Supporting Information

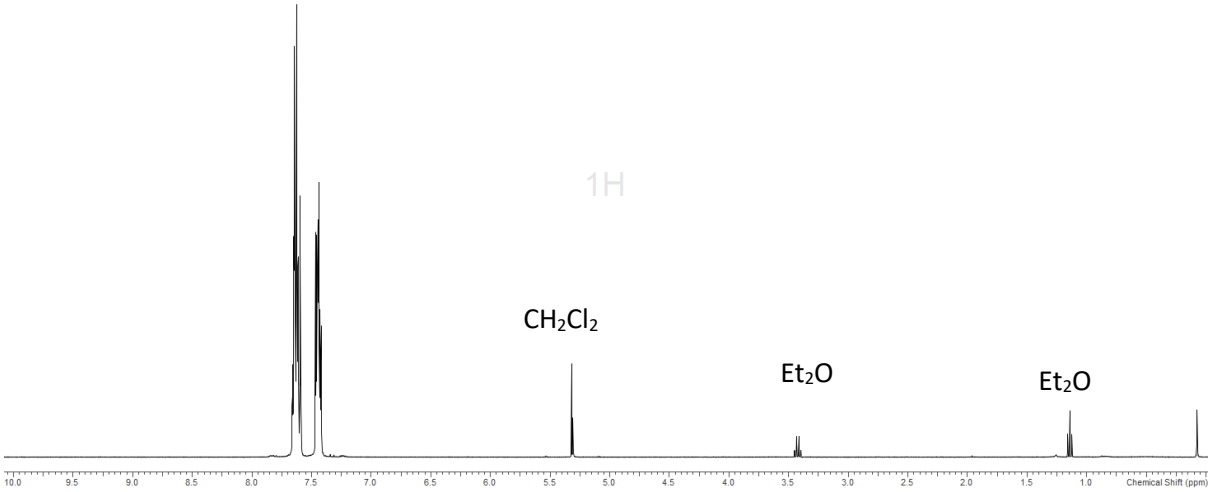
Structural diversity of Sn(II) phosphine oxide complexes with weakly coordinating anions and comparisons with related Ge(II) and Pb(II) species

Rhys P. King*,[a] Kelsey R. Cairns, [a] Charlotte Denman, [a] William Levason, [a] Mark E. Light[a] and Gillian Reid[a]

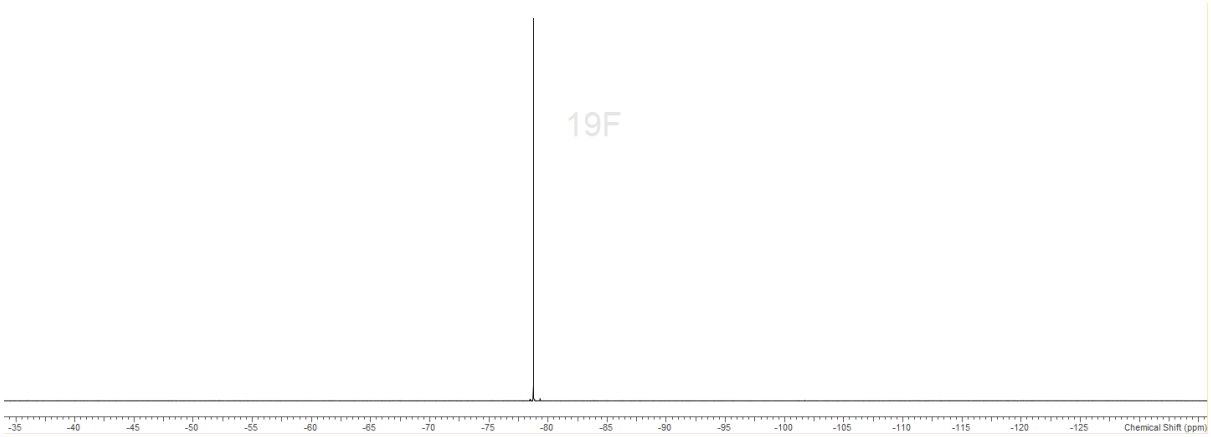
[a] School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK; email: R.P.King@soton.ac.uk

S1.0 - $[Sn(OTf)_2(OPPh_3)_2]$

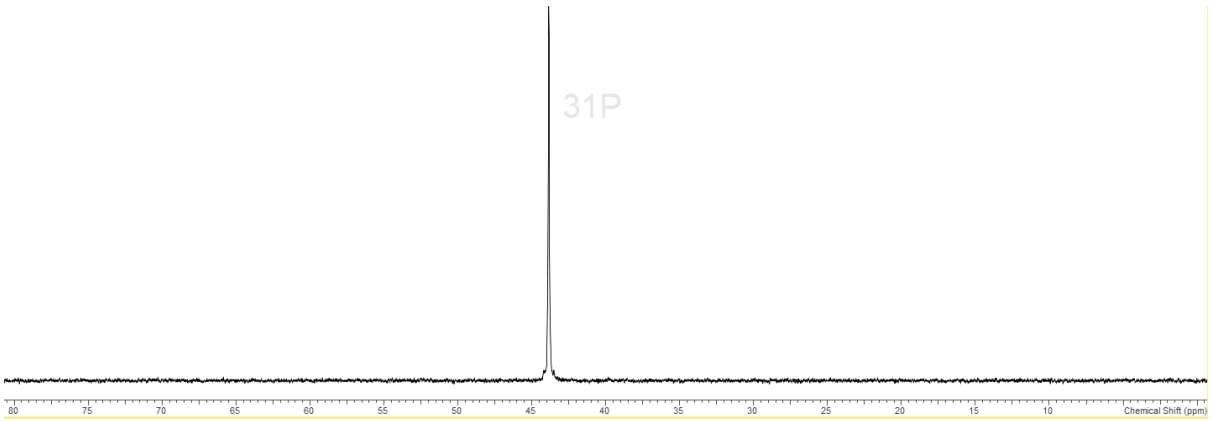
S1.1 - ^{1}H NMR spectrum (298 K, CD_2Cl_2)



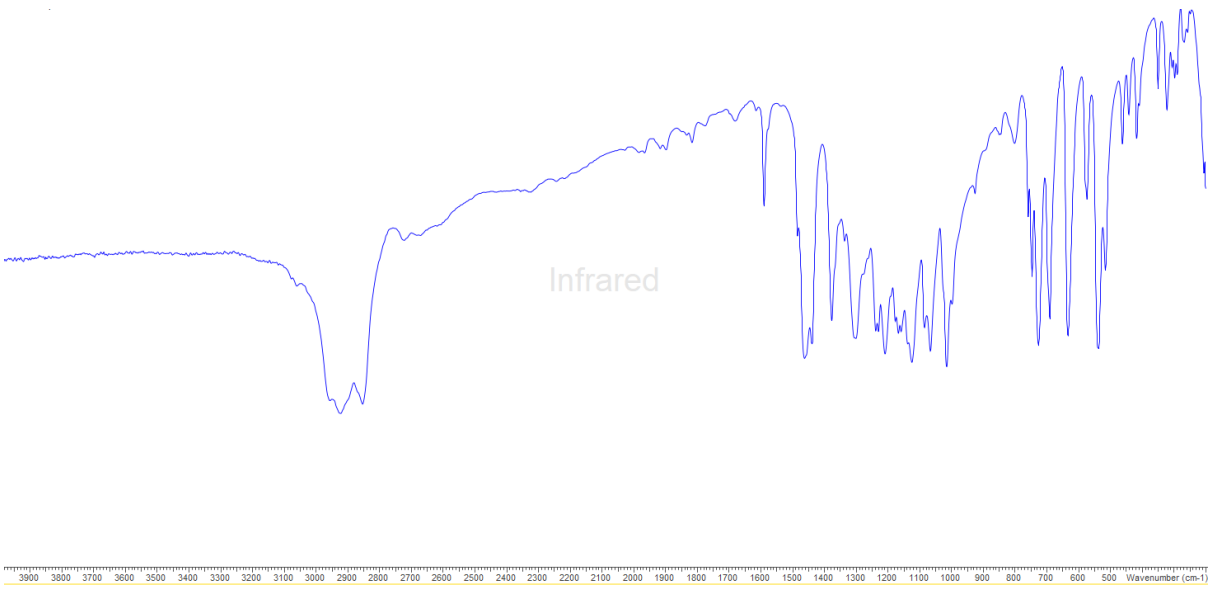
S1.2 - $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S1.3 - $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

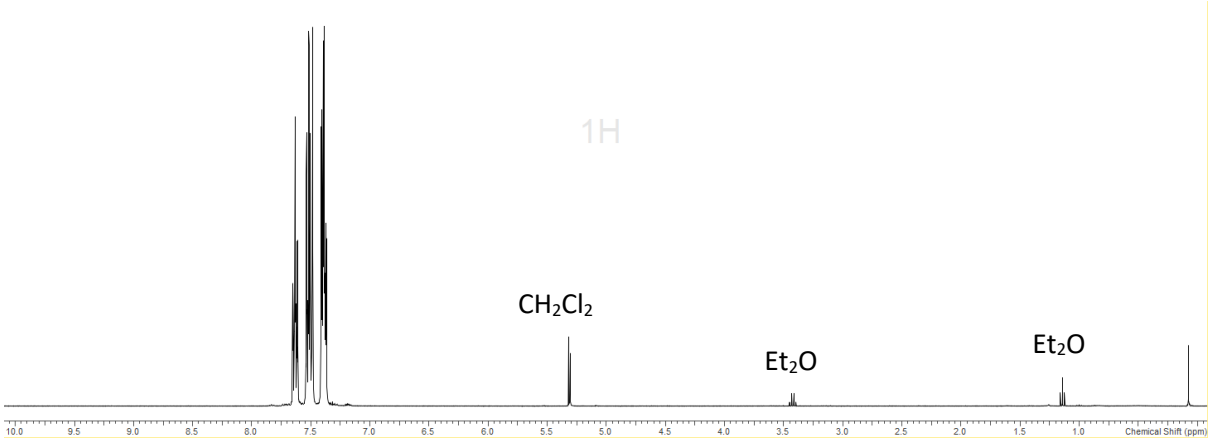


S1.4 - IR spectrum NMR spectrum (Nujol)

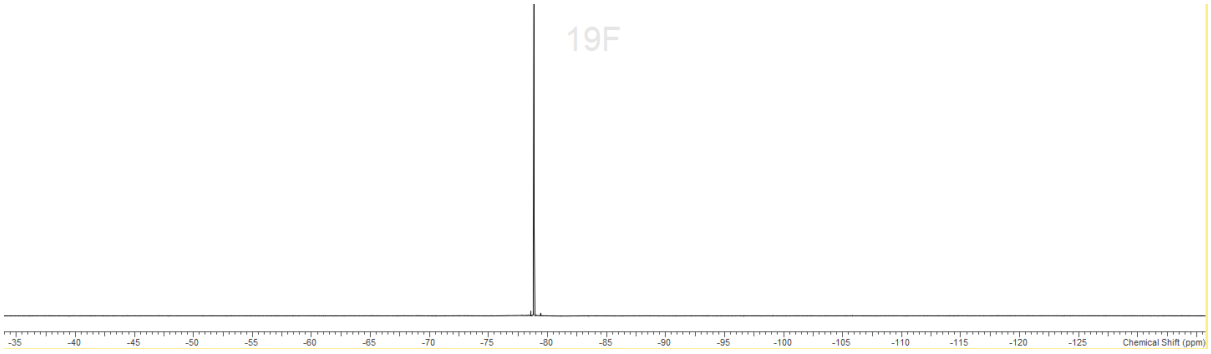


S2.0 - $[Sn(OTf)(OPPh_3)_3][OTf]$

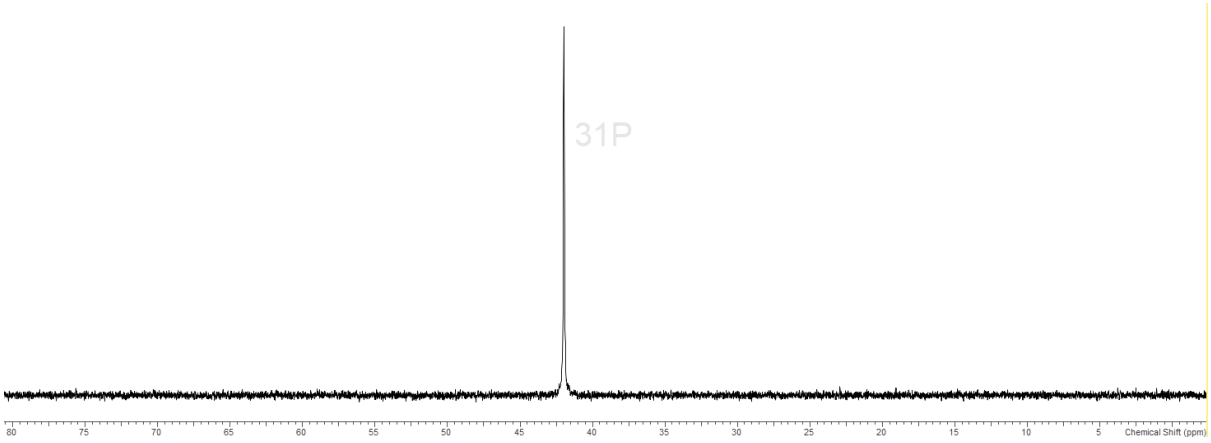
S2.1 - ^{1}H NMR spectrum (298 K, CD_2Cl_2)



