University of Southampton

Faculty of Engineering and Physical Sciences

School of Chemistry

Synthesis of Organic Chromophores for use in Electro-Optic Polymers

by

Matthew Owen Jenner

Thesis for the degree of MPhil Chemistry

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Abstract

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One of the most rapidly advancing technologies in the field of optoelectronics is optical modulation, with recent research focusing on the use of organic chromophore-containing polymers to achieve this modulation. These polymer-based optical modulators achieve modulation speeds far beyond their mechanical or electronic counterparts, and further success in this field could pave the way for future technologies such as LiFi (light-based WiFi) communications and LiDAR (Light Detection And Ranging).

In collaboration with the Optoelectronics Research Centre at the University of Southampton, this project has been centred around synthesising organic chromophores and chromophore-containing polymers for use in the department's optical modulators, with an aim of synthesising several novel chromophores by the end of the project.

Over the course of the project a PMMA-chromophore copolymer was made from the commercially available chromophore Disperse Red 1 and several steps of a multi-step chromophore synthesis were completed. However, due to repeated failures of several of the steps the final stage of the chromophore synthesis was not completed, although the results from tests of these steps under different conditions may prove useful for future attempts of this project.

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Research Thesis: Declaration of Authorship

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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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I would also like to thank all the members of the Rios group for their helpful advice and informative discussion throughout my time in the group. I would particularly like to thank Dr Marta Meazza for her invaluable help and advice over the course of the project. Furthermore, I would like to thank Teerapat Rutirawut and Dr Frederic Gardes from the optoelectronics department for their help explaining the optoelectronics principles and technologies described in this report.

Finally, I would like to thank Dr Neil Wells for his help with NMR acquisition, Ms Julie Herniman for her help with mass spectrometry acquisition, Professor Richard Brown and his research group for allowing the use of their IR spectrometer and Dr Thomas Logothetis for allowing the use of the level 5 teaching laboratory's melting point apparatus.

Definitions and Abbreviations

Ac – Acetyl

AIBN – Azobisisobutyronitrile

AMA – Anthracenylmethacrylate

Bu – Butyl

cm – Centimetre(s)

CPU – Central processing unit

DCM – Dichloromethane

DIBAL – Diisobutylaluminium hydride

DIPA – Diisopropylamine

DMF – N,N-Dimethylformamide

DMSO – Dimethyl sulfoxide

DR1MA – Disperse Red 1 methacrylate

EM – Electromagnetic

EO Polymer – Electro-optic polymer

ESI – Electrospray ionisation

Et – Ethyl

g – Gram(s)

h – Hour(s)

HRMS – High-resolution mass spectrometry

Hz – Hertz

IR – Infrared

LED – Light-emitting diode

LIDAR – Light detection and ranging

LiFi – Light-based WiFi

M – Molar

Me – Methyl

MEMS – Micro-electromechanical systems

mg – Milligram(s)

MHz – Megahertz

min – Minute(s)

MIT – Massachusetts Institute of Technology

ml – Millilitre(s)

mmol – Millimole(s)

MOM – Methoxymethyl

mp – Melting point

m/z – Mass/charge ratio

NMBS – Non-mechanical beam steering

NMR – Nuclear magnetic resonance

pm – Picometre(s)

PMMA – Poly(methylmethacrylate)

r_{33} – Intrinsic electro-optic coefficient

RADAR – Radio detection and ranging

rt – Room temperature

TBDMS – *tert*-Butyldimethylsilyl

tert – Tertiary

T_g – Glass transition temperature

Definitions and Abbreviations

THF – Tetrahydrofuran

THz – Terahertz

UC Berkeley – University of California, Berkeley

UCSB – University of California at Santa Barbara

V – Volt(s)

VLC – Visible light communication

2D – Two-dimensional

3D – Three-dimensional

°C – Degrees Celsius

µL – Microlitre(s)

µmol – Micromole(s)

Chapter 1 Introduction

1.1 Optical Modulation

Optical modulation is the process of varying one or more properties (usually intensity or phase) of a beam of visible light, which has many optoelectronic applications. One example of such an application is in a photonic circuit - a device similar to an electronic circuit, which uses visible light to transmit data rather than electricity. In a photonic circuit, optical modulation is implemented by devices which either cause direct changes in the optical intensity of the light *via* absorption, or cause changes in the refractive index of the material.[1] This latter effect is useful as it changes the phase of the incoming wave, which can be converted into an intensity change *via* either an interferometer[2] or a resonant device.[3] These refractive index changes are typically produced via an applied electrical field, which cause the change of refractive index in different ways depending on the type of optical modulator. For this joint project which our group is carrying out with members of the optoelectronic department, the optical modulators in question are those formed of a chromophore-containing polymer, the synthesis of which it has been my aim to complete.

1.2 EO polymer optical modulators

In an optical modulator which uses an EO polymer (electro-optic polymer) to function, the change in refractive index is caused by the applied electric field interacting with the polar chromophore molecules and causing them to align (see Figure 1 below).

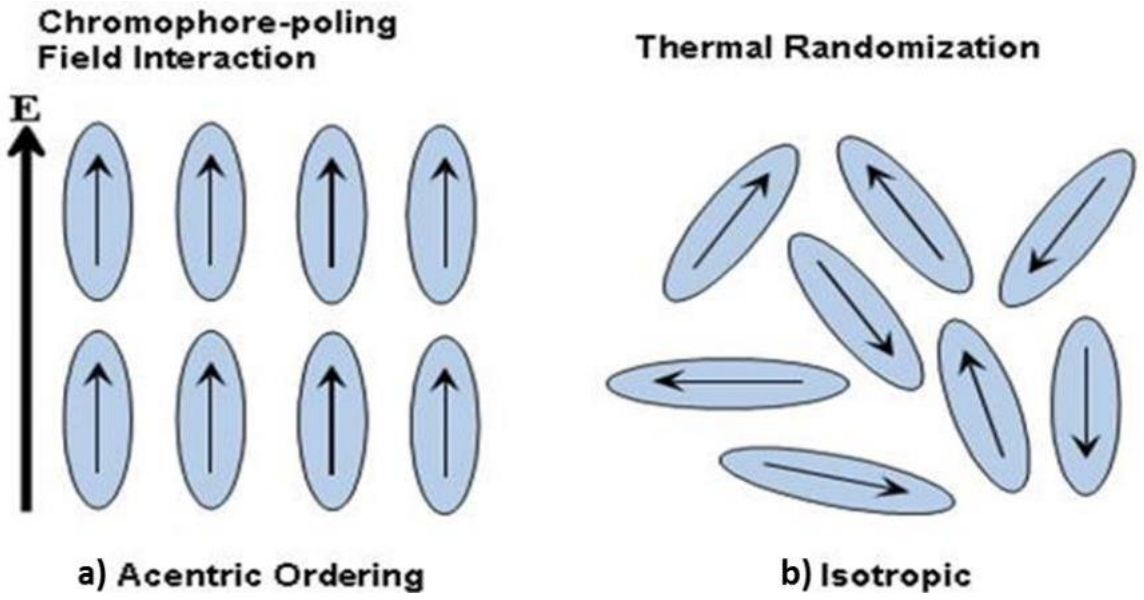

Figure 1 Diagram detailing the effects of an applied electrical field on chromophore molecules within a polymer[4]

This alignment changes how the light passing through the polymer interacts with the molecules of the chromophore, thus altering the amount of refraction the light undergoes. The most prominent effect of this is found when combining two channels of light which have undergone differing amounts of refraction. Refraction of a light wave changes the phase of the wave, and when two waves with exactly opposite phases are combined this results in a wave with an intensity of zero – effectively 'turning off' the signal. In this way optical modulation is able to convert digital electronic data - comprising of a collection of signals, each being either a '1' (signal on) or a '0' (signal off) – into a corresponding optical signal, the applications of which are extremely vast.

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[4] Diagram originated from Teerapat Rutirawut's 16 month progress report, which used a diagram adapted from R.W. Boyd's book 'Nonlinear Optics' – [5]

1.3 Applications of optical modulators - LiFi

Originating from recent advances in visible light communication (VLC), LiFi (light-based WiFi) is fast becoming a superior alternative to WiFi for high speed data communication. First coined by Harald Haas in 2011 at a TED Global talk, with a publication being released a few years later in 2016,[6] LiFi is a relatively new technology which enables data transmission via visible light through small changes in the intensity of the light, which can in turn be translated into a digital signal. This method of data transfer is extremely fast in comparison to current WiFi technologies due to the frequency difference of the electromagnetic radiation used (the light radiation used in LiFi can have a frequency of up to 800 THz, over 10,000 times faster than the radio frequency radiation used for WiFi). This advanced method of data communication can be applied to almost any environment where LED lights are present (see Figure 2), with the only modification needed being an optical modulator which can modulate the light as fast as the data is being received. Of course, there are still some disadvantages of LiFi – namely the installation cost. As each room must first be fitted with a light modulation system before LiFi can be used, the initial cost of equipping a whole building will be very high, but if this financial barrier can be overcome then the actual maintenance costs or likelihood of network downtime will actually be very low. Although the optical modulator itself is certainly not new technology, the idea of using optoelectronic polymers in place of the usual lithium niobite crystal (which also changes its refractive index relative to the input electric field) is a much less explored area, especially considering these organic materials have equally fast data translation speeds as their inorganic counterparts.

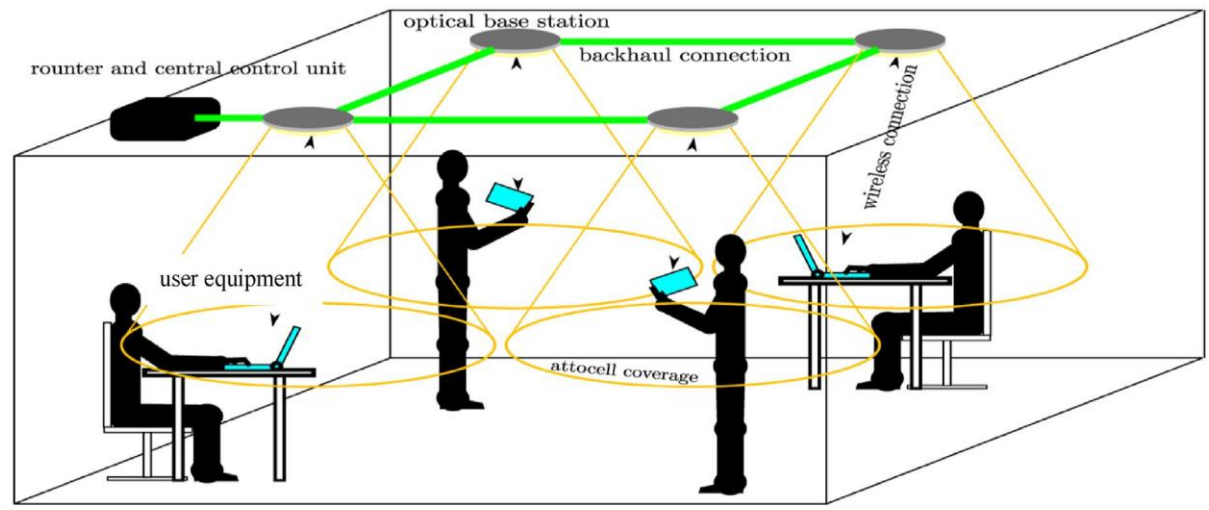


Figure 2 Diagram demonstrating the applications of LiFi technology[7]

1.4 Applications of optical modulators - NMBS

Another key function which an optical modulator can be used for is to steer a light signal via a process known as non-mechanical beam steering (NMBS). In common mechanical beam steering moving parts such as gimbals or prisms are needed in order to steer the light, but moving these mechanically is far too slow a process to adequately be of use for most electronic beam scanning purposes. In response to this very obvious technological need, various solutions to the problem began surfacing from MIT in 2013 (Figure 3(b)),[8] UC Berkeley in 2014 (Figure 3(a))[9] and UCSB in 2015,[10] each of which employing a different, yet equally successful, optoelectronic method of steering a narrow beam of visible light.

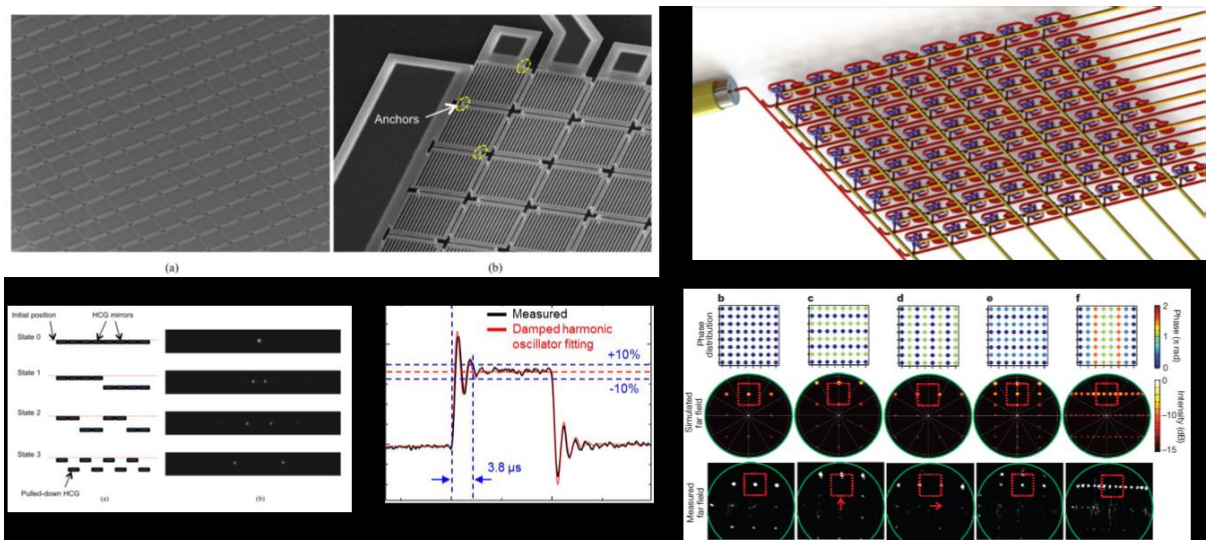


Figure 3[11] (a) (left) UC Berkely's device, which employs an array of MEMS (micro-electro-mechanical systems) to configure diffraction gratings which angle the light[9] - the top left shows microscope images of the gratings, while the bottom left shows the light patterns possible from each digital signal. (b) (right) MIT's device, which uses a 2D array of optical phase modulators to angle the resulting light beam[8] - the top right is a computer-generated image of the array in full, the bottom right shows the different light signals possible from each phase modulation combination.

1.5 Applications of optical modulators - LIDAR

With the technological setback of beam steering circumvented, new ideas for ways to apply this advancement began to appear, the most revolutionary of which was LIDAR (Light Detection and Ranging). LIDAR uses a similar principle to RADAR (Radio Detection and Ranging) – it sends out pulses of electromagnetic radiation and records the time taken for each pulse to be reflected and return to the device to determine the reflecting object's distance – however its use of visible light instead of radio waves allows it both a higher accuracy (due to ease of beam focusing) and higher processing speed (due to higher EM frequency), while background light interference can be avoided by narrowing the detected frequency to the exact light frequency that was emitted. With this key application the advantages of optical modulation can really be applied, as a beam of light steered solely by electrical signals will be able to collect a full 3D scan in a fraction of the time that it would take to even just rotate the beam in one dimension mechanically. Again, as with LiFi, there is still the disadvantage of installation cost, as these optical modulator-based scanners require much more precise manufacturing techniques than the standard mechanical versions. However, since the only real disadvantages are cost and ease of production, it seems that the pros definitely outweigh the cons when it comes to LIDAR. With this innovation of optical modulator-driven LIDAR beam steering comes further possible innovations in the optical modulator itself, the most prominent of which for this project is via the use of electro-optic polymers.

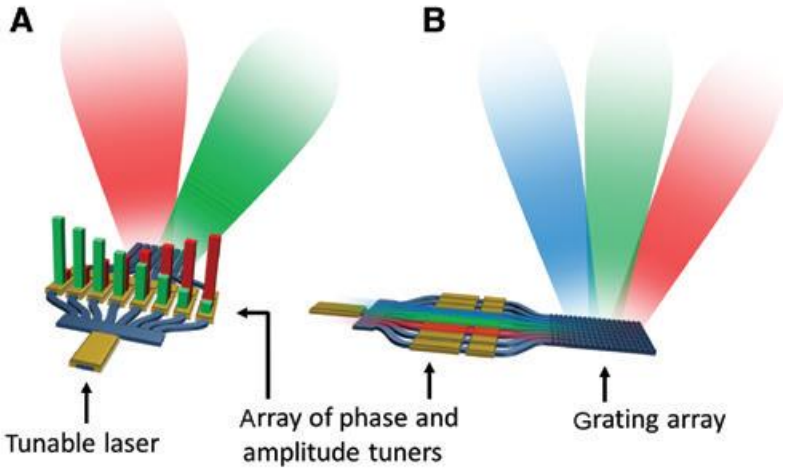


Figure 4 Examples of optical modulator-driven beam steering via either (**A**) applying and changing a linear phase profile over an array of phase tuners (with the size of the bars representing the amount of phase tuning) or (**B**) changing the wavelength of the light using a tuneable laser and passing it through an multi-angled, wavelength-specific grating[12]

1.6 Electro-optic polymers - Key physical properties

When devising electro-optic polymers for synthesis there are several important physical properties to take into account. One of the most basic properties which is key to a polymer's success as an optical modulator is its glass transition temperature (T_g). Optical modulators – when applied to an optoelectronic circuit inside such devices as a computer's CPU, for example – are often subjected to high levels of heat from the many surrounding components of the CPU, and it is this heat which can be particularly problematic for EO polymers. The glass transition temperature is the temperature at which a polymer transitions from a clear, rigid, glassy-like state to a rubbery and translucent semi-solid. The translucency of this semi-solid state makes it much harder for light to pass through the material, and this effectively renders any electro-optic polymer useless, so it is understandable why a high T_g is such an important property to have.

Related to this, another important intrinsic property of an EO polymer is its optical absorption. All electro-optic polymers have certain regions of the EM spectrum which they absorb more than others, and this property can seriously affect the efficiency of the optical modulator if this region coincides with the intended frequency of the incident light. The optical absorption range is determined by many factors, such as the chromophore used, the comonomer used, and the ratio of the two, and it is this latter variable which is often used to tune the optical absorption so that the region falls outside of the frequency range at which the optical modulator operates, thus maximising efficiency.

The final key property to consider is the electro-optic coefficient (or electro-optic efficiency) of the polymer, as this is the feature which has possibly the strongest influence on the overall efficiency of the optical modulator. As mentioned previously, in an EO polymer optical modulator the greater the refractive index change needed, the greater the required electric field strength, however the correlation between these two variables is not the same for all EO polymers. Each polymer has an intrinsic electro-optic coefficient (often represented as r_{33}) of units pmV^{-1}, which is used to express its efficiency as a ratio of refractive index change per each unit of voltage applied. This property is also what gives organic polymer optical modulators an edge over inorganic crystal optical modulators like $LiNbO_3$, as EO polymers commonly have much higher r_{33} values in comparison.

1.7 Electro-optic polymers - Compatible chromophores

Along with the physical properties of the polymer, there are also some chemical properties which have to be considered when selecting a chromophore to synthesise and copolymerise. In many literature examples[13,14] the upper section of the chromophore is synthesised with a hydroxy group connected to the optically active part of the chromophore by a short alkyl chain and an amine (see Figure 5). This hydroxy group is essential for the connection of the chromophore to the polymer chain, usually carried out via a simple esterification reaction with methacryloyl chloride to form the monomer (see Figure 6). This is important as most compatible electro-optic polymers are primarily a chain of methacrylate-based monomers, which is due to mainly to the polymer's key intrinsic property of a high transparency for visible light.

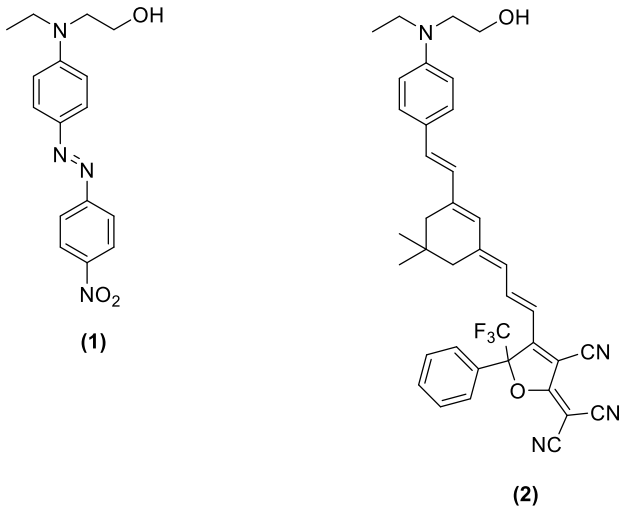


Figure 5 Two examples of chromophores used for electro-optic polymer synthesis, Disperse Red 1 **(1)**[13] and AJL6 **(2)**,[14]

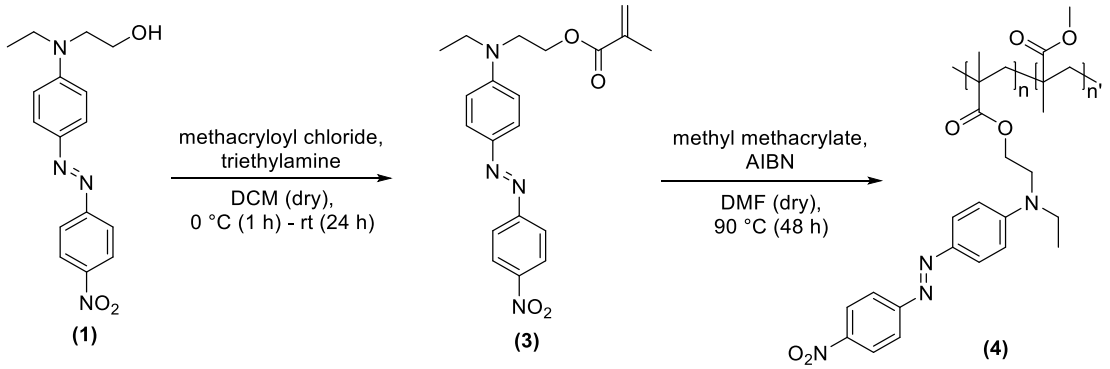


Figure 6 An example of the necessary esterification and radical copolymerisation reactions needed to form an electro-optic polymer **(4)** from an organic chromophore **(1)**[13]

The amine functional group is also a key component of the chromophore, not only because it allows facile linkage to the benzene ring via nucleophilic aromatic substitution (see Figure 7), but also because its electron-donating properties increase the polarity of the chromophore, which is crucial for the chromophore-poling field interaction described in Figure 1. However, many of these chromophores are relatively long molecules, so in order to give them the high polarity that is needed there must not only be an electron-donating amine on one end, but also an electron-withdrawing group at the other end. In chromophore **1** this electron-withdrawing property is present in the nitro group, and in chromophore **2** this is present in the many nitrile groups attached to the furan-like ring in the lower section of the molecule.

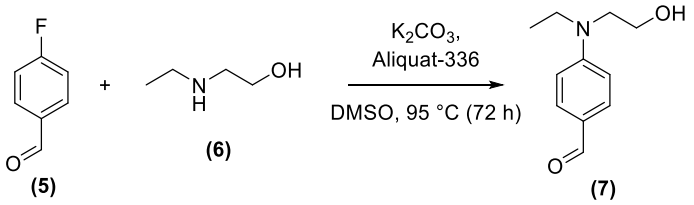


Figure 7 An example of a nucleophilic aromatic substitution reaction, used to form the upper section of the chromophore[15]

The final key feature is a fully conjugated π-system, seen in both chromophores **1** and **2**, as this elongated system is what lowers the π-π* energy gap and allows these transitions to happen at visible wavelengths, thus providing the optical properties of the chromophore. Further modifications such as side chains (see Figure 8) allow for more than one polymerisation site, creating dendrimers rather than chains (see **1.9** for more information), which have been shown to give advanced electro-optic activities.[14]

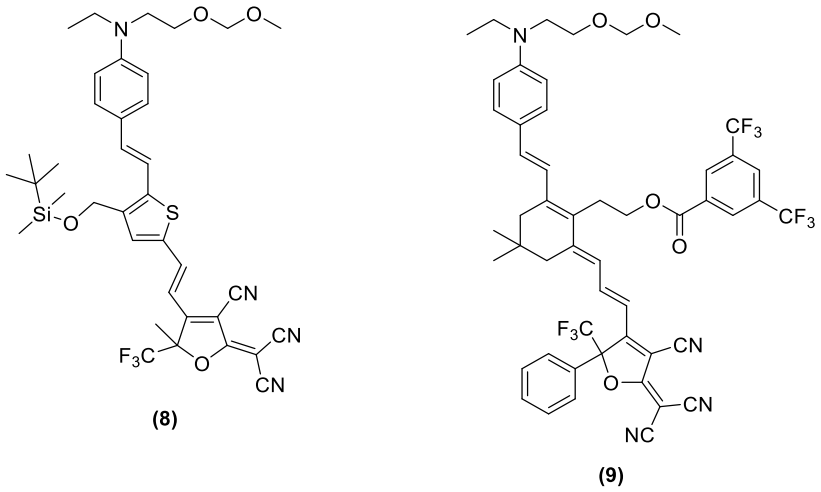
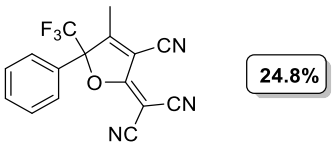


Figure 8 Two examples of chromophores with side chains for dendrimeric polymer synthesis[14]

1.8 Possible chromophore modifications

From the literature procedures studied for this project, one of the earliest reported chromophore syntheses comes from a 2003 paper by Alex Jen *et al*.[16] This paper was primarily focused on the newly devised furan derivative electron acceptors, as seen in the lower section of chromophores **2**, **8** and **9**. As was mentioned in **1.7**, an effective chromophore requires three key components – an electron donor, a conjugating bridge, and an electron acceptor – and the most under-researched of these at the time of release of this paper was the latter, especially in terms of chromophore-compatible acceptors. However, although this paper does go into great detail about how to form chromophores from the aforementioned acceptors, it's actually a cited paper by Mingquian He *et al* in 2002[17] which provides the essential library of electron acceptors needed for the modification of these literature chromophores into novel chromophores with (hopefully) improved optoelectronic properties. Shown below in Figure 10 are a few examples of the acceptors which were synthesised, pictured alongside the overall calculated yields for the two steps needed for their synthesis. These all show promise from a yield perspective as, according to the aforementioned paper,[17] they all have a higher overall yield than acceptor **10** - the most commonly used acceptor by Tae-Dong Kim *et al* in their paper on EO polymers[14] (see chromophores **2** and **9** for examples). This provides a good starting point for chromophore optimisation, as the effect on the optical properties from the substituents alone is a rather under-studied field, with few indications as to which acceptor substituents produce which changes in optical properties, so this kind of chromophore optimisation can only really be determined by trial and error.



