ESI for

Synthesis, spectroscopic and structural properties of Sn(II) and Pb(II) triflate complexes with soft phosphine and arsine coordination

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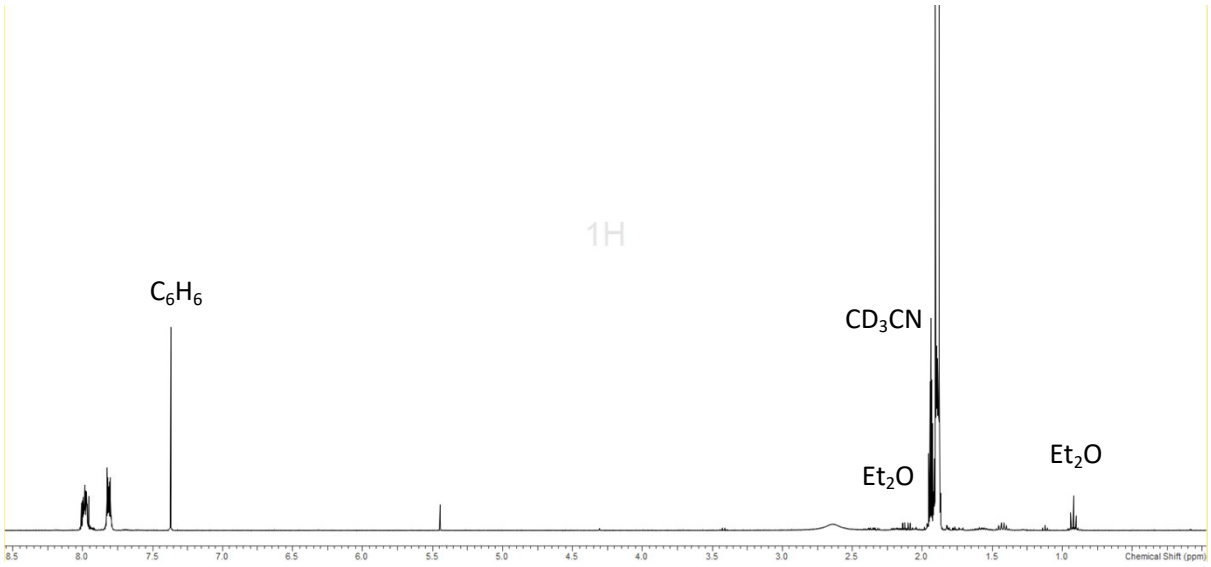
Figure S17 – IR spectrum for Pb(OTf)$_2$

Table S1 - X-ray crystallographic parameters

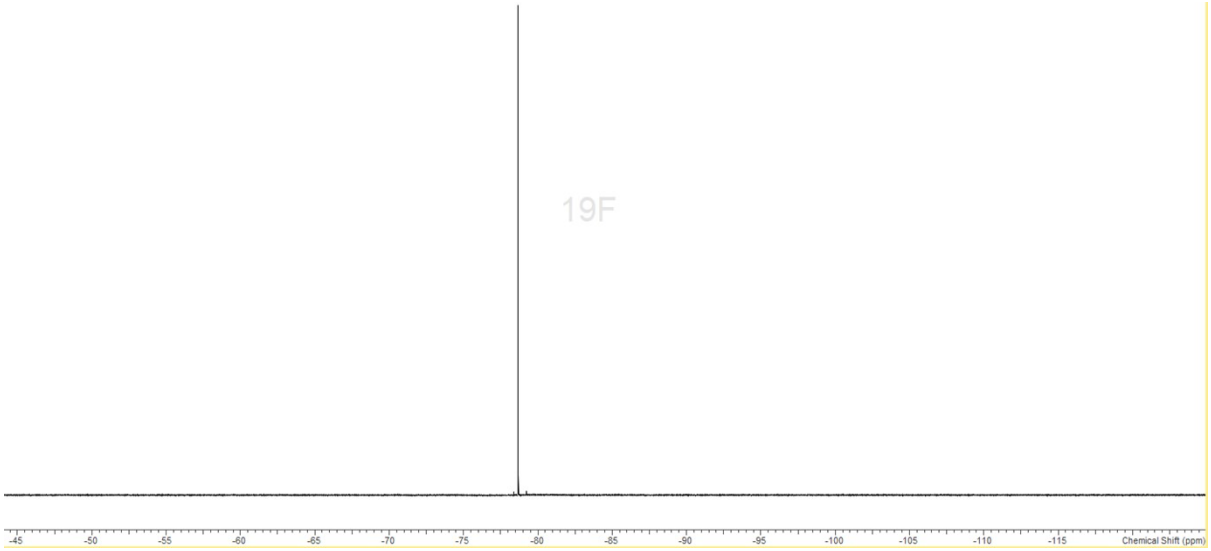
Table S2 – Experimental (X-ray) *vs.* calculated (DFT, B3LYP-D3) metrics for [M{MeC(CH$_2$PPh$_2$)$_3$}]$^{2+}$ (M = Ge, Sn, Pb)