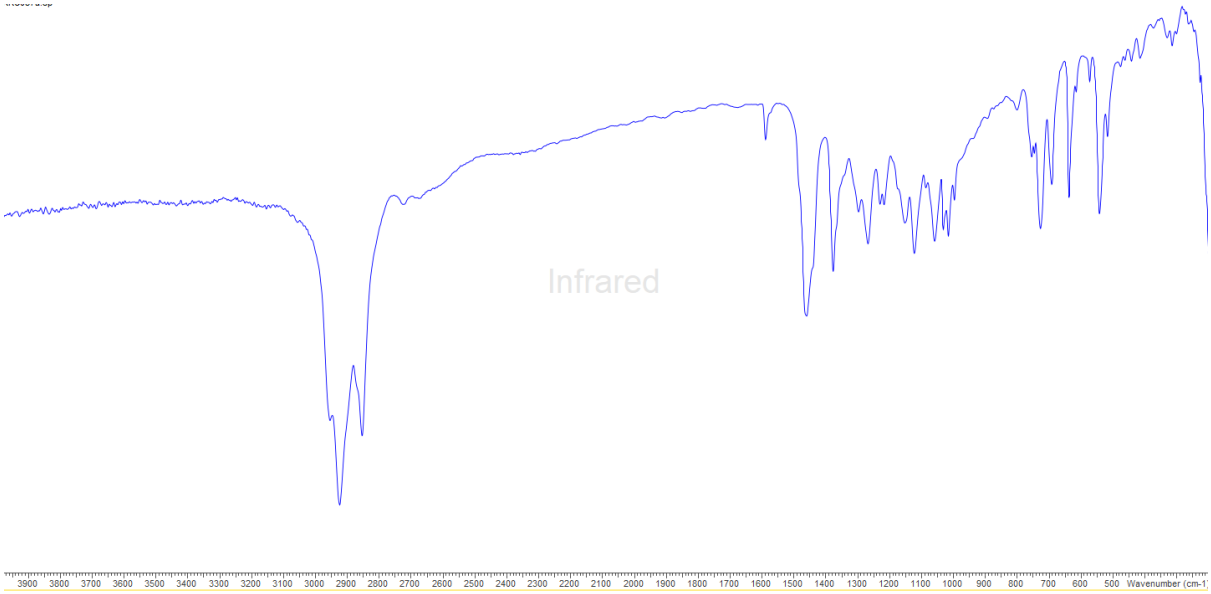
S2.2 - $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S2.3 - $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

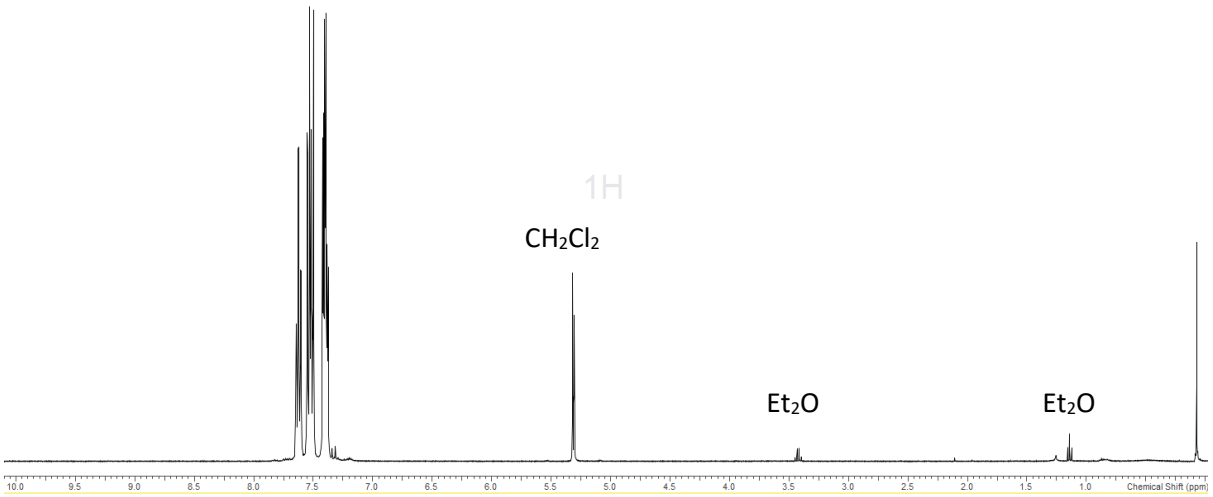


S2.4 - IR spectrum (Nujol)

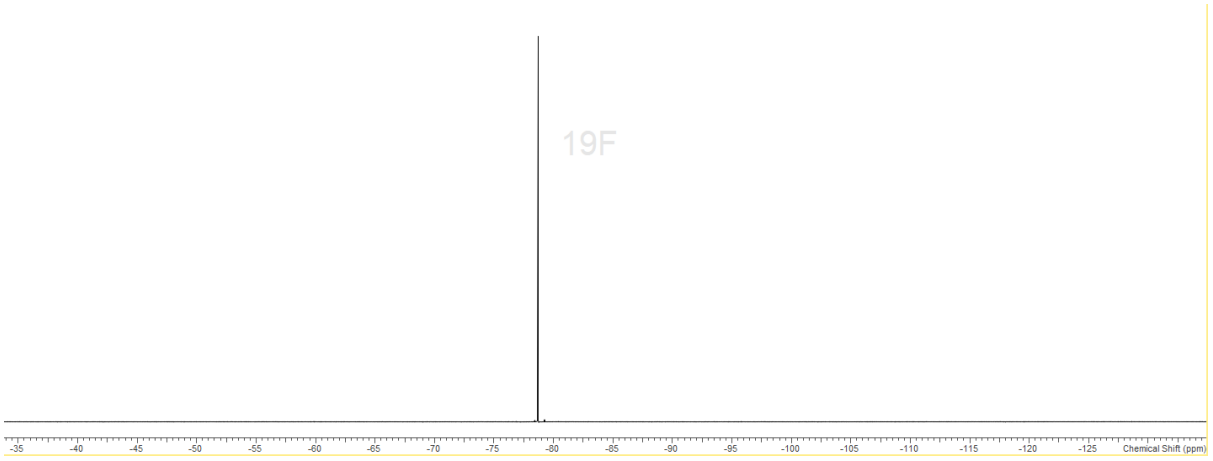


S3.0 - $[Sn(OPPh_3)_4][OTf]_2$

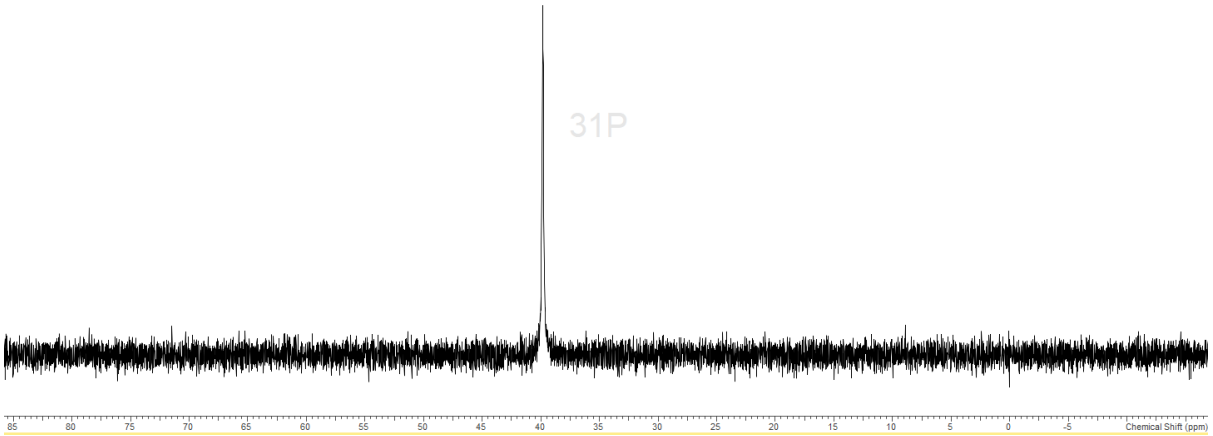
S3.1 - ^{1}H NMR spectrum (298 K, CD_2Cl_2)



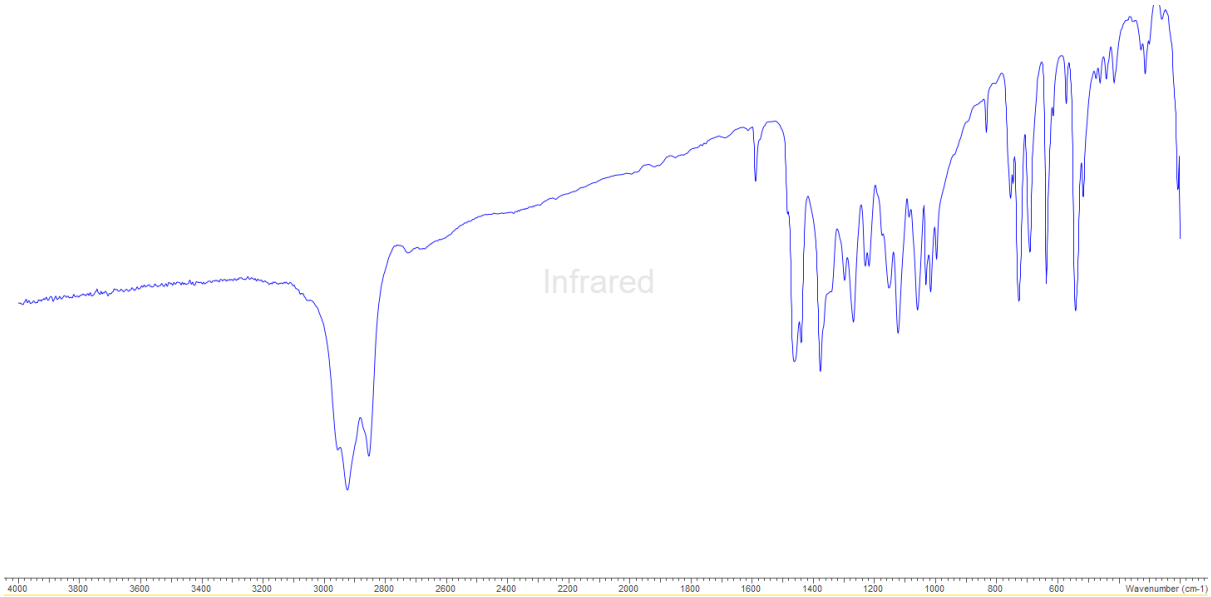
S3.2 - $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S3.3 - $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

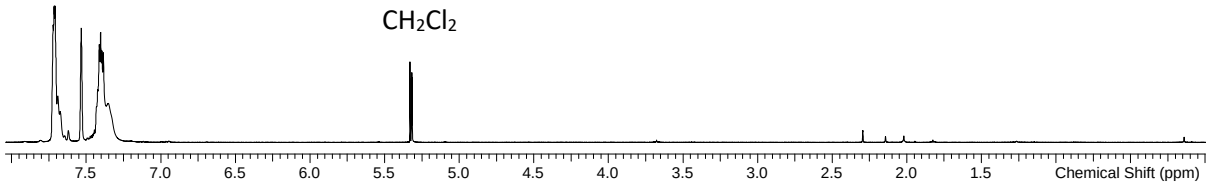


S3.4 – IR spectrum (Nujol)