(10)

Figure 9 Acceptor **10**, a commonly-used electron acceptor, alongside it's overall two-step yield from the 2002 paper by Mingquian He *et al*[17]

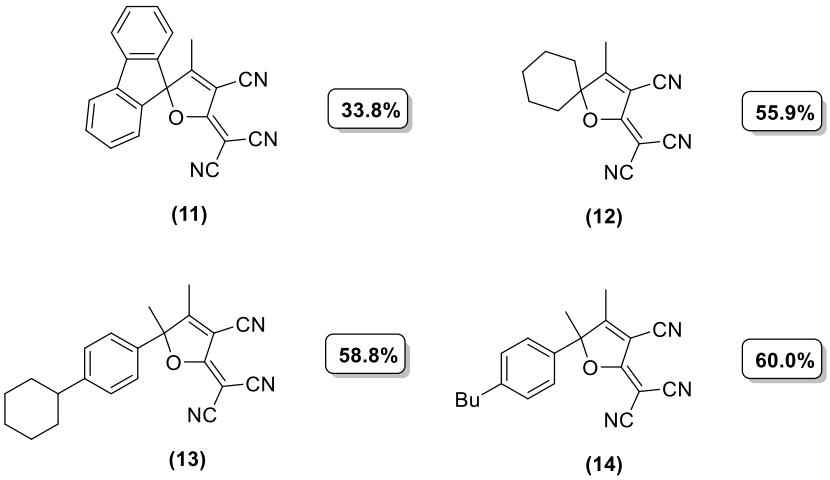


Figure 10 A few examples of other possible electron acceptors, alongside their overall two-step yields from the 2002 paper by Mingquian He *et al*[17]

Another possible modification, first shown in the aforementioned paper by Alex Jen *et al*[16] is to use a thiophene-based group as the mid-section of the conjugating bridge instead of the cyclohexene-based version. The copolymeristion of this type of chromophore, however, has already been attempted by Tae-Dong Kim *et al* in a later paper,[14] and it was found that the polymer gave a much lower electro-optic coefficient than its cyclohexene-based equivalent. Nevertheless, the possibility of furan or pyrrole-based conjugating bridges has not yet been explored, so chromophores such as those shown in Figure 11 still have the possibility of demonstrating a greater electro-optic efficiency.

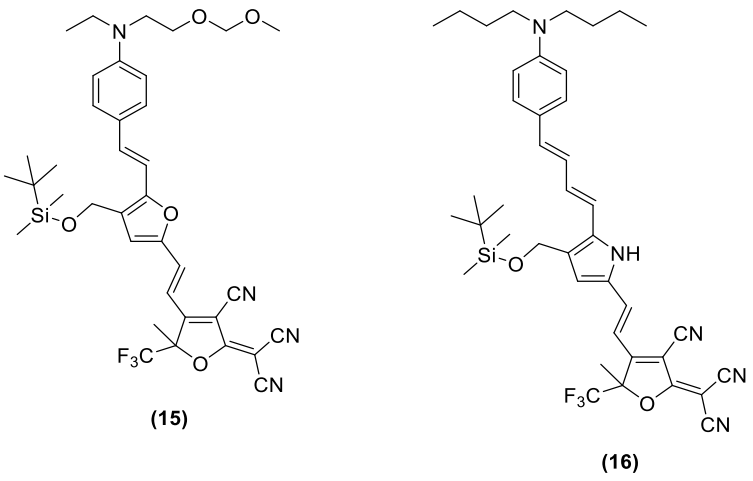
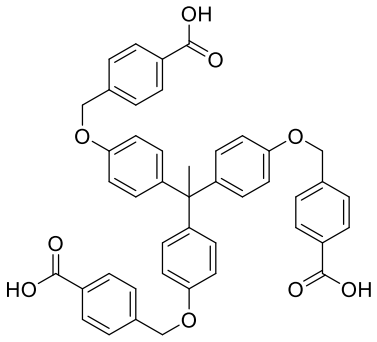


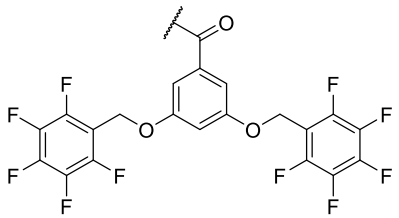
Figure 11 Possible novel furan-containing **(15)** or pyrrole-containing **(16)** chromophore conjugating bridge designs, based on chromophores from [14] and [16] respectively

1.9 Possible copolymerisation methods

Alongside modifications to the chromophores, there is also the possibility of modifying the copolymerisation methods to form more complex structures than simple linear polymerisation allows. The aforementioned 2008 paper by Tae-Dong Kim *et al*[14] provides a great starting point for such innovations, as it describes a wide range of different strategies, comonomers and crosslinkers for chromophore copolymerisation, each with a plethora of analytical data to support their use. One technique which gave a particularly high optical activity was the synthesis of dendritic copolymers like compound **19**. Throughout their research, Kim *et al* found that the electro-optic activity of polymers would always increase as chromophore concentration was increased, but this also increased the chance of chromophore aggregation, an effect which greatly disrupts the poling process (see Figure 1). In order to combat this, branched core molecules like compound **17** were synthesised which caused the copolymer units to form spherical shapes rather than chains. This, combined with the addition of electronically-shielding substituent **18** to the chromophore side chain, gave protection from aggregation, and allowed the use of much higher chromophore concentrations (thus achieving a much higher EO activity).

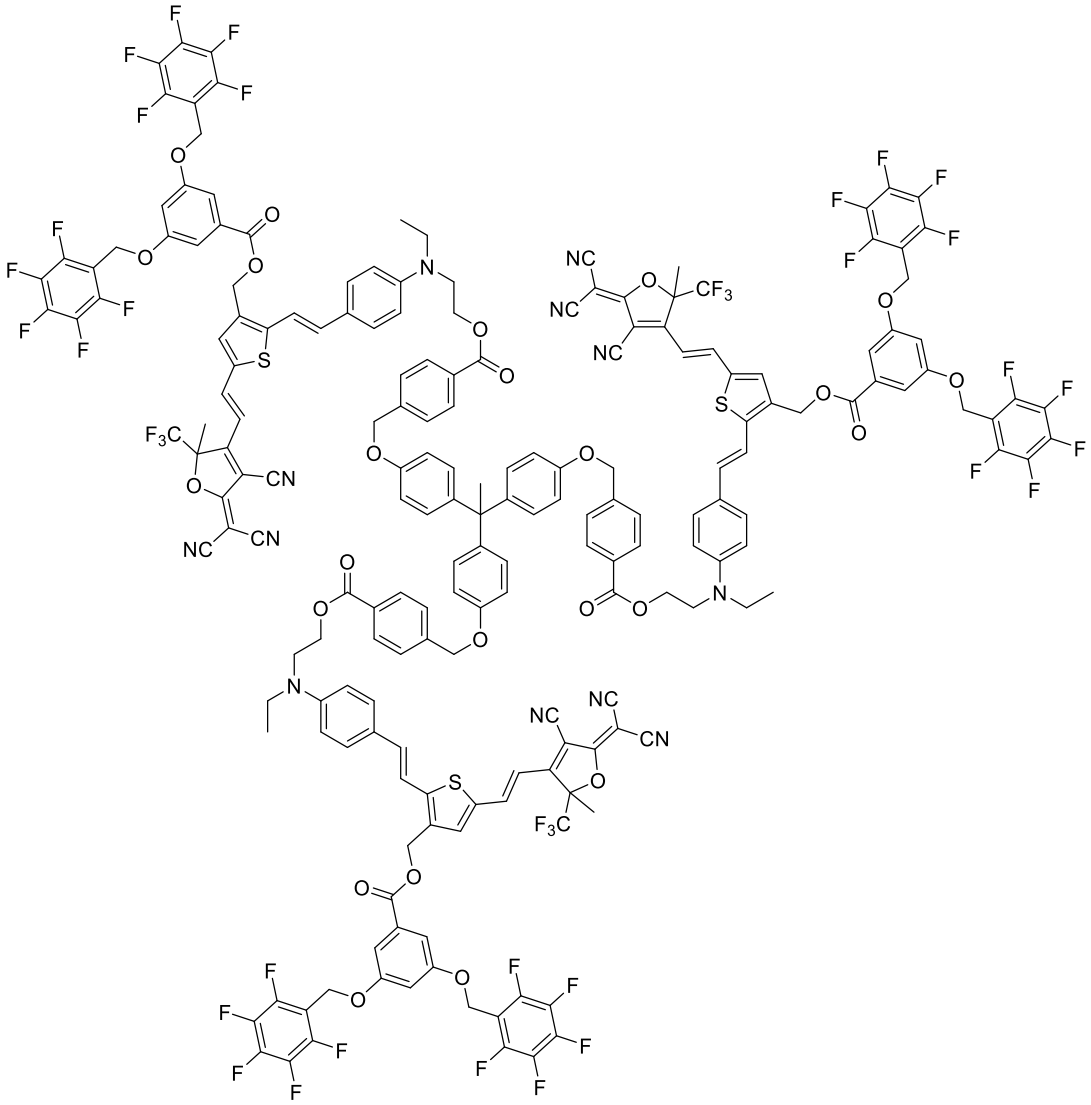


(17)



(18)

Figure 12 Branched core **(17)** and electronically-shielding chromophore substituent **(18)** for the synthesis of dendritic EO polymers[14]



(19)

Figure 13 An example of one of the electro-optic dendrimers synthesised by Tae-Dong Kim *et al*[14]

An alternative strategy for the synthesis of non-linear polymers, also from the same paper, is by the use of the polymer PMMA-AMA10 (**20**) and crosslinkers like compound **21** to form lattice-like structures. The advantage of these lattices is that they boast a much-improved temporal stability. This is a rather unique property which means the polymer will retain its spatial conformation for much longer than common linear polymers, or even dendritic polymers like **19**, thus giving these lattice-like polymers a much greater lifespan than other polymers. PMMA-AMA10 is a copolymer of methyl methacrylate and 9-anthracenylmethyl methacrylate in a 9:1 ratio, which is able to react with compound **21** in a Diels-Alder reaction to form the lattice. Chromophores can be bonded onto the polymer in a similar way (demonstrated in Figure 15), thus creating an easily modifiable cross-linked polymer with greatly improved stability.

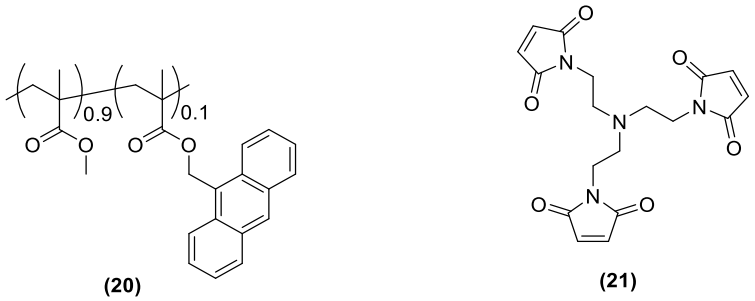


Figure 14 PMMA-AMA10 **(20),** and a crosslinker **(21)** which is able to join separate chains of PMMA-AMA10 together via Diels-Alder reactions with the anthracene moieties on the chain[14]

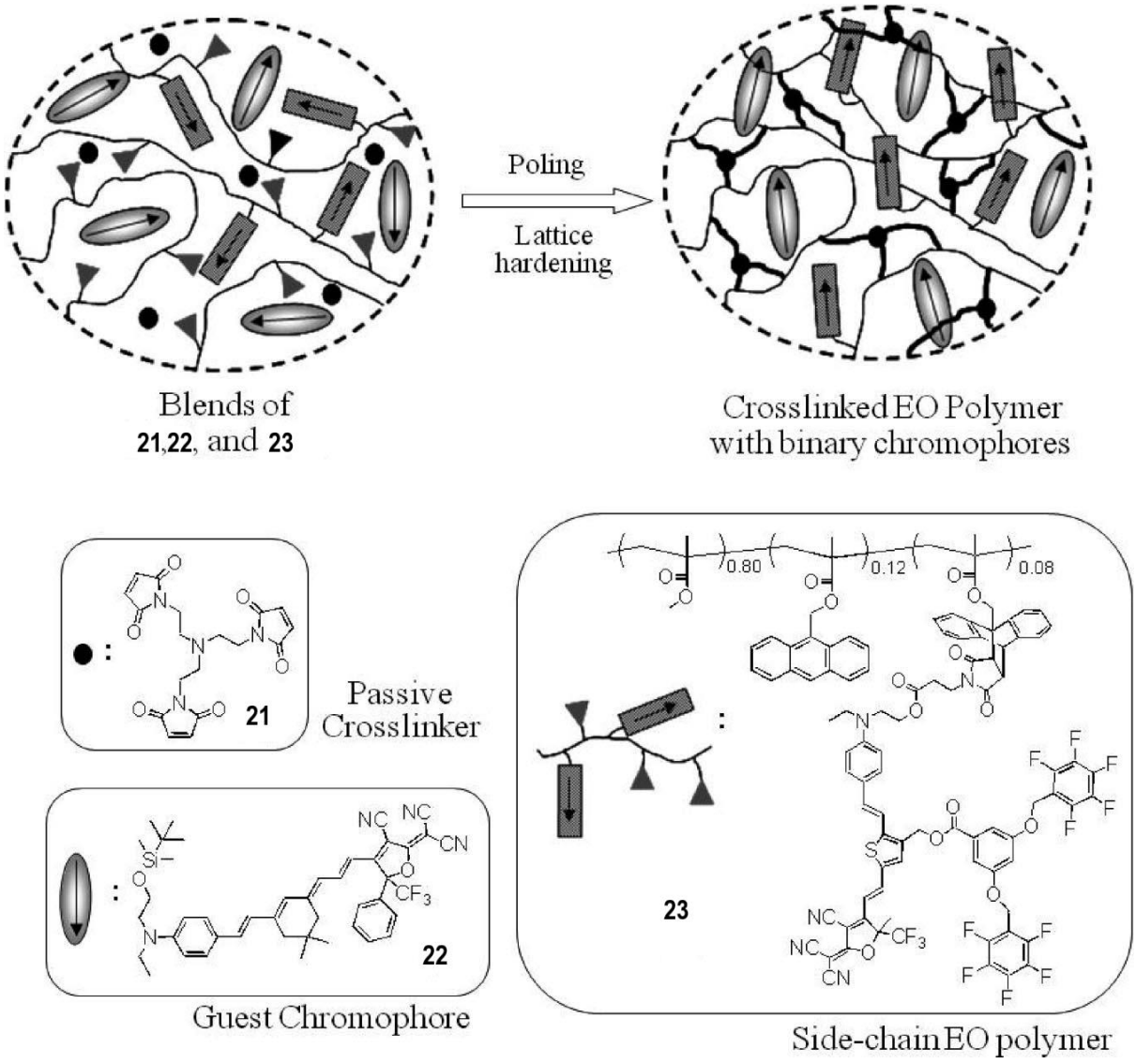


Figure 15 Modified diagram from [14] demonstrating a cross-linked polymer with one chromophore bonded via a Diels-Alder reaction to the anthracene moiety on the chain (**23**) and an additional chromophore included in the polymer in a guest-host-type system (**22**)

One final method for the formation of non-linear polymers, mentioned previously in section **1.7**, is *via* the incorporation of an ethoxy side chain on the central cyclohexene or heterocyclic ring of the conjugation bridge of the chromophore (see compounds **8** and **9**). A much more common form of dendronization which can be found in many papers on the subject,[14,16,18] this method simply involves an esterification where 2 equivalents of methacryloyl chloride are reacted with the chromophore, one for each hydroxy group, followed by a standard polymerisation with methyl methacrylate to form the polymer.

1.10 Aims of this project

Building upon the modifications studied in the literature – the range of different electron acceptors,[17] the option of side-chains[14,16,18] or heterocycles[16] in the conjugating bridge, and the variety of different linear or dendrimeric copolymerisation strategies[14] – the main aim of this project is to devise and synthesise a selection of novel electro-optic polymers for use in the novel optical modulator system which the optoelectronics department has devised.

For electron acceptors **11**-**14** the most predictable improvement will be an increase in overall yield, while hopefully improving the electro-optic efficiency of the chromophore in the progress. The inclusion of more side-chains gives more options for physical property modification, while also allowing for the formation of dendrimeric copolymers, which have been proven to be more stable than simple linear polymers. The effects of including heterocycles in the chromophore or other copolymerisation strategies for the formation of the polymer are less predictable and will need to be found experimentally, but both should definitely be trialled if the optimal chromophore and polymer structure is to be discovered.

The polymers produced will ideally have improved physical properties – such as a high glass transition temperature, high electro-optic coefficient, and an optical absorption optimized for the purpose – resulting in an optical modulator which is both highly durable and, most importantly, highly efficient.

Chapter 2 Results

2.1 Synthesis of PMMA-*co*-DR1MA copolymers

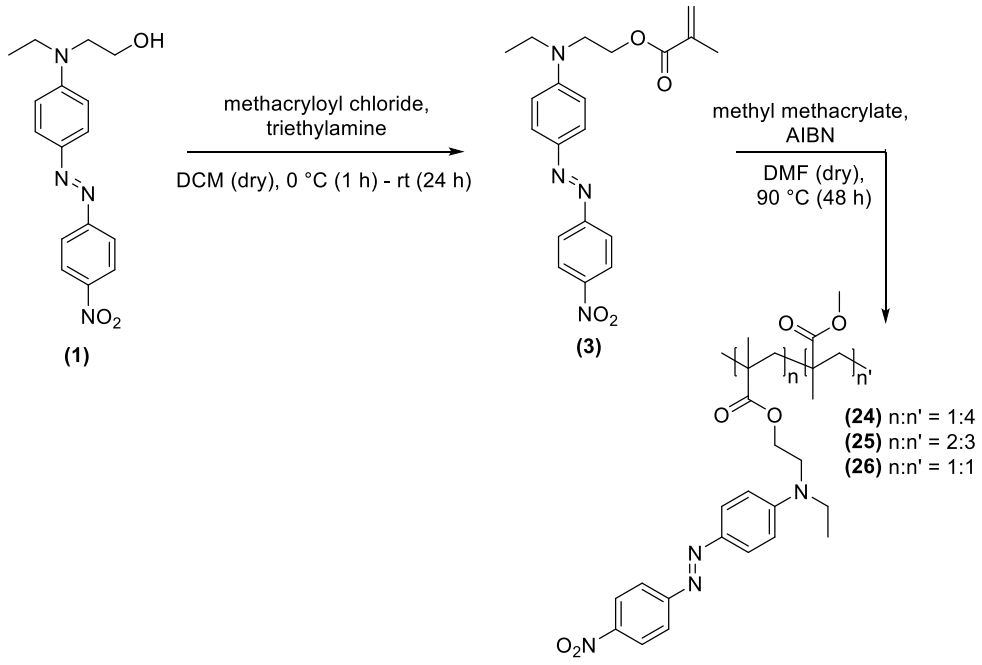


Figure 16 PMMA-*co*-DR1MA copolymer synthesis

The first procedure carried out was the copolymerisation of the commercially available chromophore Disperse Red 1 (compound **1** above), as outlined by Yee Song Ko et al.[13] This synthesis involved an esterification step with methacryloyl chloride followed by a radical copolymerisation step with methyl methacrylate, both of which were completed with no difficulty. The aforementioned paper also detailed the synthesis of a range of different DR1MA:PMMA ratios (from 9:1 to 1:9), three of which were successfully synthesised (1:4, 2:3 and 1:1 DR1MA:PMMA). The mechanisms for the formation of the methacrylate and the polymer are shown on the following page:

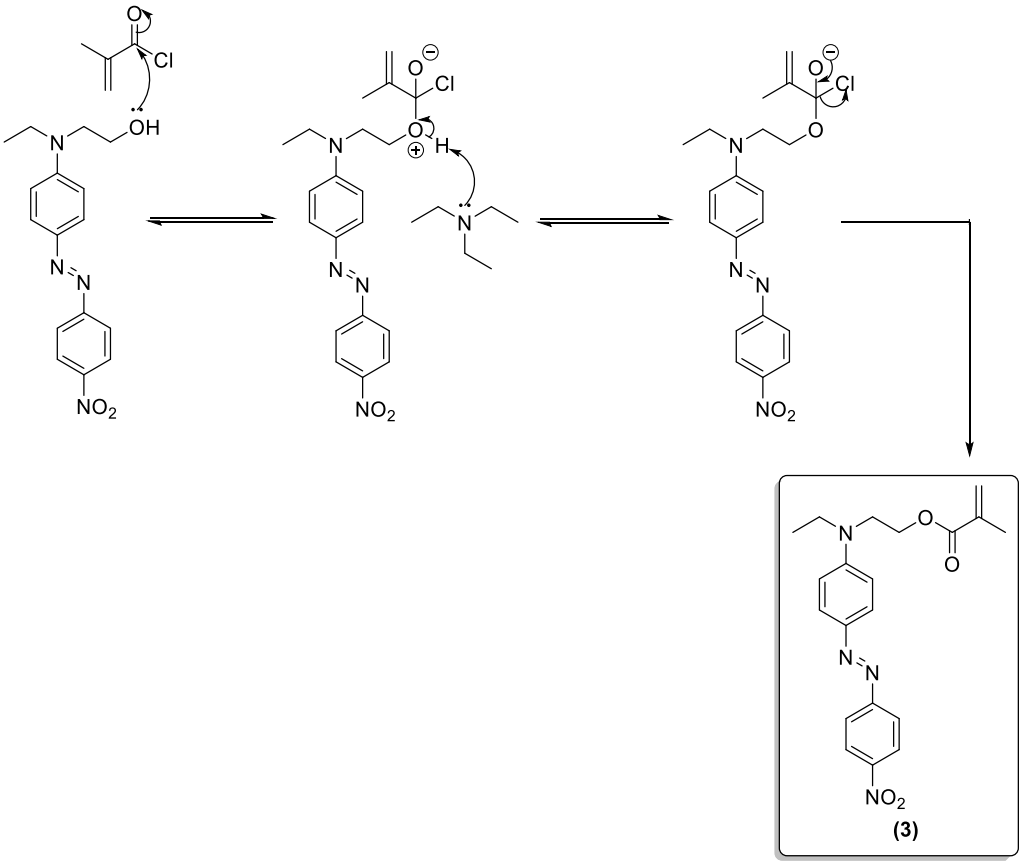


Figure 17 Mechanism for the formation of compound **3**

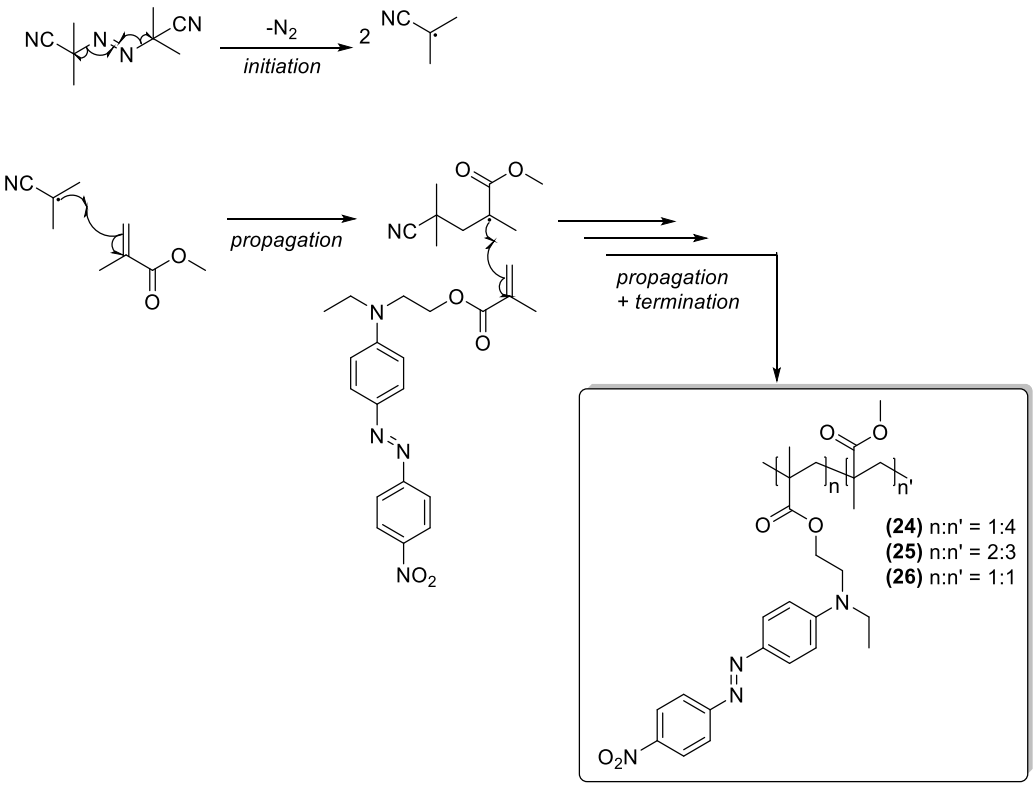


Figure 18 – Mechanism for the formation of compounds **24, 25** and **26**

2.2 Attempted synthesis of chromophore 27

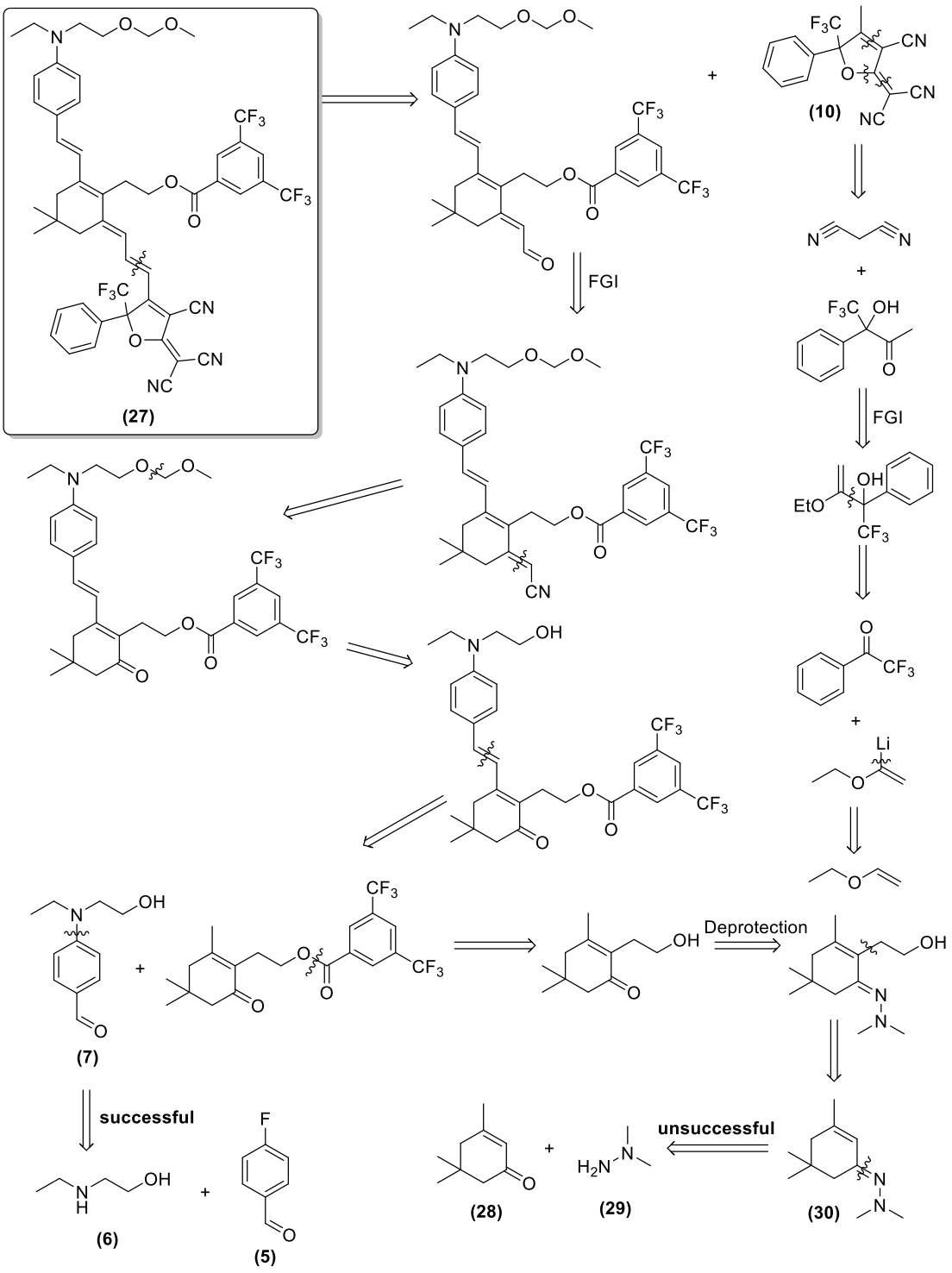


Figure 19 Chromophore **27** retrosynthesis

After synthesis of the PMMA-*co*-DR1MA copolymer was completed and a sample was sent to the optoelectronics department for testing, research was carried out into other possible chromophores for optoelectronics purposes. In 2008, Tae-Dong Kim *et al* reported on several

possible synthetic chromophores which would be compatible for optoelectronic copolymers,[14] which, thanks to their detailed analysis of the chromophores' physical properties, proved to be a very useful paper when selecting which chromophores to synthesise. The first synthesis attempted was that of chromophore **27** above - the chromophore from the paper which had the highest optical efficiency - however the branched nature of this chromophore did give some issues. No problems were encountered in the synthesis of compound **7**, as this was achieved via a fairly straightforward nucleophilic aromatic substitution reaction, the mechanism of which is shown below:

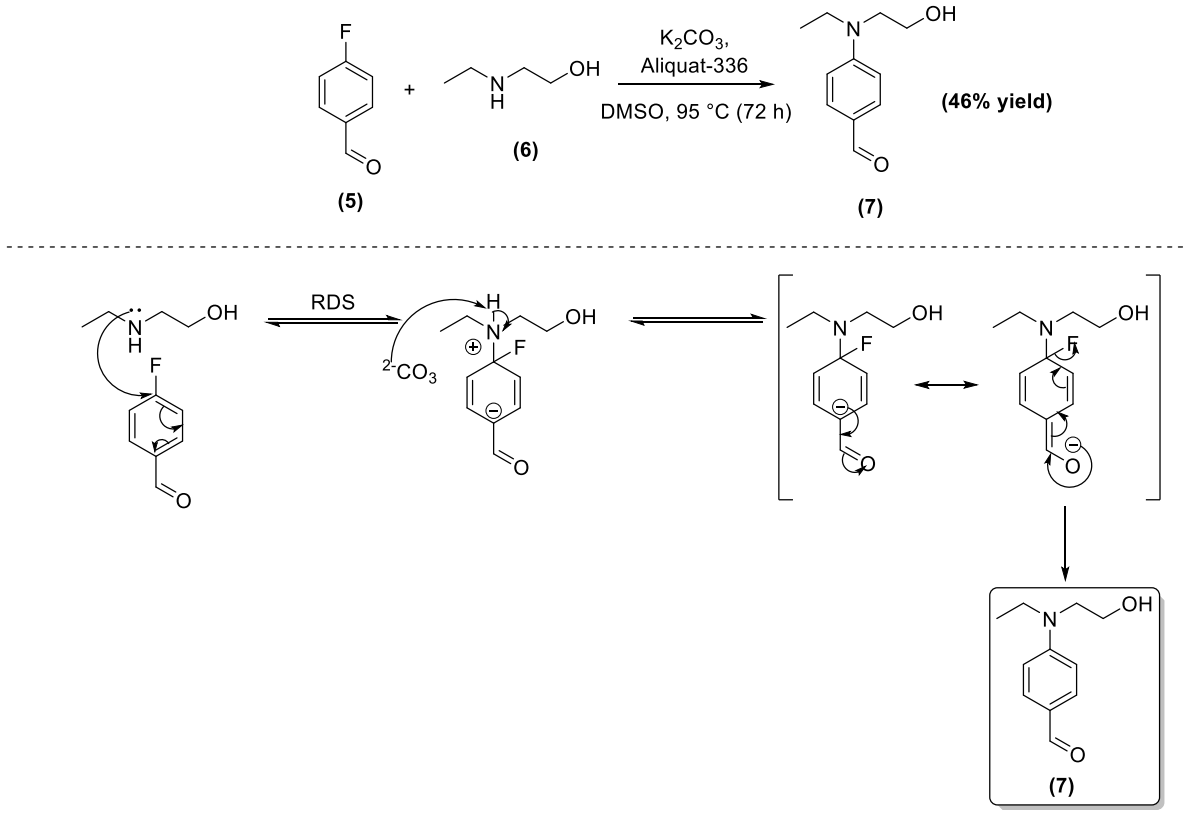


Figure 20 Reaction conditions and mechanism for the formation of compound **7**

However, literature procedures for the modification of isophorone (compound **28**) in the specific way needed were rare, and when attempts were made to carry out an imine protection of the ketone functional group with N,N-dimethylhydrazine (compound **29**) the reaction was repeatedly unsuccessful. It was decided that a different, unbranched chromophore should be attempted instead.

2.3 Attempted synthesis of chromophore 31

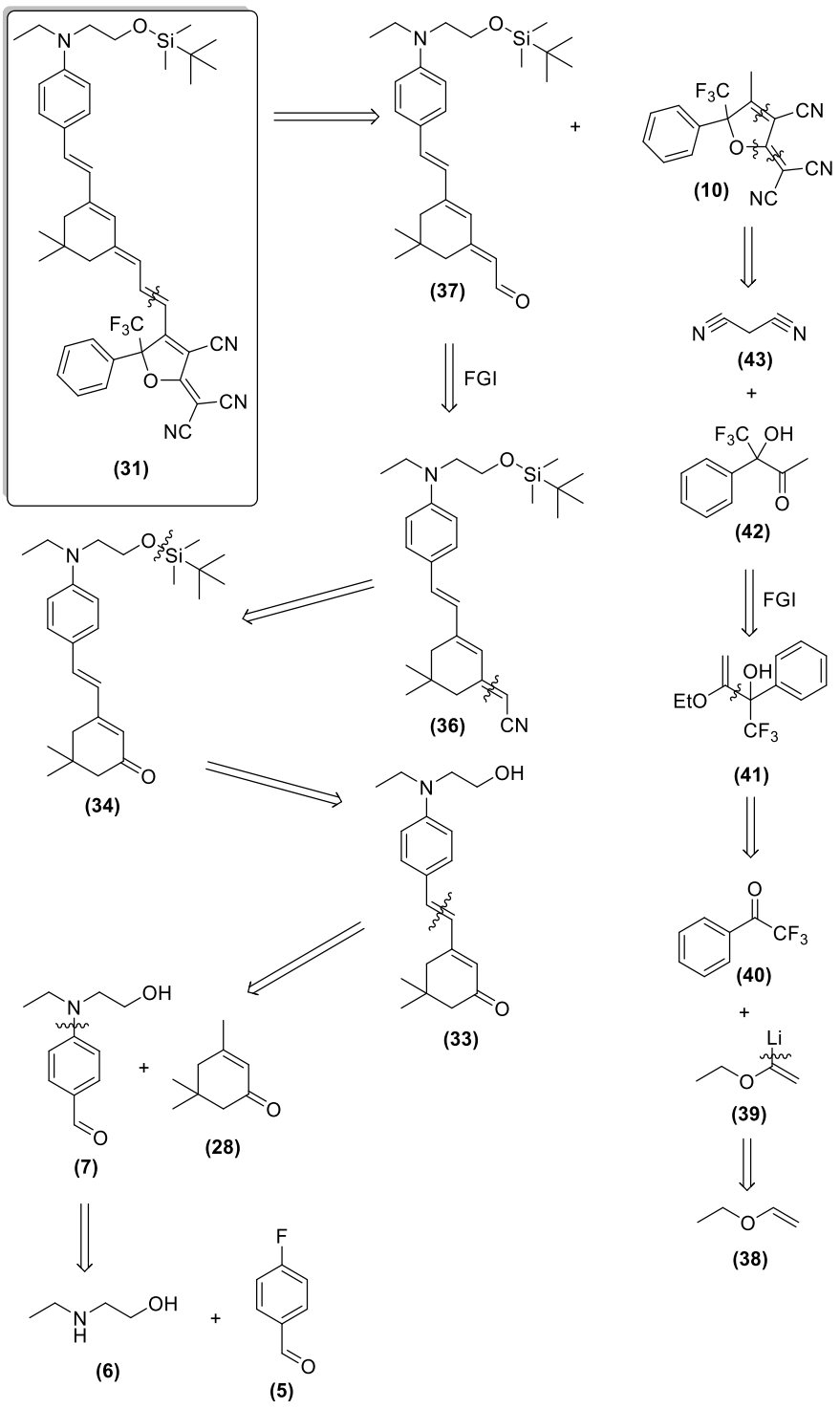


Figure 21 Retrosynthesis of chromophore **31**

Taken from the previously mentioned paper by Alex Jen *et al*,[14] chromophore **31** also had a very high optical activity but proved to be a much more promising molecule to synthesise. The lack of the branched structure from the central cyclohexene ring meant that no modification of the isophorone (compound **28**) was needed before attempting the condensation reaction with compound **7**, and it was this ease of synthesis compared to other possible chromophores which drove us to attempt to synthesise this one next. After synthesising more of compound **7**, an acetyl protection of the hydroxy group was carried out, as described in literature.[19] The mechanism for the acetyl protection of compound **7** is shown below:

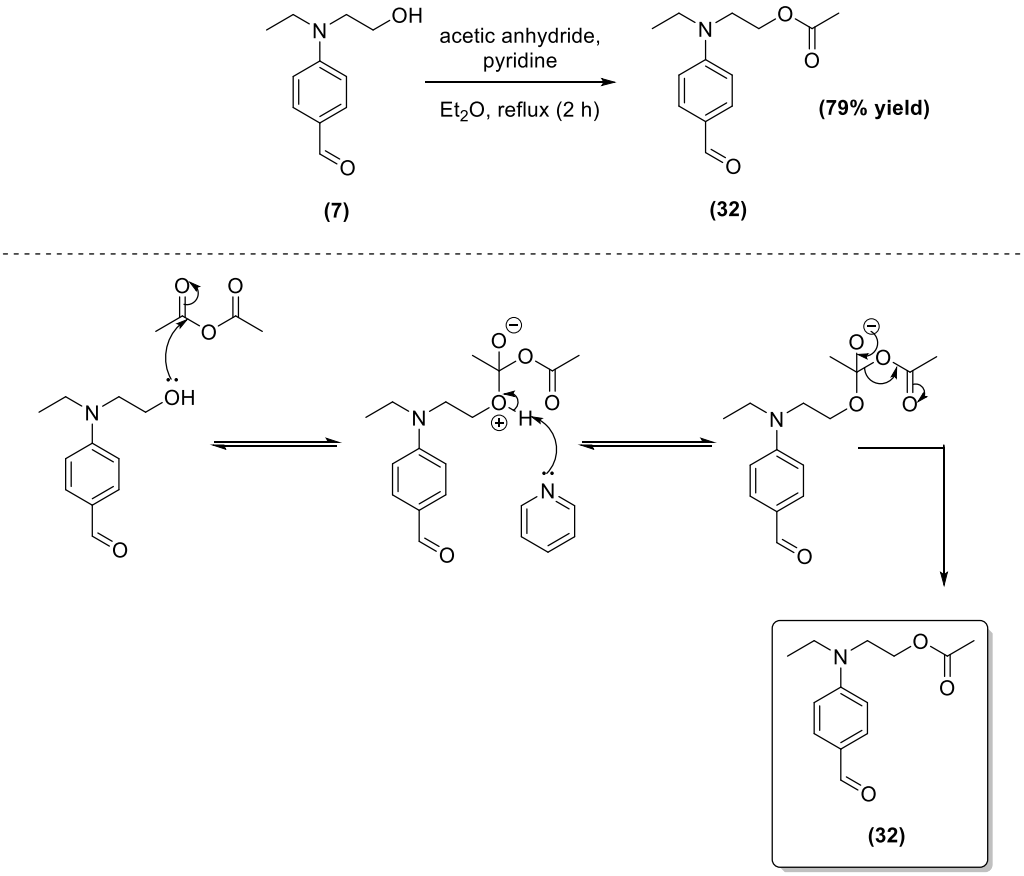


Figure 22 – Reaction conditions and mechanism for the formation of compound **32**

The synthesis of compound **33** gave some complications at first – several different reaction conditions were attempted, each resulting in very little or no product. However, a method was eventually found which not only gave high conversion, but which was also a relatively green form of chemistry, as no solvent was needed in this instance. This method was also tested with the unprotected version of the starting material (compound **7**) and was found to still give high conversion with no by-products, thus the acetyl protection step was skipped in later repeats as it was deemed to be unnecessary. The mechanism for the formation of compound **33** is shown on the following page:

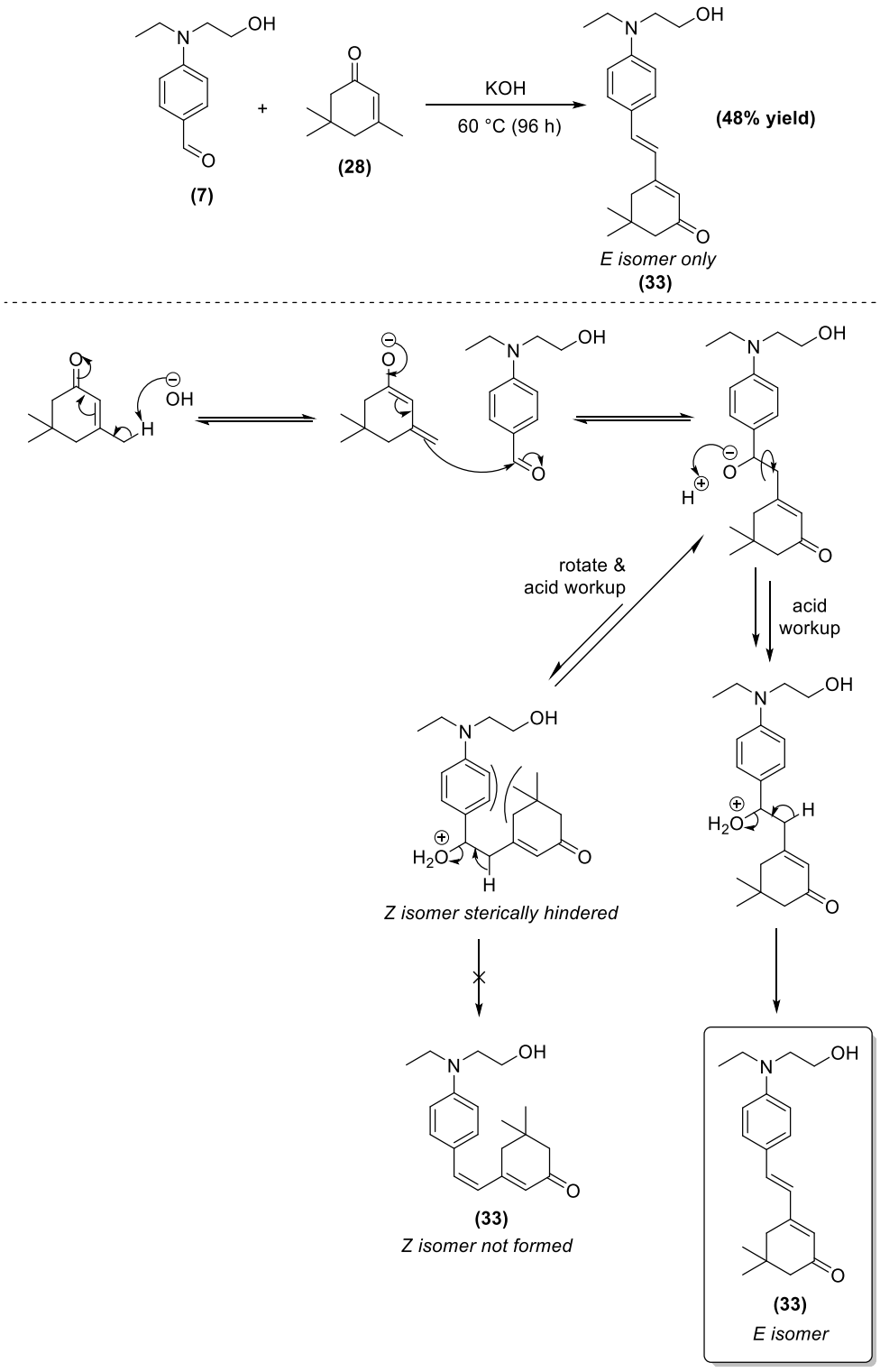


Figure 23 Reaction conditions and mechanism for the formation of the E isomer of compound **33**. The Z isomer is not formed, which can be proven by the fact that the proton NMR only has one set of peaks for each proton environment (see appendix for spectrum)

Reagents / Conditions	**Conversion (%)***	**Reference**
piperidine, EtOH, 50 °C, (120 h)	0	-
cetyltrimethylammonium chloride, NaOH, H_2O 60 °C (96 h)	36	[19]
NaOEt, EtOH, 65 °C, (120 h)	23	[18]
KOH, (no solvent), 60 °C, (16 h)	95	[20]

Table 1 Reagents and conditions for compound **33** synthesis attempts

*The conversion of starting material to product is shown above to compare the effectiveness of the conditions, rather than yield, as each of these conditions was only tested on a milligram scale with no workup – thus providing no yield to work with.