Figure S1 – [Sn(OTf)$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}]

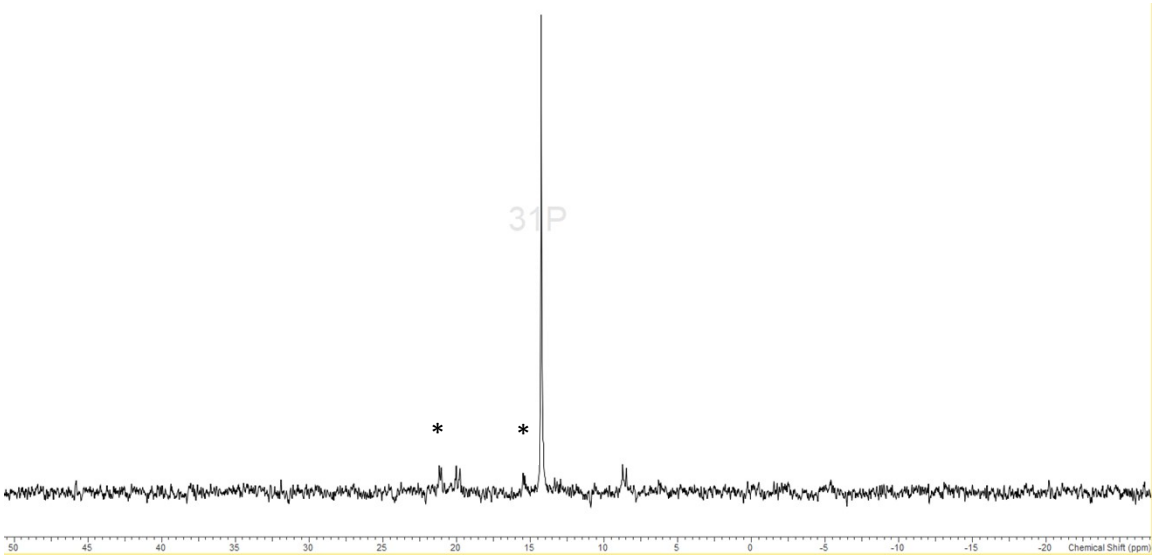
S1.1 – ^{1}HMR spectrum (298 K, CD_3CN)



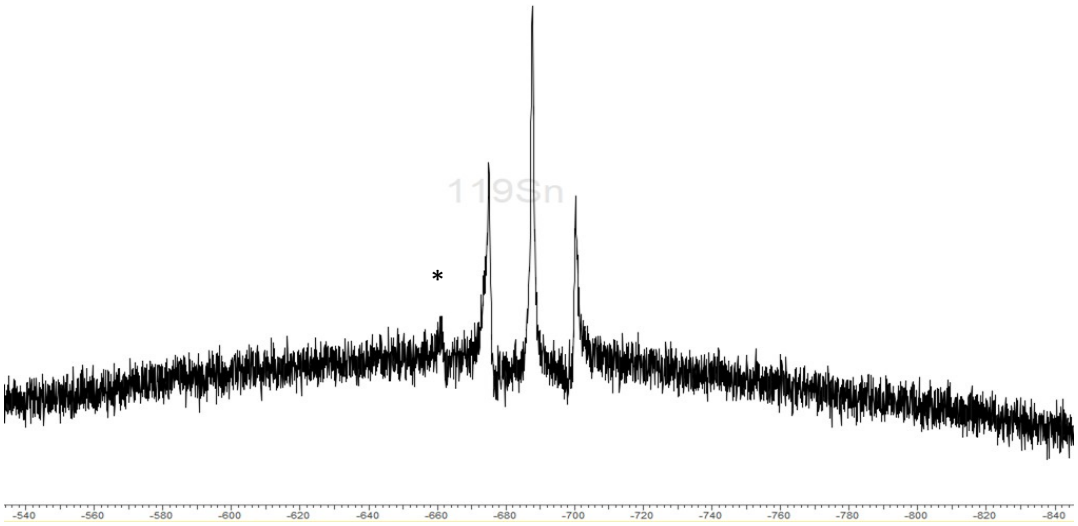
S1.2 – ^{19}F{^{1}H} NMR spectrum (298 K, CD_3CN)