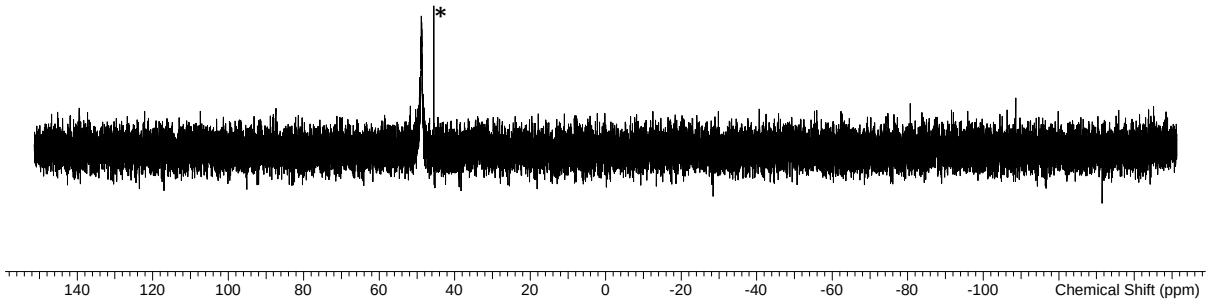


S4.0 $[Sn(OPPh_3)_3][BAr^F]_2$

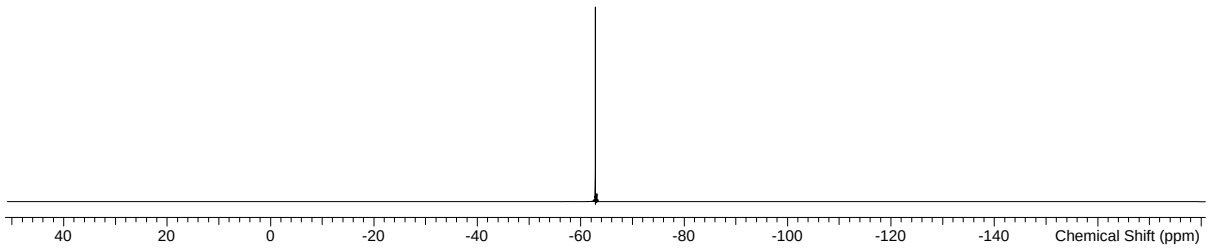
S4.1 ^1H NMR spectrum (298 K, CD_2Cl_2)



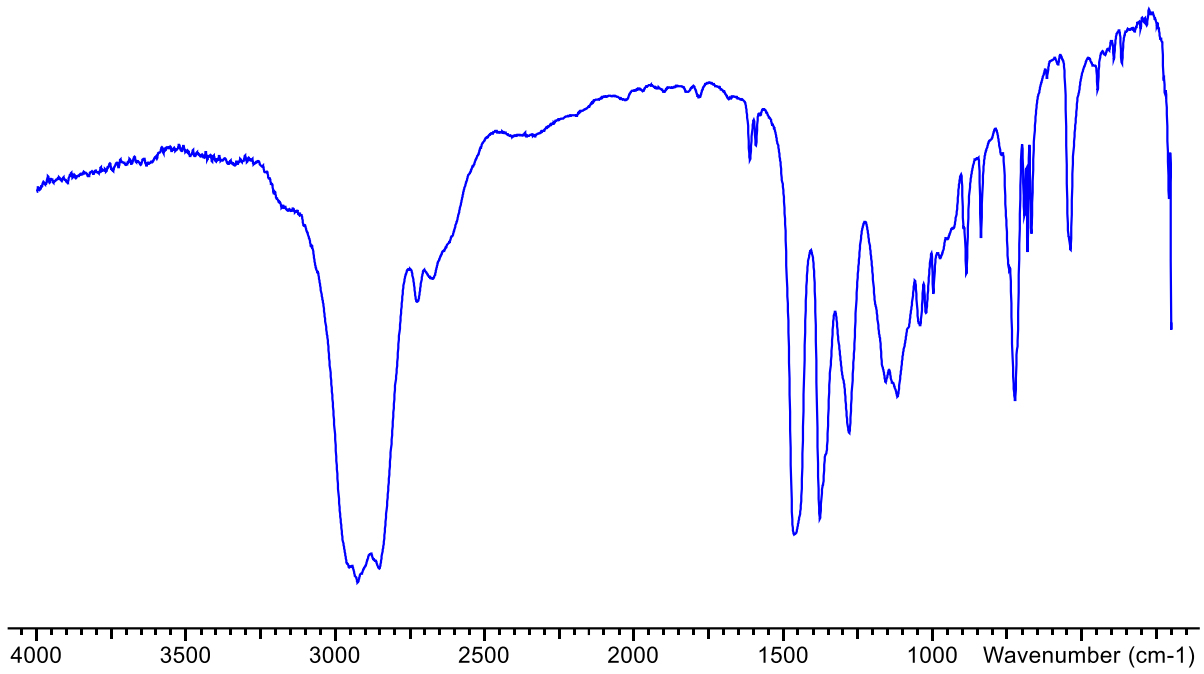
S4.2 $^{31}P\{^1H\}$ NMR spectrum (298 K, CD_2Cl_2) (* A very minor unknown impurity)



S4.3 $^{19}F\{^1H\}$ NMR spectrum (298 K, CD_2Cl_2)

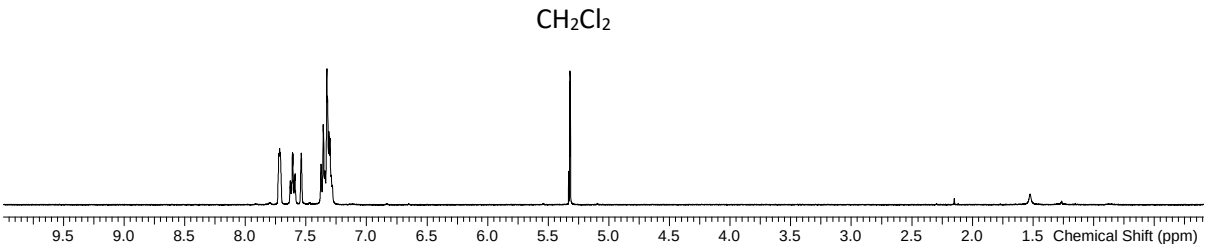


S4.4 – IR spectrum (Nujol)

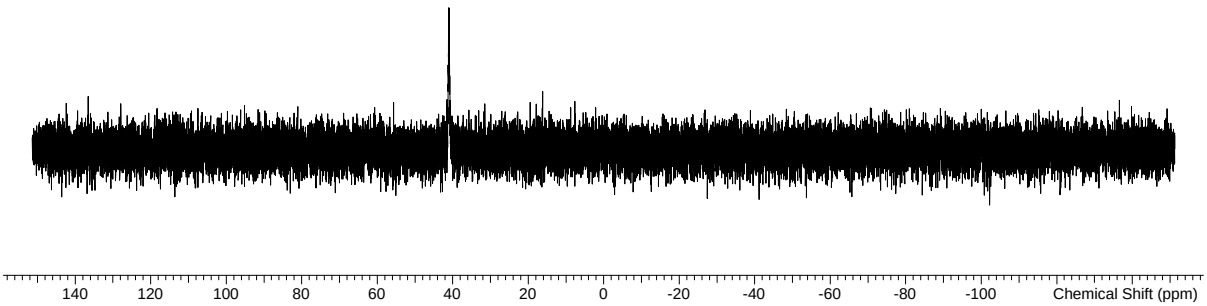


S5.0 $[Sn(OPPh_3)_4][BAr^F]_2$

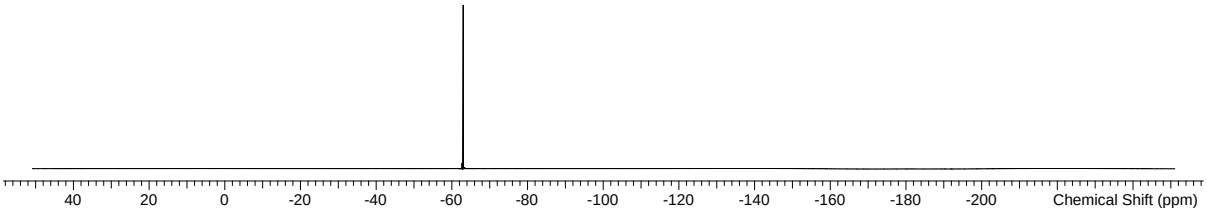
S5.1 ^1H NMR spectrum (298 K, CD_2Cl_2)



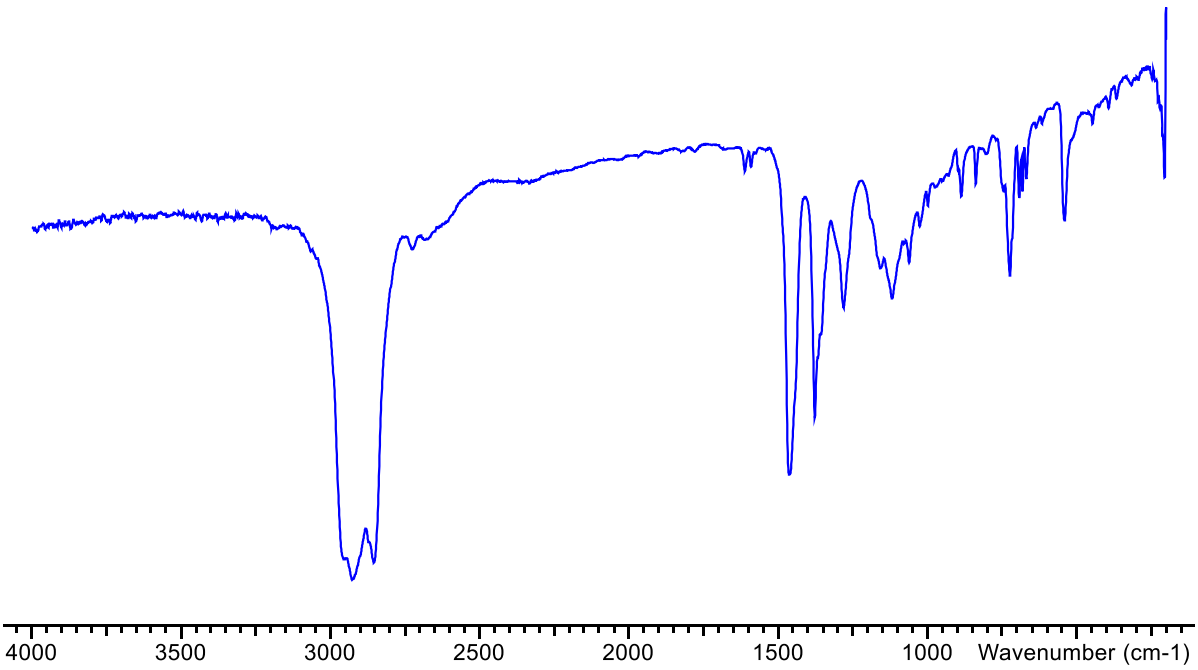
S5.2 $^{31}P\{^1H\}$ NMR spectrum (298 K, CD_2Cl_2)



S5.3 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

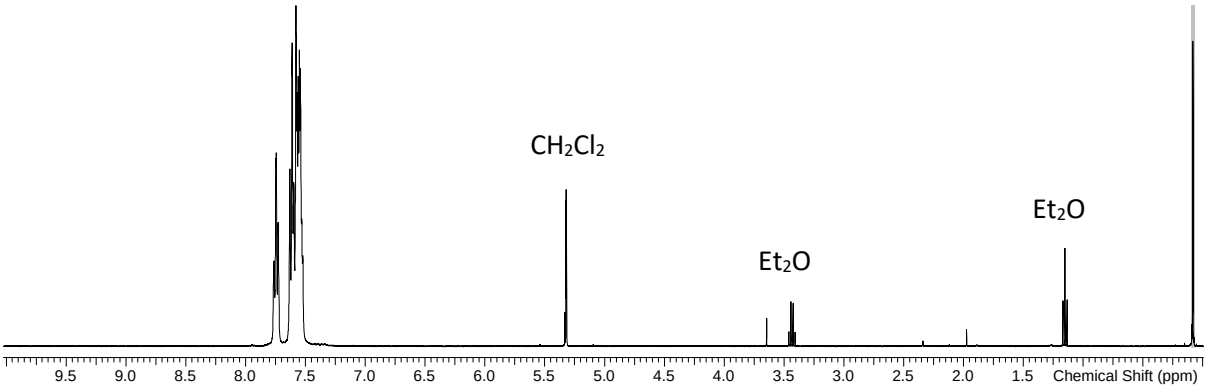


S5.4 – IR spectrum (Nujol)