In order to carry out later steps without unwanted by-products being formed, a protecting group needed to be added to the hydroxy group of compound **33**. One possible option from literature[18] was a MOM (methoxymethyl) protecting group, however the reagents needed for this protection were deemed to be both too toxic and too expensive for this application. An alternative was chosen instead – the TBDMS (*tert*-butyldimethylsilyl) protecting group – as this was much cheaper and much less toxic, but was still shown to be compatible for this application in literature.[19,21] The mechanism for the TBDMS protection is shown on the following page:

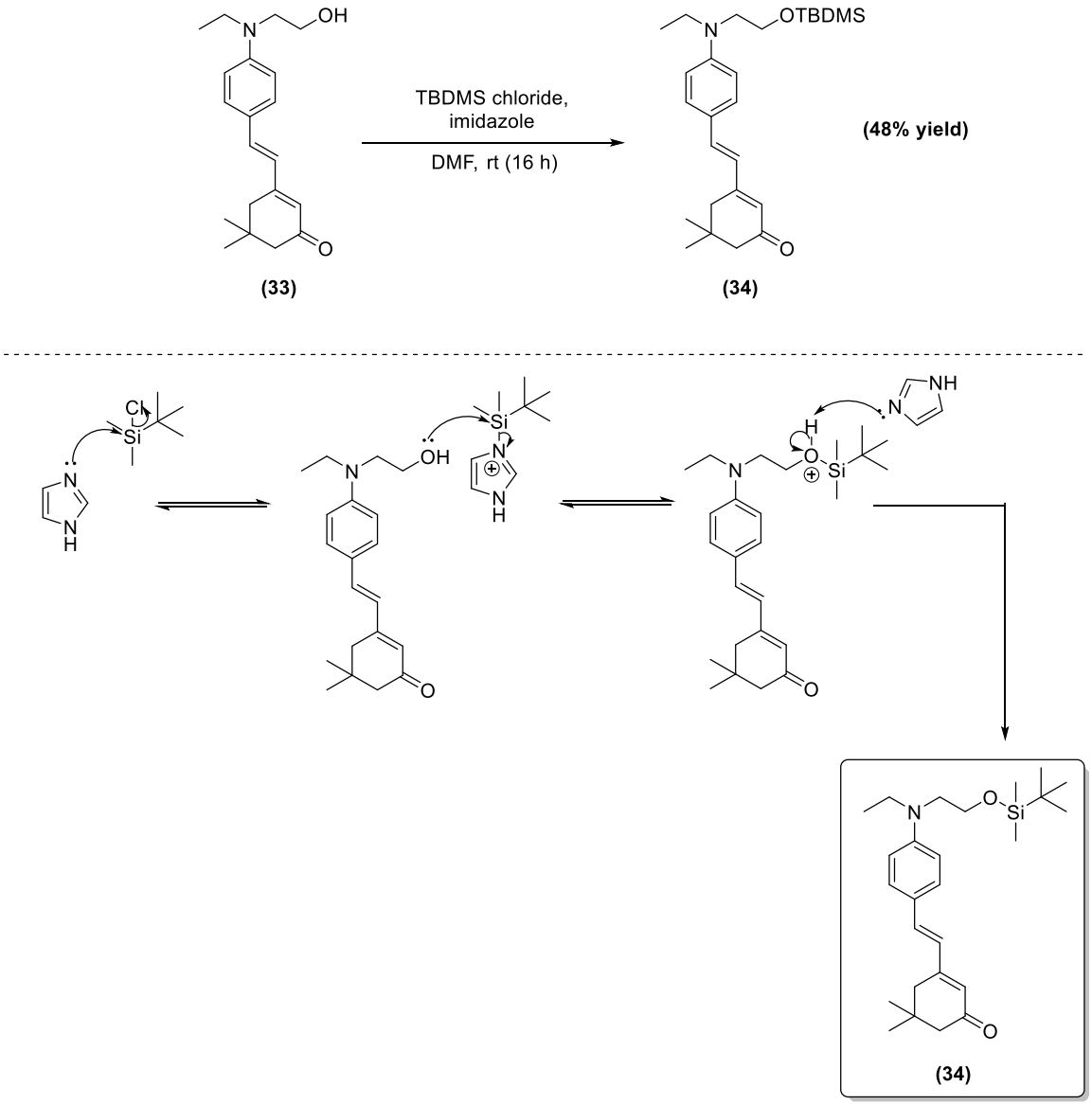


Figure 24 Reaction conditions and mechanism for the formation of compound **34**

For the synthesis of compound **36** (shown on the following page), two different methods were trialled. One literature method for the synthesis of a similar compound detailed a two-step reaction using DIPA (N,N-diisopropylamine), n-BuLi and acetonitrile to form the 1-acetonitrile-2-hydroxy compound shown on the following page, followed by a dehydration reaction with acetic acid to form the product:[18]

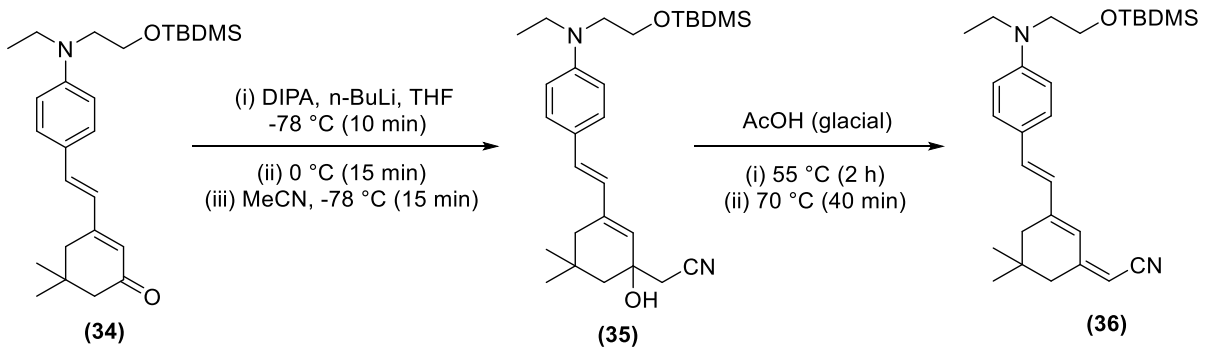


Figure 25 First attempted method for the synthesis of compound **36**

However, although the synthesis of compound **35** was found to be successful by crude NMR, due to the acid-labile nature of the TBDMS protecting group the following step deprotected the alcohol and a wide variety of products were produced, none of which were compound **36**. An alternative method, which worked much more successfully, was the Horner-Wadsworth-Emmons reaction proposed by Alex Jen *et al* for their synthesis of chromophore **31**.[21] This reaction was much more successful, and was trialled first for 3 h, and then overnight in an attempt to improve yield (however it was found that this actually reduced the yield, proving that the 3 h reaction time was the better option). The mechanism for the synthesis of compound **36** via this Horner-Wadsworth-Emmons method is shown on the following page, along with the isomeric ratio of the product:

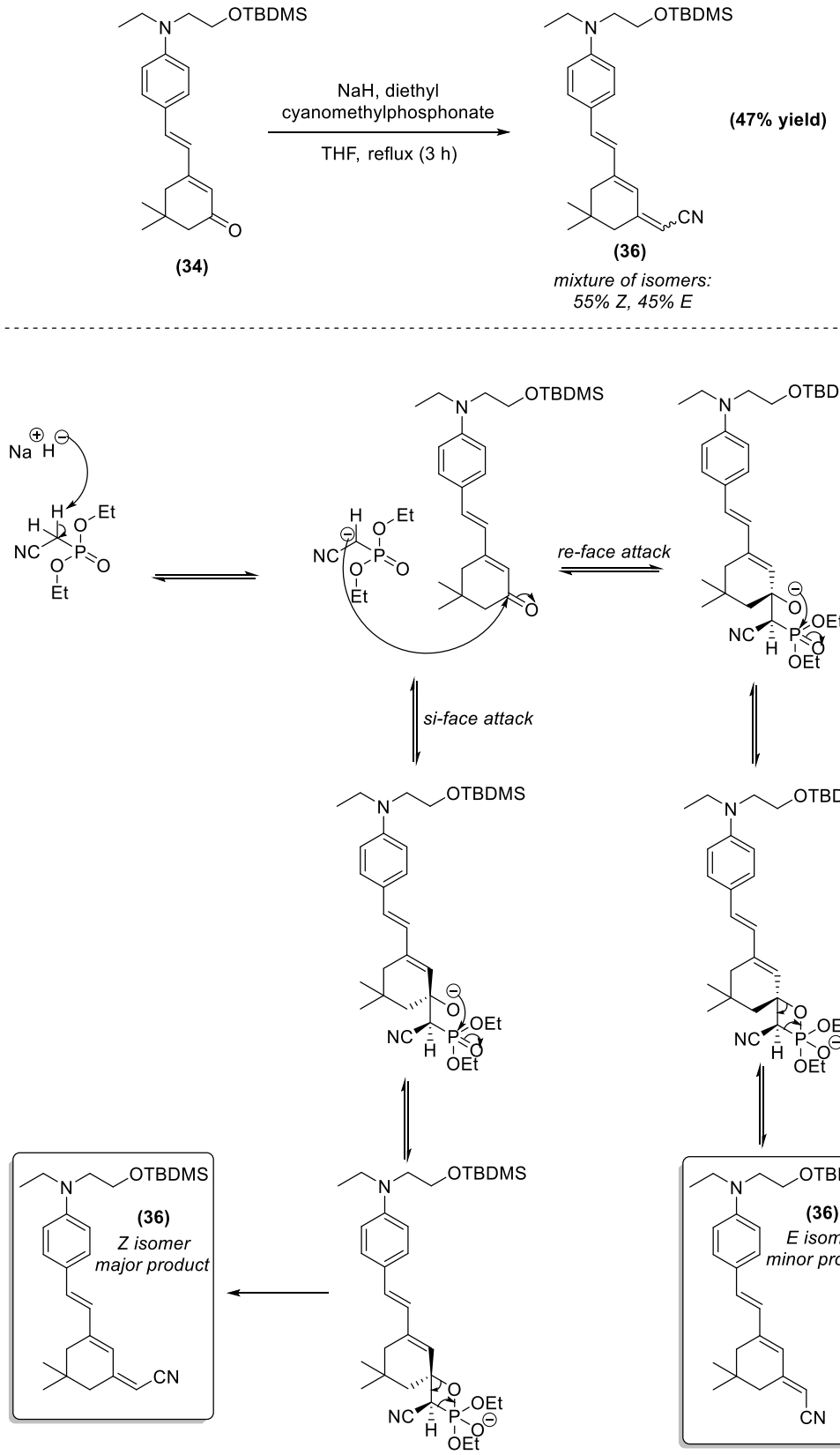


Figure 26 Reaction conditions and mechanism for the formation of both isomers of compound **36** (as per the literature, the isomers did not need to be separated to carry out the next step)

Reagents / Conditions	**Yield (%)**	**Reference**
(i) DIPA, n-BuLi, MeCN, THF, -78 °C - 0 °C (40 m) (ii) AcOH, 55 °C (2 h) – 70 °C (40 m)	0	[18]
NaH, diethyl cyanomethylphosphonate, THF, reflux (3 h)	47	[21]
NaH, diethyl cyanomethylphosphonate, THF, reflux (16 h)	34	[21]

Table 2 Reagents and conditions for the compound **36** synthesis attempts

The synthesis of compound **37** produced far fewer obstacles, and although the yield was fairly low (32%) this nitrile reduction reaction was still successful on the first attempt. However, due to the low yield (and recurring low yield from previous steps), not enough of the product was present to carry out the final step and complete the chromophore **31** synthesis, so more had to be synthesised by starting again from step one on a much larger, several-batch scale. The mechanism for the compound **37** synthesis is shown on the following page, along with the isomeric ratio of the product:

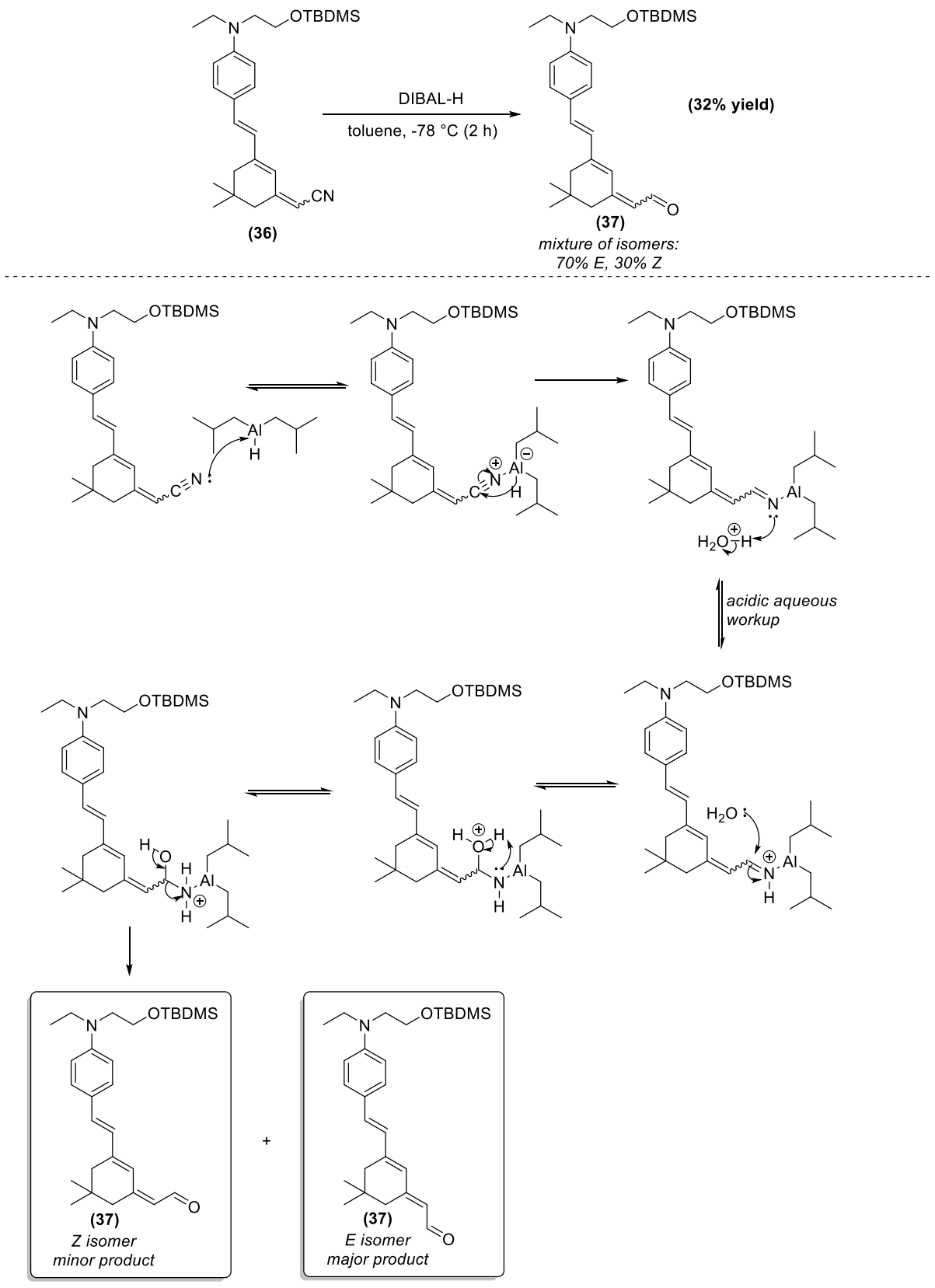


Figure 27 Reaction conditions and mechanism for the formation of both isomers of compound **37** (as per the literature, the isomers did not need to be separated to carry out the next step)

In terms of the lower half of chromophore **31**, the synthesis of compound **42** was carried out via a deprotonation of ethyl vinyl ether (compound **38**) with t-BuLi (a weaker base such as n-BuLi would not have been sufficient due to the relatively high pKa of the vinyl proton). This reaction was unsuccessful to begin with as the high reactivity of t-BuLi gave many by-products under the initial test conditions, however this problem was eventually circumvented by trialling reaction conditions from several different literature procedures until the product was synthesised successfully. The mechanism for this synthesis is shown below:

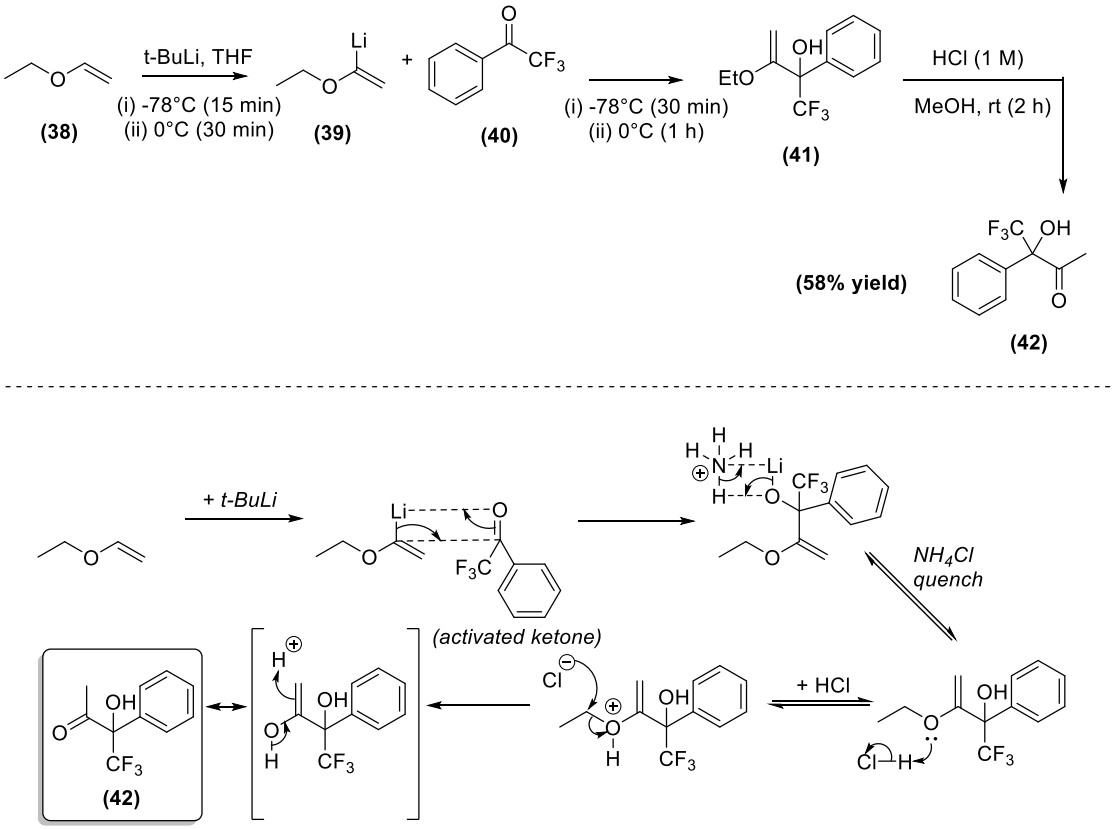


Figure 28 Reaction conditions and mechanism for the formation of compound **42**

Conditions	**Yield (%)**	**Reference**
-78 °C (30 min)	0	[22]
-78 °C (5 min) – -10 °C (5 min) – rt (16 h)	0	[17]
-78 °C (15 min) – 0 °C (30 min) – -78 °C (30 min) – 0 °C (1 h)	58	[16]

Table 3 Reagents and conditions for compound **42** synthesis attempts

The following step, synthesising furan derivative **10**, also produced many problems, but this too was eventually synthesised successfully (after a few failed attempts – detailed below).

Reagents / Conditions	**Conversion** (%)**	**Notes**	**Reference**
NaOEt, EtOH, rt (20 h)	0	no product present in crude NMR	[22]
NaOEt, THF, reflux (16 h)	46	purified by column, product degraded on the column	[17]
NaOEt, THF, reflux (96 h)	0	no product present in crude NMR	[17]
NaOEt, THF, reflux (48 h)	93	purified by recrystallization, product did not degrade	[17]
LiOEt, THF, reflux (64 h)	51	purified by recrystallization, product did not degrade	[17]

Table 4 Reagents and conditions for compound **10** synthesis attempts

**Conversion was again used to compare effectiveness, as some reactions were effective but product was lost during purification, meaning yield would be insufficient for comparing every set of conditions.

It appeared that, for this step, the product was quite unstable – degrading quickly on a chromatography column and even degrading if the reaction was left any longer than 48 hours (which was determined to be the optimal reaction time). However, a method for purification via recrystallization, rather than column chromatography, was eventually devised and proven to work, meaning that the pure product could finally be synthesised without risk of degradation, thus completing the lower half of the chromophore. The mechanism for the synthesis of compound **10** is shown on the following page:

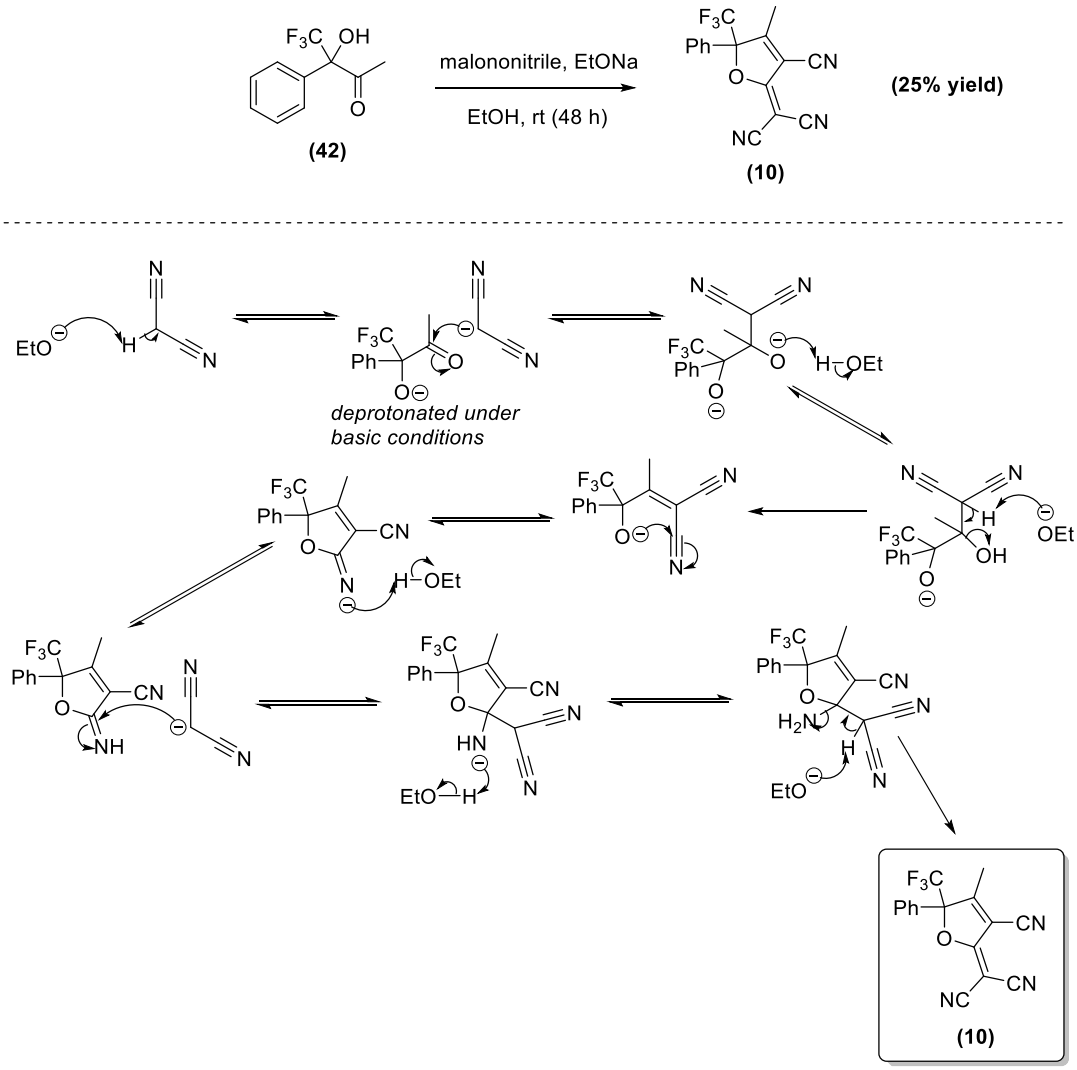


Figure 29 Reaction conditions and mechanism for the formation of compound **10**

The final few months of this project were spent repeating the earlier steps of this synthesis on a larger scale, with an aim to synthesise the final chromophore on a large enough scale to be used by the optoelectronics department in their studies. However, despite trying the exact literature conditions multiple times, as well as a few slight variations to these conditions, each attempted synthesis of compound **33** resulted in either no product at all, or very little (along with a large amount of by-product). Although proton NMRs of each crude product were recorded and analysed thoroughly, no concrete evidence explaining the failure of these attempts was found, leaving the synthesis of chromophore **31** one final step short of a complete synthesis. There is a speculative reason for the synthesis of compound **33** repeatedly failing – it's possible that a competing reaction could have been hindering the formation of compound **33**, a theory which is reinforced by the presence of an unknown by-product in the crude NMR spectrum – however, further testing would need to be carried out before this competing reaction can be identified.

2.4 Future Work

The first and most prominent objective for future work in this project will be to complete the synthesis of chromophore **31** on a large enough scale that a copolymerisation of the chromophore can also be carried out. Although many copolymerisation strategies have been mentioned previously, to ensure the group is able to provide the optoelectronics department with a large enough sample to test with, the simpler and more reliable method of radical copolymerisation with PMMA (the same method used for the PMMA-*co*-DR1MA copolymerisation seen in Figure 16) will most likely be carried out first.

Following this, the main focus of the project will then be pursued – synthesis of novel chromophores and chromophore copolymers. Building upon many of the chromophores from the literature mentioned previously, there are several routes which can be pursued in the goal of creating a novel chromophore with improved optical properties. One route is to increase the dendritic nature of the resulting polymer, as this has been shown to increase optical activity, so a chromophore with multiple polymerisation sites would be one way of doing so (see chromophore **44** below).

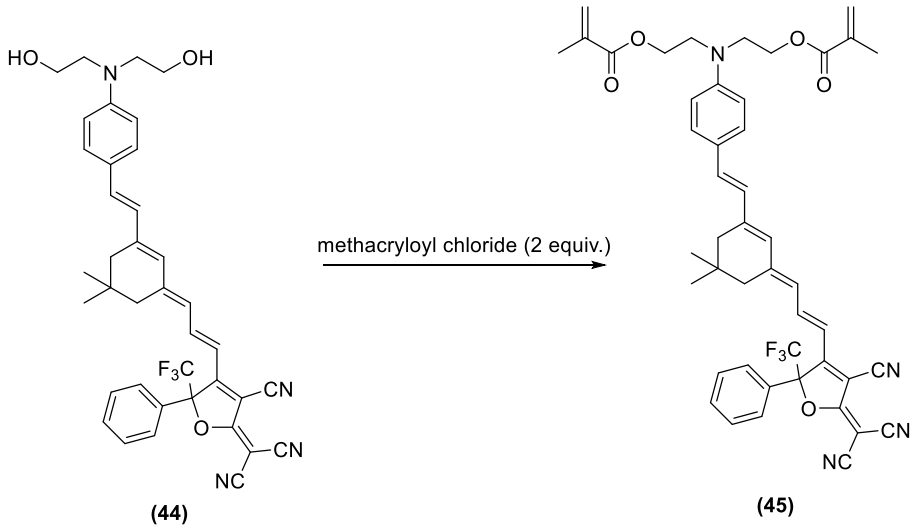


Figure 30 Possible novel chromophore **44**, before and after preparation for polymerisation with methacryloyl chloride

Further to this, the introduction of a side chain has given much better optical activities in the literature due to this increased dendronization, and although the initial attempt of doing this during the synthesis of chromophore **27** was unsuccessful, other methods (such as via an ether moiety) can also be attempted (see chromophore **46** on the following page).

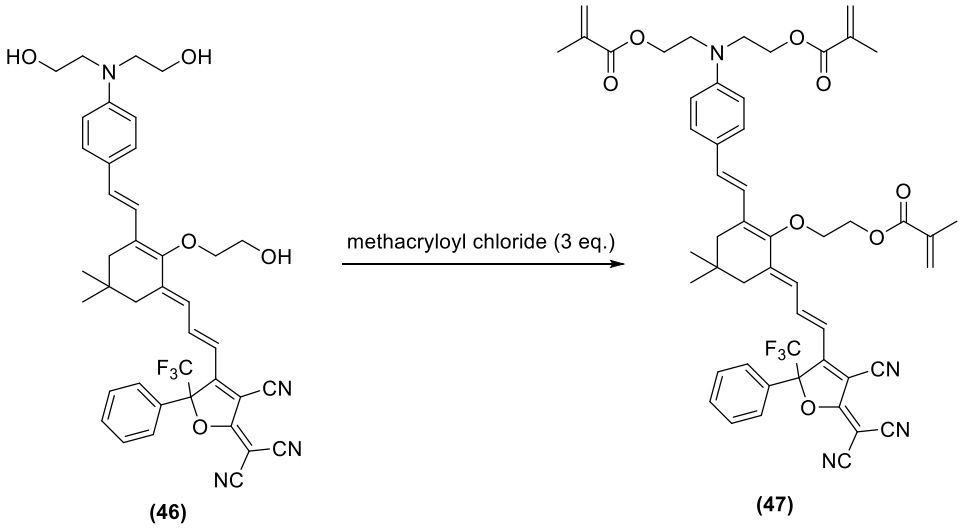


Figure 31 Possible novel chromophore **46**, before and after preparation for polymerisation with methacryloyl chloride

Finally, another modification which has not been fully explored is the possibility of changing the acceptor in the lower section of the molecule. As mentioned in section **1.8**, many other acceptors have been shown to be much more reliable to synthesise than acceptor **10** (due to higher overall yields), so using these acceptors in the synthesis of new chromophores may also improve the overall yield in addition to the possible increase in optical activity (see chromophores **48**-**50** below).

