0.1163425
H	-3.2423554	0.6676992	-0.2853405
H	-2.6532174	-0.9381678	-0.7272875
C	-3.6790364	-0.8693108	1.1712655
H	-4.6690404	-1.1142048	0.7635565
H	-3.2311864	-1.7939868	1.5586495
H	-3.8199214	-0.1842908	2.0193915

E = -679.707973996, G = -679.539703

3.26

C	1.4911906	-0.1578667	-0.3523458
H	1.1065366	-1.0968327	-0.7718358
H	1.7613466	0.4868813	-1.2061498
C	0.3656726	0.4856503	0.4462292
H	0.1046166	-0.1676767	1.2921482
H	0.6910726	1.4561323	0.8580232
C	-0.9059394	0.6937023	-0.3833398
H	-0.7297274	1.4927733	-1.1306068
C	-2.0928034	1.0338203	0.5208142
H	-1.7826804	1.7481233	1.3088822
C	-3.2586474	1.6230713	-0.2687638
H	-4.1286564	1.7422863	0.3892582
H	-2.9934994	2.6023363	-0.6951948
H	-3.5248864	0.9323273	-1.0794608
Mn	-2.1815584	-1.6016697	0.0396352
O	-2.4744154	-0.1720857	1.1402942
O	-1.2589234	-0.4821897	-1.0704108
O	-1.1770764	-2.6014197	0.7007332
O	-3.5242714	-2.0408807	-0.6284088
C	2.7321736	-0.4362067	0.4900032
H	3.1047206	0.5062563	0.9218502
H	2.4433646	-1.0766927	1.3360182
C	3.8468846	-1.1113217	-0.3057468
H	4.7285836	-1.3164707	0.3165962
H	3.4936836	-2.0643617	-0.7217508
H	4.1632396	-0.4776867	-1.1464698

E = -679.873721128, G = -679.701005

3.27

C	1.8432528	-0.5568986	-0.0009231
H	2.0830288	-1.6228586	-0.0029891
C	2.8513138	0.3210014	0.0011579
H	3.8839228	-0.0219556	0.0005929
H	2.6912728	1.3982674	0.0033919
C	0.4001708	-0.2460246	-0.0005751
C	-0.5199872	-1.3018456	-0.0000521

C	-0.0935992	1.0674134	-0.0008241
C	-1.8930872	-1.0605086	0.0005039
H	-0.1505072	-2.3277396	-0.0000101
C	-1.4626242	1.3109084	-0.0003101
H	0.5965808	1.9093734	-0.0015561
H	-2.5905412	-1.8971396	0.0009819
H	-1.8283212	2.3369764	-0.0005511
C	-2.3696832	0.2482654	0.0003949
H	-3.4411922	0.4427644	0.0007669

E = -309.560056677, G = -309.456615

3.28

C	3.4541680	-1.2325009	-0.9225167
H	3.2603350	-1.2287739	-1.9943237
Mn	0.8132660	-2.5250849	0.4135203
O	1.2056780	-1.3730639	-0.6338397
O	2.1762920	-3.3214859	0.5989593
O	-0.3368610	-3.4056879	-0.2044557
O	0.3869700	-1.8324399	1.7712173
N	-1.9317960	0.2352921	-0.0664987
C	-2.9199920	1.3619771	-0.1932377
H	-3.0460680	1.7667671	0.8146593
H	-2.4249730	2.1255701	-0.7993187
C	-0.6081350	0.8476651	0.3905783
H	-0.8672090	1.5004051	1.2297183
H	0.0024420	0.0204171	0.7616233
C	-2.3873120	-0.7782239	0.9649053
H	-3.4006700	-1.0666719	0.6765723
H	-1.7307250	-1.6442089	0.8478293
C	-1.7171440	-0.4688459	-1.3995597
H	-1.7711260	0.3203471	-2.1572027
H	-0.6928520	-0.8530169	-1.3663697
C	3.8853010	-2.3795039	-0.3247417
H	4.0338180	-3.2832579	-0.9087087
H	4.3053900	-2.3611939	0.6779953
C	3.4426470	0.0775541	-0.2479497
C	3.1079220	0.1898541	1.1114713
C	3.7483190	1.2435351	-0.9625667
C	3.1089130	1.4341221	1.7379373
H	2.8141070	-0.7017859	1.6656083
C	3.7586420	2.4875871	-0.3329207
H	3.9956590	1.1679541	-2.0217907
H	2.8463400	1.5045591	2.7931313
H	4.0172930	3.3803801	-0.9011337
C	0.1529160	1.6174421	-0.6724517
H	1.0377810	2.0337031	-0.1768697
H	0.5192110	0.9596001	-1.4640637
H	-0.4099440	2.4535811	-1.1036517
C	-4.2694840	1.0269011	-0.8051097
H	-4.8021900	0.2411491	-0.2600057
H	-4.8813990	1.9347371	-0.7577807
H	-4.1823920	0.7411081	-1.8575897
C	-2.6544290	-1.6268849	-1.7167977
H	-3.7178370	-1.3871219	-1.6373637
H	-2.4505960	-1.9110349	-2.7555857
H	-2.4174470	-2.4959299	-1.0967737
C	-2.3383270	-0.2983239	2.4042853
H	-2.7906590	-1.0866889	3.0157853
H	-1.3065530	-0.1789059	2.7447163
H	-2.9081390	0.6216561	2.5812343
C	3.4408590	2.5883241	1.0222063

H 3.4499910 3.5584481 1.5172223
E = -1085.57205027, G = -1085.191973

3.29

C	2.5920324	0.4078293	-0.0181359
H	2.9344444	1.4445703	-0.0641729
C	3.5109354	-0.5625987	0.0248441
H	4.5718314	-0.3211977	0.0140211
H	3.2473514	-1.6183887	0.0716481
C	1.1266144	0.2401483	-0.0106349
C	0.3105684	1.3744473	-0.0609199
C	0.5010624	-1.0158447	0.0450641
C	-1.0801986	1.2655373	-0.0560739
H	0.7728294	2.3611763	-0.1047009
C	-0.8826866	-1.1208417	0.0497561
H	1.1021734	-1.9227237	0.0852641
C	-1.7006646	0.0180143	-0.0007349
H	-1.6901266	2.1681613	-0.0960919
H	-1.3451916	-2.1079207	0.0935421
C	-3.2005456	-0.1211137	0.0054461
H	-3.5406666	-0.7134487	-0.8539299
H	-3.5407666	-0.6341667	0.9143371
H	-3.6889966	0.8583603	-0.0385269

E = -348.861894387, G = -348.7323402

3.30

C	2.7012608	-2.3017489	-1.1452954
H	2.4180428	-2.3200689	-2.1970644
Mn	-0.0359172	-2.8226369	0.4925616
O	0.5163268	-1.8812049	-0.6850244
O	1.1133418	-3.9092119	0.6506526
O	-1.4138522	-3.4412199	0.0468826
O	-0.1582472	-1.9484849	1.8070596
N	-2.0713702	0.4953941	-0.0205064
C	-2.7690222	1.8180721	-0.1792404
H	-2.6934242	2.3147611	0.7919716
H	-2.1678042	2.3889951	-0.8919884
C	-0.6019432	0.7926251	0.2751026
H	-0.6141142	1.5486301	1.0662376
H	-0.1759262	-0.1315219	0.6749096
C	-2.6548002	-0.2951259	1.1339726
H	-3.7305502	-0.3477619	0.9518806
H	-2.2368382	-1.3012359	1.0509086
C	-2.1593562	-0.3377109	-1.2927414
H	-2.0954602	0.3821441	-2.1160754
H	-1.2585642	-0.9590039	-1.2993824
C	2.9009118	-3.4784079	-0.4856464
H	2.7759008	-4.4276449	-0.9984494
H	3.4051498	-3.4972279	0.4774186
C	3.0594858	-0.9879109	-0.5827314
C	2.8832628	-0.7080589	0.7795586
C	3.5686378	0.0258631	-1.4060594
C	3.2329658	0.5379221	1.2979036
H	2.4389138	-1.4622819	1.4292446
C	3.9250978	1.2649401	-0.8806504
H	3.6989918	-0.1683489	-2.4710564
C	3.7656928	1.5423741	0.4825076
H	3.0854128	0.7337311	2.3606786
H	4.3346768	2.0318791	-1.5398144
C	0.2150068	1.2727041	-0.9099204
H	1.2152258	1.4997791	-0.5222634

H	0.3424798	0.4881021	-1.6595384
H	-0.1752072	2.1844481	-1.3770454
C	-4.2129442	1.7805501	-0.6495954
H	-4.8602252	1.1903581	0.0069056
H	-4.5843362	2.8114431	-0.6396394
H	-4.2998342	1.4063521	-1.6739974
C	-3.3723312	-1.2489169	-1.4260324
H	-4.3347452	-0.7464269	-1.3001224
H	-3.3376832	-1.6598469	-2.4415224
H	-3.2964052	-2.0953729	-0.7377464
C	-2.3547432	0.2620151	2.5137786
H	-2.9118202	-0.3522939	3.2295296
H	-1.2942962	0.1590571	2.7580176
H	-2.6797142	1.3005041	2.6498786
C	4.1590408	2.8857621	1.0428786
H	5.2375858	3.0563301	0.9304156
H	3.6425468	3.7009951	0.5193966
H	3.9155188	2.9539431	2.1088976

E = -1124.87321485, G = -1124.468838

3.31

C	1.0544660	1.1998376	-1.8265719
H	0.8566460	0.8559436	-2.8438809
C	1.8588780	2.2527936	-1.6519669
H	2.3054710	2.7543136	-2.5079789
H	2.1016320	2.6522356	-0.6682269
C	0.3824290	0.4261396	-0.7653679
C	-0.4309290	-0.6558464	-1.1321629
C	0.5242370	0.7293796	0.5988451
C	-1.0897940	-1.4219224	-0.1764429
H	-0.5485630	-0.9006244	-2.1872019
C	-0.1243280	-0.0222754	1.5677641
H	1.1488110	1.5630036	0.9116651
C	-0.9226440	-1.0884364	1.1607931
H	-1.7225470	-2.2624234	-0.4480609
H	-0.0251980	0.1990646	2.6270341
N	-1.6135290	-1.8896484	2.1857871
O	-2.3047090	-2.8152864	1.8067711
O	-1.4503290	-1.5762474	3.3492031

E = -514.036151602, G = -513.932722

3.32

C	-2.0158727	3.1031064	-1.0274304
H	-1.7203667	3.1275914	-2.0750644
Mn	0.6708543	2.5900964	0.6730776
O	-0.0899127	1.9450064	-0.5839364
O	-0.0895687	3.9725514	0.8883126
O	2.1895953	2.7731124	0.3085006
O	0.4547613	1.6438914	1.9206596
N	1.7410023	-1.1350156	0.0206816
C	2.0456023	-2.5897256	-0.2161544
H	1.7663113	-3.1088656	0.7047486
H	1.3577423	-2.9140376	-1.0016274
C	0.2303443	-1.0180466	0.2071106
H	-0.0354887	-1.8031416	0.9213186
H	0.0536043	-0.0442136	0.6706646
C	2.4316153	-0.6276076	1.2715456
H	3.4889963	-0.8759536	1.1542796
H	2.3253343	0.4599574	1.2532856
C	2.1600623	-0.2757526	-1.1645244
H	1.9484603	-0.8814526	-2.0524314

H	1.4838073	0.5848054	-1.1591474
C	-1.8609227	4.2184524	-0.2561014
H	-1.4565777	5.1302334	-0.6860614
H	-2.3644397	4.3075604	0.7031876
C	-2.7480147	1.9121424	-0.5783914
C	-2.7142577	1.5136854	0.7711086
C	-3.4626907	1.1287804	-1.4987264
C	-3.3841317	0.3728424	1.1911376
H	-2.1193957	2.0837894	1.4834366
C	-4.1514787	-0.0079256	-1.0925764
H	-3.4842837	1.4252344	-2.5467634
C	-4.0960087	-0.3706026	0.2503776
H	-3.3579657	0.0448544	2.2268086
H	-4.7194067	-0.6169036	-1.7906664
N	-4.7867507	-1.5913836	0.6838076
O	-4.7016907	-1.9074426	1.8567876
O	-5.3994967	-2.2266686	-0.1554934
C	-0.5922647	-1.1471926	-1.0619604
H	-1.6429247	-1.1123786	-0.7521214
H	-0.4317197	-0.3017496	-1.7353004
H	-0.4402757	-2.0920746	-1.5961934
C	3.4695453	-2.9387996	-0.6137124
H	4.2110363	-2.6039726	0.1186976
H	3.5311953	-4.0313236	-0.6701264
H	3.7280443	-2.5403626	-1.5990654
C	3.5933483	0.2386454	-1.1581704
H	4.3533763	-0.5369676	-1.0360574
H	3.7528273	0.7155414	-2.1319294
H	3.7227233	1.0147884	-0.3992914
C	1.8765983	-1.1683716	2.5771006
H	2.5283583	-0.7975876	3.3755476
H	0.8742503	-0.7782016	2.7715466
H	1.8765113	-2.2629476	2.6352966

E = -1290.05031772, G = -1289.669915

3.33

C	2.0020397	-0.1961957	0.1204605
C	3.1365507	-0.8679147	-0.0863565
H	3.8496487	-0.4880577	-0.8264885
H	1.2648547	-0.5925327	0.8252445
C	3.5055297	-2.1444267	0.6132775
C	1.6143457	1.0603153	-0.6081885
H	1.7363857	1.9291653	0.0603515
H	2.2968617	1.2082953	-1.4575205
C	0.1570347	1.0277523	-1.0877405
H	4.4450387	-2.0382647	1.1757935
H	2.7124487	-2.4416807	1.3093005
H	3.6497757	-2.9611707	-0.1084435
H	-0.0082383	1.8439333	-1.8066065
H	-0.0328613	0.0823353	-1.6179165
C	-0.8311913	1.1475593	0.0441185
C	-2.1325713	1.4961753	-0.1571855
H	-0.4464763	1.0974543	1.0631355
C	-3.0901553	1.7206273	0.9771855
H	-2.4473913	1.8095643	-1.1525575
H	-2.7484493	1.1702193	1.8629285
H	-3.1772913	2.7881383	1.2335735
H	-4.0844803	1.3430323	0.7121645
Mn	-2.2927003	-1.6601497	-0.2207265
O	-3.0274013	-0.3586447	-0.8218705
O	-1.0071243	-1.0132697	0.5020335

O	-1.8273283	-2.6030567	-1.3897885
O	-3.2168543	-2.3592037	0.8418215

E = -717.769414290, H = -717.642026
G = -717.591599

3.33-extended

C	-4.2640205	-1.3004959	-0.5735223
H	-4.2147325	-1.6092129	-1.6277023
H	-4.8644715	-0.3836459	-0.5093763
H	-4.7914335	-2.0988739	-0.0312843
C	-2.8883875	-1.0817759	-0.0140333
H	-2.1977615	-1.9310929	-0.0311053
C	-2.4406725	0.0763651	0.4761077
H	-3.1097515	0.9460651	0.4736037
C	-1.0387495	0.2746651	0.9753457
H	-0.5719925	-0.6973439	1.1648537
H	-1.0453195	0.8372751	1.9222467
C	-0.1810165	1.0277251	-0.0513203
H	-0.1651595	0.4394551	-0.9795913
H	-0.6606665	1.9948291	-0.2838503
C	1.2480855	1.2469541	0.3727067
H	1.4503145	1.4970221	1.4144307
C	2.2428495	1.3472671	-0.5559703
H	1.9821265	1.4029301	-1.6113213
C	3.6770505	1.5756611	-0.1842313
H	4.2913555	0.7492411	-0.5664793
H	4.0665265	2.5154331	-0.6044413
H	3.7893025	1.6009091	0.9069457
Mn	1.9412095	-1.7568599	-0.0180883
O	2.2438695	-0.7554019	-1.2426903
O	1.6736405	-0.7149809	1.1844247
O	0.6169705	-2.5671999	-0.2905553
O	3.2108335	-2.6349139	0.2848987

E = -717.769518003, H = -717.543076
G = -717.588520

3.33 • TMA

C	-0.7511158	2.4643065	-0.0454693
C	0.2199082	3.3575335	-0.2492433
H	0.0725522	4.1335615	-1.0068873
H	-0.6081968	1.6726325	0.6970857
C	1.5080762	3.4158055	0.5198307
C	-2.0833398	2.5018215	-0.7457183
H	-2.7959848	3.0373995	-0.0973093
H	-1.9861698	3.0961405	-1.6644093
C	-2.6870428	1.1334565	-1.0710113
H	1.6378862	4.3956735	0.9982907
H	1.5195582	2.6546865	1.3119107
H	2.3778062	3.2677495	-0.1366163
H	-3.5932808	1.2871675	-1.6735383
H	-1.9888528	0.5458865	-1.6879603
C	-3.0401088	0.3355915	0.1545847
C	-3.8847388	-0.7363165	0.1137837
H	-2.7301538	0.7256085	1.1255767
C	-4.3693338	-1.4452055	1.3457737
H	-4.4105718	-0.9420105	-0.8193893
H	-3.6633308	-1.2952605	2.1719117
H	-5.3559118	-1.0722775	1.6557177
H	-4.4541578	-2.5217345	1.1592247
Mn	-1.0383058	-2.0812845	-0.4045693
O	-2.6028088	-2.3102265	-0.6422353

O	-0.9711198	-0.6557825	0.3143557
O	-0.2792188	-1.9727485	-1.7891683
O	-0.4002828	-3.1586555	0.5561807
N	2.7192922	-1.1657285	-0.0112423
C	2.5907402	-2.4259285	-0.8142203
H	3.0735282	-3.2311335	-0.2532963
H	1.5314092	-2.6367645	-0.9834393
H	3.1030362	-2.2670895	-1.7684263
C	2.1020422	-1.3613765	1.3391897
H	2.6020732	-2.2032255	1.8254247
H	2.2562042	-0.4437245	1.9147577
H	1.0345272	-1.5687165	1.2179627
C	4.1627262	-0.8553235	0.1598927
H	4.6090922	-0.6974175	-0.8260493
H	4.2607112	0.0514965	0.7640617
H	4.6478322	-1.6971325	0.6629857
C	2.0327912	-0.0304245	-0.7087473
H	0.9584982	-0.2334195	-0.7528643
H	2.2243582	0.8822585	-0.1397163
H	2.4493762	0.0501335	-1.7169763

E = -931.946785242, H = -931.546488
G = -931.609429

3.33_{Na}

C	2.0173315	0.6398878	-0.1670128
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H	3.3708285	1.7283878	1.0008502
H	1.3613075	0.6509068	-1.0424438
C	2.7098435	2.9944808	-0.6967768
C	2.0274555	-0.6139442	0.6608202
H	2.4711745	-1.4398832	0.0820552
H	2.6663325	-0.4566132	1.5400782
C	0.6239405	-1.0378642	1.1125192
H	3.7088665	3.2248968	-1.0925908
H	2.0145675	2.9026388	-1.5395358
H	2.4005625	3.8521588	-0.0834978
H	0.7056525	-1.8397442	1.8596222
H	0.1308755	-0.1890662	1.6094802
C	-0.2472895	-1.5101722	-0.0202548
C	-1.3865465	-2.2301832	0.1735672
H	0.1199515	-1.3803712	-1.0389538
C	-2.2259055	-2.7554762	-0.9495278
H	-1.6297955	-2.5652172	1.1822422
H	-1.9131405	-2.3137432	-1.9031858
H	-2.1446375	-3.8489872	-1.0235308
H	-3.2820415	-2.5095502	-0.7829098
Mn	-2.4717745	0.7889618	0.1503082
O	-2.7799495	-0.5856472	0.8593312
O	-1.1269255	0.5079838	-0.6224568
O	-2.2794625	1.9659188	1.2258552
O	-3.6537925	1.1947748	-0.8584498
Na	-3.9150205	3.0923668	0.2491882

E = -879.974955880, H = -879.743699
G = -879.794409

3.34s

C	1.9814372	-0.0987836	0.3018855
C	3.2551752	-0.3221536	-0.0291725
H	3.8910812	0.5261794	-0.3076945
H	1.3295382	-0.9382516	0.5541555
O	-0.9866658	-0.3494116	1.0058665

O	-0.1959928	-2.3777576	-0.6920005
O	-2.5419608	-2.6466216	0.7176065
O	-2.3029188	-0.6056416	-1.1527945
C	1.3235602	1.2511744	0.2991725
H	1.0892032	1.5419194	1.3363225
H	2.0321662	1.9926494	-0.0989885
C	0.0154512	1.2617944	-0.5115295
H	-0.1629268	2.2679944	-0.9215195
H	0.0918502	0.5631654	-1.3574175
C	-2.4412518	0.6597344	-0.5511045
C	-3.7285258	0.7267004	0.2678905
H	-2.4756998	1.4236924	-1.3522085
H	-4.5847148	0.4612334	-0.3645415
H	-3.6659338	0.0035194	1.0915165
H	-3.8833618	1.7353704	0.6791765
Mn	-1.4763268	-1.7777316	-0.0225635
C	3.8832682	-1.6865986	-0.0645985
H	4.3121552	-1.9002756	-1.0546725
H	4.6993772	-1.7769026	0.6682675
H	3.1292212	-2.4525496	0.1525215
C	-1.2038158	0.8634764	0.3250815
H	-1.3833888	1.6540754	1.0813425

E = -717.932167120, H = -717.700013
G = -717.756930

3.34s_{Na}

C	2.0199652	0.1258938	-0.3761905
C	3.2059782	0.5052698	0.1019685
H	3.8714232	-0.2506732	0.5316095
H	1.3420582	0.8753728	-0.7902665
O	-0.9723488	0.1415978	-0.9842115
O	-0.3589308	2.2408507	0.7062175
O	-2.6706438	2.3438527	-0.6573605
O	-2.2831638	0.2383018	1.1314645
C	1.5063022	-1.2857433	-0.3423295
H	1.3278952	-1.6411023	-1.3697755
H	2.2804892	-1.9314543	0.0938245
C	0.2034032	-1.4314082	0.4616925
H	0.1115782	-2.4633652	0.8300595
H	0.2301942	-0.7708073	1.3405665
C	-2.2998018	-1.0576132	0.5428105
C	-3.5887358	-1.2626513	-0.2397895
H	-2.2337188	-1.7875272	1.3655495
H	-4.4528918	-1.0619093	0.4032785
H	-3.6173518	-0.5722733	-1.0929735
H	-3.6535808	-2.2933023	-0.6121205
Mn	-1.5688558	1.4455268	0.0532155
C	3.7044122	1.9206898	0.1076375
H	3.9182262	2.2582648	1.1315065
H	4.6362472	2.0188098	-0.4666855
H	2.9543212	2.5925638	-0.3268595
C	-1.0570548	-1.1251562	-0.3437625
H	-1.1750718	-1.8789503	-1.1402175
Na	-1.3803428	4.1069428	-0.0588575

E = -880.133572482, H = -879.901243
G = -879.950635

3.34s_H

C	2.0540051	-0.1607523	-0.4627288
C	3.1328431	0.2486307	0.2066052
H	3.6148681	-0.4434723	0.9050362

H	1.5651391	0.5270077	-1.1562038
O	-0.8527429	0.2600377	-0.9564147
O	-2.1322289	0.5542977	1.1237933
C	3.7346181	1.6168377	0.0887292
C	1.4198351	-1.5130833	-0.2862648
H	1.2382551	-1.9784883	-1.2673207
H	2.1213721	-2.1613483	0.2555792
C	0.0984771	-1.4677263	0.4974082
H	3.7133871	2.1357917	1.0571572
H	4.7850611	1.5651317	-0.2284398
H	3.1793311	2.2224917	-0.6371617
H	-0.1454479	-2.4761323	0.8616822
H	0.2154831	-0.8208103	1.3788863
C	-1.1020249	-0.9917503	-0.3151238
C	-2.3298299	-0.7480063	0.5628363
H	-1.3125849	-1.7093013	-1.1234958
C	-3.6360769	-0.7771473	-0.2131638
H	-2.3606059	-1.4548993	1.4050663
H	-4.4625179	-0.4549053	0.4292252
H	-3.5731609	-0.1003373	-1.0746627
H	-3.8411149	-1.7941493	-0.5703917
Mn	-1.1651609	1.5947977	0.1222542
O	0.1388031	1.9777527	0.7906732
O	-2.1805739	2.7116637	-0.7425897
H	-1.9174069	3.6378687	-0.6509708

E = -718.381417672, H = -718.1402606
G = -718.186500

3.34s_{H2O}

C	-2.1714299	0.0839374	-0.2680651
C	-3.3651699	-0.2708796	0.2112249
H	-3.9832329	0.4834974	0.7115129
H	-1.5348439	-0.6649516	-0.7438461
O	0.7982411	-0.0824846	-0.9886301
O	1.0865941	-2.4676756	-1.4324871
O	2.5301281	-2.6958546	0.5151629
O	2.2948191	-0.3030186	0.9887019
C	-3.9169129	-1.6659756	0.1408819
C	-1.5803879	1.4590434	-0.1451041
H	-1.4266339	1.8845664	-1.1506881
H	-2.3001549	2.1067254	0.3777329
C	-0.2305479	1.4671324	0.5934329
H	-4.1377529	-2.0531546	1.1462089
H	-4.8534359	-1.7037336	-0.4353431
H	-3.1878269	-2.3381236	-0.3267661
H	-0.0542119	2.4676154	1.0184889
H	-0.2552169	0.7508324	1.4272109
C	0.9570061	1.1337104	-0.3135421
C	2.2614241	1.0008224	0.4797119
H	1.0460161	1.9395424	-1.0699501
C	3.4837841	1.2520024	-0.4009241
H	2.2667141	1.7176044	1.3248819
H	4.3977311	1.0109964	0.1558399
H	3.4283651	0.5998714	-1.2826441
H	3.5293001	2.3014064	-0.7282561
O	-0.0040449	-1.8212676	0.9666399
H	0.6553401	-1.8519766	-2.0389991
H	3.0574731	-2.2113296	1.1627199
Mn	1.2088671	-1.5288816	0.1048939

E = -794.359999821, H = -794.099600
G = -794.161190

3.34s_{H2O} (optimiation by M06-2X/aug-cc-pVDZ)

E = -794.359899385, H = -794.104357

G = -794.150139

3.34s_H • H₂O

C	2.3002133	0.2204613	0.3844792
C	3.3089273	-0.3692287	-0.2592338
H	3.8394173	0.1901093	-1.0369438
H	1.7619163	-0.3357597	1.1549642
O	-0.6209997	0.1181003	1.0063272
O	-1.4996347	-2.16s485647	1.4556922
O	-2.2669247	-2.7075877	-0.8589418
O	-2.0643997	-0.1915937	-0.9401108
C	3.7629213	-1.7765357	-0.0116678
C	1.7986873	1.6037573	0.0774722
H	1.7156643	2.1915083	1.0050872
H	2.5327583	2.1102393	-0.5635718
C	0.4376133	1.6085473	-0.6368308
H	3.6737003	-2.3795127	-0.9260148
H	4.8171993	-1.8083147	0.2955952
H	3.1548483	-2.2477447	0.7693222
H	0.2663503	2.5982093	-1.0850258
H	0.4524243	0.8773273	-1.4578308
C	-0.7504497	1.3265193	0.2786662
C	-2.0594347	1.1636553	-0.5044688
H	-0.8363447	2.1368073	1.0213062
C	-3.2903737	1.4339423	0.3449392
H	-2.0623577	1.8012943	-1.4017108
H	-4.1984117	1.1730713	-0.2104678
H	-3.2458257	0.8305783	1.2607512
H	-3.3411477	2.4950173	0.6195562
H	-1.2431707	-1.6169357	2.2205182
H	-2.9632397	-2.1593817	-1.2501638
Mn	-1.0157697	-1.2878977	-0.0199418
O	0.2729813	-1.7227807	-0.6645458
H	-2.6371377	-3.1273067	-0.0672068

E = -794.832122241, H = -794.561606

G = -794.610080

3.34s • TMA

C	0.6536995	2.4208990	0.5009687
C	-0.4031725	3.0196350	-0.0532893
H	-0.2572075	3.6553350	-0.9319503
H	0.5094935	1.7686490	1.3694327
O	1.3888865	-0.2127600	-0.4326513
O	0.5835165	-0.4658960	2.1533907
O	0.3873275	-2.6058850	0.4622237
O	2.9320935	-1.5382380	1.0461357
C	2.0779115	2.6098560	0.0473097
H	2.0945025	2.8572730	-1.0247953
H	2.4823425	3.4863750	0.5768747
C	3.0019525	1.4240530	0.3362587
H	4.0454835	1.7353320	0.1833567
H	2.9006635	1.1242980	1.3901677
C	3.5801075	-1.0010480	-0.0939323
C	3.6900445	-2.0586750	-1.1844333
H	4.5876335	-0.6749230	0.2160527
H	4.1897735	-2.9501130	-0.7889543
H	2.6829165	-2.3418910	-1.5171773
H	4.2617145	-1.6795070	-2.0423973

Mn	1.1575675	-1.3225450	0.9779947
C	-1.8113855	2.8972380	0.4572787
H	-2.2088155	3.8695540	0.7787007
H	-2.4908465	2.5235140	-0.3254113
H	-1.8499505	2.2192770	1.3217797
C	2.7396055	0.1986940	-0.5356233
H	2.9343225	0.4520360	-1.5929753
C	-2.6905725	-2.5083490	-0.6594863
H	-1.7409895	-3.0177900	-0.4630303
H	-3.5259805	-3.0317660	-0.1841493
H	-2.8632545	-2.4117070	-1.7357633
C	-1.4701875	-0.4075050	-0.7738353
H	-1.8570295	-0.0466230	-1.7314383
H	-1.1273795	0.4256310	-0.1548253
H	-0.6395675	-1.0953190	-0.9292803
C	-2.3075215	-1.2635680	1.3933527
H	-2.1485165	-0.2619140	1.7998107
H	-3.1766845	-1.7410420	1.8564397
H	-1.4047755	-1.8633560	1.5266577
C	-3.8567255	-0.3954550	-0.2591893
H	-4.0814495	-0.3389560	-1.3278863
H	-4.6575065	-0.9210820	0.2689777
H	-3.7273695	0.6090600	0.1538377
N	-2.5846685	-1.1407960	-0.0745253

E = -932.105731856, H = -931.702863
G = -931.760177

3.34t

C	-1.9803551	-0.1133371	-0.2891698
C	-3.2682501	-0.3074281	0.0030712
H	-3.9106151	0.5594089	0.1987252
H	-1.3269301	-0.9749691	-0.4505698
O	1.0333619	-0.3310931	-1.0254568
O	0.1877479	-2.4476101	0.6638112
O	2.5052489	-2.7323331	-0.7221858
O	2.2625139	-0.5657701	1.1935542
C	-1.3138351	1.2315949	-0.3506678
H	-1.0624761	1.4644739	-1.3981418
H	-2.0218331	1.9990059	-0.0043568
C	-0.0186181	1.2750369	0.4801292
H	0.1421889	2.2889069	0.8777842
H	-0.0982771	0.5884809	1.3350472
C	2.4455039	0.6861689	0.5621842
C	3.7450979	0.7092869	-0.2358018
H	2.4809219	1.4611979	1.3511862
H	4.5862759	0.4525819	0.4193562
H	3.6880339	-0.0364991	-1.0392048
H	3.9191929	1.7038069	-0.6721348
Mn	1.4949609	-1.7475331	0.0353682
C	-3.9038761	-1.6654781	0.1007412
H	-4.3701271	-1.8154841	1.0854852
H	-4.6927271	-1.7985841	-0.6548978
H	-3.1450291	-2.4439671	-0.0411678
C	1.2176939	0.8864769	-0.3328258
H	1.4042059	1.6736589	-1.0898618

E = -717.953326765, H = -717.721903
G = -717.781310

3.34t_H

C	-2.1180357	0.1429559	-0.4917101
C	-3.1505857	-0.3433581	0.1989209

H	-3.6137227	0.2844539	0.9674899
H	-1.6510597	-0.4817321	-1.2557311
O	0.8017023	-0.1882401	-1.0262861
O	2.0258253	-0.5278231	1.1181419
C	-3.7221478	-1.7167981	0.0136489
C	-1.5106197	1.4982279	-0.2482751
H	-1.3504167	2.0210039	-1.2036131
H	-2.2196907	2.0996519	0.3357129
C	-0.1810267	1.4421059	0.5224179
H	-3.6391257	-2.3002911	0.9408289
H	-4.7881247	-1.6721841	-0.2477101
H	-3.1891127	-2.2547571	-0.7788381
H	0.0416743	2.4348389	0.9403459
H	-0.2776607	0.7445539	1.3667559
C	1.0221013	1.0382939	-0.3191721
C	2.2646413	0.7603109	0.5330009
H	1.2210923	1.8025869	-1.0868961
C	3.5535193	0.7542689	-0.2692481
H	2.3339503	1.4647809	1.3765939
H	4.3864103	0.4261169	0.3623229
H	3.4613313	0.0728659	-1.1240761
H	3.7722293	1.7631379	-0.6410481
Mn	1.1208613	-1.5941301	0.0046989
O	-0.1266717	-2.2768311	0.6568259
O	2.3748603	-2.6851951	-0.6056451
H	3.1578033	-2.7088151	-0.0394551

E = -718.421790789, H = -718.183193
G = -718.229460

3.34t_{H2O}

C	3.7026227	-1.3766130	0.0629742
H	4.7295057	-1.3448250	-0.3314188
H	3.7367827	-1.9092690	1.0244392
H	3.0728747	-1.9585000	-0.6202068
C	3.1313797	0.0004240	0.2397382
H	3.6393857	0.6657830	0.9475082
C	2.0272037	0.4278690	-0.3784158
H	1.5065987	-0.2391710	-1.0695728
C	1.3859797	1.7668770	-0.1385358
H	2.0729007	2.3858430	0.4583292
H	1.2301357	2.2779280	-1.1026918
C	0.0304307	1.6685180	0.5839802
H	-0.2323303	2.6554940	0.9971592
H	0.1095717	0.9636100	1.4227852
C	-1.1148743	1.2220780	-0.3311168
H	-1.3134293	2.0411890	-1.0536198
C	-2.3862473	0.8920160	0.4692262
H	-2.4796053	1.5820860	1.3324402
Mn	-1.0743513	-1.4887940	-0.0582828
O	-0.7942083	0.0690580	-1.0616548
O	-2.2489553	-0.4223290	0.9390642
O	-1.6909503	-3.0375850	0.8121282
H	-0.9522443	-3.6386420	0.9566532
O	0.4525717	-1.4851750	0.9626062
O	-0.4399943	-2.4597740	-1.5104698
H	-0.6298153	-3.3830030	-1.3108588
C	-3.6379333	1.0150350	-0.3990338
H	-4.5046343	0.6178680	0.1437902
H	-3.8323613	2.0637240	-0.6699588
H	-3.4960093	0.4282790	-1.3169848

E = -794.395587204, H = -794.144060

G = -794.193104

4.34d

C	-1.9547323	0.2792737	-0.4864368
C	-2.9183373	-0.2893443	0.2508052
H	-3.2213983	0.1956007	1.1850042
H	-1.6615723	-0.2035843	-1.4213758
O	0.8207097	-0.4019783	-0.9755458
O	-0.5545313	-1.9253843	0.8928702
O	1.5852067	-3.0613853	-0.6127548
O	2.1547567	-0.8147063	1.1102562
C	-1.2449863	1.5537557	-0.1072958
H	-1.0885573	2.1728337	-1.0029738
H	-1.8889493	2.1226017	0.5762922
C	0.1068207	1.3472637	0.5905922
H	0.4585177	2.3109387	0.9837552
H	-0.0205543	0.6700387	1.4461812
C	2.4688167	0.4425497	0.4782892
C	3.7035177	0.3020847	-0.3885058
H	2.6426447	1.1635317	1.2891742
H	4.5404847	-0.0828883	0.2053362
H	3.5087057	-0.3890473	-1.2188258
H	3.9855387	1.2801347	-0.7972688
Mn	1.0279097	-1.8013433	0.1358952
C	-3.6293153	-1.5567923	-0.1123348
H	-3.5188443	-2.3095453	0.6804502
H	-4.7069773	-1.3799413	-0.2346298
H	-3.2353033	-1.9727513	-1.0478298
C	1.2097097	0.8111707	-0.3110988
H	1.4307207	1.5369137	-1.1080248

E = -717.741917659, H = -717.515410
G = -717.559999

3.34s (optimisation by M06-2X/aug-cc-pVDZ)

E = -717.931981118, H = -717.703210
G = -717.748228

3.34s • MnO₄⁻

C	-8.5310879	-0.2650424	-0.2540515
C	-9.5570939	0.4213986	-0.7668585
H	-10.5783929	0.1101836	-0.5198105
H	-7.5061909	0.0231336	-0.5009335
O	-5.7691969	-1.5024594	0.2336235
O	-6.0009209	-1.0195564	-2.4795815
O	-3.5061239	-1.3235804	-1.3518905
O	-5.3052599	-3.4426934	-1.3190025
C	-8.6793539	-1.4569394	0.6508685
H	-8.3266459	-1.1965564	1.6623565
H	-9.7476809	-1.7003474	0.7377475
C	-7.8953669	-2.6914324	0.1764725
H	-8.3671249	-3.5993044	0.5803775
H	-7.9301769	-2.7605404	-0.9207745
C	-5.6485699	-3.8507524	-0.0050255
C	-4.4004309	-4.1995984	0.7948965
H	-6.2890729	-4.7463034	-0.0873245
H	-3.8007429	-4.9469344	0.2587685
H	-3.7856389	-3.3011664	0.9414595
H	-4.6695259	-4.6098334	1.7779065
Mn	-5.0385739	-1.6534854	-1.4166785
C	-9.4229829	1.6151346	-1.6655995
H	-9.9145769	1.4395456	-2.6332275

H	-9.9044199	2.4988186	-1.2214635
H	-8.3675759	1.8526456	-1.8513255
C	-6.4320589	-2.6951804	0.6187565
H	-6.4024569	-2.7548134	1.7216585
Mn	38.3560141	9.1500716	1.3681215
O	37.7526171	7.9964156	0.4765735
O	39.7062661	9.6590046	0.7307605
O	37.3268471	10.3427646	1.4403855
O	38.6354991	8.6074026	2.8228145

E = -1122.58405569, H = -1122.335357
G = -1122.395512

3.34s_{H2O} • MnO₄⁻

C	-2.4330813	1.6133608	-0.2954335
C	-2.5740493	2.9394778	-0.3876225
H	-2.6361193	3.3975778	-1.3808445
H	-2.3526423	1.1507338	0.6914365
O	-1.2657593	-1.0341482	0.7209005
O	-0.8243033	-0.5443232	3.0808615
O	1.5814967	-0.8939272	2.7295605
O	1.1434587	-1.4266432	0.3719615
C	-2.6366253	3.8711468	0.7870485
C	-2.3339503	0.6860108	-1.4749535
H	-3.1698763	-0.0322302	-1.4527285
H	-2.4427663	1.2789088	-2.3938815
C	-1.0189573	-0.1089742	-1.5320805
H	-1.8231063	4.6095958	0.7465545
H	-3.5793393	4.4370018	0.7980385
H	-2.5529583	3.3175268	1.7308215
H	-0.8609193	-0.4614752	-2.5618925
H	-0.1721063	0.5449258	-1.2772015
C	-0.9986133	-1.3411962	-0.6279955
C	0.3672977	-2.0396392	-0.6325915
H	-1.7835943	-2.0351032	-0.9797725
C	0.2507677	-3.5336162	-0.3559595
H	0.8653117	-1.8886542	-1.6065795
H	1.2482767	-3.9761212	-0.2402235
H	-0.3135593	-3.6956042	0.5732625
H	-0.2649813	-4.0470062	-1.1790285
O	0.4022667	1.0623648	1.2568255
H	-1.7217523	-0.6268812	2.7345485
H	2.2719347	-1.2369922	2.1485855
Mn	0.2294307	-0.3998732	1.5962515
Mn	5.8786627	0.0827828	-0.3173645
O	5.2114307	-0.9985372	-1.2428145
O	4.7609547	0.9227238	0.3981665
O	6.7762747	1.0358508	-1.1888475
O	6.7714967	-0.6290442	0.7629905

E = -1199.00971178, H = -1198.734741
G = -1198.794831

3.34d_{H2O}

C	2.2876185	0.0161605	0.2880472
C	3.3792265	-0.4899985	-0.2863578
H	3.9217995	0.1225235	-1.0084918
H	1.7403805	-0.5888835	1.0081452
O	-0.7876155	-0.2019415	0.8464702
O	-1.3484055	-2.4862805	1.3332892
O	-3.0108955	-2.4588325	-0.4808158
O	-2.3962255	-0.1496205	-0.9364898
C	3.9446015	-1.8550225	-0.0277648

C	1.7339235	1.3867975	0.0076342
H	1.6926955	1.9675275	0.9401932
H	2.4283035	1.9204815	-0.6500128
C	0.3369705	1.4122115	-0.6479808
H	3.9846245	-2.4481425	-0.9482748
H	4.9719645	-1.7954735	0.3495962
H	3.3486475	-2.4089755	0.7015802
H	0.1602905	2.4209715	-1.0432798
H	0.3147385	0.7336325	-1.5072468
C	-0.8339045	1.1067865	0.2881942
C	-2.2057825	1.1590495	-0.4116528
H	-0.8103295	1.7984055	1.1411872
C	-3.3591125	1.5496135	0.5049892
H	-2.1702395	1.8322625	-1.2780278
H	-4.3114775	1.4488425	-0.0200098
H	-3.3866215	0.9132405	1.3930942
H	-3.2577905	2.5902125	0.8275442
O	-0.4407255	-2.0030045	-1.1574128
H	-0.7991885	-2.0096755	1.9743982
H	-3.6053145	-1.9445575	-1.0469498
Mn	-1.5221565	-1.5383105	-0.1535938

E = -794.150737278, H = -793.899533
G = -793.947745

3.35s

C	1.6550163	0.5710091	0.4704938
C	2.2757133	-0.3830399	-0.3442232
H	2.5850443	-0.0242759	-1.3291542
H	1.7301673	0.4673181	1.5510858
O	-0.3452467	-0.2429419	0.7860728
O	1.0500843	-1.4801259	-1.0533992
O	-0.7506027	-3.0884609	0.4458238
O	-1.8396477	-0.9580429	-1.1680652
C	3.1937803	-1.4006219	0.2915378
C	1.0817713	1.8479551	-0.0822182
H	0.9518433	2.5814311	0.7268678
H	1.7704073	2.2863061	-0.8216752
C	-0.2781967	1.5774571	-0.7431492
H	2.7192693	-1.8008839	1.1972528
H	3.3596753	-2.2370289	-0.3964802
H	4.1656633	-0.9613959	0.5635318
H	-0.7734317	2.5111461	-1.0519182
H	-0.1384977	0.9420811	-1.6287542
C	-1.1367297	0.7966841	0.2507908
C	-2.3377147	0.1233911	-0.4327012
H	-1.4623287	1.4669521	1.0706718
C	-3.3738477	-0.3333939	0.5938428
H	-2.8137757	0.8468211	-1.1270782
H	-4.1725317	-0.8865349	0.0841468
H	-2.8916267	-1.0065889	1.3150148
H	-3.8141477	0.5227921	1.1276658
Mn	-0.4101107	-1.7380099	-0.2959832

E = -717.881809380, H = -717.655194
G = -717.696952

3.35s_{Na}

C	1.0611231	1.3655922	0.4542348
C	2.1109841	0.8709372	-0.3069202
H	2.2009701	1.2340632	-1.3297202
H	1.1545941	1.3395792	1.5386458
O	-0.2767449	-0.2783328	0.7396138

O	-1.2740539	-1.6703298	-1.1146092
C	3.3812891	0.4104902	0.3590958
C	-0.0297269	2.2220812	-0.1362022
H	-0.4920559	2.8267652	0.6547328
H	0.3927291	2.9116372	-0.8793442
C	-1.1008099	1.3394442	-0.7908942
H	3.1449381	-0.1665248	1.2663028
H	3.9848931	-0.2002978	-0.3297612
H	4.0154191	1.2537032	0.6642708
H	-1.9757899	1.9276082	-1.0976732
H	-0.6872339	0.8400362	-1.6782952
C	-1.4842499	0.2656282	0.2204778
C	-2.2383249	-0.9123508	-0.4162592
H	-2.0531949	0.7113622	1.0535798
C	-2.9546019	-1.7575698	0.6299328
H	-2.9708059	-0.5305278	-1.1486032
H	-3.3982269	-2.6372928	0.1504768
H	-2.2354179	-2.0991128	1.3862098
H	-3.7499939	-1.1828838	1.1233238
Mn	0.3141111	-1.6527478	-0.2831842
O	1.5561651	-0.8754838	-1.0422332
O	0.7776861	-2.9802518	0.5051908
Na	2.8263281	-2.5752208	-0.1923892

E = -880.094385036, H = -879.863425
G = -879.907747

3.35s_H

C	1.7616157	0.6613270	0.4975035
C	2.4177497	-0.2043250	-0.3452145
H	2.5935307	0.1228030	-1.3715355
H	1.7858617	0.4606180	1.5674535
O	-0.3888523	-0.2131120	0.7719225
O	-1.8359743	-0.7910650	-1.1803825
C	3.2560747	-1.3385140	0.1681485
C	1.1526127	1.9523560	0.0305945
H	0.9944277	2.6215250	0.8857435
H	1.8374287	2.4554080	-0.6657845
C	-0.1880203	1.7036420	-0.6751505
H	2.8588737	-1.7042090	1.1227165
H	3.2663097	-2.1680960	-0.5469125
H	4.2928807	-1.0100610	0.3242045
H	-0.6665403	2.6512780	-0.9560595
H	-0.0258783	1.1178280	-1.5905885
C	-1.0937063	0.9114520	0.2608845
C	-2.3229773	0.3365910	-0.4655915
H	-1.3841453	1.5374920	1.1197445
C	-3.4234163	-0.0747840	0.4992895
H	-2.7069493	1.0594950	-1.2022685
H	-4.2234733	-0.5873900	-0.0458655
H	-3.0153233	-0.7581230	1.2547995
H	-3.8452693	0.8063200	0.9993375
Mn	-0.4715713	-1.5510430	-0.3957535
O	0.9139557	-1.4023090	-1.1131885
O	-0.7829423	-2.8634640	0.7394185
H	-0.7562823	-3.7316410	0.3125335

E = -718.364617281, H = -718.124522
G = -718.166994

3.35s_{H2O}

C	1.8869322	0.5861277	0.4000928
C	2.3498112	-0.4954143	-0.3294552

H	2.6128592	-0.3157233	-1.3731852
H	1.9730682	0.5588987	1.4846098
O	-0.1674528	0.1703807	0.7852698
O	-1.9169148	-0.3666913	-0.9672932
C	2.9961112	-1.6710993	0.3531228
C	1.5724562	1.9069057	-0.2577502
H	1.6119712	2.7156067	0.4860848
H	2.3189852	2.1295047	-1.0338602
C	0.1673722	1.8485277	-0.8677382
H	2.4472142	-1.9013673	1.2751458
H	2.9496072	-2.5565433	-0.2909902
H	4.0496502	-1.4696253	0.6005158
H	-0.1657878	2.8328747	-1.2295502
H	0.1538372	1.1398147	-1.7075522
C	-0.7578788	1.3116777	0.2203278
C	-2.1168628	0.8629097	-0.3324712
H	-0.8906088	2.0882007	1.0002738
C	-3.1479538	0.7238137	0.7866678
H	-2.4770958	1.6040667	-1.0737152
H	-4.0795728	0.3118497	0.3797198
H	-2.7557328	0.0296797	1.5419228
H	-3.3593998	1.6958137	1.2569868
Mn	-0.6064428	-1.3937533	-0.1991812
O	-0.6887098	-2.2564413	1.3644128
H	-1.0828148	-3.0957913	1.0861628
O	-1.4983248	-2.9253623	-0.9139452
H	-2.1648308	-2.5604063	-1.5041912
O	0.7865072	-1.5084333	-0.9404382

E = -794.323463050, H = -794.068969
G = -794.113387

3.35s_H • H₂O

C	2.0621959	0.6267757	0.4175001
C	2.4851959	-0.4977773	-0.2410769
H	2.6632949	-0.4239663	-1.3154489
H	2.0965869	0.6357267	1.5056161
O	-0.1835361	0.2806417	0.9092381
O	-1.9211891	-0.2714963	-0.7966179
C	3.0620199	-1.6823633	0.4764921
C	1.7077579	1.9035167	-0.2930889
H	1.7706229	2.7478977	0.4051151
H	2.4232369	2.0881687	-1.1055809
C	0.2875809	1.8299517	-0.8716759
H	2.6344549	-1.7612193	1.4832101
H	2.8436739	-2.6084083	-0.0667699
H	4.1533859	-1.5888163	0.5646641
H	-0.0125691	2.7936007	-1.3054079
H	0.2475249	1.0704457	-1.6646029
C	-0.6704241	1.4289137	0.2442211
C	-2.0636431	1.0435327	-0.2862729
H	-0.7452461	2.2467427	0.9803851
C	-3.1168491	1.0735557	0.8101911
H	-2.3548021	1.7048287	-1.1182429
H	-4.0686981	0.6889157	0.4264771
H	-2.7884251	0.4446067	1.6475581
H	-3.2717461	2.0991327	1.1688941
Mn	-0.6451981	-1.2119833	0.0104311
O	-0.9422461	-2.0490363	1.5365061
H	-1.2702541	-2.9373273	1.3427281
O	-1.6548271	-2.8162953	-0.9927549
H	-2.3380021	-2.2573033	-1.3971429

O	0.6864719	-1.5011753	-0.7630269
H	-1.0763491	-3.0997853	-1.7115179

E = -794.809326209, H = -794.540687
G = -794.585902

3.35t

C	-1.8382529	-0.6599036	0.3191913
C	-2.5630479	0.3372924	-0.2698717
H	-1.7876069	-0.6836836	1.4074383
O	0.5802291	0.1941034	0.9817563
O	2.1707121	1.1656234	-0.8220637
C	-3.6015999	1.1241894	0.4799293
C	-1.0404849	-1.6966836	-0.4294917
H	-0.9128139	-2.5769976	0.2193883
H	-1.6210009	-2.0249676	-1.3056467
C	0.3488601	-1.2488186	-0.9179417
H	-4.5905399	0.6484484	0.3885323
H	-3.3347719	1.1780014	1.5427883
H	-3.6576479	2.1442884	0.0862583
H	0.8322411	-2.0832446	-1.4509747
H	0.2293031	-0.4270956	-1.6405417
C	1.2531111	-0.7675176	0.2206403
C	2.5296691	-0.0934966	-0.3311527
H	1.5136891	-1.6385606	0.8588923
C	3.5890201	0.0353614	0.7633813
H	3.9490271	-0.9516636	1.0922703
H	4.4380631	0.6203854	0.3881243
H	3.1497651	0.5610054	1.6218043
Mn	0.5166101	1.7778954	-0.0638787
O	0.8515211	3.5698654	-0.2481617
O	-1.2858639	1.8875844	-0.3770857
H	-2.6626949	0.3199614	-1.3573197
H	2.9445051	-0.7113726	-1.1562637

E = -717.947183678, H = -717.723273
G = -717.768335

3.35s . TMA

C	-2.2160379	1.9432976	0.5235653
C	-1.2173719	2.3093116	-0.3696867
H	-1.5408039	2.6470966	-1.3541807
H	-1.9952909	1.9778886	1.5891183
O	-2.0113679	-0.1851554	0.7598783
O	-0.5044649	0.7120586	-1.1735007
O	0.5395611	-1.4562154	0.2480583
O	-1.9548569	-1.8131544	-1.1801347
C	-3.6570389	1.8020696	0.1060053
H	-4.3085639	1.8787586	0.9867293
H	-3.9307139	2.6128646	-0.5835387
C	-3.8779799	0.4430936	-0.5707607
H	-4.9418829	0.2598196	-0.7743327
H	-3.3273949	0.4028096	-1.5209377
C	-3.0886129	-1.9682604	-0.3587917
C	-2.8949429	-3.1078844	0.6359343
H	-3.9595319	-2.1867644	-1.0031657
H	-2.6483339	-4.0284084	0.0944143
H	-2.0630349	-2.8661084	1.3102763
H	-3.8052889	-3.2755124	1.2279803
Mn	-0.7329669	-0.7215404	-0.4246057
C	0.0876111	2.8687546	0.1364613
H	0.8297201	2.8835796	-0.6706077
H	-0.0262509	3.8938726	0.5154653

H	0.4668501	2.2362236	0.9522623
C	-3.2993999	-0.6234774	0.3525993
H	-3.9343139	-0.7329804	1.2492943
C	3.0426241	-0.3366634	1.3741873
H	1.9917491	-0.6573674	1.3525623
H	3.6594861	-1.0298084	1.9546223
H	3.1512611	0.6810746	1.7614533
C	2.7332651	0.6249696	-0.8456737
H	2.8923801	1.6223206	-0.4255217
H	3.0884031	0.5882296	-1.8797557
H	1.6746941	0.3480436	-0.7891357
C	3.3626421	-1.7226944	-0.6123007
H	3.7338761	-1.7092814	-1.6414967
H	3.9508281	-2.4186024	-0.0063027
H	2.2911741	-1.9590274	-0.5677457
C	4.9696001	0.0342126	-0.0776007
H	5.0811081	1.0324526	0.3556653
H	5.5462231	-0.6929914	0.5016623
H	5.3074421	0.0382226	-1.1180617
N	3.5359461	-0.3491254	-0.0403567

E = -932.056554866, H = -931.657783
G = -931.712994

3.35_{sH2O}

C	1.8245932	0.9624197	0.4565466
C	2.5633052	0.2306767	-0.4237804
H	2.6650022	0.6056267	-1.4463264
H	1.7590022	0.6135257	1.4862886
O	-0.5781338	0.0500607	1.0842676
O	-1.8539308	-0.8884043	-0.9173054
C	3.4751212	-0.8834343	0.0013506
C	0.9921722	2.1522017	0.0628116
H	0.7824702	2.7580217	0.9568046
H	1.5670732	2.7790787	-0.6361634
C	-0.3434428	1.7714717	-0.6040254
H	3.1033022	-1.3169373	0.9365586
H	3.4835792	-1.6740583	-0.7575804
H	4.5042662	-0.5161193	0.1360396
H	-0.8473558	2.6839117	-0.9607804
H	-0.1431828	1.1264647	-1.4682864
C	-1.2750128	1.0225977	0.3579096
C	-2.3970488	0.2968687	-0.4078244
H	-1.7024238	1.7572267	1.0726616
C	-3.5834378	-0.0051693	0.5078536
H	-2.7479958	0.9352137	-1.2459504
H	-4.3063598	-0.6395753	-0.0203544
H	-3.2219538	-0.5449093	1.3937856
H	-4.0860918	0.9193117	0.8307836
Mn	-0.3504228	-1.5250713	0.0696756
O	0.7971762	-2.2017483	1.3691726
H	0.9277312	-3.1184013	1.0961556
O	-0.6414528	-3.2464983	-0.5918204
H	-1.3682628	-3.1345163	-1.2158944
O	1.0017152	-0.9698353	-1.1225734

E = -794.395151859, H = -794.143582
G = -794.190994

3.35q

C	-1.8422227	-0.6214459	0.2978608
C	-2.6138917	0.3447171	-0.2739932
H	-1.7587247	-0.6302839	1.3844778

O	0.6354393	0.1780611	1.0234038
O	2.2039493	1.1560061	-0.7895582
C	-3.6555957	1.1115581	0.4920978
C	-1.0376917	-1.6494579	-0.4569862
H	-0.9407197	-2.5455279	0.1762668
H	-1.6040927	-1.9507409	-1.3515242
C	0.3703353	-1.2247059	-0.9103802
H	-4.6365567	0.6166791	0.4139478
H	-3.3729337	1.1684221	1.5503728
H	-3.7361157	2.1311901	0.1024008
H	0.8402843	-2.0622999	-1.4508642
H	0.2786123	-0.3932279	-1.6267622
C	1.2838503	-0.7805239	0.2392658
C	2.5625683	-0.1124309	-0.3130742
H	1.5367453	-1.6696289	0.8552418
C	3.6296173	0.0033541	0.7739758
H	3.9897413	-0.9882619	1.0884588
H	4.4776793	0.5907601	0.4002028
H	3.1959803	0.5186561	1.6412398
Mn	0.5501433	1.7482701	-0.0556222
O	0.7149603	3.5194451	-0.4263522
O	-1.3237727	1.9151881	-0.2719432
H	-2.7156707	0.3454391	-1.3619422
H	2.9680833	-0.7192099	-1.1502112

E = -717.940965270, H = -717.717043
G = -717.762670

3.35q_{H2O}

C	1.7770959	0.9904632	0.4430514
C	2.6219369	0.3564282	-0.4060576
H	2.7367829	0.7492772	-1.4206486
H	1.6646259	0.5889862	1.4497394
O	-0.6465781	0.0425492	1.1303204
O	-1.8245011	-0.9780178	-0.8762826
C	3.5369999	-0.7538598	0.0177454
C	0.9009729	2.1508222	0.0535674
H	0.6840429	2.7530342	0.9488854
H	1.4486609	2.7916632	-0.6539086
C	-0.4300021	1.7316362	-0.5989926
H	3.1599259	-1.1992498	0.9456194
H	3.5589309	-1.5354808	-0.7504326
H	4.5626979	-0.3829968	0.1692784
H	-0.9521471	2.6285942	-0.9686346
H	-0.2131981	1.0785992	-1.4532576
C	-1.3558481	0.9786142	0.3666334
C	-2.4310081	0.1952772	-0.4072446
H	-1.8226651	1.7142802	1.0545134
C	-3.6259051	-0.1412718	0.4840144
H	-2.7846741	0.7994152	-1.2683586
H	-4.3060701	-0.8185228	-0.0479176
H	-3.2634521	-0.6448218	1.3904584
H	-4.1774321	0.7664032	0.7724424
Mn	-0.2821831	-1.4965868	0.1104644
O	0.8197829	-2.1412208	1.4513414
H	1.0734189	-3.0185358	1.1379244
O	-0.3797351	-3.1809088	-0.6631256
H	-1.0792971	-3.0908188	-1.3219196
O	1.0288229	-0.9337498	-1.0892186