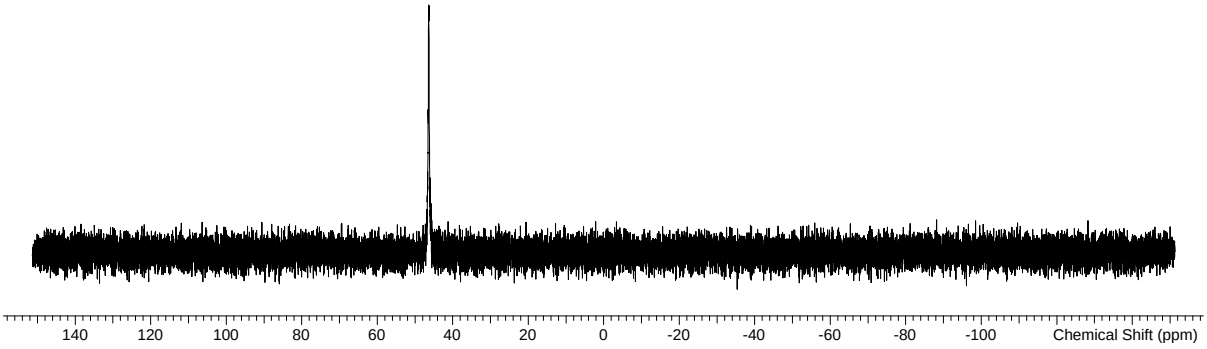


S6.0 $[Ge(OTf)_2(OPPh_3)_2]$

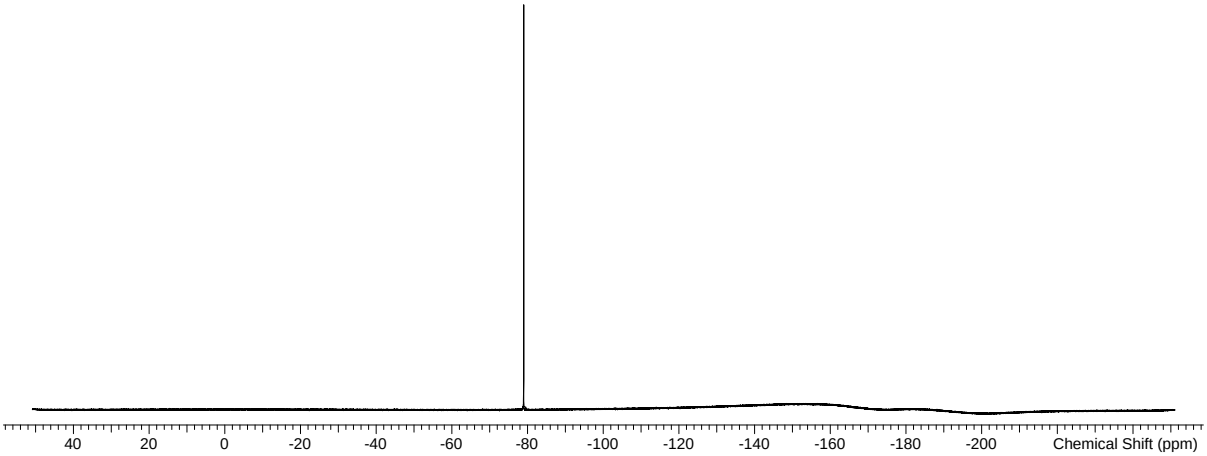
S6.1 ^{1}H NMR spectrum (298 K, CD_2Cl_2)



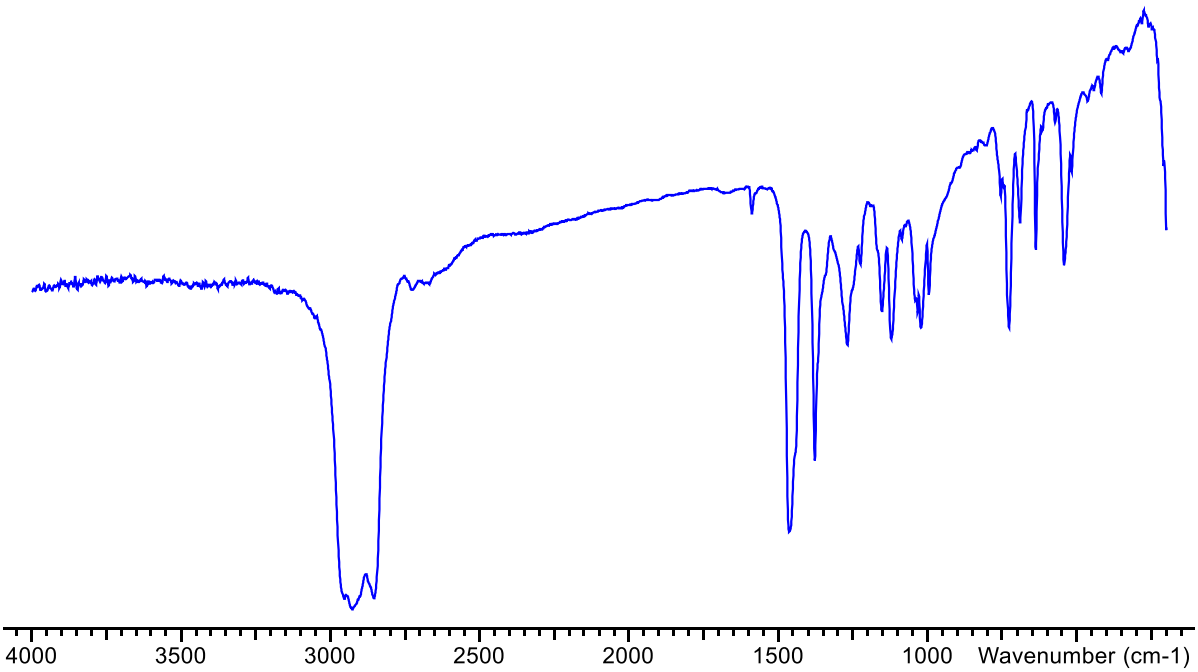
S6.2 $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S6.3 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

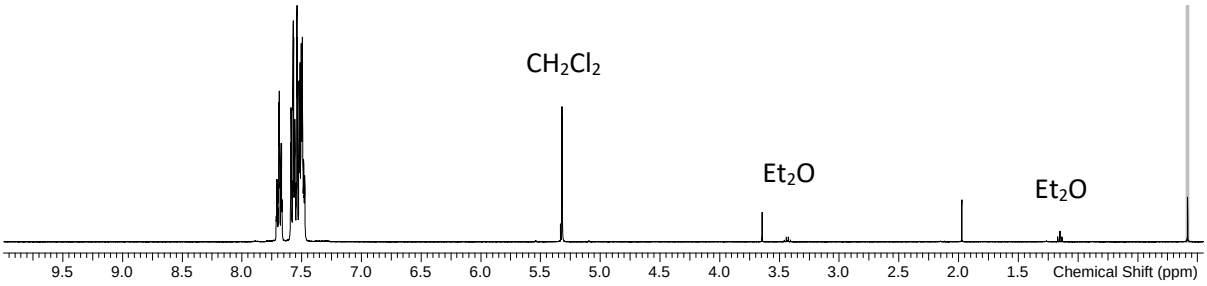


S6.4 – IR spectrum (Nujol)

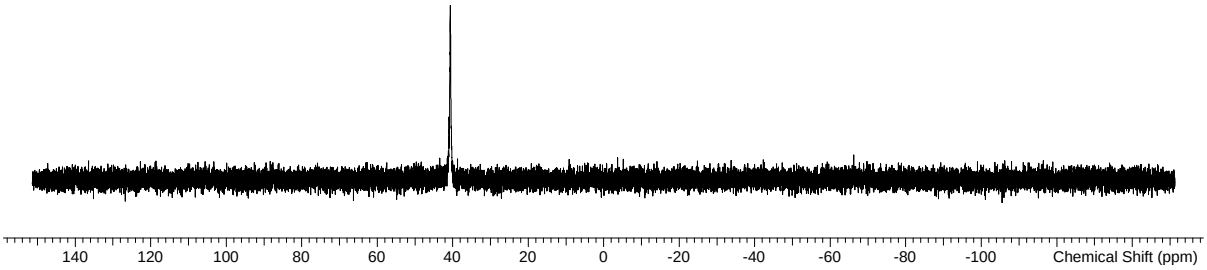


S7.0 $[Ge(OPPh_3)_3][OTf]_2$

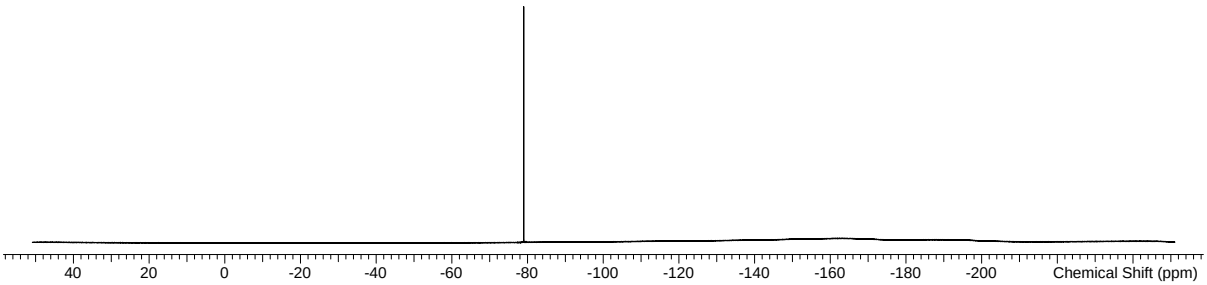
S7.1 ^{1}H NMR spectrum (298 K, CD_2Cl_2)



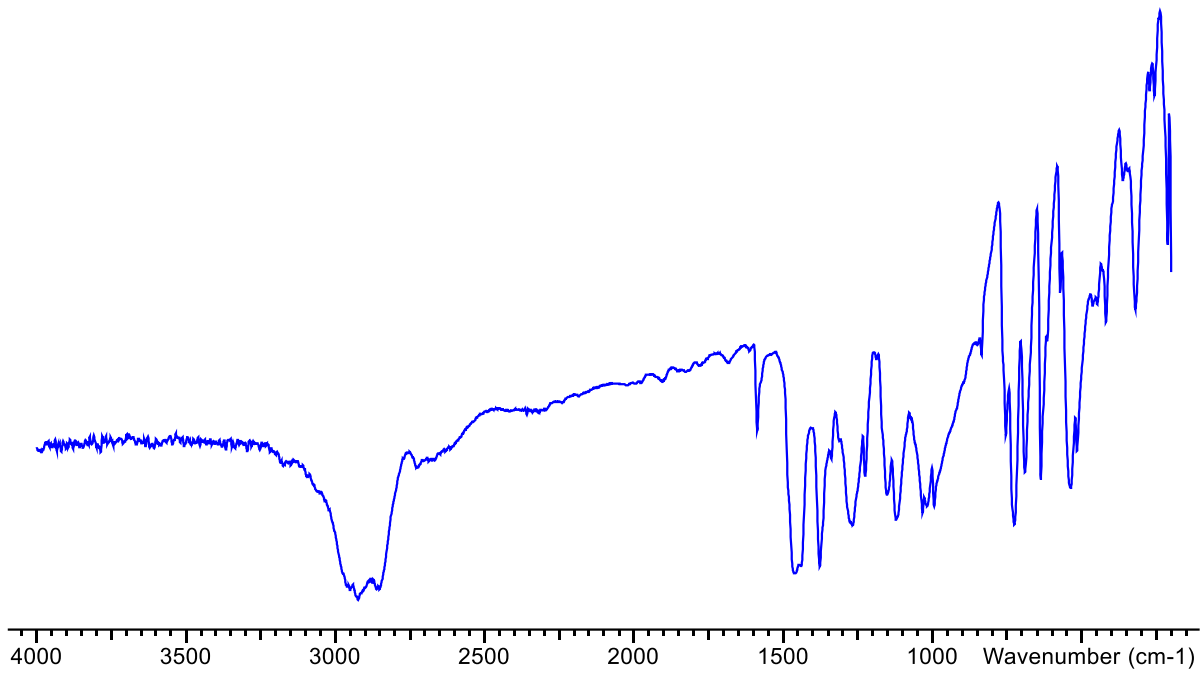
S7.2 $^{31}P\{^{1}H\}$ (298 K, CD_2Cl_2)



S7.3 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

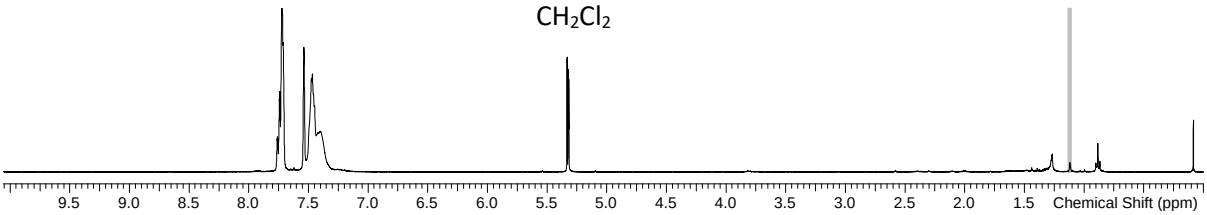


S7.4 – IR spectrum (Nujol)