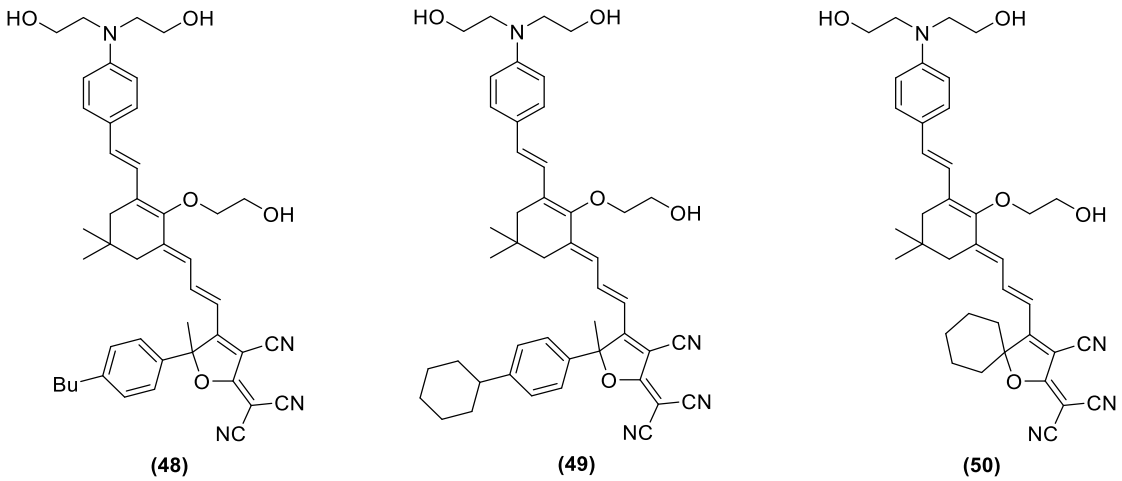
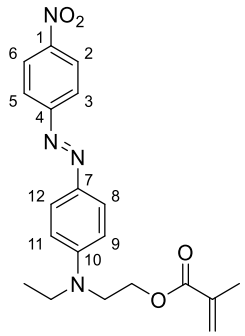


Figure 32 Possible novel chromophores **48-50**

Chapter 3 Experimental

(E)-2-(Ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl methacrylate (DR1MA) (3)



Following a literature procedure,[13] Disperse Red 1 (1.00 g, 3.18 mmol) and triethylamine (690 µL, 4.95 mmol) were dissolved in dry DCM (12.0 mL) at 0 °C under Ar atmosphere. Methacryloyl chloride (430 µL, 4.40 mmol) was added, the reaction was stirred under Ar atmosphere at 0 °C for 1 h, then at rt overnight. The reaction mixture was washed with brine, dried over $MgSO_4$ and the crude product was purified by column chromatography (EtOAc:hexanes 1:6) to give the title compound (1.20g, 99%) as a red solid.

IR ($CDCl_3$, solid film) 1717 (C=O), 1517 (asymmetric N-O), 1383 (symmetric N-O), 1333 (C-O), 1283 (C-O) cm^{-1}.

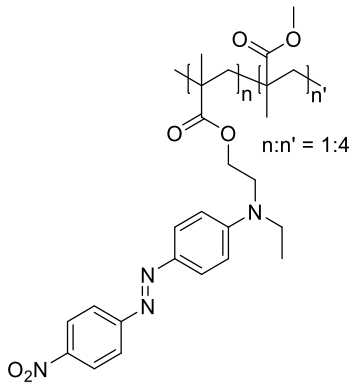
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, 2H, ArC(2,6)*H*), 7.92 (m, 4H, ArC(3,5,8,12)*H*), 6.83 (d, 2H, ArC(9,11)*H*), 6.11 (m, 1H, CC*H*H), 5.60 (m, 1H, CCH*H*), 4.38 (t, *J* = 6.4 Hz, 2H, CH_2O), 3.74 (t, *J* = 6.4 Hz, 2H, CH_2CH$_2$O), 3.55 (q, *J* = 7.2 Hz, 2H, CH_2CH$_3$), 1.94 (dd, 3H, CCH_3), 1.27 (t, *J* = 6.8 Hz, 3H, CH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 (C), 156.9 (C), 151.4 (C), 147.6 (C), 144.0 (C), 136.0 (C), 126.4 (CH_2), 124.8 (2CH), 122.8 (2CH), 111.7 (2CH), 77.4 (2CH), 61.9 (CH_2), 48.9 (CH_2), 45.8 (CH_2), 18.5 (CH_3), 12.4 (CH_3).

mp (°C) 94.8 – 100.3

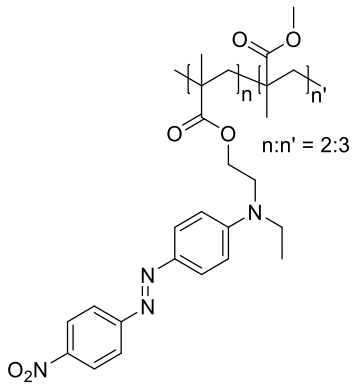
HRMS *m/z* (ESI+) Exact mass calculated for $C_{20}H_{23}N_4O_4$ $[M+H]^+$: 383.1714, found: 383.1717.

PMMA-*co*-DR1MA(20%) copolymer (24)



Following a literature procedure,[13] DR1MA (255 mg, 667 µmol), AIBN (6.00 mg, 36.5 µmol) and methyl methacrylate (240 µL, 2.24 mmol) were dissolved in dry DMF (3.00 mL) under Ar atmosphere. The solution underwent three freeze-pump-thaw cycles, followed by rigorous bubbling of Ar for 30 min. The reaction was then heated to 90 °C and stirred under Ar atmosphere for 48 h. The mixture was cooled to room temperature, further DMF (3.00 mL) was added and the product was precipitated into methanol (30.0 mL). The precipitate was collected by vacuum filtration, washed with water and dried to give the title compound (183 mg, 42%) as a pale red solid.

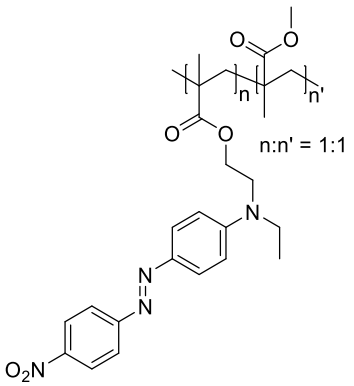
PMMA-*co*-DR1MA(40%) copolymer (25)



Following a literature procedure,[13] DR1MA (510 mg, 1.33 mmol), AIBN (12.0 mg, 71.8 µmol) and methyl methacrylate (210 µL, 2.00 mmol) were dissolved in dry DMF (3.00 mL) under Ar atmosphere. The solution underwent three freeze-pump-thaw cycles, followed by rigorous bubbling of Ar for 30 min. The reaction was then heated to 90 °C and stirred under Ar atmosphere for 48 h. The mixture was cooled to room temperature, further DMF (3.00 mL) was added and the product was precipitated into methanol (30.0 mL). The

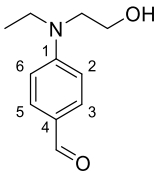
precipitate was collected by vacuum filtration, washed with water and dried to give the title compound (442 mg, 63%) as a pale red solid.

PMMA-*co*-DR1MA(50%) copolymer (26)



Following a literature procedure,[13] DR1MA (923 mg, 2.41 mmol), AIBN (11.0 mg, 67.0 µmol) and methyl methacrylate (260 µL, 2.43 mmol) were dissolved in anhydrous DMF (3.40 mL) under Ar atmosphere. The solution underwent three freeze-pump-thaw cycles, followed by rigorous bubbling of Ar for 30 min. The reaction was then heated to 90 °C and stirred under Ar atmosphere for 48 h. The mixture was cooled to room temperature, further DMF (3.40 mL) was added and the product was precipitated into methanol (34.0 mL). The precipitate was collected by vacuum filtration, washed with water and dried to give the title compound (448 mg, 38%) as a pale red solid.

4-(Ethyl(2-hydroxyethyl)amino)benzaldehyde (7)



Following a modified literature procedure,[15] 4-fluorobenzaldehyde (4.32 mL, 40.3 mmol) and 2-(ethylamino)ethanol (11.8 mL, 121 mmol) were dissolved in DMSO (50.0 mL), potassium carbonate (8.35 g, 60.5 mmol) and Aliquat-336 (200 µL, 437 µmol) were added and the reaction was stirred at 95 °C for 88 h. The reaction was cooled to rt, poured into an ice-water mixture (100 mL) and the water layer was extracted with DCM (3 x 50.0 mL).

The organic phase was washed with more ice-water mixture (2 x 100 mL), then dried over $MgSO_4$ and evaporated. The orange oil was dissolved in Et_2O (50.0 mL), poured into 1M HCl (160 mL) and stirred for 10 min. The mixture was separated, the water phase was neutralised with saturated aqueous Na_2CO_3 and extracted with DCM (3 x 50.0 mL). The organic phase was dried over $MgSO_4$, evaporated and purified by column chromatography (EtOAc:hexanes 1:1) to give the title compound (3.60 g, 46%) as an orange oil.

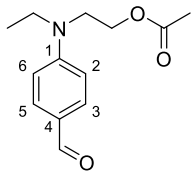
IR ($CDCl_3$, liquid film) 3391 (O-H), 2971 (alkane C-H), 2738 (aldehyde C-H), 1653 (C=O), 1588 (aromatic C-C), 1552 (aromatic C-C), 1524 (aromatic C-C), 1437 (alkane C-H), 1403 (alkane C-H), 1351 (alkane C-H), 1314 (alcohol C-O), 1243 (C-N), 1164 (C-N), 1048 (C-N) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H, C*H*O), 7.70 (d, *J* = 9.2 Hz, 2H, ArC(3,5)*H*), 6.75 (d, *J* = 9.2 Hz, 2H, ArC(2,6)*H*), 3.86 (m, 2H, CH_2OH), 3.58 (t, *J* = 6.0 Hz, 2H, CH_2CH$_2$OH), 3.52 (q, *J* = 6.8 Hz, 2H, CH_2CH$_3$), 1.86 (bs, 1H, O*H*), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4 (CH), 152.9 (C), 132.4 (2CH), 125.0 (C), 111.1 (2CH), 60.0 (CH_2), 52.3 (CH_2), 45.8 (CH_2), 12.0 (CH_3).

HRMS *m/z* (ESI+) Exact mass calculated for $C_{11}H_{16}NO_2$ $[M+H]^+$: 194.1176, found: 194.1179.

2-(Ethyl(4-formylphenyl)amino)ethyl acetate (32)



Following a literature procedure,[19] 4-(ethyl(2-hydroxyethyl)amino)benzaldehyde (1.66 g, 8.57 mmol) and pyridine (700 µL, 8.65 mmol) were dissolved in Et_2O (5.20 mL) and stirred at 0 °C as acetic anhydride (860 µL, 9.10 mmol) was added dropwise to the solution. The reaction was heated to reflux and stirred for 72 h. The mixture was extracted with Et_2O, washed with H_2O and 0.3 M HCl, dried over $MgSO_4$ and concentrated under vacuum to give the title compound (1.59 g, 79%) as an orange oil.

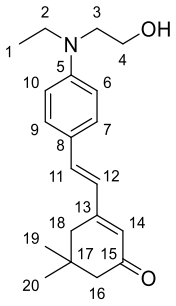
IR ($CDCl_3$, liquid film) 2933 (aldehyde C-H), 1750 (C=O), 1667 (C=O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H, C*H*O), 7.73 (d, *J* = 8.8 Hz, 2H, ArC(3,5)*H*), 6.75 (d, *J* = 9.2 Hz, 2H, ArC(2,6)*H*), 4.26 (t, *J* = 6.4 Hz, 2H, CH_2O), 3.64 (t, *J* = 6.0 Hz, 2H, CH_2CH$_2$O), 3.49 (q, *J* = 7.2 Hz, 2H, CH_2CH$_3$), 2.04 (s, 3H, COCH_3), 1.22 (t, *J* = 6.8 Hz, 3H, CH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3 (CH), 171.0 (C), 152.4 (C), 132.4 (2CH), 125.6 (C), 111.1 (2CH), 61.3 (CH_2), 48.8 (CH_2), 45.7 (CH_2), 21.0 (CH_3), 12.2 (CH_3).

HRMS *m/z* (ESI+) Exact mass calculated for $C_{13}H_{17}NNaO_3$ $[M+Na]^+$: 258.1101, found: 258.1103.

(E)-3-(4-(Ethyl(2-hydroxyethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-one (33)



Following a literature procedure,[20] isophorone (3.00 mL, 20.0 mmol) and freshly powdered potassium hydroxide (1.12 g, 20.0 mmol) were vigorously stirred at room temperature for 5 min. 4-(Ethyl(2-hydroxyethyl)amino)benzaldehyde (3.22 g, 16.7 mmol) was then added and the reaction was stirred at 60 °C for 16 h. The mixture was dissolved in $CHCl_3$ (26.0 mL), added to a solution of glacial acetic acid (900 µL, 16.7 mmol) in water (26.0 mL) and stirred at room temperature for 30 min. The organic layer was separated, and the aqueous phase was extracted with $CHCl_3$ (2 x 26.0 mL). The combined organic extracts were washed with water (26.0 mL) and brine (26.0 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (EtOAc:hexanes 1:1) to give the title compound (2.54 g, 48%) as an orange-red oil.

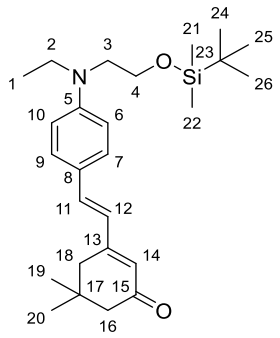
IR ($CDCl_3$, liquid film) 3386 (O-H), 2955 (alkane C-H), 2868 (alkane C-H), 1637 (C=O), 1591 (aromatic C-C), 1567 (aromatic C-C), 1518 (aromatic C-C), 1377 (alkane C-H), 1275 (alcohol C-O), 1177 (C-N), 1150 (C-N), 1048 (C-N), 996 (alkene C-H), 961 (alkene C-H), 806 (alkene C-H) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.2 Hz, 2H, ArC(7,9)*H*), 6.92 (d, *J* = 16.0 Hz, 1H, C(11)*H*), 6.76-6.68 (m, 3H, C(6,10,12)*H*), 6.01 (s, 1H, C(14)*H*), 3.86-3.80 (m, 2H, C(4)H_2), 3.52 (t, *J* = 6.0 Hz, 2H, C(3)H_2), 3.47 (q, *J* = 6.8 Hz, 2H, C(2)H_2), 2.46 (s, 2H, C(18)H_2), 2.29 (s, 2H, C(16)H_2), 1.68 (bs, 1H, O*H*), 1.19 (t, *J* = 7.2 Hz, 3H, C(1)H_3), 1.10 (s, 6H, C(19,20)H_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3 (C^{15}), 156.1 (C), 149.1 (C), 135.5 (C^{14}), 129.1 ($C^{7,9}$), 125.3 ($C^{11/12}$), 125.1 ($C^{11/12}$), 124.3 (C), 112.4 ($C^{6,10}$), 60.4 (CH_2), 52.5 (CH_2), 51.6 (CH_2), 45.7 (CH_2), 39.3 (CH_2), 33.5 (C^{5}), 28.7 ($C^{19,20}$), 12.1 (C^{1}).

HRMS *m/z* (ESI+) Exact mass calculated for $C_{20}H_{28}NO_2$ $[M+H]^+$: 314.2115, found: 314.2111.

(E)-3-(4-((2-((tert-Butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-one (34)



Following a literature procedure,[19] (E)-3-(4-(ethyl(2-hydroxyethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-one (1.18 g, 3.75 mmol) and *tert*-butyldimethylsilyl chloride (679 mg, 4.50 mmol) were dissolved in anhydrous DMF (7.60 mL) under Ar atmosphere. Imidazole (332 mg, 4.88 mmol) was added and the reaction was stirred under Ar atmosphere at room temperature for 4 h. The reaction was poured into water (15.0 mL) and extracted with Et_2O (3 x 15.0 mL). The organic layer was washed with brine (15.0 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (EtOAc:hexanes:Et_3N 1:18:1) to give the title compound (772 mg, 48%) as an orange oil.

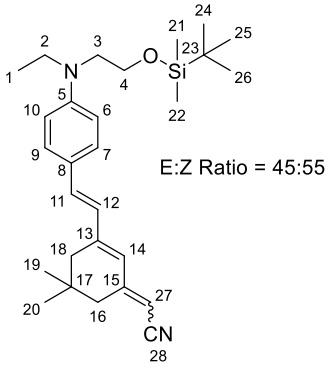
IR ($CDCl_3$, liquid film) 2954 (alkane C-H), 2928 (alkane C-H), 2857 (alkane C-H), 1654 (C=O), 1596 (aromatic C-C), 1574 (aromatic C-C), 1519 (aromatic C-C), 1376 (alkane C-H), 1359 (alkane C-H), 1275 (silyl ether C-O), 1246 (Si-C), 1182 (C-N), 1146 (C-N), 1100 (Si-O), 1004 (C-N), 834 (alkene C-H), 808 (alkene C-H), 776 (alkene C-H) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H, ArC(7,9)*H*), 6.92 (d, *J* = 16.0 Hz, 1H, C(11)*H*), 6.74-6.63 (m, 3H, C(6,10,12)*H*), 6.00 (s, 1H, C(14)*H*), 3.77 (t, *J* = 6.4 Hz, 2H, C(4)H_2), 3.50-3.40 (m, 4H, C(2,3)H_2), 2.46 (s, 2H, C(18)H_2), 2.29 (s, 2H, C(16)H_2),1.18 (t, *J* = 6.8 Hz, 3H, C(1)H_3), 1.10 (s, 6H, C(19,20)H_3), 0.89 (s, 9H, C(24,25,26)H_3), 0.04 (s, 6H, C(21,22)H_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3 (C^{15}), 156.2 (C), 148.9 (C), 135.8 (C^{14}), 129.1 ($C^{7,9}$), 125.1 ($C^{11/12}$), 124.5 ($C^{11/12}$), 123.6 (C), 111.7 ($C^{6,10}$), 60.7 (CH_2), 52.6 (CH_2), 51.6 (CH_2), 45.7 (CH_2), 39.3 (CH_2), 33.5 (C^5), 31.7 (C^{23}), 28.7 ($C^{19,20}$), 26.0 ($C^{24,25,26}$), 12.3 (C^1), -5.2 ($C^{21,22}$).

HRMS *m/z* (ESI+) Exact mass calculated for $C_{26}H_{42}NO_2Si$ $[M+H]^+$: 428.2979, found: 428.2987.

(E)-2-(3-((E)-4-((2-((tert-Butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetonitrile (36)



Following a literature procedure,[21] sodium hydride (60% in mineral oil, 37.0 mg, 935 µmol) was dissolved in anhydrous THF (1.33 mL) under Ar atmosphere and cooled to 0 °C. Diethyl cyanomethylphosphonate (150 µL, 935 µmol) was added dropwise and the reaction was stirred until the solution became clear. A solution of (E)-3-(4-((2-((tert-butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-one (284 mg, 664 µmol) in anhydrous THF (500 µL) was added dropwise at rt and the reaction was heated to reflux and stirred for 3 h. The mixture was poured into a saturated aqueous solution of NH_4Cl (5.00 mL) and extracted with EtOAc (20.0 mL x 3). The organic layer was washed with brine (20.0 mL), dried over $MgSO_4$ and evaporated, and the crude product was purified by column chromatography (EtOAc:hexanes 1:9) to give the title compound (140 mg, 47%) as an orange-red oil.

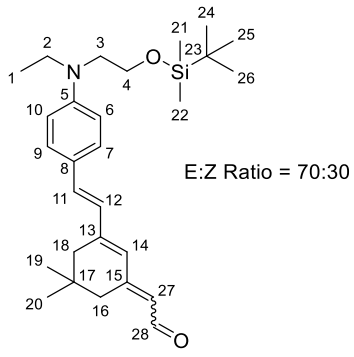
IR ($CDCl_3$, liquid film) 2954 (alkane C-H), 2928 (alkane C-H), 2857 (alkane C-H), 2203 (C≡N), 1605 (alkene C=C), 1574 (aromatic C-C), 1519 (aromatic C-C), 1393 (alkane C-H), 1360 (alkane C-H), 1250 (Si-C), 1182 (C-N), 1147 (C-N), 1101 (Si-O), 1005 (C-N), 957 (alkene C-H), 837 (alkene C-H), 809 (alkene C-H), 776 (alkene C-H) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H, ArC(7,9)*H*), 6.74-6.62 (m, 4.55H, C(6,10,11,12,14$_Z$)*H*), 6.21 (s, 0.45H, C(14$_E$)*H*), 5.06 (s, 0.45H, C(27$_E$)*H*), 4.89 (s, 0.55H, C(27$_Z$)*H*), 3.79-3.75 (m, 2H, C(4)H_2), 3.48-3.43 (m, 4H, C(2,3)H_2), 2.46 (s, 0.9H, C(16$_E$)H_2), 2.30 (s, 2H, C(18)H_2), 2.22 (s, 1.1H, C(16$_Z$)H_2), 1.19-1.16 (m, 3H, C(1)H_3), 1.03 (s, 2.7H, C(19$_E$,20$_E$)H_3), 1.00 (s, 3.3H, C(19$_Z$,20$_Z$)H_3), 0.89 (s, 9H, C(24,25,26)H_3), 0.04 (s, 6H, C(21,22)H_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (C^8), 148.3 (C^{15}), 146.1 (C^{13}), 132.6 (C^{14}), 128.5 ($C^{7,9}$) 125.5 ($C^{11/12}$), 124.1 ($C^{11/12}$), 122.7 (C^{17}), 118.0 (C^{28}), 111.7 ($C^{6,10}$), 90.3 (C^{27}), 60.7 (CH_2), 52.5 (CH_2), 45.6 (CH_2), 44.8 (CH_2), 39.1 (CH_2), 31.3 (C^5), 28.2 ($C^{19,20}$), 26.0 ($C^{24,25,26}$), 18.4 (C^{23}), 12.3 (C^1), -5.3 ($C^{21,22}$).

HRMS *m/z* (ESI+) Exact mass calculated for $C_{28}H_{43}N_2OSi$ $[M+H]^+$: 451.3139, found: 451.3133.

(E)-2-(3-((E)-4-((2-((tert-Butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetaldehyde (37)



Following a literature procedure,[18] (E)-2-(3-((E)-4-((2-((tert-butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetonitrile (202 mg, 448 µmol) was dissolved in anhydrous toluene (5.60 mL) under Ar atmosphere and the solution was cooled to -78 °C. A 1 M solution of DIBAL-H in hexane (1.29 mL, 1.29 mmol) was added dropwise and the reaction was stirred under Ar

atmosphere at -78 °C for 2 h. Wet silica gel (170 mg) in Et_2O (600 µL) was added to quench the reaction and the mixture was stirred at 0 °C for 1 h. The silica was filtered from the mixture and washed with EtOAc. The organic phase was dried over $MgSO_4$, evaporated and purified by column chromatography (EtOAc:hexanes:Et_3N 2:14:1) to give the title compound (65.0 mg, 32%) as a dark orange-red oil.