E = -794.378706260, H = -794.126682
G = -794.174471

3.35d

C	1.7854189	0.5876401	0.4747168
C	2.4583519	-0.3096599	-0.3091922
H	2.6052789	-0.0630579	-1.3620472
H	1.7848379	0.4340751	1.5534408
O	-0.4494341	-0.3259119	0.8508188
O	0.8575119	-1.5520349	-1.0513922
O	-0.7154131	-3.0362969	0.5158748
O	-1.8875791	-1.0209959	-1.0784502
C	3.2788119	-1.4299679	0.2568768
C	1.1146349	1.8214991	-0.0589802
H	0.9665989	2.5426891	0.7547268
H	1.7610139	2.2951721	-0.8102302
C	-0.2418911	1.5064141	-0.7118702
H	2.9325839	-1.6918069	1.2637948
H	3.2127679	-2.3184799	-0.3797592
H	4.3353909	-1.1349249	0.3185898
H	-0.7309281	2.4329401	-1.0414862
H	-0.0892521	0.8725941	-1.5958352
C	-1.1507251	0.7724511	0.2692838
C	-2.3754051	0.1507971	-0.4261452
H	-1.4487481	1.4426691	1.0903838
C	-3.4816961	-0.2028059	0.5528898
H	-2.7569971	0.8244371	-1.2091252
H	-4.2704441	-0.7592819	0.0358948
H	-3.0799961	-0.8262839	1.3616628
H	-3.9150651	0.7084611	0.9842498
Mn	-0.4996261	-1.7203299	-0.2486912

E = -717.747429709, H = -717.520173
G = -717.562446

3.35d_{H2O}

C	1.8513376	0.6517734	0.5875597
C	2.3997956	-0.2153746	-0.3918452
H	2.4151496	0.1539814	-1.4194152
H	2.0055646	0.3911894	1.6348948
O	-0.5869994	-0.2308786	0.9411777
O	0.9472506	-1.4219736	-0.9053053
O	-1.7726484	-0.8779856	-1.1166722
C	3.4118236	-1.2430656	-0.0248502
C	1.1245426	1.9062944	0.2444988
H	0.9013956	2.4679744	1.1579168
H	1.7843206	2.5310394	-0.3774922
C	-0.1718604	1.6527604	-0.5488422
H	3.1961246	-1.6874856	0.9524398
H	3.4806176	-2.0199416	-0.7917063
H	4.3911116	-0.7426456	0.0305868
H	-0.5967704	2.6137904	-0.8627293
H	0.0422006	1.0781344	-1.4612602
C	-1.1980424	0.9085824	0.2980768
C	-2.3493874	0.3178744	-0.5236933
H	-1.5593154	1.5460704	1.1176968
C	-3.5685494	-0.0493446	0.2949278
H	-2.6111774	0.9678724	-1.3694543
H	-4.2823944	-0.6014236	-0.3240103
H	-3.2831564	-0.6671716	1.1549858
H	-4.0549134	0.8639664	0.6576147
Mn	-0.4876024	-1.5649286	-0.2045223
O	-0.7601294	-2.9234046	0.8221437
H	-0.6682894	-3.8056806	0.4272788

E = -794.189283799, H = -793.938818

G = -793.985398

3.36s

C	1.1802604	0.7683419	0.3181476
C	2.1918604	-0.2226541	-0.2781564
H	3.0340304	0.3890789	-0.6690604
H	1.5131344	1.1433659	1.2992266
O	-0.0365816	0.0182829	0.5236316
O	1.5816884	-0.9152091	-1.3136054
O	0.0509124	-3.2246301	-0.1821844
O	-1.7185066	-1.0560311	-1.2327814
C	2.7495964	-1.1597161	0.7989816
C	0.8109584	1.9286289	-0.6283004
H	1.4625374	1.9209449	-1.5088374
H	0.9281064	2.8919629	-0.1150964
C	-0.6531316	1.6718549	-1.0046484
H	3.4300004	-1.8777111	0.3258536
H	3.2956364	-0.6010441	1.5755646
H	1.9318914	-1.7311801	1.2587926
H	-1.2401076	2.5905479	-1.1237664
H	-0.7126146	1.0724359	-1.9202264
C	-1.1773556	0.8080669	0.1366636
C	-2.2585646	-0.1909051	-0.2953004
H	-1.4917026	1.4183779	1.0023126
C	-2.8386926	-0.9342631	0.9115546
H	-3.0712546	0.4129149	-0.7561274
H	-3.5930876	-1.6482471	0.5604586
H	-2.0406326	-1.5015791	1.4084726
H	-3.3031186	-0.2420051	1.6314856
Mn	-0.0252616	-1.7296301	-0.7230534

E = -717.988086948, H = -717.757245
G = -717.798544

3.36s_{Na}

C	1.5729096	-0.0067697	0.2170658
C	1.7735856	-1.4427367	-0.2788542
H	2.7552376	-1.4814487	-0.7847182
H	2.1268906	0.1856323	1.1460548
O	0.1537986	0.0977103	0.5292537
O	0.7642656	-1.7165237	-1.2129842
O	-2.0345304	0.1055743	-0.9839912
C	1.7789316	-2.4464057	0.8730967
C	1.8477066	1.0763993	-0.8452952
H	2.2929656	0.6295083	-1.7395413
H	2.5416746	1.8264593	-0.4500022
C	0.4759866	1.6943923	-1.1477422
H	1.8542776	-3.4601927	0.4651538
H	2.6255106	-2.2690347	1.5508528
H	0.8429716	-2.3796007	1.4445607
H	0.5203866	2.7701553	-1.3474993
H	0.0062796	1.1892573	-1.9992752
C	-0.3393484	1.3866113	0.1018588
C	-1.8393264	1.2148403	-0.1430092
H	-0.1447454	2.1161323	0.9040348
C	-2.6037994	1.0583053	1.1703278
H	-2.1856654	2.1293943	-0.6577112
H	-3.6818234	0.9725003	0.9705488
H	-2.2625094	0.1540573	1.6921738
H	-2.4589604	1.9245043	1.8290377
Mn	-0.8967984	-1.3525427	-0.5337832
O	-1.8849144	-2.5220257	0.0059147

Na -3.6009574 -1.4541527 -0.7755273
 E = -880.212517546, H = -879.977756
 G = -880.021945

3.36s_H

C	1.1958993	0.8042797	0.3877936
C	2.1659873	-0.1156803	-0.3704064
H	2.9148863	0.5229818	-0.8660554
H	1.5746443	1.0051038	1.3978336
O	-0.0526197	0.0583467	0.5448556
O	1.4585203	-0.8208243	-1.3725674
O	-1.6685637	-0.8794873	-1.3027214
C	2.8772133	-1.0837643	0.5690766
C	0.8222253	2.1076248	-0.3406134
H	1.5230223	2.3159518	-1.1548814
H	0.8518483	2.9500638	0.3597806
C	-0.6034237	1.8736547	-0.8432724
H	3.5072343	-1.7614173	-0.0174644
H	3.5117053	-0.5367453	1.2788976
H	2.1438763	-1.6816863	1.1257656
H	-1.1934047	2.7935278	-0.9073004
H	-0.5966327	1.3807568	-1.8223554
C	-1.1794197	0.9130177	0.1846596
C	-2.2655987	-0.0145963	-0.3569794
H	-1.5053107	1.4365168	1.0956866
C	-2.9513617	-0.8100183	0.7469196
H	-3.0056427	0.6128347	-0.8811584
H	-3.6835667	-1.4933613	0.3037106
H	-2.2092147	-1.4040893	1.2958246
H	-3.4691187	-0.1402173	1.4460326
Mn	-0.0828667	-1.4773193	-0.7775504
O	-0.0450817	-2.8441382	0.3512976
H	-0.0352367	-3.7113162	-0.0748084

E = -718.495612830, H = -718.251140
 G = -718.292532

3.36s_{H2O}

C	1.5264509	0.6801223	0.2126421
C	2.1115819	-0.6747027	-0.2028099
H	3.0557349	-0.4606847	-0.7453119
H	2.0559229	1.0863603	1.0896341
O	0.1631809	0.4251993	0.5938591
O	-1.9046111	-0.2842797	-0.9519739
C	2.4441599	-1.5341497	1.0189301
C	1.4774579	1.7122503	-0.9331119
H	1.9751629	2.6425953	-0.6313469
H	1.9868959	1.3168123	-1.8186249
C	-0.0168971	1.9329253	-1.1933839
H	1.5348569	-1.7089057	1.6077781
H	2.8241059	-2.5046447	0.6772801
H	3.2113549	-1.0494037	1.6424491
H	-0.2688971	2.9742873	-1.4271199
H	-0.3668411	1.2827253	-2.0027669
C	-0.6877391	1.4675083	0.0961081
C	-2.0594591	0.8284763	-0.1328599
H	-0.7335921	2.2779983	0.8459971
C	-2.7303251	0.4680393	1.1942291
H	-2.6789031	1.5885153	-0.6530719
H	-3.7204311	0.0412023	0.9924901
H	-2.1258281	-0.2889417	1.7100131
H	-2.8487661	1.3563353	1.8337961

Mn	-0.5262121	-1.4367587	-0.4786669
O	-0.7350441	-2.2176967	1.1539161
H	-1.0588381	-3.0938857	0.9074451
O	-1.1425921	-2.9013117	-1.4866049
H	-1.9846301	-2.6146717	-1.8569299
O	1.2227419	-1.3113167	-1.0619829

E = -794.451114480, H = -794.193276
G = -794.237596

3.36s_H • H₂O

C	1.0172478	1.3461112	0.3734854
C	2.1498458	0.3953332	-0.0503506
H	2.8586958	0.9762602	-0.6632296
H	1.2999718	1.8773282	1.2914964
O	-0.1379762	0.5189582	0.6980024
O	-1.4944352	-1.1106708	-0.8989266
C	2.8850208	-0.1708468	1.1605284
C	0.5482218	2.3298432	-0.7141906
H	0.4272598	3.3318922	-0.2865336
H	1.2772738	2.3926632	-1.5281516
C	-0.7997682	1.7756312	-1.1762656
H	2.1793288	-0.6882528	1.8232484
H	3.6397638	-0.8907578	0.8245164
H	3.3859728	0.6309682	1.7189774
H	-1.4909172	2.5525772	-1.5191776
H	-0.6656152	1.0368552	-1.9744776
C	-1.3260352	1.0654612	0.0619714
C	-2.2492892	-0.1141528	-0.2429106
H	-1.7929672	1.7703722	0.7663724
C	-2.9058462	-0.6734948	1.0138054
H	-3.0258502	0.2517282	-0.9360436
H	-3.5391582	-1.5263238	0.7457874
H	-2.1348592	-1.0192608	1.7143504
H	-3.5274002	0.0881842	1.5027864

Mn 0.1221938 -1.3512008 -0.1630496
O 0.2198838 -2.2659488 1.3509054
H 0.3565898 -3.2070818 1.1846944
O 0.3769428 -3.0082928 -1.3764796
H -0.4085432 -2.9446268 -1.9393076
O 1.6248848 -0.6468508 -0.8473056
H 1.1295638 -2.7224038 -1.9145286

E = -794.945972935, H = -794.673494
G = -794.718338

3.36s • TMA

C	-2.4114561	1.4635315	0.4420509
C	-0.9891731	1.9153715	0.0875029
H	-1.0734051	2.9268255	-0.3527821
H	-2.7540571	1.9269925	1.3788509
O	-2.3273671	0.0366575	0.6651029
O	-0.4615691	1.0328395	-0.8619891
O	0.6649129	-1.3166375	0.4481939
O	-1.8764921	-1.9343965	-1.0024941
C	-3.4410531	1.6601995	-0.6882921
H	-4.2908061	2.2500485	-0.3264631
H	-2.9858181	2.1917225	-1.5301571
C	-3.8710021	0.2406695	-1.0858581
H	-4.9379901	0.1647405	-1.3204111
H	-3.2868121	-0.1128145	-1.9427541
C	-3.0473021	-2.0339955	-0.2446531

C	-2.8516701	-2.9012935	0.9970969
H	-3.8474761	-2.4767065	-0.8683061
H	-2.4918311	-3.8900895	0.6920149
H	-2.0952351	-2.4484545	1.6516419
H	-3.7907771	-3.0197455	1.5561309
Mn	-0.6586751	-0.7438775	-0.3057641
C	-0.1041671	2.0024825	1.3342249
H	0.9024959	2.3319775	1.0443479
H	-0.5057291	2.7213975	2.0612879
H	-0.0260441	1.0133575	1.8058929
C	-3.4994851	-0.6166565	0.1186959
H	-4.2858011	-0.6098175	0.8902759
C	3.1950589	0.0246465	1.1747629
H	2.1570229	-0.3279005	1.2770499
H	3.8846909	-0.5976125	1.7536709
H	3.3069009	1.0762155	1.4570839
C	2.6597209	0.7819715	-1.0778701
H	2.8708219	1.8191975	-0.7992121
H	2.8841199	0.6245125	-2.1368571
H	1.6141449	0.5365215	-0.8595551
C	3.3606579	-1.5280035	-0.7025021
H	3.6333029	-1.6005565	-1.7600191
H	4.0209889	-2.1563955	-0.0967301
H	2.3013769	-1.7726055	-0.5282761
C	4.9713829	0.2915925	-0.4804361
H	5.1012649	1.3258635	-0.1478601
H	5.6163819	-0.3734765	0.1013739
H	5.2086769	0.2072955	-1.5452401
N	3.5572729	-0.1055945	-0.2727711

E = -932.167375821, H = -931.764600
G = -931.819680

3.36t

C	1.1317980	-1.0510726	0.2288677
C	0.0287590	-2.0538256	-0.1475573
H	0.5634100	-2.9434976	-0.5478313
H	1.7654640	-1.5039276	1.0107167
O	0.5471360	0.1311524	0.7769547
O	-0.8012990	-1.5461436	-1.1375823
O	-3.5678150	-0.6115976	-0.1774743
O	-1.4580280	1.4744084	-1.0239583
C	-0.7456140	-2.4913836	1.0979917
C	1.9738870	-0.5900826	-0.9702943
H	1.9513420	-1.3322486	-1.7764473
H	3.0167410	-0.4331296	-0.6609483
C	1.3212860	0.7332064	-1.3740993
H	-1.5640310	-3.1568316	0.7991397
H	-0.0898060	-3.0156946	1.8099357
H	-1.1841810	-1.6130796	1.5892277
H	2.0241410	1.4382164	-1.8350333
H	0.4817840	0.5525784	-2.0512843
C	0.7736160	1.2728984	-0.0532323
C	-0.5222940	2.0888734	-0.2083413
H	1.5239810	1.9135854	0.4502127
C	-1.1035930	2.4312104	1.1651407
H	-0.2014040	3.0382504	-0.6914443
H	-1.9922200	3.0604564	1.0357047
H	-1.4008300	1.5037794	1.6704847
H	-0.3703920	2.9622464	1.7915227
Mn	-2.1018370	-0.2583476	-0.7703703

E = -718.021713506, H = -717.791586

G = -717.834950

3.36t_H

C	1.1829630	0.9961087	0.2759988
C	2.2440660	-0.0186393	-0.1599262
H	3.0788230	0.5339897	-0.6219252
H	1.4621380	1.4858937	1.2185818
O	-0.0048240	0.1989017	0.5319548
O	1.6594540	-0.8494813	-1.1320452
O	-1.6388870	-1.1072973	-1.0179982
C	2.7687200	-0.8305113	1.0212648
C	0.7736600	2.0174847	-0.8016632
H	1.3920830	1.8948667	-1.6963872
H	0.9089450	3.0366867	-0.4248132
C	-0.7054900	1.7193387	-1.0999062
H	3.4533390	-1.6037273	0.6581728
H	3.2982170	-0.1893613	1.7378818
H	1.9404850	-1.3257413	1.5498998
H	-1.3024720	2.6239407	-1.2519552
H	-0.7982580	1.0799097	-1.9850222
C	-1.1844210	0.9310587	0.1131308
C	-2.2315860	-0.1447813	-0.1858962
H	-1.4916260	1.5863717	0.9416708
C	-2.7739160	-0.7772903	1.0914838
H	-3.0578150	0.3358927	-0.7373912
H	-3.4711790	-1.5808413	0.8327918
H	-1.9515830	-1.2085793	1.6784648
H	-3.2970450	-0.0358033	1.7096628
Mn	0.0774980	-1.5666423	-0.6070492
O	0.1120300	-3.3461133	-0.5204522
H	-0.4433200	-3.8556333	-1.1185292
E = -718.535618077, H = -718.292327			
G = -718.337290			

3.36t_{H2O}

C	1.3631879	0.9338031	0.1700284
C	2.2418419	-0.2718899	-0.2051396
H	3.1284439	0.1475751	-0.7296216
H	1.7623649	1.4705081	1.0459494
O	0.0790909	0.3935511	0.5300544
O	-1.9239921	-0.6490519	-0.9191976
C	2.7347119	-1.0111629	1.0415084
C	1.0991169	1.8982691	-1.0058286
H	1.4745199	2.9021211	-0.7707606
H	1.6113549	1.5330071	-1.9025416
C	-0.4267461	1.8894181	-1.1954006
H	1.8792229	-1.4000789	1.6060824
H	3.3500469	-1.8634239	0.7280664
H	3.3431229	-0.3451509	1.6738654
H	-0.8483321	2.8846051	-1.3801726
H	-0.7081131	1.2209651	-2.0169916
C	-0.9631241	1.2837281	0.1005034
C	-2.2172161	0.4201041	-0.0814796
H	-1.1097191	2.0550851	0.8777254
C	-2.7472951	-0.0619759	1.2717524
H	-2.9822721	1.0743261	-0.5517796
H	-3.6506091	-0.6618579	1.1073554
H	-1.9900281	-0.6988519	1.7488034
H	-2.9945601	0.7826561	1.9332654
Mn	-0.2593441	-1.4983089	-0.5310556
O	-0.0630711	-2.3941399	1.1029594

H	-0.4127651	-3.2737799	0.9225024
O	-0.7107641	-2.9473479	-1.5784356
H	-1.5866681	-2.7323259	-1.9208736
O	1.5275949	-1.0803759	-1.0711446

E = -794.488183338, H = -794.231106
G = -794.277874

3.36q

C	1.1319536	0.8839520	0.3388061
C	2.1907286	-0.0619760	-0.2613769
H	3.0337056	0.6012220	-0.5666999
H	1.4888466	1.3070530	1.2925381
O	-0.0552874	0.1109020	0.6174651
O	1.6704026	-0.7318310	-1.3479829
O	0.3894856	-3.6181020	-0.0520279
O	-1.7369474	-1.1860060	-1.2309379
C	2.7338386	-1.0141730	0.8161711
C	0.7014416	1.9937510	-0.6391869
H	1.4114836	2.0650020	-1.4705879
H	0.6599256	2.9636430	-0.1247719
C	-0.6906894	1.5619900	-1.1027309
H	3.4551306	-1.6984600	0.3534651
H	3.2302106	-0.4632160	1.6302941
H	1.9253876	-1.6230610	1.2473721
H	-1.3481414	2.4030920	-1.3552579
H	-0.6183864	0.8771530	-1.9548389
C	-1.2200724	0.7669920	0.0822581
C	-2.2536314	-0.3049320	-0.3080959
H	-1.6307494	1.4381860	0.8606281
C	-2.7711464	-1.0254390	0.9447811
H	-3.1074214	0.2680770	-0.7409529
H	-3.5207484	-1.7675900	0.6447981
H	-1.9432004	-1.5539000	1.4378071
H	-3.2236364	-0.3243850	1.6636841
Mn	0.0975166	-1.8679450	-0.7746199

E = -718.093160374, H = -717.864538
G = -717.909862

3.36q_{H2O}

C	1.2707276	0.8858905	0.0247707
C	2.2434526	-0.3073195	0.0470547
H	3.1712576	0.0451995	-0.4540903
H	1.6524856	1.7080555	0.6584387
O	0.0489876	0.4016585	0.5825057
O	-1.9986634	-0.9039355	-0.7554153
C	2.5881106	-0.6729385	1.4959967
C	0.8898146	1.3895035	-1.3747783
H	1.4730496	2.2776315	-1.6455143
H	1.0804006	0.5902615	-2.1006113
C	-0.6281254	1.6745075	-1.2904823
H	1.6682806	-0.9568585	2.0237277
H	3.2757026	-1.5276305	1.4943367
H	3.0640226	0.1662285	2.0265297
H	-0.8578694	2.7421995	-1.3894383
H	-1.1616714	1.1196635	-2.0694703
C	-1.0643224	1.1518755	0.0940017
C	-2.2558584	0.1761205	0.0774157
H	-1.2603894	1.9869755	0.7904487
C	-2.5946634	-0.2805305	1.4994247
H	-3.1161174	0.7540485	-0.3258693
H	-3.4953104	-0.9055895	1.4678417

H	-1.7669454	-0.8926695	1.8781997
H	-2.7738284	0.5748645	2.1696407
Mn	-0.1832674	-1.5831795	-0.7269163
O	-0.3242584	-2.6586005	0.8086077
H	0.5816406	-2.8747565	1.0566647
O	-0.1697394	-1.4380665	-2.6025753
H	-1.0899274	-1.2456375	-2.8188333
O	1.7330246	-1.3969715	-0.6416113

E = -794.555736372, H = -794.299051
G = -794.345006

3.36q_H

C	-1.2531563	-0.8961711	-0.0123079
C	-2.3143943	0.2102319	-0.0317059
H	-3.1817293	-0.1717891	-0.5991699
H	-1.4868563	-1.6833031	0.7183751
O	-0.0400853	-0.2326341	0.4399261
O	-1.7876253	1.3220519	-0.7046009
O	1.8258417	1.2205509	-0.6631099
C	-2.7647133	0.5781609	1.3789951
C	-0.8749763	-1.4763681	-1.3834079
H	-1.2893063	-0.8355581	-2.1693769
H	-1.2892873	-2.4817631	-1.5033709
C	0.6726647	-1.4668211	-1.4258229
H	-3.4682213	1.4150269	1.3248161
H	-3.2545013	-0.2696981	1.8760741
H	-1.9022053	0.8894369	1.9848931
H	1.0970897	-2.4520411	-1.6407799
H	1.0366727	-0.7630181	-2.1832279
C	1.1124287	-0.9736231	-0.0435919
C	2.2600317	0.0420369	-0.0319009
H	1.2881847	-1.8043001	0.6547251
C	2.7421377	0.3251089	1.3871471
H	3.0905807	-0.3870271	-0.6192869
H	3.5207247	1.0943319	1.3571521
H	1.9108477	0.6957919	2.0029251
H	3.1520327	-0.5787411	1.8569471
Mn	0.0271377	1.6246539	-0.4345659
O	0.1229087	3.3989169	-0.7141569
H	1.0477747	3.6565579	-0.8215939

E = -718.607690921, H = -718.364215
G = -718.409362

3.36d

C	1.1986476	0.7095906	0.3541466
C	2.1817246	-0.2483894	-0.3322004
H	2.9548506	0.3579396	-0.8313684
H	1.5393236	0.9694676	1.3639046
O	-0.0416714	-0.0554194	0.5132366
O	1.4743226	-0.9606174	-1.3222294
O	-0.0028134	-3.0358554	0.0054846
O	-1.6494494	-1.0577314	-1.2423164
C	2.8494476	-1.1909754	0.6632066
C	0.8149276	1.9585236	-0.4587174
H	1.4869546	2.0844096	-1.3131254
H	0.8882266	2.8523556	0.1705466
C	-0.6324474	1.7170316	-0.9005624
H	3.4632426	-1.9163814	0.1189516
H	3.4887976	-0.6318594	1.3588766
H	2.0949606	-1.7440544	1.2389116
H	-1.2184034	2.6387826	-0.9706544

H	-0.6623534	1.1960566	-1.8641254
C	-1.1866644	0.7868366	0.1656986
C	-2.2630324	-0.1777904	-0.3285494
H	-1.4875714	1.3247186	1.0760306
C	-2.9309794	-0.9372064	0.8111216
H	-3.0176784	0.4138126	-0.8732874
H	-3.6428034	-1.6596234	0.3988696
H	-2.1793054	-1.4878854	1.3923136
H	-3.4664914	-0.2501274	1.4794846
Mn	-0.0537624	-1.6556094	-0.6736464

E = -717.868001402, H = -717.634830
G = -717.676050

3.36d_{H2O}

C	1.2315525	0.6982226	0.4398569
C	2.1419655	-0.1865724	-0.4394501
H	2.7381745	0.4502156	-1.1045891
H	1.6241445	0.7470296	1.4599319
O	-0.0727765	-0.0133974	0.5415409
O	1.3078395	-0.9834714	-1.2991771
O	-1.6122575	-0.9372834	-1.2481671
C	3.0408035	-1.0950644	0.3800419
C	0.8774445	2.0809846	-0.1167801
H	1.6406425	2.4351106	-0.8153481
H	0.8044205	2.8041306	0.7022829
C	-0.4899875	1.8885986	-0.7771391
H	3.6264515	-1.7419184	-0.2801621
H	3.7314445	-0.4895334	0.9787909
H	2.4431665	-1.7183534	1.0591809
H	-1.0520975	2.8231526	-0.8621301
H	-0.3976985	1.4384366	-1.7736291
C	-1.1720135	0.9205576	0.1653119
C	-2.2678575	0.0381946	-0.4255841
H	-1.4939595	1.4027766	1.0960069
C	-3.1221785	-0.6496704	0.6248809
H	-2.8866815	0.6476166	-1.0975911
H	-3.8313005	-1.3289744	0.1422799
H	-2.4962685	-1.2225774	1.3218119
H	-3.6868715	0.0982626	1.1933819
Mn	-0.1430525	-1.5410064	-0.6018391
O	-0.1887385	-2.8243434	0.5183039
H	-0.2943105	-3.7411224	0.2179829

E = -794.312943564, H = -794.052367
G = -794.096326

3.38d

C	-2.0656011	0.3369177	-0.3425335
C	-2.9762171	-0.2742383	0.4212375
H	-3.2538071	0.1964867	1.3738995
H	-1.7826671	-0.1198943	-1.2987965
O	0.8788399	-0.2025223	-1.2173195
O	-0.8042041	-2.4911883	-0.3633985
O	1.7320359	-3.4055223	0.1652355
O	2.2732549	-0.8242803	0.9750975
C	-1.3838401	1.6180657	0.0445815
H	-1.4540541	2.3567787	-0.7712595
H	-1.8885101	2.0559827	0.9194025
C	0.1101729	1.4269187	0.4153645
H	0.5161749	2.3794467	0.7879765
H	0.1847119	0.6740027	1.2180495
C	2.8246099	0.2711747	0.6744985

C	3.9408709	0.3113767	-0.3163975
H	2.6172089	1.1523907	1.3042915
H	4.8307729	-0.1734923	0.1201435
H	3.6565449	-0.2722653	-1.2067025
H	4.2003349	1.3382607	-0.6026705
Mn	0.8794779	-1.8580253	-0.1326415
C	-3.6618701	-1.5596473	0.0816515
H	-3.4363181	-2.3252223	0.8392455
H	-4.7546561	-1.4244773	0.0614195
H	-3.3210461	-1.9443903	-0.8876275
C	0.8992659	0.9893737	-0.7787285
H	1.2385139	1.7679907	-1.4840185

E = -717.7119193725, H = -1764.486527
G = -1764.549889

3.38s

C	-1.8619484	-0.1489357	-0.4602203
C	-2.9677754	-0.6427367	0.1014357
H	-3.7534114	0.0453263	0.4372837
H	-1.0733504	-0.8359447	-0.7753203
O	0.9743356	0.3014583	-1.3806213
O	0.2529216	-2.8163777	-0.0536383
O	2.8250096	-2.1610837	-0.9793393
O	1.5030786	-0.5244177	1.0729717
C	-1.5737564	1.3132663	-0.6432863
H	-1.4465874	1.5340663	-1.7136883
H	-2.4263344	1.9024363	-0.2724393
C	-0.2949074	1.7397583	0.1011627
H	-0.2660254	2.8353463	0.2060677
H	-0.3346094	1.3117243	1.1125327
C	2.1594946	0.5812153	0.9579587
C	3.4997796	0.5900453	0.2824577
H	1.9962906	1.3129133	1.7661307
H	4.1847366	-0.1000837	0.8000767
H	3.3939456	0.2182693	-0.7469233
H	3.9249246	1.6017983	0.2927517
Mn	1.5094146	-1.8708997	-0.1722263
C	-3.1919984	-2.1122777	0.3226807
H	-3.4154654	-2.3207087	1.3792977
H	-4.0449104	-2.4824177	-0.2668303
H	-2.2893864	-2.6713647	0.0460657
C	0.9867656	1.2976583	-0.6135893
H	1.7297696	2.1019673	-0.8007523

E = -717.835996543, H = -717.611826
G = -717.659245

3.38s_{H2O}

C	2.1386400	0.8374491	0.3520295
C	2.8041130	0.0147361	-0.4593685
H	2.8071530	0.2394351	-1.5307075
H	2.0645470	0.5921441	1.4157285
O	-0.6631260	-0.2181359	0.8991535
O	0.6285800	-2.5773239	1.0041075
O	-1.7581870	-2.7837189	-0.2470555
O	-2.2814420	-0.2539369	-1.3072625
C	3.4264250	-1.2829649	-0.0532485
C	1.3479700	2.0193411	-0.1428485
H	1.3113670	2.8054291	0.6263405
H	1.8467720	2.4492421	-1.0240865
C	-0.0935030	1.6414041	-0.5571505
H	2.7763400	-2.1025779	-0.3967185

H	4.4245250	-1.4113329	-0.4942475
H	3.5092330	-1.3570369	1.0387685
H	-0.6168200	2.5525491	-0.8837325
H	-0.0596870	0.9297571	-1.3945715
C	-0.8757490	1.0079321	0.5588465
C	-2.6630430	0.6038061	-0.4770055
H	-1.1963510	1.6712881	1.3787465
C	-3.5503740	0.1760821	0.6748055
H	-2.7360290	1.6671331	-0.7923905
H	-4.5482560	-0.0682129	0.2789405
H	-3.1239670	-0.7296739	1.1226965
H	-3.6534000	0.9656701	1.4306295
O	0.4011960	-1.4940009	-1.5583145
H	1.1271420	-1.9378849	1.5263255
H	-2.4272120	-2.3268589	-0.7753715
Mn	-0.3668580	-1.6297389	-0.2130385

E = -794.296766945, H = -793.045442
G = -794.094744

3.38q_H

C	-0.5238812	-1.3295173	1.8160169
C	-1.7446852	-1.4704553	1.2965869
H	-2.4390402	-0.6257633	1.3485699
H	0.1845528	-2.1574723	1.7324599
O	-0.4030242	0.4756327	-0.6292061
O	1.9171178	0.5147027	-1.3831301
C	-2.2145092	-2.6887903	0.5657109
C	0.0083488	-0.0495663	2.3834659
H	-0.8143672	0.6394187	2.6201859
H	0.5625478	-0.2330613	3.3137339
C	0.9894798	0.6274687	1.3882939
H	-3.1597792	-3.0673373	0.9761759
H	-2.3861662	-2.4399693	-0.4915681
H	-1.4590082	-3.4813603	0.6070839
H	1.5358888	1.4352767	1.8910719
H	1.7068618	-0.1169193	1.0217579
C	0.2016708	1.2188847	0.2450929
C	1.6626708	1.7419917	-1.0224081
H	-0.3499752	2.1371147	0.5059159
C	0.9577608	2.6530917	-1.9900571
H	2.4241748	2.1943457	-0.3714001
H	1.6746798	2.9638187	-2.7632711
H	0.1277238	2.1192837	-2.4665501
H	0.5907798	3.5522767	-1.4827131
Mn	0.6294448	-0.7369313	-1.5420311
O	0.8843538	-2.1093643	-0.8958531
O	-0.4775842	-0.6856043	-2.9424911
H	-0.0860362	-1.0811943	-3.7314441

E = -718.347260368, H = -718.109124
G = -718.154923

3.39d

C	1.4576242	-0.2173537	-0.6315408
C	1.7077152	1.0678593	-0.3763068
H	2.4794412	1.3268093	0.3566282
H	0.6760462	-0.4597917	-1.3588948
O	-0.8763558	-2.6295837	-0.4616348
O	-1.6883728	-0.0588957	-1.6867798
O	-3.6598028	-1.4185007	0.0162352
O	-1.2329938	-0.0223947	1.1377012
C	2.1334372	-1.3612737	0.0662052

H	2.6591942	-2.0044097	-0.6562358
H	2.8835852	-0.9851557	0.7723352
C	1.1078132	-2.2148427	0.8572172
H	1.6449512	-2.9558677	1.4636122
H	0.4942102	-1.5708747	1.4938702
C	-1.3117538	1.1887903	1.2759372
C	-2.2868858	2.0452793	0.5456882
H	-0.6107708	1.6646773	1.9865242
H	-2.0081318	2.0292833	-0.5191708
H	-3.2847198	1.5908743	0.6128142
H	-2.2910328	3.0667683	0.9343032
Mn	-2.2611488	-0.9468577	-0.4985438
C	0.9773092	2.1982323	-1.0398498
H	0.5651972	2.8943573	-0.2933268
H	1.6521612	2.7899053	-1.6727218
H	0.1585382	1.8081303	-1.6575548
C	0.2396822	-2.9559127	-0.1064298
H	0.6750622	-3.8692507	-0.5600818

E = -717.7331854479, G = -717.563273

3.39qr

C	-1.9054893	-0.3299479	-0.4826163
C	-1.9781383	-1.1651329	0.5571227
H	-2.2662453	-0.7557599	1.5325477
H	-1.6196353	-0.7239899	-1.4642243
O	0.8083437	1.0336441	-1.7916153
O	0.1054597	-2.0522809	-2.0770663
O	3.3582617	-0.9017929	-1.1621093
O	1.2327547	-0.6716069	0.9470617
C	-2.1544593	1.1479901	-0.3590603
H	-2.7620953	1.5172021	-1.1975343
H	-2.7074653	1.3614041	0.5636927
C	-0.8268013	1.9505051	-0.2944753
H	-1.0451393	3.0124251	-0.1211883
H	-0.2033843	1.5502591	0.5123637
C	2.0888197	-0.1020309	1.6038907
C	3.1261957	0.8099131	1.0513537
H	2.1056967	-0.2826609	2.6961267
H	4.0535617	0.2224381	0.9631357
H	2.8661557	1.1576911	0.0460657
H	3.3042487	1.6409711	1.7435347
Mn	1.4624547	-1.0311209	-1.2527603
C	-1.6852073	-2.6322089	0.5025127
H	-0.8626383	-2.8752839	1.1898267
H	-2.5591993	-3.2142339	0.8245037
H	-1.3902033	-2.9331729	-0.5087773
C	-0.1010723	1.8162631	-1.5905853
H	-0.4447793	2.4505161	-2.4317273

E = -717.846978644, H = -717.622403
G = -717.677137

3.39s

C	-1.8895398	0.5545765	-0.4064873
C	-2.8744528	-0.2199365	0.0505117
H	-3.5181878	0.1559965	0.8549537
H	-1.2115528	0.1320575	-1.1540153
O	2.0471852	2.1221145	0.2795587
O	2.3077682	-1.2004745	1.0089447
C	-3.0803108	-1.6386005	-0.3858293
C	-1.5325978	1.8885205	0.1860777
H	-1.4265148	2.6583835	-0.5950133

H	-2.3332938	2.2172395	0.8634007
C	-0.2196478	1.8006105	0.9916557
H	-2.8090798	-2.3048965	0.4458377
H	-4.1236158	-1.8324595	-0.6772563
H	-2.4082158	-1.8777875	-1.2183073
H	-0.0298378	2.7077295	1.5799647
H	-0.2930268	0.9325525	1.6665387
C	0.9809962	1.5552185	0.1167337
C	3.2783412	-0.7189425	0.4369647
H	0.8588422	0.8006105	-0.6892873
C	3.3725082	-0.5151055	-1.0346193
H	4.1331802	-0.4116625	1.0660747
H	4.3429302	-0.8848815	-1.3930673
H	2.5204932	-1.0074465	-1.5259043
H	3.3376262	0.5704625	-1.2153083
Mn	0.5542012	-1.7712965	0.3939747
O	-0.4401778	-2.2218005	1.5681747
O	0.4559792	-1.4907815	-1.2142713

E = -717.886644247, H = -717.661806
G = -717.711369

3.39q

C	-2.0071131	-0.0319191	-0.3975436
C	-3.1566101	-0.4103541	0.1643684
H	-3.8360871	0.3483539	0.5714314
H	-1.3259721	-0.8059221	-0.7599196
O	0.9755819	-0.1023321	-1.2638526
O	-0.1157091	-2.5764861	0.1749574
O	2.6636689	-2.6183821	-0.6949286
O	1.9682689	-0.4587001	1.3327824
C	-1.5092031	1.3826139	-0.4636716
H	-1.4417171	1.7214529	-1.5095276
H	-2.2160971	2.0473669	0.0548224
C	-0.1134451	1.5020329	0.1948054
H	0.0840279	2.5431459	0.4877454
H	-0.1023411	0.8733659	1.0972784
C	2.5223169	0.5919869	0.8927124
C	3.7347009	0.5122759	0.0063034
H	2.3431459	1.5380679	1.4357474
H	4.5960359	0.1823809	0.6079734
H	3.5707119	-0.2460411	-0.7717866
H	3.9646579	1.4891219	-0.4380236
Mn	1.3287279	-1.8437111	-0.1303416
C	-3.5526951	-1.8528561	0.3065154
H	-3.8112301	-2.0838821	1.3499574
H	-4.4326291	-2.0967781	-0.3080586
H	-2.7096141	-2.4917621	0.0143404
C	0.9937719	1.0481779	-0.7274656
H	1.5848469	1.8387829	-1.2266216

E = -717.939453179, H = -717.715302
G = -717.765686

3.39s_{H2O}

C	3.0191017	0.5070880	0.5518961
C	2.1537347	-0.4826630	0.7953781
H	1.4607637	-0.8211850	0.0168841
H	3.7105097	0.8174260	1.3429391
O	-0.3338703	1.7255090	-0.5806759
O	-1.1285583	-0.4066680	0.9971431
O	-2.5458683	0.3981680	-1.7456819
O	-5.3697713	-0.5699360	1.2681331

C	2.0388967	-1.2035230	2.1033031
C	3.1330227	1.2450250	-0.7631449
H	3.4467587	2.2835030	-0.5668049
H	3.9289057	0.8055550	-1.3825909
C	1.8279387	1.2558250	-1.5734589
H	0.9940937	-1.1688390	2.4399821
H	2.2926047	-2.2653160	1.9748941
H	2.6989987	-0.7717030	2.8678231
H	2.0071417	1.7732430	-2.5307259
H	1.4205677	0.2519600	-1.7802149
C	0.8004137	2.0698510	-0.8520939
C	-4.2977993	-0.6352440	0.6956981
H	1.1144197	3.0911110	-0.5432559
C	-3.7602143	-1.8795080	0.0604711
H	-3.6398413	0.2496020	0.6092521
H	-4.4634013	-2.7101290	0.1847411
H	-3.5635663	-1.6608330	-0.9988629
H	-2.7838113	-2.0951750	0.5170391
O	0.0028067	-1.2185750	-1.6264969
H	-0.7046973	0.3424260	1.4307241
H	-2.4264373	1.3038540	-2.0490509
Mn	-1.0328433	-0.2308500	-0.8632419

E = -794.359113905, H = -794.122879
G = -794.163179

3.39q_{H2O}

C	2.2656177	-0.0265828	0.2085136
C	3.4110887	-0.5551028	-0.2250484
H	4.0951797	0.0661462	-0.8143834
H	1.5561727	-0.6494788	0.7583336
O	-0.7219643	0.1436102	1.1043706
O	-1.8073183	-2.2688828	1.5872306
O	-2.9107503	-2.4852958	-0.9406224
O	-2.2109163	0.1971402	-1.2622684
C	3.8162847	-1.9821128	0.0077876
C	1.8164767	1.3774602	-0.0775254
H	1.8495507	1.9801002	0.8457136
H	2.5133967	1.8415392	-0.7909584
C	0.3828857	1.4163502	-0.6444164
H	3.9835337	-2.5025748	-0.9461574
H	4.7505137	-2.0499368	0.5852036
H	3.0256377	-2.5151138	0.5482106
H	0.2072487	2.3819952	-1.1402954
H	0.2432557	0.6060272	-1.3684754
C	-0.6373813	1.2518932	0.4696866
C	-2.3321963	1.2585182	-0.5572844
H	-0.8049413	2.1813662	1.0602656
C	-3.3436803	1.2764352	0.5733166
H	-2.2037923	2.2327792	-1.0764084
H	-4.3548773	1.2974192	0.1406546
H	-3.2388573	0.3661462	1.1761826
H	-3.2147033	2.1596502	1.2131656
O	-0.0663983	-1.8450338	-0.8494284
H	-1.3731453	-1.6340868	2.1708036
H	-3.1861063	-1.8832098	-1.6431154
Mn	-1.5098133	-1.6371638	-0.1130504

E = -794.380772433, H = -794.130390
G = -794.185238

3.39s_H

C	-1.9273476	0.2615505	-0.9225458

C	-2.7620476	-0.6512565	-0.4256168
H	-3.6361046	-0.3116325	0.1397342
H	-1.0303516	-0.0798595	-1.4475498
O	1.0709524	1.1572815	-0.0274498
O	2.5275394	-0.4026025	1.8711072
C	-2.5528936	-2.1288415	-0.5267268
C	-2.0847086	1.7354615	-0.6843918
H	-1.9830746	2.3090095	-1.6180498
H	-3.0792226	1.9482945	-0.2748918
C	-1.0406306	2.2436635	0.3514782
H	-2.4089676	-2.5439885	0.4807982
H	-3.4245806	-2.6266515	-0.9722818
H	-1.6562926	-2.3481395	-1.1151858
H	-1.2155456	3.3079745	0.5571982
H	-1.1144456	1.6436785	1.2679812
C	0.3133814	2.0916225	-0.2432238
C	3.6087784	-0.4534035	1.3039812
H	0.6414914	2.8537775	-0.9748098
C	3.8013344	-0.6403525	-0.1592238
H	4.5100604	-0.3503925	1.9346752
H	4.4790784	-1.4908695	-0.3143228
H	2.8425754	-0.8043945	-0.6634878
H	4.3171824	0.2483975	-0.5509228
Mn	0.6628024	-0.4552575	1.1856822
O	-0.5008546	-0.4623885	2.2268452
O	0.7256044	-1.5649075	-0.3023308
H	0.9162884	-2.4857735	-0.0964688

E = -718.410476401, H = -718.171463
G = -718.222044

3.39q_H

C	2.0245135	-0.0024551	0.5016623
C	2.3973455	-1.0646091	-0.2216147
H	2.9720415	-0.8958601	-1.1373247
H	1.4187485	-0.1556141	1.4009373
O	-0.8107505	1.3564819	0.2399773
O	-2.7328365	-0.2083761	-1.3640137
C	2.0636115	-2.4876521	0.1017753
C	2.3816895	1.4085849	0.1142953
H	2.6243465	2.0021499	1.0067983
H	3.2727525	1.4004479	-0.5238307
C	1.2598255	2.1149569	-0.6992827
H	1.4845535	-2.9289361	-0.7220297
H	2.9809365	-3.0819721	0.2084633
H	1.4809095	-2.5515361	1.0269533
H	1.5948905	3.1190439	-0.9859677
H	1.0348355	1.5021159	-1.5831547
C	0.0381775	2.2276009	0.1467223
C	-3.6918175	0.0708999	-0.6660597
H	-0.0833445	3.1401809	0.7643683
C	-3.7010735	0.0555989	0.8227273
H	-4.6270685	0.3742719	-1.1783967
H	-4.6538065	-0.3598581	1.1734753
H	-2.8423695	-0.5053271	1.2151413
H	-3.6634755	1.1036769	1.1575573
Mn	-0.6656265	-0.7224441	-0.6638777
O	0.4477925	-0.6245081	-2.2347497
O	-1.1005805	-1.6824501	0.9644603
H	-0.9042205	-2.6044111	1.1349873

E = -718.532999987, H = -718.296774
G = -718.351752

3.40s

C	1.7372761	0.9576780	0.3310602
C	2.3579731	0.0036290	-0.4836568
H	2.6673041	0.3623930	-1.4685878
H	1.8124271	0.8539870	1.4116522
O	-0.2629869	0.1437270	0.6466392
O	1.1323441	-1.0934570	-1.1928328
O	-0.6683429	-2.7017920	0.3063902
O	-1.7573879	-0.5713740	-1.3074988
C	3.2760401	-1.0139530	0.1521042
H	2.8015291	-1.4142150	1.0578192
H	3.4419351	-1.8503600	-0.5359138
H	4.2479231	-0.5747270	0.4240982
C	-1.0544699	1.1833530	0.1113572
C	-2.2554549	0.5100600	-0.5721348
H	-1.3800689	1.8536210	0.9312382
C	-3.2915879	0.0532750	0.4544092
H	-2.7315159	1.2334900	-1.2665118
H	-4.0902719	-0.4998660	-0.0552868
H	-2.8093669	-0.6199200	1.1755812
H	-3.7318879	0.9094610	0.9882322
Mn	-0.3278509	-1.3513410	-0.4354168
H	-0.4363919	1.7454500	-0.6042028
H	1.3228331	1.8808810	-0.0685378
E = -640.45555629			

3.40s_{H2O}

C	2.0440357	0.9450929	0.2475441
C	2.5069147	-0.1364491	-0.4820039
H	2.7699627	0.0432419	-1.5257339
H	2.1301717	0.9178639	1.3320611
O	-0.0103493	0.5293459	0.6327211
O	-1.7598113	-0.0077261	-1.1198419
C	3.1532147	-1.3121341	0.2005741
H	2.6043177	-1.5424021	1.1225971
H	3.1067107	-2.1975781	-0.4435389
H	4.2067537	-1.1106601	0.4479671
C	-0.6007753	1.6706429	0.0677791
C	-1.9597593	1.2218749	-0.4850199
H	-0.7335053	2.4471659	0.8477251
C	-2.9908503	1.0827789	0.6341191
H	-2.3199923	1.9630319	-1.2262639
H	-3.9224693	0.6708149	0.2271711
H	-2.5986293	0.3886449	1.3893741
H	-3.2022963	2.0547789	1.1044381
Mn	-0.4493393	-1.0347881	-0.3517299
O	-0.5316063	-1.8974761	1.2118641
H	-0.9257113	-2.7368261	0.9336141
O	-1.3412213	-2.5663971	-1.0664939
H	-2.0077273	-2.2014411	-1.6567399
O	0.9436107	-1.1494681	-1.0929869
H	0.0711027	2.0604809	-0.7223289
H	1.8172477	1.8975869	-0.2268669
E = -716.89765546			

3.40s_{Na}

C	0.9378050	1.7423313	0.3106948
C	1.9876660	1.2476763	-0.4504602
H	2.0776520	1.6108023	-1.4732603
H	1.0312760	1.7163183	1.3951057

O	-0.4000630	0.0984063	0.5960737
O	-1.3973720	-1.2935907	-1.2581493
C	3.2579710	0.7872293	0.2155558
H	3.0216200	0.2102143	1.1227627
H	3.8615750	0.1764413	-0.4733012
H	3.8921010	1.6304423	0.5207308
C	-1.6075680	0.6423673	0.0769378
C	-2.3616430	-0.5356117	-0.5597992
H	-2.1765130	1.0881013	0.9100397
C	-3.0779200	-1.3808307	0.4863928
H	-3.0941240	-0.1537887	-1.2921433
H	-3.5215450	-2.2605537	0.0069368
H	-2.3587360	-1.7223737	1.2426697
H	-3.8733120	-0.8061447	0.9797837
Mn	0.1907930	-1.2760087	-0.4267242
O	1.4328470	-0.4987447	-1.1857733
O	0.6543680	-2.6035127	0.3616508
Na	2.7030100	-2.1984817	-0.3359292
H	-1.3303280	1.4187733	-0.6543182
H	0.1504400	2.3605373	-0.1154762

E = -802.66836333

3.40s_H

C	1.8542735	1.0539265	0.3843376
C	2.5104075	0.1882745	-0.4583804
H	2.6861885	0.5154025	-1.4847014
H	1.8785195	0.8532175	1.4542876
O	-0.2961945	0.1794875	0.6587566
O	-1.7433165	-0.3984655	-1.2935484
C	3.3487325	-0.9459145	0.0549826
H	2.9515315	-1.3116095	1.0095506
H	3.3589675	-1.7754965	-0.6600784
H	4.3855385	-0.6174615	0.2110386
C	-1.0010485	1.3040515	0.1477186
C	-2.2303195	0.7291905	-0.5787574
H	-1.2914875	1.9300915	1.0065786
C	-3.3307585	0.3178155	0.3861236
H	-2.6142915	1.4520945	-1.3154344
H	-4.1308155	-0.1947905	-0.1590314
H	-2.9226655	-0.3655235	1.1416336
H	-3.7526115	1.1989195	0.8861716
Mn	-0.3789135	-1.1584435	-0.5089194
O	1.0066135	-1.0097095	-1.2263544
O	-0.6902845	-2.4708645	0.6262526
H	-0.6636245	-3.3390415	0.1993676
H	-0.3475375	1.8756675	-0.5276914
H	1.4130965	1.9891805	0.0460966

E = -640.93674052

3.40s_{H3O}

C	2.1145170	0.9255916	0.1496213
C	2.6316710	-0.2701184	-0.3012597
H	2.9975750	-0.3295544	-1.3253037
H	2.0782580	1.0768456	1.2285733
O	0.0720490	0.5011016	0.4725113
O	-1.8992710	0.1748716	-0.9840117
C	2.8014960	-1.4377654	0.6111293
H	1.8669700	-1.6024174	1.1684353
H	3.0527910	-2.3473614	0.0581193
H	3.6010500	-1.2439724	1.3411763
C	-0.4121620	1.7333006	-0.0101037

C	-1.8850480	1.4436446	-0.3789067
H	-0.3448340	2.4872026	0.7910133
C	-2.7890010	1.4626916	0.8451493
H	-2.2240220	2.1846836	-1.1206387
H	-3.8023560	1.1640026	0.5560503
H	-2.4105540	0.7527686	1.5915183
H	-2.8275800	2.4671096	1.2858283
Mn	-0.6443800	-0.9406944	-0.4425877
O	-0.6788030	-1.7798924	1.0840443
H	-1.1942350	-2.5792144	0.8883323
O	-1.5966710	-2.3832174	-1.1194447
H	-2.2250640	-2.0811534	-1.7838787
O	0.7621240	-1.1596254	-1.4185697
H	0.7902880	-2.0419604	-1.8157777
H	0.2019700	2.0326356	-0.8747697
H	1.9632220	1.7904966	-0.4962497

E = -717.33851467

3.40s • TMAI

C	-2.6363589	2.0738351	0.4724265
C	-1.6376929	2.4398491	-0.4208255
H	-1.9611249	2.7776341	-1.4053195
H	-2.4156119	2.1084261	1.5379795
O	-2.4316889	-0.0546179	0.7087395
O	-0.9247859	0.8425961	-1.2246395
O	0.1192401	-1.3256779	0.1969195
O	-2.3751779	-1.6826169	-1.2312735
C	-3.5089339	-1.8377229	-0.4099305
C	-3.3152639	-2.9773469	0.5847955
H	-4.3798529	-2.0562269	-1.0543045
H	-3.0686549	-3.8978709	0.0432755
H	-2.4833559	-2.7355709	1.2591375
H	-4.2256099	-3.1449749	1.1768415
Mn	-1.1532879	-0.5910029	-0.4757445
C	-0.3327099	2.9992921	0.0853225
H	0.4093991	3.0141171	-0.7217465
H	-0.4465719	4.0244101	0.4643265
H	0.0465291	2.3667611	0.9011235
C	-3.7197209	-0.4929399	0.3014605
H	-4.3546349	-0.6024429	1.1981555
C	2.6072461	-0.1950779	1.3102595
H	1.5563711	-0.5157819	1.2886345
H	3.2241081	-0.8882229	1.8906945
H	2.7158831	0.8226601	1.6975255
C	2.2978871	0.7665551	-0.9096015
H	2.4570021	1.7639061	-0.4894495
H	2.6530251	0.7298151	-1.9436835
H	1.2393161	0.4896291	-0.8530635
C	2.9272641	-1.5811089	-0.6762285
H	3.2984981	-1.5676959	-1.7054245
H	3.5154501	-2.2770169	-0.0702305
H	1.8557961	-1.8174419	-0.6316735
C	4.5342221	0.1757981	-0.1415285
H	4.6457301	1.1740381	0.2917375
H	5.1108451	-0.5514059	0.4377345
H	4.8720641	0.1798081	-1.1819895
N	3.1005681	-0.2075399	-0.1042845
H	-4.1386379	0.2793041	-0.3670935
H	-3.6767699	1.9718681	0.1709455

E = -854.63105015

3.40s_{aa}

C	2.7087188	-1.0651023	-0.5641472
C	1.8471568	-2.1364073	-0.6505072
H	3.2830138	-0.9256293	0.3496358
O	1.5203138	0.5722127	0.3345858
O	-0.6459702	1.4564837	-0.5711572
C	1.7308868	-3.1419503	0.4618048
H	2.5071888	-3.9182173	0.3875268
H	1.8274268	-2.6314193	1.4285298
H	0.7482758	-3.6261483	0.4342388
C	1.7037348	1.5329927	-0.6723202
C	0.4134358	2.3654027	-0.6907312
H	2.5781308	2.1657387	-0.4221082
C	0.3826798	3.3726867	0.4553078
H	1.1667808	4.1343007	0.3352378
H	-0.5958332	3.8668807	0.4830068
H	0.5346508	2.8363787	1.4012128
Mn	-0.2476932	-0.0377503	0.3415728
O	-0.1677962	-0.0744783	2.1226378
H	-1.0706372	-0.2994453	2.3846298
O	-2.1987612	-0.3338253	0.6002498
O	0.0098818	-1.4013013	-0.4000122
H	0.3211318	2.8965607	-1.6571492
H	1.5267848	-2.4480243	-1.6455002
C	-3.0193612	-0.5900543	-0.3613852
O	-2.7401322	-0.8152973	-1.5353832
C	-4.4816832	-0.5906313	0.0895648
H	-5.1245682	-0.9570673	-0.7164212
H	-4.7661932	0.4363277	0.3536428
H	-4.5964822	-1.2088803	0.9881408
H	1.8859638	1.0187017	-1.6365502
H	2.9589538	-0.4530393	-1.4281532

E = -869.54344008

3.40s_H • H₂O

C	-1.8964643	-1.5444816	-0.0658234
C	-2.5972073	-0.4603336	-0.5250134
H	-2.7379643	-0.3623206	-1.6029854
H	-1.9385553	-1.7785626	0.9965756
O	0.1703337	-0.7327646	0.6229356
O	1.7154347	0.5794884	-0.8347654
C	-3.4765423	0.3665804	0.3659746
H	-3.0960123	0.3515204	1.3943136
H	-3.5074643	1.4065364	0.0226036
H	-4.5042743	-0.0224846	0.3659566
C	0.9527617	-1.5591566	-0.2153474
C	2.1981617	-0.7279146	-0.5745374
H	1.2353397	-2.4592156	0.3559876
C	3.2097367	-0.7014476	0.5605356
H	2.6638107	-1.1116316	-1.4965964
H	4.0284507	-0.0146286	0.3172456
H	2.7167467	-0.3590406	1.4794156
H	3.6288297	-1.7018866	0.7277226
Mn	0.2264787	0.9765404	0.0536926
O	0.2735827	1.5406984	1.7262076
H	0.3547737	2.5038224	1.7250616
O	0.7820047	2.9543224	-0.5621964
H	1.5937037	2.6838194	-1.0212204
O	-1.1259503	1.0584294	-0.7333554
H	0.1563897	3.2153094	-1.2493024
H	0.3710797	-1.8521196	-1.1042914

H	-1.3971853	-2.2490796	-0.7287934
E = -717.38271816			

3.41s

O	1.4273874	0.0869636	0.7052133
O	2.8227184	-1.1502204	-1.1342587
O	1.0220314	-2.7585554	0.3649643
O	-0.0670136	-0.6281374	-1.2489247
C	0.6359044	1.1265896	0.1699313
C	-0.5650806	0.4532966	-0.5135607
H	0.3103054	1.7968576	0.9898123
C	-1.6012136	-0.0034884	0.5129833
H	-1.0411416	1.1767266	-1.2079377
H	-2.3998976	-0.5566294	0.0032873
H	-1.1189926	-0.6766834	1.2341553
H	-2.0415136	0.8526976	1.0468063
Mn	1.3625234	-1.4081044	-0.3768427
H	1.2539824	1.6886866	-0.5456287
E = -522.64124597			

3.41s_{H2O}

O	1.4213760	0.3825555	0.6722858
O	-0.3280860	-0.1545165	-1.0802772
C	0.8309500	1.5238525	0.1073438
C	-0.5280340	1.0750845	-0.4454552
H	0.6982200	2.3003755	0.8872898
C	-1.5591250	0.9359885	0.6736838
H	-0.8882670	1.8162415	-1.1866992
H	-2.4907440	0.5240245	0.2667358
H	-1.1669040	0.2418545	1.4289388
H	-1.7705710	1.9079885	1.1440028
Mn	0.9823860	-1.1815785	-0.3121652
O	0.9001190	-2.0442665	1.2514288
H	0.5060140	-2.8836165	0.9731788
O	0.0905040	-2.7131875	-1.0269292
H	-0.5760020	-2.3482315	-1.6171752
O	2.3753360	-1.2962585	-1.0534222
H	1.5028280	1.9136905	-0.6827642
E = -599.07040890			

3.41s_{Na}

O	0.9478107	0.8638725	0.6662305
O	-0.0494983	-0.5281245	-1.1879925
C	-0.2596943	1.4078335	0.1470945
C	-1.0137693	0.2298545	-0.4896425
H	-0.8286393	1.8535675	0.9801965
C	-1.7300463	-0.6153645	0.5565495
H	-1.7462503	0.6116775	-1.2219865
H	-2.1736713	-1.4950875	0.0770935
H	-1.0108623	-0.9569075	1.3128265
H	-2.5254383	-0.0406785	1.0499405
Mn	1.5386667	-0.5105425	-0.3565675
O	2.7807207	0.2667215	-1.1156165
O	2.0022417	-1.8380465	0.4318075
Na	4.0508837	-1.4330155	-0.2657725
H	0.0175457	2.1842395	-0.5841615
E = -684.84455681			

3.41s_H

O	1.3296225	0.1761222	0.6958989
O	-0.1174995	-0.4018308	-1.2564061

C	0.6247685	1.3006862	0.1848609
C	-0.6045025	0.7258252	-0.5416151
H	0.3343295	1.9267262	1.0437209
C	-1.7049415	0.3144502	0.4232659
H	-0.9884745	1.4487292	-1.2782921
H	-2.5049985	-0.1981558	-0.1218891
H	-1.2968485	-0.3688888	1.1787759
H	-2.1267945	1.1955542	0.9233139
Mn	1.2469035	-1.1618088	-0.4717771
O	2.6324305	-1.0130748	-1.1892121
O	0.9355325	-2.4742298	0.6633949
H	0.9621925	-3.3424068	0.2365099
H	1.2782795	1.8723022	-0.4905491