S1.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN) * = unidentified impurity



S1.4 – ^{119}Sn NMR spectrum (298 K, CD_3CN) * = unidentified impurity



S1.5 – IR spectrum (Nujol)

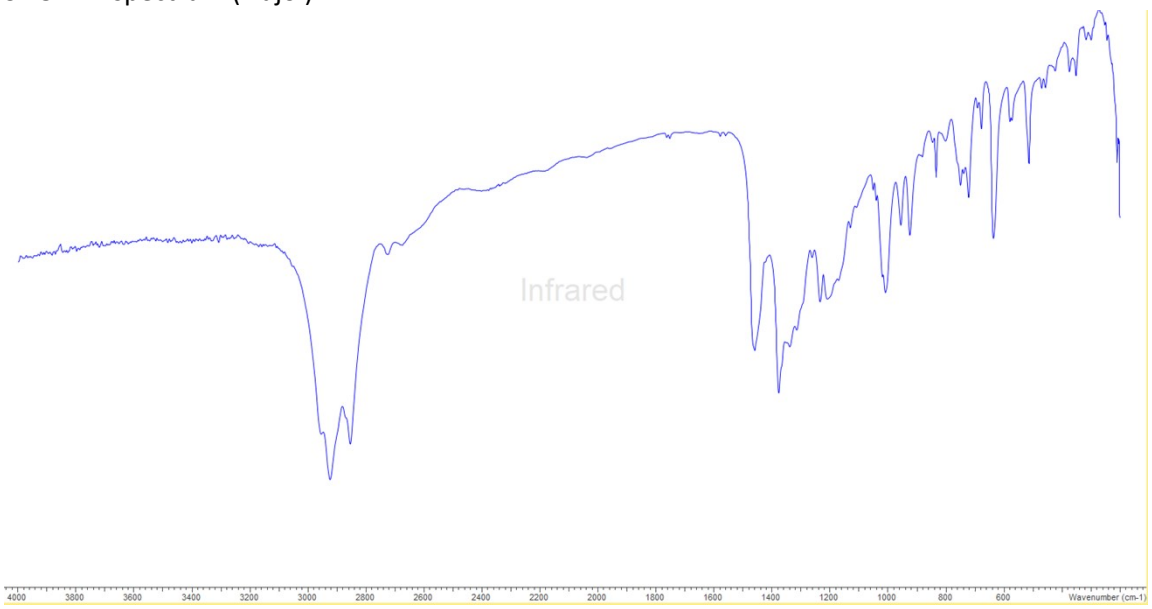
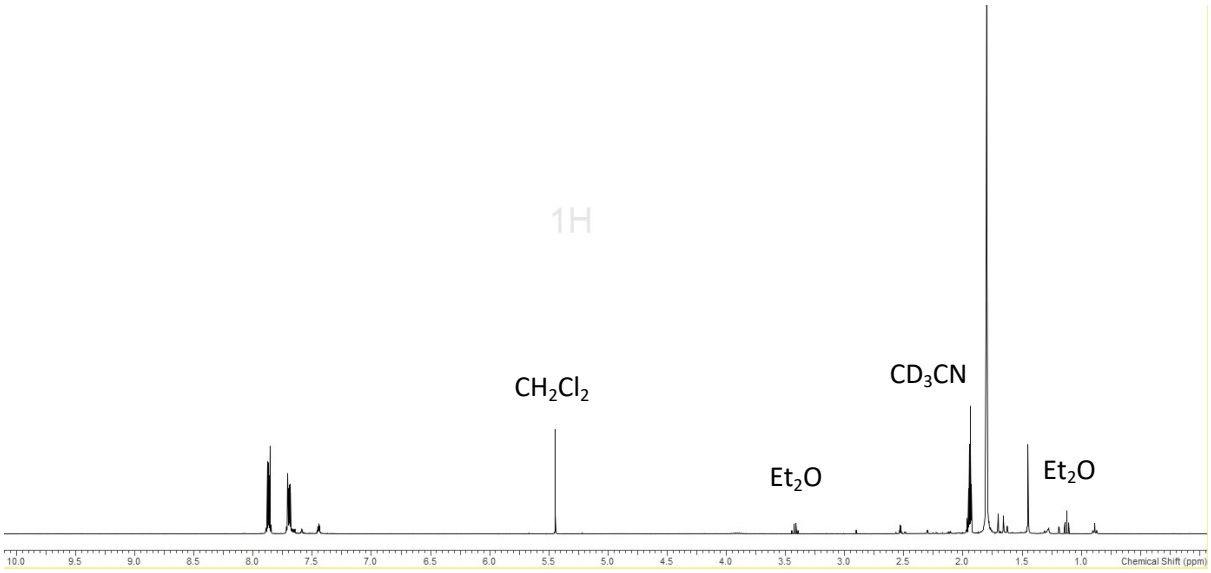
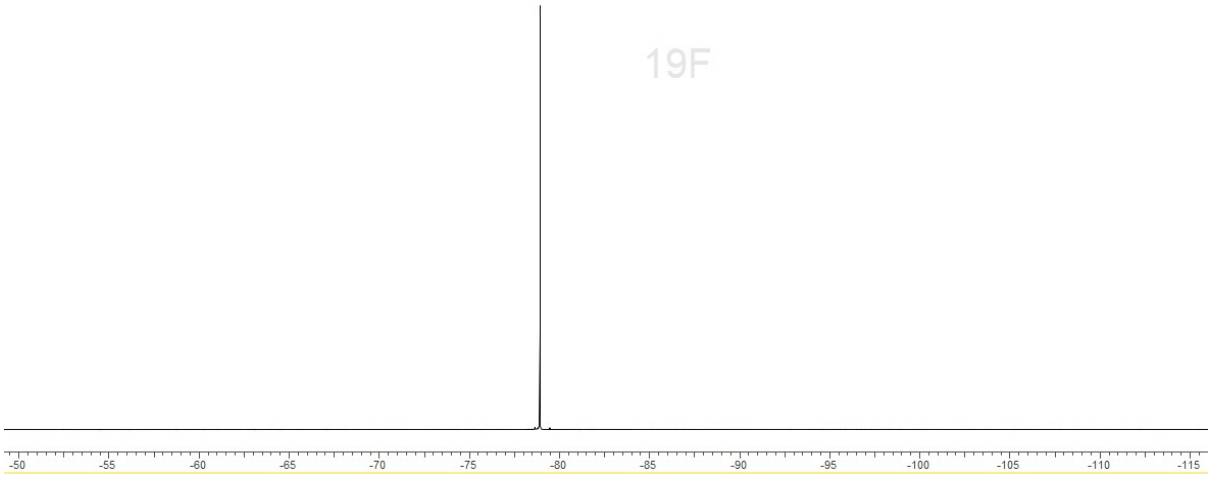