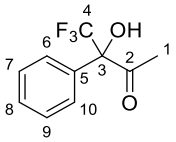
IR ($CDCl_3$, liquid film) 2955 (alkane C-H), 2928 (alkane C-H), 2857 (alkane C-H), 1653 (C=O), 1603 (alkene C=C), 1560 (aromatic C-C), 1520 (aromatic C-C), 1395 (alkane C-H), 1360 (alkane C-H), 1250 (Si-C), 1180 (C-N), 1149 (C-N), 1105 (Si-O), 1005 (C-N), 958 (alkene C-H), 836 (alkene C-H), 807 (alkene C-H), 777 (alkene C-H) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (d, *J* = 8.0 Hz, 0.3H, C(28$_Z$)*H*), 10.05 (d, *J* = 8.4 Hz, 0.7H, C(28$_E$)*H*), 7.35-7.31 (m, 2H, ArC(7,9)*H*), 6.75-6.64 (m, 4.3H, C(6,10,11,12,14$_Z$)*H*), 6.26 (s, 0.7H, C(14$_E$)*H*), 5.91 (d, *J* = 8.0 Hz, 0.7H, C(27$_E$)*H*), 5.70 (d, *J* = 8.0 Hz, 0.3H, C(27$_Z$)*H*), 3.77 (t, *J* = 6.4 Hz, 2H, C(4)H_2), 3.48-3.43 (m, 4H, C(2,3)H_2), 2.68 (s, 1.4H, C(16$_E$)H_2), 2.35 (s, 2H, C(18)H_2), 2.28 (s, 0.6H, C(16$_Z$)H_2), 1.17 (t, *J* = 7.2 Hz, 3H, C(1)H_3), 1.06 (s, 4.2H, C(19$_E$,20$_E$)H_3), 1.03 (s, 1.8H, C(19$_Z$,20$_Z$)H_3), 0.89 (s, 9H, C(24,25,26)H_3), 0.04 (s, 6H, C(21,22)H_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1 (C^{28}), 157.6 (C^{8}), 148.7 (C^{15}), 147.3 (C^{13}), 140.4 (C^{27}), 132.9 (C^{14}), 128.9 ($C^{7,9}$) 126.0 ($C^{11/12}$), 124.5 ($C^{11/12}$), 122.3 (C^{17}), 112.1 ($C^{6,10}$), 61.1 (CH_2), 52.9 (CH_2), 46.0 (CH_2), 39.7 (CH_2), 39.4 (CH_2), 31.6 (C^{5}), 30.2 (C^{23}), 28.9 ($C^{19,20}$), 26.4 ($C^{24,25,26}$), 12.7 (C^{1}), -4.9 ($C^{21,22}$).

HRMS *m/z* (ESI+) Exact mass calculated for $C_{28}H_{44}NO_2Si$ $[M+H]^+$: 454.3136, found: 454.3133.

4,4,4-Trifluoro-3-hydroxy-3-phenylbutan-2-one (42)



Following a literature procedure,[16] ethyl vinyl ether (5.11 mL, 53.4 mmol) was dissolved in dry THF (17.8 mL) under Ar atmosphere and the solution was cooled to -78 °C. A 1.7 M solution of *tert*-butyl lithium (21.0 mL, 35.7 mmol) in pentanes was added dropwise and

the solution was stirred at -78 °C for 15 min, then at 0 °C for 30 min. The solution was re-cooled to -78 °C and a solution of 2,2,2-trifluoroacetophenone (2.50 mL, 17.8 mmol) in dry THF (3.60 mL) was added. The mixture was stirred at -78 °C for 30 min, 0 °C for 1 h, then warmed to room temperature. The reaction was quenched with a saturated aqueous solution of NH_4Cl (25.0 mL), the crude product was extracted with Et_2O (3 x 25.0 mL) and the organic phase was washed with brine (25.0 mL) and dried over $MgSO_4$. The solvent was removed under vacuum to give the crude phenylbutenol intermediate (4.43 g) as a brown oil, which was determined pure enough to use in the next step by NMR. The crude 3-ethoxy-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (4.43 g) was dissolved in methanol (9.00 mL), a water bath was used to maintain the temperature at rt and 1 M aqueous HCl (19.8 mL, 19.8 mmol) was added dropwise. The reaction was stirred at rt for 2 h, the solution was neutralised with saturated aqueous $NaHCO_3$ solution and the methanol was removed under vacuum. The crude product was extracted with DCM (3 x 20.0 mL), washed with brine (20.0 mL), dried over $MgSO_4$ and purified by column chromatography (EtOAc:hexanes 1:9) to give the title compound (2.23 g, 58%) as a pale yellow oil.

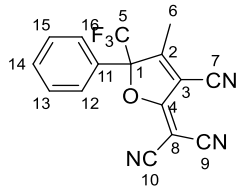
IR ($CDCl_3$, liquid film) 3433 (O-H), 1717 (C=O), 1150 (C-O), 700 (C-F) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.40 (m, 5H, ArC*H*), 4.96 (s, 1H, O*H*), 2.32 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9 (C^2), 133.8 (C^5), 130.0 (C^8), 129.5 ($C^{7,9}$), 127.0 (q, *J* = 2.0 Hz, $C^{6,10}$), 124.0 (q, *J* = 287.9 Hz, C^4), 83.0 (q, *J* = 28.3 Hz, C^3), 25.6 (q, *J* = 3.0 Hz, C^1).

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.6

2-(3-Cyano-4-methyl-5-phenyl-5-(trifluoromethyl)furan-2(5H)-ylidene)malononitrile (10)



Following a literature procedure,[17] 4,4,4-trifluoro-3-hydroxy-3-phenylbutan-2-one (2.23 g, 10.2 mmol) and distilled malononitrile* (1.29 mL, 20.5 mmol) were dissolved in THF (4.40 mL). A solution of sodium ethoxide (38.0 mg, 556 µmol) in ethanol (560 µL) was

added and the reaction was stirred at reflux for 48 h. The mixture was concentrated under reduced pressure, the residue was extracted with DCM (3 x 5.00 mL) and the organic phase was washed with water (5.00 mL) and brine (5.00 mL) and dried over $MgSO_4$. The crude product was recrystallized by dissolving in a small amount of hot ethanol, placing the flask in an ice bath and scratching the inside of the flask with a glass rod to give the title compound (808 mg, 25%) as a green powder.

IR ($CHCl_3$, solid film) 2926 (alkane C-H), 2236 (C≡N), 1621 (alkene C=C), 1497 (aromatic C-C), 1453 (aromatic C-C), 1431 (aromatic C-C), 1364 (alkane C-H), 1201 (C-F), 1180 (C-F), 1164 (C-F), 1275 (C-O), 1010 (conjugated C-O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.51 (m, 3H, ArC(13,14,15)*H*), 7.47-7.40 (m, 2H, ArC(12,16)*H*), 2.48 (s, 3H, C(6)H_3)

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0 (C^7), 171.9 ($C^{9,10}$), 131.9 (C^{14}), 130.2 ($C^{13,15}$), 127.5 (C^{11}), 125.7 (q, *J* = 1.0 Hz, $C^{12,16}$), 121.7 (q, *J* = 288.9 Hz, C^5), 109.4 (C), 109.0 (C), 108.0 (C), 98.4 (q, *J* = 32.3 Hz, C^1), 63.2 (C^2), 15.4 (q, *J* = 1.0 Hz, C^6).

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5.

mp (°C) 146.6 – 150.8

HRMS *m/z* (ESI+) Exact mass calculated for $C_{16}H_8F_3N_3NaO$ $[M+Na]^+$: 338.0512, found: 338.0515.

*Distillation of malononitrile was carried out under reduced pressure using a distillation apparatus fitted with a condenser. The crude brown solid was heated slowly under reduced pressure using an oil bath and hot plate until the solid had melted and was just boiling. At this point the temperature of the oil bath was kept constant and any solidified malononitrile inside the fractionating column section of the apparatus was melted back into the flask with a heat gun. By this point the pure malononitrile had begun to collect as a clear liquid in the flask attached to the end of the apparatus, and this process was continued until no more pure malononitrile was produced.

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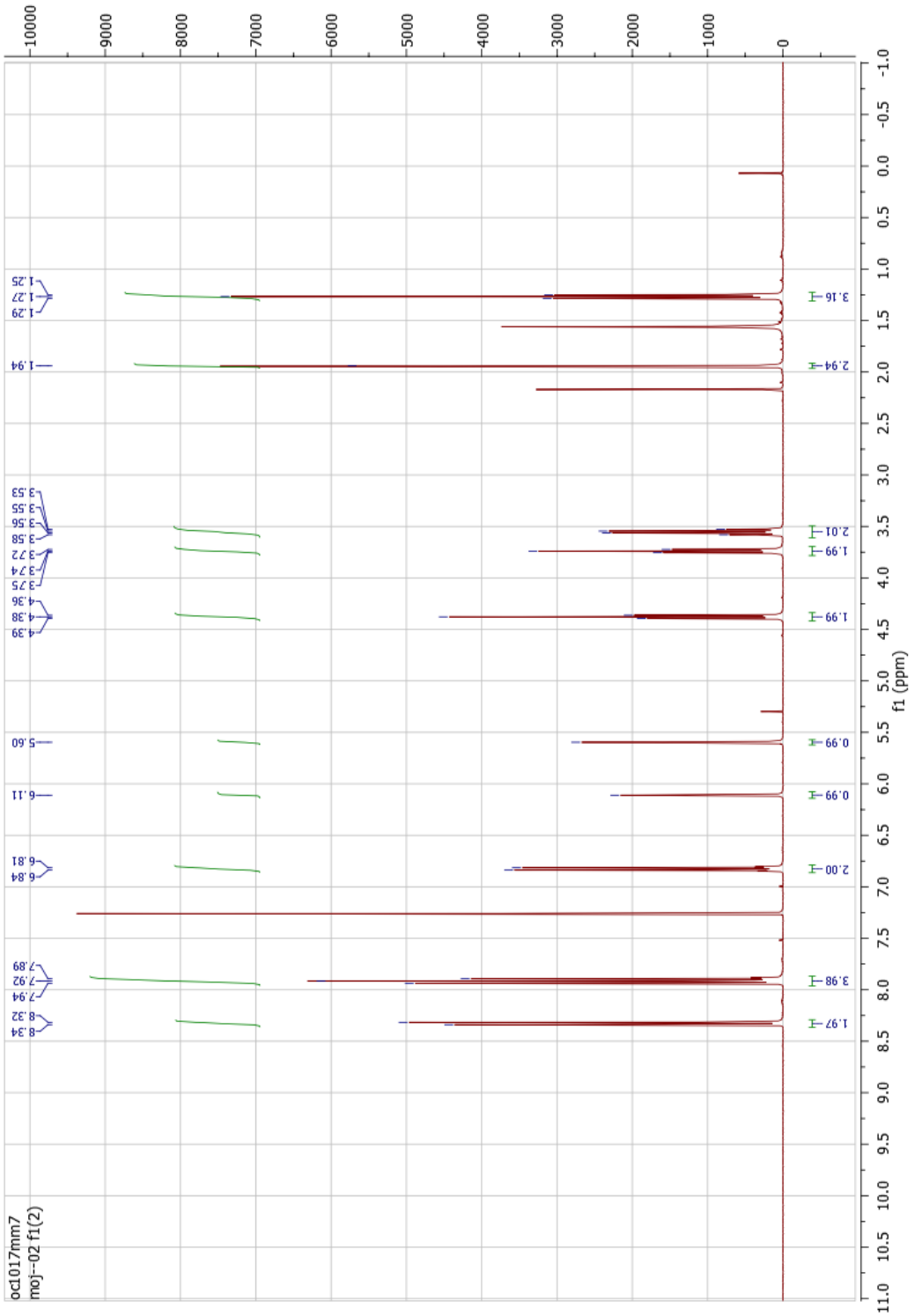
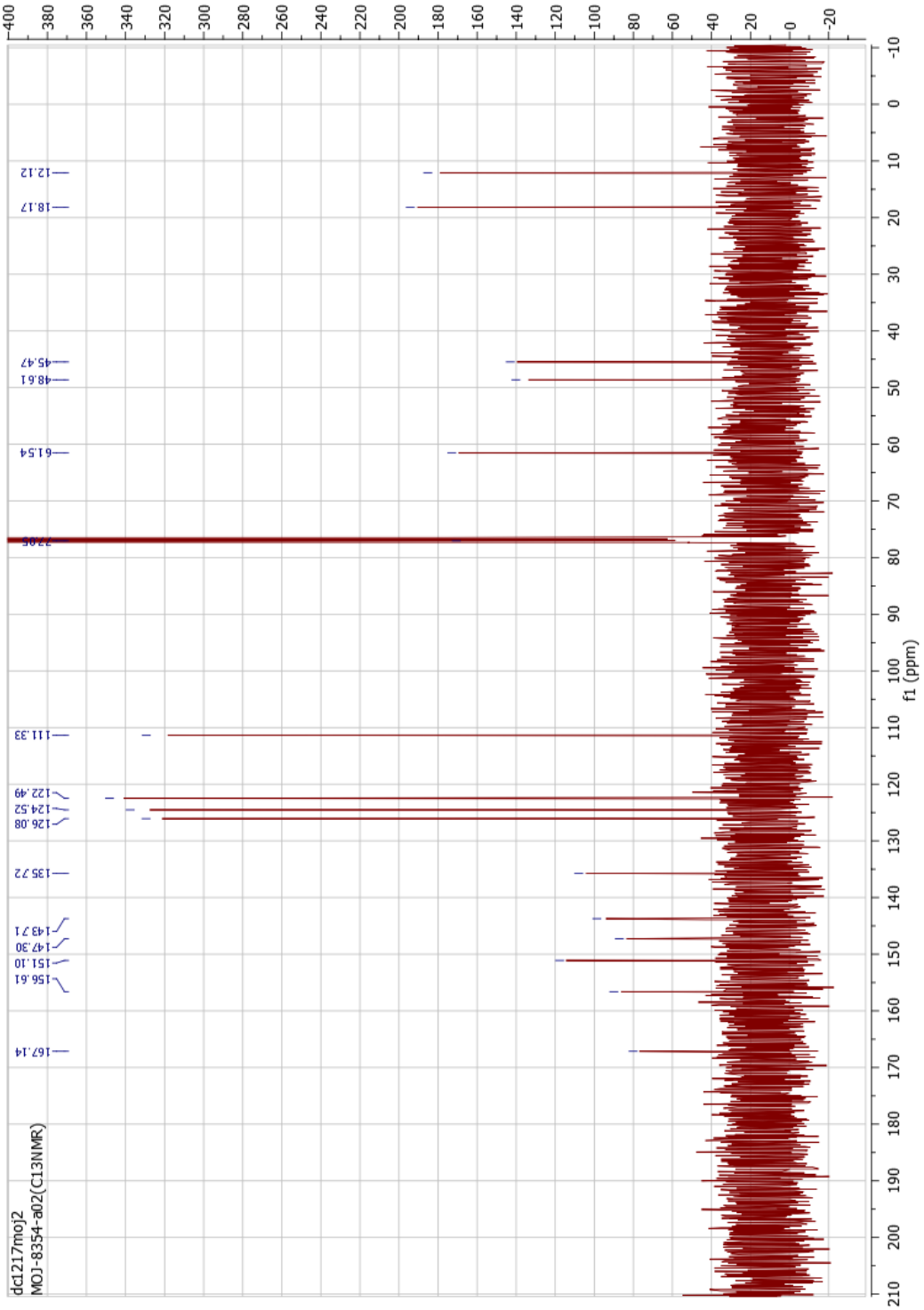
Appendix

(E)-2-(Ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl methacrylate (DR1MA) (3)

^{1}H NMR (400 MHz, $CDCl_3$)

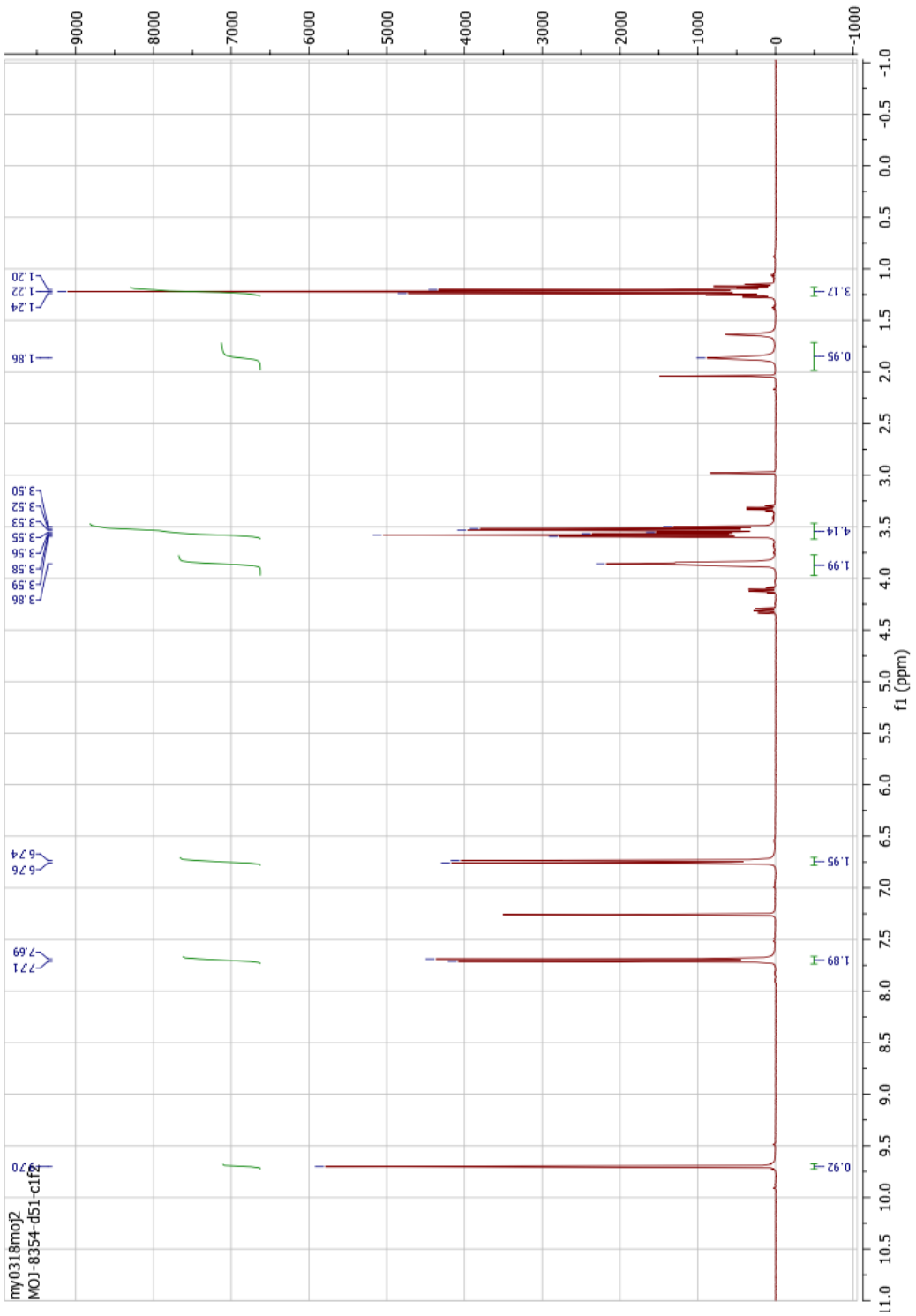


^{13}C NMR (101 MHz, $CDCl_3$)

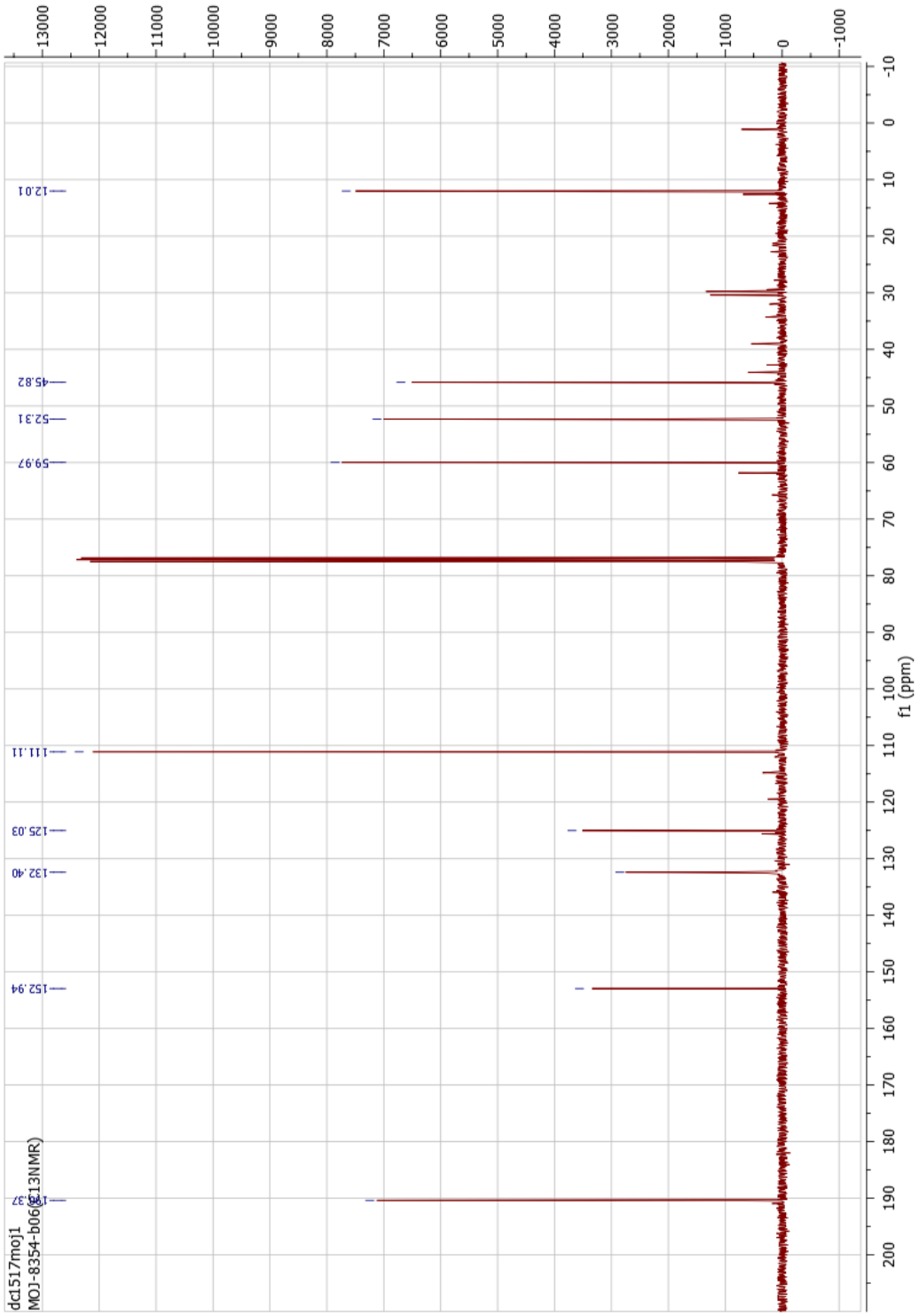


4-(Ethyl(2-hydroxyethyl)amino)benzaldehyde (7)

^{1}H NMR (400 MHz, $CDCl_3$)

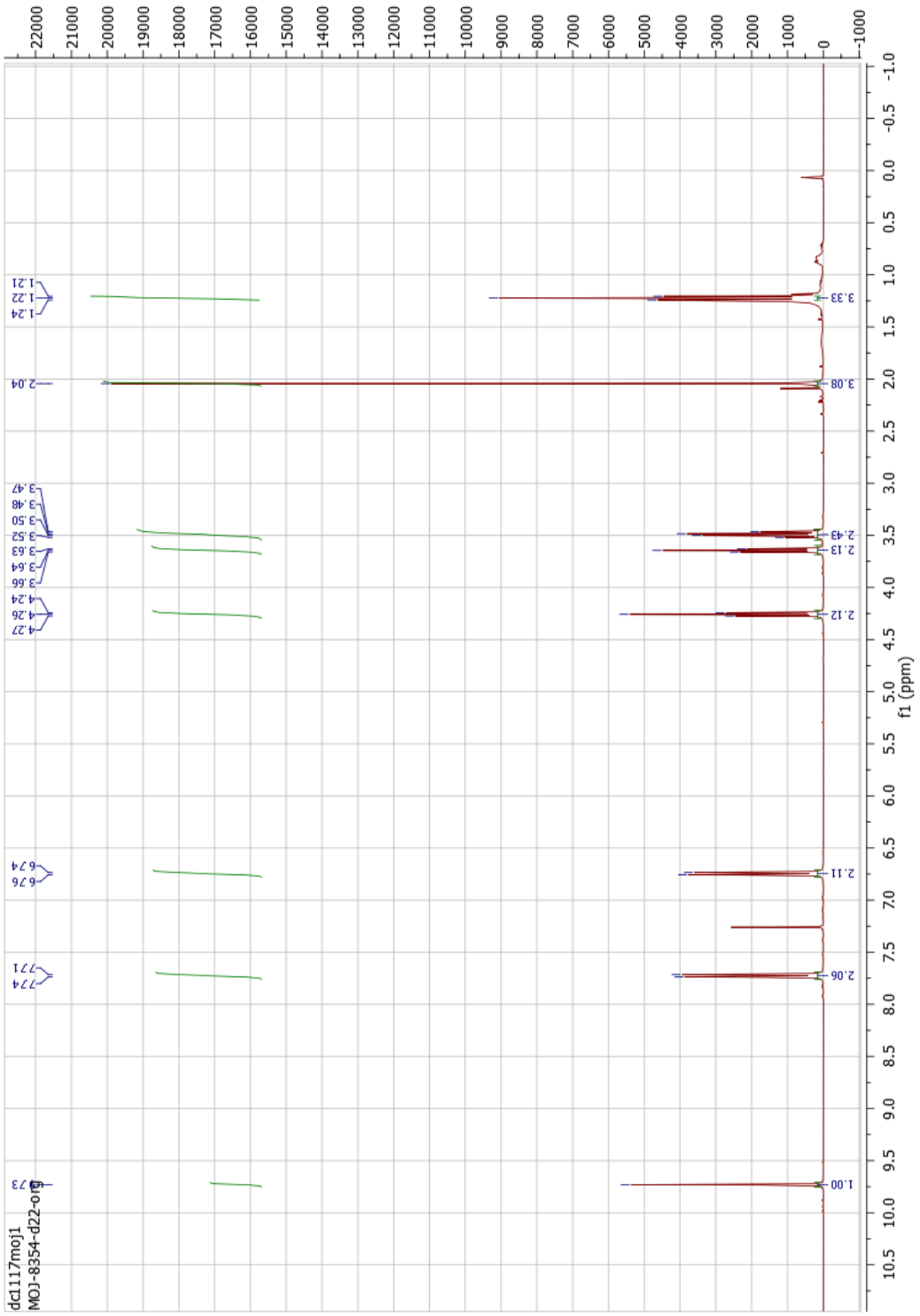


^{13}C NMR (101 MHz, $CDCl_3$)