E = -523.09676854

3.41s_{H3O}

O	1.3558018	0.3100874	0.6077469
O	-0.6155182	-0.0161426	-0.8487761
C	0.8715908	1.5422864	0.1251319
C	-0.6012952	1.2526304	-0.2436711
H	0.9389188	2.2961884	0.9262489
C	-1.5052482	1.2716774	0.9803849
H	-0.9402692	1.9936694	-0.9854031
H	-2.5186032	0.9729884	0.6912859
H	-1.1268012	0.5617544	1.7267539
H	-1.5438272	2.2760954	1.4210639
Mn	0.6393728	-1.1317086	-0.3073521
O	0.6049498	-1.9709066	1.2192799
H	0.0895178	-2.7702286	1.0235679
O	-0.3129182	-2.5742316	-0.9842091
H	-0.9413112	-2.2721676	-1.6486431
O	2.0458768	-1.3506396	-1.2833341
H	2.0740408	-2.2329746	-1.6805421
H	1.4857228	1.8416214	-0.7395341

E = -599.49728923

3.41s • TMAI

O	-2.8397828	0.7123561	0.7437147
O	-1.3328798	1.6095701	-1.1896643
O	-0.2888538	-0.5587039	0.2318947
O	-2.7832718	-0.9156429	-1.1962983
C	-3.9170278	-1.0707489	-0.3749553
C	-3.7233578	-2.2103729	0.6197707
H	-4.7879468	-1.2892529	-1.0193293
H	-3.4767488	-3.1308969	0.0782507
H	-2.8914498	-1.9685969	1.2941127
H	-4.6337038	-2.3780009	1.2118167
Mn	-1.5613818	0.1759711	-0.4407693
C	-4.1278148	0.2740341	0.3364357
H	-4.7627288	0.1645311	1.2331307
C	2.1991522	0.5718961	1.3452347
H	1.1482772	0.2511921	1.3236097
H	2.8160142	-0.1212489	1.9256697
H	2.3077892	1.5896341	1.7325007
C	1.8897932	1.5335291	-0.8746263
H	2.0489082	2.5308801	-0.4544743
H	2.2449312	1.4967891	-1.9087083
H	0.8312222	1.2566031	-0.8180883
C	2.5191702	-0.8141349	-0.6412533
H	2.8904042	-0.8007219	-1.6704493

H	3.1073562	-1.5100429	-0.0352553
H	1.4477022	-1.0504679	-0.5966983
C	4.1261282	0.9427721	-0.1065533
H	4.2376362	1.9410121	0.3267127
H	4.7027512	0.2155681	0.4727097
H	4.4639702	0.9467821	-1.1470143
N	2.6924742	0.5594341	-0.0693093
H	-4.5467318	1.0462781	-0.3321183

E = -736.81440419

3.41s_{aa}

O	2.3027542	-0.4676040	0.6276915
O	0.3386612	0.5438390	-0.5615985
C	2.6767262	0.5203200	-0.2968365
C	1.4374582	1.4089270	-0.4776945
H	3.5249552	1.1043280	0.1118005
C	1.2671572	2.3740190	0.6921635
H	2.0886892	3.1042000	0.7269165
H	0.3156732	2.9095320	0.5902495
H	1.2498282	1.7973120	1.6262765
Mn	0.5333132	-0.9988690	0.3365105
O	0.3339712	-1.1041680	2.1054365
H	-0.6064888	-1.2985360	2.2155675
O	-1.4440528	-1.2178900	0.2791175
O	0.8511462	-2.3444290	-0.4144985
H	1.5166792	1.9786110	-1.4231025
C	-2.1143358	-1.4023640	-0.8073765
O	-1.6647748	-1.5966320	-1.9330445
C	-3.6279338	-1.3549500	-0.5871155
H	-4.1511598	-1.6629750	-1.4973595
H	-3.9108978	-0.3267860	-0.3260815
H	-3.9043478	-1.9999710	0.2557335
H	2.9869782	0.0340870	-1.2427565

E = -751.70964394

3.41s_H • H₂O

O	0.0707649	-1.6163633	0.4845468
O	-0.1066991	0.5330977	-0.7734532
C	1.1786829	-1.3956503	-0.3649472
C	1.2384909	0.1272997	-0.5841482
H	2.0851399	-1.7516743	0.1527048
C	1.8452249	0.8491377	0.6088318
H	1.8001789	0.3618507	-1.5027082
H	1.7713549	1.9335607	0.4682238
H	1.3005119	0.5686207	1.5194468
H	2.9032329	0.5815277	0.7249078
Mn	-1.2864111	-0.5123793	0.0507168
O	-1.6706191	-0.2991633	1.7608988
H	-2.3979251	0.3327787	1.8375478
O	-2.5649571	1.1550207	-0.3789902
H	-1.8776891	1.6907897	-0.8071772
O	-2.1736261	-1.4768113	-0.8083142
H	-3.1631151	0.8703757	-1.0809932
H	1.0474589	-1.9520183	-1.3070932

E = -599.54145846

3.42s

O	1.4394894	0.1120375	0.7384811
O	2.6916564	-1.3409585	-1.2671399
O	0.9423254	-2.6074325	0.4315031

O	-0.0004286	-0.5962655	-1.2413349
C	0.6384884	1.1340755	0.2089771
C	-0.5384786	0.4724495	-0.5004069
H	0.3057004	1.8059155	1.0232031
C	-1.5831976	-0.0376585	0.4925961
H	-1.0164546	1.1835765	-1.2022429
H	-2.3448616	-0.6218275	-0.0392459
H	-1.0898836	-0.6905325	1.2247691
H	-2.0718666	0.7972935	1.0177901
Mn	1.4177244	-1.3464855	-0.3621539
H	1.2097864	1.7358125	-0.5247959

E = -522.65659297

3.42s_{H2O}

O	1.2185994	0.2093164	0.8470336
O	-0.3720956	-0.1897436	-1.0231354
C	0.8093664	1.3889554	0.2241626
C	-0.5254456	1.0792494	-0.4483224
H	0.7196164	2.1979974	0.9735076
C	-1.6784366	1.0645794	0.5545256
H	-0.7384646	1.8176854	-1.2457764
H	-2.5883506	0.6857294	0.0717286
H	-1.4144156	0.3966774	1.3850786
H	-1.8762586	2.0732314	0.9476856
Mn	1.0275294	-1.1927796	-0.3266304
O	1.4190634	-2.2069706	1.1103266
H	1.0289344	-3.0606756	0.8825006
O	-0.0441816	-2.6137616	-0.7948784
H	-0.7340296	-2.2121376	-1.3352474
O	2.2097454	-1.1456446	-1.2751834
H	1.5388234	1.7082914	-0.5473764

E = -599.08502138

3.42s_{Na}

O	0.9392489	0.9380091	0.7081842
O	0.0413849	-0.4766499	-1.1416478
C	-0.2816671	1.4303501	0.1839122
C	-0.9838971	0.2507681	-0.4748228
H	-0.8685241	1.8651121	1.0071632
C	-1.6905521	-0.6456729	0.5334012
H	-1.6949731	0.5922911	-1.2433358
H	-2.0473391	-1.5560829	0.0388692
H	-0.9911851	-0.9302839	1.3304472
H	-2.5475811	-0.1243499	0.9797462
Mn	1.5885819	-0.3723359	-0.2893548
O	2.7789749	0.1304461	-1.2141528
O	1.8933919	-1.6867359	0.5513442
Na	3.9382879	-1.6300419	-0.4085798
H	-0.0741511	2.2151771	-0.5611738

E = -684.85734151

3.42s_H

O	1.3217087	0.1829245	0.7285727
O	-0.0990963	-0.4177445	-1.1976683
C	0.6172077	1.3051395	0.2117417
C	-0.5929523	0.7421185	-0.5193213
H	0.3502407	1.9567625	1.0548427
C	-1.7187383	0.3420115	0.4214237
H	-0.9545553	1.4365145	-1.2910993
H	-2.4963443	-0.1980755	-0.1288843
H	-1.3264233	-0.3103175	1.2120167

H	-2.1643423	1.2336655	0.8803457
Mn	1.2663007	-1.1447835	-0.4033613
O	2.5108757	-1.0929265	-1.2658973
O	0.7527257	-2.5470755	0.4855957
H	1.2652657	-3.3451515	0.2948387
H	1.2681277	1.8569385	-0.4831463

E = -523.10460599

3.42s_{H3O}

O	1.2384174	0.2218363	0.7323674
O	-0.5864906	-0.0656337	-0.7953326
C	0.8700184	1.4570503	0.1780194
C	-0.5855496	1.2399443	-0.2404866
H	0.9829384	2.2483543	0.9310224
C	-1.5579786	1.3191133	0.9243584
H	-0.8735716	1.9328653	-1.0446306
H	-2.5600536	1.0222193	0.5965644
H	-1.2298506	0.6463583	1.7263384
H	-1.6033806	2.3446223	1.3115234
Mn	0.7045224	-1.1350857	-0.2521946
O	0.7686174	-2.0573327	1.2110604
H	0.2783554	-2.8736437	1.0199984
O	-0.3242136	-2.4776977	-0.8775286
H	-0.9554126	-2.1370537	-1.5241016
O	2.0319284	-1.2924857	-1.3142436
H	1.9121884	-2.0723257	-1.8775056
H	1.4895144	1.6788943	-0.7052286

E = -599.50585065

3.42s • TMAI

O	1.6519510	0.8642484	-0.4814976
O	0.6891760	0.8515164	2.0708404
O	0.5734760	-1.4269766	0.5741964
O	3.0906540	-0.3370796	1.2077504
C	3.8061700	0.0482994	0.0469674
C	3.9301080	-1.1329236	-0.9087546
H	4.8082620	0.3832934	0.3628084
H	4.3750190	-1.9879316	-0.3870526
H	2.9310160	-1.4210786	-1.2615206
H	4.5587310	-0.8746896	-1.7718686
Mn	1.3290070	-0.1048626	1.0126144
C	3.0219340	1.2048334	-0.5608356
H	3.2903000	1.3830904	-1.6148186
C	-2.3724600	-1.2780406	-0.6238176
H	-1.3776420	-1.7039066	-0.4522636
H	-3.1559700	-1.9318156	-0.2278876
H	-2.5394770	-1.0852126	-1.6880416
C	-1.4079340	0.9526224	-0.4953756
H	-1.8184270	1.3312124	-1.4363796
H	-1.2104400	1.7676874	0.2059694
H	-0.4822690	0.4069114	-0.6823296
C	-2.1500110	-0.2183826	1.5578564
H	-2.1052960	0.7465834	2.0681244
H	-2.9657250	-0.8336936	1.9501424
H	-1.1881040	-0.7292586	1.6435534
C	-3.7772910	0.6336094	-0.0331726
H	-4.0056550	0.7541144	-1.0959526
H	-4.5135450	-0.0226866	0.4394754
H	-3.7698740	1.6089114	0.4623824
N	-2.4284230	0.0252544	0.1038584
H	3.2127390	2.1263524	0.0150304

E = -736.82759995

3.42s_{aa}

O	2.1255306	0.3877476	1.0063996
O	0.2292246	0.4566726	-0.5633484
C	2.3687016	1.2411686	-0.0707484
C	0.9924586	1.6396266	-0.5953094
H	2.9554026	2.1145256	0.2677076
C	0.3313286	2.7030866	0.2768126
H	0.8533376	3.6668916	0.1876296
H	-0.7146884	2.8355406	-0.0255124
H	0.3596026	2.3690136	1.3221716
Mn	0.8596986	-0.8401754	0.5079986
O	0.6067166	-1.0449324	2.2636196
H	-0.2152114	-1.5504784	2.3159606
O	-0.9536924	-1.5722444	0.4098256
O	1.6496516	-1.9383934	-0.1604704
H	1.0492236	1.9902456	-1.6417054
C	-1.4870594	-1.9724934	-0.7049944
O	-0.9172174	-2.1531304	-1.7709024
C	-2.9861914	-2.2286424	-0.5703834
H	-3.3719794	-2.6792844	-1.4892894
H	-3.4888314	-1.2714224	-0.3818404
H	-3.1778174	-2.8801814	0.2906766
H	2.9318106	0.7268586	-0.8742984

E = -751.71940698

3.42s_H • H₂O

O	1.3099676	0.4327746	0.9040616
O	-0.3211894	-0.0812304	-0.8510524
C	0.9006046	1.5868166	0.2049936
C	-0.4793684	1.2473826	-0.3577424
H	0.8793946	2.4338966	0.9055736
C	-1.5700814	1.2841006	0.6998356
H	-0.7368174	1.8921276	-1.2111414
H	-2.5068834	0.8885146	0.2908416
H	-1.2659164	0.6728166	1.5586916
H	-1.7429784	2.3149136	1.0336716
Mn	0.9779576	-0.9978964	-0.0736294
O	0.7357936	-1.8879624	1.4269096
H	0.4555196	-2.7858574	1.2002046
O	-0.1033304	-2.5942364	-1.0306954
H	-0.8004364	-2.0436784	-1.4228224
O	2.2269396	-1.2694904	-0.8949274
H	0.4427496	-2.9054874	-1.7639544
H	1.5980746	1.8124966	-0.6188174

E = -599.54724406

3.47s

C	1.6407033	0.6077624	0.0704553
C	2.2087783	-0.7655926	-0.2878187
H	3.0674583	-0.5993356	-0.9599507
H	2.2868723	1.1260854	0.7952873
O	0.3535373	0.3685774	0.7030443
O	1.2343873	-1.4999466	-1.0025357
O	-1.5662387	0.0029624	-1.0274077
C	2.6615903	-1.5365346	0.9470023
C	1.3107293	1.4975934	-1.1182507
H	0.9605603	0.8707664	-1.9461717
H	2.1820443	2.0722664	-1.4476957
C	0.1833463	2.3804734	-0.5783287

H	3.0341383	-2.5203346	0.6428353
H	3.4633963	-0.9995726	1.4704543
H	1.8133583	-1.6817206	1.6278533
H	0.5934503	3.2707404	-0.0884257
H	-0.5045747	2.7114154	-1.3629857
C	-0.5312347	1.4942254	0.4610963
C	-1.8951197	0.9570844	-0.0035687
H	-0.6692267	2.0203784	1.4142673
C	-2.7242537	0.3485314	1.1132853
H	-2.4436517	1.7825854	-0.4775327
H	-3.6294617	-0.1133106	0.7011563
H	-2.1539497	-0.4135096	1.6570023
H	-3.0289187	1.1414014	1.8070943
Mn	-0.3959917	-1.3511266	-0.3381327
O	-0.7423427	-2.2269556	1.1504373
H	-1.2380837	-3.0137036	0.8807923
O	-1.7668687	-2.3387396	-1.3395627
H	-2.1665387	-0.7947466	-1.3128027
H	-1.5378957	-2.7977196	-2.1508937

E = -794.908454423, H = -794.639360
G = -794.682877

3.47q

C	1.6407033	0.6077624	0.0704553
C	2.2087783	-0.7655926	-0.2878187
H	3.0674583	-0.5993356	-0.9599507
H	2.2868723	1.1260854	0.7952873
O	0.3535373	0.3685774	0.7030443
O	1.2343873	-1.4999466	-1.0025357
O	-1.5662387	0.0029624	-1.0274077
C	2.6615903	-1.5365346	0.9470023
C	1.3107293	1.4975934	-1.1182507
H	0.9605603	0.8707664	-1.9461717
H	2.1820443	2.0722664	-1.4476957
C	0.1833463	2.3804734	-0.5783287
H	3.0341383	-2.5203346	0.6428353
H	3.4633963	-0.9995726	1.4704543
H	1.8133583	-1.6817206	1.6278533
H	0.5934503	3.2707404	-0.0884257
H	-0.5045747	2.7114154	-1.3629857
C	-0.5312347	1.4942254	0.4610963
C	-1.8951197	0.9570844	-0.0035687
H	-0.6692267	2.0203784	1.4142673
C	-2.7242537	0.3485314	1.1132853
H	-2.4436517	1.7825854	-0.4775327
H	-3.6294617	-0.1133106	0.7011563
H	-2.1539497	-0.4135096	1.6570023
H	-3.0289187	1.1414014	1.8070943
Mn	-0.3959917	-1.3511266	-0.3381327
O	-0.7423427	-2.2269556	1.1504373
H	-1.2380837	-3.0137036	0.8807923
O	-1.7668687	-2.3387396	-1.3395627
H	-2.1665387	-0.7947466	-1.3128027
H	-1.5378957	-2.7977196	-2.1508937

E = -795.022968607, H = -794.757310
G = -794.803121

3.48s

C	0.9831042	1.2837685	0.3074703
C	2.1475122	0.3640555	-0.0537277
H	2.9190062	0.9640905	-0.5561057

H	1.2506972	1.8356265	1.2188853
O	-0.1573318	0.4567135	0.5985453
O	-1.6903458	-1.0621675	-0.9402307
C	2.7286172	-0.3803275	1.1326323
C	0.5512092	2.2466995	-0.8209057
H	0.5215842	3.2735275	-0.4405867
H	1.2513712	2.2174195	-1.6622457
C	-0.8488008	1.7642145	-1.2144007
H	1.9430312	-0.9351485	1.6578223
H	3.5022842	-1.0843745	0.8002263
H	3.1978502	0.3410865	1.8126323
H	-1.5112528	2.5788335	-1.5232937
H	-0.7972378	1.0208905	-2.0180947
C	-1.3458128	1.0742685	0.0486093
C	-2.3364338	-0.0616695	-0.1923657
H	-1.7325278	1.7982175	0.7827643
C	-2.8912408	-0.6201875	1.1138603
H	-3.1620908	0.3462165	-0.8011557
H	-3.5742048	-1.4471455	0.8912283
H	-2.0691488	-1.0007415	1.7328823
H	-3.4406748	0.1532925	1.6669583
Mn	-0.0421038	-1.5213715	-0.4278297
O	0.1484542	-2.1895755	1.2379443
H	0.1491262	-3.1521215	1.1748733
O	0.5310532	-2.8603925	-1.5299017
H	-0.0215558	-3.6401915	-1.6325507
O	1.5883572	-0.5388315	-1.0350827
H	2.2075062	-1.2246735	-1.3288567

E = -794.919377362, H = -794.647346
G = -794.693163

3.48q

C	1.2260327	1.0051640	-0.0438739
C	2.2821227	-0.0584890	-0.2973459
H	3.0647827	0.4093620	-0.9134849
H	1.6146377	1.7389030	0.6797151
O	0.0556137	0.3896790	0.5383441
O	-1.9240673	-0.4079940	-0.9803609
C	2.8886987	-0.5956840	0.9893331
C	0.6818207	1.6988920	-1.2824979
H	1.3647207	2.4717480	-1.6499259
H	0.5291617	0.9500200	-2.0683199
C	-0.6605983	2.2515230	-0.7920819
H	2.1114597	-1.0211670	1.6322891
H	3.6231367	-1.3783300	0.7633321
H	3.4059827	0.2151150	1.5159151
H	-0.5554423	3.2825470	-0.4371599
H	-1.4215393	2.2252640	-1.5776539
C	-1.0589763	1.3227720	0.3722041
C	-2.2783923	0.4562140	0.0650391
H	-1.1663733	1.8681440	1.3194261
C	-2.7632693	-0.3026650	1.3032191
H	-3.0870913	1.1252500	-0.2765339
H	-3.5767483	-0.9782400	1.0182891
H	-1.9556293	-0.9023160	1.7544761
H	-3.1272183	0.3888880	2.0741221
Mn	-0.5212473	-1.5026680	-0.3700359
O	0.5306827	-2.5673840	0.7648811
H	0.2361517	-3.4835400	0.7209601
O	-1.1046493	-2.9342500	-1.3200129
H	-1.8871393	-2.6416170	-1.8057199

O	1.6764247	-1.0909700	-1.0864419
H	1.7969527	-1.9341700	-0.6100959

E = -795.037801210, H = -794.766254
G = -794.813437

3.49s

C	1.6407402	-0.5870683	1.0549813
C	2.4016142	-1.0478183	-0.1869597
H	3.4634472	-1.1322733	0.1051183
H	1.8859652	-1.2895823	1.8636383
O	0.2334372	-0.6607003	0.8577433
O	-1.8972068	-0.4673603	-0.8731047
C	1.8927632	-2.3867343	-0.6943327
C	1.9182052	0.8643867	1.4594503
H	1.8229992	0.9639037	2.5467543
H	2.9197892	1.1913217	1.1617573
C	0.8093362	1.6490357	0.7468663
H	1.9913392	-3.1552283	0.0820573
H	0.8356832	-2.2972923	-0.9689947
H	2.4709922	-2.7121633	-1.5694117
H	0.5007892	2.5408627	1.3010083
H	1.1434832	1.9481317	-0.2516797
C	-0.3316488	0.6285777	0.6307573
C	-1.0123068	0.6427677	-0.7324487
H	-1.0961108	0.7853727	1.4127603
C	-1.7683548	1.9388867	-0.9721687
H	-0.2264758	0.5059747	-1.4893277
H	-2.2943528	1.8919807	-1.9320207
H	-2.5122498	2.1053477	-0.1776547
H	-1.0864248	2.7975697	-0.9864017
Mn	-3.4178718	-0.6556133	0.2643243
O	-5.0385408	-0.0173023	0.1589313
H	-5.7634718	-0.2909483	-0.4093427
O	-2.5672848	-1.9397623	0.8161003
O	2.2695412	-0.0334613	-1.1824397
H	2.6029852	-0.3803823	-2.0158717
H	-1.7908098	-1.4004303	-0.0200877

E = -794.810507783, H = -794.543955
G = -794.593360

3.49q

C	-1.0696609	-0.5214939	-0.7819282
C	-1.2965359	-1.0063939	0.6587588
H	-1.2456009	-0.1470289	1.3416508
H	-1.3187519	-1.3325869	-1.4784332
O	0.3164091	-0.2406939	-1.0003232
O	2.2821381	0.1501051	0.8488588
C	-2.6352719	-1.7075789	0.8097848
C	-1.7542779	0.8021001	-1.1160612
H	-1.9129559	0.8646501	-2.1974352
H	-2.7234879	0.9122411	-0.6184332
C	-0.7305139	1.8603511	-0.6570712
H	-3.4638339	-1.0397249	0.5454618
H	-2.6752709	-2.5841889	0.1487998
H	-2.7694479	-2.0406949	1.8440168
H	-0.7293139	2.7355401	-1.3123952
H	-0.9545529	2.2049491	0.3600558
C	0.6236611	1.1263161	-0.6754662
C	1.3651341	1.2192631	0.6697258
H	1.2887411	1.4692641	-1.4782992
C	2.0626241	2.5639731	0.7959678

H	0.6339201	1.1026281	1.4832328
H	2.5435031	2.6481591	1.7755368
H	2.8311951	2.6577111	0.0179178
H	1.3467161	3.3885741	0.6810948
Mn	1.7257631	-1.6912999	-0.1016972
O	1.0715291	-3.4519209	-0.4519542
H	1.5549831	-4.1030839	-0.9615982
O	3.2081881	-1.2376019	-0.9206432
O	-0.2274489	-1.8593919	1.0640348
H	-0.2895799	-2.7390639	0.6323048
H	2.9420011	-0.0030789	0.0745368

E = -795.003600548, H = -794.734472
G = -794.781595

3.50s

C	2.4185952	1.7183661	-1.1898809
C	3.4403482	0.7079661	-0.6607039
O	2.8447772	0.2232481	0.5672351
C	2.2115632	1.3644141	1.2368721
C	1.6932122	2.2297961	0.0776191
C	3.7558352	-0.5118329	-1.5309079
C	1.1716892	0.7908261	2.2239401
C	1.8505572	0.3671561	3.5231171
O	0.4964722	-0.3120339	1.6786631
C	4.8773272	-1.3551339	-0.9525609
O	2.6140902	-1.3794859	-1.6197129
Mn	1.5119522	-1.1342849	0.1919721
O	1.6031812	-2.7891779	0.7740311
C	-4.7365388	-0.7116629	0.2915341
C	-3.5946488	-1.3423919	-0.5294469
O	-2.7190818	-0.2480659	-0.9158089
C	-3.3988118	1.0091981	-0.6953969
C	-4.3078718	0.7437211	0.4959811
C	-2.7198438	-2.3299679	0.2484441
C	-2.3050508	2.0397911	-0.4311979
C	-1.5279588	2.3740511	-1.7038899
O	-1.4492668	1.5349361	0.5656031
C	-1.8886578	-3.2106239	-0.6807139
O	-1.8931928	-1.6099789	1.1326981
Mn	-1.0497518	-0.2195809	0.3892851
O	0.2158492	-0.6302919	-0.8594769
H	2.9185742	2.5144501	-1.7497629
H	1.6965012	1.2246811	-1.8507709
H	4.3805742	1.2101791	-0.3896829
H	3.0162042	1.8751511	1.7830791
H	1.9088692	3.2842701	0.2758741
H	0.6114692	2.1099391	-0.0105729
H	4.0197092	-0.1514869	-2.5356079
H	0.4534982	1.6041511	2.4217801
H	2.6060912	-0.4039239	3.3186111
H	2.3358222	1.2177441	4.0196581
H	1.1002532	-0.0579859	4.1970071
H	1.8989212	-0.9888239	-2.1498539
H	5.7896402	-0.7573239	-0.8448649
H	4.5805562	-1.7435749	0.0293021
H	5.0807222	-2.2036329	-1.6126479
H	1.0711912	-2.8549219	1.5804371
H	-4.8696198	-1.2373559	1.2422841
H	-5.6781288	-0.7679649	-0.2665909
H	-3.9728198	-1.8020759	-1.4524669
H	-3.9779008	1.2543701	-1.5996729

H	-5.1502938	1.4425601	0.5260421
H	-3.7194388	0.8485111	1.4143771
H	-3.3899498	-2.9714819	0.8451441
H	-2.7959988	2.9524531	-0.0511439
H	-2.2009948	2.7384651	-2.4907289
H	-0.7862438	3.1549871	-1.4985859
H	-1.0105708	1.4737881	-2.0628739
H	-1.2298338	-3.8508359	-0.0841609
H	-2.5388068	-3.8445259	-1.2981369
H	-1.2627688	-2.5887449	-1.3327669

E = -1437.03610482, H = -1436.543833

G = -1436.606997

HMnO₂ (singlet)

Mn	-0.7364470	-0.0117635	-0.0021170
O	1.0186970	0.0053745	-0.0032640
H	1.9704750	-0.0012785	0.0068660
O	-2.2527250	0.0076675	-0.0014850

H = -254.746524

G = -254.770164

HMnO₂ (quintet)

Mn	0.6308005	-0.0322600	-0.1345892
O	-1.1978375	-0.1217960	-0.0896162
H	-1.8992485	0.1485350	0.5012638
O	2.4662855	0.0055210	-0.2770583

E = -254.944333600, H = -254.928270

G = -254.953784

H₂O

O	-0.2260083	-0.3197947	0.0000000
H	0.7352557	-0.2798667	0.0000000
H	-0.5092473	0.5996613	0.0000000

E = -76.4161650778, H = -76.391530

G = -76.409194

CH₃CO₂H

C	0.5134454	0.2751442	-0.0001085
O	1.0529294	1.3519913	-0.0000615
C	-0.9671336	0.0280683	-0.0000475
H	-1.2373376	-0.5592058	0.8848935
H	-1.4908786	0.9853852	-0.0000685
H	-1.2374386	-0.5594587	-0.8847995
O	1.2142584	-0.8820978	-0.0000935
H	2.1521554	-0.6398267	0.0002855

E = -229.041345386, H = -228.974649

G = -229.000989

CH₃CO₂Na

O	1.0370626	-1.1122261	-0.0168410
C	0.4375566	0.0046009	-0.0218660
C	-1.0792704	0.0024799	-0.0061990
H	-1.4596864	-0.8516261	-0.5748480
H	-1.4083524	-0.1090591	1.0352290
H	-1.4674574	0.9469489	-0.3974220
O	1.0401996	1.1192529	-0.0167770
Na	2.8999476	-0.0003711	-0.0012760

E = -390.782152904, H = -390.732065

G = -390.761059

(CH₃CO₂)N(CH₃)₄

N	1.3402070	-0.3001530	-0.0054325
C	2.8180310	-0.3162720	-0.1292275
H	3.1073020	-1.1181870	-0.8150915
H	3.1496220	0.6501210	-0.5201555
H	3.2544000	-0.4915080	0.8587205
C	0.7215780	-0.0676470	-1.3502775
H	1.0537200	0.9082380	-1.7153285
H	1.0588930	-0.8698220	-2.0148275
H	-0.3633680	-0.0597540	-1.2145795
C	0.8536500	-1.6101780	0.5297975
H	-0.2398980	-1.5347970	0.5962155
H	1.1660180	-2.3983400	-0.1627615
H	1.3108600	-1.7679850	1.5118575
C	0.9221360	0.7908280	0.9329425
H	1.4041290	0.6024850	1.8978775
H	1.2478820	1.7465290	0.5128945
H	-0.1693380	0.7688700	0.9944715
O	-1.9037130	-0.4709080	0.3463615
C	-2.3747280	0.6460870	-0.0334895
C	-3.8909370	0.8067180	0.0402255
H	-4.1943660	1.7978750	-0.3082945
H	-4.3653230	0.0288270	-0.5704905
H	-4.2191780	0.6523580	1.0754055
O	-1.6875780	1.6066150	-0.4568135

E = -442.734187923, H = -442.510010
G = -442.551769

MnO₂

Mn	0.0000000	0.0000000	0.0003807
O	0.0000000	1.6792210	-0.0001903
O	0.0000000	-1.6792210	-0.0001903

E = -254.208086080, H = -254.201883
G = -254.194678

Mn(OAc)₂

Mn	0.0000000	0.0000000	0.0226641
O	0.7793570	1.7809010	-0.7581169
O	-0.7793570	-1.7809010	-0.7581169
C	0.0000000	2.4231880	0.0163651
C	0.0000000	-2.4231880	0.0163651
C	-0.0279780	3.9230340	-0.0051319
H	-0.2072100	4.3041660	1.0041271
H	0.9024050	4.3135120	-0.4238839
H	-0.8663930	4.2328140	-0.6418629
C	0.0279780	-3.9230340	-0.0051319
H	0.2072100	-4.3041660	1.0041271
H	-0.9024050	-4.3135120	-0.4238839
H	0.8663930	-4.2328140	-0.6418629
O	-0.7751890	1.7815980	0.7971711
O	0.7751890	-1.7815980	0.7971711

E = -560.929817872, H = -560.817343
G = -560.859560

Propene

C	1.3780556	0.1822691	0.0000504
C	0.2317536	-0.4981339	0.0000694
H	0.2682456	-1.5909419	-0.0000406
H	1.3880926	1.2733151	-0.0000266
C	-1.1323414	0.1237261	0.0000114
H	-1.7050314	-0.1911949	-0.8829796
H	-1.7049314	-0.1906599	0.8832874

H	-1.0646914	1.2180951	-0.0002896
H	2.3408486	-0.3264749	-0.0000826

E = -117.854834956

Propene'

C	-0.8921951	1.0459766	0.2399449
C	-0.2714981	0.0919276	-0.5747721
H	0.0378329	0.4506916	-1.5597031
H	-0.8170441	0.9422856	1.3205369
C	0.6465689	-0.9256544	0.0609889
H	0.1720579	-1.3259164	0.9667039
H	0.8124639	-1.7620614	-0.6270291
H	1.6184519	-0.4864284	0.3329829
H	-1.3066381	1.9691796	-0.1596531

E = -117.83604080

Propene''

C	-1.2307020	-0.5679641	0.3519562
C	-0.2320360	-0.2019501	-0.5412958
H	-0.5554680	0.1358349	-1.5257898
H	-1.0099550	-0.5333731	1.4175092
C	1.0729470	0.3574929	-0.0351478
H	1.8150560	0.3723179	-0.8422168
H	0.9590850	1.3826109	0.3438562
H	1.4521860	-0.2750381	0.7806532
H	-2.2711130	-0.6699311	0.0504752

E = -117.84056690

Propene'''

C	-0.6603342	1.2223638	0.1728108
C	-0.1974552	0.1408218	-0.5567372
H	0.0655928	0.3205128	-1.6004672
H	-0.5741982	1.1951348	1.2573278
C	0.4488448	-1.0348632	0.1258408
H	-0.1000522	-1.2651312	1.0478638
H	0.4023408	-1.9203072	-0.5182722
H	1.5023838	-0.8333892	0.3732338
H	-0.8871222	2.1748578	-0.3016002

E = -117.84350268

Propene''''

C	-1.3086512	0.4665543	0.1937668
C	-0.2587902	-0.0281007	-0.5673882
H	-0.1688042	0.3350253	-1.5901882
H	-1.2151802	0.4405413	1.2781778
C	1.0115148	-0.4885477	0.0986278
H	0.7751638	-1.0655627	1.0058348
H	1.6151188	-1.0993357	-0.5902292
H	1.6456448	0.3546653	0.4038028
H	-2.0960162	1.0847603	-0.2324042

E = -117.84152575

Propene'''''

C	0.6865454	1.1835650	-0.2815019
C	-0.1911036	0.1551620	-0.5452459
H	1.1167074	1.2640840	0.7148641
C	-0.5168686	-0.8842650	0.4917401
H	0.2315564	-1.6907700	0.5044651
H	-0.5524716	-0.4141690	1.4828311
H	-1.5008926	-1.3233370	0.2926301
H	-0.3645166	-0.1054450	-1.5901219

H 1.0910434 1.8151750 -1.0696609
E = -117.846392959

Propene''''''

C -0.5829551 1.2655308 0.1144828
C -0.1599551 0.1409778 -0.5440942
H 0.0181439 0.2147888 -1.6184662
H -0.5485641 1.2744818 1.2025988
C 0.4168689 -1.0436082 0.1734748
H -0.0106961 -1.1224642 1.1801928
H 0.1985229 -1.9696532 -0.3697872
H 1.5082349 -0.9500612 0.2616468
H -0.8396001 2.1900078 -0.4000482
E = -117.84953302

Propene''''''

C -0.8554216 1.0595354 0.3224339
C -0.1992876 0.1938834 -0.5202841
H -0.0235066 0.5210114 -1.5466051
H -0.8311756 0.8588264 1.3923839
C 0.6390374 -0.9403056 -0.0069211
H 0.2418364 -1.3060006 0.9476469
H 0.6492724 -1.7698876 -0.7219821
H 1.6758434 -0.6118526 0.1491349
H -1.2965986 1.9947894 -0.0158071
E = -117.84843593

Propene''''''

C -0.4529886 1.3076200 -0.1208500
C 0.0641654 0.1119100 -0.5717310
H 0.4300694 0.0524740 -1.5957750
H -0.4892476 1.4588740 0.9581020
C 0.2339904 -1.0557370 0.3406580
H -0.7005356 -1.2203890 0.8979640
H 0.4852854 -1.9653330 -0.2123520
H 1.0335444 -0.8619440 1.0707050
H -0.6042836 2.1725250 -0.7667210
E = -117.84510713

5.3.2 Osmium-mediated oxidative cyclisation computational and cartesian coordinates data accounted from (SMD)–M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of theory

5.3.2.1 Computational and cartesian coordinates data accounted (SMD)–M06-2X/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of the

(E)-2-Butene

C	-0.547575000	1.880648000	-0.000222000
H	-1.068732000	2.274102000	-0.883797000
H	-1.068970000	2.274718000	0.882945000
H	0.476920000	2.271671000	-0.000235000
C	-0.547575000	0.380777000	0.000410000
H	-1.526234000	-0.109943000	-0.000047000
C	0.547575000	-0.380777000	0.000410000
H	1.526234000	0.109943000	-0.000047000
C	0.547575000	-1.880648000	-0.000222000
H	1.068732000	-2.274102000	-0.883797000
H	1.068970000	-2.274718000	0.882945000
H	-0.476920000	-2.271671000	-0.000235000

E = -157.157162422, H = -157.043635
G = -157.077229

(E)-2-Butene (in *t*-butanol at 273.15 K)

E = -157.156478277, H = -157.043127
G = -157.07323

3.1

E = -313.128808624, H = -312.920784
G = -312.967719

3.1'

E = -313.129564994, H = -312.921538
G = -312.971065

3.1''

C	-1.818606000	0.547142000	-0.360613000
C	-1.641777000	-0.651986000	0.196738000
H	-0.740644000	-0.845269000	0.781834000
H	-2.723030000	0.710254000	-0.956383000
C	-2.605631000	-1.793981000	0.063400000
C	-0.903569000	1.736343000	-0.247514000
H	-0.661805000	2.093305000	-1.261566000
H	-1.463607000	2.557656000	0.224636000
C	0.400935000	1.518178000	0.524036000
H	-2.123017000	-2.660275000	-0.409567000
H	-2.963192000	-2.123628000	1.048575000
H	-3.474349000	-1.508064000	-0.541668000
H	0.866366000	2.504329000	0.670724000
H	0.190071000	1.117272000	1.525598000
C	1.381767000	0.626593000	-0.185987000
C	2.064999000	-0.369240000	0.379895000
H	1.546296000	0.840483000	-1.248089000
C	3.066210000	-1.232578000	-0.327971000
H	1.892591000	-0.585422000	1.439506000

H	2.778451000	-2.291747000	-0.278440000
H	3.151548000	-0.945981000	-1.382942000
H	4.058351000	-1.145735000	0.135881000

E = -313.128847534, H = -312.920550
G = -312.965511

3.2

E = -540.015159387, H = -539.762870
G = -539.815162

4.1

Os	0.786818000	-0.000013000	0.000000000
O	1.694375000	-1.225341000	0.752520000
O	-0.369767000	0.676944000	1.097438000
O	-0.369831000	-0.676977000	-1.097377000
O	1.694309000	1.225314000	-0.752584000
C	-2.441909000	-0.527339000	-0.439879000
H	-2.594983000	-0.314062000	-1.498154000
C	-2.441870000	0.527424000	0.439896000
H	-2.594960000	0.314193000	1.498178000
C	-2.570038000	1.952719000	-0.004634000
H	-1.989806000	2.618929000	0.643318000
H	-2.217639000	2.069158000	-1.037072000
H	-3.620181000	2.273925000	0.038021000
C	-2.570296000	-1.952628000	0.004625000
H	-3.620487000	-2.273673000	-0.038102000
H	-1.990129000	-2.618906000	-0.643306000
H	-2.217977000	-2.069133000	1.037083000

E = -548.824692205, H = -548.690178
G = -548.739793

4.1 (In t-butanol at 273.15 K)

E = -548.837992659, H = -548.704988
G = -548.7489997

4.2

Os	0.000000000	0.000000000	0.735280000
O	0.000000000	1.476619000	1.556650000
O	1.242278000	-0.049475000	-0.695604000
O	-1.242278000	0.049475000	-0.695604000
O	0.000000000	-1.476619000	1.556650000
C	-0.685054000	0.325502000	-1.995789000
H	-1.360270000	-0.160539000	-2.712864000
C	0.685054000	-0.325502000	-1.995789000
H	1.360270000	0.160539000	-2.712864000
C	0.638732000	-1.826451000	-2.219613000
H	1.628341000	-2.264243000	-2.052539000
H	-0.074414000	-2.289587000	-1.524566000
H	0.322270000	-2.046577000	-3.246621000
C	-0.638732000	1.826451000	-2.219613000
H	-0.322270000	2.046577000	-3.246621000
H	-1.628341000	2.264243000	-2.052539000
H	0.074414000	2.289587000	-1.524566000

E = -548.927838790, H = -548.789443
G = -548.835380

4.2 (In t-butanol at 273.15 K)

E = -548.942066023, H = -548.806632

G = -548.847841

4.2_H+ • NMO

C	3.3545287	-1.0001195	0.1612681
O	3.0715757	-0.0749565	-0.9041249
Os	1.4321107	0.8316435	-0.6982429
O	0.9912597	-0.7527695	0.2407161
C	2.0399887	-1.7452835	0.3810851
C	1.7935917	-2.8547505	-0.6216909
O	-0.4719763	1.0053415	-1.2368309
O	1.7118007	2.1841135	0.2209111
H	4.1209937	-1.6785295	-0.2330819
H	1.9700037	-2.1132715	1.4126221
H	0.7918777	-3.2779095	-0.4905929
H	1.8915637	-2.4696375	-1.6450569
H	2.5247537	-3.6583025	-0.4779089
C	-3.9178123	1.5594185	-0.1262109
C	-2.6950673	0.9912185	1.7664321
C	-1.3751483	1.0040905	1.0028011
H	-4.6113643	2.3162275	-0.5058379
H	-2.4949773	1.3182225	2.7914441
H	-3.1246843	-0.0232365	1.8098421
H	-0.9443003	2.0109635	1.0127331
H	-0.6666303	0.2748205	1.4026211
H	-4.4232793	0.5814415	-0.1715279
N	-1.5904253	0.6799095	-0.4506549
O	-3.6110393	1.9005335	1.2066061
C	-2.6648683	1.5955315	-0.9898739
H	-2.8485823	1.2879055	-2.0232769
H	-2.2160563	2.5929875	-0.9768949
C	-1.9256323	-0.7535235	-0.6940869
H	-1.1312883	-1.3601165	-0.2601999
H	-1.9681793	-0.8838345	-1.7775099
H	-2.8907303	-0.9827645	-0.2390519
O	1.5792077	1.1091365	-2.5516419
H	2.4875477	0.9278205	-2.8441789
C	3.8562777	-0.2694095	1.3928991
H	4.2003687	-0.9955365	2.1383021
H	4.6932217	0.3854355	1.1305241
H	3.0613707	0.3371905	1.8476711

E = -951.590709186, H = -951.259123

G = -951.323666

4.3

C	-2.962305000	0.340536000	0.000000000
H	-2.801430000	1.417678000	0.000000000
H	-3.994917000	-0.002258000	0.000000000
C	-1.954417000	-0.537496000	0.000000000
H	-2.193930000	-1.603533000	0.000000000
C	-0.511439000	-0.226524000	0.000000000
C	0.408836000	-1.282291000	0.000000000
C	-0.017465000	1.086738000	0.000000000
C	1.781911000	-1.041192000	0.000000000
H	0.039494000	-2.308284000	0.000000000

C	1.351640000	1.330330000	0.000000000
H	-0.707215000	1.929128000	0.000000000
C	2.258511000	0.267669000	0.000000000
H	2.479150000	-1.877932000	0.000000000
H	1.717197000	2.356408000	0.000000000
H	3.330010000	0.462172000	0.000000000

E = -309.556672386, H = -309.413690
G = -309.456948

4.4

Os	-1.415647000	-0.205516000	-0.082398000
O	-1.102196000	-1.837242000	0.272141000
O	-0.184835000	0.441302000	-1.112249000
O	-1.071208000	0.799705000	1.292910000
O	-2.961099000	0.120946000	-0.710453000
C	0.522436000	2.142279000	1.066098000
H	0.819457000	1.810562000	2.057155000
H	-0.139204000	3.003150000	1.015379000
C	1.235787000	1.755039000	-0.044689000
H	1.161793000	2.351179000	-0.952752000
C	2.300647000	0.742934000	-0.005251000
C	3.310447000	0.761293000	-0.975650000
C	2.309529000	-0.270401000	0.965192000
C	4.325882000	-0.190783000	-0.960545000
H	3.298047000	1.534853000	-1.743857000
C	3.319363000	-1.227521000	0.973635000
H	1.509786000	-0.323368000	1.704852000
C	4.334021000	-1.186740000	0.015817000
H	5.110674000	-0.158902000	-1.715152000
H	3.311101000	-2.015641000	1.725327000
H	5.123556000	-1.936928000	0.024898000

E = -701.238380716, H = -701.077666
G = -701.136303

4.5

Os	1.419531000	-0.196145000	-0.042164000
O	1.080920000	-1.795016000	-0.472709000
O	0.163726000	0.421892000	1.242700000
O	0.537972000	1.081692000	-1.128781000
O	2.994005000	0.319424000	0.279942000
C	-0.306550000	2.002342000	-0.429815000
H	-1.064911000	2.350906000	-1.139511000
H	0.304097000	2.849952000	-0.088798000
C	-0.895444000	1.252434000	0.750112000
H	-1.140189000	1.942499000	1.569695000
C	-2.126541000	0.442932000	0.390981000
C	-2.143631000	-0.949832000	0.448986000
C	-3.283634000	1.126003000	-0.000521000
C	-3.301794000	-1.650711000	0.104247000
H	-1.258577000	-1.495326000	0.768687000
C	-4.438394000	0.428014000	-0.339178000
H	-3.284972000	2.216940000	-0.033882000
C	-4.448459000	-0.967496000	-0.290572000
H	-3.303415000	-2.738831000	0.148377000
H	-5.332821000	0.972468000	-0.638896000
H	-5.349892000	-1.517655000	-0.555893000

E = -701.333423573, H = -701.166952

G = -701.223483

4.6

C	-3.434712000	-0.503514000	0.000066000
H	-3.201305000	-1.567417000	0.000070000
H	-4.488291000	-0.231761000	0.000127000
C	-2.488511000	0.441289000	0.000010000
H	-2.801201000	1.488399000	0.000038000
C	-1.028462000	0.231805000	-0.000028000
C	-0.180409000	1.343511000	-0.000040000
C	-0.438969000	-1.042736000	-0.000063000
C	1.206682000	1.194930000	-0.000025000
H	-0.614356000	2.343975000	-0.000015000
C	0.941217000	-1.187205000	-0.000064000
H	-1.065720000	-1.933000000	-0.000037000
C	1.791337000	-0.070976000	-0.000025000
H	1.842085000	2.080711000	0.000004000
H	1.375422000	-2.188013000	-0.000051000
C	3.286621000	-0.252915000	0.000083000
H	3.802808000	0.713232000	-0.000453000
H	3.610870000	-0.815115000	0.885440000
H	3.610931000	-0.816142000	-0.884614000

E = -348.858429643, H = -348.685704

G = -348.733256

4.7

Os	1.635951000	-0.305627000	0.078979000
O	1.070493000	-1.878202000	-0.229303000
O	0.553301000	0.532611000	1.137033000
O	1.392659000	0.720069000	-1.304056000
O	3.235806000	-0.201328000	0.644269000
C	0.038823000	2.298583000	-1.041381000
H	-0.298058000	2.034006000	-2.039456000
H	0.816494000	3.054926000	-0.970440000
C	-0.725647000	1.996277000	0.062081000
H	-0.575434000	2.564391000	0.978572000
C	-1.901774000	1.120800000	0.014556000
C	-2.877943000	1.211915000	1.012570000
C	-2.058878000	0.149564000	-0.988282000
C	-3.994413000	0.379411000	0.995530000
H	-2.760726000	1.947211000	1.808528000
C	-3.170371000	-0.683047000	-0.994311000
H	-1.296014000	0.030568000	-1.758207000
C	-4.159657000	-0.579921000	-0.006630000
H	-4.747595000	0.473620000	1.777699000
H	-3.271987000	-1.437853000	-1.774680000
C	-5.354912000	-1.495916000	-0.032828000
H	-5.921639000	-1.369045000	-0.964301000
H	-5.039938000	-2.546046000	0.020231000
H	-6.026828000	-1.295337000	0.808233000

E = -740.541683102, H = -740.348749

G = -740.413263

4.8

Os	1.644299000	-0.288668000	-0.062602000

O	1.061251000	-1.832309000	-0.424107000
O	0.557690000	0.538780000	1.258384000
O	0.904249000	1.078006000	-1.146063000
O	3.292482000	-0.000915000	0.162999000
C	0.197685000	2.107863000	-0.444745000
H	-0.537234000	2.526561000	-1.140558000
H	0.913839000	2.885081000	-0.143290000
C	-0.430957000	1.456998000	0.771963000
H	-0.579766000	2.189930000	1.577119000
C	-1.740392000	0.752995000	0.470958000
C	-1.914857000	-0.610411000	0.694469000
C	-2.817935000	1.497445000	-0.023974000
C	-3.138508000	-1.220315000	0.406687000
H	-1.099803000	-1.205758000	1.100090000
C	-4.033812000	0.886240000	-0.302874000
H	-2.710003000	2.571039000	-0.186673000
C	-4.212435000	-0.488705000	-0.097113000
H	-3.253911000	-2.289911000	0.582060000
H	-4.861715000	1.483787000	-0.686517000
C	-5.531603000	-1.142811000	-0.416443000
H	-6.353194000	-0.646306000	0.115030000
H	-5.747007000	-1.079575000	-1.491004000
H	-5.526419000	-2.200375000	-0.131818000

E = -740.635504055, H = -740.439545
G = -740.499760

4.9

C	4.190457000	-0.641886000	-0.337800000
H	3.925365000	-1.680965000	-0.146940000
H	5.235210000	-0.434914000	-0.560049000
C	3.294193000	0.349271000	-0.303704000
H	3.636956000	1.367463000	-0.502004000
C	1.851813000	0.223957000	-0.019897000
C	1.064293000	1.381687000	0.019357000
C	1.227150000	-1.010964000	0.213264000
C	-0.300410000	1.314265000	0.286726000
H	1.532256000	2.349736000	-0.159880000
C	-0.133994000	-1.078692000	0.478520000
H	1.809211000	-1.930221000	0.186959000
C	-0.913556000	0.083432000	0.521838000
H	-0.896175000	2.226986000	0.308845000
H	-0.605078000	-2.046852000	0.650736000
C	-2.381991000	0.004535000	0.800817000
H	-2.758874000	0.925198000	1.253296000
H	-2.631513000	-0.852974000	1.430490000
Cl	-3.331476000	-0.216300000	-0.730363000

E = -808.455805183, H = -808.291183
G = -808.341183

4.10

Os	2.178580000	-0.357904000	0.055167000
O	1.495087000	-1.910625000	-0.038353000
O	1.223826000	0.664670000	1.072834000
O	1.908000000	0.525659000	-1.418061000
O	3.815376000	-0.307357000	0.508754000
C	0.663251000	2.199526000	-1.264550000

H	0.225527000	1.831109000	-2.188149000
H	1.479511000	2.911067000	-1.359899000
C	-0.016429000	2.088172000	-0.073202000
H	0.239004000	2.756923000	0.746755000
C	-1.244477000	1.296139000	0.075943000
C	-2.146019000	1.594533000	1.104104000
C	-1.517594000	0.207884000	-0.769097000
C	-3.306806000	0.844940000	1.268333000
H	-1.934335000	2.424932000	1.777204000
C	-2.671447000	-0.544219000	-0.595988000
H	-0.811447000	-0.063740000	-1.554198000
C	-3.578861000	-0.232010000	0.422441000
H	-4.006203000	1.094004000	2.066417000
H	-2.874670000	-1.388590000	-1.254965000
C	-4.821544000	-1.048918000	0.600420000
H	-5.261012000	-0.908781000	1.590728000
H	-4.637619000	-2.111007000	0.418696000
Cl	-6.099388000	-0.562367000	-0.591004000

E = -1200.13790002, H = -1199.955506
G = -1200.016507

4.11

Os	2.215757000	-0.330746000	-0.034649000
O	1.590647000	-1.833646000	-0.487461000
O	1.095911000	0.482184000	1.268163000
O	1.582194000	1.109108000	-1.090146000
O	3.858693000	-0.118090000	0.286842000
C	0.895053000	2.141750000	-0.374679000
H	0.216134000	2.628864000	-1.082979000
H	1.631892000	2.867303000	-0.003669000
C	0.177930000	1.468244000	0.779160000
H	0.019454000	2.169961000	1.609990000
C	-1.146819000	0.846185000	0.379699000
C	-1.398836000	-0.515632000	0.529100000
C	-2.153755000	1.672155000	-0.137072000
C	-2.633171000	-1.046166000	0.147464000
H	-0.638612000	-1.170668000	0.948461000
C	-3.380156000	1.142990000	-0.513376000
H	-1.979772000	2.743883000	-0.241576000
C	-3.628977000	-0.228323000	-0.380551000
H	-2.817387000	-2.113952000	0.265002000
H	-4.159029000	1.796788000	-0.906349000
C	-4.951772000	-0.799272000	-0.793104000
H	-5.296040000	-0.383575000	-1.743872000
H	-4.919188000	-1.889546000	-0.853143000
Cl	-6.244207000	-0.395317000	0.411910000

E = -1200.23259774, H = -1200.045929
G = -1200.107447

4.12

C	-4.426205000	-0.598930000	0.011895000
H	-4.146044000	-1.651442000	0.005751000
H	-5.490826000	-0.375033000	0.020745000
C	-3.525183000	0.388017000	0.008845000
H	-3.881633000	1.420311000	0.015428000
C	-2.057108000	0.237428000	-0.002327000

C	-1.259721000	1.387866000	-0.006159000
C	-1.422560000	-1.015580000	-0.010299000
C	0.131026000	1.303541000	-0.017789000
H	-1.738004000	2.367028000	-0.001681000
C	-0.038786000	-1.109854000	-0.021331000
H	-2.014960000	-1.928083000	-0.009910000
C	0.737216000	0.052545000	-0.025948000
H	0.739146000	2.205390000	-0.023153000
H	0.446132000	-2.084952000	-0.031243000
C	2.233131000	-0.074448000	0.000351000
F	2.680624000	-0.453287000	1.216292000
F	2.851572000	1.080658000	-0.300042000
F	2.673951000	-1.002565000	-0.871735000

E = -646.555840910, H = -646.404784
G = -646.455684

4.13

Os	2.323097000	-0.401917000	0.081490000
O	1.605478000	-1.919939000	-0.171399000
O	1.336939000	0.571136000	1.118329000
O	2.169521000	0.602232000	-1.330542000
O	3.931092000	-0.438108000	0.626103000
C	1.037786000	2.340932000	-1.090332000
H	0.642191000	2.103818000	-2.073975000
H	1.909504000	2.989634000	-1.059548000
C	0.271963000	2.165064000	0.038836000
H	0.513715000	2.730692000	0.936255000
C	-1.019638000	1.462518000	0.022771000
C	-1.959747000	1.706624000	1.029963000
C	-1.318696000	0.518322000	-0.973885000
C	-3.188606000	1.051580000	1.030676000
H	-1.728146000	2.422453000	1.817783000
C	-2.539344000	-0.141406000	-0.975321000
H	-0.585070000	0.288470000	-1.746236000
C	-3.474028000	0.133090000	0.025003000
H	-3.921391000	1.249745000	1.809571000
H	-2.766949000	-0.876350000	-1.746112000
C	-4.788405000	-0.594611000	-0.005632000
F	-5.460109000	-0.356796000	-1.150678000
F	-4.620536000	-1.929513000	0.066834000
F	-5.596149000	-0.240140000	1.007911000

E = -1038.23797090, H = -1038.067711
G = -1038.133227

4.14

Os	2.384337000	-0.358768000	-0.057835000
O	1.705091000	-1.881990000	-0.326629000
O	1.362252000	0.601343000	1.227800000
O	1.699950000	0.981086000	-1.209977000
O	4.047509000	-0.151134000	0.132373000
C	1.096561000	2.104089000	-0.559213000
H	0.375394000	2.536611000	-1.261355000
H	1.878515000	2.840191000	-0.327122000
C	0.455501000	1.582349000	0.713594000
H	0.397429000	2.371190000	1.476586000
C	-0.928455000	1.002570000	0.492895000

C	-1.209784000	-0.345081000	0.705010000
C	-1.953427000	1.861806000	0.075507000
C	-2.499372000	-0.836715000	0.489913000
H	-0.428946000	-1.019786000	1.047212000
C	-3.237601000	1.381282000	-0.134900000
H	-1.746520000	2.921229000	-0.080021000
C	-3.504529000	0.025622000	0.071659000
H	-2.716805000	-1.890257000	0.650628000
H	-4.033160000	2.050245000	-0.459669000
C	-4.908406000	-0.467736000	-0.136831000
F	-4.997173000	-1.806515000	-0.084175000
F	-5.749211000	0.021123000	0.798234000
F	-5.399933000	-0.079786000	-1.330185000

E = -1038.33285495, H = -1038.158494
G = -1038.221416

4.15

C	3.815244000	-0.552620000	0.000000000
H	3.559894000	-1.611519000	0.000000000
H	4.874153000	-0.303006000	0.000000000
C	2.890171000	0.412234000	0.000000000
H	3.223527000	1.452590000	0.000000000
C	1.426098000	0.230863000	0.000000000
C	0.601207000	1.362591000	0.000000000
C	0.815287000	-1.032087000	0.000000000
C	-0.787435000	1.253112000	0.000000000
H	1.055227000	2.353631000	0.000000000
C	-0.568012000	-1.161769000	0.000000000
H	1.424111000	-1.934199000	0.000000000
C	-1.359183000	-0.013597000	0.000000000
H	-1.420758000	2.137398000	0.000000000
H	-1.038292000	-2.142798000	0.000000000
Cl	-3.098713000	-0.173203000	0.000000000

E = -769.153031580, H = -769.017938
G = -769.064557

4.16

Os	-1.872701000	-0.355756000	-0.080224000
O	-1.227834000	-1.901764000	0.201824000
O	-0.838591000	0.549808000	-1.131702000
O	-1.671422000	0.662831000	1.315611000
O	-3.479967000	-0.323332000	-0.629714000
C	-0.428170000	2.323114000	1.059414000
H	-0.063038000	2.075809000	2.052108000
H	-1.254858000	3.026858000	1.004523000
C	0.341601000	2.080897000	-0.054863000
H	0.147092000	2.645967000	-0.964385000
C	1.576372000	1.287865000	-0.018408000
C	2.540550000	1.448088000	-1.022125000
C	1.802059000	0.333470000	0.985509000
C	3.716194000	0.704356000	-1.014136000
H	2.370651000	2.172185000	-1.818330000
C	2.968721000	-0.422625000	1.002900000
H	1.051822000	0.163328000	1.757656000
C	3.919154000	-0.224278000	0.003531000
H	4.469726000	0.836147000	-1.787296000

H 3.141074000 -1.167978000 1.775973000
 Cl 5.387435000 -1.164735000 0.022219000
 E = -1160.83585003, H = -1160.681225
 G = -1160.743550

4.17

Os 1.899684000 -0.328283000 -0.061320000
 O 1.263254000 -1.860876000 -0.378082000
 O 0.844574000 0.570096000 1.241067000
 O 1.193882000 1.027711000 -1.180760000
 O 3.555972000 -0.084994000 0.148790000
 C 0.543766000 2.109269000 -0.504431000
 H -0.180088000 2.540204000 -1.204668000
 H 1.297665000 2.862280000 -0.235706000
 C -0.098000000 1.525624000 0.739848000
 H -0.199624000 2.287844000 1.524764000
 C -1.448940000 0.886735000 0.478758000
 C -1.682227000 -0.468418000 0.709683000
 C -2.498203000 1.687142000 0.014709000
 C -2.938889000 -1.024493000 0.465710000
 H -0.885518000 -1.104163000 1.088760000
 C -3.757382000 1.149690000 -0.227957000
 H -2.338601000 2.752845000 -0.154531000
 C -3.962630000 -0.209936000 -0.001224000
 H -3.123071000 -2.082074000 0.641104000
 H -4.574989000 1.771936000 -0.585357000
 Cl -5.539892000 -0.895795000 -0.300748000
 E = -1160.93034966, H = -1160.770861
 G = -1160.832391