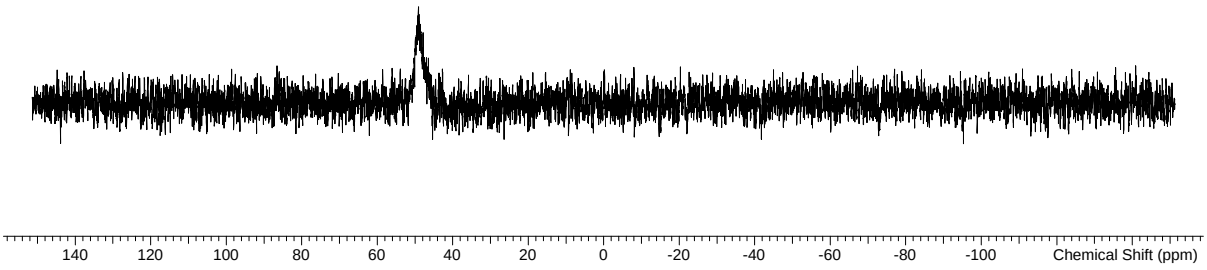


S8.0 $[Ge(OPPh_3)_3][BAr^F]_2$

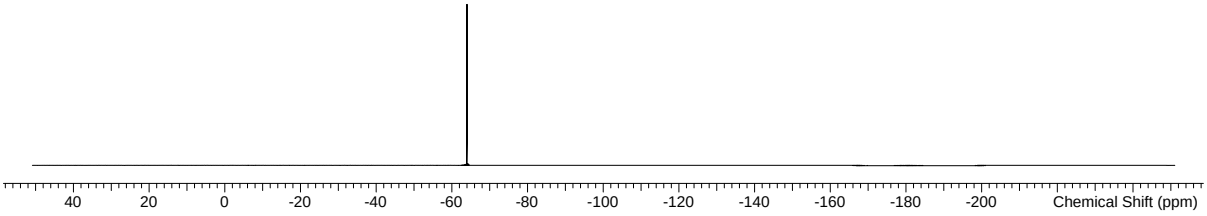
S8.1 ^1H NMR spectrum (298 K, CD_2Cl_2)



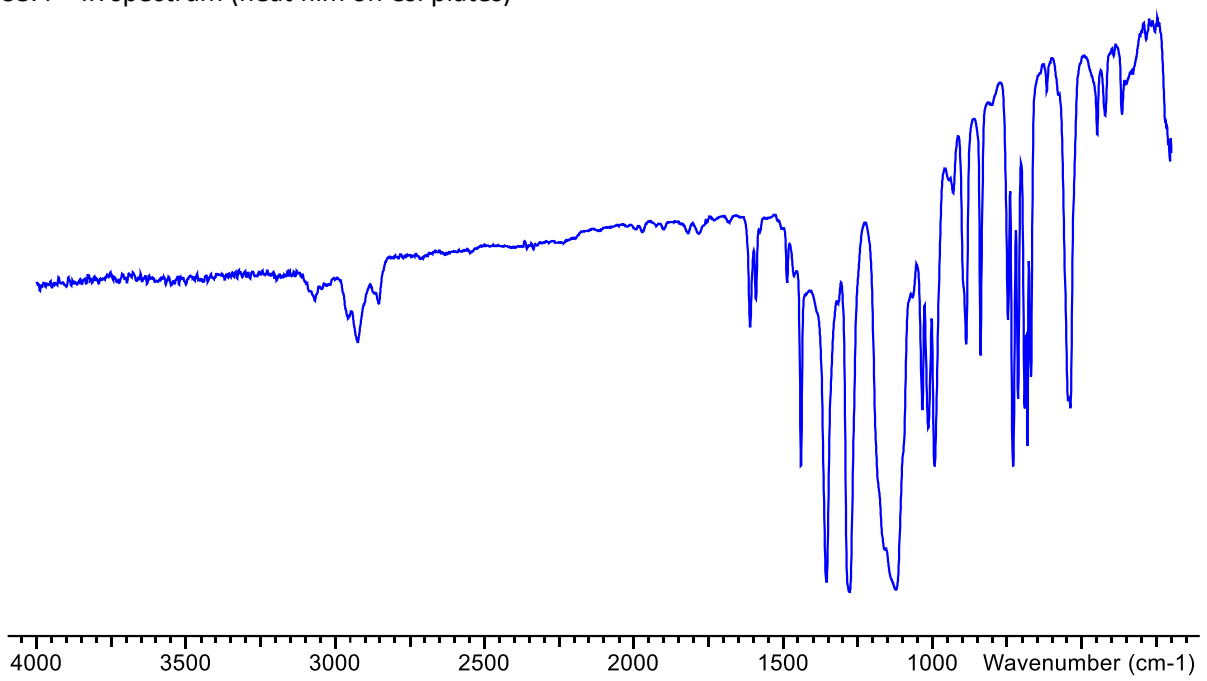
S8.2 $^{31}P\{^1H\}$ NMR spectrum (298 K, CD_2Cl_2)



S8.3 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

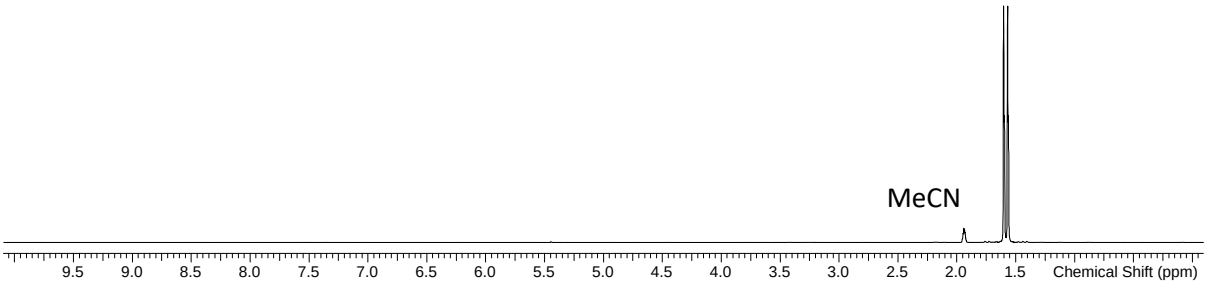


S8.4 – IR spectrum (neat film on CsI plates)

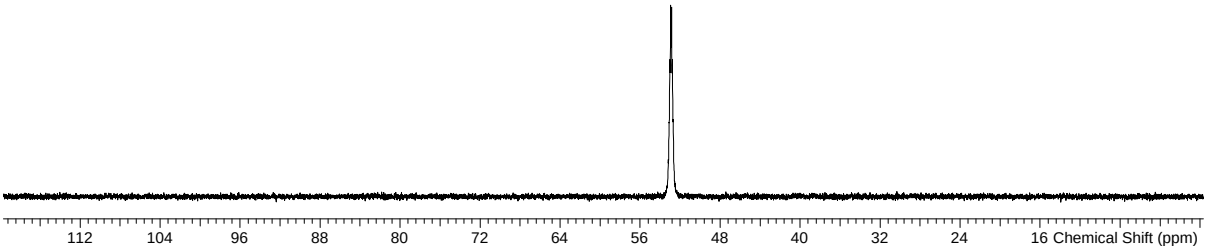


S9.0 $[Pb(OPMe_3)_4][OTf]_2$

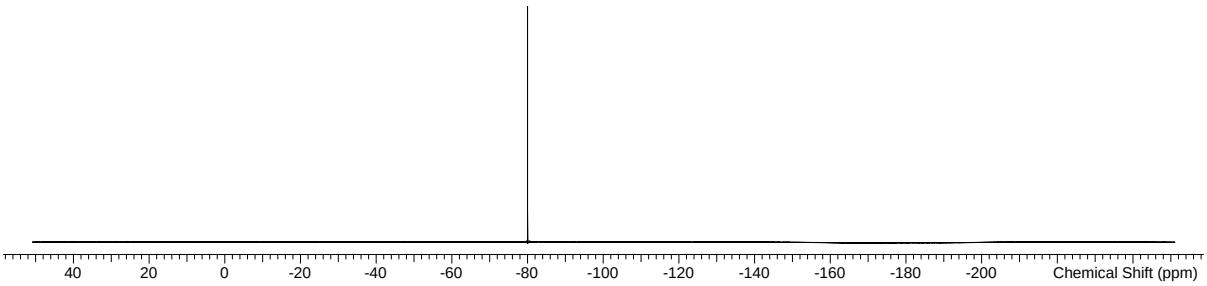
S9.1 ^{1}H NMR spectrum (298 K, d-MeCN)



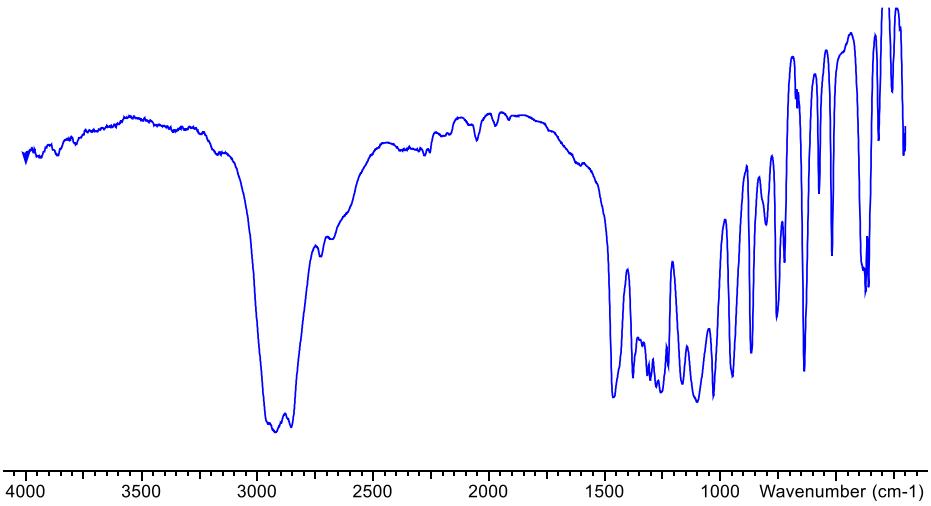
S9.2 $^{31}P\{^{1}H\}$ NMR spectrum (298 K, d-MeCN)



S9.3 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, d-MeCN)

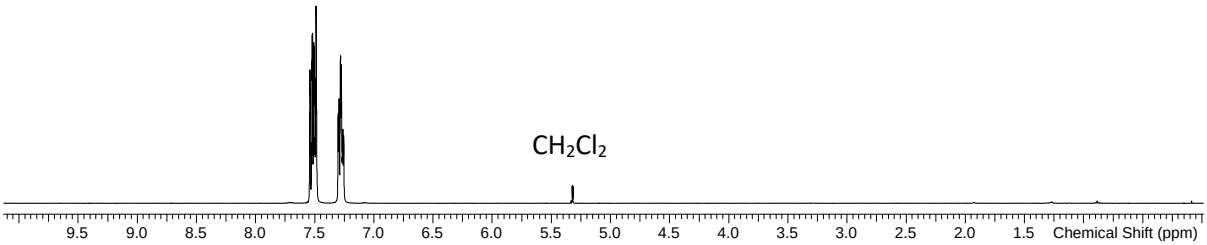


S9.4 – IR spectrum (Nujol)

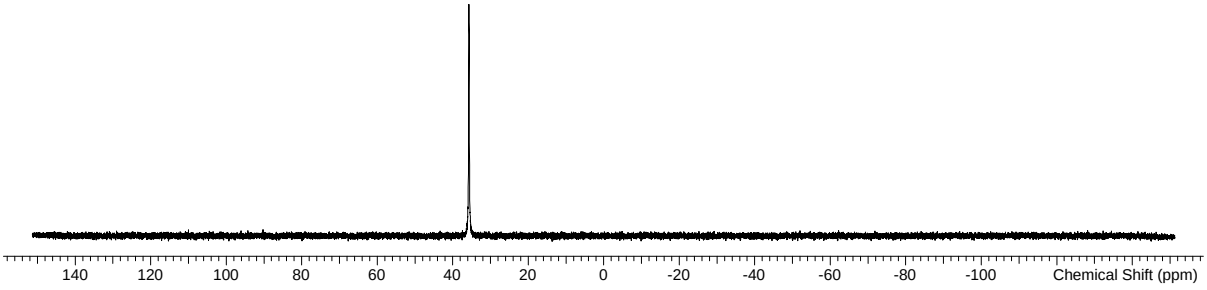


S10.0 $[Pb(OTf)_2(OPPh_3)_4]$

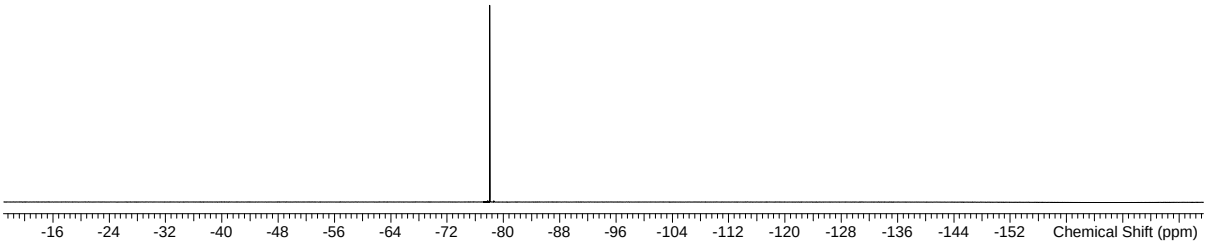
S10.1 ^{1}H NMR spectrum (298 K, CD_2Cl_2)