Figure S2 [$Sn(OTf)_2\{o\text{-}C_6H_4(AsMe_2)_2\}$]

S2.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



S2.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



S2.3 – ^{119}Sn NMR spectrum (258 K, CD_3CN)

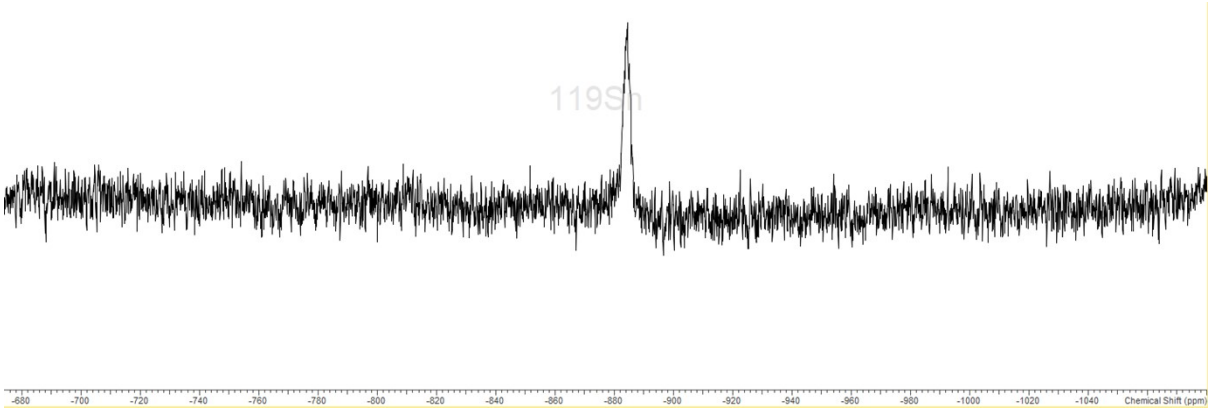
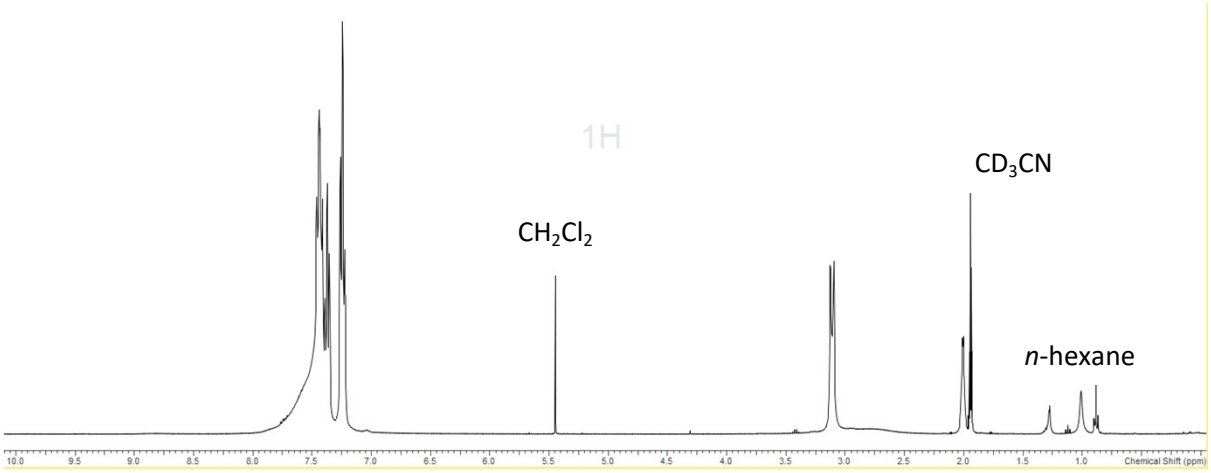
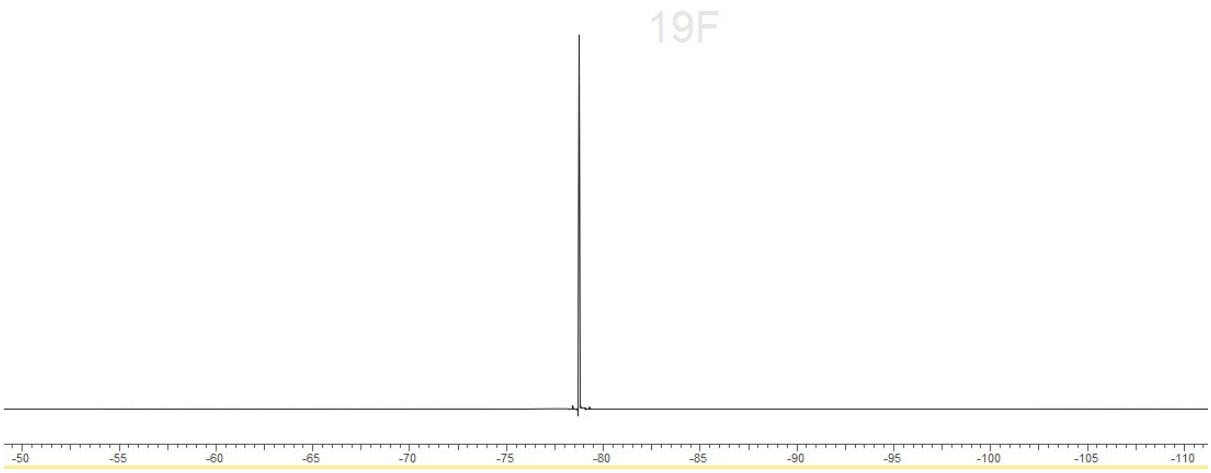