4.18

C -1.615745000 1.613334000 0.547445000
 H -2.180243000 2.536031000 0.755326000
 H -1.490395000 1.087643000 1.504707000
 C -2.434575000 0.748237000 -0.415654000
 H -1.893691000 -0.191254000 -0.601749000
 H -2.512149000 1.261632000 -1.386223000
 C -6.065284000 -0.702298000 -0.343838000
 H -6.584254000 0.252913000 -0.176571000
 H -6.004124000 -1.199039000 0.635485000
 C -3.834855000 0.442800000 0.106355000
 H -4.367118000 1.389373000 0.289152000
 H -3.759250000 -0.064419000 1.080586000
 C -4.653703000 -0.419081000 -0.849817000
 H -4.129748000 -1.372450000 -1.020591000
 H -4.712852000 0.081613000 -1.828824000
 C -6.874294000 -1.564652000 -1.308679000
 H -6.388750000 -2.537543000 -1.461786000
 H -7.887597000 -1.747438000 -0.931398000
 H -6.960108000 -1.075207000 -2.287962000
 C 0.899899000 1.633405000 0.528964000
 H 0.949279000 1.073249000 1.463886000
 H 1.843559000 1.910430000 0.061595000
 C -0.270754000 1.967963000 -0.013938000
 H -0.276991000 2.528503000 -0.953960000
 E = -314.345672159, H = -314.112829

G = -314.162389

4.19

C	-1.655915000	1.529514000	0.550052000
C	-0.291808000	1.892322000	0.025032000
O	0.385588000	-0.182341000	-0.166890000
Os	1.601274000	-0.662623000	0.969913000
O	2.993727000	-1.220075000	0.171406000
O	0.953781000	-1.731859000	2.122040000
O	1.864129000	0.903527000	1.660124000
H	-2.176324000	2.458246000	0.832826000
H	-1.539252000	0.948631000	1.477924000
H	-0.155811000	1.900815000	-1.056786000
C	-2.517257000	0.757982000	-0.446081000
H	-2.002039000	-0.168142000	-0.732481000
H	-2.626085000	1.357313000	-1.362898000
C	-6.149517000	-0.683162000	-0.346968000
H	-6.661169000	0.249383000	-0.067189000
H	-6.043778000	-1.270214000	0.576941000
C	0.667162000	2.474941000	0.812395000
H	1.557115000	2.918290000	0.372959000
H	0.447957000	2.728160000	1.848012000
C	-3.899416000	0.424050000	0.105642000
H	-4.415116000	1.354360000	0.390870000
H	-3.789900000	-0.167399000	1.027687000
C	-4.762465000	-0.348076000	-0.887611000
H	-4.247310000	-1.279806000	-1.168418000
H	-4.865221000	0.240281000	-1.812811000
C	-6.999171000	-1.455320000	-1.352152000
H	-6.515608000	-2.403403000	-1.622840000
H	-7.992015000	-1.685790000	-0.947928000
H	-7.134431000	-0.873796000	-2.273843000

E = -706.025629174, H = -705.773633
G = -705.839312

4.20

C	-1.523698000	1.367182000	0.465869000
C	-0.111534000	1.572412000	-0.065277000
O	0.492484000	0.297177000	-0.363515000
Os	1.369138000	-0.548126000	1.089586000
O	2.989660000	-0.898183000	0.766603000
O	0.338557000	-1.681147000	1.804510000
O	1.222798000	1.184787000	1.844847000
H	-1.969170000	2.357857000	0.640896000
H	-1.461568000	0.866590000	1.445015000
H	-0.131824000	2.118482000	-1.018298000
C	-2.407542000	0.558419000	-0.477562000
H	-1.947470000	-0.424148000	-0.648016000
H	-2.448547000	1.061231000	-1.456282000
C	-6.136997000	-0.605435000	-0.343317000
H	-6.583535000	0.382160000	-0.156134000
H	-6.087950000	-1.114858000	0.629967000
C	0.813480000	2.219166000	0.938643000
H	1.706210000	2.634347000	0.451148000
H	0.322193000	2.996335000	1.536826000
C	-3.823137000	0.377332000	0.060690000

H	-4.274975000	1.364654000	0.244080000
H	-3.776137000	-0.130462000	1.036162000
C	-4.721135000	-0.419514000	-0.880415000
H	-4.268282000	-1.405846000	-1.064483000
H	-4.766268000	0.088382000	-1.856482000
C	-7.026974000	-1.399459000	-1.295251000
H	-6.606390000	-2.397076000	-1.478409000
H	-8.037354000	-1.527279000	-0.888650000
H	-7.112903000	-0.889170000	-2.263824000

E = -706.129550485, H = -705.871189
G = -705.935406

4.21

C	-3.072383000	0.150324000	-0.387724000
C	-4.169062000	-0.425026000	0.106941000
H	-5.007598000	0.209602000	0.399334000
H	-2.235925000	-0.475988000	-0.687460000
O	-0.004454000	0.286800000	-1.028967000
O	0.084497000	-2.004753000	0.677971000
O	2.440536000	-1.214335000	-0.838155000
O	1.358837000	0.531921000	1.154848000
C	-4.362581000	-1.900194000	0.299554000
C	-2.897653000	1.633079000	-0.569372000
H	-2.670269000	1.856594000	-1.619645000
H	-3.850771000	2.125882000	-0.352973000
C	-1.807095000	2.276628000	0.323166000
H	-4.583096000	-2.137782000	1.346401000
H	-5.210400000	-2.269949000	-0.288654000
H	-3.474782000	-2.465836000	0.007521000
H	-2.107694000	3.320154000	0.501400000
H	-1.796855000	1.803850000	1.310704000
C	-0.412108000	2.352581000	-0.233213000
C	0.693226000	2.558013000	0.560941000
H	-0.321453000	2.549506000	-1.297187000
C	2.012231000	3.030098000	0.030896000
H	0.542134000	2.637763000	1.632861000
H	2.845328000	2.601062000	0.591273000
H	2.138585000	2.783027000	-1.025918000
H	2.086715000	4.120274000	0.128724000
Os	1.009254000	-0.730372000	-0.015251000

E = -704.791168218, H = -704.565715
G = -704.622232

4.21'

C	-1.829886000	1.652909000	0.175898000
C	-0.486805000	2.135191000	-0.294491000
C	0.504543000	2.486491000	0.588198000
C	1.793359000	3.113015000	0.154379000
O	0.324600000	0.282560000	-1.153450000
Os	1.210320000	-0.667121000	-0.004231000
O	2.781459000	-1.004602000	-0.560346000
O	0.291032000	-2.014733000	0.475385000
O	1.252918000	0.542272000	1.236995000
H	-2.437661000	2.531742000	0.446682000
H	-1.700196000	1.072611000	1.101031000
H	-0.383059000	2.421529000	-1.341957000

H	0.260567000	2.517084000	1.650043000
H	2.629857000	2.737926000	0.755619000
H	1.992681000	2.897829000	-0.902371000
H	1.754873000	4.203421000	0.284875000
C	-2.607320000	0.817264000	-0.848716000
H	-2.053047000	-0.100644000	-1.075098000
H	-2.682862000	1.390167000	-1.785606000
C	-3.976968000	0.466087000	-0.344346000
H	-4.685976000	1.291438000	-0.218525000
C	-4.359636000	-0.769051000	-0.015836000
H	-3.640649000	-1.585357000	-0.138736000
C	-5.712124000	-1.135908000	0.516542000
H	-6.356103000	-0.251887000	0.594328000
H	-6.204273000	-1.868409000	-0.137622000
H	-5.629483000	-1.596225000	1.510491000

E = -704.796502406, H = -704.569656
G = -704.631868

4.21''

C	-2.275492000	-1.353827000	-0.493535000
C	-2.107999000	-1.387973000	0.830112000
H	-2.370102000	-0.517776000	1.434732000
H	-1.985361000	-2.238670000	-1.068233000
O	-0.037789000	0.578959000	-1.265482000
O	0.894741000	-1.913820000	-0.234635000
O	2.608529000	0.376970000	-0.308130000
O	0.295334000	0.440721000	1.285803000
C	-1.536147000	-2.550414000	1.583205000
C	-2.828898000	-0.209315000	-1.299655000
H	-2.228088000	-0.095367000	-2.211515000
H	-3.845042000	-0.467992000	-1.633334000
C	-2.884134000	1.132821000	-0.559439000
H	-0.616414000	-2.250010000	2.105381000
H	-2.240667000	-2.909473000	2.345336000
H	-1.293388000	-3.377854000	0.907628000
H	-3.518038000	1.813432000	-1.144352000
H	-3.381474000	0.998062000	0.409159000
C	-1.561601000	1.829859000	-0.353299000
C	-1.011526000	2.060294000	0.890943000
H	-1.208321000	2.448118000	-1.178277000
C	0.061711000	3.087939000	1.101879000
H	-1.563943000	1.721883000	1.767958000
H	0.678340000	2.842345000	1.972544000
H	0.709374000	3.152604000	0.217799000
H	-0.387384000	4.076930000	1.267249000
Os	1.026691000	-0.219936000	-0.147550000

E = -704.797450994, H = -704.567408
G = -704.625524

4.22

C	-2.791470000	0.698710000	-0.529280000
C	-3.735032000	0.084185000	0.185666000
H	-4.267387000	0.651623000	0.956401000
H	-2.257278000	0.134457000	-1.296537000
O	0.111183000	0.708507000	-0.998731000
O	-0.654948000	-1.569598000	0.697785000

O	1.917429000	-1.660396000	-0.746588000
O	1.415956000	0.561683000	1.109360000
C	-4.113294000	-1.357486000	0.029192000
C	-2.370985000	2.127625000	-0.311002000
H	-2.267188000	2.646266000	-1.276194000
H	-3.161061000	2.643590000	0.249961000
C	-1.057956000	2.266382000	0.476784000
H	-3.929089000	-1.908321000	0.961671000
H	-5.180341000	-1.464636000	-0.208425000
H	-3.525911000	-1.829028000	-0.767167000
H	-0.965208000	3.294217000	0.856638000
H	-1.084795000	1.598992000	1.351313000
C	0.202467000	1.979721000	-0.328427000
C	1.443081000	1.886343000	0.540219000
H	0.322435000	2.721383000	-1.130982000
C	2.738070000	2.082122000	-0.227461000
H	1.384744000	2.572830000	1.395610000
H	3.594399000	1.843184000	0.411785000
H	2.760286000	1.424729000	-1.106875000
H	2.825378000	3.122419000	-0.564123000
Os	0.678221000	-0.794459000	0.008660000

E = -704.899619947, H = -704.667315
G = -704.723515

4.22-extended

C	1.614189000	1.429501000	0.178669000
H	1.498387000	0.709371000	1.002904000
H	2.024776000	2.352730000	0.613515000
C	0.240253000	1.745098000	-0.397716000
H	0.305226000	2.541118000	-1.152890000
C	-0.788818000	2.057173000	0.671210000
H	-0.340096000	2.609793000	1.507865000
C	-2.018688000	2.771697000	0.141394000
H	-2.784883000	2.832645000	0.921361000
H	-1.757579000	3.787960000	-0.178494000
H	-2.431955000	2.226901000	-0.717948000
O	-1.169363000	0.777395000	1.217265000
O	-0.274986000	0.594869000	-1.096458000
O	-0.096216000	-1.905201000	0.425500000
O	-2.744646000	-0.992979000	-0.521807000
Os	-1.168050000	-0.671812000	-0.004657000
C	2.581679000	0.857764000	-0.860952000
H	2.166304000	-0.074341000	-1.263070000
H	2.663260000	1.566868000	-1.699469000
C	3.938140000	0.596578000	-0.272958000
H	4.518126000	1.471967000	0.038502000
C	4.454544000	-0.618822000	-0.084299000
H	3.865196000	-1.488112000	-0.392576000
C	5.794546000	-0.896186000	0.527587000
H	6.434558000	-1.455973000	-0.167963000
H	6.305191000	0.036459000	0.795181000
H	5.691894000	-1.509155000	1.433452000

E = -704.900707036, H = -704.669584
G = -704.725177

4.22 • NMO

C	1.7067206	3.9995958	-1.1444822
C	2.5935206	3.2247048	-0.2010892
C	2.9937086	1.9725108	-0.4267902
C	3.8171466	1.1644558	0.5352628
C	3.0545416	-0.0266122	1.1394858
C	2.9632636	-1.2435642	0.2213488
O	2.4116826	-0.9021002	-1.0502402
Os	0.4873876	-0.9866512	-1.0695382
O	0.7146806	-1.9427642	0.5713428
C	2.0806646	-2.3406342	0.8068338
C	2.3265066	-3.6970982	0.1687348
O	-1.6959414	-1.2206432	-1.1315662
O	0.2027856	0.6935878	-0.8359082
O	0.3191196	-2.0340932	-2.4004962
H	2.9025956	3.7188768	0.7249798
H	2.6765726	1.4648768	-1.3398842
H	4.7203386	0.7839198	0.0325198
H	4.1508326	1.8219058	1.3497558
H	0.7312446	3.5051708	-1.2461842
H	1.5387726	5.0222638	-0.7887522
H	2.1499086	4.0614468	-2.1466242
H	3.5610426	-0.3528332	2.0598878
H	2.0389416	0.2914948	1.4185688
H	3.9763926	-1.6291132	0.0261838
H	2.1947536	-2.3972862	1.8988318
H	1.5867786	-4.4222422	0.5254528
H	2.2445916	-3.6144762	-0.9228722
H	3.3301416	-4.0605072	0.4219908
C	-4.9603184	-0.5792682	0.3939958
C	-3.9702284	1.4796598	-0.0537532
C	-2.8023714	0.8284738	-0.7751182
H	-5.8867424	-1.1398442	0.2309348
H	-4.1780054	2.4456728	-0.5244332
H	-3.7386154	1.6610268	1.0094638
H	-3.0324384	0.6793228	-1.8341902
H	-1.8705834	1.3907538	-0.6821292
H	-4.8030194	-0.4936672	1.4821258
N	-2.5320734	-0.5560492	-0.2542652
O	-5.1449564	0.7001088	-0.1734852
C	-3.8193534	-1.3263392	-0.2818732
H	-3.6152044	-2.2939772	0.1868418
H	-4.0249044	-1.4766742	-1.3452442
C	-1.9575234	-0.5408572	1.1229768
H	-1.1143384	0.1519988	1.1349028
H	-1.6090564	-1.5560562	1.3258918
H	-2.7189624	-0.2284772	1.8406058

E = -1107.09760275, H = -1106.685677
G = -1106.761644

4.22_{H2O}

C	2.849392000	0.868419000	0.464917000
C	3.423736000	-0.078411000	-0.278195000
H	3.654350000	0.144425000	-1.325360000
H	2.604794000	0.648560000	1.506527000
Os	-0.540883000	-0.687240000	-0.088837000
O	0.055985000	0.764629000	0.997684000

O	-0.360814000	-1.664515000	1.527865000
O	-2.114239000	-1.742537000	-0.258312000
O	-1.683972000	0.672871000	-0.789696000
C	3.754000000	-1.458875000	0.202543000
C	2.455392000	2.224104000	-0.065012000
H	2.532893000	2.978225000	0.731433000
H	3.160621000	2.517847000	-0.853794000
C	1.040720000	2.270079000	-0.662102000
H	3.198885000	-2.210906000	-0.374776000
H	4.823201000	-1.677095000	0.079944000
H	3.494698000	-1.575690000	1.261803000
H	0.869270000	3.260259000	-1.108824000
H	0.965652000	1.533136000	-1.475744000
C	-0.080270000	2.030192000	0.340731000
C	-1.465272000	2.005744000	-0.310878000
H	-0.040412000	2.791241000	1.133855000
C	-2.582377000	2.362962000	0.653627000
H	-1.484052000	2.664398000	-1.190801000
H	-3.555862000	2.198867000	0.179446000
H	-2.515731000	1.732839000	1.550191000
H	-2.508549000	3.415910000	0.952402000
O	0.611460000	-1.168297000	-1.187238000
H	0.200954000	-1.154986000	2.131223000
H	-2.732901000	-1.279292000	-0.842106000

E = -781.347805736, H = -781.086756
G = -781.146522

4.22_{H2O}-extended

Os	-0.971921000	-0.608621000	-0.027995000
O	-0.277369000	0.719728000	1.157138000
O	-1.729618000	-1.305130000	1.564111000
O	-2.648593000	-1.138312000	-0.754163000
O	-1.266507000	0.921988000	-1.129869000
C	1.629608000	1.500574000	-0.151431000
H	2.058520000	2.428300000	-0.557846000
H	1.503192000	0.812546000	-1.000692000
C	0.265866000	1.835711000	0.441102000
C	-0.768099000	2.172209000	-0.631995000
H	0.356529000	2.651851000	1.171838000
C	-1.935440000	2.989259000	-0.108167000
H	-0.284692000	2.679021000	-1.479340000
H	-2.703176000	3.090478000	-0.882548000
H	-2.377507000	2.491491000	0.764766000
H	-1.598132000	3.990502000	0.186960000
O	0.247835000	-1.591551000	-0.589527000
H	-1.268080000	-0.911832000	2.320243000
H	-2.825905000	-0.605202000	-1.543149000
C	2.588032000	0.873479000	0.863755000
H	2.151097000	-0.059260000	1.241598000
H	2.694622000	1.554560000	1.722286000
C	3.930537000	0.590219000	0.254756000
H	4.535514000	1.456961000	-0.031853000
C	4.402849000	-0.634003000	0.013830000
H	3.787969000	-1.494080000	0.296968000
C	5.724311000	-0.932496000	-0.627823000
H	6.264582000	-0.007917000	-0.863194000

H 6.352584000 -1.544293000 0.033423000
H 5.586938000 -1.501438000 -1.557482000
E = -781.349389300, H = -781.087334
G = -781.151658

4.22_[ox]

C -3.336881000 -1.191094000 0.347713000
C -2.926140000 0.242849000 0.497977000
C -2.539309000 1.025042000 -0.514455000
C -2.097579000 2.462921000 -0.360034000
C -0.777309000 2.607009000 0.408127000
C 0.451150000 2.106086000 -0.346122000
O 0.203374000 0.881310000 -1.019543000
Os 0.407204000 -0.780841000 -0.042818000
O 1.211925000 0.548899000 1.152632000
C 1.603775000 1.786700000 0.604175000
C 2.955327000 1.691750000 -0.083053000
O -0.249607000 -1.468689000 1.362343000
O -0.666926000 -1.359901000 -1.235293000
O 1.861416000 -1.553111000 -0.435678000
H -2.943012000 0.653903000 1.513281000
H -2.502970000 0.596290000 -1.517889000
H -2.000073000 2.928533000 -1.349584000
H -2.868014000 3.025730000 0.183178000
H -2.636397000 -1.851806000 0.880748000
H -4.332206000 -1.361124000 0.778864000
H -3.353784000 -1.482197000 -0.708186000
H -0.597467000 3.662251000 0.657295000
H -0.853896000 2.057506000 1.356566000
H 0.751395000 2.815556000 -1.131634000
H 1.631544000 2.513050000 1.429775000
H 3.700491000 1.288215000 0.610301000
H 2.898449000 1.034669000 -0.959804000
H 3.278764000 2.687671000 -0.410424000
E = -780.025053532, H = -779.788611
G = -779.845480

4.22_[ox]-extended

C -2.018800000 0.868025000 0.244748000
C -0.769463000 1.393552000 -0.444203000
O -0.018011000 0.324957000 -1.003472000
Os 1.419796000 -0.482043000 0.018925000
O 0.862761000 1.023127000 1.131153000
C 0.193962000 2.097115000 0.510565000
C 1.169376000 3.027140000 -0.191125000
O 1.399823000 -1.421262000 1.429021000
O 1.252758000 -1.673281000 -1.189610000
O 2.967523000 0.137507000 -0.284843000
H -2.592650000 1.728700000 0.617119000
H -1.710315000 0.279756000 1.122458000
H -1.034036000 2.043197000 -1.292264000
H -0.362058000 2.628707000 1.295758000
H 1.931921000 3.374998000 0.513551000
H 1.668888000 2.510063000 -1.020373000
H 0.633904000 3.896491000 -0.592472000
C -2.903230000 0.022914000 -0.675628000

H	-2.306774000	-0.816410000	-1.059896000
H	-3.214437000	0.624201000	-1.541782000
C	-4.115830000	-0.490370000	0.044706000
H	-3.929183000	-1.153949000	0.895968000
C	-5.375706000	-0.181139000	-0.265727000
H	-5.556611000	0.481475000	-1.118226000
C	-6.585775000	-0.681251000	0.464918000
H	-7.188184000	0.155308000	0.844362000
H	-7.232608000	-1.266971000	-0.202341000
H	-6.298374000	-1.314601000	1.312349000

E = -780.023872816, H = -779.787487
G = -779.848907

4.22_{[ox]H⁺}

C	-3.333809000	-1.047828000	0.387510000
C	-2.845627000	0.349887000	0.519374000
C	-2.488019000	1.133009000	-0.521209000
C	-2.008994000	2.549452000	-0.365068000
C	-0.678320000	2.635601000	0.403514000
C	0.505990000	2.081344000	-0.364709000
C	1.688730000	1.720694000	0.574063000
C	3.019024000	1.568491000	-0.132234000
O	0.238854000	0.821434000	-0.994726000
Os	0.410763000	-0.760500000	-0.011866000
O	1.240519000	0.498683000	1.143260000
O	-0.355721000	-1.480230000	1.315420000
H	-2.792047000	0.755051000	1.534895000
H	-2.560760000	0.726792000	-1.532141000
H	-1.907056000	3.026430000	-1.346657000
H	-2.750329000	3.127572000	0.201502000
H	-2.583638000	-1.750264000	0.821579000
H	-4.238301000	-1.218920000	0.985172000
H	-3.544266000	-1.312052000	-0.655112000
H	-0.448402000	3.684505000	0.630225000
H	-0.772612000	2.109261000	1.362741000
H	0.821986000	2.745569000	-1.179492000
H	1.730122000	2.444977000	1.398036000
H	3.768009000	1.165901000	0.557326000
H	2.938628000	0.904640000	-1.001910000
H	3.357998000	2.552710000	-0.475675000
O	1.748527000	-1.632366000	-0.503025000
O	-0.860136000	-1.345479000	-1.270895000
H	-1.487532000	-2.004429000	-0.926387000

E = -780.413901380, H = -780.167040
G = -780.224537

4.22_{[ox]H⁺}-extended

C	6.229133000	-0.656560000	-0.333005000
C	5.001607000	-0.125372000	0.323733000
C	3.759189000	-0.206205000	-0.186549000
C	2.551230000	0.332561000	0.490711000
C	1.709428000	1.233391000	-0.426605000
C	0.485188000	1.747639000	0.313477000
O	-0.126753000	0.699889000	1.038758000
Os	-1.162445000	-0.546778000	0.077139000
O	-1.212703000	0.943994000	-1.063872000

C	-0.675545000	2.198793000	-0.619386000
C	-1.728034000	3.037864000	0.066269000
O	0.043801000	-1.738085000	0.040465000
O	-2.285515000	-0.792771000	1.289761000
H	5.133185000	0.360359000	1.295505000
H	3.612981000	-0.696965000	-1.153501000
H	1.889155000	-0.508805000	0.805565000
H	2.831371000	0.868878000	1.407150000
H	6.964512000	0.146486000	-0.478793000
H	6.709592000	-1.404469000	0.313607000
H	6.004444000	-1.115739000	-1.301317000
H	2.298320000	2.087587000	-0.783093000
H	1.389644000	0.665027000	-1.313269000
H	0.717720000	2.534227000	1.043689000
H	-0.272741000	2.682442000	-1.518376000
H	-2.578096000	3.188128000	-0.607051000
H	-2.077008000	2.555354000	0.988335000
H	-1.309213000	4.019040000	0.317691000
O	-2.056835000	-1.241321000	-1.433121000
H	-1.857153000	-2.172737000	-1.626509000

E = -780.405517726, H = -780.159180
G = -780.223338

• **4.22'**_{[ox]H⁺}

•	C	-2.8249021	-2.3183310	0.6867928
•	C	-2.2577441	-0.9714570	1.0097878
•	C	-2.1956141	0.0649150	0.1625378
•	C	-1.6726561	1.4338480	0.5478308
•	C	-0.1676781	1.4634170	0.8503338
•	C	0.6994219	1.3194710	-0.3865572
•	O	0.2646919	0.1795600	-1.1850042
•	Os	0.4956649	-1.5889330	-0.7394622
•	O	2.1637719	-0.2720870	0.4171908
•	C	2.1787109	1.0753610	-0.1004262
•	C	3.0706359	1.1963180	-1.3181772
•	O	0.4465999	-2.2341060	0.8109028
•	H	-1.8918011	-0.8338050	2.0334838
•	H	-2.5819121	-0.0617910	-0.8525462
•	H	-1.8975241	2.1550940	-0.2482472
•	H	-2.2009851	1.7821300	1.4432118
•	H	-2.0716161	-3.1087120	0.8296758
•	H	-3.6507391	-2.5525680	1.3703888
•	H	-3.1993341	-2.3604810	-0.3418212
•	H	0.1053119	2.4239910	1.3073338
•	H	0.0934189	0.6769610	1.5731658
•	H	0.5640929	2.1660720	-1.0713552
•	H	2.4969669	1.7475190	0.7073788
•	H	4.1018629	0.9169250	-1.0704772
•	H	2.7144059	0.5559010	-2.1344642
•	H	3.0842039	2.2356030	-1.6655092
•	O	1.8672739	-2.1820460	-1.5135762
•	O	-0.7914701	-2.2667530	-1.5689282
•	H	3.0569409	-0.6420150	0.4465358

• E = -780.439497304, H = -780.189203
• G = -780.251164

•

4.22'_{[ox]H⁺}-extended

6	4.418773000	-0.712952000	-0.326960000
6	5.522405000	-0.661632000	0.421219000
1	5.415458000	-0.519641000	1.501665000
1	4.509622000	-0.865795000	-1.406598000
76	-1.675136000	-0.460997000	0.000479000
8	0.144373000	-0.296447000	-0.097390000
8	-1.140886000	1.856433000	0.186369000
6	6.918703000	-0.798994000	-0.100072000
6	3.026523000	-0.571607000	0.218860000
1	2.429296000	-1.459061000	-0.036619000
1	3.066582000	-0.503260000	1.315126000
6	2.332951000	0.674915000	-0.343191000
1	7.514949000	0.087908000	0.150911000
1	7.417719000	-1.660826000	0.362037000
1	6.925813000	-0.931946000	-1.187502000
1	2.926115000	1.563068000	-0.084398000
1	2.268880000	0.627332000	-1.439171000
6	0.950506000	0.896091000	0.228881000
6	0.190687000	2.082786000	-0.330249000
1	0.964919000	0.940206000	1.327360000
6	0.737177000	3.418854000	0.127770000
1	0.161055000	2.010839000	-1.427315000
1	0.083709000	4.230255000	-0.212461000
1	0.809280000	3.454390000	1.220651000
1	1.727058000	3.585712000	-0.310386000
8	-2.560747000	0.160502000	-1.291153000
8	-2.380938000	-0.091514000	1.477637000
8	-1.776835000	-2.125078000	-0.149867000
1	-1.776227000	2.480624000	-0.192030000

E = -780.434311492, H = -780.183271

G = -780.247792

•

4.22_{H⁺}

•	C	2.702104000	0.902106000	0.601750000
•	C	3.258078000	-0.037239000	-0.179035000
•	H	3.433456000	0.195709000	-1.234736000
•	H	2.568090000	0.689874000	1.665053000
•	O	-0.018359000	0.651848000	0.959980000
•	O	0.801761000	-1.181280000	-0.954729000
•	O	-1.572276000	0.502286000	-0.956948000
•	C	3.740113000	-1.372212000	0.300384000
•	C	2.293827000	2.269170000	0.108707000
•	H	2.304503000	2.985343000	0.940754000
•	H	3.029039000	2.623686000	-0.624707000
•	C	0.919726000	2.309132000	-0.572639000
•	H	3.329198000	-2.187832000	-0.308706000
•	H	4.832642000	-1.433286000	0.210250000
•	H	3.473982000	-1.537073000	1.351331000
•	H	0.724110000	3.317786000	-0.961800000
•	H	0.909837000	1.627376000	-1.437455000
•	C	-0.237576000	1.960273000	0.353570000
•	C	-1.574600000	1.841763000	-0.363868000
•	H	-0.283304000	2.643338000	1.211059000

- C -2.785872000 1.973369000 0.537254000
- H -1.629177000 2.517393000 -1.225143000
- H -3.697218000 1.716980000 -0.011557000
- H -2.692566000 1.315242000 1.411454000
- H -2.868434000 3.009229000 0.885687000
- Os -0.553693000 -0.770575000 -0.091726000
- O -1.669678000 -1.868784000 0.877151000
- H -1.579867000 -2.830773000 0.979345000
- E = -705.279898712, H = -705.039096
- G = -705.095356

4.22_H⁺-extended

C	-1.609041000	1.408280000	-0.162880000
H	-1.500367000	0.708269000	-1.006782000
H	-2.010160000	2.341627000	-0.582299000
C	-0.236405000	1.729719000	0.408967000
H	-0.294727000	2.484160000	1.203578000
C	0.801102000	2.070387000	-0.646612000
H	0.345123000	2.566209000	-1.511204000
C	2.012940000	2.819923000	-0.131590000
H	2.779281000	2.889808000	-0.909701000
H	1.714328000	3.835182000	0.153833000
H	2.434866000	2.317910000	0.749388000
O	1.248538000	0.773913000	-1.172498000
O	0.295462000	0.550516000	1.094220000
O	-0.027126000	-1.739100000	-0.522935000
Os	1.125987000	-0.661283000	-0.023499000
C	-2.580242000	0.831876000	0.871396000
H	-2.184240000	-0.112429000	1.268330000
H	-2.655578000	1.532822000	1.716758000
C	-3.935446000	0.592574000	0.269107000
H	-4.492093000	1.477200000	-0.054669000
C	-4.478158000	-0.615353000	0.107158000
H	-3.914494000	-1.490972000	0.446632000
C	-5.825034000	-0.876814000	-0.491816000
H	-6.480674000	-1.371402000	0.236928000
H	-6.302544000	0.055420000	-0.813517000
H	-5.743805000	-1.547173000	-1.357337000
O	2.808567000	-1.000131000	0.626226000
H	3.228205000	-1.874294000	0.703474000

E = -705.279807542, H = -705.038820
G = -705.095647

4.22_H⁺ • NMO

C	2.4605980	3.3817811	-2.5267524
C	2.8883210	2.9888151	-1.1456024
C	3.5735410	1.8825611	-0.8447154
C	3.9661340	1.4969501	0.5590666
C	2.9102140	0.6533151	1.2880366
C	2.6369460	-0.7020569	0.6519466
O	2.1607030	-0.5773829	-0.6996354
Os	0.3421930	-0.1024919	-0.8181824
O	0.2813270	-1.0119879	0.8422426
C	1.5434860	-1.4946959	1.3702556
C	1.6252810	-2.9903899	1.1384156
O	-1.5414010	-0.6567269	-1.1652094

O	0.2686900	1.5538451	-0.7671884
H	2.6194270	3.6755241	-0.3358704
H	3.8636440	1.2044781	-1.6508144
H	4.9168320	0.9463661	0.5479996
H	4.1307360	2.4059821	1.1511016
H	1.3695570	3.4987101	-2.5795954
H	2.8989760	4.3465751	-2.8123744
H	2.7696630	2.6308991	-3.2638534
H	3.2436570	0.4616511	2.3175886
H	1.9709930	1.2237271	1.3579296
H	3.5615730	-1.2905099	0.5880836
H	1.5324820	-1.2571839	2.4414386
H	0.7639550	-3.4984649	1.5854056
H	1.6537930	-3.2066599	0.0626116
H	2.5349800	-3.3904459	1.5999286
C	-5.0441810	-0.4295489	-0.1172534
C	-3.7688570	0.3923731	1.6441836
C	-2.4773370	0.3117691	0.8366606
H	-5.9026800	-0.1773709	-0.7472294
H	-3.6905500	1.2467481	2.3236256
H	-3.9183350	-0.5149359	2.2522716
H	-2.3224400	1.2410121	0.2782316
H	-1.6147270	0.0919991	1.4702766
H	-5.2709190	-1.3739739	0.4032086
N	-2.5619530	-0.7679289	-0.2073394
O	-4.8761010	0.6221321	0.8062656
C	-3.8202600	-0.5539609	-1.0140064
H	-3.8879010	-1.3892559	-1.7170084
H	-3.6481660	0.3764891	-1.5628024
C	-2.5149080	-2.1458619	0.3641396
H	-1.5945710	-2.2356829	0.9403406
H	-2.5134260	-2.8350349	-0.4829994
H	-3.3920610	-2.3068779	0.9930046
O	0.4693630	-0.8147959	-2.5538844
H	1.4037100	-0.9094769	-2.8019444

E = -1107.56325303, H = -1107.044417
G = -1107.213497

4.22_H+ • NMO-extended

C	5.3152901	3.3401895	-0.3185759
C	4.5619031	2.0897755	-0.6545939
C	4.5643811	0.9748955	0.0781551
C	3.8020801	-0.2680755	-0.2799229
C	2.7141591	-0.5830415	0.7503891
C	1.9249391	-1.8413325	0.4171151
O	1.4433081	-1.8083365	-0.9395449
Os	-0.0288259	-0.6550845	-1.1640329
O	-0.3367109	-1.1522685	0.6362371
C	0.6631851	-1.9995705	1.2619381
C	0.1326041	-3.4177455	1.3191051
O	-1.9918399	-0.4520245	-1.4094459
O	0.5747731	0.8674565	-1.4302929
H	3.9808981	2.1013645	-1.5827319
H	5.1489571	0.9462175	1.0030041
H	3.3442541	-0.1415545	-1.2697859
H	4.4851361	-1.1286925	-0.3469769

H	6.0470821	3.5721825	-1.1037559
H	4.6362591	4.2001325	-0.2482419
H	5.8484051	3.2360285	0.6331591
H	3.1622091	-0.7251045	1.7439971
H	2.0317861	0.2769105	0.8376021
H	2.5611621	-2.7330895	0.4817951
H	0.8176241	-1.5886815	2.2676651
H	-0.8318939	-3.4482415	1.8376361
H	0.0110041	-3.8208475	0.3056801
H	0.8340141	-4.0563335	1.8678281
C	-5.0344959	1.3520625	-0.4618449
C	-3.4276719	1.8800705	1.1327731
C	-2.3293189	1.1438745	0.3720101
H	-5.7567559	1.8160765	-1.1406279
H	-2.9702929	2.7332205	1.6432161
H	-3.8884129	1.2320145	1.8962001
H	-1.8517689	1.8180255	-0.3468889
H	-1.5887139	0.7093995	1.0477861
H	-5.5877579	0.6883595	0.2219561
N	-2.9049939	0.0259915	-0.4546989
O	-4.4010629	2.3886615	0.2528841
C	-4.0225029	0.5867735	-1.3027399
H	-4.4646499	-0.2588305	-1.8374339
H	-3.5285129	1.2547005	-2.0142249
C	-3.3744339	-1.1320715	0.3612461
H	-2.5324799	-1.4827255	0.9571761
H	-3.7006909	-1.8996245	-0.3438569
H	-4.2023869	-0.8147485	0.9971981
O	-0.3220049	-1.6558915	-2.7282739
H	0.4727651	-2.1704685	-2.9452589

E = -1107.56433057, H = -1107.138050
G = -1107.212849

4.22'_{H+}

C	-2.0832229	-0.0277781	-0.5770591
C	-2.9279619	-0.6879801	0.2196389
H	-3.3075169	-0.1839941	1.1149739
H	-1.7260599	-0.5121251	-1.4894791
O	0.7774431	-0.2494131	-1.0055481
O	2.2327491	-2.7696151	-0.8211361
O	2.0415671	-0.3653281	1.1034889
C	-3.4219399	-2.0803481	-0.0232051
C	-1.5967149	1.3711489	-0.2927531
H	-1.5149799	1.9475339	-1.2251941
H	-2.3367979	1.8836429	0.3337259
C	-0.2555609	1.4291769	0.4550829
H	-3.1728059	-2.7362581	0.8216819
H	-4.5149049	-2.0901291	-0.1222581
H	-2.9871799	-2.5011991	-0.9375371
H	-0.0758369	2.4532009	0.8131099
H	-0.3084929	0.7804429	1.3440409
C	0.9547801	1.0429599	-0.3839941
C	2.2403781	0.9668289	0.4217649
H	1.0852781	1.7339299	-1.2275081
C	3.5188221	0.9288719	-0.3758051
H	2.2562201	1.6942429	1.2402549

H	4.3846361	0.7063259	0.2587479
H	3.4558821	0.1917289	-1.1860391
H	3.6781201	1.9186689	-0.8197751
Os	1.1451661	-1.7967251	0.0019269
O	-0.2659429	-2.4533911	0.6057099
H	2.7248751	-0.5944201	1.7531439

E = -705.291177992, H = -705.046888
G = -705.105267

4.22' _{H+} • NMO

C	1.8830942	3.9926005	-0.3854520
C	2.9206522	3.0237395	0.0940930
C	3.1901722	1.8568955	-0.4943440
C	4.2090322	0.8778775	0.0212460
C	3.5933172	-0.3638705	0.6845330
C	3.0191142	-1.3768425	-0.3028490
O	2.0368522	-0.8045785	-1.1647600
Os	0.2587242	-0.7359585	-0.4318150
C	2.3976182	-2.5806015	0.4043940
C	2.0994972	-3.7616185	-0.4854740
O	-1.5525728	-0.9402745	0.5928960
O	0.2622242	0.9226415	-0.0670610
O	-0.4437528	-1.4993295	-1.7784850
H	3.4864892	3.3093085	0.9864770
H	2.6361232	1.5733455	-1.3913890
H	4.8742302	0.5516965	-0.7923750
H	4.8366172	1.3812645	0.7672200
H	1.1234842	4.1656185	0.3895910
H	2.3315112	4.9674425	-0.6166720
H	1.3853422	3.6146645	-1.2860020
H	4.3678662	-0.8860115	1.2649250
H	2.8125722	-0.0476305	1.3940440
H	3.8212172	-1.7457315	-0.9586790
H	2.9479812	-2.8507055	1.3115230
H	1.5292212	-4.5341485	0.0448090
H	1.5518972	-3.4435315	-1.3812340
H	3.0496522	-4.2080315	-0.8005340
C	-5.1788648	-0.3423495	0.4404900
C	-4.2117098	0.8811435	-1.2845730
C	-2.8360478	0.2769755	-1.0280670
H	-5.9823078	-1.0583775	0.6397510
H	-4.3034438	1.0708675	-2.3584350
H	-4.3400798	1.8401245	-0.7566810
H	-2.6994198	-0.6378025	-1.6110540
H	-2.0350418	0.9895105	-1.2487140
H	-5.3606818	0.5534175	1.0565120
N	-2.6811518	-0.1390115	0.4100160
O	-5.2329878	-0.0234065	-0.9312950
C	-3.8522158	-1.0061385	0.7828210
H	-3.7529918	-1.2279935	1.8495720
H	-3.7202078	-1.9216145	0.1988600
C	-2.5496548	1.0333715	1.3225310
H	-1.6702268	1.5980655	1.0088530
H	-2.4096938	0.6361375	2.3298290
H	-3.4485418	1.6506065	1.2721350
O	1.0981512	-2.0031035	0.9012870

H 0.5389422 -2.6286535 1.3875380
 E = -1107.51480381, H = -1107.088574
 G = -1107.167639

4.22_H+ • H₂O

C	2.3603918	0.0578043	-0.4434203
C	2.4971168	-1.0724057	-1.1523953
H	2.2949458	-1.0421817	-2.2283373
H	2.6069768	0.0450853	0.6208647
Os	-1.0833982	-1.1573907	0.3248257
O	-0.0390152	0.2560683	0.9393587
O	-1.0280002	-1.8845947	2.0567007
O	-2.7893282	-2.4173927	0.2630207
O	-2.2746252	0.1929803	-0.1431963
C	2.9737058	-2.3780657	-0.5956133
C	1.9130588	1.3687223	-1.0393453
H	2.3226488	2.2050193	-0.4577653
H	2.3119348	1.4603283	-2.0571483
C	0.3874848	1.5179403	-1.1247443
H	2.2719368	-3.1890717	-0.8308493
H	3.9373458	-2.6543517	-1.0431723
H	3.1033718	-2.3213617	0.4916327
H	0.1337308	2.4776823	-1.5951693
H	-0.0257212	0.7285563	-1.7710183
C	-0.3057622	1.4892443	0.2290617
C	-1.8359222	1.5580823	0.1254757
H	0.0775768	2.2847353	0.8800087
C	-2.5147602	2.0509553	1.3857537
H	-2.1426512	2.1392703	-0.7516413
H	-3.6010102	1.9448963	1.3004857
H	-2.1633702	1.4864213	2.2594497
H	-2.2823512	3.1111563	1.5383477
O	-0.1593272	-1.8752687	-0.8516923
H	-0.3791272	-1.4470307	2.6317587
H	-3.6212832	-2.0281197	-0.0485403
H	-2.9465742	-2.9077137	1.0873037

E = -781.757928807, H = -781.484275
 G = -781.548004

4.22_H+ • H₂O-extended

C	2.7027135	-0.9614649	-0.0247315
C	3.9731235	-0.6725089	0.2621775
H	4.1781165	0.0295701	1.0767265
H	2.4861535	-1.6678359	-0.8327615
Os	-2.2875455	-1.0430049	0.0431975
O	-1.3051045	0.0689441	1.1624365
O	-3.4699445	-1.3047359	1.4799155
O	-4.0410185	-1.5623459	-0.9977185
O	-2.3409615	0.4664001	-1.0451165
C	5.1616865	-1.2490379	-0.4423995
C	1.5187295	-0.3726429	0.6867415
H	0.9027645	-1.1763679	1.1196965
H	1.8593485	0.2558951	1.5212545
C	0.6524355	0.4601281	-0.2626475
H	5.7772875	-0.4532319	-0.8817675
H	5.8006075	-1.7965269	0.2629625

H	4.8542065	-1.9350569	-1.2397345
H	1.2446745	1.2859631	-0.6797055
H	0.3380165	-0.1539149	-1.1218905
C	-0.5670875	1.0698541	0.4137145
C	-1.5926295	1.6308121	-0.5751895
H	-0.2760395	1.8209021	1.1582065
C	-2.5621725	2.6237001	0.0291495
H	-1.0959975	2.0354321	-1.4651035
H	-3.3518795	2.8732171	-0.6867175
H	-3.0141545	2.2135441	0.9416385
H	-2.0277185	3.5448791	0.2880875
O	-1.2906545	-2.3019109	-0.3581425
H	-3.1121965	-0.9887929	2.3264145
H	-4.3097295	-0.9865149	-1.7317355
H	-4.8050295	-1.7533459	-0.4269595

E = -781.757106278, H = -781.482649

G = -781.547109

4.22' $\text{H}^+ \bullet \text{H}_2\text{O}$

C	2.2926865	-0.5138460	-0.4380660
C	2.5627175	-1.5515590	-1.2335100
H	2.6951455	-1.3733010	-2.3057510
H	2.1842755	-0.6829020	0.6359190
Os	-1.2874025	-0.8356760	0.9132950
O	0.0408825	0.4769330	1.1651870
O	-1.8684985	-0.9503810	2.5027490
O	-3.0056935	-2.4010600	0.6450230
C	2.7093255	-2.9664260	-0.7661090
C	2.1195555	0.8953140	-0.9394580
H	2.6614325	1.6038530	-0.2957960
H	2.5611365	0.9712040	-1.9407110
C	0.6536095	1.3444270	-1.0482390
H	1.9842245	-3.6191160	-1.2709500
H	3.7080065	-3.3543200	-1.0038980
H	2.5544495	-3.0416550	0.3164660
H	0.5993355	2.2774290	-1.6279040
H	0.0800565	0.5839840	-1.6011640
C	-0.0160845	1.6202750	0.2927000
C	-1.4790315	2.0214090	0.1570540
H	0.5222045	2.4114870	0.8318650
C	-2.1088655	2.6146680	1.3918520
H	-1.6607685	2.6080280	-0.7493280
H	-3.1920335	2.7375510	1.2727180
H	-1.9001865	1.9974040	2.2745580
H	-1.6791245	3.6097740	1.5556260
O	-0.4615915	-1.9895810	0.0053420
H	-2.7401485	-3.1908870	0.1510270
H	-3.3391695	-2.7014260	1.5039620
O	-2.1160825	0.6811570	-0.1239700
H	-3.0743635	0.7172390	-0.2704900

E = -781.72617941, H = -781.453127

G = -781.521516

4.22t

C	2.523756000	1.225479000	0.562987000
C	3.305356000	0.436303000	-0.175906000
H	3.561704000	0.752780000	-1.192761000

H	2.254193000	0.908914000	1.572601000
O	-0.272962000	0.704419000	1.036192000
O	0.808175000	-1.493821000	-1.027350000
O	-0.879375000	-1.935025000	1.190435000
O	-1.662037000	0.297522000	-0.974156000
C	3.845388000	-0.888712000	0.268871000
C	1.927811000	2.516481000	0.060593000
H	1.835855000	3.239136000	0.884017000
H	2.606515000	2.958161000	-0.680665000
C	0.556233000	2.341736000	-0.610338000
H	3.472108000	-1.689839000	-0.382934000
H	4.942356000	-0.906446000	0.219424000
H	3.537904000	-1.109416000	1.298186000
H	0.248542000	3.293607000	-1.067071000
H	0.647175000	1.608875000	-1.427001000
C	-0.562814000	1.916327000	0.331853000
C	-1.872373000	1.606055000	-0.407502000
H	-0.712463000	2.680442000	1.108550000
C	-3.086045000	1.589385000	0.500671000
H	-2.021491000	2.285418000	-1.257907000
H	-3.961485000	1.225031000	-0.047070000
H	-2.900562000	0.932516000	1.359863000
H	-3.295661000	2.602289000	0.866216000
Os	-0.447223000	-0.839797000	-0.082129000

E = -704.869085081, H = -704.636744
G = -704.697675

4.22t_{H2O}

C	2.994729000	0.534852000	0.377708000
C	3.992209000	-0.144639000	-0.189359000
H	4.631999000	0.363987000	-0.917963000
H	2.347891000	0.029498000	1.097245000
Os	-0.746076000	-0.641682000	-0.006918000
O	0.037218000	0.852435000	1.023494000
O	-1.199220000	-1.326105000	1.676195000
O	-1.868416000	-1.934341000	-0.896458000
O	-1.513880000	0.771413000	-0.951808000
C	4.294117000	-1.587192000	0.086007000
C	2.653062000	1.961381000	0.051973000
H	2.637434000	2.567831000	0.971247000
H	3.440777000	2.372430000	-0.593312000
C	1.300339000	2.115816000	-0.661641000
H	4.234614000	-2.180256000	-0.836879000
H	5.308502000	-1.713501000	0.488324000
H	3.577695000	-2.000436000	0.805414000
H	1.262947000	3.095612000	-1.160233000
H	1.207329000	1.349412000	-1.445108000
C	0.094158000	2.051050000	0.271051000
C	-1.233905000	2.115982000	-0.495137000
H	0.146918000	2.886692000	0.986957000
C	-2.397402000	2.587777000	0.355557000
H	-1.140746000	2.721529000	-1.406733000
H	-3.342799000	2.448029000	-0.178939000
H	-2.427839000	2.017921000	1.293303000
H	-2.278729000	3.651852000	0.592873000
O	0.679413000	-1.279556000	-0.710821000

H -0.802555000 -0.760890000 2.359634000
H -1.366456000 -2.562780000 -1.431794000
E = -781.306767001, H = -781.046663
G = -781.111060

4.22t_H+

C 1.927539000 1.749117000 0.540334000
C 2.669446000 0.721703000 -0.073882000
H 2.742659000 0.722722000 -1.164137000
H 1.973885000 1.814909000 1.627645000
O -0.047600000 0.774175000 0.855531000
O -1.842200000 -0.146099000 -0.663264000
C 3.362671000 -0.345571000 0.666705000
C 1.333752000 2.873409000 -0.233805000
H 1.196121000 3.742167000 0.417939000
H 2.015822000 3.148299000 -1.050561000
C -0.028301000 2.459916000 -0.837358000
H 3.100951000 -1.325874000 0.241575000
H 4.449045000 -0.239326000 0.506089000
H 3.155205000 -0.319701000 1.740533000
H -0.535180000 3.340643000 -1.246475000
H 0.113620000 1.742027000 -1.658232000
C -0.845643000 1.820550000 0.273968000
C -2.156003000 1.177018000 -0.185617000
H -1.030918000 2.548137000 1.075902000
C -3.178373000 1.060639000 0.928542000
H -2.570033000 1.722665000 -1.043894000
H -4.039394000 0.480284000 0.582867000
H -2.737392000 0.557564000 1.799205000
H -3.524930000 2.055976000 1.230460000
Os -0.201222000 -0.900309000 -0.177628000
O 0.912519000 -1.204152000 -1.399906000
O 0.000729000 -1.844001000 1.430326000
H 0.285265000 -1.307102000 2.186014000
E = -705.286173565, H = -705.043539
G = -705.102858

4.23

C 2.150016000 1.220828000 0.539588000
C 2.673000000 0.094786000 -0.101827000
H 3.061630000 0.249668000 -1.108287000
H 2.190085000 1.247517000 1.627417000
O 0.103415000 0.772882000 0.850555000
O 1.216821000 -0.862374000 -0.877944000
O -1.025901000 -2.239187000 0.574676000
O -1.668268000 0.343388000 -0.884864000
C 3.302853000 -1.011931000 0.699996000
C 1.862562000 2.513954000 -0.179639000
H 1.978662000 3.353656000 0.517028000
H 2.578874000 2.655504000 -0.998847000
C 0.430361000 2.512182000 -0.741374000
H 3.307426000 -1.945448000 0.128238000
H 4.339710000 -0.762359000 0.962507000
H 2.739871000 -1.174593000 1.627966000
H 0.123274000 3.515958000 -1.061910000
H 0.369006000 1.842192000 -1.609962000

C	-0.495417000	1.979330000	0.343098000
C	-1.871720000	1.564952000	-0.167083000
H	-0.566527000	2.683352000	1.185062000
C	-2.886927000	1.383244000	0.949226000
H	-2.241362000	2.292939000	-0.904412000
H	-3.813398000	0.964988000	0.541949000
H	-2.495861000	0.694785000	1.709952000
H	-3.111676000	2.345993000	1.425459000
Os	-0.374429000	-0.837183000	-0.123598000

E = -704.861451374, H = -704.629334
G = -704.683390

4.23_{H2O}

C	2.549302000	0.323281000	0.488016000
C	2.553091000	-0.888346000	-0.213073000
H	2.903560000	-0.850081000	-1.244947000
H	2.667240000	0.281667000	1.569227000
Os	-0.601010000	-0.524950000	-0.090796000
O	0.566395000	0.758810000	0.862634000
O	0.772401000	-1.249331000	-0.846629000
O	-1.114092000	-1.251220000	1.577720000
O	-1.344880000	1.029454000	-0.852408000
C	2.736253000	-2.188164000	0.518903000
C	2.834683000	1.628166000	-0.209985000
H	3.223009000	2.360746000	0.507969000
H	3.593461000	1.483638000	-0.989172000
C	1.531708000	2.153164000	-0.820287000
H	2.372905000	-3.025799000	-0.086168000
H	3.797014000	-2.361480000	0.744315000
H	2.178017000	-2.169984000	1.463734000
H	1.634355000	3.181242000	-1.189605000
H	1.219337000	1.516483000	-1.660415000
C	0.487614000	2.068298000	0.280730000
C	-0.945705000	2.250763000	-0.222097000
H	0.712073000	2.798112000	1.073370000
C	-1.918707000	2.586470000	0.896422000
H	-0.971920000	3.027383000	-1.000606000
H	-2.943045000	2.582495000	0.509439000
H	-1.838013000	1.839184000	1.697325000
H	-1.699386000	3.577385000	1.313285000
O	-2.132607000	-1.502718000	-0.870601000
H	-2.233142000	-2.402647000	-0.539504000
H	-1.885883000	-1.823868000	1.454741000

E = -781.302023679, H = -781.041830
G = -781.099533

4.23_[ox]

C	3.080974000	-1.771730000	0.502487000
C	2.700383000	-0.521216000	-0.235503000
C	2.530889000	0.685032000	0.431515000
C	2.575475000	2.015231000	-0.269503000
C	1.185727000	2.382703000	-0.804763000
C	0.181660000	2.126175000	0.309228000
C	-1.263493000	2.108963000	-0.186333000
C	-2.279623000	2.229826000	0.937504000
O	0.399871000	0.822594000	0.808349000

Os	-0.603701000	-0.689791000	-0.053224000
O	-1.406659000	0.881215000	-0.873047000
O	0.916699000	-1.184459000	-0.756162000
O	-0.769293000	-1.422050000	1.473051000
H	2.961618000	-0.470712000	-1.293706000
H	2.608847000	0.677523000	1.517755000
H	2.912968000	2.788354000	0.431886000
H	3.293658000	1.977312000	-1.098475000
H	2.780326000	-2.659950000	-0.062805000
H	4.168801000	-1.810205000	0.649547000
H	2.595295000	-1.797698000	1.485801000
H	1.145013000	3.427562000	-1.138131000
H	0.927832000	1.738229000	-1.656239000
H	0.313806000	2.843684000	1.133974000
H	-1.419781000	2.900512000	-0.933713000
H	-3.289742000	2.082608000	0.541645000
H	-2.085444000	1.470970000	1.707701000
H	-2.219724000	3.222585000	1.400697000
O	-1.776135000	-1.534373000	-0.995781000

E = -780.006653366, H = -779.771497
G = -779.826747

4.23_{[ox]H⁺}

C	3.355126000	-1.428837000	0.347804000
C	2.975560000	-0.114577000	-0.248354000
C	2.575547000	0.970065000	0.485193000
C	2.320142000	2.320111000	-0.114998000
C	0.899283000	2.429860000	-0.701517000
C	-0.133982000	2.075456000	0.353485000
C	-1.564289000	1.956931000	-0.215131000
C	-2.659335000	2.073058000	0.820868000
O	0.125244000	0.782634000	0.899582000
Os	-0.536022000	-0.712168000	-0.125824000
O	-1.586232000	0.636287000	-0.809060000
O	0.855349000	-0.834596000	-1.083164000
H	3.176548000	0.030307000	-1.313302000
H	2.530061000	0.869429000	1.570739000
H	2.459950000	3.098887000	0.643525000
H	3.036816000	2.508323000	-0.924405000
H	2.949649000	-2.262903000	-0.238367000
H	4.449238000	-1.534916000	0.323272000
H	3.020108000	-1.510197000	1.387228000
H	0.711494000	3.451474000	-1.055865000
H	0.796846000	1.755664000	-1.563718000
H	-0.115493000	2.787866000	1.188806000
H	-1.713787000	2.647927000	-1.054547000
H	-3.629129000	1.823470000	0.379093000
H	-2.458538000	1.406682000	1.669660000
H	-2.700653000	3.105247000	1.186970000
O	-1.561769000	-2.046011000	-0.400432000
O	-0.070924000	-1.464527000	1.556316000
H	-0.477109000	-2.335215000	1.693516000

E = -780.404017409, H = -780.156548
G = -780.216637

• 4.23'_{[ox]H⁺}

- C 2.6212157 -2.5352015 -0.6273056
- C 2.0790217 -1.1466745 -0.5153336
- C 1.9743087 -0.4858905 0.6873454
- C 1.8843917 1.0009625 0.8422714
- C 0.7606337 1.6209095 0.0235514
- C -0.6100943 1.2732525 0.6117054
- C -1.7081583 1.4404845 -0.4375456
- C -3.1133503 1.4693905 0.1304314
- O -0.6303283 -0.0852455 1.0744764
- Os -1.3682553 -1.6033315 0.2308264
- O -1.4739503 0.2895645 -1.2736626
- O 0.0610357 -2.0511115 -0.6151546
- H 2.0103477 -0.5665255 -1.4392556
- H 2.1115147 -1.0780605 1.5964854
- H 1.7723007 1.2595155 1.9015814
- H 2.8399517 1.4348945 0.5084724
- H 2.1349397 -3.0883215 -1.4384746
- H 3.6929277 -2.4802585 -0.8650946
- H 2.5052057 -3.0842995 0.3135434
- H 0.8457657 2.7148825 0.0118244
- H 0.8019757 1.2758605 -1.0165706
- H -0.8211253 1.8817145 1.5000674
- H -1.5002373 2.3442955 -1.0245786
- H -3.8610273 1.4141085 -0.6700896
- H -3.2939713 0.6429665 0.8303604
- H -3.2666023 2.4106125 0.6698574
- O -2.7688663 -1.8122375 -0.7011976
- O -1.4621313 -2.6056925 1.5688844
- H -2.2174383 0.1494355 -1.8774206
- E = -780.425962889, H = -780.177232
- G = -780.236513

4.23_H+

C	2.271739000	1.220856000	0.620833000
C	2.846273000	0.241607000	-0.166684000
H	3.051734000	0.489601000	-1.210153000
H	2.253284000	1.062197000	1.699720000
O	-0.070594000	0.658921000	0.953256000
O	1.161905000	-0.825470000	-0.909449000
O	-1.663365000	0.257128000	-0.953996000
C	3.549710000	-0.947262000	0.406311000
C	1.822854000	2.548514000	0.092965000
H	1.777162000	3.276928000	0.910629000
H	2.548603000	2.915081000	-0.645023000
C	0.447109000	2.463691000	-0.589770000
H	3.468990000	-1.811687000	-0.261614000
H	4.618748000	-0.718467000	0.514951000
H	3.152604000	-1.205892000	1.394979000
H	0.122017000	3.459356000	-0.915585000
H	0.499631000	1.827455000	-1.485159000
C	-0.578403000	1.893851000	0.379242000
C	-1.908252000	1.526209000	-0.281903000
H	-0.715359000	2.558937000	1.241806000
C	-3.054674000	1.375472000	0.697215000
H	-2.154251000	2.230833000	-1.085510000

H	-3.937428000	0.982383000	0.183169000
H	-2.778777000	0.694054000	1.513127000
H	-3.307978000	2.351964000	1.126108000
Os	-0.368945000	-0.808826000	-0.164191000
O	-0.904042000	-2.045581000	1.126792000
H	-1.128516000	-2.939585000	0.815016000