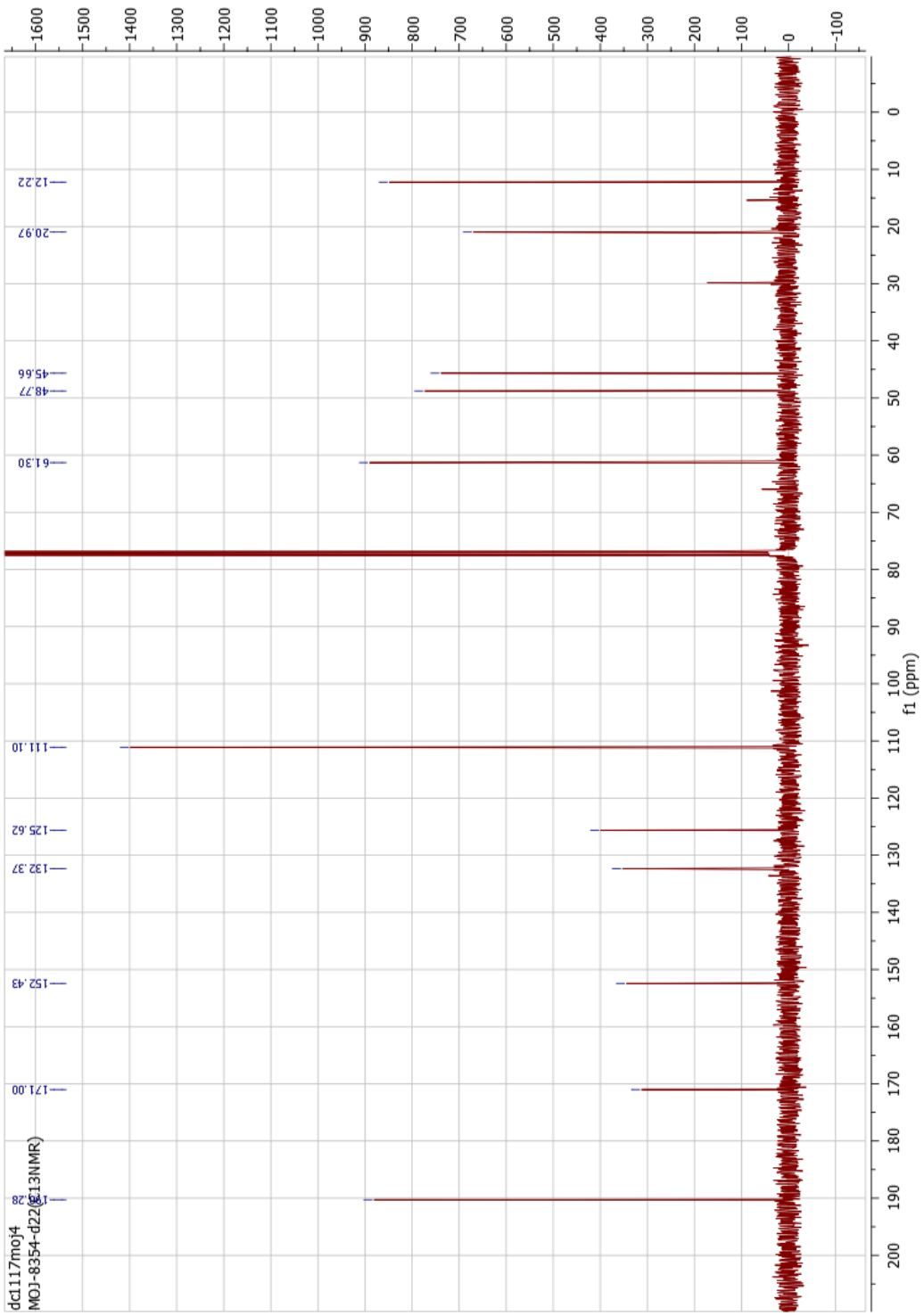


2-(Ethyl(4-formylphenyl)amino)ethyl acetate (32)

^{1}H NMR (400 MHz, $CDCl_3$)

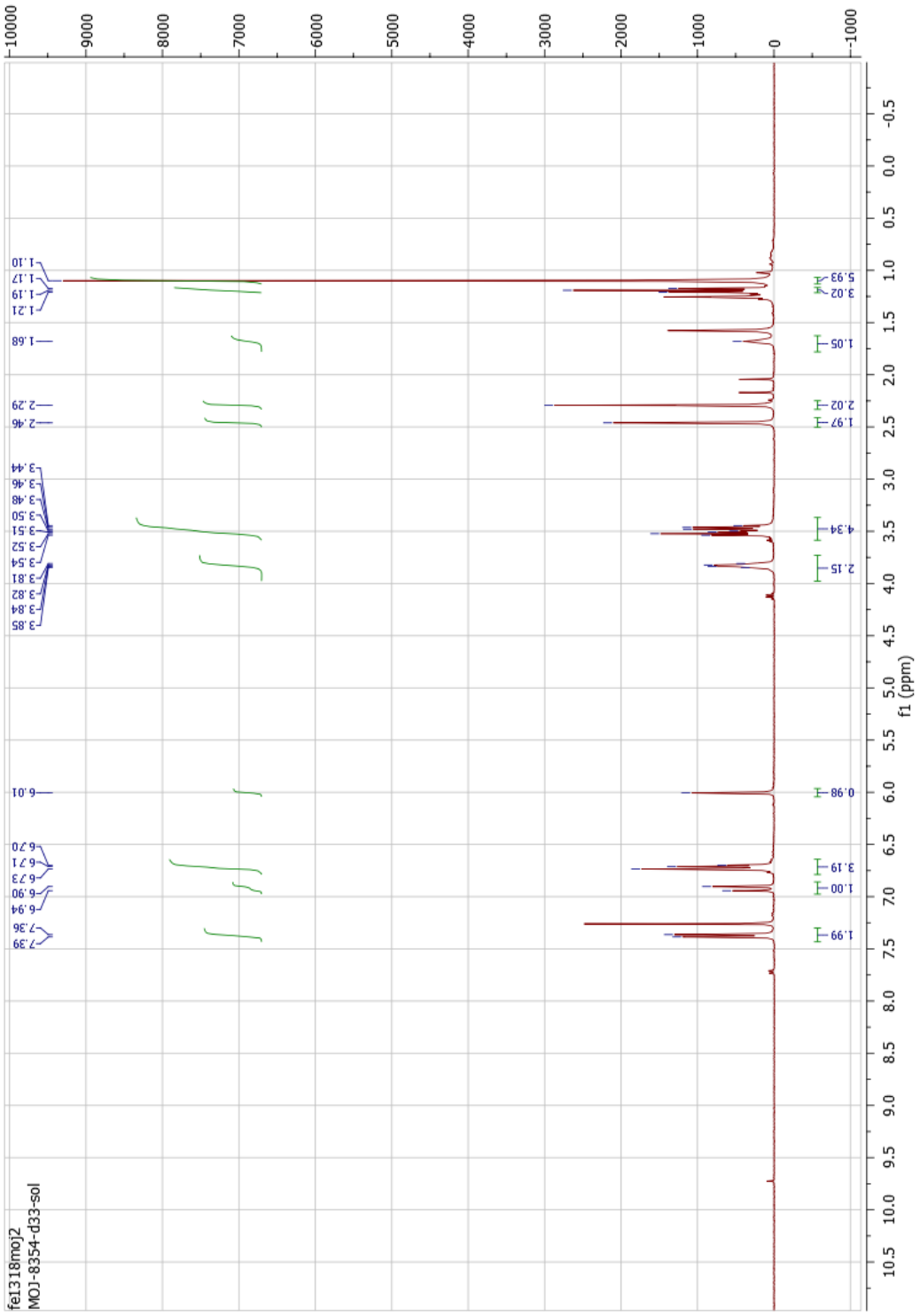


^{13}C NMR (101 MHz, $CDCl_3$)

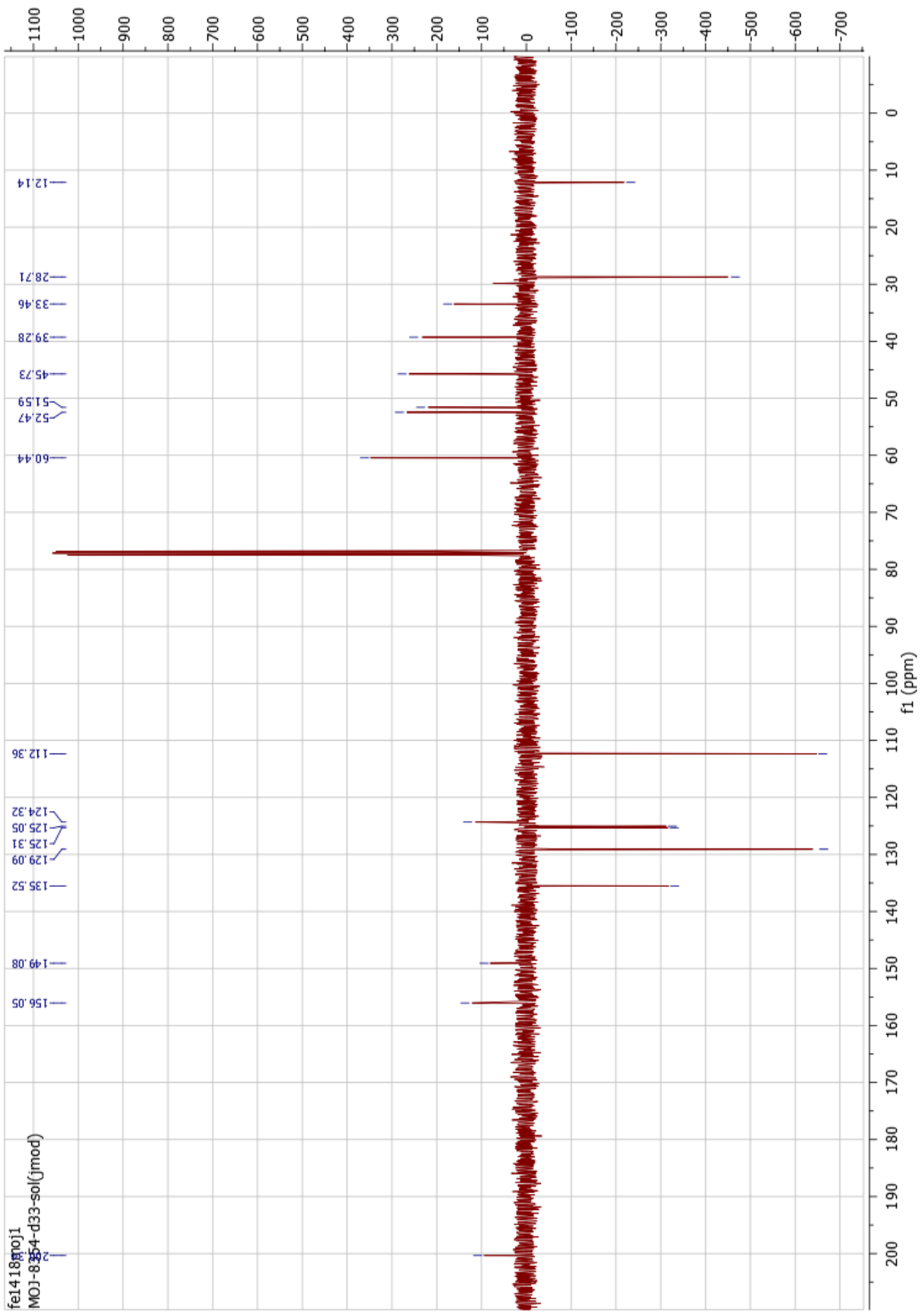


(E)-3-(4-(Ethyl(2-hydroxyethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-one (33)

^{1}H NMR (400 MHz, $CDCl_3$)

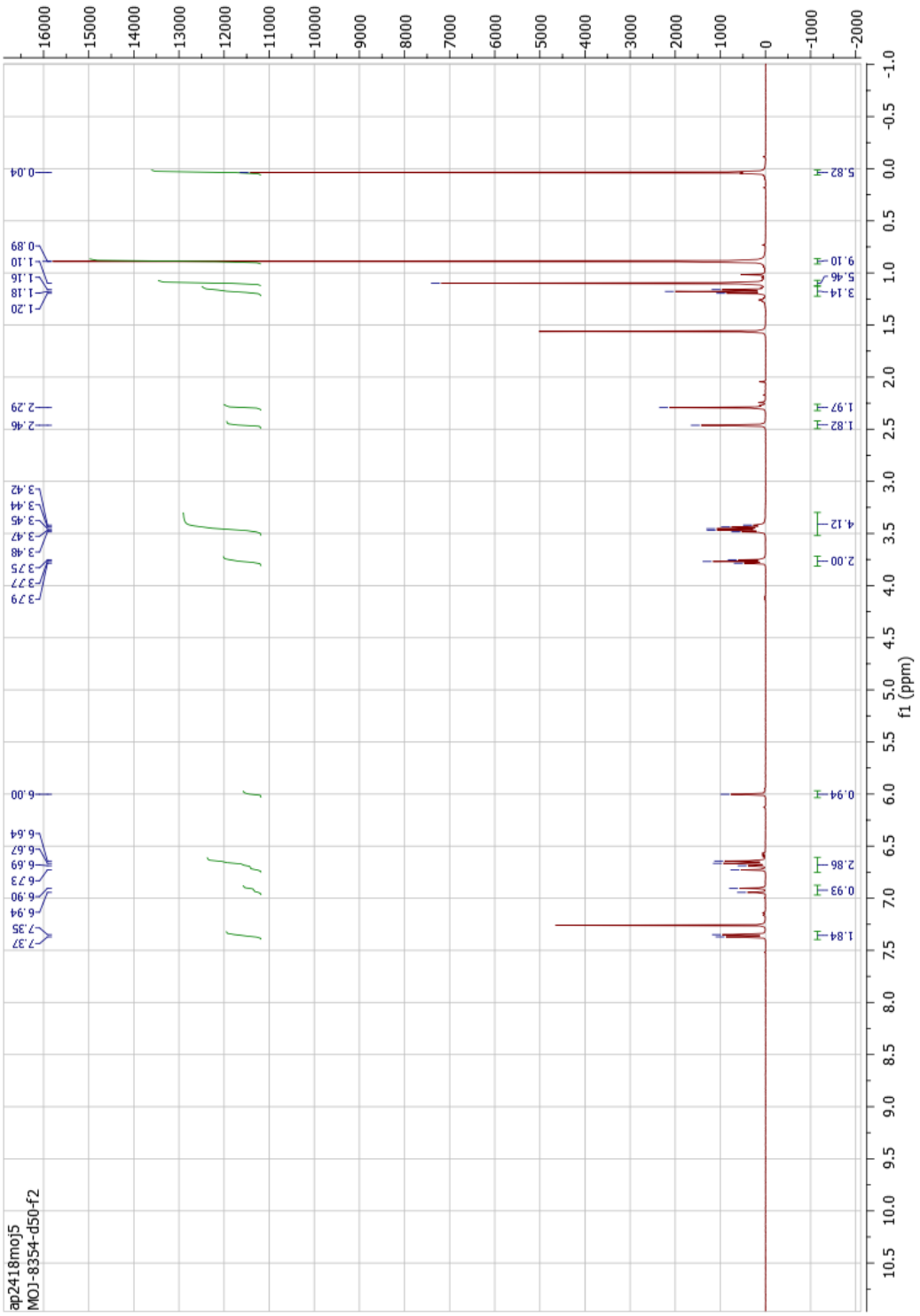


^{13}C (JMOD) NMR (101 MHz, $CDCl_3$)

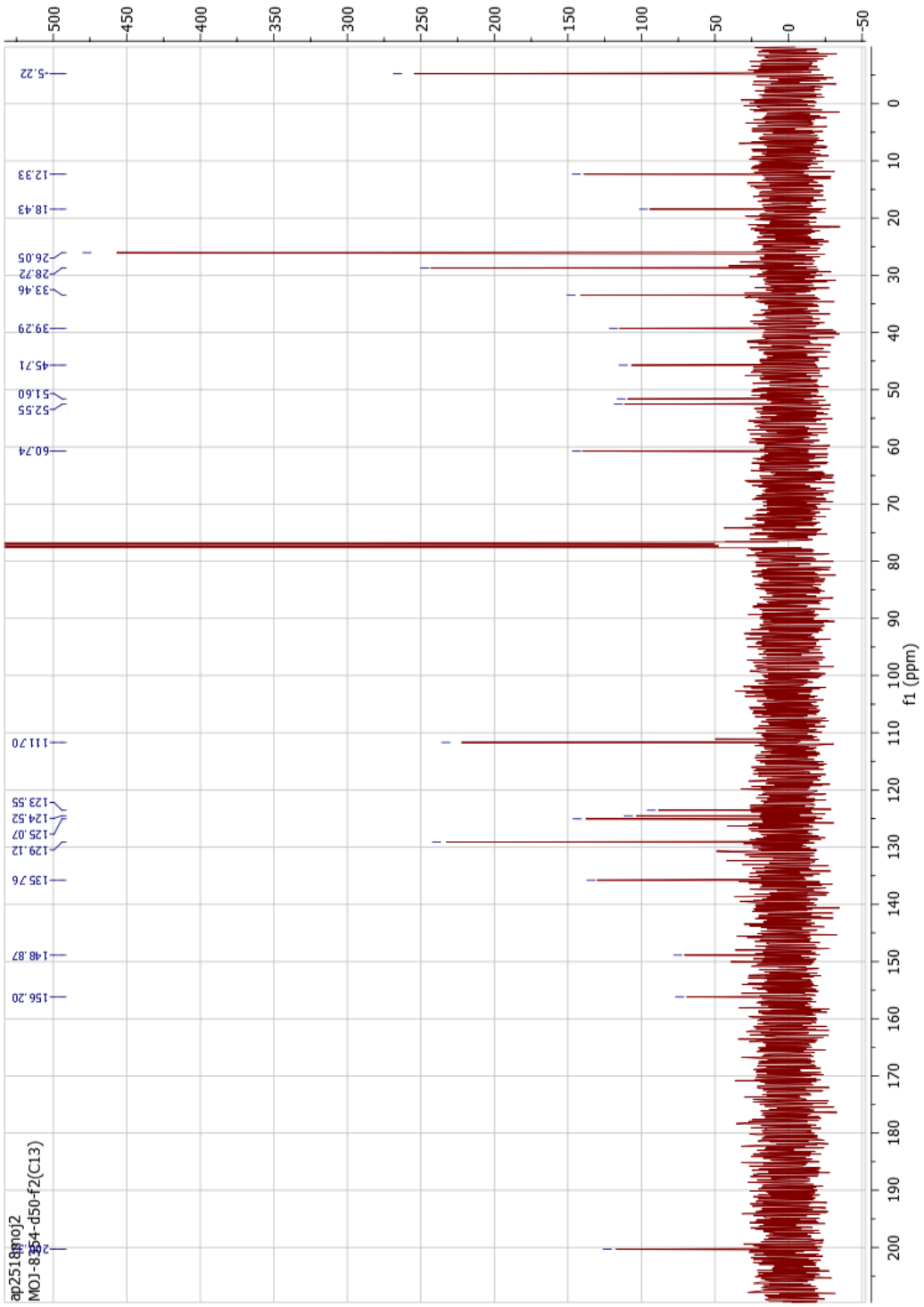


(E)-3-(4-((2-((tert-Butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-one (34)

^{1}H NMR (400 MHz, $CDCl_3$)

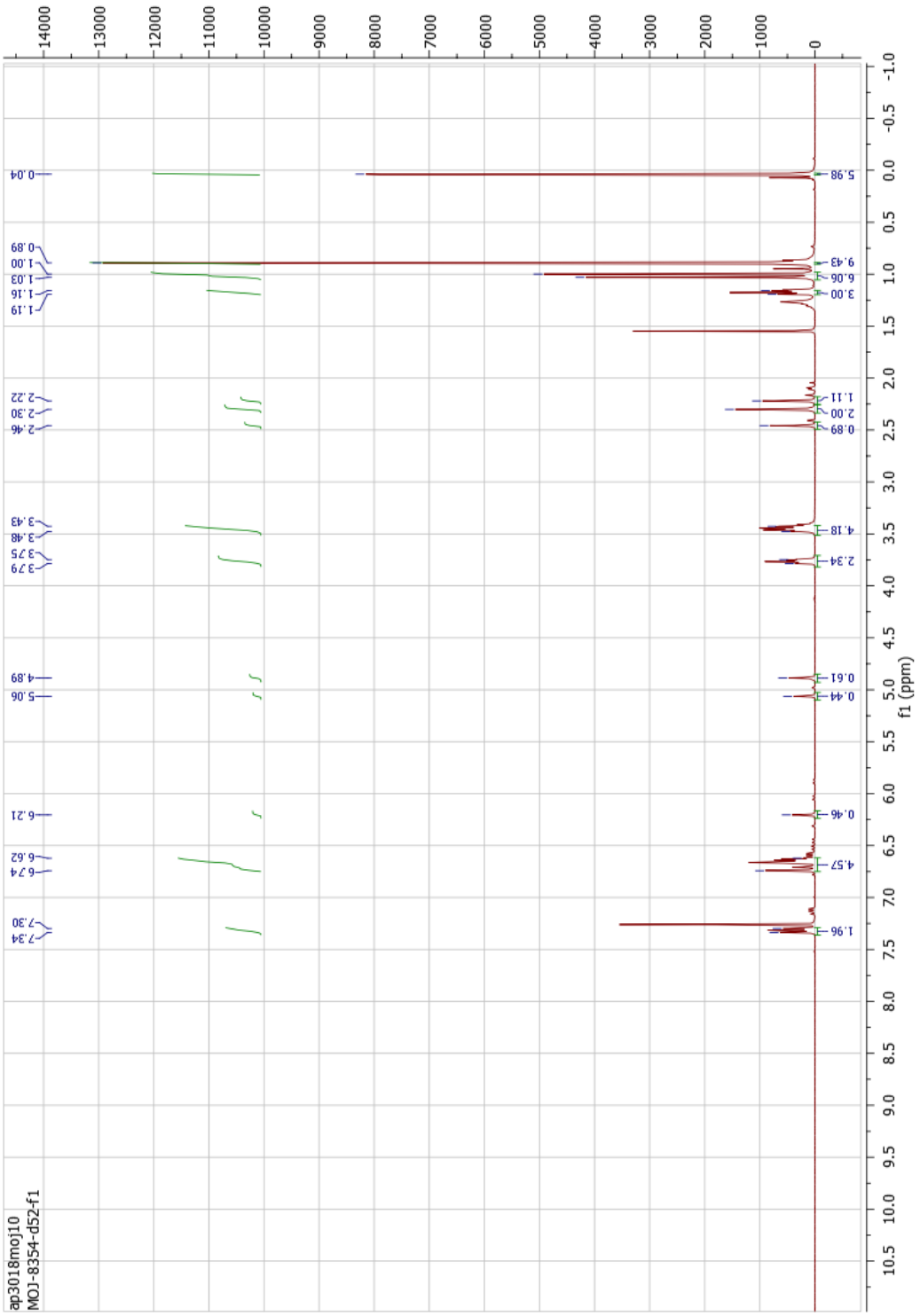


^{13}C NMR (101 MHz, $CDCl_3$)