Figure S3 – $[Sn(OTf)_2\{MeC(CH_2PPh_2)_3\}]$

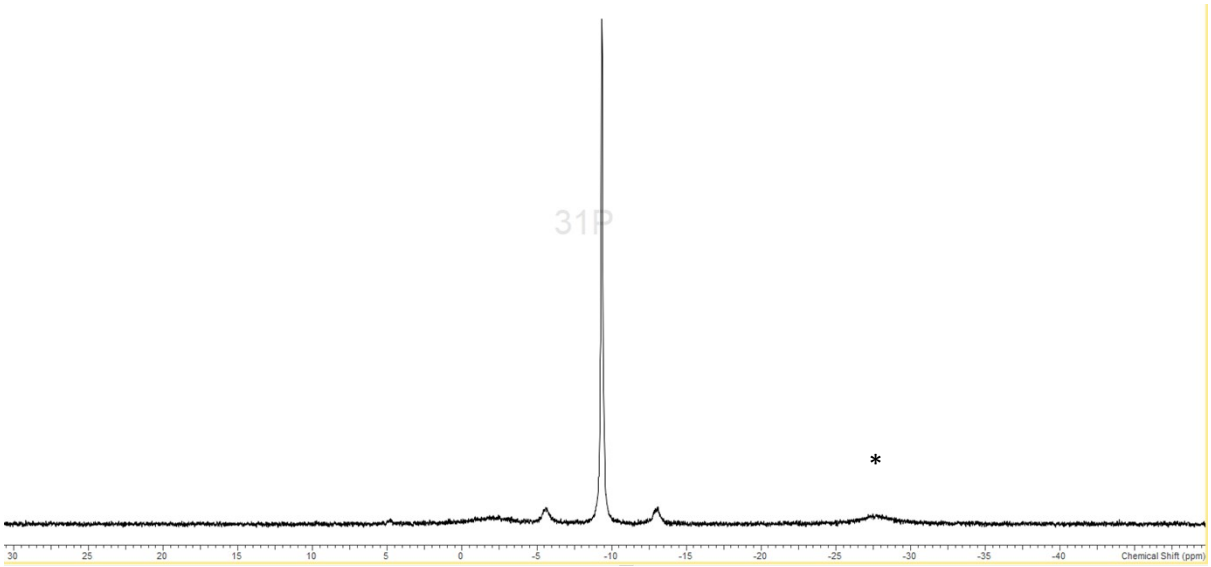
S3.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



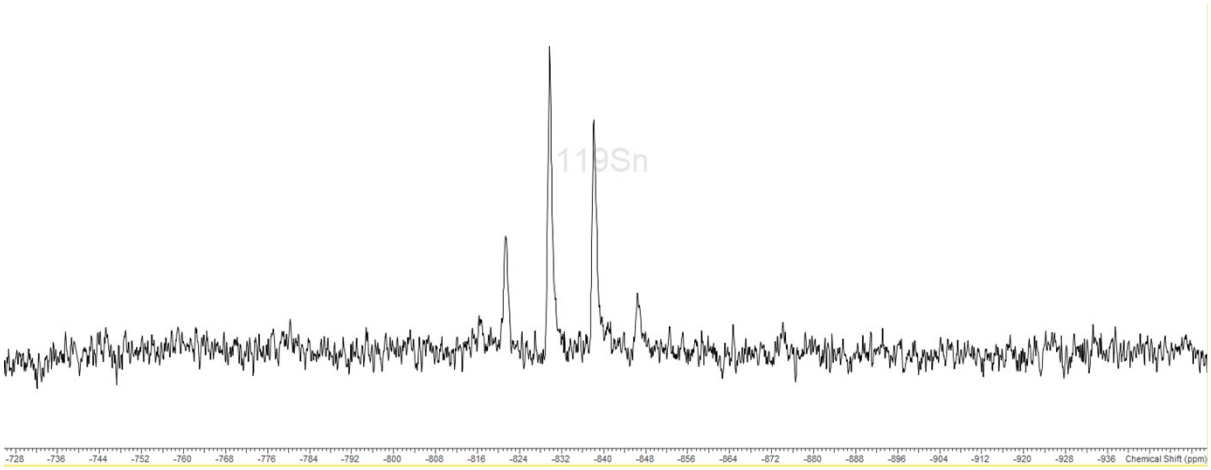
S3.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



S3.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN) * = unidentified impurity



S3.4 – ^{119}Sn NMR spectrum (298 K, CD_3CN)



S3.5 – IR spectrum (Nujol)