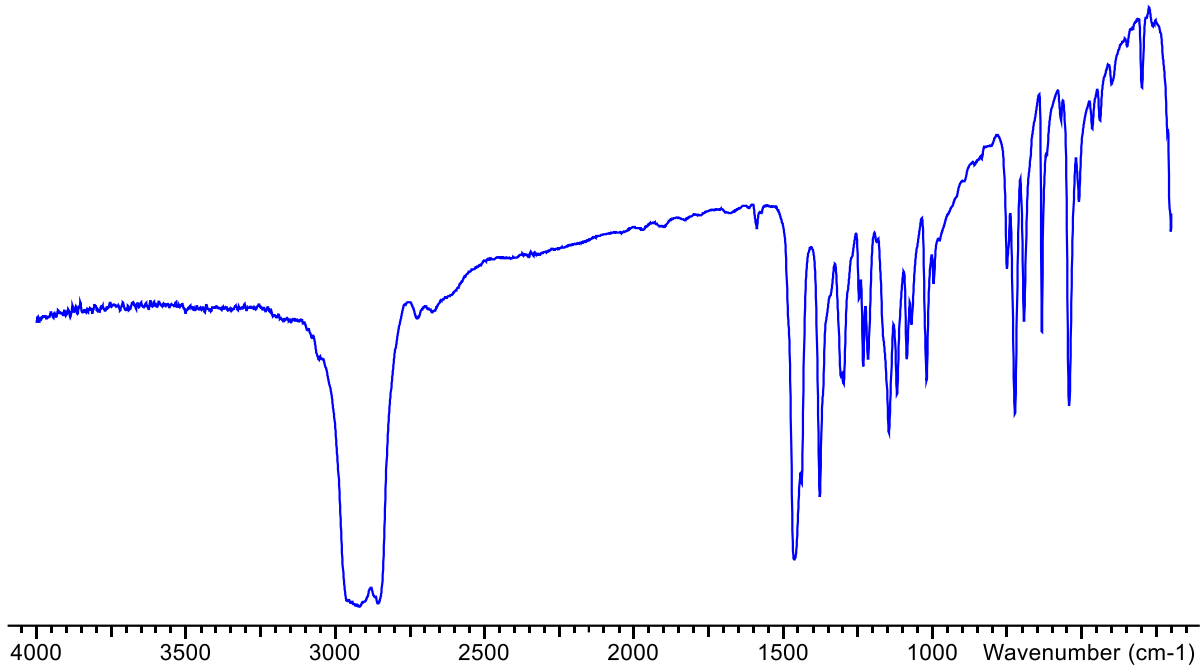
S10.2 $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S10.3 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

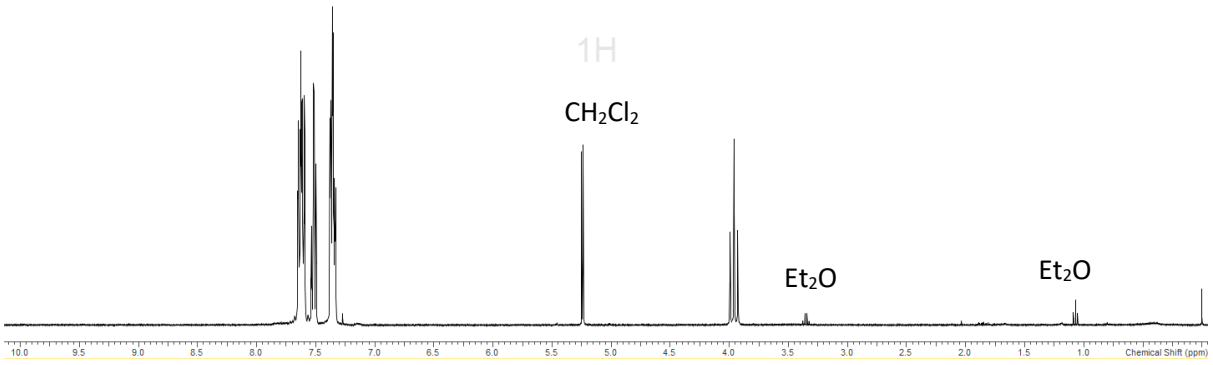


S10.4 – IR spectrum (Nujol)

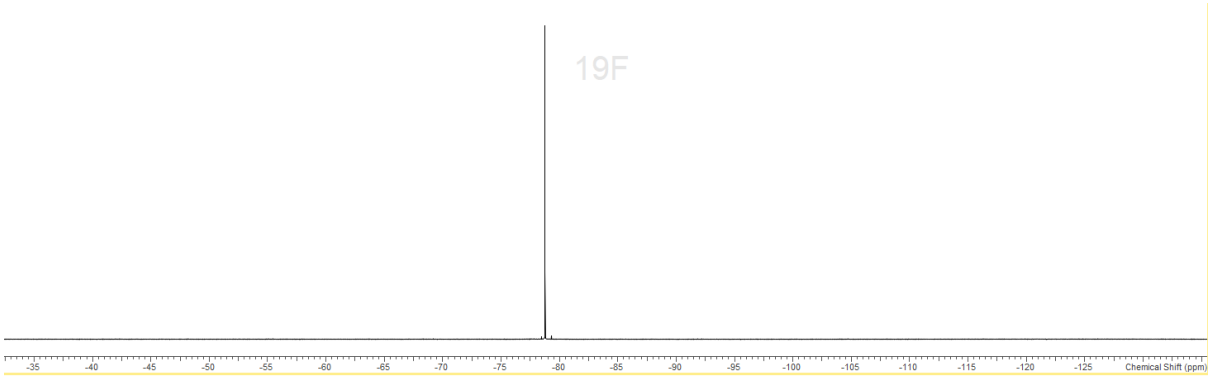


S11.0 [$Sn(OTf)_2(dppmO_2)$]

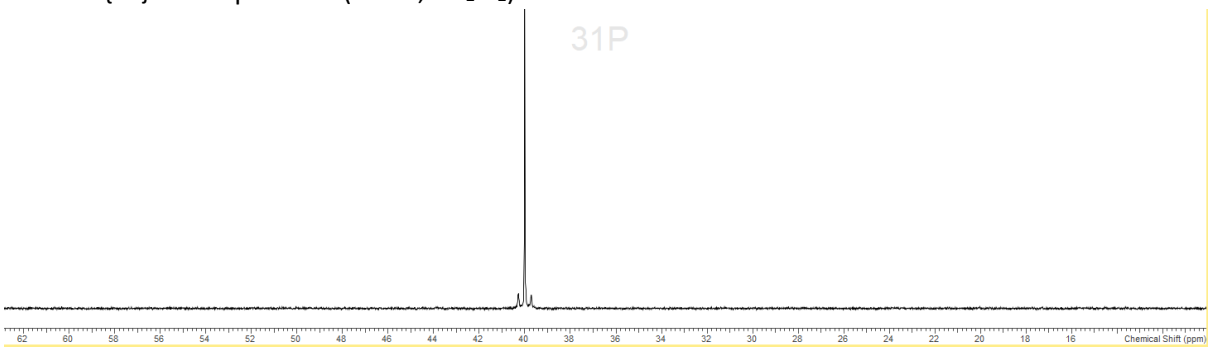
11.1 ^1H NMR spectrum (298 K, CD_2Cl_2)



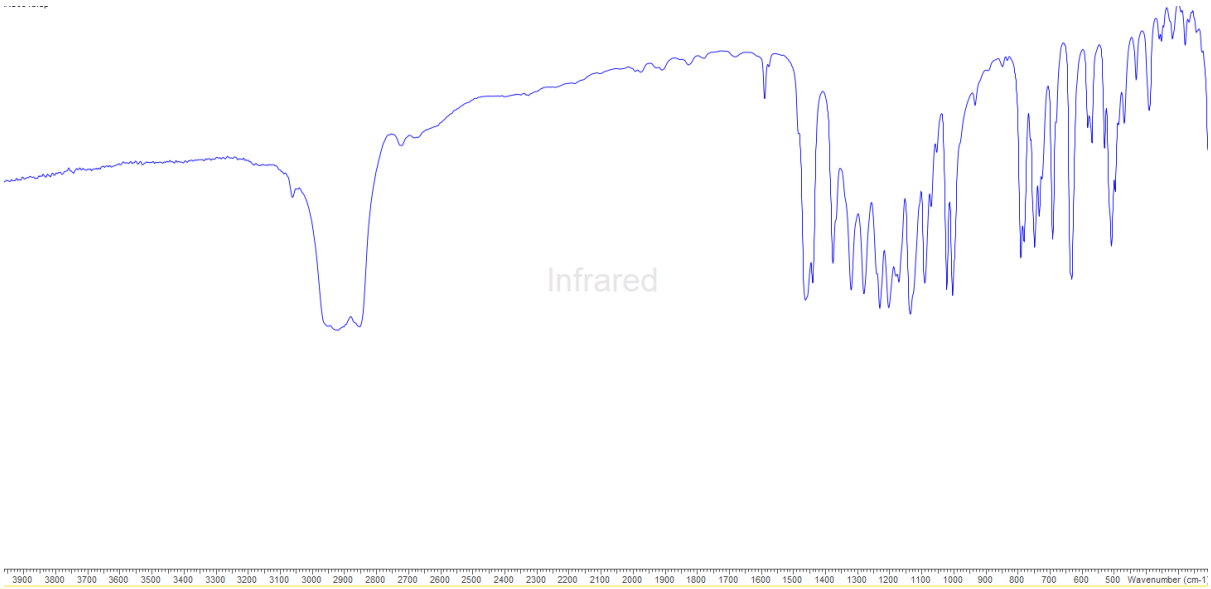
11.2 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



11.3 $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

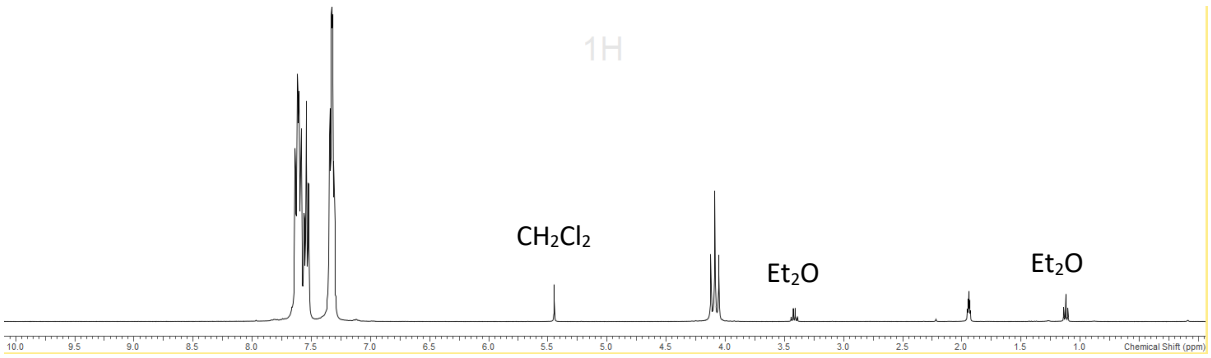


11.4 IR spectrum (Nujol)

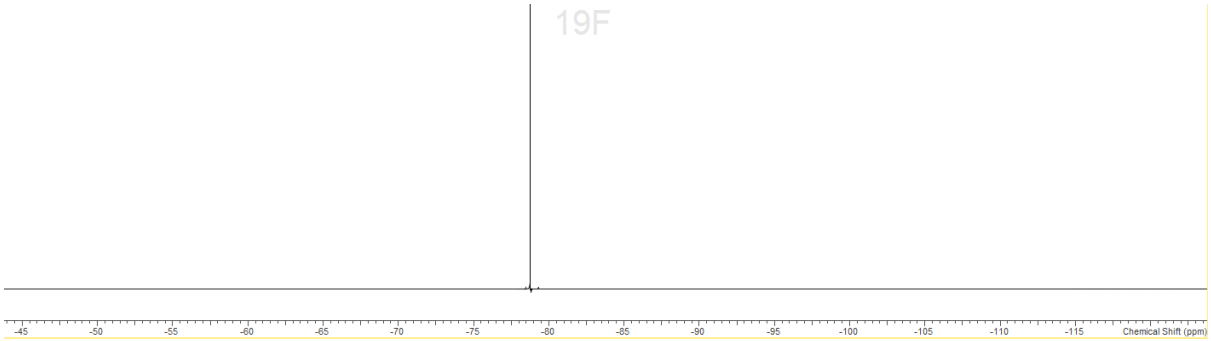


S12.0 $[Sn(OTf)(dppmO_2)_2][OTf]$

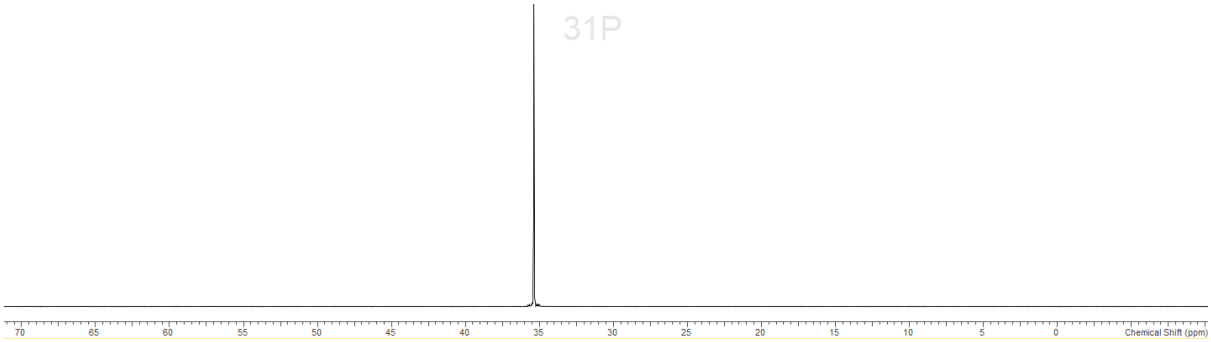
S12.1 ^{1}H NMR spectrum (298 K, CH_2Cl_2)