E = -705.279797089, H = -705.037627
G = -705.092027

4.23' _{H+}

C	1.7973626	0.6506376	0.3464639
C	2.5628816	-0.3782154	-0.1868841
H	2.9348746	-0.2450994	-1.2031141
H	1.7293816	0.7225376	1.4317429
O	-0.2748224	-0.2555054	0.7250249
O	1.1777956	-1.5711874	-1.0586191
O	-2.0290184	-0.9651854	-0.8788141
C	3.2863946	-1.3581674	0.6856159
C	1.2206536	1.7762316	-0.4642241
H	1.2006026	2.6867056	0.1465249
H	1.8499606	1.9717556	-1.3407031
C	-0.2126954	1.4652986	-0.9473601
H	3.4052216	-2.3201674	0.1764649
H	4.2912206	-0.9788454	0.9149729
H	2.7533206	-1.5121234	1.6316519
H	-0.7013204	2.3766936	-1.3140921
H	-0.1680314	0.7531936	-1.7845591
C	-1.0162674	0.8536066	0.1954109
C	-2.3878904	0.3257256	-0.2142411
H	-1.1385344	1.5685756	1.0202509
C	-3.3271784	0.0439406	0.9315689
H	-2.8420864	0.9423226	-0.9980291
H	-4.2275614	-0.4748004	0.5857939
H	-2.8284384	-0.5598624	1.6993009
H	-3.6339384	0.9968806	1.3789469
Os	-0.3338924	-1.8975504	-0.2804601
O	-0.5247134	-3.3987414	0.4447279
H	-2.5632804	-1.2186534	-1.6433611

E = -705.268514455, H = -705.025237
G = -705.080606

4.23 • NMO

C	0.1432036	2.8390000	-0.6983403
C	-1.2172074	2.1884190	-0.6594343
C	-1.8506564	2.0084940	0.5771717
C	-3.3477854	2.0329080	0.7119137
C	-3.9271724	0.7596460	0.0961117
C	-3.2630184	-0.4221440	0.7895497
O	-1.8515334	-0.1412050	0.8865637
Os	-0.8104734	-0.9915770	-0.5193663
C	-3.4289644	-1.7198370	-0.0060993
C	-3.1946964	-2.9649540	0.8394157
O	-0.8498864	0.5848240	-1.4178773
H	-1.8813204	2.4672950	-1.4804073
H	-1.2467014	2.0878800	1.4799377
H	-3.6289684	2.0907530	1.7713997

H	-3.7609254	2.9182730	0.2079957
H	0.7224566	2.5344560	0.1793697
H	0.6834816	2.5479370	-1.6083083
H	0.0442376	3.9328010	-0.6974143
H	-5.0185494	0.7072240	0.2067537
H	-3.6823774	0.7101300	-0.9742053
H	-3.6402534	-0.5279180	1.8180987
H	-4.4429684	-1.7541570	-0.4355133
H	-3.1894484	-3.8509430	0.1953527
H	-2.2273384	-2.9080950	1.3554947
H	-3.9886974	-3.0735290	1.5897217
C	4.2698996	-1.7065010	0.2893467
C	4.5868196	0.5932460	0.1139427
C	3.0992826	0.8583470	0.3064967
H	4.4852526	-1.8716850	-0.7798743
H	5.1464256	1.4199090	0.5644037
H	4.8526186	0.5477700	-0.9553913
H	2.8600346	1.0019550	1.3640977
H	2.7603676	1.7256240	-0.2673963
H	4.6253126	-2.5795100	0.8457397
N	2.2459166	-0.2986840	-0.1177263
O	4.9959616	-0.5886050	0.7678917
C	2.7816546	-1.5410800	0.5375917
H	2.1815966	-2.3742920	0.1646357
H	2.5788806	-1.3941340	1.6025677
O	-2.5215444	-1.6471370	-1.1007373
O	0.1306516	-2.4364120	-0.4876033
C	2.2176336	-0.4119140	-1.6051213
H	1.7374936	-1.3593140	-1.8573563
H	1.6103656	0.4240410	-1.9606053
H	3.2328786	-0.3732220	-2.0062813
O	0.9780606	-0.0440810	0.3734927

E = -1107.04577856, H = -1106.633754
G = -1106.704239

4.23_H+ • NMO

C	-1.0392709	3.2581261	-0.4276506
C	-2.2113069	2.3219291	-0.4710146
C	-2.6850689	1.7066101	0.6879294
C	-4.0537459	1.0871741	0.7428984
C	-3.9785709	-0.3297799	0.1638184
C	-2.8192439	-1.0250959	0.8582854
O	-1.6649649	-0.1617719	0.7950574
Os	-0.6300809	-0.4683879	-0.8364686
C	-2.4262759	-2.3517129	0.2045594
C	-1.6225429	-3.2539619	1.1231764
O	-1.3097179	0.9216461	-1.5648036
H	-2.9230649	2.4535081	-1.2864126
H	-2.1754829	1.9253071	1.6250724
H	-4.4059439	1.0428091	1.7797404
H	-4.7653149	1.6928921	0.1686144
H	-0.5635239	3.3335651	-1.4120686
H	-1.3668819	4.2650531	-0.1383076
H	-0.3048699	2.9145601	0.3130794
H	-4.9117189	-0.8826969	0.3247524
H	-3.7883279	-0.2926059	-0.9183356

H	-3.0463429	-1.1773229	1.9222754
H	-3.3211669	-2.8699749	-0.1645106
H	-1.2696089	-4.1321129	0.5732554
H	-0.7583029	-2.7076289	1.5263594
H	-2.2425379	-3.5899069	1.9622124
C	4.3668521	-1.1797849	-0.2893686
C	4.4315621	0.8452521	0.8480424
C	2.9123701	0.8916601	0.9561724
H	4.7110391	-0.7233319	-1.2319536
H	4.8491041	1.3174471	1.7430154
H	4.7951651	1.4019771	-0.0308946
H	2.5765671	0.3915451	1.8687844
H	2.5191741	1.9123011	0.9258194
H	4.7560531	-2.2015619	-0.2466146
N	2.2522791	0.1351241	-0.1681146
O	4.8905131	-0.4851869	0.8210024
C	2.8476991	-1.2488779	-0.2284246
H	2.4067371	-1.7451439	-1.0947146
H	2.5228111	-1.7314489	0.6990374
O	-1.6353139	-2.0420419	-0.9614966
C	2.3509861	0.8851391	-1.4532986
H	1.9218221	0.2659311	-2.2426596
H	1.7891241	1.8136791	-1.3204876
H	3.4011711	1.1021391	-1.6554536
O	0.9031321	0.0613831	0.2547614
O	0.5935101	-1.3365739	-2.1194346
H	0.1215181	-2.0098459	-2.6252346

E = -1107.52383868, H = -1107.098750

G = -1107.171440

4.23'_{H+} • NMO

C	-0.3372553	3.0731435	-1.1381046
C	-1.5539103	2.2325195	-0.8608836
C	-2.0238843	2.1117575	0.4474174
C	-3.4762843	1.9302665	0.7732234
C	-3.9368273	0.5808295	0.2420544
C	-3.0713183	-0.4927015	0.8989394
O	-1.7049623	-0.0410755	0.9531644
Os	-0.4833183	-0.8417735	-0.3553366
C	-3.1943103	-1.8166465	0.1457624
C	-2.7347563	-3.0327195	0.9258904
O	-0.7072523	0.6143215	-1.3636836
H	-2.3024813	2.1996455	-1.6549286
H	-1.3508373	2.3990725	1.2561164
H	-3.6276713	1.9782095	1.8578934
H	-4.0661093	2.7377815	0.3184674
H	0.1049067	2.8065305	-2.1048226
H	-0.6068953	4.1361795	-1.1701386
H	0.4049357	2.9351035	-0.3403866
H	-4.9947433	0.3914495	0.4630314
H	-3.8029823	0.5346225	-0.8471686
H	-3.3889473	-0.6492325	1.9393124
H	-4.2318923	-1.9422675	-0.1881726
H	-2.6781643	-3.9179415	0.2803244
H	-1.7560613	-2.8787575	1.3914314
H	-3.4719203	-3.2361975	1.7111644

C	4.4187307	-1.6165375	-0.1264766
C	4.6921847	0.5687245	0.6273584
C	3.2005127	0.7190495	0.9002364
H	4.6579117	-1.3457815	-1.1682546
H	5.2353547	1.1578955	1.3727384
H	4.9653607	0.9490255	-0.3706226
H	2.9618627	0.4073305	1.9210124
H	2.8395277	1.7377525	0.7288094
H	4.7783357	-2.6348075	0.0491424
N	2.3817997	-0.1860985	0.0207194
O	5.0973627	-0.7719695	0.7766674
C	2.9184217	-1.5883365	0.1293874
H	2.3564317	-2.2097655	-0.5730606
H	2.6931827	-1.8969595	1.1546514
O	-2.3962413	-1.5940855	-1.0653006
H	-2.2791743	-2.4320545	-1.5367726
O	0.0209937	-2.4799805	-0.5099306
C	2.3483347	0.3056895	-1.3842396
H	1.8558277	-0.4454015	-2.0063216
H	1.7777217	1.2364095	-1.3924476
H	3.3714757	0.4620925	-1.7292696
O	1.0970267	-0.1543095	0.6014074

E = -1107.49217207, H = -1107.066503
G = -1107.139156

4.23_H+ • H₂O

C	2.1821319	-0.1681917	0.3803867
C	2.1881839	-1.3803297	-0.2774623
H	2.3877759	-1.3724087	-1.3506413
H	2.2264509	-0.1759887	1.4693697
Os	-1.1339841	-0.9163717	-0.0226283
O	-0.0666121	0.3339913	0.9015237
O	0.1379909	-1.7034267	-0.8411463
O	-1.7640091	-1.5772267	1.6140967
O	-1.9512251	0.5630933	-0.7980733
C	2.3316699	-2.6847227	0.4414097
C	2.3125249	1.1475893	-0.3269853
H	2.7002469	1.9053113	0.3636307
H	3.0235689	1.0537353	-1.1577393
C	0.9589599	1.6131033	-0.8855533
H	1.8153159	-3.4890777	-0.0940213
H	3.3939909	-2.9586247	0.4979947
H	1.9405419	-2.6159367	1.4635217
H	1.0414399	2.6199793	-1.3130413
H	0.6297159	0.9391253	-1.6899813
C	-0.0698681	1.6158403	0.2345327
C	-1.5063621	1.8411933	-0.2617233
H	0.1958419	2.3535443	1.0022537
C	-2.4551431	2.2839453	0.8332217
H	-1.5184011	2.5368143	-1.1095813
H	-3.4821351	2.3109023	0.4550227
H	-2.4006331	1.5949483	1.6865817
H	-2.1855861	3.2894763	1.1761087
O	-2.7222831	-2.1440517	-0.9446073
H	-2.4617821	-2.9431697	-1.4250143
H	-2.4600101	-2.2464527	1.5165407

H -3.2883161 -1.6266117 -1.5379953
 E = -781.741284440, H = -781.470275
 G = -781.529354

4.23' _{H+} • H₂O

C	2.0774618	-0.0465334	0.4189989
C	2.1699428	-1.3026914	-0.1838091
H	2.5246838	-1.3217674	-1.2149201
H	2.1275608	-0.0029554	1.5059189
Os	-1.0446492	-1.0795364	-0.1332681
O	-0.0861842	0.2655486	0.8454259
O	0.4010908	-1.7248474	-0.8645531
O	-1.8387142	-1.8418734	1.2100669
C	2.4060458	-2.5326514	0.6428699
C	2.1826678	1.2447266	-0.3432761
H	2.6028708	2.0207416	0.3072229
H	2.8559248	1.1215786	-1.2005321
C	0.8046578	1.7061326	-0.8512251
H	2.0938358	-3.4306944	0.1004979
H	3.4751858	-2.6317024	0.8708489
H	1.8554878	-2.4737634	1.5899549
H	0.8489638	2.7370096	-1.2235101
H	0.4816478	1.0645546	-1.6846861
C	-0.1893422	1.5851246	0.2989049
C	-1.6432052	1.8191526	-0.1025981
H	0.0661328	2.2853496	1.1059969
C	-2.6029322	1.9380986	1.0565539
H	-1.7295582	2.6433636	-0.8193941
H	-3.6412832	1.9907106	0.7081229
H	-2.4864982	1.0891516	1.7418509
H	-2.3872922	2.8642276	1.6016599
O	-2.2331872	-2.6775104	-1.1463181
H	-2.5696312	-3.1764194	-0.3797481
H	-1.7310052	-3.2918444	-1.7004351
O	-1.9541662	0.5816846	-0.8789041
H	-2.8365132	0.5776336	-1.2777171

E = -781.699019342, H = -781.426867
 G = -781.487412

4.23t

C	2.344930000	1.296264000	0.565557000
C	2.826424000	0.274024000	-0.231855000
H	2.980855000	0.494853000	-1.289926000
H	2.341677000	1.146552000	1.644551000
O	-0.144689000	0.740263000	0.995376000
O	1.284845000	-0.853810000	-0.758656000
O	-0.820506000	-2.258482000	0.755287000
O	-1.668379000	0.253979000	-0.960642000
C	3.635131000	-0.851302000	0.342545000
C	1.793999000	2.584116000	0.028741000
H	1.729208000	3.320300000	0.840436000
H	2.483665000	2.988405000	-0.725790000
C	0.407025000	2.438714000	-0.626449000
H	3.566644000	-1.738303000	-0.294460000
H	4.690736000	-0.554554000	0.412757000
H	3.276927000	-1.106004000	1.347038000

H	0.081460000	3.413710000	-1.014630000
H	0.473716000	1.747773000	-1.478829000
C	-0.634375000	1.916734000	0.356507000
C	-1.939981000	1.516901000	-0.328253000
H	-0.811656000	2.656651000	1.152307000
C	-3.101289000	1.373711000	0.638225000
H	-2.189181000	2.219052000	-1.136730000
H	-3.963741000	0.935232000	0.124887000
H	-2.814632000	0.720669000	1.472942000
H	-3.388937000	2.353730000	1.039561000
Os	-0.390238000	-0.854587000	-0.089673000

E = -704.837647054, H = -704.607585
G = -704.665175

4.23t_{H2O}

C	2.492414000	1.140627000	0.508399000
C	2.779700000	0.019457000	-0.266314000
H	3.002152000	0.201716000	-1.320464000
H	2.496804000	1.036547000	1.591671000
Os	-0.426451000	-0.686612000	-0.017815000
O	-0.024787000	0.985915000	1.018666000
O	1.186900000	-0.863142000	-0.779348000
O	-0.729463000	-1.617767000	1.573567000
O	-1.590916000	0.467296000	-0.888092000
C	3.448399000	-1.177317000	0.351009000
C	2.128221000	2.468204000	-0.084340000
H	2.143727000	3.239004000	0.697088000
H	2.877304000	2.750198000	-0.839632000
C	0.744997000	2.454392000	-0.751950000
H	3.266886000	-2.074070000	-0.250192000
H	4.532222000	-1.012578000	0.410311000
H	3.065035000	-1.344469000	1.365006000
H	0.539010000	3.429717000	-1.215357000
H	0.731645000	1.700121000	-1.552300000
C	-0.346352000	2.130498000	0.271209000
C	-1.688302000	1.828148000	-0.404141000
H	-0.461590000	2.981138000	0.963772000
C	-2.868930000	1.924990000	0.542481000
H	-1.843629000	2.448470000	-1.298114000
H	-3.772053000	1.526958000	0.067657000
H	-2.655050000	1.352149000	1.453775000
H	-3.045481000	2.972895000	0.814388000
O	-0.998379000	-2.306431000	-0.957744000
H	-0.347619000	-2.564008000	-1.622461000
H	-1.006827000	-2.522216000	1.354276000

E = -781.272799513, H = -781.015903
G = -781.075413

4.23t_{H+}

C	2.283275000	0.492219000	0.331179000
C	2.622317000	-0.932969000	0.342868000
H	3.123194000	-1.343607000	-0.531297000
H	2.712201000	1.009034000	1.201691000
O	0.769810000	0.703209000	0.630894000
O	0.448746000	-1.427624000	-1.176616000
O	-1.571339000	0.958355000	-0.373648000

C	2.445367000	-1.770462000	1.555027000
C	2.496616000	1.262547000	-0.976645000
H	3.375186000	1.907100000	-0.876402000
H	2.676240000	0.566180000	-1.801128000
C	1.211962000	2.085427000	-1.211097000
H	2.072903000	-2.768827000	1.290484000
H	3.416125000	-1.928201000	2.053576000
H	1.767266000	-1.306901000	2.281747000
H	1.415986000	3.112057000	-1.527887000
H	0.579445000	1.613742000	-1.973785000
C	0.496720000	2.057728000	0.129006000
C	-1.017552000	2.188649000	0.125277000
H	0.947874000	2.747685000	0.853109000
C	-1.594554000	2.480760000	1.499389000
H	-1.306168000	2.965639000	-0.594791000
H	-2.687507000	2.452242000	1.458109000
H	-1.246257000	1.738071000	2.230237000
H	-1.284221000	3.477328000	1.835107000
Os	-0.603019000	-0.652682000	-0.134931000
O	-2.195381000	-1.564471000	0.143672000
H	-3.012400000	-1.176873000	-0.208492000

E = -705.275705066, H = -705.033621
G = -705.090929

4.23q

C	2.252990000	0.409430000	0.003035000
C	2.490014000	-1.048769000	0.082743000
H	2.804717000	-1.545091000	-0.831898000
H	2.967206000	0.955981000	0.643694000
O	0.934474000	0.738997000	0.567623000
O	0.537599000	-1.865831000	-0.080340000
O	-2.224525000	-1.505743000	-0.417361000
O	-1.447450000	1.212328000	-0.401436000
C	2.831290000	-1.677997000	1.388057000
C	2.187792000	1.030210000	-1.391327000
H	3.185336000	1.306838000	-1.746148000
H	1.770238000	0.292765000	-2.088314000
C	1.241117000	2.239602000	-1.232351000
H	2.575524000	-2.742766000	1.371224000
H	3.908301000	-1.588193000	1.605415000
H	2.277002000	-1.199982000	2.205361000
H	1.762725000	3.194754000	-1.346601000
H	0.425509000	2.199613000	-1.961711000
C	0.665529000	2.107201000	0.188187000
C	-0.849709000	2.270951000	0.293772000
H	1.189930000	2.758450000	0.902160000
C	-1.316404000	2.309750000	1.745997000
H	-1.120500000	3.216104000	-0.204949000
H	-2.409799000	2.350851000	1.776471000
H	-0.986847000	1.404509000	2.276366000
H	-0.910074000	3.185498000	2.268707000
Os	-0.748102000	-0.635126000	-0.114294000

E = -704.829362451, H = -704.601197
G = -704.654218

4.23q_{H2O}

C	2.187508000	1.316645000	0.504262000
C	2.672665000	0.299323000	-0.341585000
H	2.828220000	0.547268000	-1.390257000
H	2.285244000	1.167426000	1.577977000
Os	-0.342378000	-0.737814000	-0.008773000
O	0.033612000	0.998831000	0.973016000
O	0.826732000	-0.546144000	-1.364488000
O	0.431943000	-1.644673000	1.524975000
O	-1.632021000	0.428039000	-0.942049000
C	3.243683000	-0.969017000	0.175506000
C	1.837706000	2.662499000	-0.038218000
H	1.826718000	3.402863000	0.770124000
H	2.599543000	2.959588000	-0.773604000
C	0.457575000	2.617267000	-0.722119000
H	3.122794000	-1.765294000	-0.564519000
H	4.322421000	-0.823214000	0.348298000
H	2.763958000	-1.258546000	1.116180000
H	0.183271000	3.613435000	-1.090407000
H	0.469385000	1.914580000	-1.565394000
C	-0.537071000	2.119573000	0.320911000
C	-1.871243000	1.657433000	-0.291023000
H	-0.706779000	2.902802000	1.077909000
C	-2.957730000	1.520678000	0.769265000
H	-2.191954000	2.384262000	-1.055718000
H	-3.854826000	1.080094000	0.321363000
H	-2.612720000	0.867819000	1.583287000
H	-3.215969000	2.498900000	1.195980000
O	-1.070066000	-2.436121000	-0.574232000
H	-1.028947000	-2.563851000	-1.529410000
H	0.310217000	-2.600091000	1.445144000
E = -781.245938244, H = -780.990407			
G = -781.051308			

4.23q_H⁺

C	-2.533604000	1.078909000	-0.410861000
C	-2.841295000	-0.097665000	0.318956000
H	-2.656809000	-0.085766000	1.395385000
H	-2.710887000	1.049032000	-1.486377000
O	-0.061568000	0.845175000	-0.895264000
O	-1.219767000	-1.303538000	-0.046342000
O	1.686052000	0.426555000	0.801180000
C	-3.818452000	-1.087450000	-0.197989000
C	-2.123457000	2.366693000	0.218101000
H	-2.198195000	3.168538000	-0.524228000
H	-2.831954000	2.595895000	1.028734000
C	-0.702580000	2.355939000	0.819426000
H	-3.671491000	-2.063893000	0.271926000
H	-4.825999000	-0.732203000	0.072650000
H	-3.761055000	-1.172379000	-1.287759000
H	-0.504676000	3.336666000	1.268211000
H	-0.629282000	1.607198000	1.622150000
C	0.339845000	2.043040000	-0.248853000
C	1.736329000	1.772378000	0.331411000
H	0.381317000	2.838091000	-1.005990000
C	2.840950000	1.913000000	-0.701338000
H	1.926716000	2.412388000	1.203498000

H	3.792619000	1.567988000	-0.285494000
H	2.603566000	1.322460000	-1.595660000
H	2.947327000	2.964808000	-0.992060000
Os	0.474559000	-0.796718000	-0.026417000
O	1.629489000	-2.238061000	0.234017000
H	2.412268000	-2.168353000	0.800845000

E = -705.245602054, H = -705.005952
G = -705.061909

4.24

C	1.858560000	-1.176844000	0.386101000
C	0.804803000	-2.254678000	0.148057000
H	1.271851000	-3.079257000	-0.412093000
H	2.500310000	-1.418808000	1.244521000
O	1.094274000	0.001283000	0.731141000
O	-0.172045000	-1.686079000	-0.713179000
O	-2.566755000	-0.003351000	0.144842000
O	-0.176658000	1.686081000	-0.712837000
C	0.201953000	-2.786648000	1.440235000
C	2.670222000	-0.769799000	-0.850619000
H	3.680235000	-1.188002000	-0.803709000
H	2.176541000	-1.154677000	-1.748840000
C	2.667170000	0.775796000	-0.851676000
H	-0.635593000	-3.451766000	1.204777000
H	0.951846000	-3.349782000	2.010698000
H	-0.169856000	-1.959956000	2.058793000
H	3.675560000	1.198143000	-0.806882000
H	2.170508000	1.157462000	-1.749639000
C	1.855580000	1.181182000	0.385535000
C	0.799270000	2.256691000	0.148097000
H	2.497410000	1.424598000	1.243493000
C	0.195741000	2.787020000	1.440621000
H	1.264192000	3.082447000	-0.412089000
H	-0.643324000	3.450386000	1.205635000
H	-0.174055000	1.959357000	2.059086000
H	0.944621000	3.351623000	2.010961000
Os	-0.937639000	-0.001073000	-0.212928000

E = -704.947096787, H = -704.710782
G = -704.765579

4.24 • NMO

C	3.8206669	-2.7381150	-0.1427321
C	2.8888199	-1.5637970	-0.4036261
C	3.3618969	-0.3358460	0.4117889
C	4.2132599	0.6002600	-0.4468951
C	3.1462679	1.5103970	-1.0672821
C	2.2442499	1.7683890	0.1260239
O	2.2368689	0.4952690	0.8384339
Os	0.4011159	-0.5392740	0.4875799
C	0.7908219	2.1835340	-0.1426121
C	0.1737309	2.8445110	1.0854199
O	1.5559879	-1.9540010	-0.1501411
H	2.9530139	-1.2939580	-1.4739851
H	3.8495009	-0.6579340	1.3387919
H	4.8999109	1.1900020	0.1724809
H	4.7986809	0.0431580	-1.1862481

H	3.5291359	-3.5853530	-0.7721391
H	4.8652309	-2.4773600	-0.3619031
H	3.7399169	-3.0388820	0.9094279
H	3.5541399	2.4384210	-1.4802081
H	2.5814229	0.9865830	-1.8499231
H	2.7139849	2.4996240	0.7996929
H	0.8057089	2.8975430	-0.9822521
H	-0.8704861	3.1012110	0.8703729
H	0.2065349	2.1475170	1.9347299
H	0.7130829	3.7631590	1.3492049
C	-4.0124081	0.3102760	-1.3797971
C	-4.1409901	0.5152650	0.9458879
C	-2.7954731	-0.1704990	1.1270509
H	-4.8568241	-0.3972090	-1.4426661
H	-4.2494101	1.2745240	1.7265559
H	-4.9863491	-0.1874300	1.0358869
H	-1.9975211	0.5725790	1.0673649
H	-2.6814851	-0.7153430	2.0680619
H	-4.0154941	0.9192050	-2.2895871
N	-2.5356521	-1.1461670	0.0163549
O	-4.1995891	1.1953260	-0.2946101
C	-2.6765181	-0.4163670	-1.2864751
H	-2.5522381	-1.1630320	-2.0769121
H	-1.8439941	0.2945400	-1.3065531
O	-0.0045051	1.0761190	-0.5403541
C	-3.4467651	-2.3166490	0.0964309
H	-3.1379911	-3.0025820	-0.6952191
H	-3.2792361	-2.7790170	1.0714599
H	-4.4894581	-2.0173680	-0.0262031
O	-0.0025181	-0.4186900	2.2229539
O	-1.2690461	-1.7125400	0.0963669

E = -1107.11783380, H = -1106.701815
G = -1106.773268

4.24_{H2O}

C	2.031244000	-1.078914000	0.433802000
C	1.038393000	-2.167388000	0.028528000
H	1.575509000	-2.916544000	-0.571743000
H	2.580533000	-1.383099000	1.333540000
O	1.233860000	0.086318000	0.796673000
O	-0.257443000	1.693787000	-0.720158000
C	0.391076000	-2.842750000	1.229719000
C	2.988063000	-0.619089000	-0.682749000
H	4.022410000	-0.648290000	-0.324107000
H	2.912332000	-1.272845000	-1.557223000
C	2.557149000	0.815781000	-1.003829000
H	-0.096490000	-2.101901000	1.876349000
H	-0.365169000	-3.554980000	0.882944000
H	1.146705000	-3.385080000	1.812151000
H	3.395383000	1.465956000	-1.272758000
H	1.825207000	0.829264000	-1.819533000
C	1.876401000	1.281498000	0.275643000
C	0.768112000	2.304629000	0.061246000
H	2.601013000	1.628366000	1.026354000
C	0.203439000	2.847735000	1.365613000
H	1.178153000	3.126150000	-0.545942000

H	-0.627401000	3.527268000	1.149468000
H	-0.169257000	2.026623000	1.991202000
H	0.976442000	3.396806000	1.918014000
O	-1.849148000	-0.203757000	1.380794000
H	-2.766390000	-0.263110000	1.057895000
O	-2.583053000	-0.123136000	-0.986256000
H	-2.565001000	-0.001560000	-1.938904000
O	0.045162000	-1.599877000	-0.826984000
Os	-0.782398000	-0.033536000	-0.163396000

E = -781.380927807, H = -781.116938
G = -781.175635

4.24_[ox]

C	2.110335000	1.068804000	0.132956000
O	1.505990000	0.038304000	0.940174000
C	2.053048000	-1.243835000	0.586192000
C	3.190226000	-0.962640000	-0.401815000
C	2.764656000	0.357179000	-1.042294000
C	0.901129000	-2.067815000	-0.020918000
C	0.033610000	-2.709374000	1.057133000
Os	-1.063134000	0.023552000	-0.109703000
O	-0.090729000	1.493721000	-0.870333000
C	1.043763000	2.085918000	-0.242579000
C	0.610692000	2.931891000	0.947931000
O	0.197856000	-1.199851000	-0.884096000
O	-1.370871000	0.553961000	1.470184000
H	1.321163000	-2.854728000	-0.664221000
H	2.410466000	-1.724153000	1.506345000
H	4.133600000	-0.832880000	0.142691000
H	3.318047000	-1.777389000	-1.121696000
H	-0.883331000	-3.119368000	0.618200000
H	0.591962000	-3.528060000	1.527631000
H	-0.231931000	-1.984470000	1.837810000
H	3.605559000	0.933675000	-1.441504000
H	2.022466000	0.195204000	-1.830182000
H	2.872293000	1.574648000	0.747889000
H	1.473856000	2.739653000	-1.017550000
H	-0.209904000	3.594169000	0.652723000
H	0.280167000	2.298955000	1.778898000
H	1.454999000	3.544862000	1.287571000
O	-2.442995000	-0.587494000	-0.879277000

E = -780.109693283, H = -779.869800
G = -779.928207

4.24_[ox] • NMO

C	4.0132136	-2.6767816	-0.2026631
C	3.0517056	-1.4959026	-0.2268001
C	3.2330836	-0.6093436	1.0130839
C	4.4808976	0.2664914	0.9352999
C	3.9895786	1.4149184	0.0483479
C	2.5188416	1.5636254	0.4534879
O	2.1577766	0.3454544	1.1229189
Os	0.2301766	-0.8586646	-0.1459261
C	1.5327366	1.7598084	-0.7218701
C	0.3590536	2.6426144	-0.3065431
O	1.7509466	-2.0300126	-0.2699101

H	3.2260606	-0.8886456	-1.1290041
H	3.1731256	-1.2318856	1.9141179
H	4.7435456	0.6315394	1.9352029
H	5.3442186	-0.2602026	0.5170029
H	3.8116206	-3.3193556	-1.0660921
H	5.0593336	-2.3509486	-0.2453221
H	3.8568706	-3.2664066	0.7097049
H	4.5440486	2.3462424	0.2024299
H	4.0608726	1.1449194	-1.0115991
H	2.3951896	2.3723434	1.1870379
H	2.0729876	2.2686874	-1.5370821
H	-0.3908344	2.6788174	-1.1032201
H	-0.1193784	2.2708304	0.6064549
H	0.7351116	3.6569324	-0.1168261
C	-5.0761054	0.6101284	0.5352449
C	-4.4862124	-1.6383546	0.4782189
C	-3.0034604	-1.3148336	0.3854899
H	-5.5412934	0.5769224	-0.4642621
H	-4.5988324	-2.5686796	1.0436679
H	-4.9272234	-1.7908726	-0.5206411
H	-2.5455804	-1.2347986	1.3756129
H	-2.4622614	-2.0535616	-0.2105901
H	-5.6227044	1.3414194	1.1397059
N	-2.7685854	0.0258164	-0.2554181
O	-5.2039024	-0.6399616	1.1779869
C	-3.6174124	1.0326844	0.4610719
H	-3.4760144	1.9855474	-0.0580161
H	-3.1823544	1.0983994	1.4624329
C	-3.0518534	0.0174004	-1.7198251
H	-2.8482054	1.0295434	-2.0769301
H	-2.3527264	-0.6907686	-2.1658801
H	-4.0918144	-0.2612946	-1.9072991
O	-0.6132734	-1.6688376	-1.4291471
O	1.1854636	0.5003574	-1.2270431
O	-1.4677614	0.4683534	-0.0748441
O	-0.0786684	-1.1996866	1.4882309

E = -1182.31856573, H = -1181.897802
G = -1181.971372

4.24_{[ox]H⁺}

C	0.702083000	-3.266826000	0.488030000
C	1.127989000	-2.035078000	-0.291714000
C	1.951284000	-1.006515000	0.524839000
C	3.210528000	-0.498761000	-0.192276000
C	2.728680000	0.785607000	-0.876260000
C	1.840594000	1.355372000	0.211973000
C	0.755572000	2.363886000	-0.162854000
C	0.281941000	3.214414000	0.999160000
O	1.134075000	0.193143000	0.716874000
Os	-0.974938000	-0.015164000	-0.142695000
O	-0.367759000	1.618684000	-0.679476000
O	0.014789000	-1.379231000	-0.921714000
H	1.721894000	-2.355495000	-1.158486000
H	2.160036000	-1.406608000	1.521700000
H	3.991516000	-0.262194000	0.539271000
H	3.611078000	-1.239886000	-0.889527000

H	0.105791000	-3.923232000	-0.153410000
H	1.604961000	-3.811857000	0.790925000
H	0.129528000	-3.001480000	1.379861000
H	3.545917000	1.461567000	-1.144077000
H	2.136732000	0.567717000	-1.776361000
H	2.444335000	1.764635000	1.033545000
H	1.086133000	2.987498000	-1.002958000
H	-0.574299000	3.826019000	0.698915000
H	-0.000051000	2.578614000	1.848982000
H	1.093586000	3.879247000	1.315905000
O	-2.616142000	-0.082663000	-0.434572000
O	-1.053349000	-0.965196000	1.495419000
H	-1.446819000	-0.462594000	2.222882000

E = -780.52860307, H = -780.275360
G = -780.332910

4.24_{[ox]H+} • NMO

C	-4.1778810	-2.4144483	0.2140227
C	-3.1074910	-1.3485013	0.3428777
C	-2.6549990	-0.7938263	-1.0116413
C	-3.5931480	0.1852087	-1.6919473
C	-3.2969430	1.4959507	-0.9553843
C	-1.8174220	1.3918887	-0.5567223
O	-1.4525370	-0.0043113	-0.7657113
Os	-0.3298870	-0.9393733	1.0146027
C	-1.5314070	1.7609227	0.9303347
C	-0.3981420	2.7611677	1.1197257
O	-1.9389390	-1.9642823	0.8866997
H	-3.4388150	-0.5337463	0.9988737
H	-2.3359650	-1.6232203	-1.6533983
H	-3.3368150	0.2594957	-2.7538293
H	-4.6410450	-0.1186333	-1.6104663
H	-4.3883660	-2.8472863	1.1967517
H	-5.1053320	-1.9786603	-0.1747333
H	-3.8477990	-3.2140303	-0.4600433
H	-3.4825330	2.3771177	-1.5755803
H	-3.9208450	1.5785697	-0.0588893
H	-1.1671440	1.9663727	-1.2254943
H	-2.4418040	2.2254297	1.3364667
H	-0.1853790	2.8680237	2.1891557
H	0.5079680	2.4610467	0.5896337
H	-0.7178220	3.7388807	0.7377567
C	4.4748580	0.7455917	-1.0504753
C	4.3442000	-1.4576293	-0.3231063
C	2.8421070	-1.3593623	-0.0830023
H	5.0638760	1.0664897	-0.1761403
H	4.5652540	-2.4810863	-0.6411603
H	4.9232350	-1.2542713	0.5919277
H	2.2861780	-1.6188233	-0.9851953
H	2.5182650	-1.9960653	0.7455037
H	4.7837980	1.3518307	-1.9078513
N	2.4437930	0.0546807	0.2451657
O	4.7439320	-0.5997473	-1.3675883
C	2.9825730	0.9595357	-0.8330423
H	2.7441220	1.9839477	-0.5322963
H	2.4160290	0.6918947	-1.7291993

C	2.9092090	0.4726577	1.5993967
H	2.5405920	1.4872247	1.7641117
H	2.4772880	-0.2141873	2.3303127
H	3.9985530	0.4402367	1.6443967
O	0.3890660	-1.3012723	2.4680097
O	-1.4048830	0.5580617	1.6464397
O	1.0597050	0.2809127	0.2071647
O	0.1851950	-2.2008753	-0.3221463
H	-0.4864520	-2.8994993	-0.3542843

E = -1182.77909751, H = -1182.344552
G = -1182.417736

4.24_{[ox][ox]} • NMM-H⁺

C	1.6529193	0.5094516	3.3305377
C	2.1169283	0.4804456	1.8835477
C	1.1219803	1.2294146	0.9581967
C	1.6066473	2.6038046	0.5203387
C	2.5379933	2.2877476	-0.6696773
C	2.0926963	0.8988886	-1.1557733
O	0.9991903	0.5082196	-0.2824413
Os	1.1206413	-1.8004234	0.2299707
C	3.1915163	-0.1713624	-1.0569213
C	4.1134993	-0.1388084	-2.2636103
O	2.3042083	-0.8465524	1.4394307
H	3.1008873	0.9686506	1.8039467
H	0.1230953	1.2332696	1.4060037
H	0.7551063	3.2109596	0.1970707
H	2.1182443	3.1343336	1.3297857
H	2.3998163	0.0394776	3.9768757
H	1.5163983	1.5499316	3.6545637
H	0.7026253	-0.0265564	3.4276977
H	2.4525423	3.0397256	-1.4577503
H	3.5872373	2.2532886	-0.3544703
H	1.6711713	0.8955656	-2.1669573
H	3.7699723	-0.0221034	-0.1338423
H	4.8964683	-0.8951774	-2.1581873
H	3.5465183	-0.3374924	-3.1801733
H	4.5887783	0.8469936	-2.3413163
C	-3.5769407	0.5833586	-1.4561153
C	-4.6039197	-0.0770474	0.5290807
C	-3.3467817	-0.7761564	1.0212587
H	-4.2113867	-0.0907104	-2.0551483
H	-5.1476187	0.3243726	1.3895747
H	-5.2713567	-0.7750744	-0.0029033
H	-2.7288717	-0.0820044	1.6010267
H	-3.5739677	-1.6564444	1.6308837
H	-3.3652117	1.4718706	-2.0582033
N	-2.4967837	-1.2240124	-0.1335213
O	-4.2678077	1.0140166	-0.3019713
C	-2.2626857	-0.0805424	-1.0799743
H	-1.7290757	-0.4785284	-1.9472953
H	-1.6104697	0.6227386	-0.5504183
C	-3.0055817	-2.4489404	-0.8061683
H	-3.9895637	-2.2544854	-1.2380263
H	-2.2918447	-2.7267264	-1.5853603
H	-3.0766777	-3.2461074	-0.0612303

O	1.5421453	-3.3625284	0.6788997
O	2.5644663	-1.4275474	-0.9904093
O	0.0906733	-1.9918214	-1.1332743
O	-0.1528247	-1.3232934	1.3280057
H	-1.5749967	-1.4460774	0.2844447

E = -1182.74333943, H = -1182.309394
G = -1182.386008

4.24' _{[ox]H+}

C	-1.1339506	-0.9075929	0.1368072
O	-0.1402036	-0.0510029	0.7572692
C	-0.5427956	1.3376661	0.5881932
C	-1.9318026	1.2831201	-0.0465998
C	-1.8659416	-0.0151089	-0.8496988
C	0.5218944	2.0446681	-0.3006298
C	1.4691184	2.9292111	0.4923102
Os	2.1681314	-0.3232639	-0.1346728
O	0.7596414	-1.6051559	-1.1319628
C	-0.4341786	-2.1276009	-0.4297728
C	-0.0502836	-3.1679359	0.5992882
O	2.2508944	-1.1767409	1.3107542
H	0.0180684	2.6359661	-1.0761338
H	-0.5452146	1.7878921	1.5865472
H	-2.7011576	1.2071571	0.7303272
H	-2.1423106	2.1684461	-0.6529448
H	2.2448424	3.3403441	-0.1613788
H	0.9037484	3.7605451	0.9300702
H	1.9411344	2.3729291	1.3132572
H	-2.8506736	-0.4144869	-1.1096208
H	-1.2712246	0.1093211	-1.7640288
H	-1.8175606	-1.2486879	0.9273762
H	-1.0578456	-2.5607659	-1.2219418
H	0.5723724	-3.9557599	0.1577192
H	0.4716454	-2.7191519	1.4504872
H	-0.9688066	-3.6412479	0.9660742
O	3.7022374	0.2417881	-0.4797048
O	1.2256584	1.0360451	-1.0082908
H	1.2045614	-2.3405979	-1.5790998

E = -780.521690820, H = -780.268385
G = -780.322642

4.24' _{[ox]H+} • NMO

C	-4.1069480	-2.6556451	0.1431606
C	-3.1132940	-1.5142741	0.2669096
C	-2.9102190	-0.7863941	-1.0575184
C	-4.0076180	0.1696949	-1.4810544
C	-3.7067340	1.4156939	-0.6446294
C	-2.1791450	1.4662479	-0.5817214
O	-1.7397380	0.1054879	-0.8779954
Os	-0.3013470	-1.0025571	0.3156456
C	-1.6181560	1.9171569	0.7823726
C	-0.4004280	2.8134109	0.6844206
O	-1.8647450	-2.0624841	0.6659336
H	-3.4557130	-0.7936021	1.0279576
H	-2.5980480	-1.4969541	-1.8308074
H	-3.9274310	0.3836299	-2.5520264

H	-5.0026770	-0.2388461	-1.2826374
H	-4.1471130	-3.1997921	1.0917276
H	-5.1126790	-2.2850761	-0.0872824
H	-3.7860960	-3.3503341	-0.6419764
H	-4.1107070	2.3323949	-1.0836924
H	-4.1193600	1.3107739	0.3648366
H	-1.7591940	2.0902999	-1.3781294
H	-2.4197930	2.4309989	1.3278566
H	-0.0229350	3.0589259	1.6854256
H	0.3907840	2.3332529	0.1011866
H	-0.6913850	3.7537939	0.2015426
C	4.9154840	0.4452719	-0.8487704
C	4.4672810	-1.7162711	-0.1126214
C	2.9643720	-1.4661641	-0.0955954
H	5.3960390	0.7385859	0.0991246
H	4.6330600	-2.7644421	-0.3798974
H	4.9214570	-1.5421351	0.8761216
H	2.5219270	-1.7044301	-1.0658554
H	2.4659810	-2.0345261	0.6948796
H	5.4081320	0.9908369	-1.6595804
N	2.6541130	-0.0106761	0.1351456
O	5.1018230	-0.9297271	-1.0966124
C	3.4347890	0.7974039	-0.8638654
H	3.2504240	1.8504759	-0.6304754
H	2.9882830	0.5510909	-1.8312884
C	2.9529960	0.4109379	1.5335706
H	2.6861720	1.4676089	1.6075956
H	2.3315320	-0.1947171	2.1937126
H	4.0126250	0.2684879	1.7526236
O	0.3932370	-1.2612421	1.8606586
O	-1.3460620	0.6891929	1.4860796
H	-0.9110980	0.8548709	2.3329496
O	1.3154170	0.2880839	-0.1229514
O	0.1527350	-1.9243221	-1.0244534

E = -1182.76471624, H = -1182.329887

G = -1182.403866

4.24_{[ox]H2O}

C	1.574944000	1.604706000	0.428953000
O	1.091182000	0.351957000	0.972089000
C	2.022373000	-0.708619000	0.684006000
C	3.375386000	-0.014334000	0.659957000
C	3.036932000	1.339839000	0.026259000
C	1.580306000	-1.383497000	-0.618928000
C	2.300094000	-2.699094000	-0.858826000
Os	-1.057958000	-0.243986000	-0.036923000
O	0.001108000	0.891907000	-1.222764000
C	0.675364000	2.036370000	-0.771024000
C	-0.195897000	3.255987000	-0.502907000
O	0.204114000	-1.665502000	-0.451218000
O	-2.407507000	-0.475565000	-0.968203000
O	-1.472651000	1.190041000	1.158301000
O	-1.244128000	-1.264704000	1.570513000
H	1.494725000	2.333605000	1.243366000
H	1.913697000	-1.431419000	1.502764000
H	3.741499000	0.110371000	1.684952000

H	4.125202000	-0.573614000	0.090764000
H	3.700229000	2.142214000	0.363453000
H	3.115380000	1.275707000	-1.064705000
H	1.733035000	-0.701064000	-1.466573000
H	1.883204000	-3.189442000	-1.744657000
H	3.371437000	-2.533715000	-1.025031000
H	2.169783000	-3.366729000	0.002432000
H	1.350930000	2.302081000	-1.599960000
H	-0.807934000	3.460980000	-1.388756000
H	-0.846211000	3.113338000	0.361182000
H	0.453667000	4.125407000	-0.329168000
H	-1.760985000	0.788621000	1.991552000
H	-0.826798000	-2.126661000	1.429824000

E = -856.570374998, H = -856.301157
G = -856.359460

4.24_H+

C	1.348332000	1.581559000	0.623047000
C	2.304774000	0.568375000	-0.003142000
H	3.047027000	1.107518000	-0.604444000
H	1.668206000	1.838148000	1.637720000
O	0.043202000	0.864188000	0.816429000
O	1.562083000	-0.246237000	-0.941022000
O	-1.695235000	-0.100751000	-0.854584000
C	2.993447000	-0.318273000	1.019324000
C	1.016133000	2.823969000	-0.216149000
H	1.103577000	3.720845000	0.404834000
H	1.706409000	2.925209000	-1.058504000
C	-0.430041000	2.629016000	-0.682304000
H	3.593450000	-1.077529000	0.507637000
H	3.657681000	0.283080000	1.650895000
H	2.258845000	-0.818636000	1.666136000
H	-0.961498000	3.576223000	-0.812563000
H	-0.472653000	2.072633000	-1.626740000
C	-1.053820000	1.802803000	0.422558000
C	-2.224851000	0.924401000	0.017112000
H	-1.265469000	2.389027000	1.324777000
C	-2.960557000	0.297485000	1.186897000
H	-2.907031000	1.518839000	-0.604372000
H	-3.722708000	-0.394666000	0.815566000
H	-2.266182000	-0.252387000	1.836903000
H	-3.455979000	1.074373000	1.780790000
Os	-0.079986000	-0.830215000	-0.283167000
O	-0.122165000	-2.218406000	0.957401000
H	-0.168323000	-3.112690000	0.572190000

E = -705.362175050, H = -705.113739
G = -705.168079

4.24_H+ • NMO

C	3.2365534	-3.0947708	-0.1329518
C	2.8881444	-1.6555888	-0.4596508
C	2.8678644	-0.7861948	0.8126392
C	4.1519574	0.0301892	0.9412822
C	3.8186604	1.2669732	0.0998472
C	2.3939374	1.5549132	0.5350302
O	1.8072534	0.2258202	0.7380532

Os	0.4267894	-0.2715818	-0.8378298
C	1.4832404	2.3119922	-0.4342468
C	0.3364194	3.0108232	0.2785262
O	1.6488084	-1.6261368	-1.1823618
H	3.6335714	-1.2444018	-1.1564548
H	2.6301854	-1.3929568	1.6926742
H	4.3326734	0.3111152	1.9847272
H	5.0208554	-0.5254808	0.5745002
H	3.2999374	-3.6846928	-1.0520898
H	4.2047194	-3.1451238	0.3810022
H	2.4682174	-3.5283968	0.5187282
H	4.4832134	2.1134082	0.2949812
H	3.8440344	1.0396192	-0.9743358
H	2.3840784	2.0495662	1.5148022
H	2.0860154	3.0384142	-0.9950718
H	-0.3281366	3.4767522	-0.4565878
H	-0.2302196	2.2848452	0.8789272
H	0.7190784	3.7899632	0.9473832
C	-4.3309776	0.6805612	-0.9260878
C	-4.5892666	-0.0224848	1.2734302
C	-3.0838946	-0.1720048	1.4551472
H	-4.7813396	-0.2407998	-1.3298698
H	-5.0195616	0.2849432	2.2317752
H	-5.0602946	-0.9738398	0.9782962
H	-2.6461106	0.7685432	1.8017532
H	-2.8194026	-0.9788208	2.1448562
H	-4.5839636	1.5037802	-1.6009068
N	-2.3978826	-0.4665218	0.1493672
O	-4.8788376	0.9891832	0.3374302
C	-2.8145256	0.5734902	-0.8576958
H	-2.3647586	0.2925842	-1.8143488
H	-2.3859146	1.5105502	-0.4856928
O	0.9358804	1.4167302	-1.4220938
C	-2.6519986	-1.8657548	-0.3008928
H	-2.1236576	-2.0027948	-1.2468848
H	-2.2625626	-2.5230258	0.4802202
H	-3.7271996	-2.0120468	-0.4204598
O	-1.0195756	-0.3287108	0.4702132
O	-0.7631156	-0.8521038	-2.3352408
H	-0.2388916	-1.1305268	-3.0938368

E = -1107.59981486, H = -1107.170666

G = -1107.243875

4.24_H+ • 2 NMO

C	-3.8861817	-1.4557697	-1.7138099
C	-3.2111357	-0.4884487	-0.7560179
C	-3.1130407	0.9093533	-1.3821209
C	-4.2692287	1.8409173	-1.0505069
C	-3.8861837	2.4367793	0.3244201
C	-2.3655417	2.2533483	0.4416931
O	-1.9711807	1.6081633	-0.8147539
Os	-0.4332137	0.2394053	-0.5121189
C	-1.9194337	1.3820983	1.6270681
C	-1.8156127	2.2260913	2.8861411
O	-1.9195977	-0.9947427	-0.4184139
H	-3.8003827	-0.4259367	0.1725621

H	-2.8875657	0.8330433	-2.4511899
H	-4.3371957	2.6278123	-1.8075449
H	-5.2258697	1.3093023	-1.0209999
H	-3.9986117	-2.4370167	-1.2408349
H	-4.8824257	-1.0956327	-1.9993379
H	-3.2747437	-1.5593637	-2.6188339
H	-4.1715097	3.4895643	0.3932111
H	-4.3875907	1.9021963	1.1391731
H	-1.8089547	3.1968153	0.4445001
H	-2.6797467	0.5959233	1.7809431
H	-1.5287057	1.5961913	3.7341001
H	-1.0529437	3.0033363	2.7493381
H	-2.7721327	2.7103983	3.1206581
C	4.1108463	3.4765003	-0.2319899
C	4.4746413	1.3296583	-1.0546259
C	2.9826133	1.0607753	-1.1875849
H	4.4929413	3.2270883	0.7718701
H	4.9974353	0.7968003	-1.8547169
H	4.8636383	0.9640883	-0.0892779
H	2.6101013	1.3832633	-2.1649429
H	2.7328093	0.0107873	-1.0153539
H	4.3526063	4.5244433	-0.4345759
N	2.1900103	1.8653133	-0.1981809
O	4.7626513	2.7011053	-1.2142919
C	2.6009223	3.3049013	-0.3192889
H	2.0686123	3.8503823	0.4653951
H	2.2310153	3.6177633	-1.2995749
C	2.3359293	1.3768953	1.2008971
H	1.6308823	1.9471183	1.8083881
H	2.0605483	0.3213593	1.2085741
H	3.3646693	1.5228663	1.5353921
O	1.1092133	-1.1635117	-0.1857279
O	-0.6888847	0.7410603	1.3603571
O	0.8463073	1.8497313	-0.5567939
O	-0.0971767	-0.0252537	-2.3854469
H	0.6649823	-0.6010947	-2.5345139
C	2.0321373	-4.5758367	0.8037561
C	0.0766983	-4.7120387	-0.4504479
C	0.1137493	-3.2297797	-0.7880229
C	2.1501123	-3.0793147	0.5433251
H	-0.3626057	-5.2499117	-1.2960439
H	1.5151323	-4.7836127	1.7545101
H	3.0412113	-4.9948237	0.8711651
H	0.7108643	-3.0611687	-1.6893649
H	-0.8804887	-2.7918797	-0.9075039
H	2.7274643	-2.8963147	-0.3674609
H	2.6022313	-2.5439157	1.3841801
H	-0.5438587	-4.9092587	0.4391051
C	0.0153953	-2.3486517	1.5429351
H	-0.0641217	-3.3369457	1.9986761
H	0.5399363	-1.6533997	2.2013251
H	-0.9695947	-1.9555197	1.2882421
N	0.8153893	-2.4418407	0.2864271
O	1.3817613	-5.2216597	-0.2661139

E = -1509.82500848, H = -1509.216082
 G = -1509.305175

4.24'_{H+}

C	0.3589141	1.4720011	0.1308751
C	1.8696331	1.4274991	-0.0678409
H	2.1853701	2.3206861	-0.6228189
H	0.0872851	2.0467251	1.0237081
O	-0.0060579	0.0767841	0.4066841
O	2.1064991	0.3228161	-0.9559429
O	-0.4506509	-2.1320459	-0.8140759
C	2.6510221	1.3068281	1.2286331
C	-0.4877019	1.8588921	-1.0966819
H	-1.0053539	2.8042041	-0.9133869
H	0.1476391	1.9822061	-1.9787879
C	-1.4841029	0.6936551	-1.2938349
H	3.7064671	1.1221601	1.0049181
H	2.5748681	2.2380401	1.8022001
H	2.2698411	0.4831001	1.8468531
H	-2.5067029	1.0307831	-1.4854429
H	-1.1705939	0.0662801	-2.1393559
C	-1.3878699	-0.0978829	0.0064081
C	-1.6101899	-1.6025989	-0.0589959
H	-2.0199289	0.3295961	0.7961861
C	-1.6412999	-2.2864049	1.2874771
H	-2.4983479	-1.8309689	-0.6584909
H	-1.7081739	-3.3715469	1.1648081
H	-0.7442779	-2.0396139	1.8678901
H	-2.5229589	-1.9439879	1.8415431
Os	1.4104021	-1.3495699	-0.4658509
O	2.5394911	-2.5079819	-0.1438869
H	-0.6632219	-2.4196549	-1.7127899

E = -705.362797728, H = -705.113603
G = -705.169155

4.24'_{H+} • NMO

C	2.5479093	-3.0624439	0.8561157
C	2.8755253	-1.7031319	0.2608147
C	2.3519563	-0.5340769	1.1520817
C	3.4361713	0.4715401	1.5139567
C	3.4552293	1.3451741	0.2593287
C	1.9669553	1.5312931	0.0143277
O	1.3738073	0.2509191	0.3841267
Os	0.5059623	-1.1986449	-1.1808593
C	1.5531273	1.9177691	-1.4073503
C	0.3462743	2.8354041	-1.4674223
O	2.3759813	-1.5384159	-1.0499243
H	3.9681663	-1.6065179	0.1735917
H	1.8059083	-0.9234779	2.0191177
H	3.1487663	1.0643381	2.3906647
H	4.3899363	-0.0211939	1.7225587
H	2.9231223	-3.8556469	0.2018437
H	3.0195013	-3.1695409	1.8416677
H	1.4624283	-3.1833499	0.9710097
H	3.9674913	2.3019471	0.3968377
H	3.9042233	0.8092821	-0.5875673
H	1.5625693	2.2766491	0.7134247
H	2.4130073	2.4039791	-1.8876453

H	0.0620133	3.0353891	-2.5079653
H	-0.5047587	2.3855881	-0.9488743
H	0.5990193	3.7949411	-1.0018003
C	-4.0887407	-1.5747949	0.4084677
C	-4.4575337	0.7117161	0.2368647
C	-3.1476647	0.9199641	-0.5117713
H	-3.9520257	-1.5273279	1.5016877
H	-5.1830867	1.4413441	-0.1356563
H	-4.3387377	0.8724911	1.3211677
H	-3.2990967	0.8145861	-1.5896083
H	-2.6946187	1.8916181	-0.2941193
H	-4.5456267	-2.5396329	0.1674897
N	-2.1253867	-0.1286099	-0.1656053
O	-4.9790727	-0.5699539	-0.0224253
C	-2.7586997	-1.4846029	-0.3280093
H	-2.0419237	-2.2270019	0.0324047
H	-2.8975757	-1.6052469	-1.4065463
C	-1.5814427	0.0717891	1.2033637
H	-0.8583427	-0.7232559	1.3944067
H	-1.0850867	1.0441251	1.2196867
H	-2.3968257	0.0365981	1.9277347
O	-1.1117677	0.0432291	-1.1216643
O	-0.2522387	-2.6208109	-1.5772043
O	1.3263593	0.6782141	-2.1082873
H	0.9588403	0.8477921	-2.9844383

E = -1107.58719268, H = -1107.157134
G = -1107.229930

4.24_H+ • H₂O

C	1.3351395	-1.1218490	0.2630453
C	0.3591115	-2.2048600	-0.2063387
H	0.8832135	-2.8693060	-0.9044047
H	1.8325735	-1.4459090	1.1828013
O	0.5231395	0.0614490	0.6487803
O	-0.9949075	1.6759950	-0.8086847
C	-0.2277925	-3.0060470	0.9434013
C	2.3412475	-0.6200610	-0.7850307
H	3.3422305	-0.5757110	-0.3448397
H	2.3805865	-1.2900390	-1.6488077
C	1.8570005	0.7811440	-1.1619367
H	-0.7001565	-2.3430030	1.6814933
H	-0.9762235	-3.7088520	0.5632953
H	0.5618435	-3.5774550	1.4448203
H	2.6719035	1.4466050	-1.4615067
H	1.1230225	0.7423600	-1.9764457
C	1.1838105	1.2722720	0.1056073
C	0.0928305	2.3138140	-0.1006787
H	1.9072425	1.5946310	0.8642723
C	-0.4130915	2.9288030	1.1917513
H	0.4802875	3.0875760	-0.7765307
H	-1.2435115	3.6095010	0.9793103
H	-0.7578655	2.1492660	1.8842863
H	0.3881035	3.4987340	1.6764653
O	-2.3787995	-0.1932330	1.3903883
H	-3.3342695	-0.2684100	1.2312953
O	-3.2834485	-0.1194940	-1.2020427

H	-3.3696765	-0.8648360	-1.8149777
O	-0.7100745	-1.5968890	-0.9690897
Os	-1.3889025	-0.0407350	-0.1852647
H	-3.4845685	0.6845380	-1.7044347

E = -781.827775268, H = -781.551387
G = -781.608803

4.24'_{H+} • H₂O

C	1.3218541	-1.0943087	0.1771501
C	0.4266461	-2.3137187	-0.0355799
H	1.0012361	-3.0591027	-0.6028189
H	2.0321171	-1.2537677	0.9976401
O	0.4281281	0.0023713	0.6061741
C	-0.0883209	-2.9104887	1.2625931
C	1.9871141	-0.5414467	-1.0773479
H	2.9675691	-0.9983467	-1.2360439
H	1.3635581	-0.7722427	-1.9499539
C	2.0753291	0.9777613	-0.8419239
H	-0.6477969	-2.1629137	1.8396631
H	-0.7524299	-3.7513607	1.0400361
H	0.7472441	-3.2790817	1.8694281
H	3.0850301	1.2841533	-0.5554609
H	1.7995361	1.5371483	-1.7416529
C	1.1009221	1.2665333	0.3157471
C	0.0234671	2.3075763	0.0379131
H	1.6293541	1.5558203	1.2313121
C	-0.8095699	2.6924483	1.2400881
H	0.4875531	3.1770203	-0.4417299
H	-1.6005399	3.3960013	0.9554431
H	-1.2622829	1.8090513	1.7079001
H	-0.1638589	3.1929563	1.9709821
O	-2.4983869	-0.2998637	0.9161141
O	-3.2492379	-0.5481767	-1.4271639
H	-3.7846159	-0.6400277	-0.6072969
O	-0.6687109	-1.9243227	-0.8857249
Os	-1.3781869	-0.2339657	-0.4423269
H	-3.3024039	-1.3885797	-1.9052469
O	-0.8323959	1.6733123	-0.9977979
H	-1.4379219	2.2995613	-1.4201159

E = -781.779500587, H = -781.502437
G = -781.561766

4.24_{[ox][ox]}

C	1.863510000	-1.034347000	-0.590219000
O	1.033749000	0.061628000	-1.039817000
C	1.621421000	1.297630000	-0.606975000
C	3.113759000	1.050336000	-0.777712000
C	3.267717000	-0.437591000	-0.395476000
C	1.198205000	1.576178000	0.862776000
C	0.905658000	3.055156000	1.068014000
Os	-1.124899000	-0.050423000	-0.090796000
O	-0.140904000	-1.629041000	0.544717000
C	1.248260000	-1.615364000	0.694158000
C	1.734714000	-3.036088000	0.934304000
O	0.104465000	0.778129000	1.231534000
O	-2.465765000	-0.166463000	0.925524000