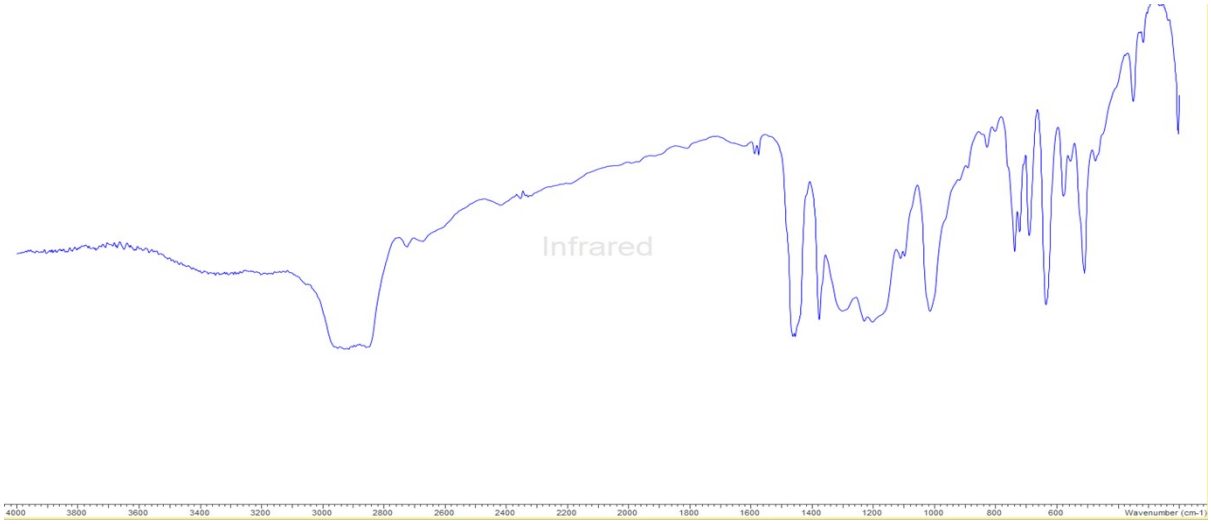
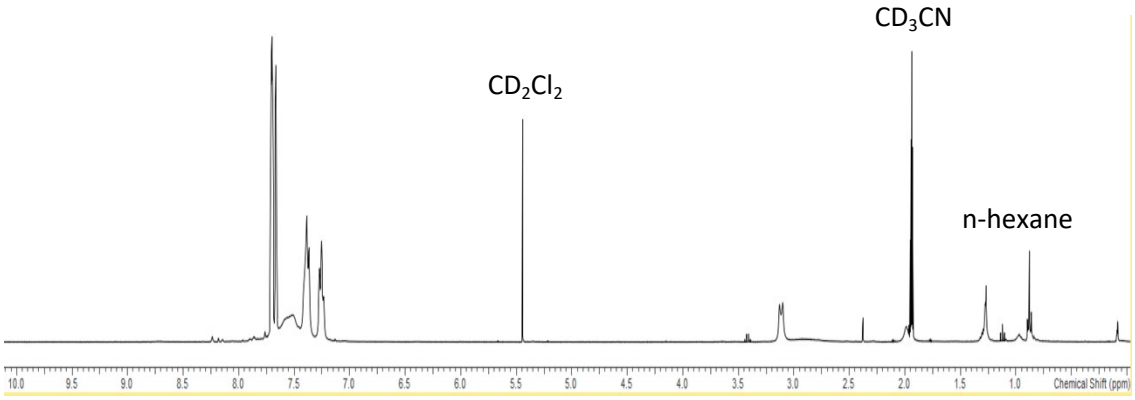
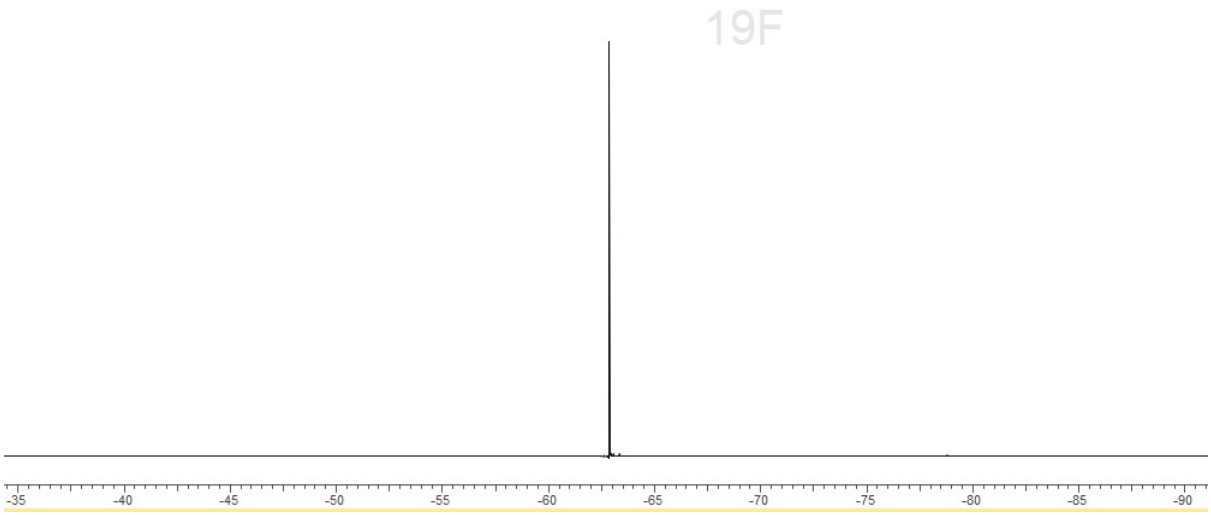