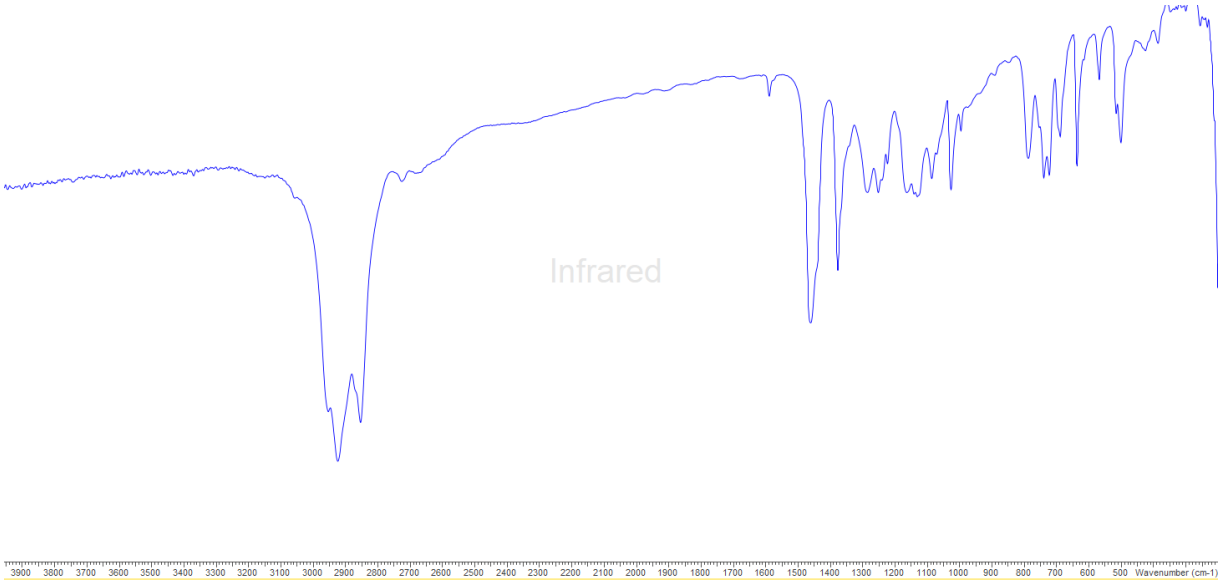
S12.2 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



12.3 $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

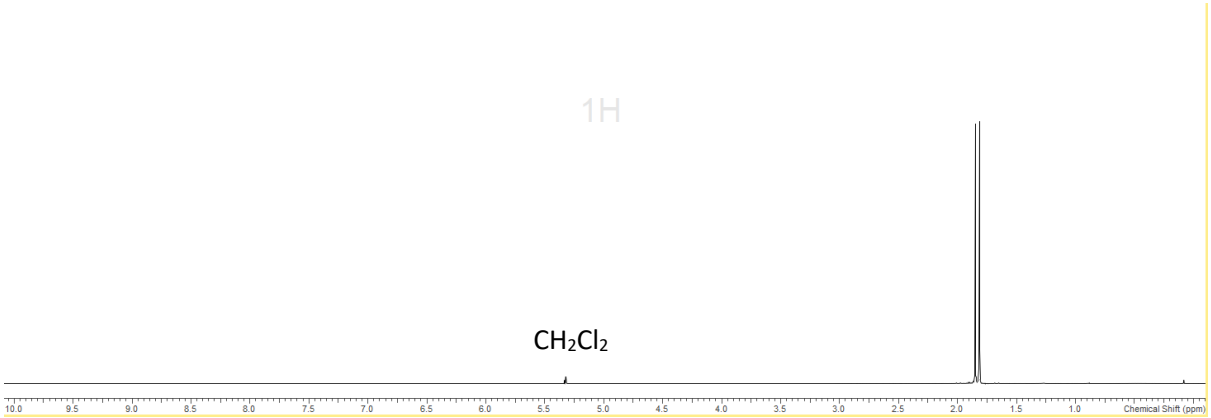


12.4 IR spectrum (Nujol)

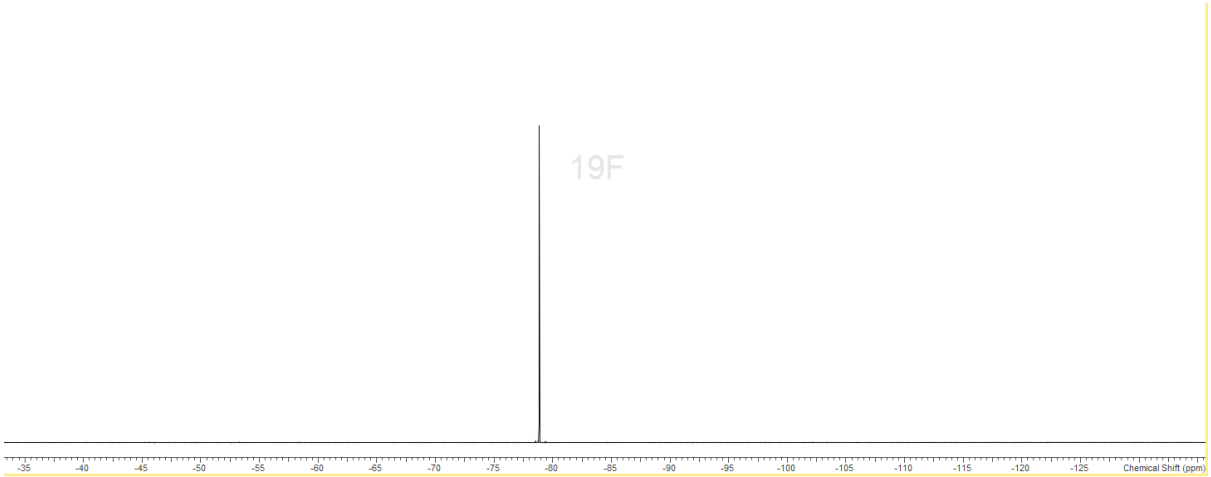


S13 $[Sn(OTf)_2(OPMe_3)_2]$

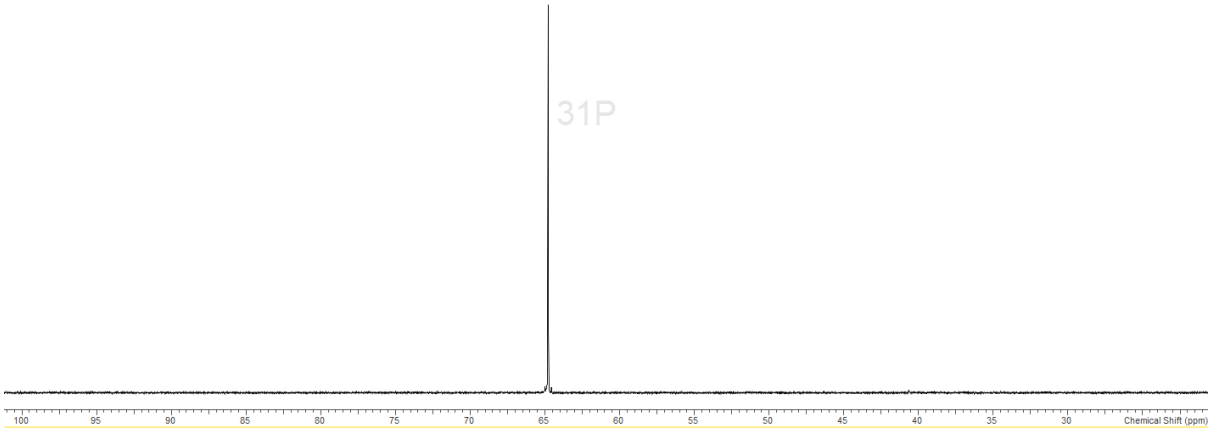
S13.1 ^{1}H NMR spectrum (298 K, CD_2Cl_2)



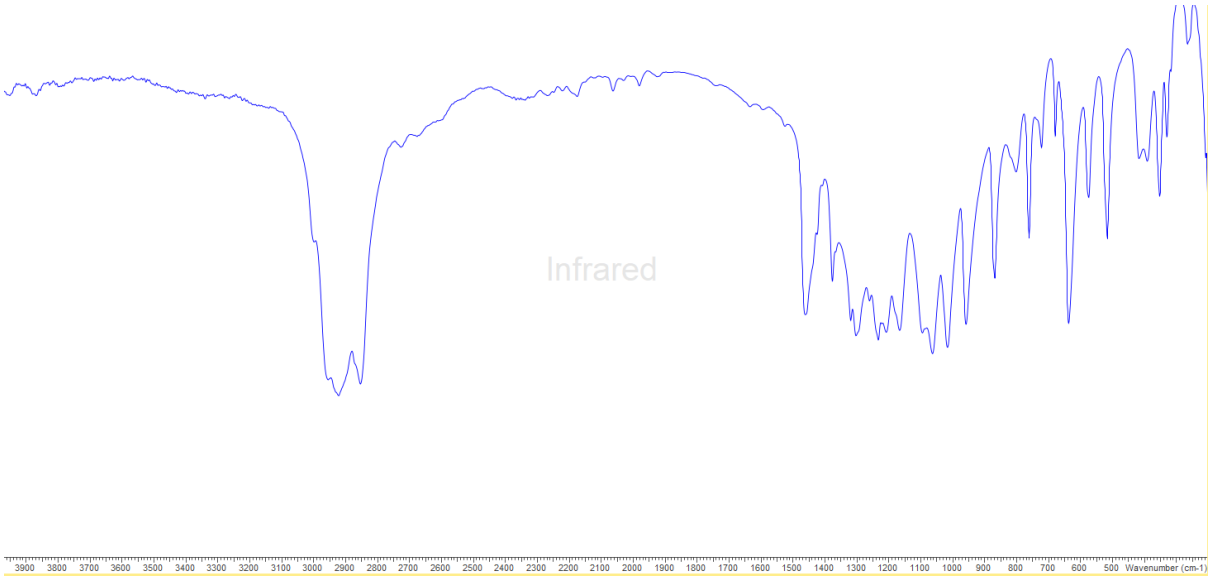
S13.2 $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S13.3 $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



S13.4 IR spectrum (Nujol)



S14 Disorder in crystal structure of $[Pb(OTf)_2(OPPh_3)_4]$

$[Pb(OTf)_2(OPPh_3)_4]$

For the triflate ligands above the lead (yellow and purple) the oxygen contact is displaced from the symmetry axis so none of the triflate atoms are coincident, but the triflates interpenetrate. For the triflate ligands below the lead (orange and magenta) the contact oxygen falls along the symmetry axis so is shared between both triflates (as does the carbon of the triflate) and again the triflates interpenetrate.