O	-1.523489000	-0.984295000	-1.457309000
H	1.806589000	-1.783139000	-1.388362000
H	1.219079000	2.066655000	-1.272472000
H	3.397159000	1.212298000	-1.822918000
H	3.714919000	1.714545000	-0.147382000
H	4.013807000	-0.940469000	-1.016673000
H	3.573348000	-0.547150000	0.652006000
H	2.034513000	1.277479000	1.519416000
H	0.683332000	3.251928000	2.121641000
H	1.776185000	3.657867000	0.773422000
H	0.043186000	3.345963000	0.458083000
H	1.521600000	-0.978315000	1.548205000
H	1.297175000	-3.429941000	1.856930000
H	1.438463000	-3.681214000	0.098755000
H	2.828373000	-3.050638000	1.030967000
O	-1.204914000	1.512647000	-0.785190000

E = -855.259978582, H = -855.014427
G = -855.070387

4.24_{[ox][ox]H⁺}

C	1.834695000	-1.075239000	-0.618381000
O	0.988937000	0.048839000	-0.999604000
C	1.626680000	1.279346000	-0.602137000
C	3.107837000	0.996859000	-0.798015000
C	3.244305000	-0.497150000	-0.432498000
C	1.230072000	1.564911000	0.864753000
C	1.118673000	3.051501000	1.156257000
Os	-1.096310000	-0.093445000	-0.057021000
O	-0.177186000	-1.623232000	0.520350000
C	1.237616000	-1.672029000	0.661568000
C	1.660016000	-3.109789000	0.892548000
O	0.008971000	0.887948000	1.162170000
O	-2.458626000	-0.230106000	0.897586000
O	-1.541003000	-0.699215000	-1.562010000
H	1.749527000	-1.794540000	-1.439387000
H	1.231453000	2.049570000	-1.270640000
H	3.374149000	1.166929000	-1.845200000
H	3.735442000	1.641397000	-0.174247000
H	3.971941000	-1.001385000	-1.072561000
H	3.569248000	-0.626110000	0.606763000
H	1.979156000	1.125155000	1.538834000
H	0.801746000	3.216003000	2.190233000
H	2.099644000	3.521944000	1.015153000
H	0.414352000	3.549759000	0.476726000
H	1.491407000	-1.046974000	1.530528000
H	1.209440000	-3.496827000	1.810751000
H	1.356762000	-3.736777000	0.047125000
H	2.751329000	-3.151107000	0.995816000
O	-1.281936000	1.631710000	-0.846247000
H	-1.088687000	2.326774000	-0.198815000

E = -855.666825649, H = -855.408848
G = -855.465677

4.24'_{[ox][ox]H⁺}

6	1.936112000	-0.801020000	-0.649085000
8	0.914129000	0.195006000	-0.969752000

6	1.377908000	1.503731000	-0.571853000
6	2.868702000	1.461134000	-0.859076000
6	3.256092000	-0.012542000	-0.599915000
6	0.991766000	1.683736000	0.909053000
6	0.599420000	3.114300000	1.223133000
76	-1.141857000	-0.110142000	-0.107173000
8	0.213578000	-1.770869000	0.777096000
6	1.627292000	-1.485491000	0.687927000
6	2.433305000	-2.757501000	0.859326000
8	-0.108713000	0.815656000	1.198292000
8	-2.351228000	-0.575837000	0.956622000
8	-1.160466000	-1.300816000	-1.320243000
1	1.880019000	-1.526712000	-1.467906000
1	0.822037000	2.212086000	-1.196298000
1	3.048797000	1.732622000	-1.902879000
1	3.425187000	2.156331000	-0.222349000
1	3.965905000	-0.375602000	-1.346447000
1	3.721128000	-0.128773000	0.385523000
1	1.818100000	1.359424000	1.557595000
1	0.371490000	3.224709000	2.286846000
1	1.432080000	3.783811000	0.970104000
1	-0.278207000	3.402500000	0.632168000
1	1.811274000	-0.796598000	1.517619000
1	3.505735000	-2.533897000	0.828303000
1	2.207465000	-3.223154000	1.823609000
1	2.213260000	-3.469322000	0.051838000
8	-1.723110000	1.252340000	-0.904160000
1	0.019723000	-2.608530000	0.327511000

E = -855.685771563, H = -855.426059

G = -855.483724

4.24t

C	0.969490000	1.997230000	0.014574000
C	2.178880000	1.090705000	0.236337000
H	3.011109000	1.461380000	-0.381938000
H	1.078101000	2.939447000	0.571396000
O	-0.129486000	1.263786000	0.583112000
O	1.852354000	-0.199895000	-0.236207000
O	0.268063000	-2.618622000	-0.408781000
O	-1.773224000	-0.571007000	-0.234932000
C	2.597939000	1.039497000	1.698813000
C	0.550342000	2.239046000	-1.443732000
H	0.870220000	3.229478000	-1.781099000
H	1.018095000	1.484727000	-2.085778000
C	-0.990726000	2.079423000	-1.444986000
H	3.415086000	0.321038000	1.818394000
H	2.938869000	2.025954000	2.038676000
H	1.752028000	0.716416000	2.318120000
H	-1.506528000	2.982583000	-1.784643000
H	-1.293127000	1.244039000	-2.085749000
C	-1.353438000	1.759478000	0.013145000
C	-2.354787000	0.627422000	0.235276000
H	-1.650317000	2.661043000	0.568736000
C	-2.757531000	0.495917000	1.697295000
H	-3.244115000	0.821103000	-0.384446000
H	-3.413866000	-0.371786000	1.818137000

H	-1.865357000	0.352032000	2.319268000
H	-3.290781000	1.394660000	2.033137000
Os	0.097341000	-0.950375000	-0.113791000

E = -704.935000557, H = -704.700293
G = -704.754156

4.24t_{H2O}

C	2.048309000	-0.901188000	0.638803000
C	1.300525000	-1.925809000	-0.250916000
H	2.042919000	-2.425740000	-0.891565000
H	2.273584000	-1.328625000	1.622611000
O	1.133760000	0.223998000	0.877287000
O	-0.304405000	1.443806000	-1.058762000
C	0.581130000	-2.988822000	0.578096000
C	3.275019000	-0.277942000	-0.028818000
H	4.002183000	0.039295000	0.729118000
H	3.764231000	-0.988447000	-0.701934000
C	2.692805000	0.939102000	-0.743684000
H	-0.091126000	-2.533525000	1.320752000
H	-0.009802000	-3.629324000	-0.085231000
H	1.307027000	-3.609424000	1.119399000
H	3.443051000	1.699875000	-0.982218000
H	2.152601000	0.646177000	-1.651343000
C	1.695722000	1.447913000	0.278240000
C	0.543917000	2.274196000	-0.290495000
H	2.198128000	1.986326000	1.093933000
C	-0.227245000	3.019453000	0.796354000
H	0.986524000	3.005454000	-0.985805000
H	-1.071094000	3.548802000	0.340827000
H	-0.618111000	2.323135000	1.550916000
H	0.420549000	3.750417000	1.297039000
O	-1.839719000	-0.103990000	1.572254000
H	-2.787289000	-0.153771000	1.383197000
O	-2.487421000	-0.449310000	-0.974984000
H	-2.601106000	0.215055000	-1.666217000
O	0.423991000	-1.226370000	-1.105705000
Os	-0.819513000	-0.147002000	-0.050522000

E = -781.357929089, H = -781.096061
G = -781.152668

4.24t_{H+}

C	-1.888926000	1.174980000	0.121333000
C	-0.853993000	2.290028000	0.214818000
H	-1.146045000	3.125301000	-0.433733000
H	-2.715615000	1.350960000	0.820670000
O	-1.170237000	0.001340000	0.593178000
O	0.342899000	1.744026000	-0.371574000
O	0.338728000	-1.744906000	-0.371204000
C	-0.586588000	2.759179000	1.631981000
C	-2.371762000	0.778101000	-1.278433000
H	-3.360793000	1.198905000	-1.477193000
H	-1.679014000	1.165323000	-2.033674000
C	-2.373133000	-0.771966000	-1.278823000
H	0.257244000	3.455680000	1.640840000
H	-1.470230000	3.278682000	2.020805000
H	-0.358368000	1.908301000	2.286045000

H	-3.362741000	-1.190981000	-1.478497000
H	-1.680506000	-1.160021000	-2.033763000
C	-1.891848000	-1.170351000	0.120999000
C	-0.859759000	-2.288001000	0.214625000
H	-2.719218000	-1.344302000	0.820047000
C	-0.594010000	-2.758098000	1.631785000
H	-1.153705000	-3.122398000	-0.434201000
H	0.247987000	-3.456814000	1.640784000
H	-0.363760000	-1.907931000	2.286058000
H	-1.479137000	-3.275349000	2.020238000
Os	0.901006000	-0.001064000	-0.117854000
O	2.720426000	-0.003404000	-0.322556000
H	3.173018000	-0.004159000	-1.180008000

E = -705.362523589, H = -705.114100
G = -705.170021

4.24q

C	1.185119000	1.809179000	-0.021275000
C	2.311334000	0.791133000	0.213392000
H	3.172408000	1.115277000	-0.393740000
H	1.404776000	2.756117000	0.491363000
O	-0.000087000	1.243269000	0.600227000
O	1.929659000	-0.495907000	-0.232114000
O	0.000161000	-2.553348000	-0.612871000
O	-1.929614000	-0.496185000	-0.231973000
C	2.715800000	0.740310000	1.683062000
C	0.774577000	2.034757000	-1.484260000
H	1.190119000	2.974754000	-1.858752000
H	1.167915000	1.219778000	-2.103230000
C	-0.774679000	2.034408000	-1.484373000
H	3.490827000	-0.020537000	1.817914000
H	3.102238000	1.709569000	2.023975000
H	1.849454000	0.468445000	2.301417000
H	-1.190617000	2.974098000	-1.859196000
H	-1.167550000	1.219063000	-2.103165000
C	-1.185305000	1.809006000	-0.021403000
C	-2.311448000	0.790887000	0.213311000
H	-1.405063000	2.755997000	0.491097000
C	-2.716043000	0.740227000	1.682948000
H	-3.172493000	1.114867000	-0.393953000
H	-3.491044000	-0.020641000	1.817828000
H	-1.849735000	0.468473000	2.301403000
H	-3.102555000	1.709510000	2.023709000
Os	0.000056000	-0.875353000	-0.071464000

E = -704.918516462, H = -704.685057
G = -704.737440

4.24q_{H2O}

C	2.167782000	-1.076556000	0.602950000
C	1.159712000	-2.051838000	-0.032858000
H	1.726932000	-2.767537000	-0.647319000
H	2.572566000	-1.526662000	1.519314000
O	1.455735000	0.122036000	0.987240000
O	-0.053189000	1.560008000	-0.849551000
C	0.397783000	-2.826441000	1.037816000
C	3.286526000	-0.622157000	-0.342781000

H	4.215344000	-0.467692000	0.220061000
H	3.476172000	-1.364561000	-1.124384000
C	2.766493000	0.705621000	-0.885218000
H	-0.043242000	-2.149982000	1.781730000
H	-0.412721000	-3.404565000	0.585057000
H	1.091006000	-3.503282000	1.553534000
H	3.561450000	1.379374000	-1.221477000
H	2.051188000	0.542631000	-1.698119000
C	2.023902000	1.268556000	0.316333000
C	0.898679000	2.228698000	-0.052706000
H	2.718650000	1.761764000	1.015786000
C	0.268848000	2.872320000	1.179346000
H	1.345938000	3.018910000	-0.677516000
H	-0.530992000	3.560194000	0.878575000
H	-0.146988000	2.112332000	1.852910000
H	1.023050000	3.447241000	1.731164000
O	-2.126305000	-1.499430000	0.291170000
H	-2.941042000	-1.144310000	0.672741000
O	-2.366390000	1.085828000	0.488250000
H	-2.174556000	2.020485000	0.348710000
O	0.321201000	-1.335582000	-0.914763000
Os	-0.963152000	-0.052190000	-0.233511000

E = -781.360256493, H = -781.098637
G = -781.156101

4.24q_H⁺

C	1.215497000	1.805553000	0.023772000
C	2.343103000	0.782561000	0.189912000
H	3.170463000	1.062462000	-0.476332000
H	1.383702000	2.687903000	0.652321000
O	0.015258000	1.135340000	0.561903000
O	1.866255000	-0.494717000	-0.251177000
O	-1.877295000	-0.448848000	-0.251649000
C	2.826754000	0.672134000	1.626558000
C	0.801343000	2.169929000	-1.405322000
H	1.229998000	3.135308000	-1.687437000
H	1.184074000	1.419109000	-2.106406000
C	-0.750456000	2.189570000	-1.403195000
H	3.562062000	-0.133436000	1.710200000
H	3.295833000	1.611575000	1.942329000
H	1.987365000	0.457979000	2.302480000
H	-1.155357000	3.165779000	-1.683086000
H	-1.153731000	1.449459000	-2.104099000
C	-1.169981000	1.834054000	0.026677000
C	-2.321840000	0.838522000	0.194034000
H	-1.315786000	2.719673000	0.656227000
C	-2.803277000	0.736005000	1.632014000
H	-3.144061000	1.140256000	-0.469025000
H	-3.558381000	-0.051013000	1.716044000
H	-1.967183000	0.498678000	2.304278000
H	-3.247351000	1.685949000	1.952369000
Os	-0.010269000	-0.845680000	-0.065384000
O	-0.030632000	-2.655562000	-0.515259000
H	-0.126735000	-3.037690000	-1.397907000

E = -705.359222234, H = -705.111080
G = -705.167779

4.25

C	-2.809950000	3.547971000	0.029070000
C	-3.528072000	2.234738000	-0.052394000
C	-3.201837000	1.154866000	0.658874000
C	-3.864361000	-0.186162000	0.501920000
C	-3.003192000	-1.202294000	-0.265724000
C	-1.840020000	-1.775371000	0.534372000
O	-0.972638000	-0.775435000	1.031709000
Os	0.340269000	-0.041812000	-0.221367000
O	-0.058538000	-1.775208000	-0.994358000
C	-0.929016000	-2.664621000	-0.309923000
C	-0.116344000	-3.648494000	0.513453000
O	-0.548183000	1.183965000	-0.969909000
O	1.084454000	0.590384000	1.191210000
O	1.790362000	-0.195435000	-1.146933000
H	-4.356127000	2.167869000	-0.765739000
H	-2.371870000	1.215885000	1.366239000
H	-4.114659000	-0.606358000	1.488291000
H	-4.808383000	-0.051724000	-0.042700000
H	-2.370468000	3.807294000	-0.944158000
H	-3.492791000	4.362322000	0.306170000
H	-2.001412000	3.499628000	0.767999000
H	-3.629252000	-2.055094000	-0.567025000
H	-2.619850000	-0.738884000	-1.186942000
H	-2.219807000	-2.325912000	1.408850000
H	-1.504751000	-3.187340000	-1.087609000
H	0.628019000	-4.143072000	-0.119407000
H	0.399495000	-3.118307000	1.325009000
H	-0.772682000	-4.410379000	0.951628000
C	3.262777000	1.505105000	0.718130000
H	3.212749000	1.413297000	1.803719000
C	3.781633000	0.481711000	-0.000948000
H	3.974052000	0.634556000	-1.063563000
C	4.211534000	-0.823061000	0.590946000
H	3.952053000	-0.874668000	1.654738000
H	3.722516000	-1.654548000	0.066030000
H	5.295692000	-0.963905000	0.484365000
C	2.825992000	2.801967000	0.114177000
H	1.774427000	3.004042000	0.362533000
H	3.417216000	3.640049000	0.506972000
H	2.926884000	2.778664000	-0.976957000

E = -937.189345787, H = -936.837978

G = -936.914240

4.26

C	2.877535000	-3.255677000	0.035199000
C	3.487944000	-1.888355000	-0.037592000
C	3.149995000	-0.869293000	0.753603000
C	3.695455000	0.525927000	0.599023000
C	2.765901000	1.463175000	-0.190251000
C	1.513412000	1.896938000	0.561651000
O	0.766492000	0.773184000	1.041067000
Os	-0.327612000	-0.022928000	-0.295012000
O	-0.265512000	1.743360000	-1.012713000
C	0.542237000	2.691305000	-0.308358000

C	-0.367365000	3.603967000	0.497028000
O	0.550473000	-1.094244000	-1.220153000
O	-1.123764000	-0.926108000	1.179145000
O	-2.145392000	0.083165000	-0.871772000
H	4.238337000	-1.725336000	-0.818257000
H	2.392960000	-1.024666000	1.524983000
H	3.893958000	0.969435000	1.586205000
H	4.654916000	0.473452000	0.067308000
H	2.363040000	-3.496242000	-0.905440000
H	3.641393000	-4.027951000	0.196493000
H	2.145523000	-3.310016000	0.849973000
H	3.313659000	2.379733000	-0.453519000
H	2.476421000	0.978765000	-1.135072000
H	1.797398000	2.471804000	1.455244000
H	1.088968000	3.264290000	-1.071438000
H	-1.143118000	4.023194000	-0.152216000
H	-0.848503000	3.033433000	1.302480000
H	0.207972000	4.425109000	0.942382000
C	-2.373569000	-1.543290000	0.847204000
H	-2.898960000	-1.694903000	1.800228000
C	-3.116092000	-0.532463000	-0.021327000
H	-3.831203000	-1.044735000	-0.681667000
C	-3.812646000	0.547493000	0.789695000
H	-3.104774000	0.989463000	1.503282000
H	-4.183295000	1.333711000	0.123756000
H	-4.657312000	0.124246000	1.347591000
C	-2.139326000	-2.875017000	0.153304000
H	-1.475064000	-3.502413000	0.757463000
H	-3.092772000	-3.399087000	0.013892000
H	-1.680300000	-2.721878000	-0.832451000

E = -937.330659016, H = -936.973227
G = -937.043847

4.27

C	-1.208971000	3.292437000	0.471945000
C	-1.994628000	2.189458000	-0.181424000
C	-2.672238000	1.252807000	0.613869000
C	-3.763680000	0.383339000	0.043233000
C	-3.127816000	-0.889270000	-0.530150000
C	-2.133777000	-1.374546000	0.512019000
O	-1.332770000	-0.249809000	0.908758000
Os	0.246249000	-0.029855000	-0.262885000
O	-0.207366000	-1.779136000	-0.841004000
C	-1.168029000	-2.437550000	-0.014038000
C	-0.459112000	-3.186733000	1.103943000
O	-0.524828000	1.322583000	-1.024413000
O	1.342024000	0.463396000	1.193748000
O	1.990355000	-0.309740000	-1.136733000
H	-2.425664000	2.395689000	-1.161089000
H	-2.643380000	1.393782000	1.692793000
H	-4.476982000	0.112328000	0.831288000
H	-4.311318000	0.923240000	-0.739207000
H	-0.504596000	3.738647000	-0.238079000
H	-1.875308000	4.082273000	0.843475000
H	-0.640629000	2.888045000	1.320311000
H	-3.877309000	-1.660236000	-0.748480000

H	-2.587308000	-0.661246000	-1.459306000
H	-2.662290000	-1.736963000	1.406703000
H	-1.711092000	-3.142320000	-0.661457000
H	0.301976000	-3.849960000	0.679470000
H	0.027931000	-2.473511000	1.782935000
H	-1.173705000	-3.787985000	1.679709000
C	2.682350000	0.839098000	0.822609000
H	3.294038000	0.696450000	1.724940000
C	3.108334000	-0.111389000	-0.293619000
H	3.909178000	0.358689000	-0.888113000
C	3.587614000	-1.453977000	0.245201000
H	2.829609000	-1.876067000	0.919783000
H	3.739070000	-2.150457000	-0.586206000
H	4.529832000	-1.343715000	0.798440000
C	2.698337000	2.297325000	0.394212000
H	2.229617000	2.926273000	1.160040000
H	3.731033000	2.635532000	0.243557000
H	2.152713000	2.416132000	-0.551882000

E = -937.285552313, H = -936.930168
G = -936.997070

4.28

C	-0.709135000	2.944460000	0.942607000
C	-1.465867000	2.196846000	-0.147953000
C	-2.476297000	1.199312000	0.420185000
C	-3.516817000	0.677678000	-0.589543000
C	-3.172157000	-0.803332000	-0.780959000
C	-2.432746000	-1.170746000	0.498699000
O	-1.711559000	0.038024000	0.856743000
Os	0.241313000	-0.020510000	-0.244824000
O	-0.381595000	-1.773623000	-0.574324000
C	-1.379907000	-2.258191000	0.323807000
C	-0.751410000	-2.697325000	1.637811000
O	-0.560070000	1.511599000	-1.012576000
O	1.454387000	0.171431000	1.182418000
O	1.895502000	0.042908000	-1.339777000
H	-2.013956000	2.915522000	-0.775098000
H	-4.525767000	0.798610000	-0.181375000
H	-3.460206000	1.232594000	-1.531186000
H	0.043469000	3.594862000	0.483946000
H	-1.399385000	3.562897000	1.529992000
H	-0.201390000	2.240414000	1.615216000
H	-4.054086000	-1.434099000	-0.930296000
H	-2.495306000	-0.937594000	-1.632514000
H	-3.122291000	-1.408971000	1.321334000
H	-1.858230000	-3.115555000	-0.173171000
H	0.014258000	-3.455472000	1.442169000
H	-0.279098000	-1.842990000	2.139099000
H	-1.510221000	-3.127337000	2.303467000
C	2.837755000	0.361715000	0.798414000
H	3.432614000	-0.133040000	1.579894000
C	3.017425000	-0.311785000	-0.557491000
H	3.911018000	0.098416000	-1.056343000
C	3.157893000	-1.827135000	-0.434487000
H	2.311284000	-2.248625000	0.125342000
H	3.162725000	-2.275344000	-1.434085000

H	4.088359000	-2.094520000	0.084197000
C	3.126506000	1.852546000	0.762188000
H	2.816170000	2.324341000	1.702034000
H	4.198594000	2.031774000	0.614124000
H	2.574942000	2.306671000	-0.071928000
H	-2.958095000	1.619252000	1.312261000

E = -937.360687977, H = -937.002045
G = -937.069781

4.29 • NMO

C	-4.0915889	-1.0554064	2.0726253
C	-3.7784849	0.4110746	2.0717613
C	-3.4236849	1.1049776	0.9897013
C	-3.0682759	2.5644556	1.0099363
C	-1.5807839	2.8435086	0.7451623
C	-1.1520329	2.6909896	-0.7101217
O	-1.3841319	1.3850066	-1.2320817
Os	-0.1173899	0.0799066	-0.6696847
O	0.9997221	1.7388956	-0.5057707
C	0.3502931	2.9403226	-0.8931697
C	0.7059181	3.2803296	-2.3329887
O	1.6251351	-0.9131354	-0.9628477
H	-3.8375229	0.9289596	3.0350183
H	-3.3482509	0.5954046	0.0271423
H	-3.6643449	3.1071416	0.2594933
H	-3.3334209	2.9760876	1.9934493
H	-3.3374089	-1.6162714	2.6432323
H	-5.0673179	-1.2532334	2.5360583
H	-4.1088709	-1.4467554	1.0490283
H	-1.3567039	3.8807446	1.0353033
H	-0.9630309	2.1891296	1.3786753
H	-1.7411219	3.3812766	-1.3341897
H	0.6853701	3.7465906	-0.2209907
H	1.7952171	3.3260086	-2.4504787
H	0.3083261	2.5060886	-3.0021977
H	0.2824071	4.2506006	-2.6219597
C	3.6758511	-0.0814714	2.0614323
C	4.8739611	0.5064876	0.1414963
C	3.6672281	0.2501586	-0.7529547
H	3.3838541	0.3182896	3.0375433
H	5.4476361	1.3371266	-0.2817587
H	5.5379041	-0.3728814	0.1927073
H	3.0473421	1.1449576	-0.8611697
H	3.9517861	-0.1364284	-1.7364297
H	4.2520471	-1.0058374	2.2312183
N	2.7492791	-0.7687554	-0.1422767
O	4.4831761	0.8985566	1.4416583
C	2.4097581	-0.3286304	1.2527043
H	1.7594491	-1.0968414	1.6831483
H	1.8672141	0.6136706	1.1416783
C	3.3437251	-2.1335794	-0.1502837
H	3.5004081	-2.3987504	-1.1975997
H	2.6051411	-2.8033954	0.2956613
H	4.2823531	-2.1515344	0.4049663
O	-0.8404139	-0.8592344	0.5618263
O	-0.6353439	-1.0644454	-2.0231197

C	-1.7979729	-2.5173624	-1.5910487
H	-1.2458329	-3.0551854	-2.3620407
C	-1.5456339	-2.8557904	-0.2782227
H	-2.3117209	-2.6932144	0.4765233
C	-3.1282589	-1.9386904	-1.9913207
H	-3.0303269	-1.3657214	-2.9178167
H	-3.8810199	-2.7257144	-2.1360327
H	-3.4879689	-1.2578654	-1.2096107
C	-0.3231429	-3.6277104	0.1210133
H	0.1118951	-3.2174724	1.0449773
H	-0.5473549	-4.6878784	0.3112133
H	0.4269621	-3.5675524	-0.6781887

E = -1264.20491241, H = -1263.676944
G = -1263.766578

4.30 • NMO

C	-3.9768080	-1.0510650	2.0312074
C	-3.6247250	0.4042940	2.1009504
C	-3.4409390	1.1802160	1.0321424
C	-3.0111080	2.6174080	1.0921694
C	-1.5388720	2.8256780	0.7118624
C	-1.1970630	2.5686210	-0.7536556
O	-1.4335660	1.2294050	-1.1846596
Os	-0.1399690	-0.0388820	-0.6146706
O	0.9539070	1.6329510	-0.5604816
C	0.2972800	2.8009130	-1.0225996
C	0.5900070	3.0177810	-2.5001276
O	1.6017470	-1.0297560	-0.8048896
H	-3.4920550	0.8370520	3.0981444
H	-3.5575760	0.7470180	0.0383264
H	-3.6390140	3.2282530	0.4256264
H	-3.1618450	2.9930530	2.1136064
H	-3.1715990	-1.6635770	2.4611494
H	-4.8953780	-1.2700880	2.5922534
H	-4.1207020	-1.3583070	0.9881514
H	-1.2663430	3.8707500	0.9226924
H	-0.9044120	2.1869370	1.3436884
H	-1.8182670	3.2172370	-1.3912736
H	0.6592480	3.6611530	-0.4365136
H	1.6732790	3.0505480	-2.6676116
H	0.1641250	2.1914110	-3.0834426
H	0.1547880	3.9629970	-2.8488296
C	3.7586860	0.1824320	2.0170824
C	4.8728600	0.5194670	-0.0061076
C	3.6358330	0.1439520	-0.8107376
H	3.5010200	0.7033240	2.9444914
H	5.4254970	1.2867750	-0.5572956
H	5.5437770	-0.3445160	0.1389954
H	3.0037860	1.0142350	-1.0103456
H	3.8838860	-0.3668700	-1.7460846
H	4.3568180	-0.7056240	2.2804574
N	2.7494350	-0.7908900	-0.0394746
O	4.5258590	1.0807960	1.2428234
C	2.4623970	-0.1826470	1.3037464
H	1.8547670	-0.9036180	1.8602984
H	1.8895090	0.7250750	1.0997664

C	3.3481170	-2.1459340	0.0963434
H	3.4691170	-2.5379930	-0.9152236
H	2.6283550	-2.7565890	0.6462284
H	4.3056120	-2.0986860	0.6173514
O	-1.0525280	-1.2982810	0.4518064
O	-0.6520330	-1.4140180	-1.9966246
C	-1.7075100	-2.2550930	-1.6044566
H	-1.6203750	-3.1897710	-2.1856306
C	-1.4746330	-2.5461810	-0.1309756
H	-2.3960800	-2.8361690	0.3941054
C	-3.0696140	-1.6230320	-1.8716346
H	-3.1569000	-1.3832430	-2.9368456
H	-3.8863690	-2.3018430	-1.5892946
H	-3.1631350	-0.6878670	-1.3084596
C	-0.3844420	-3.5842990	0.0946684
H	-0.0943850	-3.6076780	1.1532184
H	-0.7441480	-4.5808150	-0.1898556
H	0.4826790	-3.3263990	-0.5255496

E = -1264.29593778, H = -1263.763942
G = -1263.850202

4.31

6	4.601576000	-0.722598000	-0.124700000
6	5.825493000	-0.358713000	0.261859000
1	5.931409000	0.217215000	1.186991000
1	4.489640000	-1.301018000	-1.048140000
76	-1.693482000	-0.339444000	-0.152762000
8	0.349525000	-0.394173000	0.652207000
8	-1.124472000	1.526137000	0.024967000
6	7.089832000	-0.690134000	-0.472979000
6	3.335986000	-0.381513000	0.605934000
1	2.795422000	-1.299246000	0.876894000
1	3.582134000	0.145586000	1.538940000
6	2.403960000	0.487442000	-0.242143000
1	7.636944000	0.221826000	-0.747615000
1	7.761061000	-1.291520000	0.155052000
1	6.873643000	-1.254593000	-1.387676000
1	2.909949000	1.428301000	-0.502399000
1	2.161919000	-0.027591000	-1.183495000
6	1.095901000	0.803803000	0.461244000
6	0.214464000	1.780987000	-0.339749000
1	1.290455000	1.242578000	1.455008000
6	0.535348000	3.237440000	-0.069199000
1	0.327893000	1.546803000	-1.413879000
1	-0.099983000	3.886277000	-0.680291000
1	0.362947000	3.466864000	0.989476000
1	1.584550000	3.445291000	-0.311615000
8	-1.191189000	-0.361335000	-1.773241000
8	-3.330229000	0.074156000	-0.136603000
8	-1.636775000	-1.980921000	0.275888000
8	-1.508778000	-0.125990000	2.002966000
1	-0.342799000	-0.279352000	1.615959000
1	-1.640599000	0.807070000	2.215613000

E = -856.427488813, H = -856.167518
G = -856.229862

4.32

6	5.378919000	-0.614702000	-0.162609000
6	6.535304000	0.048252000	-0.107097000
1	6.661110000	0.816133000	0.662752000
1	5.247949000	-1.384149000	-0.930760000
76	-2.185432000	-0.100106000	-0.126597000
8	1.356275000	-1.066418000	1.227203000
8	-0.609769000	0.627851000	0.816585000
6	7.699756000	-0.181723000	-1.023309000
6	4.208023000	-0.376938000	0.745561000
1	3.930374000	-1.310856000	1.253683000
1	4.484681000	0.352561000	1.520139000
6	2.986244000	0.132573000	-0.023566000
1	7.958212000	0.736113000	-1.568658000
1	8.591360000	-0.480692000	-0.455600000
1	7.474900000	-0.967584000	-1.754008000
1	3.217695000	1.106438000	-0.474817000
1	2.748057000	-0.558819000	-0.845967000
6	1.748135000	0.258986000	0.845970000
6	0.581701000	0.932284000	0.110180000
1	1.978442000	0.838033000	1.755053000
6	0.719582000	2.443815000	0.013260000
1	0.540244000	0.501661000	-0.906130000
1	-0.161329000	2.860421000	-0.486105000
1	0.793193000	2.875042000	1.019007000
1	1.610466000	2.719081000	-0.563441000
8	-2.128190000	1.237800000	-1.172858000
8	-3.079631000	0.160720000	1.286031000
8	-3.185440000	-1.160414000	-1.006402000
8	-0.952823000	-1.547113000	-0.299748000
1	0.788528000	-0.985578000	2.003068000
1	-0.120432000	-1.384427000	0.196318000

E = -856.436255737, H = -856.170977

G = -856.237558

4.33

6	5.757711000	-0.312061000	-0.413779000
6	6.805912000	0.213857000	0.222640000
1	6.767611000	0.293854000	1.313825000
1	5.791905000	-0.394322000	-1.505604000
76	-2.388051000	0.052955000	-0.074835000
8	1.811718000	-1.818390000	0.088545000
8	-0.359153000	-0.250374000	0.638325000
6	8.056058000	0.705002000	-0.444265000
6	4.501617000	-0.792537000	0.251564000
1	4.319284000	-1.846371000	0.004390000
1	4.615697000	-0.724952000	1.343240000
6	3.280447000	0.024479000	-0.182339000
1	8.232891000	1.765269000	-0.217679000
1	8.935042000	0.149224000	-0.089887000
1	7.990016000	0.589441000	-1.532660000
1	3.447418000	1.077540000	0.074941000
1	3.159263000	-0.036430000	-1.274464000
6	1.995499000	-0.461339000	0.471657000
6	0.775622000	0.371419000	0.056637000
1	2.092707000	-0.393875000	1.568888000

6	0.866226000	1.817724000	0.517075000
1	0.694510000	0.318475000	-1.042767000
1	-0.083098000	2.331728000	0.330367000
1	1.077782000	1.859355000	1.593354000
1	1.651515000	2.354891000	-0.024801000
8	-1.682484000	1.086790000	-1.219078000
8	-2.673877000	0.837787000	1.393866000
8	-3.924661000	-0.284319000	-0.701589000
8	-1.895504000	-1.712055000	-0.039877000
1	1.211551000	-2.235994000	0.713396000
1	-0.855082000	-1.407193000	0.276234000

E = -856.415138460, H = -856.154423

G = -856.220180

4.34

C	-4.342397000	-0.885781000	0.515421000
C	-3.389914000	0.210699000	0.139630000
C	-2.154165000	0.016620000	-0.325037000
C	-1.209319000	1.128485000	-0.688511000
C	0.122728000	1.089732000	0.079101000
C	1.166158000	0.179791000	-0.548720000
C	2.524266000	0.300977000	0.148640000
C	3.546642000	-0.686384000	-0.399216000
H	-3.752166000	1.236791000	0.261683000
H	-1.775041000	-1.001025000	-0.440917000
H	-0.995385000	1.094819000	-1.769139000
H	-1.710334000	2.086348000	-0.494173000
H	-4.646522000	-0.800828000	1.567919000
H	-5.258662000	-0.837727000	-0.089302000
H	-3.881248000	-1.869338000	0.367225000
H	0.553080000	2.100355000	0.115648000
H	-0.041961000	0.769386000	1.115002000
H	1.324091000	0.496581000	-1.596880000
H	2.878276000	1.330013000	-0.041507000
H	4.534834000	-0.507182000	0.043780000
H	3.249808000	-1.713473000	-0.150380000
H	3.646380000	-0.584460000	-1.488328000
O	0.658808000	-1.147455000	-0.528256000
H	1.261281000	-1.722630000	-1.009616000
O	2.322493000	0.111518000	1.541161000
H	3.179181000	0.085032000	1.977900000

E = -464.779554931, H = -464.534519

G = -464.588678

4.35_H+

C	1.982027000	2.011132000	0.380827000
C	2.765624000	1.109319000	-0.313370000
H	2.911255000	1.285090000	-1.381283000
H	1.998125000	1.967936000	1.470499000
O	-0.171806000	0.972338000	0.822091000
O	1.369372000	-0.383910000	-0.903452000
O	-1.627961000	0.020304000	-0.997032000
C	3.719882000	0.178226000	0.364135000
H	3.839059000	-0.747971000	-0.208425000
H	4.708697000	0.653193000	0.424501000
H	3.390145000	-0.057029000	1.382946000

C	-0.946031000	1.992187000	0.134416000
C	-2.156230000	1.265078000	-0.455077000
H	-1.232221000	2.696795000	0.926083000
C	-3.240169000	0.963726000	0.559782000
H	-2.554502000	1.806308000	-1.321820000
H	-4.009471000	0.328768000	0.109205000
H	-2.818082000	0.453036000	1.435682000
H	-3.709658000	1.897461000	0.890491000
Os	-0.126549000	-0.635022000	-0.129921000
O	-0.368830000	-1.816462000	1.294168000
H	-0.383577000	-2.765996000	1.082026000
H	-0.333631000	2.470965000	-0.600865000
H	1.454735000	2.816965000	-0.085538000
E=	-627.849709681		

4.35_[ox]

C	3.608039000	0.267125000	0.370259000
C	2.662505000	1.031106000	-0.510400000
C	1.936015000	2.109309000	-0.022172000
C	-0.818309000	2.212530000	-0.139521000
C	-2.078713000	1.422121000	-0.487339000
C	-3.015798000	1.245014000	0.696149000
O	0.008689000	1.282827000	0.529650000
Os	-0.144471000	-0.651386000	0.007985000
O	-1.615495000	0.173300000	-0.962011000
O	1.418700000	-0.481165000	-0.752250000
O	0.079470000	-1.087048000	1.636846000
H	2.856815000	1.008907000	-1.583871000
H	2.017851000	2.334746000	1.040152000
H	3.770131000	-0.742269000	-0.021826000
H	4.579633000	0.777258000	0.417628000
H	3.204816000	0.190377000	1.387601000
H	-1.042711000	3.041348000	0.549821000
H	-2.605776000	1.895638000	-1.328492000
H	-3.831747000	0.567213000	0.424985000
H	-2.471217000	0.821757000	1.551167000
H	-3.440074000	2.211748000	0.994680000
O	-0.769607000	-2.105107000	-0.679207000
H	-0.295228000	2.562915000	-1.004689000
H	1.500792000	2.849981000	-0.660048000
E=	-702.577983223		

4.35_{[ox]H⁺}

C	3.698147000	0.235680000	0.255173000
C	2.846495000	1.215832000	-0.480180000
C	2.069016000	2.162334000	0.131547000
C	-0.857897000	2.143222000	0.014930000
C	-2.139476000	1.420212000	-0.451931000
C	-3.192157000	1.260524000	0.621507000
O	-0.125973000	1.130730000	0.704825000
Os	-0.176824000	-0.629616000	-0.083692000
O	-1.662540000	0.118749000	-0.871526000
O	1.152869000	-0.353861000	-1.095264000
H	2.972728000	1.276120000	-1.564584000
H	2.070050000	2.203685000	1.221912000
H	3.635921000	-0.762165000	-0.196611000

H	4.750848000	0.544596000	0.182184000
H	3.423694000	0.179917000	1.313863000
H	-1.106632000	2.919235000	0.750842000
H	-2.543349000	1.881294000	-1.362280000
H	-3.997301000	0.607343000	0.270711000
H	-2.750083000	0.842519000	1.535108000
H	-3.619491000	2.242220000	0.855623000
O	-0.622478000	-2.274639000	-0.128380000
O	0.546290000	-0.911867000	1.651069000
H	0.500627000	-1.843168000	1.920329000
H	-0.282069000	2.541539000	-0.794184000
H	1.533572000	2.917991000	-0.404347000

E = -702.974049489

4.35'_{[ox]H+}

C	-3.6227287	-0.5985462	0.5420518
C	-2.4934827	0.3658748	0.3711318
C	-2.0618807	0.7914008	-0.8644592
C	1.0536333	1.1583358	-0.7456372
C	2.0755673	0.8938038	0.3590408
C	3.3466763	0.2186698	-0.1168532
O	0.4507583	-0.0915332	-1.1123142
Os	0.3744723	-1.6952382	-0.1207612
O	1.3106323	0.0624228	1.2547198
O	-1.1202707	-1.3533112	0.6589138
H	-2.1864757	0.9297948	1.2558138
H	-2.4354877	0.2498738	-1.7380672
H	-3.4712887	-1.2375992	1.4190238
H	-4.5512487	-0.0334342	0.7052278
H	-3.7514777	-1.2219202	-0.3495712
H	1.5467513	1.5170958	-1.6578172
H	2.2974193	1.8404918	0.8682318
H	3.9614943	-0.1028782	0.7325688
H	3.1396513	-0.6573722	-0.7454962
H	3.9346343	0.9293508	-0.7081262
O	1.4918523	-2.4420132	0.9125878
O	0.0253223	-2.7443102	-1.3783302
H	1.8873273	-0.3498952	1.9137738
H	0.2951503	1.8652368	-0.4093442
H	-1.4970017	1.7056998	-1.0463072

E = -702.998700966

4.35_{H+} • NMO

C	-1.3062397	3.3831222	-0.1710605
C	-2.5284307	2.5127962	-0.1992785
C	-2.9793307	1.8665242	0.9519125
C	-3.2543517	-0.8595038	1.0006505
O	-2.0589357	-0.0556608	0.9200065
Os	-1.1213147	-0.3349018	-0.7740315
C	-2.9660977	-2.1708948	0.2665805
C	-2.1700087	-3.1582778	1.1003755
O	-1.7579007	1.1230982	-1.4013815
H	-3.2699927	2.7215932	-0.9708195
H	-2.4144577	2.0116462	1.8714775
H	-0.8745517	3.4821792	-1.1735265
H	-1.5641547	4.3902582	0.1812275

H	-0.5572417	2.9653982	0.5149215
H	-3.4384507	-1.0520898	2.0664085
H	-3.9045557	-2.6227538	-0.0809245
H	-1.8922207	-4.0254068	0.4928835
H	-1.2589607	-2.6785048	1.4847675
H	-2.7667357	-3.5024288	1.9528485
C	3.8496523	-1.3328538	-0.5126525
C	4.0791063	0.6272832	0.7136765
C	2.5716073	0.7476752	0.9000665
H	4.1729493	-0.8489608	-1.4489255
H	4.5640243	1.0321452	1.6076715
H	4.4302833	1.2070242	-0.1553785
H	2.2528573	0.2212772	1.8039705
H	2.2337893	1.7877342	0.9373525
H	4.1840143	-2.3744498	-0.5374195
N	1.8183043	0.0832382	-0.2238315
O	4.4628353	-0.7223698	0.6013165
C	2.3336293	-1.3253308	-0.3787485
H	1.8254043	-1.7543958	-1.2440785
H	2.0274323	-1.8355348	0.5402435
O	-2.2158797	-1.8457148	-0.9219625
C	1.8964823	0.8897162	-1.4758065
H	1.3969713	0.3336062	-2.2707415
H	1.3931863	1.8386632	-1.2715805
H	2.9461253	1.0612292	-1.7200935
O	0.4888393	0.0593302	0.2623885
O	-0.0095637	-1.2013668	-2.1561215
H	-0.5412277	-1.8231868	-2.6685455
H	-4.0861767	-0.2898438	0.5657285
H	-3.9907147	1.4688932	1.0204345

E = -1030.09671969

4.35_H+ • H₂O

C	1.9731969	1.4990864	-0.0383426
C	2.6723849	0.4096814	-0.5141736
H	2.8314639	0.3422164	-1.5920206
H	2.0139909	1.7069664	1.0307834
Os	-0.3166701	-1.0452726	0.0012484
O	-0.1578151	0.7266834	0.6270904
O	1.1767959	-1.1054206	-0.8192956
O	-0.4546421	-1.6497836	1.7698804
O	-1.8339291	-0.4465806	-0.8917836
C	3.5370679	-0.4375186	0.3652464
H	3.5744669	-1.4711086	0.0038764
H	4.5647719	-0.0496336	0.3542824
H	3.1770459	-0.4250316	1.4009354
C	-0.8946351	1.6437904	-0.2119786
C	-2.2012591	0.9292914	-0.5898596
H	-1.0993261	2.5225594	0.4125784
C	-3.2325961	0.9418004	0.5197834
H	-2.6095281	1.3367744	-1.5226886
H	-4.0899061	0.3186174	0.2456744
H	-2.7933051	0.5645774	1.4528614
H	-3.5875241	1.9651474	0.6874424
O	-0.9123331	-3.0822306	-0.5905046
H	-0.2411121	-3.6638716	-0.9757256

H	-0.6419001	-2.5995426	1.8383574
H	-1.6726881	-3.0868476	-1.1922416
H	1.5031679	2.2352534	-0.6902736
H	-0.2851821	1.9203974	-1.0811536

E = -704.31283839

4.36_H⁺

O	-0.7239247	-0.7245953	1.0986598
O	-2.8533107	-1.4438123	-0.3644132
O	-0.3426767	-0.0315993	-1.2909792
C	0.4983793	-1.2812933	0.5432548
C	0.8995273	-0.3427033	-0.5964382
H	1.2139783	-1.2510073	1.3751898
C	1.5599243	0.9378647	-0.1277162
H	1.5159003	-0.8666783	-1.3369312
H	1.6974963	1.6197467	-0.9727772
H	0.9462563	1.4311397	0.6379558
H	2.5432003	0.7133547	0.3017158
Os	-1.8617397	-0.0662193	-0.2294602
O	-2.3946887	1.5133057	0.6093458
H	-3.0197827	2.0806297	0.1253658
H	0.3214613	-2.2881333	0.2272278

E = -509.995810372

4.36_[ox]

C	1.1425787	0.9151724	0.0399151
C	-0.3025743	0.8979604	-0.4556459
C	-1.3187043	1.0188234	0.6681911
O	1.3607897	-0.3884086	0.5390361
Os	0.3572177	-1.9007936	-0.3225369
O	-0.4457403	-0.3297876	-1.1423599
O	1.8776177	-2.3954616	-1.0254749
O	0.1916257	-2.6330526	1.2037381
H	1.2747247	1.6326814	0.8646611
H	-0.4588623	1.6895094	-1.2030259
H	-2.3288233	0.8716054	0.2723321
H	-1.1245253	0.2599674	1.4383881
H	-1.2588053	2.0115824	1.1313841
O	-0.8152163	-2.7453756	-1.2650939
H	1.8486967	1.0955774	-0.7435079

E = -584.736881352

4.36_{[ox]H}⁺

C	0.9680577	1.1861934	-0.0009082
C	-0.4622493	1.0676684	-0.5695242
C	-1.5572953	1.1837954	0.4664748
O	1.2272837	-0.1066286	0.5451888
Os	0.5660177	-1.6014306	-0.4802172
O	-0.4841923	-0.2529756	-1.1634532
O	1.9573887	-1.7238586	-1.4375573
H	0.9865467	1.8986034	0.8344128
H	-0.6117473	1.7586644	-1.4089402
H	-2.5270893	0.9342074	0.0246998
H	-1.3564983	0.5174194	1.3152667
H	-1.5986133	2.2159844	0.8325768
O	-0.4597293	-2.9352736	-0.7548253

O	1.0311157	-2.3537896	1.2019228
H	0.6249307	-3.2244776	1.3391228
H	1.6960727	1.4358984	-0.7442393

E = -585.113007957

4.36' _{[ox]H+}

C	1.1192219	0.8558223	0.5985753
C	0.0211579	1.0230543	-0.4506757
C	-1.3840341	1.0519603	0.1173013
O	1.0989879	-0.5026757	1.0613463
Os	0.3610609	-2.0207617	0.2176963
O	0.2553659	-0.1278657	-1.2867927
O	1.7903519	-2.4685417	-0.6282847
H	0.9081909	1.4642843	1.4869373
H	0.2290789	1.9268653	-1.0377087
H	-2.1317111	0.9966783	-0.6832197
H	-1.5646551	0.2255363	0.8172303
H	-1.5372861	1.9931823	0.6567273
O	-1.0395501	-2.2296677	-0.7143277
O	0.2671849	-3.0231227	1.5557543
H	-0.4881221	-0.2679947	-1.8905507
H	2.0947569	1.1032463	0.1799913

E = -585.136718204

4.36_{H+} • NMO

C	-1.3062397	3.3831222	-0.1710605
C	-2.5284307	2.5127962	-0.1992785
C	-2.9793307	1.8665242	0.9519125
C	-3.2543517	-0.8595038	1.0006505
O	-2.0589357	-0.0556608	0.9200065
Os	-1.1213147	-0.3349018	-0.7740315
C	-2.9660977	-2.1708948	0.2665805
C	-2.1700087	-3.1582778	1.1003755
O	-1.7579007	1.1230982	-1.4013815
H	-3.2699927	2.7215932	-0.9708195
H	-2.4144577	2.0116462	1.8714775
H	-0.8745517	3.4821792	-1.1735265
H	-1.5641547	4.3902582	0.1812275
H	-0.5572417	2.9653982	0.5149215
H	-3.4384507	-1.0520898	2.0664085
H	-3.9045557	-2.6227538	-0.0809245
H	-1.8922207	-4.0254068	0.4928835
H	-1.2589607	-2.6785048	1.4847675
H	-2.7667357	-3.5024288	1.9528485
C	3.8496523	-1.3328538	-0.5126525
C	4.0791063	0.6272832	0.7136765
C	2.5716073	0.7476752	0.9000665
H	4.1729493	-0.8489608	-1.4489255
H	4.5640243	1.0321452	1.6076715
H	4.4302833	1.2070242	-0.1553785
H	2.2528573	0.2212772	1.8039705
H	2.2337893	1.7877342	0.9373525
H	4.1840143	-2.3744498	-0.5374195
N	1.8183043	0.0832382	-0.2238315
O	4.4628353	-0.7223698	0.6013165
C	2.3336293	-1.3253308	-0.3787485

H	1.8254043	-1.7543958	-1.2440785
H	2.0274323	-1.8355348	0.5402435
O	-2.2158797	-1.8457148	-0.9219625
C	1.8964823	0.8897162	-1.4758065
H	1.3969713	0.3336062	-2.2707415
H	1.3931863	1.8386632	-1.2715805
H	2.9461253	1.0612292	-1.7200935
O	0.4888393	0.0593302	0.2623885
O	-0.0095637	-1.2013668	-2.1561215
H	-0.5412277	-1.8231868	-2.6685455
H	-4.0861767	-0.2898438	0.5657285
H	-3.9907147	1.4688932	1.0204345

E = -912.25804720

4.36_{H+} • H₂O

Os	0.5719237	-1.2688859	-0.1046266
O	1.5017497	0.0888381	0.8166504
O	1.9243267	-1.9384829	-0.8983496
O	-0.0125843	-1.9693109	1.5325304
O	-0.3740253	0.1160921	-0.9077646
C	1.3835727	1.3569201	0.1339894
C	-0.0614143	1.4370301	-0.3819226
H	1.5669787	2.1252871	0.8956844
C	-1.0625413	1.7982171	0.6962284
H	-0.1294823	2.1188081	-1.2383346
H	-2.0823703	1.7217111	0.3056264
H	-0.9529123	1.1271941	1.5585614
H	-0.8956273	2.8288091	1.0299094
O	-0.8692743	-2.6448339	-1.0447856
H	-0.5267623	-3.4203409	-1.5122416
H	-0.6395123	-2.7036429	1.4349814
H	-1.4748263	-2.1910589	-1.6511216
H	2.1327807	1.4176501	-0.6650156

E = -586.45974657

4.37_{H+}

O	-0.705967000	0.419072000	0.740690000
O	0.293511000	-1.239016000	-1.312821000
O	-2.315752000	-0.047429000	-1.080823000
C	-1.291153000	1.643749000	0.223388000
C	-2.584696000	1.256757000	-0.461320000
H	-1.430815000	2.294102000	1.093493000
C	-3.768730000	1.099030000	0.471495000
H	-2.810832000	1.916358000	-1.306170000
H	-4.614675000	0.653148000	-0.060744000
H	-3.505825000	0.466889000	1.330491000
H	-4.071532000	2.085678000	0.840776000
Os	-1.004061000	-1.079118000	-0.300030000
O	-1.830555000	-2.357351000	0.719930000
H	-1.607226000	-3.303956000	0.759219000
H	-0.565249000	2.088557000	-0.468280000

E = -510.000849503, H = -509.881960
G = -509.926288

4.37_[ox]

C	-1.957125000	1.279649000	-0.287414000

C	-2.274382000	-0.186100000	-0.548842000
C	-2.965121000	-0.871792000	0.616067000
O	-0.821218000	1.235157000	0.531522000
Os	0.585784000	-0.026981000	0.019545000
O	-1.005290000	-0.785753000	-0.787124000
O	1.419159000	1.100687000	-0.931304000
O	1.090334000	0.029097000	1.635358000
H	-2.764191000	1.794329000	0.249777000
H	-2.843553000	-0.311686000	-1.480265000
H	-2.999996000	-1.953341000	0.449319000
H	-2.419429000	-0.669637000	1.546935000
H	-3.990561000	-0.496684000	0.720212000
O	1.243527000	-1.510650000	-0.501303000
H	-1.734214000	1.808748000	-1.227493000

E = -584.745654502, H = -584.632333
G = -584.678792

4.37_{[ox]H⁺}

C	-2.286072000	-0.052607000	-0.552181000
C	-1.903381000	1.412390000	-0.276808000
O	-1.028132000	-0.632255000	-0.913153000
Os	0.524939000	-0.087743000	0.009065000
O	-0.673965000	1.290441000	0.420910000
H	-2.906005000	-0.116359000	-1.456134000
H	-2.614067000	1.918769000	0.387126000
O	1.439324000	-0.808366000	-1.205640000
O	0.596893000	-1.048812000	1.372986000
C	-2.892317000	-0.774077000	0.630832000
H	-3.892790000	-0.369161000	0.822868000
H	-2.988246000	-1.842600000	0.414020000
H	-2.283347000	-0.640820000	1.534752000
H	-1.752592000	1.985959000	-1.198440000
O	1.713833000	1.334568000	0.309268000
H	2.648708000	1.133832000	0.120869000

E = -585.128059128, H = -585.003543
G = -585.049881

4.37'_{[ox]H⁺}

C	0.4363794	1.3916800	0.2101141
C	1.0320484	0.0132200	0.4259321
C	1.4721994	-0.6813660	-0.8463939
O	-0.8579276	1.2249380	-0.4242219
Os	-2.1190456	-0.0433300	0.0047791
O	-0.0711236	-0.6724120	1.0604161
O	-2.6038656	-0.1081210	1.6087891
H	1.0205664	2.0043020	-0.4838029
H	1.8497694	0.0944760	1.1534951
H	1.7789074	-1.7130530	-0.6363479
H	0.6690674	-0.6960430	-1.5939019
H	2.3355034	-0.1579530	-1.2726089
O	-1.9076896	-1.5823030	-0.6451999
O	-3.4007596	0.6276570	-0.8348999
H	0.0968994	-1.6241510	1.1198891
H	0.2690714	1.9224590	1.1539621

E = -585.154943696, H = -585.028935
G = -585.076415

4.37_H⁺ • NMO

C	-3.6188663	-0.3743347	1.1595706
O	-2.2713873	0.1257613	1.1111856
Os	-1.6200103	0.2543613	-0.6468224
C	-3.7027333	-1.5152947	0.1564466
C	-3.2299683	-2.8471967	0.7063306
O	-2.1341893	1.6150863	-1.4402404
H	-3.8050593	-0.7074337	2.1863776
H	-4.7155803	-1.5936237	-0.2586174
H	-3.1694033	-3.5890137	-0.0965074
H	-2.2413963	-2.7367977	1.1713636
H	-3.9346473	-3.2109467	1.4630616
C	3.4770137	-0.2903367	-0.1459224
C	3.4642427	1.8743463	0.6973186
C	1.9491347	1.8636593	0.8543486
H	3.7715087	0.0464333	-1.1538344
H	3.8816317	2.4870533	1.5023706
H	3.7750197	2.3183023	-0.2623254
H	1.6653097	1.4807763	1.8385866
H	1.4996267	2.8486693	0.6965996
H	3.9199747	-1.2766307	0.0228076
N	1.2946327	0.9214713	-0.1305254
O	3.9897347	0.5759703	0.8394566
C	1.9649417	-0.4253647	-0.0239274
H	1.5371067	-1.0614347	-0.7997834
H	1.6888197	-0.7947717	0.9685646
O	-2.8442723	-1.1460767	-0.9457234
C	1.3177357	1.4891333	-1.5080724
H	0.9198127	0.7442933	-2.1982614
H	0.7042447	2.3938563	-1.4950614
H	2.3479437	1.7353753	-1.7705884
O	-0.0239793	0.8307233	0.3584946
O	-0.5029333	-0.8931147	-1.6833174
H	-1.0502073	-1.5888897	-2.0821794
H	-4.3038023	0.4459883	0.9088276
E = -912.28368484			

4.37_H⁺ • H₂O

Os	0.6732889	-1.2837898	-0.1427113
O	1.4106699	0.0710142	0.8877917
O	1.9318599	-1.9472008	-0.9958273
O	0.1784199	-2.0362288	1.5018087
O	-0.3196931	0.0853392	-0.9022303
C	1.3580349	1.3316772	0.1978757
C	-0.0522111	1.4291082	-0.3821603
H	1.5697999	2.1122882	0.9357407
C	-1.1116291	1.7858692	0.6383107
H	-0.0822641	2.0892222	-1.2559853
H	-2.1104021	1.6893692	0.2007657
H	-1.0322971	1.1357942	1.5192557
H	-0.9749681	2.8259022	0.9562497
O	-0.9195581	-2.4844738	-0.9972943
H	-0.7568171	-3.3750118	-1.3448743
H	-0.4404621	-2.7805258	1.4279137
H	-1.4421651	-1.9911288	-1.6516193

H 2.1203939 1.3427762 -0.5930103
E = -586.46931851

4.38

C	-2.133682000	1.421141000	-0.666072000
O	-1.578484000	0.151566000	-1.076930000
C	-2.489751000	-0.894695000	-0.687726000
C	-3.853911000	-0.277356000	-0.960744000
C	-3.651668000	1.200749000	-0.565555000
C	-2.256669000	-1.259525000	0.803997000
C	-2.420284000	-2.762119000	0.997447000
Os	0.455183000	-0.317365000	-0.008226000
O	-0.112736000	1.480250000	0.552440000
C	-1.462430000	1.820091000	0.656789000
C	-1.589886000	3.313570000	0.908987000
O	-1.003093000	-0.840670000	1.269035000
O	1.704756000	-0.616066000	1.123123000
O	1.434082000	0.529344000	-1.167036000
H	-1.840279000	2.131817000	-1.447414000
H	-2.251621000	-1.745428000	-1.332144000
H	-4.094779000	-0.363274000	-2.025711000
H	-4.646213000	-0.766760000	-0.383808000
H	-4.206723000	1.876877000	-1.221701000
H	-3.983100000	1.382188000	0.463930000
H	-3.022809000	-0.735396000	1.404878000
H	-2.346244000	-3.012970000	2.060409000
H	-3.395761000	-3.100483000	0.620007000
H	-1.624054000	-3.282020000	0.450968000
H	-1.925392000	1.258756000	1.482230000
H	-1.113657000	3.573460000	1.859799000
H	-1.098848000	3.873618000	0.103882000
H	-2.647698000	3.603919000	0.955419000
O	0.200080000	-1.787337000	-0.829287000
C	3.514531000	0.944860000	-0.507627000
H	3.623413000	0.876875000	-1.590179000
C	3.784688000	-0.160522000	0.244051000
H	3.929268000	-0.040975000	1.317403000
C	4.065220000	-1.505515000	-0.349484000
H	3.508968000	-2.285623000	0.185315000
H	3.773474000	-1.530441000	-1.406166000
H	5.133392000	-1.752281000	-0.273784000
C	3.291722000	2.303000000	0.082495000
H	4.139246000	2.967176000	-0.134627000
H	2.387922000	2.756248000	-0.342799000
H	3.163449000	2.235673000	1.169128000