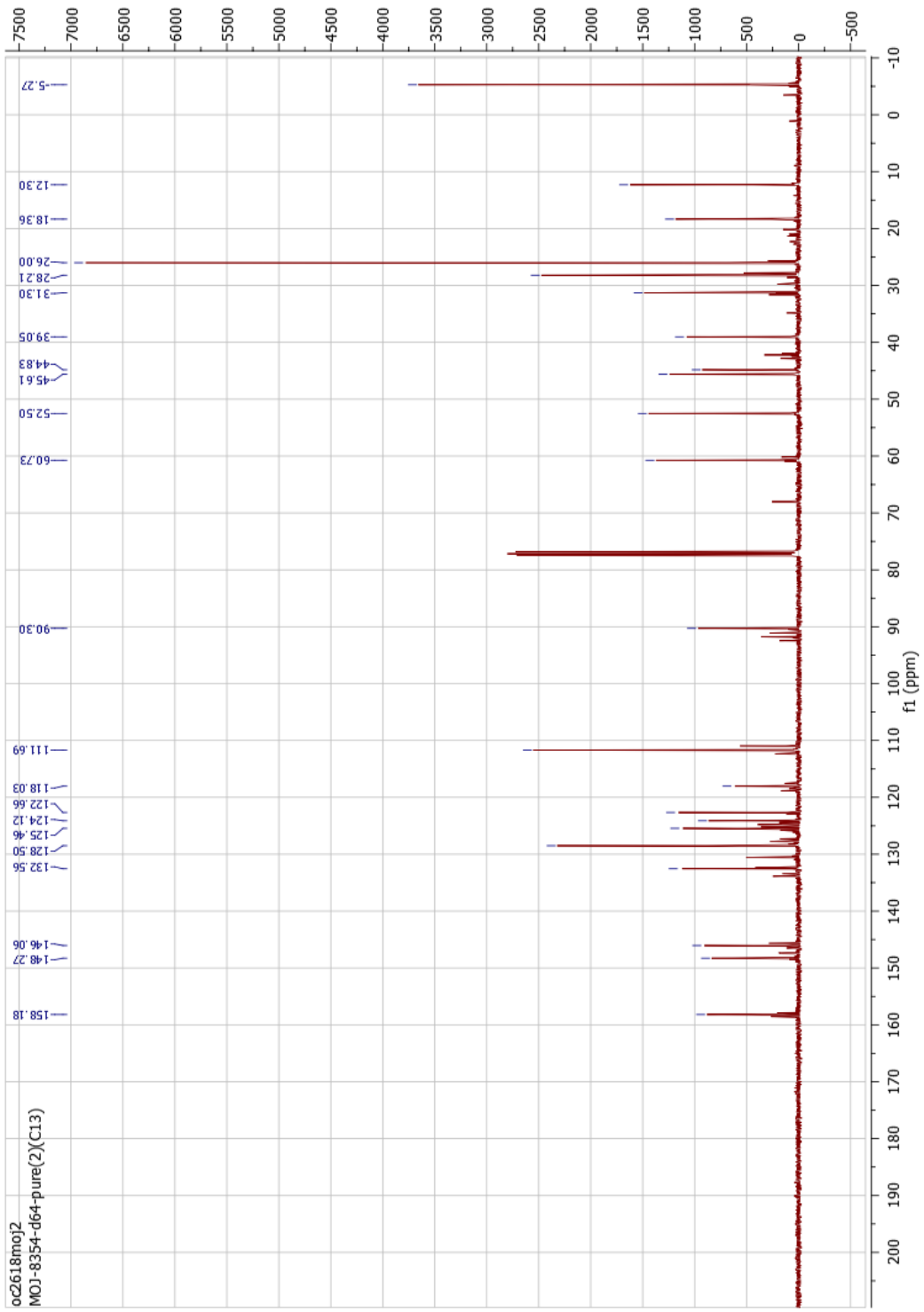


(E)-2-(3-((E)-4-((2-((tert-Butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetonitrile (36)

^{1}H NMR (400 MHz, $CDCl_3$)

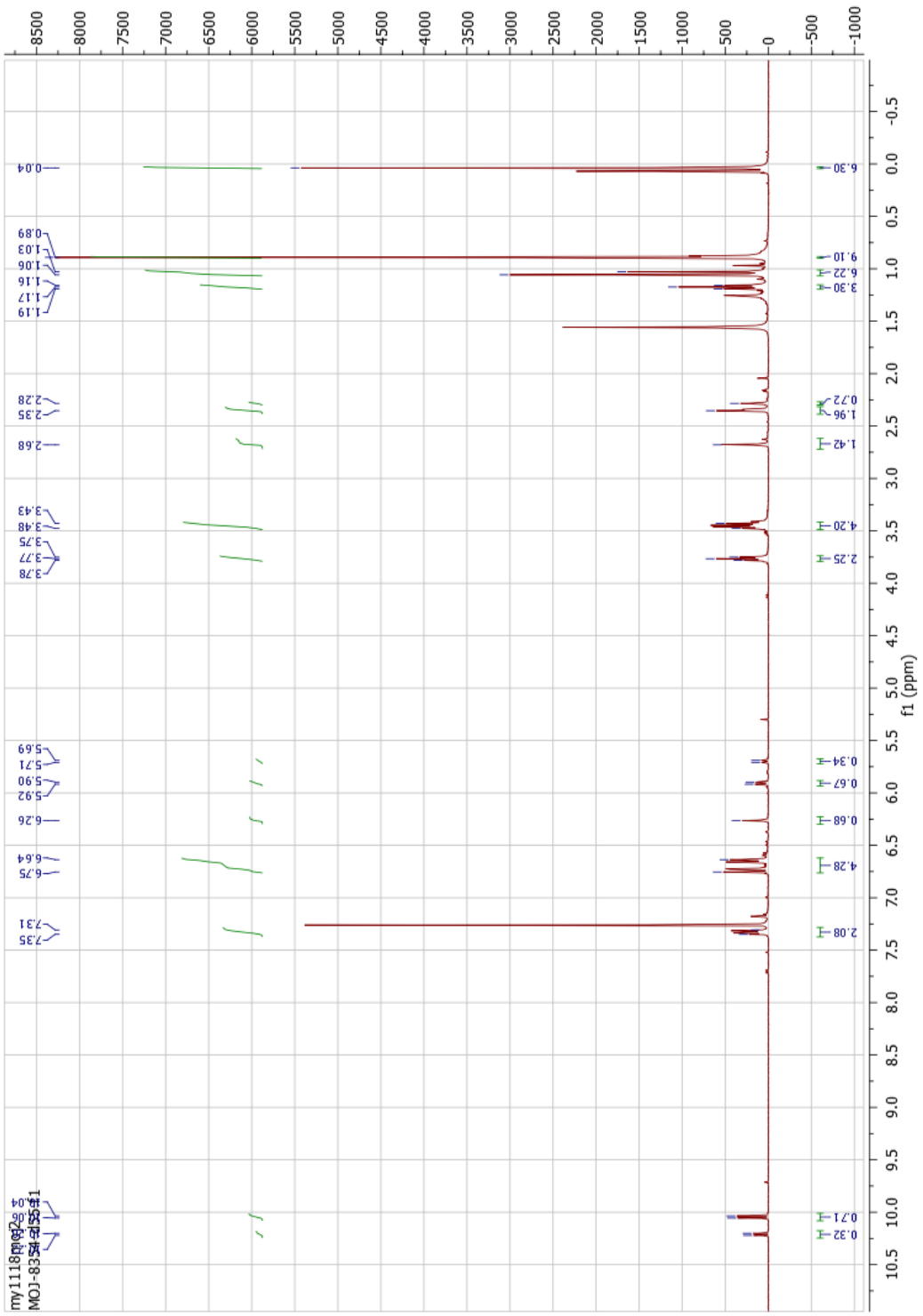


^{13}C NMR (101 MHz, $CDCl_3$)

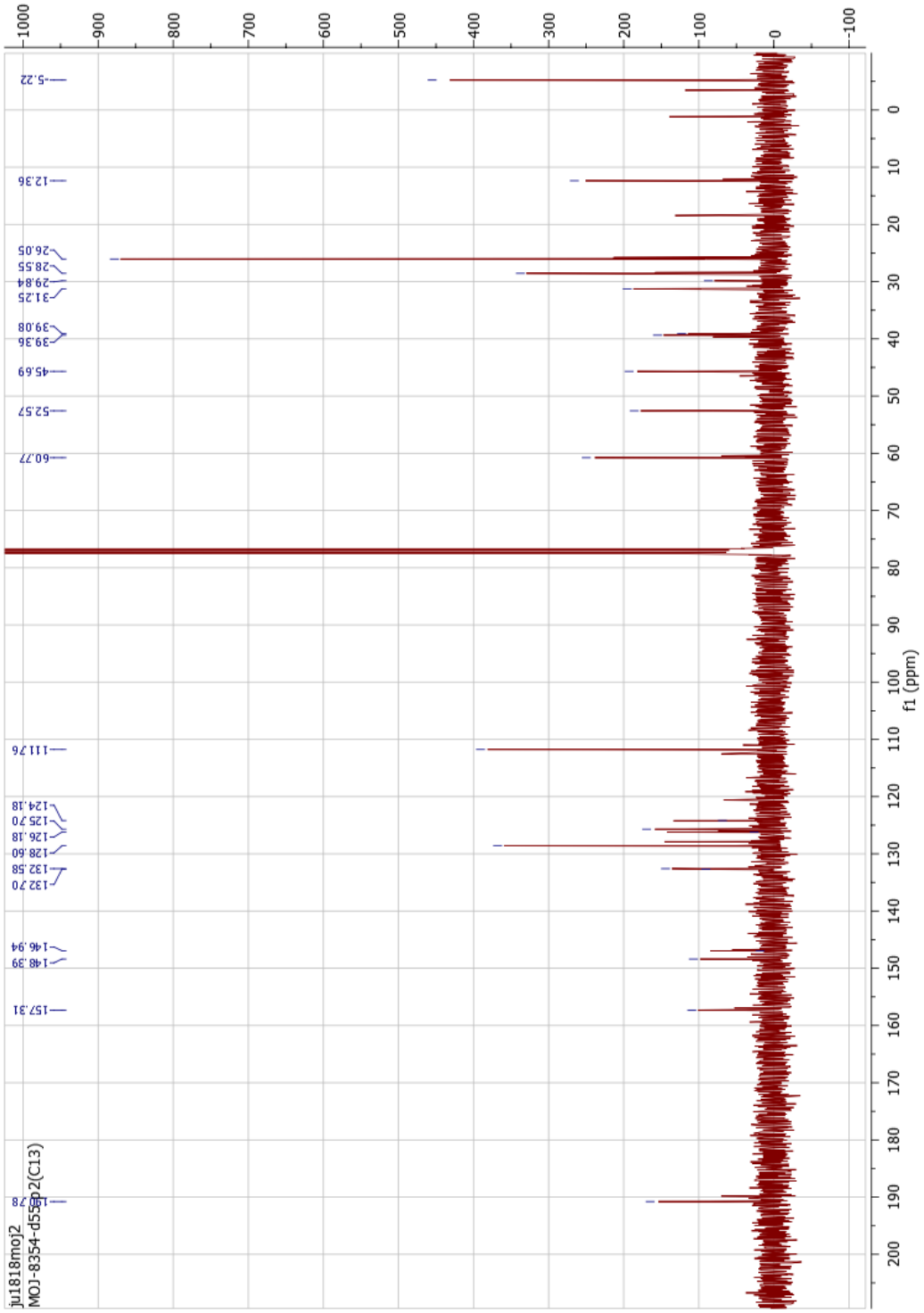


(E)-2-(3-((E)-4-((2-((tert-Butyldimethylsilyl)oxy)ethyl)(ethyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetaldehyde (37)

^{1}H NMR (400 MHz, $CDCl_3$)

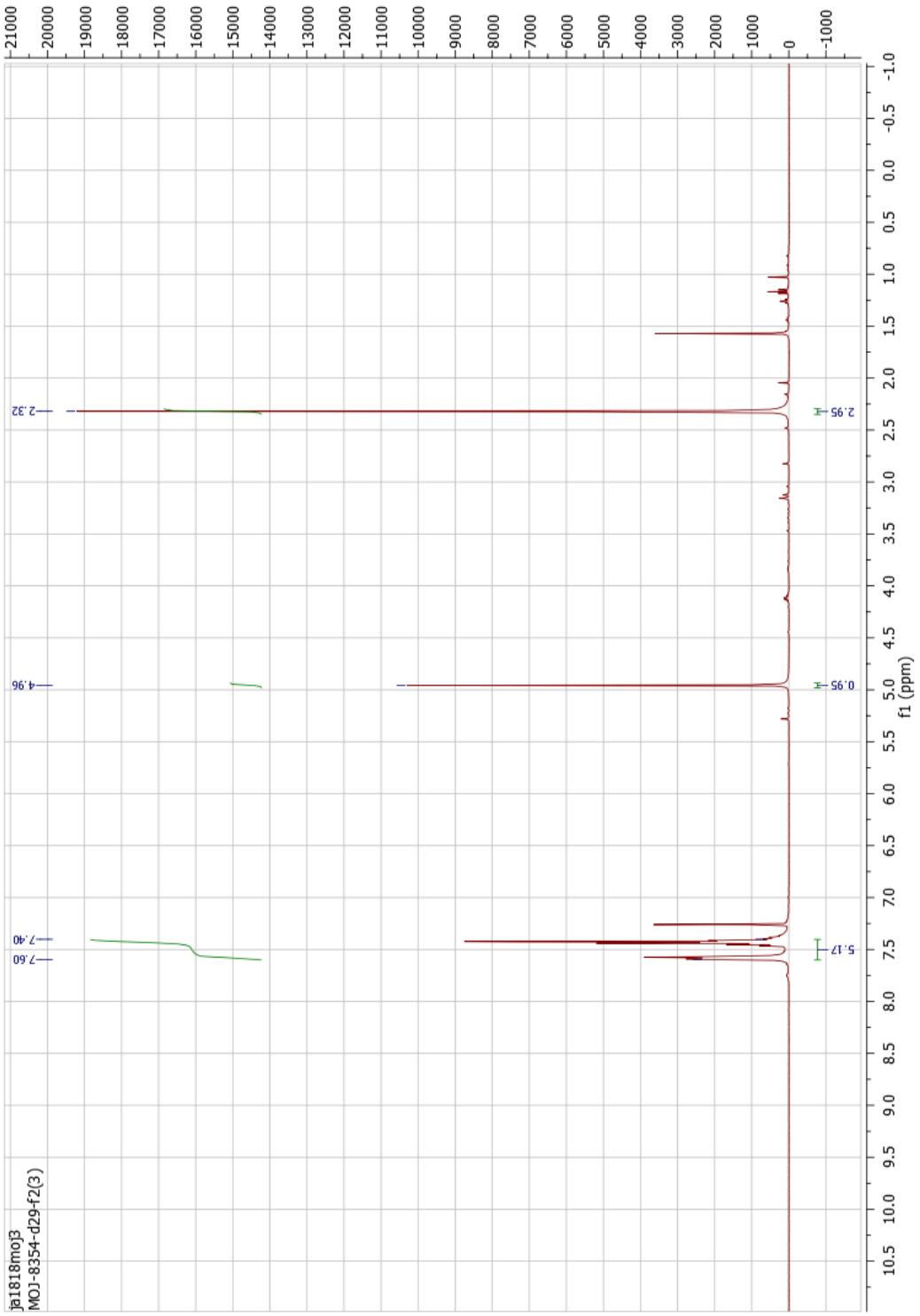


^{13}C NMR (101 MHz, $CDCl_3$)

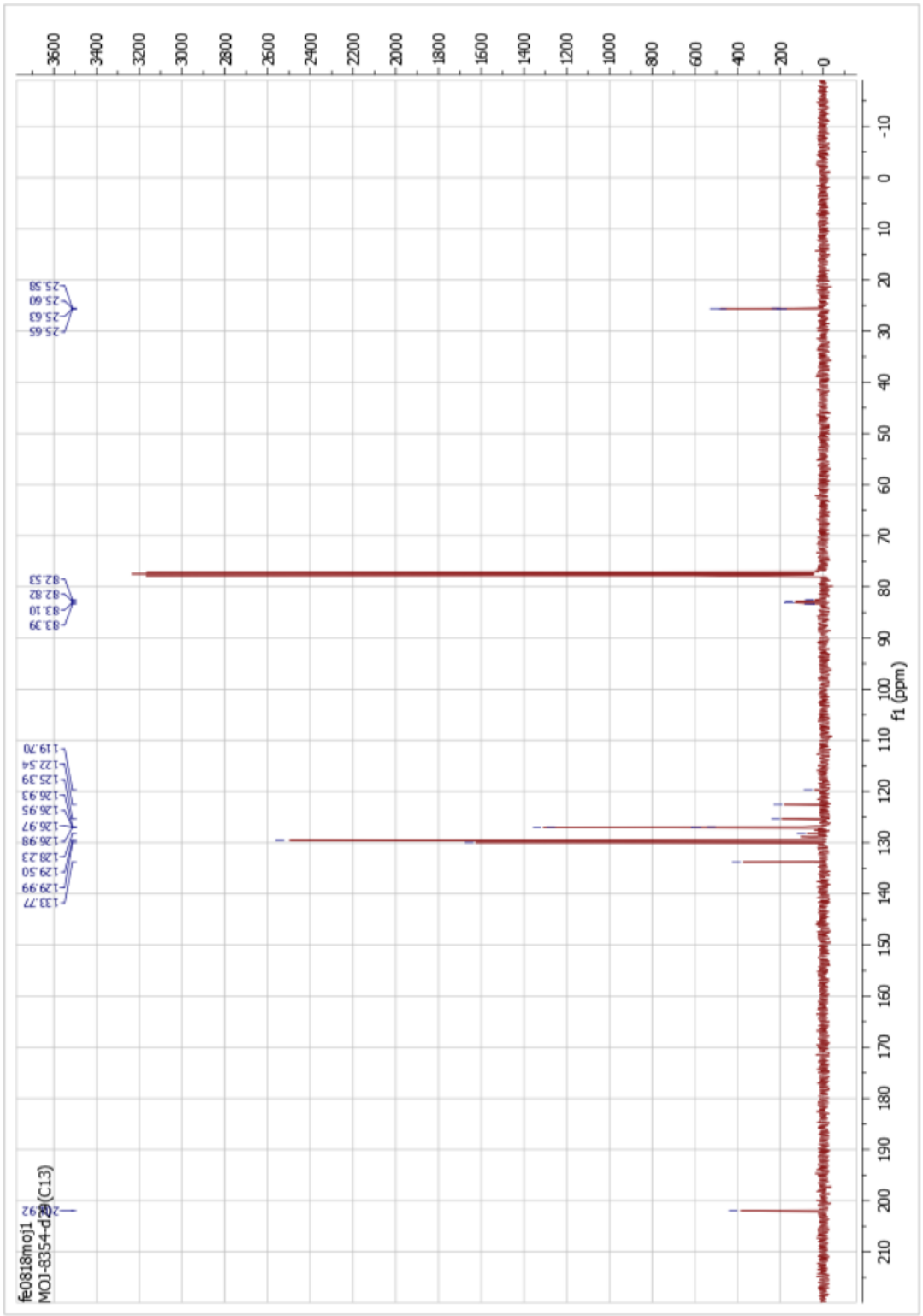


4,4,4-Trifluoro-3-hydroxy-3-phenylbutan-2-one (42)

^{1}H NMR (400 MHz, $CDCl_3$)



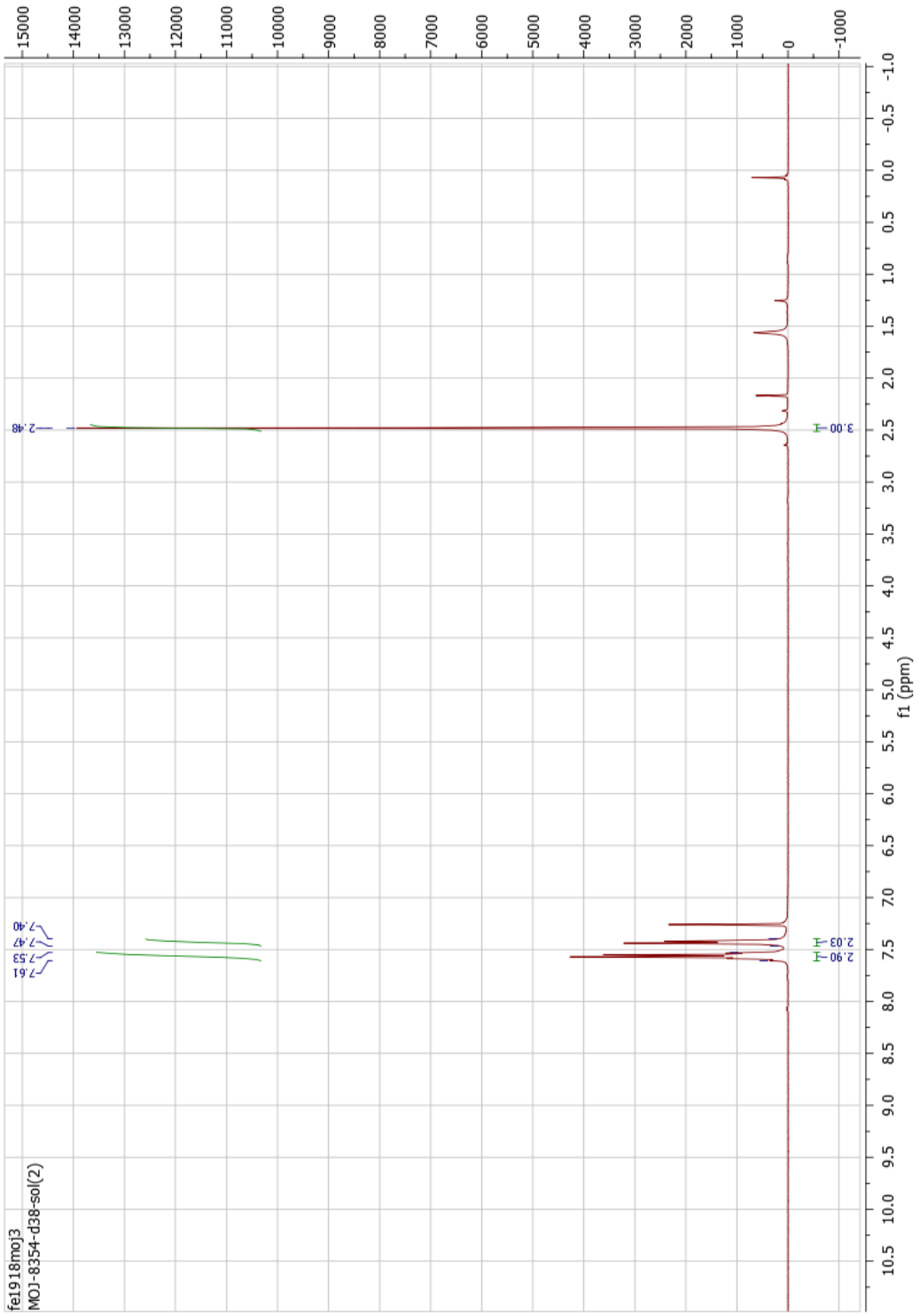
^{13}C NMR (101 MHz, $CDCl_3$)



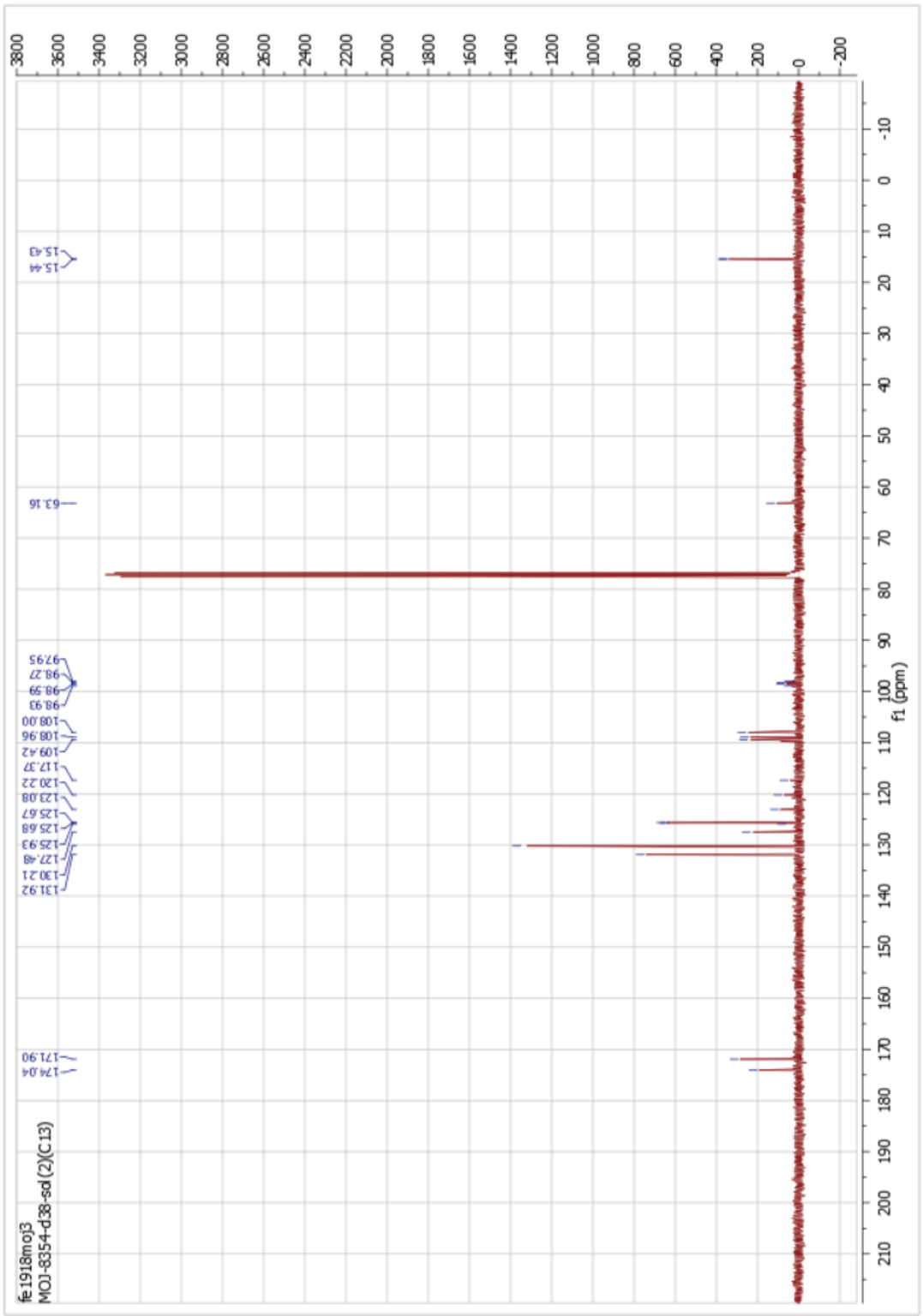
^{19}F NMR (376 MHz, $CDCl_3$)

2-(3-Cyano-4-methyl-5-phenyl-5-(trifluoromethyl)furan-2(5H)-ylidene)malononitrile (10)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)