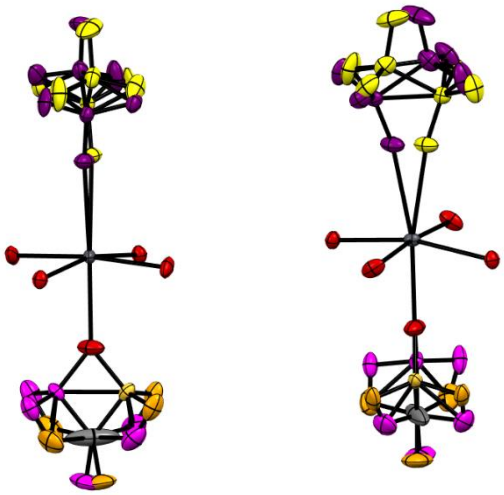
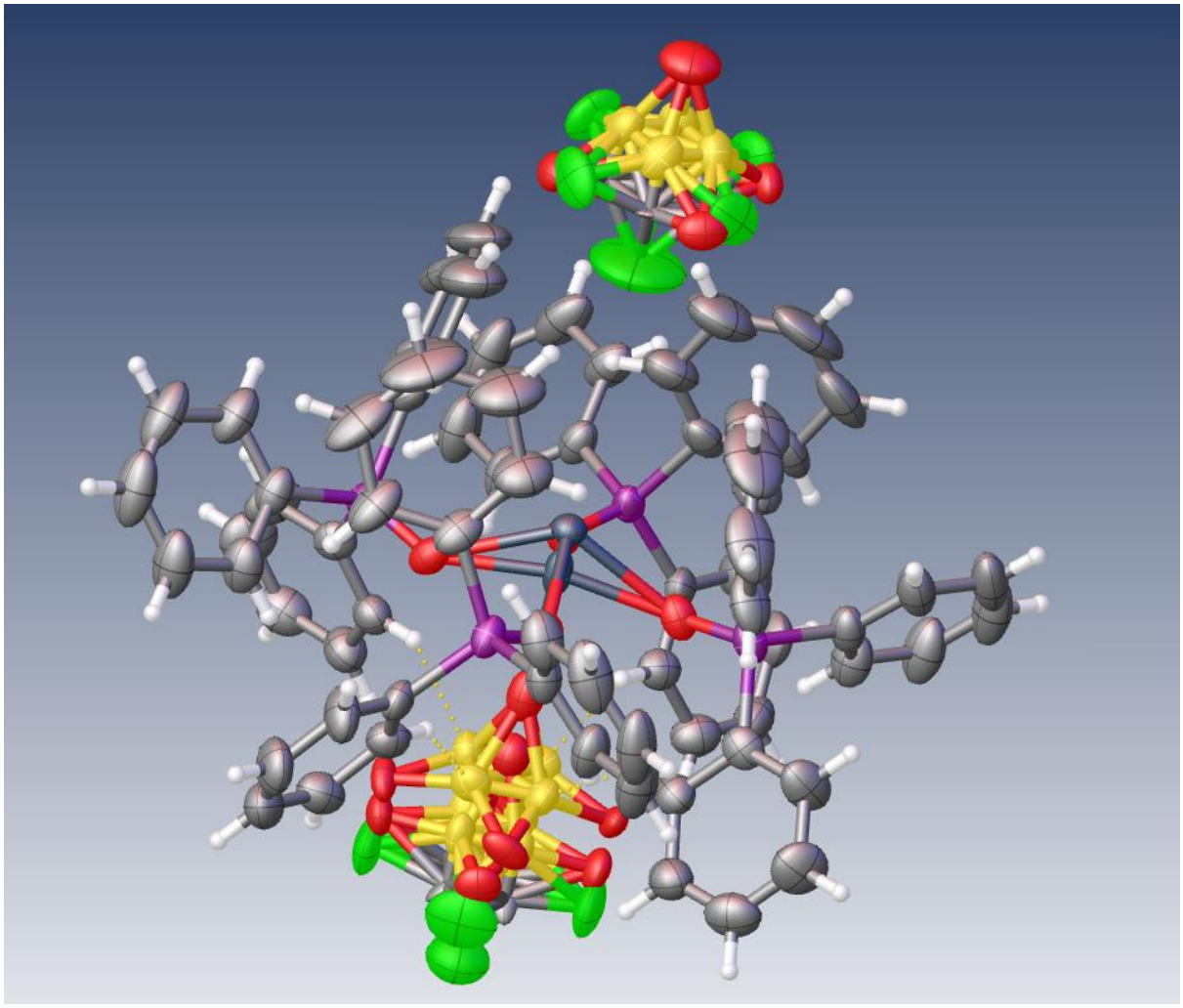


Figure S14 – The disorder of the triflate anions in $[Pb(OPPh_3)_4(OTf)_2]$ with each triflate in a different colour except where they share an atom then the regular atom colour is used; only the O atoms of $OPPh_3$ are shown.

S15 Disorder in the crystal structure of $[Sn(OPPh_3)_4][OTf]_2$

In the structure one set triflates have occupancies that sum to 100%, this set is split over a four-fold axis (seen at the top of Figure S15), So that each triflate has an occupancy of 0.25, due to symmetry one oxygen and one fluorine atom is shared by all triflates in this set (so have an occupancy of 1), the other oxygens and fluorines are shared by adjacent triflates (so have an occupancy of 0.5). The sulphur atoms and carbon atoms are not shared so have an occupancy of 0.25.

For the 80% component the position of all the triflate atoms have been located and are split in a similar way to the triflate described in the last paragraph. For the 20% component the positions of coordinating oxygen (occupancy 0.2), the non-coordinating oxygens (occupancy 0.1), the sulphurs of the triflate (occupancy 0.05) and the shared fluorine (occupancy 0.2) have been located. We were unable to locate the carbon atoms (occupancy 0.05) and the remaining fluorine atoms (occupancy 0.1) due to them not being present above the background in the difference map. There is also unmodeled hexane solvent which has been masked (described in the cif).



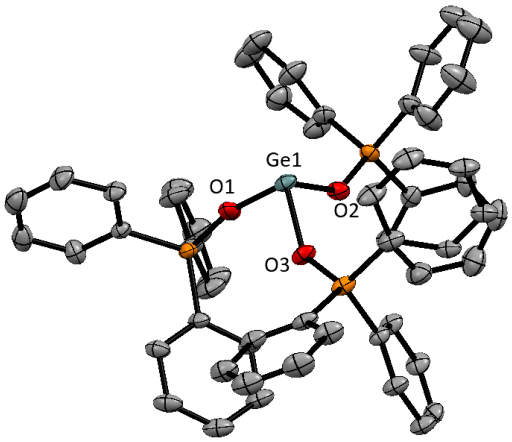


Figure S16 - Crystal structure of $[Ge(OPPh_3)_3][BAr^F]_2$ (**11**) showing the atom numbering scheme. Ellipsoids are shown at 50% probability level with H-atoms and discrete anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1-O1 = 1.881(5), Ge1-O2 = 1.920(4), Ge1-O3 = 1.908(4), O1-Ge1-O2 = 90.9(2), O1-Ge1-O3 = 90.9(2), O2-Ge1-O3 = 89.22(18)

S17 X-ray crystallographic parameters[a]

Compound	$[Sn(OPPh_3)_2(OTf)_2]$	$[Sn(OPPh_3)_3][OTf]_2$	$[Sn(OPPh_3)_4][OTf]_2$
Formula	$C_{38}H_{30}F_6O_8P_2S_2Sn$	$C_{56}H_{45}F_6O_9P_2S_2Sn$	$C_{80}H_{74}F_{5.6}O_{10}P_4S_2Sn$
M	973.437	1251.64	1608.48
Crystal system	Monoclinic	Triclinic	Tetragonal
Space group (no.)	$P2_1/n$ (14)	P-1 (2)	P4/ncc (130)
a/Å	10.8678(2)	11.75890(10)	13.6421(2)
b/Å	20.7093(3)	12.5952(2)	13.6421(2)
c/Å	17.6068(3)	19.6439(3)	39.1403(10)
α/°	90	107.9820(10)	90
β/°	106.485(2)	97.8220(10)	90
γ/°	90	97.6570(10)	90
U	3800.17(12)	2693.68(7)	7284.3(3)
Z	4	2	4
μ(Mo-K_α) /mm^{-1}	0.949	0.719	0.571
F(000)	1953	1268	3306
Total number of reflections	29496	36483	81243
R_{int}	0.037	0.030	0.043
Unique reflections	9790	10613	6164
No. of parameters, no. of restraints	514, 0	725, 7	295, 0
GOF	0.858	0.926	1.085
R_1, wR_2 $[I>2\sigma(I)]$[b]	0.036, 0.108	0.028, 0.062	0.068, 0.161
R_1, wR_2 (all data)	0.046, 0.123	0.036, 0.065	0.082, 0.167

Compound	$[Sn(OPMe_3)_2][OTf]_2$	$[Sn(dppmO_2)][OTf]_2$	$[Sn(dppmO_2)_2][OTf]_2$
Formula	$C_8H_{18}F_6O_8P_2S_2Sn$	$C_{27}H_{22}F_6O_8P_2S_2Sn$	$C_{52}H_{44}F_6O_8P_2S_2Sn$
M	600.97	833.19	1249.56
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group (no.)	$P2_1/c$ (14)	Pbca (61)	$P2_1/c$ (14)
a/Å	13.19910(10)	15.8728(2)	11.33730(10)
b/Å	11.3597(2)	17.9938(2)	28.1908(3)
c/Å	14.1089(2)	21.7167(2)	18.7751(2)
α/°	90	90	90
β/°	94.1720(10)	90	96.5430(10)
γ/°	90	90	90
U	2109.85(5)	6202.55(12)	5961.58(10)
Z	4	8	4
μ(Mo-K_α) /mm^{-1}	1.643	1.146	0.676
F(000)	1184	3312	2528
Total number of reflections	38142	111784	46260
R_{int}	0.026	0.065	0.038
Unique reflections	5446	9948	15371
No. of parameters, no. of restraints	250, 0	415, 0	676, 0
GOF	1.050	1.024	1.043
R_1, wR_2 $[I>2\sigma(I)]^b$	0.018, 0.044	0.025, 0.059	0.041, 0.094
R_1, wR_2 (all data)	0.019, 0.045	0.029, 0.060	0.053. 0.101

Compound	$[Pb(OPMe_3)_4][OTf]_2 \cdot 2CH_2Cl_2$	$[Pb(OPPh_3)_4][OTf]_2$	$[Ge(OPPh_3)_3][OTf]_2$
Formula	$C_{16}H_{40}Cl_4F_6O_{10}P_4PbS_2$	$C_{74}H_{60}F_6O_{10}P_4PbS_2$	$C_{56}H_{45}F_6GeO_9P_2S_2$
M	1043.47	1618.41	1205.54
Crystal system	Trigonal	Monoclinic	Triclinic
Space group (no.)	$P3_2$ (54)	C2/c (15)	P-1 (2)
a/Å	11.76685(12)	20.0852(4)	11.7268(2)
b/Å	11.76685(12)	16.7893(3)	12.4658(3)
c/Å	24.5584(3)	20.0561(3)	19.7335(5)
α/°	90	90	108.137(2)
β/°	90	91.055(2)	97.629(2)
γ/°	120	90	97.743(2)
U	2944.77(7)	6762.1(2)	2669.24(11)
Z	3	4	2
μ(Mo-K_α) /mm^{-1}	4.906	2.729	0.820
F(000)	1536	3248	1232
Total number of reflections	77008	48743	78057
R_{int}	0.054	0.041	0.054
Unique reflections	10133	10548	17702
No. of parameters, no. of restraints	401, 226	542, 0	722, 3
GOF	1.047	1.081	1.052
R_1, wR_2 $[I>2\sigma(I)]^b$	0.031, 0.076	0.026, 0.056	0.046, 0.105
R_1, wR_2 (all data)	0.032, 0.076	0.033, 0.058	0.073, 0.114

Compound	$[Sn(OPPh_3)_4][BAr^F]_2 \cdot 0.5CH_2Cl_2$	$[Ge(OPPh_3)_3][BAr^F]_2 \cdot 1.25CH_2Cl_2$
Formula	$C_{273}H_{170}B_4Cl_2F_{96}O_8P_8Sn_2$	$C_{119.25}H_{71.50}B_2Cl_{2.50}F_{48}GeO_3P_3$
M	6001.36	2740.01
Crystal system	Triclinic	Triclinic
Space group (no.)	P-1 (2)	P-1 (2)
a/Å	16.8883(2)	13.8582(2)
b/Å	27.7013(4)	16.6049(2)
c/Å	28.0785(3)	25.4517(3)
α/°	84.4750(10)	92.8270(10)
β/°	82.7910(10)	96.8780(10)
γ/°	87.8470(10)	90.9760(10)
U	12967.2(3)	5806.01(13)
Z	2	2
μ(Mo-K_α) /mm^{-1}	0.391	0.493
F(000)	6020	2745
Total number of reflections	183737	145261
R_{int}	0.054	0.060
Unique reflections	62759	29432
No. of parameters, no. of restraints	3619, 876	1675, 1645
GOF	1.026	1.134
R_1, wR_2 [$I>2\sigma(I)$][b]	0.068, 0.161	0.135, 0.328
R_1, wR_2 (all data)	0.121. 0.186	0.148, 0.335

[a] Common items: T = 100 K; θ(max) = 27.5°; wavelength (Mo-K_α) = 0.71073 Å;

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$