E = -1012.41680776, H = -1012.056733
G = -1012.128743

4.39

C	-2.182095000	1.351902000	-0.676743000
O	-1.603515000	0.092601000	-1.079878000
C	-2.432568000	-0.968618000	-0.555154000
C	-3.841467000	-0.431682000	-0.769231000
C	-3.683630000	1.079624000	-0.491077000
C	-2.100964000	-1.232412000	0.929713000
C	-2.392898000	-2.689723000	1.265248000

Os	0.486806000	-0.289711000	-0.108874000
O	-0.102714000	1.497382000	0.404784000
C	-1.449997000	1.806393000	0.594141000
C	-1.607048000	3.300530000	0.820809000
O	-0.755290000	-0.960045000	1.256737000
O	1.935437000	-0.608269000	1.035268000
O	1.783343000	0.792910000	-1.061203000
H	-1.955285000	2.050996000	-1.489397000
H	-2.192265000	-1.848363000	-1.160173000
H	-4.150806000	-0.604188000	-1.805308000
H	-4.568636000	-0.909726000	-0.104056000
H	-4.292908000	1.681910000	-1.170427000
H	-3.981460000	1.326892000	0.535083000
H	-2.751012000	-0.592322000	1.551026000
H	-2.217554000	-2.867554000	2.330840000
H	-3.434389000	-2.947855000	1.028404000
H	-1.722562000	-3.335905000	0.684912000
H	-1.841489000	1.254565000	1.462508000
H	-1.081478000	3.597710000	1.734074000
H	-1.179732000	3.851872000	-0.025597000
H	-2.667648000	3.564645000	0.925027000
O	0.377765000	-1.632158000	-1.109489000
C	3.027324000	0.939249000	-0.388087000
H	3.806557000	0.996103000	-1.163941000
C	3.222233000	-0.313011000	0.458119000
H	3.886854000	-0.120802000	1.311375000
C	3.708900000	-1.508175000	-0.343745000
H	3.675489000	-2.415643000	0.268739000
H	3.078755000	-1.652668000	-1.230504000
H	4.741908000	-1.339489000	-0.672053000
C	3.020425000	2.213390000	0.446461000
H	4.017297000	2.400737000	0.865448000
H	2.727179000	3.063523000	-0.178626000
H	2.296437000	2.119420000	1.264578000

E = -1012.54514767, H = -1012.180482
G = -1012.247639

4.40

C	-2.663978000	1.225842000	-0.015688000
O	-2.160636000	0.103100000	-0.746178000
C	-2.768582000	-1.119779000	-0.323455000
C	-3.883858000	-0.718406000	0.646208000
C	-3.400063000	0.634874000	1.186367000
C	-1.669532000	-2.017350000	0.294563000
C	-2.006017000	-3.492728000	0.155404000
Os	0.383043000	-0.005780000	-0.234998000
O	-0.365888000	1.809125000	-0.475705000
C	-1.471383000	2.173411000	0.302528000
C	-1.793469000	3.624742000	-0.021208000
O	-0.480159000	-1.774598000	-0.408984000
O	1.818171000	-1.240804000	0.171689000
O	1.890389000	1.167578000	0.111758000
O	0.418311000	-0.040046000	-1.943306000
C	3.179934000	0.617232000	0.018816000
C	3.036825000	-0.749460000	0.672200000
C	4.145727000	-1.727699000	0.333702000

C	4.169914000	1.543389000	0.697884000
O	-0.405645000	0.059247000	1.309528000
H	-3.364138000	1.752285000	-0.683430000
H	-3.147965000	-1.613189000	-1.227773000
H	-4.830139000	-0.601919000	0.105163000
H	-4.028412000	-1.466043000	1.434435000
H	-4.223340000	1.274042000	1.521714000
H	-2.696101000	0.494258000	2.012945000
H	-1.553337000	-1.764598000	1.359527000
H	-1.241489000	-4.101360000	0.648517000
H	-2.979098000	-3.702884000	0.618860000
H	-2.049770000	-3.767908000	-0.905152000
H	-1.232325000	2.089161000	1.373672000
H	-0.953859000	4.267338000	0.261498000
H	-1.985615000	3.737546000	-1.094641000
H	-2.685451000	3.937452000	0.537800000
H	3.436077000	0.473292000	-1.045803000
H	2.946890000	-0.611535000	1.763507000
H	3.940895000	-2.703821000	0.784920000
H	4.218223000	-1.849526000	-0.753320000
H	5.101427000	-1.356323000	0.723249000
H	5.183165000	1.132382000	0.613358000
H	4.151669000	2.527804000	0.219261000
H	3.911984000	1.659622000	1.757189000

E = -1087.61872173, H = -1087.250115

G = -1087.320120

4.41

6	-0.768181000	1.842308000	-0.238752000
8	-0.894805000	0.407337000	-0.069174000
6	-2.211272000	-0.058133000	-0.555773000
6	-2.946332000	1.244673000	-0.903119000
6	-2.193250000	2.333572000	-0.124136000
6	-2.875634000	-0.879431000	0.537408000
6	-4.187927000	-1.476683000	0.044399000
76	1.122906000	-0.524340000	-0.206634000
8	1.219718000	1.219721000	0.957961000
6	0.250739000	2.287928000	0.802890000
6	0.956433000	3.566961000	0.412448000
8	-1.948031000	-1.892339000	0.878103000
8	1.297562000	0.433593000	-1.587434000
1	-0.374492000	2.023726000	-1.249895000
1	-2.015929000	-0.695473000	-1.425773000
1	-2.885154000	1.438939000	-1.978684000
1	-4.001965000	1.196357000	-0.625632000
1	-2.324228000	3.327503000	-0.560347000
1	-2.501500000	2.360046000	0.928107000
1	-3.055405000	-0.219229000	1.403999000
1	-4.609697000	-2.122450000	0.824221000
1	-4.936124000	-0.709584000	-0.181325000
1	-4.011954000	-2.087111000	-0.849957000
1	-0.249597000	2.381730000	1.775743000
1	0.219575000	4.368647000	0.277140000
1	1.660879000	3.870468000	1.192100000
1	1.501684000	3.421926000	-0.527699000
8	0.288778000	-1.892640000	-0.704558000

8	0.644808000	-0.763048000	1.823432000
1	0.945535000	0.412107000	1.810217000
1	1.201732000	-1.377909000	2.322002000
8	2.682356000	-1.059979000	0.108590000
1	-2.374717000	-2.528208000	1.462371000

E = -932.068435765, H = -931.786149
G = -931.849396

4.42

6	-2.725395000	0.878952000	-0.345100000
8	-1.775669000	-0.088213000	-0.798425000
6	-2.259860000	-1.413011000	-0.596668000
6	-3.603937000	-1.268163000	0.143340000
6	-3.538374000	0.151660000	0.715785000
6	-1.225453000	-2.209353000	0.191630000
6	-1.577594000	-3.687527000	0.261371000
76	1.646762000	0.135047000	0.063882000
8	-1.072651000	2.549497000	-0.874251000
6	-1.944876000	2.086695000	0.143883000
6	-2.856513000	3.233174000	0.536226000
8	0.024848000	-2.036307000	-0.481250000
8	2.689090000	1.419804000	0.421869000
1	-3.361992000	1.181749000	-1.195370000
1	-2.380865000	-1.889574000	-1.581109000
1	-4.433984000	-1.354050000	-0.566640000
1	-3.742614000	-2.029170000	0.917940000
1	-4.525459000	0.596719000	0.873605000
1	-2.986882000	0.165230000	1.666029000
1	-1.148588000	-1.776486000	1.202746000
1	-0.800589000	-4.239940000	0.805783000
1	-2.525892000	-3.851323000	0.784315000
1	-1.656120000	-4.101206000	-0.752096000
1	-1.354792000	1.759717000	1.016156000
1	-3.488052000	2.953930000	1.388565000
1	-2.251823000	4.101597000	0.818173000
1	-3.494035000	3.515542000	-0.310949000
8	1.029933000	0.428286000	-1.489398000
8	0.443517000	0.137274000	1.265516000
8	2.588683000	-1.282952000	0.113396000
1	-0.666707000	1.776986000	-1.290006000
1	0.634509000	-2.726941000	-0.194640000

E = -931.706550095, H = -931.431165
G = -931.497692

4.42_H+

6	-2.353873000	1.047531000	-0.469362000
8	-1.468842000	-0.025369000	-0.776018000
6	-2.102760000	-1.297059000	-0.646799000
6	-3.568737000	-1.011019000	-0.299323000
6	-3.535191000	0.415319000	0.268362000
6	-1.323220000	-2.054721000	0.415531000
6	-1.670750000	-3.527041000	0.491613000
76	1.414653000	0.031721000	-0.038093000
8	-0.205145000	2.130978000	-0.077720000
6	-1.574775000	2.058490000	0.367016000
6	-2.221997000	3.428518000	0.379371000

8	0.075377000	-1.916323000	0.023834000
8	2.364752000	1.396688000	0.161049000
1	-2.676155000	1.511281000	-1.416315000
1	-1.997146000	-1.826092000	-1.603519000
1	-4.174098000	-1.047142000	-1.210309000
1	-3.986054000	-1.732662000	0.409875000
1	-4.472309000	0.953244000	0.100669000
1	-3.336874000	0.400090000	1.348145000
1	-1.443100000	-1.558489000	1.388357000
1	-1.055299000	-4.039766000	1.241698000
1	-2.716778000	-3.650279000	0.792162000
1	-1.526024000	-4.007684000	-0.483314000
1	-1.506200000	1.665271000	1.388679000
1	-3.245296000	3.355989000	0.766847000
1	-1.657646000	4.119369000	1.013572000
1	-2.275382000	3.839387000	-0.638098000
8	0.980200000	0.036468000	-1.657886000
8	0.443859000	0.115244000	1.575485000
1	0.481628000	0.998126000	1.980689000
8	2.528396000	-1.209893000	0.157424000
1	-0.155124000	2.666162000	-0.881691000
1	0.587293000	-2.640054000	0.409816000

E = -932.088616924, H = -931.801338

G = -931.865818

4.43

6	-2.416506000	0.848217000	-0.623870000
8	-1.682961000	-0.232626000	-1.179851000
6	-1.985403000	-1.417973000	-0.478616000
6	-3.486815000	-1.292569000	-0.204152000
6	-3.644239000	0.217424000	0.073975000
6	-1.169042000	-1.593755000	0.846799000
6	-0.605625000	-3.002267000	0.944528000
76	1.246208000	-0.031776000	-0.158827000
8	-0.203659000	1.721643000	-0.156574000
6	-1.528951000	1.653044000	0.334551000
6	-2.068794000	3.068486000	0.497119000
8	-0.152652000	-0.625461000	1.060470000
8	2.518220000	-0.856522000	0.591392000
8	2.037894000	1.194851000	-1.021652000
1	-2.694948000	1.490769000	-1.469485000
1	-1.742872000	-2.244889000	-1.155610000
1	-4.041422000	-1.575743000	-1.105046000
1	-3.827124000	-1.921711000	0.626226000
1	-4.588119000	0.607608000	-0.317502000
1	-3.619891000	0.426367000	1.151175000
1	-1.856661000	-1.422007000	1.690265000
1	-0.100712000	-3.149889000	1.904831000
1	-1.418404000	-3.735645000	0.855857000
1	0.108576000	-3.176371000	0.129469000
1	-1.529477000	1.157305000	1.318069000
1	-3.114902000	3.038120000	0.831088000
1	-1.483699000	3.624440000	1.238253000
1	-2.015987000	3.598368000	-0.461295000
8	0.753324000	-1.108284000	-1.365819000
8	1.373883000	1.399480000	1.496998000

1	0.521678000	1.880563000	0.819805000
1	0.972000000	0.989398000	2.273007000

E = -931.639307792, H = -931.370917
G = -931.431639

4.44

6	3.222958000	-0.096498000	-0.541344000
8	1.797820000	-0.116423000	-0.486478000
6	1.261766000	1.201163000	-0.521519000
6	2.457484000	2.137248000	-0.753797000
6	3.621248000	1.331190000	-0.174755000
6	0.533503000	1.477020000	0.795734000
6	-0.113446000	2.862624000	0.841678000
8	3.367525000	-2.411484000	-0.156945000
6	3.774059000	-1.163950000	0.386001000
6	5.291925000	-1.087092000	0.497699000
8	-0.382019000	0.437621000	1.123859000
1	3.543143000	-0.340895000	-1.568741000
1	0.537977000	1.261367000	-1.348981000
1	2.603867000	2.288233000	-1.829468000
1	2.331318000	3.118688000	-0.287076000
1	4.593078000	1.616281000	-0.589536000
1	3.665559000	1.437807000	0.918265000
1	1.280912000	1.402505000	1.602098000
1	-0.905789000	2.872456000	1.597646000
1	0.634490000	3.612193000	1.124991000
1	-0.546219000	3.150614000	-0.121777000
1	3.306142000	-1.010191000	1.373672000
1	5.666406000	-1.919904000	1.106672000
1	5.745933000	-1.160914000	-0.498992000
1	5.613542000	-0.152525000	0.973446000
1	3.647568000	-3.115349000	0.436136000
76	-1.770089000	-0.271228000	-0.094457000
8	-1.984102000	-1.179422000	1.586379000
1	-1.252001000	-0.887717000	2.152185000
8	-2.038252000	1.327490000	-0.617837000
8	-3.296887000	-0.968960000	-0.383988000
8	-0.743599000	-1.030013000	-1.194992000

E = -931.660350532, H = -931.388224
G = -931.452491

4.45

6	2.985878000	-0.476259000	-0.830649000
8	1.644991000	-0.002900000	-0.951619000
6	1.565064000	1.339343000	-0.488843000
6	3.002646000	1.902845000	-0.510742000
6	3.838184000	0.759924000	-1.119246000
6	0.925801000	1.407164000	0.913252000
6	0.320269000	2.781525000	1.158090000
8	2.131070000	-1.866418000	0.957587000
6	3.226904000	-1.068988000	0.565087000
6	4.465346000	-1.946584000	0.592721000
8	-0.023006000	0.373607000	1.112082000
1	3.095560000	-1.270221000	-1.579846000
1	0.915632000	1.870259000	-1.194984000
1	3.068778000	2.820410000	-1.102693000

1	3.339789000	2.137807000	0.506522000
1	3.941245000	0.892103000	-2.201595000
1	4.840466000	0.695028000	-0.682017000
1	1.713510000	1.214761000	1.658866000
1	-0.063105000	2.861792000	2.181721000
1	1.076092000	3.564113000	1.011253000
1	-0.501012000	2.958524000	0.451790000
1	3.360952000	-0.236218000	1.282207000
1	4.600843000	-2.364799000	1.595674000
1	4.340288000	-2.776066000	-0.114298000
1	5.363970000	-1.378263000	0.324255000
1	1.323197000	-1.358615000	0.788309000
76	-1.717112000	-0.231524000	-0.138724000
8	-2.181255000	0.130738000	1.595143000
1	-1.115818000	0.418710000	1.833817000
8	-1.289143000	1.041663000	-1.172910000
8	-3.299975000	-0.621293000	-0.594342000
8	-0.830237000	-1.636315000	-0.432684000

E = -931.650262028, H = -931.381029
G = -931.445580

4.46

6	2.604166000	-0.422530000	-0.344236000
8	1.421982000	0.341810000	-0.810587000
6	1.595090000	1.760706000	-0.536710000
6	3.086603000	1.933450000	-0.773830000
6	3.698416000	0.637639000	-0.193127000
6	1.171328000	2.065971000	0.916860000
6	0.491056000	3.417161000	1.005433000
76	-0.325197000	-0.647215000	-0.368529000
8	0.827198000	-1.584048000	0.822185000
6	2.181827000	-1.147753000	0.931676000
6	3.065220000	-2.351422000	1.203528000
8	0.319433000	1.000650000	1.367364000
8	-1.332808000	0.937745000	-0.701391000
8	-1.742463000	-1.050146000	0.780608000
1	2.791775000	-1.137057000	-1.154065000
1	0.947747000	2.274116000	-1.252968000
1	3.284143000	2.014238000	-1.846921000
1	3.473077000	2.831432000	-0.280573000
1	4.607124000	0.351991000	-0.728135000
1	3.953297000	0.760666000	0.865492000
1	2.061576000	2.042413000	1.560412000
1	0.244647000	3.662419000	2.044926000
1	1.159258000	4.201101000	0.629041000
1	-0.420701000	3.414177000	0.394536000
1	2.229207000	-0.445755000	1.777452000
1	2.739258000	-2.846975000	2.122591000
1	3.000373000	-3.064737000	0.373864000
1	4.109066000	-2.036115000	1.327552000
8	-0.495190000	-1.615799000	-1.696418000
6	-2.971047000	-0.384854000	0.411493000
1	-3.376781000	-0.923298000	-0.460589000
6	-2.588441000	1.026814000	-0.014275000
1	-2.431967000	1.641378000	0.891707000
6	-3.600337000	1.699225000	-0.919348000

1	-3.254798000	2.699700000	-1.199212000
1	-3.741532000	1.106452000	-1.830313000
1	-4.562052000	1.797375000	-0.402485000
6	-3.924885000	-0.455937000	1.582592000
1	-4.877947000	0.018311000	1.320684000
1	-4.119093000	-1.499609000	1.847845000
1	-3.497572000	0.056372000	2.453182000
1	-0.442297000	1.357249000	1.839769000

E = -1012.99191616, H = -1012.613608

G = -1012.682672

4.47

6	2.469413000	-0.737875000	-0.707434000
8	1.441996000	0.287318000	-0.916133000
6	1.972447000	1.602066000	-0.529099000
6	3.497751000	1.456292000	-0.623340000
6	3.751520000	-0.003608000	-1.066540000
6	1.486859000	1.912150000	0.886390000
6	1.546878000	3.385628000	1.221035000
76	-0.435208000	-0.421238000	-0.138480000
8	1.007265000	-1.142005000	1.191244000
6	2.424341000	-1.253671000	0.739602000
6	2.884738000	-2.687523000	0.854358000
8	0.118458000	1.413170000	0.994540000
8	-1.560141000	0.798142000	-0.955953000
8	-1.860132000	-0.669105000	1.005813000
1	2.210560000	-1.542172000	-1.404443000
1	1.540364000	2.301140000	-1.252795000
1	3.920761000	2.162675000	-1.340838000
1	3.954199000	1.659774000	0.352310000
1	3.905236000	-0.061113000	-2.147436000
1	4.627059000	-0.439977000	-0.574792000
1	2.044507000	1.324813000	1.623046000
1	1.199289000	3.564410000	2.243717000
1	2.583027000	3.737330000	1.151347000
1	0.944758000	3.973924000	0.515076000
1	2.988616000	-0.595137000	1.409169000
1	2.877875000	-3.024800000	1.897519000
1	2.259205000	-3.348417000	0.242078000
1	3.919815000	-2.761824000	0.497170000
8	-0.377494000	-1.747069000	-1.119066000
6	-3.161929000	-0.331337000	0.436505000
1	-3.443784000	-1.211556000	-0.162623000
6	-2.939973000	0.860367000	-0.489324000
1	-3.016716000	1.802366000	0.075989000
6	-3.856953000	0.889327000	-1.695866000
1	-3.637977000	1.760205000	-2.320606000
1	-3.739482000	-0.024999000	-2.288692000
1	-4.896589000	0.960742000	-1.354325000
6	-4.143871000	-0.092361000	1.558478000
1	-5.133844000	0.118381000	1.136492000
1	-4.225828000	-0.983682000	2.187821000
1	-3.832311000	0.759890000	2.173257000
1	-0.509654000	2.140750000	0.862788000
1	0.789770000	-1.778951000	1.891069000

E = -1013.38194743, H = -1012.991169

G = -1013.062349

4.48

C	2.5147707	-1.1333745	-0.9856658
O	1.8881627	0.0870105	-1.3626298
C	2.5497857	1.2009165	-0.7589418
C	3.8882987	0.6837445	-0.1994708
C	3.9746287	-0.7637035	-0.7222228
C	1.6544557	1.7631195	0.3442312
C	1.9624747	3.1959195	0.7069672
Os	-0.9205873	0.0112935	-0.5489678
O	0.3337657	-1.5596475	-0.0005918
C	1.8020227	-1.6915865	0.2429292
C	2.0876697	-3.1478655	0.5253242
O	0.2550457	1.6785085	-0.1400318
O	-2.2507573	1.2391275	-0.1582918
O	-2.2162403	-1.2494675	-0.1222398
H	2.3908367	-1.8295795	-1.8242288
H	2.6770237	1.9553145	-1.5444468
H	4.7317677	1.2890795	-0.5395508
H	3.8884107	0.7086155	0.8979722
H	4.5225247	-0.8012185	-1.6679648
H	4.4747277	-1.4343805	-0.0164988
H	1.6686707	1.1139185	1.2268032
H	1.3244867	3.5581355	1.5212052
H	3.0025707	3.2550635	1.0506152
H	1.8630117	3.8508275	-0.1682788
H	1.9816847	-1.0644145	1.1241062
H	1.5402417	-3.5048615	1.4050392
H	1.8430087	-3.7693655	-0.3465498
H	3.1566407	-3.2715945	0.7312772
O	-0.7697013	-0.0700635	-2.1802858
C	-3.5610913	-0.7629135	-0.4147918
H	-3.6675863	-0.8096925	-1.5098998
C	-3.5942253	0.6976255	0.0366672
H	-3.7747533	0.7538845	1.1205142
C	-4.5832513	1.5555735	-0.7230758
H	-4.5588393	2.5862155	-0.3567788
H	-4.3591513	1.5434125	-1.7958908
H	-5.5946513	1.1613475	-0.5676838
C	-4.5685113	-1.6529355	0.2738732
H	-5.5818463	-1.3009925	0.0473982
H	-4.4795233	-2.6812155	-0.0893158
H	-4.4247523	-1.6355245	1.3604172
H	-0.2157983	2.5277095	-0.1117048
H	-0.0996813	-2.4271945	-0.0679928
O	-0.6830013	0.0745585	1.7964022
H	-1.1231993	0.8049495	2.2550112
H	-0.9495403	-0.7342815	2.2572402

E = -1089.81145621, H = -1089.392638

G = -1089.467913

4.49

6	2.757101000	-1.188123000	-0.562761000
8	2.302890000	0.029449000	-1.150913000
6	2.928929000	1.131662000	-0.517224000

6	4.283431000	0.628262000	0.011504000
6	4.201581000	-0.910349000	-0.123043000
6	2.048558000	1.677380000	0.611560000
6	2.347445000	3.124715000	0.936134000
76	-0.571681000	-0.049543000	-0.350933000
8	0.470195000	-1.574644000	0.168882000
6	1.831730000	-1.597598000	0.585366000
6	2.102038000	-3.022995000	1.045252000
8	0.666907000	1.579043000	0.142567000
8	-1.825569000	1.253579000	0.252558000
8	-1.967797000	-1.239812000	0.009411000
1	2.686511000	-1.949042000	-1.348832000
1	3.029025000	1.911250000	-1.282202000
1	5.105776000	1.034464000	-0.582291000
1	4.445379000	0.938044000	1.050934000
1	4.900375000	-1.267453000	-0.883709000
1	4.447048000	-1.414712000	0.816534000
1	2.112105000	1.056439000	1.510981000
1	1.737956000	3.484349000	1.774035000
1	3.399997000	3.216703000	1.228126000
1	2.178080000	3.758426000	0.057064000
1	1.968111000	-0.909496000	1.434867000
1	1.436846000	-3.290328000	1.872899000
1	1.919668000	-3.717896000	0.217649000
1	3.137375000	-3.137251000	1.384493000
8	-0.475934000	0.015839000	-1.980058000
6	-3.249334000	-0.607528000	-0.175667000
1	-3.388860000	-0.457602000	-1.259219000
6	-3.152815000	0.757996000	0.502608000
1	-3.256355000	0.621412000	1.592791000
6	-4.165584000	1.767715000	0.004087000
1	-4.022952000	2.730786000	0.504537000
1	-4.055906000	1.908621000	-1.077469000
1	-5.181460000	1.415786000	0.218002000
6	-4.322646000	-1.514463000	0.383882000
1	-5.312075000	-1.071634000	0.221894000
1	-4.291787000	-2.485364000	-0.120034000
1	-4.171626000	-1.667785000	1.459087000
1	0.104729000	2.281751000	0.506970000
8	-0.372716000	-0.067707000	2.096230000
1	-0.418086000	-1.015831000	2.288783000
1	-1.108496000	0.345622000	2.565370000

E = -1089.40611584, H = -1089.000296

G = -1089.073204

4.50

6	2.797716000	-1.089446000	-0.725000000
8	2.212121000	0.139875000	-1.138315000
6	2.839326000	1.227654000	-0.468676000
6	4.176500000	0.700265000	0.086646000
6	4.265293000	-0.729370000	-0.484779000
6	1.902132000	1.738632000	0.623049000
6	2.218691000	3.146340000	1.072560000
76	-0.603817000	-0.036713000	-0.245824000
8	0.682573000	-1.539131000	0.467658000
6	2.122681000	-1.618490000	0.540560000

6	2.463129000	-3.077324000	0.795516000
8	0.559738000	1.710958000	0.029490000
8	-1.937283000	1.248357000	0.032490000
8	-1.953251000	-1.251937000	0.207635000
1	2.645863000	-1.798661000	-1.547247000
1	2.973605000	2.019506000	-1.216260000
1	5.019885000	1.321185000	-0.225197000
1	4.163541000	0.686072000	1.183898000
1	4.797205000	-0.728974000	-1.440959000
1	4.776715000	-1.419158000	0.193138000
1	1.866596000	1.050355000	1.473948000
1	1.536006000	3.478002000	1.864044000
1	3.235861000	3.169511000	1.481325000
1	2.170925000	3.842756000	0.226740000
1	2.443598000	-1.007943000	1.399747000
1	1.978304000	-3.428497000	1.711913000
1	2.115873000	-3.691253000	-0.043301000
1	3.545421000	-3.206229000	0.908213000
8	-0.373681000	-0.299836000	-1.858269000
6	-3.254689000	-0.731113000	-0.131930000
1	-3.347852000	-0.766326000	-1.230109000
6	-3.257344000	0.727982000	0.316639000
1	-3.382460000	0.778448000	1.409431000
6	-4.285038000	1.592589000	-0.381044000
1	-4.212176000	2.627641000	-0.032885000
1	-4.130280000	1.567196000	-1.465846000
1	-5.292383000	1.223717000	-0.155350000
6	-4.308194000	-1.592856000	0.527261000
1	-5.308179000	-1.237642000	0.253147000
1	-4.206580000	-2.629679000	0.192524000
1	-4.203362000	-1.558507000	1.618004000
1	-0.016388000	2.382650000	0.429408000
1	0.290645000	-1.068391000	1.483993000
8	-0.265629000	-0.050708000	1.903473000
1	-1.048234000	-0.245412000	2.432208000

E = -1089.37969525, H = -1088.977863
G = -1089.050066

4.51

6	2.908641000	-1.169163000	-0.668692000
8	2.337985000	0.050030000	-1.119767000
6	2.953206000	1.167192000	-0.480999000
6	4.210540000	0.641879000	0.237244000
6	4.335927000	-0.810747000	-0.252758000
6	1.974342000	1.807406000	0.497779000
6	2.367759000	3.223973000	0.859646000
76	-0.657986000	-0.001888000	-0.159214000
8	0.678657000	-1.720416000	-0.071101000
6	2.047182000	-1.736429000	0.454411000
6	2.397707000	-3.161121000	0.827890000
8	0.670069000	1.805061000	-0.149214000
8	-1.990958000	1.251484000	0.221489000
8	-1.985439000	-1.293983000	0.095695000
1	2.874456000	-1.866856000	-1.514759000
1	3.189049000	1.888456000	-1.274247000
1	5.096884000	1.233735000	-0.004771000

1	4.074189000	0.677083000	1.325486000
1	4.982090000	-0.863446000	-1.134224000
1	4.749041000	-1.478498000	0.509299000
1	1.876782000	1.188036000	1.396839000
1	1.672545000	3.656336000	1.589627000
1	3.365228000	3.221080000	1.315056000
1	2.396294000	3.856612000	-0.035616000
1	2.053928000	-1.079846000	1.334018000
1	1.709215000	-3.549121000	1.589090000
1	2.366267000	-3.810773000	-0.055134000
1	3.405835000	-3.198787000	1.253231000
8	-0.430542000	0.033030000	-1.803039000
6	-3.296627000	-0.736757000	-0.171446000
1	-3.396523000	-0.681357000	-1.267692000
6	-3.313021000	0.678814000	0.400991000
1	-3.476079000	0.630406000	1.489646000
6	-4.329902000	1.592411000	-0.248550000
1	-4.273589000	2.593481000	0.190585000
1	-4.141612000	1.663688000	-1.326176000
1	-5.341129000	1.200696000	-0.087932000
6	-4.342230000	-1.656478000	0.417354000
1	-5.345546000	-1.269494000	0.204768000
1	-4.257479000	-2.654039000	-0.024908000
1	-4.213152000	-1.734092000	1.503284000
1	0.127760000	2.514820000	0.225800000
8	-0.076180000	0.013581000	1.697567000
1	-0.759772000	0.268852000	2.330394000
1	0.162360000	-2.419642000	0.358332000

E = -1089.40007265, H = -1088.993766
G = -1089.065561

4.52

6	-2.485569000	0.912074000	-0.503785000
8	-1.518824000	-0.058676000	-1.008641000
6	-2.026332000	-1.409935000	-0.798773000
6	-3.541109000	-1.254098000	-0.609246000
6	-3.820327000	0.251596000	-0.806105000
6	-1.287599000	-1.981819000	0.415616000
6	-1.290690000	-3.496929000	0.420785000
76	0.385436000	0.371222000	-0.049726000
8	-0.785494000	1.060021000	1.239947000
6	-2.199527000	1.142098000	0.981547000
6	-2.679472000	2.505357000	1.443266000
8	1.899829000	-0.706733000	-1.186990000
8	1.835531000	0.554136000	1.117714000
8	0.532028000	1.622345000	-1.152800000
6	3.068081000	-0.139455000	0.837612000
6	3.220992000	-0.301576000	-0.674153000
6	3.622419000	0.970306000	-1.387013000
6	3.093752000	-1.449656000	1.607930000
1	-2.297664000	1.826362000	-1.077401000
1	-1.747891000	-1.961887000	-1.702890000
1	-4.099347000	-1.860900000	-1.326037000
1	-3.824879000	-1.580546000	0.397983000
1	-4.106847000	0.461823000	-1.840776000
1	-4.614047000	0.618157000	-0.147437000

1	-0.810907000	-3.882304000	-0.486991000
1	-0.754572000	-3.872103000	1.297760000
1	-2.321124000	-3.871442000	0.460087000
1	-2.677923000	0.355200000	1.582693000
1	-2.478860000	2.631084000	2.511129000
1	-2.159190000	3.294556000	0.888080000
1	-3.759188000	2.603483000	1.276033000
1	1.736511000	-1.645646000	-1.002623000
1	3.859508000	0.528484000	1.201911000
1	3.910169000	-1.120464000	-0.910358000
1	3.540646000	0.846056000	-2.471132000
1	3.002902000	1.817461000	-1.071155000
1	4.664813000	1.198216000	-1.137661000
1	4.083633000	-1.911776000	1.517820000
1	2.892048000	-1.257601000	2.665952000
1	2.335247000	-2.149974000	1.237103000
1	-1.752226000	-1.603008000	1.338703000
8	0.041724000	-1.491579000	0.367304000

E = -1012.98302958, H = -1012.604037

G = -1012.671565

4.53

6	-1.982068000	1.528718000	-0.618067000
8	-1.490621000	0.162192000	-0.919703000
6	-2.524285000	-0.847385000	-0.578702000
6	-3.813546000	-0.091337000	-0.841707000
6	-3.497296000	1.372737000	-0.458895000
6	-2.264027000	-1.270124000	0.862257000
6	-2.758804000	-2.669671000	1.161616000
76	0.298716000	-0.360319000	-0.086359000
8	0.052964000	1.370202000	0.604463000
6	-1.245241000	1.986041000	0.647943000
6	-1.127744000	3.490500000	0.739301000
8	1.952719000	-0.649290000	1.046406000
8	1.944698000	0.741996000	-1.141622000
8	0.588099000	-1.488928000	-1.284727000
6	3.159796000	0.892189000	-0.328290000
6	3.303009000	-0.430670000	0.414887000
6	3.675910000	-1.620238000	-0.435549000
6	3.099110000	2.109251000	0.571747000
1	-1.679809000	2.124494000	-1.484992000
1	-2.338381000	-1.674489000	-1.273064000
1	-4.074313000	-0.170916000	-1.900976000
1	-4.643315000	-0.497721000	-0.254371000
1	-4.035537000	2.071458000	-1.103833000
1	-3.784776000	1.582070000	0.577511000
1	-2.287150000	-3.397497000	0.491369000
1	-2.537735000	-2.933190000	2.200050000
1	-3.846000000	-2.712263000	1.022045000
1	-1.747778000	1.579307000	1.537498000
1	-0.596664000	3.774182000	1.652713000
1	-0.596744000	3.891405000	-0.132143000
1	-2.129343000	3.937077000	0.776414000
1	1.953499000	-1.380621000	1.687768000
1	3.993304000	0.963790000	-1.037976000
1	3.978746000	-0.297419000	1.266741000

1	3.629286000	-2.552155000	0.139466000
1	3.049778000	-1.700474000	-1.330689000
1	4.715932000	-1.489191000	-0.759573000
1	4.083251000	2.256883000	1.030809000
1	2.875197000	3.010343000	-0.012040000
1	2.349220000	1.997635000	1.360726000
1	-2.701718000	-0.548011000	1.564675000
8	-0.825284000	-1.228393000	1.106662000
1	1.739153000	1.587273000	-1.565941000

E = -1013.37272015, H = -1012.981997
G = -1013.051801

4.54

6	-2.788388000	1.033037000	-0.794804000
8	-2.207987000	-0.208828000	-1.177475000
6	-2.779576000	-1.249971000	-0.395486000
6	-4.238116000	-0.831716000	-0.196834000
6	-4.180195000	0.712344000	-0.214767000
6	-2.015392000	-1.386486000	0.931568000
6	-2.246352000	-2.728315000	1.601159000
76	0.477852000	-0.058927000	-0.206813000
8	-0.499214000	1.525671000	-0.109918000
6	-1.884020000	1.735282000	0.236539000
6	-2.112016000	3.233946000	0.268801000
8	2.077965000	-1.212870000	0.484976000
8	2.120929000	1.211800000	-0.369058000
8	0.473107000	-0.562660000	-1.768103000
6	3.463103000	0.706146000	0.015007000
6	3.387623000	-0.823233000	-0.112993000
6	3.522153000	-1.346633000	-1.524956000
6	3.873057000	1.216634000	1.376620000
1	-2.825490000	1.650098000	-1.699343000
1	-2.663955000	-2.176400000	-0.969737000
1	-4.833731000	-1.204113000	-1.034623000
1	-4.672453000	-1.224875000	0.727583000
1	-4.973857000	1.132357000	-0.836947000
1	-4.296106000	1.134533000	0.790702000
1	-1.916235000	-3.541795000	0.945330000
1	-1.713934000	-2.793804000	2.555248000
1	-3.316188000	-2.857207000	1.800831000
1	-2.045253000	1.308053000	1.234980000
1	-1.519406000	3.717471000	1.052254000
1	-1.859064000	3.675788000	-0.701580000
1	-3.171349000	3.431672000	0.473044000
1	1.975950000	-2.176410000	0.572080000
1	4.139169000	1.071614000	-0.766805000
1	4.141375000	-1.258903000	0.552235000
1	3.301897000	-2.419467000	-1.572910000
1	2.884127000	-0.809031000	-2.234971000
1	4.564641000	-1.213534000	-1.839153000
1	4.933399000	0.980580000	1.526336000
1	3.777239000	2.307760000	1.430649000
1	3.289472000	0.756888000	2.178008000
1	-2.292755000	-0.573969000	1.616435000
8	-0.590070000	-1.301091000	0.688856000
1	2.046681000	2.180270000	-0.350125000

8	0.833858000	0.598292000	2.017670000
1	0.407109000	1.420003000	2.299671000
1	0.641963000	-0.067847000	2.693928000

E = -1089.78630581, H = -1089.367850
G = -1089.442735

4.55

6	2.876889000	-1.080075000	-0.471341000
8	2.340869000	0.048802000	-1.151084000
6	2.797937000	1.231323000	-0.511217000
6	4.232814000	0.909656000	-0.083330000
6	4.214908000	-0.619433000	0.143258000
6	1.875911000	1.592591000	0.662080000
6	2.055856000	3.039631000	1.092349000
76	-0.465745000	-0.073403000	-0.388206000
8	0.550061000	-1.561132000	0.160192000
6	1.902522000	-1.591246000	0.602173000
6	2.204749000	-3.036114000	0.966450000
8	-1.948729000	1.326308000	-0.075147000
8	-1.904859000	-1.225466000	0.121116000
8	-0.360820000	-0.094732000	-2.031207000
6	-3.194238000	-0.655131000	-0.139056000
6	-3.213612000	0.754611000	0.438556000
6	-4.369899000	1.618324000	-0.002703000
6	-4.250387000	-1.555831000	0.468813000
8	-0.763263000	-0.016878000	2.106639000
1	2.997438000	-1.862679000	-1.229223000
1	2.735346000	2.031314000	-1.258683000
1	4.920724000	1.170621000	-0.892139000
1	4.538967000	1.461956000	0.811150000
1	5.064421000	-1.104440000	-0.343485000
1	4.260132000	-0.870541000	1.209668000
1	1.792940000	3.707425000	0.263629000
1	1.417864000	3.273141000	1.951515000
1	3.097359000	3.227768000	1.376981000
1	1.983614000	-0.970681000	1.506472000
1	1.562077000	-3.375065000	1.784914000
1	2.034373000	-3.679436000	0.095687000
1	3.251681000	-3.133455000	1.278544000
1	-1.616474000	2.091882000	0.425470000
1	-3.331689000	-0.585522000	-1.230966000
1	-3.109912000	0.711845000	1.528939000
1	-4.254848000	2.644574000	0.363903000
1	-4.449333000	1.633850000	-1.095268000
1	-5.298313000	1.218123000	0.419715000
1	-4.152708000	-1.581964000	1.560869000
1	-5.254086000	-1.205236000	0.204085000
1	-4.126177000	-2.570292000	0.078686000
1	-0.034291000	0.271241000	2.668779000
1	2.088791000	0.934023000	1.517804000
8	0.514343000	1.452308000	0.268239000
1	-0.942790000	-0.943332000	2.320412000

E = -1089.39796167, H = -1088.991311
G = -1089.066177

4.56

6	2.837761000	-1.058307000	-0.743841000
8	2.254609000	0.145062000	-1.224824000
6	2.822343000	1.238497000	-0.511880000
6	4.222529000	0.780182000	-0.052889000
6	4.305421000	-0.690230000	-0.518816000
6	1.903022000	1.626314000	0.661958000
6	2.137134000	3.055611000	1.111122000
76	-0.415747000	-0.048517000	-0.154593000
8	0.738632000	-1.368124000	0.528123000
6	2.163068000	-1.520947000	0.555857000
6	2.411727000	-2.998361000	0.815767000
8	-2.021482000	1.317531000	-0.324901000
8	-2.014161000	-1.307094000	0.320944000
8	-0.521357000	-0.424484000	-1.761055000
6	-3.231970000	-0.741125000	-0.220165000
6	-3.310009000	0.748804000	0.125893000
6	-4.435240000	1.482944000	-0.566355000
6	-4.413031000	-1.520567000	0.323799000
8	-1.127665000	0.080082000	1.873416000
1	2.684500000	-1.813678000	-1.522935000
1	2.853175000	2.079642000	-1.214234000
1	5.011315000	1.389851000	-0.500405000
1	4.321344000	0.861850000	1.036647000
1	4.845220000	-0.764856000	-1.467213000
1	4.802406000	-1.336566000	0.211669000
1	1.900440000	3.746487000	0.293485000
1	1.518263000	3.301308000	1.979592000
1	3.190795000	3.189250000	1.385688000
1	2.552774000	-0.938483000	1.402513000
1	1.965112000	-3.302377000	1.767377000
1	1.970513000	-3.596765000	0.010553000
1	3.488574000	-3.198008000	0.856294000
1	-1.848497000	2.191957000	0.057723000
1	-3.163546000	-0.847364000	-1.311830000
1	-3.345281000	0.874972000	1.214510000
1	-4.363978000	2.561001000	-0.381759000
1	-4.409586000	1.304259000	-1.647264000
1	-5.395888000	1.142908000	-0.165498000
1	-4.529900000	-1.349844000	1.401546000
1	-5.336531000	-1.228136000	-0.186844000
1	-4.248018000	-2.588126000	0.151055000
1	-0.477069000	-0.182331000	2.535826000
1	2.050948000	0.942725000	1.508024000
8	0.550712000	1.517856000	0.220671000
1	-1.791157000	-0.855875000	1.392831000

E = -1089.36702416, H = -1088.964995
G = -1089.036309

4.57

6	2.843836000	-1.148109000	-0.746215000
8	2.255268000	0.024522000	-1.289102000
6	2.855913000	1.163686000	-0.686216000
6	4.266248000	0.730246000	-0.233543000
6	4.317414000	-0.778639000	-0.557347000
6	1.998636000	1.659288000	0.491990000
6	2.281408000	3.114908000	0.813817000

76	-0.390060000	-0.005381000	0.010909000
8	0.738393000	-1.450349000	0.451832000
6	2.157798000	-1.540490000	0.570704000
6	2.459678000	-2.979397000	0.955263000
8	-2.107518000	1.351322000	-0.232411000
8	-2.168624000	-1.409429000	0.150866000
8	-0.620619000	-0.302764000	-1.617151000
6	-3.308450000	-0.710755000	-0.453533000
6	-3.346940000	0.684433000	0.164743000
6	-4.522466000	1.510587000	-0.315956000
6	-4.571132000	-1.505410000	-0.192898000
8	-0.959973000	0.155776000	1.832308000
1	2.683767000	-1.944995000	-1.482042000
1	2.871086000	1.945280000	-1.455259000
1	5.046228000	1.281972000	-0.763948000
1	4.403542000	0.914704000	0.838882000
1	4.854718000	-0.953361000	-1.493981000
1	4.806772000	-1.360122000	0.230484000
1	2.016345000	3.745119000	-0.043045000
1	1.710139000	3.437481000	1.689507000
1	3.349606000	3.243985000	1.026486000
1	2.487072000	-0.873988000	1.380705000
1	1.968709000	-3.232385000	1.900108000
1	2.099852000	-3.659450000	0.174198000
1	3.539191000	-3.122357000	1.076395000
1	-2.004045000	2.182310000	0.254758000
1	-3.104771000	-0.613224000	-1.528252000
1	-3.338021000	0.592028000	1.258165000
1	-4.423098000	2.543156000	0.038041000
1	-4.573213000	1.518914000	-1.411053000
1	-5.457575000	1.113045000	0.090719000
1	-4.817622000	-1.510758000	0.875587000
1	-5.407966000	-1.080669000	-0.756305000
1	-4.441370000	-2.540616000	-0.529423000
1	2.175500000	1.043298000	1.383247000
8	0.615485000	1.558561000	0.153860000
1	-2.045794000	-2.263579000	-0.288191000
1	-1.365470000	-0.620034000	2.238620000

E = -1089.38508378, H = -1088.978127

G = -1089.051052

4.58

C	-0.673902000	0.357807000	0.393108000
H	-0.732399000	0.913455000	1.346083000
C	0.673885000	-0.357812000	0.393125000
H	0.732363000	-0.913462000	1.346097000
C	1.836615000	0.617870000	0.302695000
H	2.793114000	0.082566000	0.374140000
H	1.790567000	1.159016000	-0.648162000
H	1.792901000	1.343204000	1.124967000
C	-1.836616000	-0.617898000	0.302663000
H	-1.792905000	-1.343232000	1.124935000
H	-2.793127000	-0.082611000	0.374083000
H	-1.790538000	-1.159021000	-0.648204000
O	0.678791000	-1.281094000	-0.688602000
H	1.587315000	-1.543695000	-0.862971000

O -0.678785000 1.281053000 -0.688651000
H -1.587225000 1.544303000 -0.862487000
E = -308.809069511, H = -308.659153
G = -308.700312

4.59

6	-2.669517000	1.181588000	-0.756141000
8	-2.236764000	-0.082700000	-1.245817000
6	-2.886823000	-1.107661000	-0.521012000
6	-4.308042000	-0.563736000	-0.331901000
6	-4.058241000	0.944264000	-0.122017000
6	-2.219484000	-1.389968000	0.834645000
6	-2.618962000	-2.767320000	1.347610000
76	0.642775000	-0.058220000	-0.199959000
8	-0.342739000	1.586750000	-0.321398000
6	-1.631819000	1.742627000	0.229108000
6	-1.861360000	3.224187000	0.482847000
8	-0.799333000	-1.345629000	0.787556000
8	2.032736000	-1.103458000	0.668254000
8	2.071189000	1.141798000	-0.450777000
1	-2.709017000	1.848811000	-1.626825000
1	-2.838667000	-2.008262000	-1.145781000
1	-4.886444000	-0.737064000	-1.245478000
1	-4.839200000	-1.025149000	0.507618000
1	-4.833085000	1.557450000	-0.591237000
1	-4.038405000	1.196274000	0.945679000
1	-2.568083000	-0.630867000	1.555866000
1	-2.196328000	-2.937396000	2.343656000
1	-3.709901000	-2.864788000	1.409293000
1	-2.229195000	-3.534764000	0.668137000
1	-1.698216000	1.203629000	1.184716000
1	-1.135673000	3.594809000	1.213488000
1	-1.734148000	3.782431000	-0.452947000
1	-2.874601000	3.400108000	0.867220000
8	0.388071000	-0.874894000	-1.619332000
6	3.377345000	0.698643000	-0.065147000
1	4.048963000	0.954287000	-0.897679000
6	3.317448000	-0.819647000	0.119810000
1	4.054094000	-1.134982000	0.873114000
6	3.547943000	-1.581103000	-1.176918000
1	3.338461000	-2.645845000	-1.028698000
1	2.899387000	-1.202600000	-1.977005000
1	4.591450000	-1.465807000	-1.496178000
6	3.783519000	1.450671000	1.191045000
1	4.831843000	1.241747000	1.437001000
1	3.659513000	2.527879000	1.039559000
1	3.153592000	1.142640000	2.035141000
8	0.321420000	0.280546000	1.945939000
1	1.110002000	-0.064148000	2.382848000
1	-0.355897000	-0.668271000	1.688439000

E = -1088.94900288, H = -1088.560964
G = -1088.630743

4.60

6	-2.270816000	1.429573000	-0.586227000
8	-2.229163000	0.008475000	-0.722226000

6	-3.539269000	-0.564598000	-0.632242000
6	-4.504734000	0.619933000	-0.728066000
6	-3.686316000	1.760397000	-0.116261000
6	-3.659430000	-1.339026000	0.684869000
6	-4.867498000	-2.258081000	0.692361000
76	0.944047000	-0.141551000	-0.175224000
8	0.102150000	1.573777000	-0.189920000
6	-1.171673000	1.871752000	0.369235000
6	-1.197293000	3.376896000	0.594906000
8	-2.517020000	-2.143570000	0.883344000
8	2.233935000	-1.149824000	0.821146000
8	2.455930000	0.962637000	-0.497232000
8	0.494351000	-0.989216000	-1.528776000
6	3.711154000	0.501797000	0.015225000
6	3.564314000	-0.988790000	0.316727000
6	3.789000000	-1.872021000	-0.898682000
6	4.057336000	1.325104000	1.244133000
8	-0.113351000	-0.533942000	1.371505000
1	-2.070742000	1.877257000	-1.574305000
1	-3.640447000	-1.271616000	-1.467199000
1	-4.735012000	0.838060000	-1.777495000
1	-5.446056000	0.436961000	-0.199179000
1	-4.011520000	2.752360000	-0.444481000
1	-3.733092000	1.725464000	0.980632000
1	-3.746661000	-0.604992000	1.508681000
1	-4.914153000	-2.798657000	1.643853000
1	-5.801535000	-1.699379000	0.559969000
1	-4.771660000	-2.992786000	-0.117107000
1	-1.308289000	1.336590000	1.318627000
1	-0.347181000	3.667992000	1.220295000
1	-1.117481000	3.904103000	-0.364339000
1	-2.124122000	3.680562000	1.095777000
1	-1.746169000	-1.558627000	0.831412000
1	4.453667000	0.659015000	-0.780166000
1	4.239264000	-1.282260000	1.132572000
1	3.523336000	-2.909118000	-0.667072000
1	3.178552000	-1.532234000	-1.745859000
1	4.844011000	-1.835995000	-1.197179000
1	5.072189000	1.091187000	1.588832000
1	3.998956000	2.392490000	1.007201000
1	3.347310000	1.102605000	2.051700000
1	0.345972000	-1.225456000	1.873262000

E = -1088.98535366, H = -1088.592074

G = -1088.667362

4.61

6	-2.786660000	1.113174000	-0.731614000
8	-2.322167000	-0.126902000	-1.242774000
6	-2.865847000	-1.166556000	-0.446730000
6	-4.306286000	-0.708137000	-0.194075000
6	-4.157096000	0.824792000	-0.078089000
6	-2.085609000	-1.356026000	0.865137000
6	-2.380112000	-2.733344000	1.452512000
76	0.557207000	-0.047907000	-0.209227000
8	-0.461846000	1.543548000	-0.261449000
6	-1.765052000	1.701207000	0.256446000

6	-1.998703000	3.189512000	0.461524000
8	2.111019000	-1.245181000	0.563556000
8	1.995126000	1.200941000	-0.386188000
8	0.483500000	-0.782870000	-1.697421000
6	3.308271000	0.776664000	-0.034541000
6	3.370355000	-0.761413000	0.044927000
6	3.625960000	-1.414298000	-1.300278000
6	3.756778000	1.478186000	1.240340000
8	0.975686000	0.254460000	1.900747000
1	-2.856149000	1.792282000	-1.590766000
1	-2.793035000	-2.083176000	-1.045155000
1	-4.930664000	-0.971608000	-1.053902000
1	-4.746429000	-1.156132000	0.703397000
1	-4.968968000	1.352914000	-0.586039000
1	-4.157272000	1.146423000	0.970896000
1	-1.993693000	-3.504614000	0.775431000
1	-1.884307000	-2.843963000	2.422766000
1	-3.458210000	-2.884094000	1.589494000
1	-1.836953000	1.191126000	1.226500000
1	-1.287275000	3.585929000	1.192445000
1	-1.857487000	3.718169000	-0.488929000
1	-3.019642000	3.371000000	0.821779000
1	1.810714000	-0.701486000	1.493572000
1	3.957422000	1.095869000	-0.865346000
1	4.141484000	-1.066177000	0.765630000
1	3.515214000	-2.501011000	-1.221693000
1	2.924214000	-1.038245000	-2.054147000
1	4.645993000	-1.183711000	-1.630110000
1	4.818649000	1.272232000	1.426686000
1	3.623328000	2.558848000	1.122743000
1	3.161393000	1.149616000	2.098093000
1	0.265814000	-0.197680000	2.371542000
1	-2.430644000	-0.600501000	1.593339000
8	-0.692221000	-1.284453000	0.704735000

E = -1088.93632284, H = -1088.546614

G = -1088.616621

5.62

6	0.765918000	2.078816000	0.218450000
8	0.912702000	0.843528000	0.953807000
6	2.320512000	0.520975000	1.015017000
6	2.965893000	1.880290000	1.247123000
6	2.103465000	2.820577000	0.377545000
6	2.780529000	-0.144996000	-0.299326000
6	3.954759000	-1.074256000	-0.017329000
76	-0.038330000	-0.985869000	-0.162850000
8	-0.440500000	0.599421000	-1.171420000
6	0.403359000	1.713396000	-1.228811000
6	-0.305343000	2.862491000	-1.924759000
8	1.763093000	-0.885905000	-0.933531000
8	-1.973635000	-1.083317000	0.106053000
1	-0.083351000	2.593682000	0.672705000
1	2.422398000	-0.175450000	1.853035000
1	2.891120000	2.152475000	2.305257000
1	4.022600000	1.887411000	0.959230000
1	1.969648000	3.798878000	0.847130000

1	2.560910000	2.980575000	-0.606045000
1	3.116676000	0.647828000	-0.990368000
1	4.334315000	-1.488275000	-0.956677000
1	4.769178000	-0.538911000	0.490070000
1	3.616361000	-1.900536000	0.620210000
1	1.316501000	1.436596000	-1.778585000
1	-0.534248000	2.592180000	-2.960753000
1	-1.236435000	3.088885000	-1.392924000
1	0.337828000	3.752644000	-1.932377000
8	0.448756000	-1.734418000	1.258206000
6	-2.766214000	-0.346597000	1.009356000
1	-3.667267000	-0.968678000	1.150622000
6	-3.296463000	0.988124000	0.451136000
1	-4.207223000	1.215290000	1.032678000
6	-3.652345000	0.902738000	-1.019154000
1	-4.101018000	1.846228000	-1.349686000
1	-2.751035000	0.695735000	-1.603409000
1	-4.372307000	0.091622000	-1.181783000
6	-2.094527000	-0.173602000	2.366867000
1	-2.781266000	0.319751000	3.069132000
1	-1.823718000	-1.150830000	2.779822000
1	-1.177451000	0.423686000	2.281697000
8	-0.463310000	-2.347525000	-1.376089000
1	-1.417327000	-2.513255000	-1.282825000
8	-2.379947000	2.072479000	0.615043000
1	-2.306350000	2.256672000	1.557188000

E = -1088.96037662, H = -1088.565527

G = -1088.636255

4.63

6	1.503829000	1.841641000	0.171336000
8	1.033851000	0.712063000	0.936716000
6	2.170975000	-0.082723000	1.333898000
6	3.220041000	0.969577000	1.669452000
6	2.953331000	2.079013000	0.627423000
6	2.596507000	-1.020873000	0.187547000
6	3.325775000	-2.232835000	0.749374000
76	-0.271970000	-0.769672000	-0.358356000
8	0.175621000	0.753426000	-1.478292000
6	1.353833000	1.490768000	-1.316961000
6	1.294508000	2.745378000	-2.171329000
8	1.500553000	-1.490571000	-0.581533000
8	-2.223079000	-0.082625000	-0.692351000
1	0.826609000	2.666269000	0.423019000
1	1.830812000	-0.666749000	2.195264000
1	3.054203000	1.345799000	2.683962000
1	4.237910000	0.570375000	1.608014000
1	3.084803000	3.075123000	1.057964000
1	3.632393000	1.991179000	-0.229056000
1	3.279878000	-0.473674000	-0.482498000
1	3.669288000	-2.870465000	-0.071049000
1	4.193347000	-1.927199000	1.349111000
1	2.639470000	-2.811759000	1.379485000
1	2.209795000	0.872565000	-1.630534000
1	1.211503000	2.475492000	-3.228588000
1	0.420314000	3.345485000	-1.890319000

1	2.202499000	3.346966000	-2.031426000
8	-0.571567000	-1.376692000	1.185585000
6	-3.257740000	0.283731000	0.227371000
1	-4.110745000	0.577109000	-0.403675000
6	-2.838333000	1.538226000	1.007186000
1	-3.745350000	1.898753000	1.513118000
6	-2.304855000	2.621767000	0.079647000
1	-2.051182000	3.514180000	0.662521000
1	-1.418771000	2.255198000	-0.454132000
1	-3.055704000	2.889481000	-0.674496000
6	-3.659718000	-0.870018000	1.128400000
1	-4.533290000	-0.577897000	1.724426000
1	-3.925186000	-1.747433000	0.527104000
1	-2.847223000	-1.128667000	1.812655000
8	-1.110737000	-1.808775000	-1.579997000
1	-2.172689000	-1.045217000	-1.311157000
8	-1.934215000	1.260439000	2.064557000
1	-1.075317000	1.000103000	1.707800000

E = -1088.93091511, H = -1088.542155

G = -1088.613758

4.64

C	-4.2402836	-2.2072116	0.8162924
C	-3.0036876	-1.3555646	0.5956354
C	-3.2869076	-0.1246676	-0.2544306
C	-4.1596696	0.9294264	0.4666684
C	-3.2347876	2.1492784	0.6003914
C	-2.2333596	1.9342684	-0.5268976
O	-2.0431336	0.5144064	-0.5486176
Os	-0.0696446	-1.7797396	-0.1610726
C	-0.8602936	2.5692644	-0.3405806
C	0.0237814	2.3439494	-1.5623156
O	-2.0225686	-2.1700906	-0.0559486
H	-2.5674036	-1.0212526	1.5524914
H	-3.7444766	-0.4479096	-1.2016426
H	-5.0431006	1.1646754	-0.1346656
H	-4.5073946	0.5752454	1.4427154
H	-4.0001946	-3.0780306	1.4364664
H	-5.0177996	-1.6320726	1.3294564
H	-4.6363766	-2.5545246	-0.1453776
H	-3.7678846	3.0999494	0.5073134
H	-2.7035796	2.1397544	1.5594594
H	-2.6545226	2.2601604	-1.4923986
H	-1.0031756	3.6465164	-0.1811836
H	1.0297404	2.7387044	-1.3726126
H	0.0766874	1.2717404	-1.7963066
H	-0.3857286	2.8599784	-2.4388276
C	5.1473764	-0.2031896	0.5281094
C	3.4825994	1.4180804	0.5933264
C	2.3749024	0.3780974	0.5150834
H	5.5021294	0.1112944	-0.4668296
H	3.1113194	2.2501574	1.1988534
H	3.7470174	1.8082154	-0.4033726
H	2.0828834	0.0510774	1.5157844
H	1.5044094	0.7743584	-0.0128866
H	6.0092174	-0.5751526	1.0912864

N	2.8421084	-0.8587916	-0.2004316
O	4.6213704	0.8925204	1.2393814
C	4.1234184	-1.3281556	0.4337184
H	4.4788354	-2.1766646	-0.1587446
H	3.8339014	-1.6660136	1.4326854
C	3.0049544	-0.6308036	-1.6644186
H	3.2458224	-1.5962526	-2.1145286
H	2.0614434	-0.2494896	-2.0580216
H	3.8067564	0.0895464	-1.8335906
O	-0.1493576	-0.9064656	1.3061124
O	-0.2337446	2.0675934	0.8347674
H	-0.5565496	1.1674714	0.9850904
O	1.9493344	-1.9286286	-0.0209986
O	-0.4501226	-3.7358036	0.0571994
H	-1.5217526	-3.4012256	0.2085924
H	0.0227164	-4.3241856	0.6613164
O	0.0147754	-1.2538426	-1.7614936

E = -1259.16318847, H = -1258.705930
G = -1258.785655

OsO₃H⁺ • NMO

Os	2.9747306	0.2353283	-0.1276504
C	-2.3638564	-0.6366907	-0.2741144
C	-1.6534884	1.5551093	0.0246576
C	-0.2017914	1.2054713	-0.2889214
H	-2.6069254	-0.7655477	0.7928686
H	-1.8361834	2.5752803	-0.3270414
H	-1.8488314	1.5267503	1.1090766
H	-0.0064514	1.2899063	-1.3630584
H	0.4934736	1.8348503	0.2760846
H	-3.0644914	-1.2423597	-0.8574504
N	0.0855916	-0.2333847	0.0581126
O	-2.5303404	0.7032233	-0.6697554
C	-0.9527144	-1.1156217	-0.5984544
H	-0.7603124	-2.1381887	-0.2592594
H	-0.7587374	-1.0310287	-1.6717544
C	0.1682286	-0.4783037	1.5266256
H	0.4993816	-1.5102027	1.6671236
H	0.8852996	0.2220343	1.9630046
H	-0.8179724	-0.3248467	1.9682396
O	3.0821296	1.7788793	-0.7844134
O	1.2953206	-0.6503997	-0.5498304
O	3.5621896	-1.0671897	-1.3543234
H	2.8378486	-1.6242937	-1.6856704
O	3.5179026	-0.1087747	1.4259036

E = -719.152209035, H = -718.945283
G = -718.998770

OsO₃ • NMO

Os	3.3069040	0.1258610	0.0704295
O	3.7627000	-1.3570910	0.7821405
C	-1.4043470	0.9177640	-1.2753935
C	-1.7162200	0.8683930	1.0377375
C	-0.3501520	0.2342120	1.2644435
H	-2.1781290	0.1543340	-1.4616925
H	-1.9355020	1.5298250	1.8822955

H	-2.5169780	0.1114620	0.9817005
H	0.4195020	0.9962940	1.4043235
H	-0.3464050	-0.4576340	2.1125815
H	-1.4042560	1.6125850	-2.1214165
N	0.0997530	-0.5584100	0.0688725
O	-1.7240490	1.6720300	-0.1249515
C	-0.0142910	0.3083480	-1.1531535
H	0.2547600	-0.3178290	-2.0100845
H	0.7233310	1.1017330	-1.0215205
O	4.6184650	0.7139660	-0.8231085
C	-0.7051010	-1.8022180	-0.0833395
H	-0.3145410	-2.3275750	-0.9574215
H	-0.5256730	-2.3989160	0.8132365
H	-1.7664760	-1.5743580	-0.1994435
O	2.3272850	1.4622650	0.5523075
O	1.3894190	-1.0150400	0.2614575

E = -718.687284012, H = -718.493240
G = -718.548180

OsO₄

O	0.373464000	1.652419000	-0.093733000
O	-0.336840000	-0.412744000	1.610467000
O	-1.358108000	-0.329320000	-0.961788000
O	1.320584000	-0.911264000	-0.551829000
Os	0.000095000	0.000096000	-0.000328000

E = -391.672383666, H = -391.653271
G = -391.688805

OsO₄ (at 325.15 K)

H = -391.652360, G = -391.688870

OsO₄ (ln *t*-butanol at 325.15 K)

E = -391.691193123, H = -391.671170
G = -391.707680

OsO₃

Os	0.000000000	0.000000000	0.000000000
O	0.000000000	1.687720000	0.000000000
O	-1.461608000	-0.843860000	0.000000000
O	1.461608000	-0.843860000	0.000000000

E = -316.499012683, H = -316.484794
G = -316.517783

NMO

C	0.334772000	-1.265606000	-1.163592000
C	0.334772000	0.250436000	-1.217986000
H	0.881074000	-1.666564000	-2.023893000
H	-0.704693000	-1.622016000	-1.177861000
H	1.360878000	0.641526000	-1.235418000
H	-0.239361000	0.617108000	-2.074679000
N	-0.368077000	0.784670000	0.000000000
O	1.003137000	-1.722105000	0.000000000
C	-0.301969000	2.266860000	0.000000000
H	-0.833687000	2.604742000	-0.892946000

H	0.740510000	2.608194000	0.000000000
O	-1.667525000	0.388406000	0.000000000

E = -402.167984215, H = -401.991146
G = -402.030004

NMM

C	0.101088000	-1.198012000	-1.164212000
C	0.101088000	0.322023000	-1.190594000
H	0.654221000	-1.600763000	-2.019907000
H	-0.939284000	-1.564544000	-1.199063000
H	1.148967000	0.684078000	-1.253326000
H	-0.438351000	0.675057000	-2.080061000
N	-0.560937000	0.838594000	0.000000000
O	0.742164000	-1.687147000	0.000000000
C	-0.583052000	2.288436000	0.000000000
H	-1.113521000	2.648602000	-0.889924000
H	0.437389000	2.723403000	0.000000000

E = -327.013913825, H = -326.843373
G = -326.881207

NMM-H⁺

C	0.123107000	-1.232113000	1.164241000
C	0.123107000	-1.232113000	-1.164241000
C	0.123107000	0.288170000	-1.233975000
H	0.668502000	-1.631996000	2.024480000
H	0.668502000	-1.631996000	-2.024480000
H	-0.910658000	-1.620291000	-1.196686000
H	1.146052000	0.681227000	-1.244056000
H	-0.428721000	0.659816000	-2.104063000
H	-0.910658000	-1.620291000	1.196686000
N	-0.532800000	0.847879000	0.000000000
O	0.780307000	-1.675088000	0.000000000
C	0.123107000	0.288170000	1.233975000
H	-0.428721000	0.659816000	2.104063000
H	1.146052000	0.681227000	1.244056000
C	-0.545949000	2.338686000	0.000000000
H	-1.063167000	2.686556000	-0.898442000
H	-1.063167000	2.686556000	0.898442000
H	0.491063000	2.686288000	0.000000000
H	-1.506808000	0.523836000	0.000000000

E = -327.477977008, H = -327.291977
G = -327.329951

H₂O

O	0.000000000	0.000000000	0.117479000
H	0.000000000	0.761964000	-0.469917000
H	0.000000000	0.761964000	-0.469917000

E = -76.4199738454, H = -76.394860
G = -76.416284

H₃O⁺

O	0.000000000	0.000000000	0.075249000
H	0.815704000	-0.470947000	-0.200663000
H	0.815704000	-0.470947000	-0.200663000

E = -76.8018462511, H = -76.764160

G = -76.786179

Propene

C	1.800317000	1.131167000	0.294770000
C	2.752137000	0.206959000	0.165023000
H	3.494712000	0.323924000	-0.628994000
H	1.039374000	1.053929000	1.072898000
C	2.891908000	-1.005410000	1.035708000
H	2.832418000	-1.924822000	0.437405000
H	3.867508000	-1.013214000	1.540700000
H	2.104409000	-1.033885000	1.798108000
H	1.749993000	1.992269000	-0.369882000

E = -117.854834956, H = -117.770406

G = -117.800432

Propene'

C	-0.7464948	1.1652574	0.2606077
C	-0.1719608	0.1860084	-0.5269093
H	0.0335002	0.4340024	-1.5703783
H	-0.7649498	1.0065984	1.3394947
C	0.5314762	-1.0028606	0.0460857
H	0.4507562	-1.8672856	-0.6218393
H	1.6005142	-0.7740656	0.1547257
H	0.1343702	-1.2614906	1.0347537
H	-1.0672118	2.1138354	-0.1165403

E = -117.848154902

Propene''

C	0.1932256	-1.1008694	0.1771572
C	-0.1873654	0.1496446	-0.5608328
C	-0.3568594	1.3558926	0.1061852
H	0.0738696	0.2001486	-1.6190358
H	-0.2789014	1.3483836	1.1924252
H	-0.1074224	-1.9890894	-0.3881348
H	1.2810526	-1.1393444	0.3242172
H	-0.2924534	-1.1268374	1.1604712
H	-0.3251454	2.3020716	-0.3924528

E = -117.843213497

Propene'''

C	0.3078907	-1.0901569	0.0843499
C	-0.0716753	0.2241031	-0.5118081
C	-0.4716883	1.3087451	0.2217389
H	0.1293127	0.3689871	-1.5767561
H	-0.5171743	1.2081091	1.3072849
H	-0.0975863	-1.9242229	-0.5018211
H	1.4020027	-1.1962359	0.0598179
H	-0.0271273	-1.1715169	1.1237739
H	-0.6539543	2.2721881	-0.2065801

E = -117.851691557

Propene''''

C	0.2836217	-0.9942073	-0.4619739
C	-0.2585723	0.3943197	-0.3500019
C	-0.3632853	1.0551037	0.8526771

H	-0.3272463	0.9744687	-1.2739239
H	-0.2260793	0.4629337	1.7618171
H	-0.2026543	-1.5473273	-1.2731429
H	1.3553337	-0.9392643	-0.6997629
H	0.1676117	-1.5433053	0.4788751
H	-0.4287293	2.1372787	0.9654361

E = -117.848086394

Propene''''

C	0.8436077	0.6540600	-0.3852474
C	-0.3284283	-0.2821370	-0.4286114
C	-0.8021903	-0.8974560	0.7303326
H	-1.0401863	-0.1505580	-1.2440094
H	-0.2926043	-0.6787590	1.6674756
H	1.3193547	0.7294990	-1.3696654
H	0.5159967	1.6609870	-0.0959044
H	1.5780087	0.3104940	0.3554826
H	-1.7935583	-1.3461300	0.7701476

E = -117.84179887

Propene''''''

C	-0.2578846	1.3765408	0.0955077
C	-0.1265056	0.1634378	-0.5473003
H	0.0852594	0.1787048	-1.6180643
H	-0.2271126	1.3851188	1.1849517
C	0.1327384	-1.1129682	0.1891667
H	-0.2967036	-1.9692962	-0.3424133
H	1.2156944	-1.2823902	0.2616487
H	-0.2763886	-1.0709492	1.2056677
H	-0.2490976	2.3318018	-0.4291643

E = -117.8484632

5.3.2.2 Supplementary computational and cartesian coordinates data accounted from (SMD)-B3LYP/aug-cc-pVDZ/Hay-Wadt VDZ (n+1) ECP level of theory in *t*-butanol at 325.15

OsO₄

76	0.000000000	0.000000000	0.000000000
8	0.991216000	0.991216000	0.991216000
8	-0.991216000	-0.991216000	0.991216000
8	0.991216000	-0.991216000	-0.991216000
8	-0.991216000	0.991216000	-0.991216000

E = -392.022454579, G = -392.043025

(*E*)-2-Butene (at 273.15 K)

6	0.539304000	0.396223000	-0.000074000
1	0.391060000	1.482444000	-0.000221000
6	-0.539304000	-0.396223000	0.000074000
1	-0.391060000	-1.482444000	0.000221000
6	-1.964505000	0.079263000	0.000067000
1	-2.019846000	1.176673000	-0.000225000
1	-2.508331000	-0.291726000	-0.883234000
1	-2.508174000	-0.291239000	0.883672000

6	1.964505000	-0.079263000	-0.000067000
1	2.508174000	0.291239000	-0.883672000
1	2.508331000	0.291726000	0.883234000
1	2.019846000	-1.176673000	0.000225000

E = -157.246231240, G = -157.163623

4.1 (at 273.15 K)

76	0.805409000	-0.000002000	0.000000000
8	1.721250000	-1.161973000	0.877881000
8	-0.400792000	0.773952000	1.027492000
8	-0.400798000	-0.773954000	-1.027489000
8	1.721249000	1.161966000	-0.877885000
6	-2.422720000	-0.533268000	-0.445651000
6	-2.422715000	0.533278000	0.445653000
1	-2.591635000	-0.309281000	-1.499681000
1	-2.591641000	0.309291000	1.499681000
6	-2.647610000	-1.952707000	-0.012995000
1	-3.722236000	-2.193087000	-0.057382000
1	-2.125609000	-2.657605000	-0.671809000
1	-2.307881000	-2.115404000	1.018477000
6	-2.647575000	1.952722000	0.012995000
1	-2.125634000	2.657617000	0.671863000
1	-2.307753000	2.115429000	-1.018445000
1	-3.722205000	2.193102000	0.057283000

E = -549.255162945, G = -549.165212

4.2 (at 273.15 K)

6	-0.252615000	0.718250000	-2.019674000
6	0.252615000	-0.718250000	-2.019674000
1	-0.350688000	-1.351023000	-2.686650000
1	0.350688000	1.351023000	-2.686650000
76	0.000000000	0.000000000	0.757982000
8	0.000000000	1.242901000	-0.683373000
8	0.000000000	-1.242901000	-0.683373000
8	1.484232000	-0.053798000	1.605662000
8	-1.484232000	0.053798000	1.605662000
6	1.733323000	-0.863736000	-2.346726000
1	2.055460000	-1.901474000	-2.196896000
1	1.916582000	-0.590120000	-3.395390000
1	2.341279000	-0.211827000	-1.704280000
6	-1.733323000	0.863736000	-2.346726000
1	-2.055460000	1.901474000	-2.196896000
1	-1.916582000	0.590120000	-3.395390000
1	-2.341279000	0.211827000	-1.704280000

E = -549.314716702, G = -549.219535

4.3

6	-2.980036000	0.337365000	0.000000000
1	-2.837317000	1.418271000	0.000001000
1	-4.010487000	-0.016180000	0.000000000
6	-1.957626000	-0.532479000	0.000000000
1	-2.194032000	-1.600551000	-0.000001000
6	-0.515954000	-0.223622000	0.000000000
6	0.408691000	-1.284420000	0.000000000
6	-0.011920000	1.092302000	0.000000000
6	1.785483000	-1.046270000	0.000000000

1	0.039115000	-2.311330000	0.000000000
6	1.361185000	1.332648000	0.000000000
1	-0.698462000	1.938486000	0.000000000
6	2.268253000	0.264801000	0.000000000
1	2.481209000	-1.886150000	0.000000000
1	1.729834000	2.359148000	0.000000000
1	3.341685000	0.456360000	0.000000000

E = -309.690492353, G = -309.591218

4.4

76	-1.513640000	-0.199754000	-0.074012000
8	-1.411201000	-1.862722000	0.351684000
8	-0.131361000	0.290377000	-1.049903000
8	-1.070684000	0.844135000	1.288565000
8	-2.994102000	0.294595000	-0.795439000
6	0.556992000	1.997530000	1.077394000
1	0.876591000	1.708714000	2.074982000
1	-0.057873000	2.891910000	1.016718000
6	1.281838000	1.597979000	-0.044104000
1	1.182399000	2.197210000	-0.947366000
6	2.421460000	0.675669000	-0.014593000
6	3.326326000	0.672451000	-1.093552000
6	2.644390000	-0.219382000	1.051240000
6	4.429160000	-0.181883000	-1.101636000
1	3.159770000	1.350785000	-1.931366000
6	3.742487000	-1.077889000	1.039235000
1	1.948163000	-0.257665000	1.888781000
6	4.641859000	-1.060021000	-0.034159000
1	5.121903000	-0.166138000	-1.943406000
1	3.897209000	-1.768990000	1.868168000
1	5.500149000	-1.732339000	-0.039779000

E = -701.699036131, G = -701.595827

4.5

76	1.478806000	-0.182265000	-0.022134000
8	1.254807000	-1.807870000	-0.504904000
8	0.095077000	0.365495000	1.170162000
8	0.616420000	1.074323000	-1.160651000
8	3.028311000	0.378959000	0.427545000
6	-0.362489000	1.943524000	-0.546907000
1	-1.103011000	2.183775000	-1.319227000
1	0.153355000	2.863076000	-0.232991000
6	-0.960846000	1.211981000	0.649675000
1	-1.179651000	1.924712000	1.459134000
6	-2.221475000	0.418989000	0.342591000
6	-2.244651000	-0.979774000	0.311918000
6	-3.408268000	1.125601000	0.089183000
6	-3.433067000	-1.659507000	0.018988000
1	-1.340566000	-1.546328000	0.523130000
6	-4.592919000	0.447821000	-0.202806000
1	-3.411412000	2.216991000	0.127092000
6	-4.607889000	-0.951191000	-0.240708000
1	-3.436209000	-2.749672000	-0.002884000
1	-5.506596000	1.011111000	-0.395322000
1	-5.532465000	-1.483416000	-0.465594000

E = -701.749926552, G = -701.642339

4.6

6	3.455178000	-0.498212000	-0.000026000
1	3.239603000	-1.567043000	-0.000070000
1	4.507223000	-0.215425000	0.000009000
6	2.493507000	0.438988000	0.000011000
1	2.802555000	1.488462000	0.000089000
6	1.035356000	0.229641000	0.000011000
6	0.180601000	1.344373000	-0.000004000
6	0.437897000	-1.047356000	0.000013000
6	-1.209444000	1.195870000	-0.000009000
1	0.612283000	2.346678000	-0.000011000
6	-0.946033000	-1.191581000	0.000009000
1	1.062195000	-1.940463000	0.000019000
6	-1.800440000	-0.072986000	0.000001000
1	-1.842543000	2.084720000	-0.000020000
1	-1.377427000	-2.194527000	0.000011000
6	-3.299800000	-0.248898000	-0.000006000
1	-3.815634000	0.719587000	-0.000119000
1	-3.634581000	-0.810603000	-0.884869000
1	-3.634610000	-0.810411000	0.884968000

E = -349.011897875, G = -348.887838

•

• 4.7

• 8	-1.477857000	-1.925382000	0.338346000
• 8	-0.474859000	0.361764000	-1.074085000
• 8	-1.412138000	0.798540000	1.289541000
• 8	-3.315265000	0.055068000	-0.752622000
• 6	0.061845000	2.132825000	1.046918000
• 1	0.412660000	1.901074000	2.048798000
• 1	-0.649289000	2.951556000	0.971627000
• 6	0.829508000	1.799739000	-0.068381000
• 1	0.669261000	2.371794000	-0.980336000
• 6	2.051058000	0.994904000	-0.026557000
• 6	2.950185000	1.047576000	-1.106744000
• 6	2.368308000	0.147435000	1.055475000
• 6	4.128673000	0.300990000	-1.098692000
• 1	2.721062000	1.684468000	-1.962085000
• 6	3.541991000	-0.599049000	1.054491000
• 1	1.684764000	0.057949000	1.899496000
• 6	4.448510000	-0.535160000	-0.019962000
• 1	4.809414000	0.366262000	-1.948560000
• 1	3.759627000	-1.251910000	1.901513000
• 6	5.718718000	-1.349219000	-0.002661000
• 1	6.299493000	-1.204359000	-0.921894000
• 1	6.356404000	-1.069889000	0.849283000
• 1	5.499540000	-2.422578000	0.096025000

E = -741.021735909, G = -740.893883

4.8

76	-1.719640000	-0.275702000	-0.105434000
8	-1.271749000	-1.924589000	-0.178089000
8	-0.400902000	0.815231000	-0.930173000
8	-1.081839000	0.603925000	1.458242000
8	-3.319126000	0.205185000	-0.469509000

6	-0.199070000	1.736067000	1.259408000
1	0.478832000	1.764711000	2.120990000
1	-0.817520000	2.645269000	1.254682000
6	0.525238000	1.560836000	-0.065102000
1	0.650181000	2.527898000	-0.570535000
6	1.860630000	0.853456000	-0.017031000
6	2.083470000	-0.261759000	0.803318000
6	2.907684000	1.298248000	-0.836552000
6	3.320981000	-0.909477000	0.799271000
1	1.290436000	-0.636493000	1.450584000
6	4.143091000	0.648852000	-0.836311000
1	2.755032000	2.163287000	-1.484002000
6	4.371341000	-0.469108000	-0.019315000
1	3.470682000	-1.776518000	1.444225000
1	4.942062000	1.016507000	-1.482581000
6	5.708017000	-1.171727000	-0.029751000
1	5.929123000	-1.585386000	-1.024819000
1	6.523623000	-0.478192000	0.221831000
1	5.730821000	-1.998085000	0.691239000

E = -741.071535013, G = -740.939233

4.9

6	4.214225000	-0.659610000	-0.348957000
1	3.955231000	-1.703718000	-0.171871000
1	5.259897000	-0.450307000	-0.571258000
6	3.312290000	0.333578000	-0.302119000
1	3.660920000	1.352525000	-0.492483000
6	1.870890000	0.219725000	-0.019365000
6	1.083739000	1.385434000	0.000460000
6	1.230503000	-1.009284000	0.237344000
6	-0.285191000	1.331461000	0.264320000
1	1.555634000	2.349766000	-0.193092000
6	-0.134629000	-1.063220000	0.500169000
1	1.804768000	-1.934845000	0.232745000
6	-0.914574000	0.105993000	0.518347000
1	-0.870324000	2.252155000	0.270408000
1	-0.607969000	-2.027392000	0.691466000
6	-2.381491000	0.041438000	0.805244000
1	-2.764503000	0.978543000	1.218622000
1	-2.639213000	-0.792846000	1.463763000
17	-3.372295000	-0.243351000	-0.728292000

E = -808.635746317, G = -808.522458

4.10

76	2.366326000	-0.303582000	0.044861000
8	2.014299000	-1.956487000	-0.271617000
8	1.123430000	0.422447000	1.060290000
8	1.985764000	0.717286000	-1.353830000
8	3.940464000	0.020759000	0.654584000
6	0.552547000	2.095075000	-1.131271000
1	0.147628000	1.809635000	-2.098373000
1	1.281146000	2.901759000	-1.142788000
6	-0.163115000	1.847511000	0.039208000
1	0.051392000	2.471453000	0.904711000
6	-1.406230000	1.073923000	0.101605000
6	-2.258912000	1.228771000	1.211074000

6	-1.780444000	0.160346000	-0.904333000
6	-3.451591000	0.515232000	1.303250000
1	-1.979754000	1.919039000	2.007699000
6	-2.969428000	-0.555776000	-0.806442000
1	-1.130006000	-0.006262000	-1.762248000
6	-3.823654000	-0.386771000	0.295717000
1	-4.100723000	0.657837000	2.167960000
1	-3.239713000	-1.260551000	-1.593673000
6	-5.101741000	-1.160204000	0.395613000
1	-5.416186000	-1.307945000	1.432468000
1	-5.044261000	-2.122639000	-0.120434000
17	-6.500387000	-0.266518000	-0.408631000

E = -1200.64400692, G = -1200.526450

4.11

76	-2.313130000	-0.329394000	-0.001696000
8	-1.860308000	-1.865810000	0.598518000
8	-0.972642000	0.363353000	-1.168292000
8	-1.719790000	1.113314000	1.087057000
8	-3.905724000	-0.052250000	-0.552161000
6	-0.866104000	2.095703000	0.458622000
1	-0.211102000	2.495516000	1.242103000
1	-1.507760000	2.900599000	0.070738000
6	-0.102123000	1.409471000	-0.669600000
1	0.027174000	2.101529000	-1.515366000
6	1.260560000	0.865969000	-0.273532000
6	1.513839000	-0.501109000	-0.121735000
6	2.307196000	1.776802000	-0.055857000
6	2.786657000	-0.945722000	0.249240000
1	0.724686000	-1.227798000	-0.299922000
6	3.573682000	1.331443000	0.315799000
1	2.134469000	2.847061000	-0.184195000
6	3.829785000	-0.039870000	0.473729000
1	2.967059000	-2.015692000	0.360372000
1	4.375550000	2.053736000	0.474221000
6	5.192176000	-0.521477000	0.868692000
1	5.707845000	0.186056000	1.524193000
1	5.160836000	-1.509830000	1.335140000
17	6.300754000	-0.711374000	-0.592440000

E = -1200.69454520, G = -1200.57381

4.12

6	-4.452724000	-0.599008000	0.001254000
1	-4.187304000	-1.656378000	-0.001138000
1	-5.516951000	-0.366578000	0.002836000
6	-3.538226000	0.383130000	0.002113000
1	-3.893364000	1.417256000	0.004308000
6	-2.071904000	0.235644000	0.000178000
6	-1.270110000	1.389923000	-0.000946000
6	-1.425080000	-1.017846000	-0.001081000
6	0.124169000	1.309744000	-0.003755000
1	-1.747321000	2.370466000	-0.000293000
6	-0.038240000	-1.107435000	-0.003748000
1	-2.011624000	-1.935259000	-0.000533000
6	0.742862000	0.058520000	-0.005584000
1	0.724280000	2.217390000	-0.005433000

1	0.443856000	-2.084333000	-0.005728000
6	2.241285000	-0.071317000	-0.000404000
9	2.693914000	-0.690268000	1.126274000
9	2.873069000	1.125483000	-0.070725000
9	2.690378000	-0.818624000	-1.046902000

E = -646.781611426, G = -646.685840

4.13

76	-2.492295000	-0.368032000	-0.074928000
8	-2.040882000	-1.968315000	0.359081000
8	-1.243810000	0.395697000	-1.055861000
8	-2.278086000	0.753639000	1.281591000
8	-4.044167000	-0.201317000	-0.793203000
6	-0.951444000	2.228102000	1.056184000
1	-0.575166000	2.030541000	2.056272000
1	-1.741981000	2.971011000	0.986151000
6	-0.158975000	1.977526000	-0.062937000
1	-0.374071000	2.536562000	-0.971463000
6	1.150462000	1.316028000	-0.014782000
6	2.055103000	1.504692000	-1.077869000
6	1.538606000	0.488117000	1.055254000
6	3.311655000	0.906547000	-1.065139000
1	1.767544000	2.132987000	-1.920984000
6	2.793234000	-0.118219000	1.071199000
1	0.853027000	0.301089000	1.880674000
6	3.684039000	0.094823000	0.013635000
1	4.002795000	1.069925000	-1.890855000
1	3.078968000	-0.757753000	1.903672000
6	5.038897000	-0.562693000	-0.002591000
9	6.031287000	0.330480000	-0.263867000
9	5.343582000	-1.161988000	1.173394000
9	5.123956000	-1.519728000	-0.967254000

E = -1038.78992594, G = -1038.688953

4.14

76	-2.466555000	-0.341833000	0.054567000
8	-1.888203000	-1.900434000	0.451520000
8	-1.304580000	0.514282000	-1.196018000
8	-1.797335000	1.029622000	1.191151000
8	-4.123234000	-0.091526000	-0.274171000
6	-1.054445000	2.094277000	0.556453000
1	-0.336430000	2.464501000	1.297933000
1	-1.761539000	2.895770000	0.297297000
6	-0.395510000	1.522498000	-0.692825000
1	-0.347545000	2.286298000	-1.484023000
6	1.001198000	0.960376000	-0.473083000
6	1.305087000	-0.389787000	-0.670872000
6	2.027256000	1.837913000	-0.083377000
6	2.606044000	-0.862458000	-0.466203000
1	0.530692000	-1.082629000	-0.990762000
6	3.324057000	1.374909000	0.119407000
1	1.816440000	2.898886000	0.059023000
6	3.613645000	0.016595000	-0.068598000
1	2.828857000	-1.916894000	-0.616049000
1	4.109151000	2.065261000	0.424889000

6	5.026835000	-0.462890000	0.132490000
9	5.124342000	-1.813554000	0.144847000
9	5.856499000	-0.017205000	-0.852427000
9	5.552533000	-0.013245000	1.303622000

E = -1038.84048766, G = -1038.725587

4.15

6	3.689209000	-1.196545000	0.000000000
1	3.944147000	-0.136443000	0.000000000
1	4.524092000	-1.896204000	0.000000000
6	2.423093000	-1.642258000	0.000000000
1	2.260264000	-2.723806000	0.000000000
6	1.189631000	-0.836419000	0.000000000
6	-0.055599000	-1.490570000	0.000000000
6	1.189468000	0.572465000	0.000000000
6	-1.258588000	-0.781451000	0.000000000
1	-0.086063000	-2.580999000	0.000000000
6	0.000000000	1.297701000	0.000000000
1	2.131515000	1.119375000	0.000000000
6	-1.218318000	0.611898000	0.000000000
1	-2.214106000	-1.302662000	0.000000000
1	0.012248000	2.386220000	0.000000000
17	-2.725028000	1.525035000	0.000000000

E = -769.312513479, G = -769.225211

4.16

76	-2.020573000	-0.325360000	-0.073162000
8	-1.644377000	-1.953016000	0.332923000
8	-0.751321000	0.385396000	-1.067513000
8	-1.722249000	0.766485000	1.292488000
8	-3.574336000	-0.066479000	-0.761256000
6	-0.324577000	2.174573000	1.060690000
1	0.041025000	1.957053000	2.060548000
1	-1.076290000	2.956844000	0.991854000
6	0.455235000	1.887723000	-0.058890000
1	0.267076000	2.458885000	-0.965848000
6	1.720820000	1.151016000	-0.020243000
6	2.620849000	1.270574000	-1.096282000
6	2.075818000	0.309628000	1.053162000
6	3.842321000	0.598709000	-1.099880000
1	2.361029000	1.904732000	-1.944376000
6	3.289595000	-0.373430000	1.062060000
1	1.393025000	0.170114000	1.890532000
6	4.166667000	-0.218640000	-0.015573000
1	4.534468000	0.702675000	-1.933236000
1	3.555075000	-1.025808000	1.891743000
17	5.702710000	-1.073948000	-0.006723000

E = -1161.32155776, G = -1161.230311

4.17

76	1.978127000	-0.308575000	-0.054100000
8	1.461428000	-1.881277000	-0.480839000
8	0.775171000	0.481719000	1.199828000
8	1.269084000	1.057568000	-1.172692000
8	3.621783000	-0.002043000	0.294019000

6	0.480782000	2.081169000	-0.524974000
1	-0.241429000	2.440935000	-1.267544000
1	1.155781000	2.901737000	-0.240290000
6	-0.171793000	1.459027000	0.702895000
1	-0.260260000	2.204841000	1.507769000
6	-1.538072000	0.837884000	0.452220000
6	-1.787773000	-0.525916000	0.640910000
6	-2.595946000	1.666985000	0.047577000
6	-3.060872000	-1.060002000	0.412996000
1	-0.990421000	-1.186707000	0.972966000
6	-3.871839000	1.151325000	-0.180814000
1	-2.433755000	2.737695000	-0.087688000
6	-4.090176000	-0.216038000	0.001792000
1	-3.248128000	-2.122628000	0.556125000
1	-4.687944000	1.799566000	-0.494530000
17	-5.696298000	-0.878712000	-0.286667000

E = -1161.37070624, G = -1161.274812

4.18

6	2.071707000	0.575364000	-0.200154000
1	1.985999000	1.273636000	-1.050720000
1	2.129335000	1.190717000	0.710902000
6	0.805399000	-0.298723000	-0.157703000
1	0.875088000	-0.988591000	0.697989000
1	0.771002000	-0.930459000	-1.060301000
6	-3.048581000	0.463504000	0.084499000
1	-3.108491000	1.156813000	-0.769891000
1	-3.010192000	1.093750000	0.987561000
6	-0.488429000	0.516069000	-0.058167000
1	-0.548343000	1.208123000	-0.914599000
1	-0.451130000	1.148881000	0.843973000
6	-1.752697000	-0.348785000	-0.016958000
1	-1.691500000	-1.042268000	0.838268000
1	-1.790280000	-0.980921000	-0.919846000
6	-4.307910000	-0.407332000	0.123710000
1	-4.292007000	-1.088980000	0.987176000
1	-5.216852000	0.205955000	0.198564000
1	-4.393104000	-1.022691000	-0.784310000
6	4.349464000	-0.248222000	0.521483000
1	4.333704000	0.353722000	1.432969000
1	5.233686000	-0.863627000	0.353193000
6	3.333330000	-0.228753000	-0.347543000
1	3.399385000	-0.852793000	-1.245930000

E = -314.514211260, G = -314.332918

4.19

6	-1.500850000	1.672629000	0.338795000
6	-0.260649000	1.991894000	-0.458364000
8	0.417385000	-0.017867000	-0.711479000
76	1.972605000	-0.423273000	0.012938000
8	3.109764000	-0.915922000	-1.178511000
8	1.775849000	-1.502159000	1.337848000
8	2.290273000	1.219683000	0.567423000
1	-1.961013000	2.630284000	0.639150000
1	-1.211520000	1.173247000	1.276613000
1	-0.359625000	1.998200000	-1.544355000

6	-2.543597000	0.836025000	-0.411926000
1	-2.093322000	-0.119009000	-0.714932000
1	-2.819817000	1.360308000	-1.341426000
6	-6.122067000	-0.530035000	0.483789000
1	-6.564751000	0.426962000	0.803764000
1	-5.842628000	-1.062409000	1.407040000
6	0.837376000	2.633555000	0.093032000
1	1.560715000	3.133643000	-0.546147000
1	0.832214000	2.926937000	1.141414000
6	-3.806151000	0.570598000	0.413926000
1	-4.249464000	1.530708000	0.726852000
1	-3.529075000	0.043876000	1.341950000
6	-4.858952000	-0.250975000	-0.337917000
1	-4.413349000	-1.208134000	-0.655401000
1	-5.138384000	0.277790000	-1.264489000
6	-7.170175000	-1.346582000	-0.278323000
1	-6.766693000	-2.323430000	-0.583750000
1	-8.060614000	-1.530725000	0.338771000
1	-7.496416000	-0.821995000	-1.188695000

E = -706.521871602 , G = -706.336496

4.20

6	1.247765000	1.432902000	-0.322086000
6	-0.010504000	1.678103000	0.511166000
8	-0.535159000	0.413062000	1.014570000
76	-1.895424000	-0.437374000	-0.011189000
8	-3.350979000	-0.670697000	0.854509000
8	-1.235608000	-1.699331000	-0.958797000
8	-1.903372000	1.251164000	-0.891711000
1	1.599836000	2.411816000	-0.686025000
1	0.974496000	0.845739000	-1.213219000
1	0.238297000	2.257936000	1.412366000
6	2.373773000	0.733787000	0.446150000
1	2.009913000	-0.231457000	0.825875000
1	2.634849000	1.336674000	1.331748000
6	6.020369000	-0.405421000	-0.495380000
1	6.373170000	0.562199000	-0.887261000
1	5.754481000	-1.013361000	-1.374962000
6	-1.151788000	2.314301000	-0.257408000
1	-1.834316000	2.861900000	0.408970000
1	-0.814716000	2.983166000	-1.060418000
6	3.628118000	0.511713000	-0.405614000
1	3.984310000	1.480847000	-0.793072000
1	3.363167000	-0.092477000	-1.288748000
6	4.766157000	-0.176786000	0.355133000
1	4.409050000	-1.144426000	0.744347000
1	5.031782000	0.428178000	1.238231000
6	7.155940000	-1.088766000	0.272174000
1	6.843144000	-2.073554000	0.649712000
1	8.036631000	-1.240072000	-0.367426000
1	7.470087000	-0.485289000	1.136845000

E = -706.582372090
G = -706.391360

5.3.2.3 Computational and cartesian coordinates data accounted from (SMD)–B3LYP/6-311+G(d)/Hay-Wadt VDZ (n+1) ECP level of theory in *t*-butanol at 325.1 K

• **OsO₄**
 • 76 0.000000000 0.000000000 0.000000000
 • 8 0.990687000 0.990687000 0.990687000
 • 8 -0.990687000 -0.990687000 0.990687000
 • 8 0.990687000 -0.990687000 -0.990687000
 • 8 -0.990687000 0.990687000 -0.990687000
 • E = -392.020558388, G = -392.042114

(*E*)-2-Butene (at 273.15)

6 0.537636000 0.393828000 -0.000074000
 1 0.392218000 1.475030000 -0.000223000
 6 -0.537636000 -0.393828000 0.000074000
 1 -0.392218000 -1.475030000 0.000223000
 6 -1.961889000 0.079511000 0.000067000
 1 -2.024807000 1.170707000 -0.000222000
 1 -2.504752000 -0.288918000 -0.877733000
 1 -2.504597000 -0.288437000 0.878167000
 6 1.961889000 -0.079511000 -0.000067000
 1 2.504597000 0.288437000 -0.878167000
 1 2.504752000 0.288918000 0.877733000
 1 2.024807000 -1.170707000 0.000222000
 E = -157.267170466, G = -157.183985

4.1

76 0.813625000 0.000000000 0.000000000
 8 1.732071000 -1.193724000 0.830935000
 8 -0.378554000 0.736611000 1.059735000
 8 -0.378553000 -0.736611000 -1.059735000
 8 1.732071000 1.193723000 -0.830935000
 6 -2.488013000 -0.531435000 -0.437859000
 6 -2.488013000 0.531436000 0.437859000
 1 -2.622263000 -0.320307000 -1.494144000
 1 -2.622264000 0.320308000 1.494145000
 6 -2.668181000 -1.954610000 -0.007750000
 1 -3.723265000 -2.242546000 -0.093659000
 1 -2.096931000 -2.637237000 -0.639776000
 1 -2.366272000 -2.106662000 1.031279000
 6 -2.668178000 1.954611000 0.007750000
 1 -2.096941000 2.637239000 0.639786000
 1 -2.366253000 2.106666000 -1.031274000

1 -3.723265000 2.242542000 0.093642000
E = -549.28157116, G = -549.1916219

4.2

6 -0.251195000 0.719640000 -2.023655000
6 0.251195000 -0.719640000 -2.023655000
1 -0.351190000 -1.351164000 -2.683522000
1 0.351190000 1.351164000 -2.683522000
76 0.000000000 0.000000000 0.761793000
8 0.000000000 1.242448000 -0.690871000
8 0.000000000 -1.242448000 -0.690871000
8 1.486403000 -0.055650000 1.604202000
8 -1.486403000 0.055650000 1.604202000
6 1.729563000 -0.868957000 -2.352364000
1 2.048829000 -1.902315000 -2.205242000
1 1.917594000 -0.597463000 -3.395273000
1 2.342139000 -0.225702000 -1.714643000
6 -1.729563000 0.868957000 -2.352364000
1 -2.048829000 1.902315000 -2.205242000
1 -1.917594000 0.597463000 -3.395273000
1 -2.342139000 0.225702000 -1.714643000
E = -549.348342671, G = -549.242718

4.3

6 -2.975269000 0.334474000 0.000000000
1 -2.840530000 1.411179000 0.000001000
1 -4.000343000 -0.018497000 0.000000000
6 -1.953766000 -0.527937000 0.000000000
1 -2.188207000 -1.591271000 -0.000001000
6 -0.514486000 -0.220036000 0.000000000
6 0.406076000 -1.279262000 0.000000000
6 -0.007960000 1.090683000 0.000000000
6 1.779193000 -1.044695000 0.000000000
1 0.037076000 -2.301072000 0.000000000
6 1.361221000 1.327347000 0.000000000
1 -0.689139000 1.934867000 0.000000000
6 2.263351000 0.260994000 0.000000000
1 2.469450000 -1.882366000 0.000000000
1 1.729458000 2.348516000 0.000000000
1 3.332081000 0.449222000 0.000000000
E = -309.725559987, G = -309.627000

4.4

76 -1.505878000 -0.200613000 -0.073334000
8 -1.335320000 -1.868936000 0.307931000
8 -0.182481000 0.346572000 -1.091489000
8 -1.055621000 0.814590000 1.298810000
8 -3.027485000 0.259987000 -0.727987000
6 0.604892000 2.070100000 1.050950000
1 0.891296000 1.781215000 2.052351000
1 -0.043190000 2.932447000 0.974363000
6 1.323084000 1.652547000 -0.051678000
1 1.216904000 2.219819000 -0.968795000
6 2.423773000 0.690954000 -0.017877000
6 3.349700000 0.676292000 -1.073820000
6 2.592455000 -0.227162000 1.033489000
6 4.422462000 -0.208347000 -1.070706000
1 3.223591000 1.368872000 -1.900411000
6 3.662000000 -1.113768000 1.033468000
1 1.876205000 -0.258424000 1.847548000
6 4.582905000 -1.106051000 -0.015991000
1 5.130713000 -0.201379000 -1.892676000
1 3.774689000 -1.820064000 1.849402000

1 5.416173000 -1.800998000 -0.013528000
E = -701.740944962, G = -701.638032

4.5

76 1.466492000 -0.188358000 -0.036087000
8 1.202550000 -1.792701000 -0.563761000
8 0.101404000 0.347138000 1.198930000
8 0.593049000 1.123819000 -1.117492000
8 3.029887000 0.342319000 0.400228000
6 -0.347595000 1.987775000 -0.450485000
1 -1.079212000 2.291327000 -1.200272000
1 0.198012000 2.867294000 -0.094235000
6 -0.951883000 1.210478000 0.712358000
1 -1.169200000 1.883526000 1.548342000
6 -2.204996000 0.423361000 0.366012000
6 -2.242051000 -0.970348000 0.410581000
6 -3.366105000 1.122999000 0.016061000
6 -3.414946000 -1.653768000 0.087031000
1 -1.361288000 -1.526252000 0.704791000
6 -4.536732000 0.441418000 -0.302074000
1 -3.361818000 2.210014000 -0.002979000
6 -4.563128000 -0.953245000 -0.270584000
1 -3.427133000 -2.738339000 0.120011000
1 -5.428702000 0.998166000 -0.570777000
1 -5.474555000 -1.487119000 -0.518908000
E = -701.798315315, G = -701.690538

4.6

6 3.450849000 -0.493004000 -0.000020000
1 3.244257000 -1.558359000 -0.000062000
1 4.497247000 -0.209365000 -0.000005000
6 2.488739000 0.435761000 0.000018000
1 2.794337000 1.481063000 0.000060000
6 1.033152000 0.225924000 0.000012000
6 0.181132000 1.337970000 0.000002000
6 0.434350000 -1.046057000 0.000015000
6 -1.204783000 1.192052000 -0.000010000
1 0.610656000 2.335954000 0.000000000
6 -0.945275000 -1.187926000 0.000004000
1 1.053618000 -1.936843000 0.000028000
6 -1.796226000 -0.072040000 -0.000008000
1 -1.832988000 2.078426000 -0.000020000
1 -1.375535000 -2.186129000 0.000006000
6 -3.294614000 -0.245541000 -0.000010000
1 -3.810077000 0.717170000 -0.000114000
1 -3.632717000 -0.802465000 -0.879764000
1 -3.632738000 -0.802283000 0.879851000
E = -349.051690090, G = -348.929096

4.7

76 -1.759994000 -0.285492000 -0.070218000
8 -1.383648000 -1.927377000 0.278599000
8 -0.539617000 0.424124000 -1.116653000
8 -1.389510000 0.758253000 1.304897000
8 -3.343819000 0.005227000 -0.673916000
6 0.096448000 2.209755000 1.029038000
1 0.414572000 1.968969000 2.033402000
1 -0.647853000 2.989649000 0.942725000
6 0.859414000 1.866464000 -0.069479000
1 0.691684000 2.408859000 -0.992377000
6 2.049420000 1.023565000 -0.029168000
6 2.966391000 1.075333000 -1.089677000
6 2.326497000 0.148165000 1.037233000

6	4.123517000	0.304655000	-1.075954000
1	2.768958000	1.731261000	-1.932231000
6	3.480348000	-0.619873000	1.043034000
1	1.628102000	0.056592000	1.862355000
6	4.404303000	-0.556788000	-0.011183000
1	4.817147000	0.370641000	-1.908875000
1	3.666628000	-1.291378000	1.876541000
6	5.650181000	-1.404868000	0.008771000
1	6.279632000	-1.216114000	-0.862933000
1	6.250696000	-1.209919000	0.902742000
1	5.403633000	-2.471405000	0.016081000

E = -741.067749614, G = -740.940677

4.8

76	-1.710773000	-0.282686000	-0.104786000
8	-1.232496000	-1.920659000	-0.207063000
8	-0.415108000	0.843682000	-0.937979000
8	-1.043276000	0.595088000	1.460780000
8	-3.322921000	0.184122000	-0.423461000
6	-0.206533000	1.753276000	1.246118000
1	0.462496000	1.822078000	2.104935000
1	-0.854848000	2.634288000	1.223713000
6	0.518174000	1.577331000	-0.076272000
1	0.644866000	2.537590000	-0.582423000
6	1.847062000	0.862392000	-0.026469000
6	2.090258000	-0.206203000	0.846223000
6	2.870562000	1.259313000	-0.888355000
6	3.320932000	-0.851495000	0.847859000
1	1.319693000	-0.538472000	1.534157000
6	4.103275000	0.608994000	-0.883771000
1	2.705285000	2.085745000	-1.573896000
6	4.349831000	-0.459253000	-0.018772000
1	3.485574000	-1.677792000	1.533792000
1	4.882784000	0.940131000	-1.563693000
6	5.675203000	-1.179702000	-0.015207000
1	6.406241000	-0.680014000	-0.654026000
1	6.096741000	-1.237980000	0.992562000
1	5.567743000	-2.207205000	-0.377702000

E = -741.125674465, G = -740.993265

4.9

6	4.217876000	-0.638891000	-0.338793000
1	3.975556000	-1.680341000	-0.153971000
1	5.257189000	-0.422967000	-0.558988000
6	3.307635000	0.339426000	-0.302249000
1	3.645595000	1.355654000	-0.497881000
6	1.868869000	0.216232000	-0.022879000
6	1.080465000	1.376313000	0.012404000
6	1.231289000	-1.013348000	0.215179000
6	-0.283767000	1.316122000	0.275243000
1	1.546835000	2.340577000	-0.167215000
6	-0.129339000	-1.073301000	0.476688000
1	1.803020000	-1.934657000	0.195168000
6	-0.909543000	0.090133000	0.512277000
1	-0.867731000	2.231676000	0.292789000
1	-0.597987000	-2.037342000	0.652146000
6	-2.373065000	0.020108000	0.804218000
1	-2.749642000	0.938751000	1.248393000
1	-2.627218000	-0.821588000	1.444707000
17	-3.379302000	-0.221561000	-0.720452000

E = -808.680291600, G = -808.567239

4.10

76	2.348358000	-0.315270000	0.044217000
8	1.912312000	-1.959075000	-0.209807000
8	1.182094000	0.483288000	1.088476000
8	1.965271000	0.670487000	-1.369635000
8	3.957441000	-0.045661000	0.584899000
6	0.530817000	2.168106000	-1.129702000
1	0.151110000	1.868952000	-2.096405000
1	1.295210000	2.933068000	-1.138866000
6	-0.178353000	1.922233000	0.029626000
1	0.050685000	2.522200000	0.902122000
6	-1.399176000	1.122288000	0.103534000
6	-2.263147000	1.287486000	1.197986000
6	-1.748025000	0.182438000	-0.882333000
6	-3.441810000	0.560151000	1.293605000
1	-2.004004000	1.995692000	1.978808000
6	-2.924202000	-0.545075000	-0.781700000
1	-1.088804000	0.006584000	-1.725318000
6	-3.789508000	-0.365812000	0.304924000
1	-4.098940000	0.711246000	2.144554000
1	-3.174713000	-1.267077000	-1.552906000
6	-5.051738000	-1.160430000	0.412424000
1	-5.370475000	-1.290145000	1.444224000
1	-4.967668000	-2.134188000	-0.064964000
17	-6.459628000	-0.329787000	-0.429022000

E = -1200.69561577, G = -1200.577873

4.11

76	-2.286568000	-0.334022000	0.026242000
8	-1.763919000	-1.830701000	0.664111000
8	-1.001634000	0.356832000	-1.220260000
8	-1.684212000	1.175720000	1.032373000
8	-3.905168000	-0.111419000	-0.469017000
6	-0.888383000	2.146005000	0.324448000
1	-0.249596000	2.626234000	1.066701000
1	-1.566032000	2.888497000	-0.108462000
6	-0.120694000	1.408602000	-0.764500000
1	0.019819000	2.053663000	-1.638347000
6	1.226766000	0.854593000	-0.331160000
6	1.516753000	-0.508444000	-0.385992000
6	2.223593000	1.739055000	0.098221000
6	2.769743000	-0.978057000	0.002749000
1	0.769323000	-1.206832000	-0.739220000
6	3.472975000	1.268558000	0.481408000
1	2.029333000	2.807732000	0.130662000
6	3.761787000	-0.100247000	0.442094000
1	2.975884000	-2.043140000	-0.043690000
1	4.234098000	1.970814000	0.807960000
6	5.103165000	-0.610142000	0.865021000
1	5.551291000	0.003454000	1.643543000
1	5.062437000	-1.644123000	1.199782000
17	6.317522000	-0.594920000	-0.515571000

E = -1200.75284184, G = -1200.632218

4.12

6	-4.451048000	-0.579549000	0.016268000
1	-4.201915000	-1.635596000	0.007514000
1	-5.508149000	-0.339723000	0.028274000
6	-3.529514000	0.388222000	0.012665000
1	-3.874121000	1.420587000	0.021805000
6	-2.066781000	0.229878000	-0.002117000
6	-1.259660000	1.377358000	-0.009048000
6	-1.427698000	-1.021564000	-0.013741000
6	0.128099000	1.288992000	-0.024747000

1	-1.727949000	2.356741000	-0.003964000
6	-0.044557000	-1.119053000	-0.029502000
1	-2.014968000	-1.932732000	-0.012412000
6	0.740919000	0.037505000	-0.037498000
1	0.728706000	2.190954000	-0.034404000
1	0.428063000	-2.094303000	-0.043473000
6	2.238514000	-0.075265000	-0.000293000
9	2.708707000	-0.167687000	1.271851000
9	2.850199000	0.994387000	-0.557135000
9	2.685616000	-1.173929000	-0.651968000

E = -646.87807357, G = -646.781816

4.13

76	-2.477779000	-0.370047000	-0.077881000
8	-1.946792000	-1.973489000	0.238709000
8	-1.320978000	0.480421000	-1.092225000
8	-2.222284000	0.673116000	1.324424000
8	-4.076255000	-0.222593000	-0.689490000
6	-0.908285000	2.267647000	1.094609000
1	-0.544308000	2.030938000	2.084417000
1	-1.727627000	2.972050000	1.048594000
6	-0.137222000	2.039987000	-0.028327000
1	-0.366732000	2.599108000	-0.927174000
6	1.146851000	1.337059000	-0.016811000
6	2.063787000	1.565167000	-1.054252000
6	1.501082000	0.437079000	1.002689000
6	3.305002000	0.941783000	-1.062907000
1	1.800347000	2.241971000	-1.860520000
6	2.738494000	-0.189907000	0.997859000
1	0.800627000	0.212392000	1.799203000
6	3.645410000	0.063085000	-0.034312000
1	4.002085000	1.131277000	-1.870366000
1	2.994342000	-0.887538000	1.786489000
6	5.007630000	-0.575290000	-0.006270000
9	5.894901000	0.170561000	0.701941000
9	4.987095000	-1.797447000	0.569743000
9	5.529827000	-0.723767000	-1.243536000

E = -1038.89398038, G = -1038.792306

4.14

76	-2.442712000	-0.352637000	0.066770000
8	-1.818680000	-1.881567000	0.503332000
8	-1.302336000	0.502055000	-1.219575000
8	-1.788275000	1.075781000	1.156517000
8	-4.106299000	-0.143778000	-0.251975000
6	-1.088751000	2.135894000	0.477479000
1	-0.398865000	2.568123000	1.203193000
1	-1.822689000	2.890683000	0.178950000
6	-0.407698000	1.531194000	-0.742439000
1	-0.358952000	2.261764000	-1.556989000
6	0.985841000	0.976945000	-0.490150000
6	1.308258000	-0.350224000	-0.771338000
6	1.986268000	1.828988000	-0.006062000
6	2.599576000	-0.826943000	-0.551844000
1	0.554967000	-1.016681000	-1.170281000
6	3.275824000	1.361834000	0.208638000
1	1.764987000	2.871565000	0.202697000
6	3.583249000	0.025670000	-0.059562000
1	2.833270000	-1.863284000	-0.763518000
1	4.038730000	2.031362000	0.589105000
6	4.992210000	-0.461934000	0.140655000
9	5.067243000	-1.807214000	0.218281000
9	5.805535000	-0.083369000	-0.879036000

9 5.543972000 0.035963000 1.272275000
E = -1038.95098783, G = -1038.844401

4.15

6 3.680626000 -1.203439000 0.000000000
1 3.943543000 -0.150660000 0.000000000
1 4.509241000 -1.902301000 0.000000000
6 2.417146000 -1.639941000 0.000000000
1 2.251916000 -2.715962000 0.000000000
6 1.187313000 -0.833111000 0.000000000
6 -0.054833000 -1.484748000 0.000000000
6 1.186013000 0.571658000 0.000000000
6 -1.253510000 -0.776753000 0.000000000
1 -0.086256000 -2.570207000 0.000000000
6 0.000000000 1.293762000 0.000000000
1 2.123294000 1.116998000 0.000000000
6 -1.215873000 0.612187000 0.000000000
1 -2.203781000 -1.297203000 0.000000000
1 0.014087000 2.377246000 0.000000000
17 -2.719608000 1.523788000 0.000000000
E = -769.351711701, G = -769.265399

4.16

76 -2.003314000 -0.331731000 -0.073642000
8 -1.540817000 -1.953826000 0.259522000
8 -0.818911000 0.452633000 -1.109329000
8 -1.688274000 0.717141000 1.312564000
8 -3.599059000 -0.118594000 -0.675413000
6 -0.297701000 2.246636000 1.052164000
1 0.041837000 2.016912000 2.052157000
1 -1.083142000 2.986384000 0.978494000
6 0.476329000 1.958078000 -0.054747000
1 0.279683000 2.504445000 -0.969204000
6 1.715711000 1.186053000 -0.022043000
6 2.636412000 1.318005000 -1.074015000
6 2.030843000 0.306195000 1.028172000
6 3.839591000 0.623394000 -1.073261000
1 2.407559000 1.978848000 -1.904079000
6 3.227835000 -0.396173000 1.040112000
1 1.330377000 0.153617000 1.841905000
6 4.127959000 -0.229409000 -0.011258000
1 4.545527000 0.737915000 -1.886959000
1 3.460301000 -1.075837000 1.851040000
17 5.641429000 -1.114483000 0.001409000
E = -1161.36757002, G = -1161.275913

4.17

76 1.958981000 -0.318066000 -0.063389000
8 1.400937000 -1.871473000 -0.504309000
8 0.779458000 0.485593000 1.219308000
8 1.252752000 1.086007000 -1.151982000
8 3.611340000 -0.040905000 0.264420000
6 0.506428000 2.113726000 -0.472135000
1 -0.195676000 2.521740000 -1.200222000
1 1.208122000 2.895249000 -0.164280000
6 -0.158867000 1.474906000 0.738828000
1 -0.244722000 2.198666000 1.556445000
6 -1.521709000 0.856880000 0.468247000
6 -1.782172000 -0.489595000 0.724223000
6 -2.561533000 1.663467000 -0.007321000
6 -3.044527000 -1.030968000 0.485155000
1 -1.001857000 -1.126277000 1.120468000
6 -3.827431000 1.138586000 -0.244872000

1	-2.395038000	2.720796000	-0.193489000
6	-4.056994000	-0.212802000	0.000182000
1	-3.236566000	-2.079550000	0.678451000
1	-4.626934000	1.769288000	-0.614849000
17	-5.650877000	-0.887403000	-0.302254000

E = -1161.42409702, G = -1161.327865

4.18

6	2.072726000	0.573719000	-0.197794000
1	1.989653000	1.273423000	-1.041213000
1	2.129810000	1.188004000	0.708168000
6	0.805731000	-0.298482000	-0.157154000
1	0.874594000	-0.988455000	0.692479000
1	0.771565000	-0.928789000	-1.055290000
6	-3.048600000	0.463575000	0.084815000
1	-3.110288000	1.157323000	-0.763117000
1	-3.012253000	1.091824000	0.983705000
6	-0.487741000	0.516311000	-0.057978000
1	-0.546944000	1.208121000	-0.908781000
1	-0.451275000	1.147924000	0.839516000
6	-1.752499000	-0.347338000	-0.018050000
1	-1.692278000	-1.041159000	0.831047000
1	-1.790645000	-0.977659000	-0.916585000
6	-4.306357000	-0.407563000	0.122764000
1	-4.293343000	-1.089321000	0.979251000
1	-5.213169000	0.199260000	0.199293000
1	-4.395027000	-1.019378000	-0.780741000
6	4.345642000	-0.249443000	0.519275000
1	4.331298000	0.344567000	1.429691000
1	5.228238000	-0.858404000	0.351773000
6	3.334361000	-0.227882000	-0.346759000
1	3.400480000	-0.844660000	-1.243917000

E = -314.553301249, G = -314.370547

4.19

6	-1.514369000	1.751659000	0.340068000
6	-0.279415000	2.084577000	-0.454783000
8	0.413869000	-0.024259000	-0.709949000
76	1.960605000	-0.434083000	0.012867000
8	3.088308000	-0.948804000	-1.178116000
8	1.754190000	-1.509839000	1.338845000
8	2.315454000	1.192636000	0.568761000
1	-1.990558000	2.699479000	0.630612000
1	-1.224916000	1.270809000	1.282144000
1	-0.369364000	2.053003000	-1.536147000
6	-2.537395000	0.891486000	-0.410161000
1	-2.062276000	-0.043258000	-0.721120000
1	-2.828279000	1.408668000	-1.334058000
6	-6.079014000	-0.568582000	0.483800000
1	-6.544118000	0.370247000	0.809890000
1	-5.789290000	-1.094807000	1.401906000
6	0.822792000	2.700151000	0.083158000
1	1.571329000	3.154802000	-0.551831000
1	0.855230000	2.967931000	1.132439000
6	-3.790474000	0.589576000	0.416440000
1	-4.255252000	1.531861000	0.736671000
1	-3.500475000	0.069030000	1.338657000
6	-4.824085000	-0.254135000	-0.336913000
1	-4.358222000	-1.194302000	-0.660252000
1	-5.116239000	0.267256000	-1.258294000
6	-7.106083000	-1.406660000	-0.281210000
1	-6.684309000	-2.367908000	-0.591988000
1	-7.988448000	-1.617095000	0.329897000

1 -7.447098000 -0.891714000 -1.185151000
E = -706.566300691, G = -706.379546

4.20

6	1.243387000	1.440565000	-0.321332000
6	-0.012275000	1.684513000	0.514706000
8	-0.533419000	0.423490000	1.019997000
76	-1.892788000	-0.440791000	-0.011671000
8	-3.353845000	-0.669192000	0.844759000
8	-1.217302000	-1.698078000	-0.953604000
8	-1.892404000	1.256726000	-0.896004000
1	1.601691000	2.417132000	-0.671867000
1	0.971184000	0.872559000	-1.219722000
1	0.237683000	2.259658000	1.412071000
6	2.362772000	0.723988000	0.438925000
1	1.995289000	-0.243213000	0.795594000
1	2.615960000	1.302361000	1.337548000
6	6.016798000	-0.398429000	-0.492198000
1	6.372075000	0.568732000	-0.869850000
1	5.761058000	-0.991142000	-1.379381000
6	-1.158166000	2.318160000	-0.249614000
1	-1.845077000	2.844283000	0.420582000
1	-0.834558000	2.998784000	-1.040102000
6	3.623810000	0.519575000	-0.406414000
1	3.980632000	1.491280000	-0.773621000
1	3.369761000	-0.064530000	-1.300579000
6	4.756290000	-0.180945000	0.351090000
1	4.398366000	-1.149563000	0.723884000
1	5.014704000	0.405860000	1.242861000
6	7.145681000	-1.090851000	0.274752000
1	6.835482000	-2.075860000	0.637872000
1	8.028481000	-1.235464000	-0.354536000
1	7.455095000	-0.503795000	1.145562000

E = -706.634500296, G = -706.442188