Figure S4 – $[Sn\{MeC(CH_2PPh_2)_3\}][BAr^F]_2$

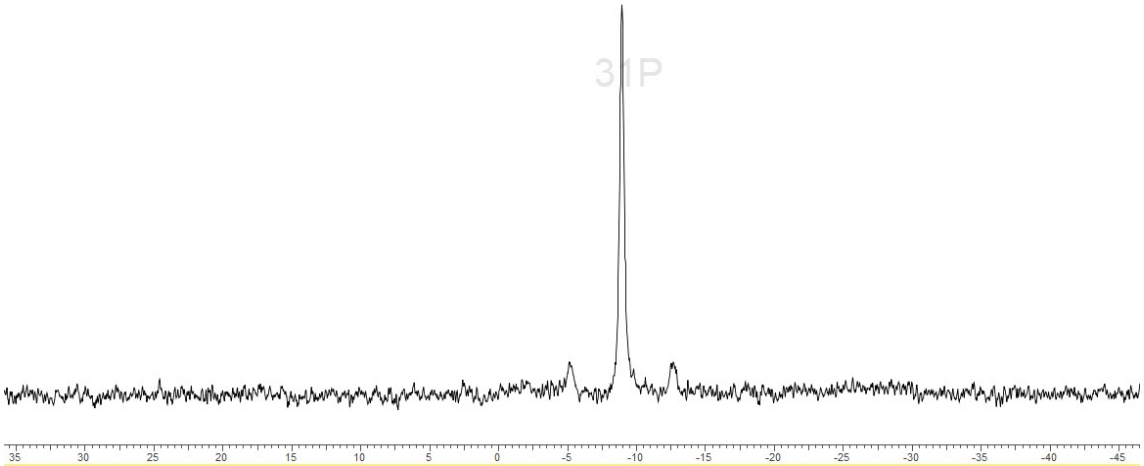
S4.1 – ^1H NMR spectrum (298 K, CD_3CN)

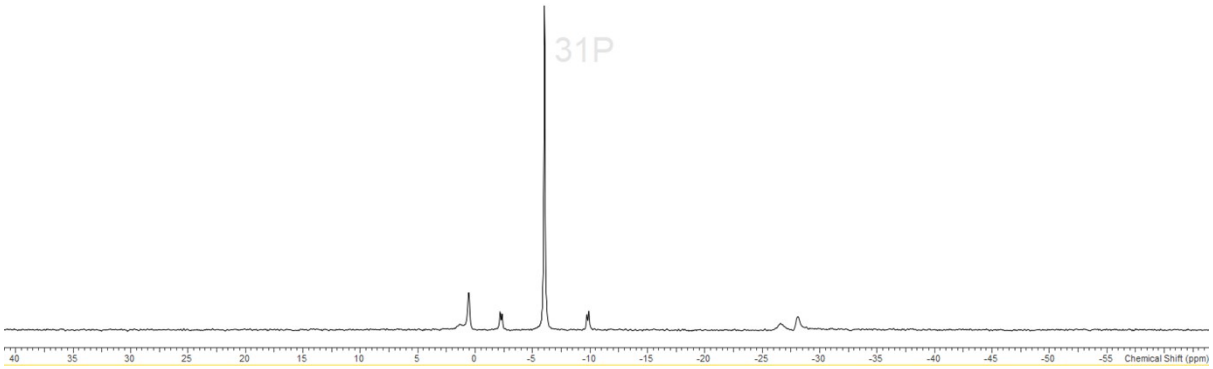


S4.2 – $^{19}F\{^1H\}$ NMR spectrum (298 K, CD_3CN)



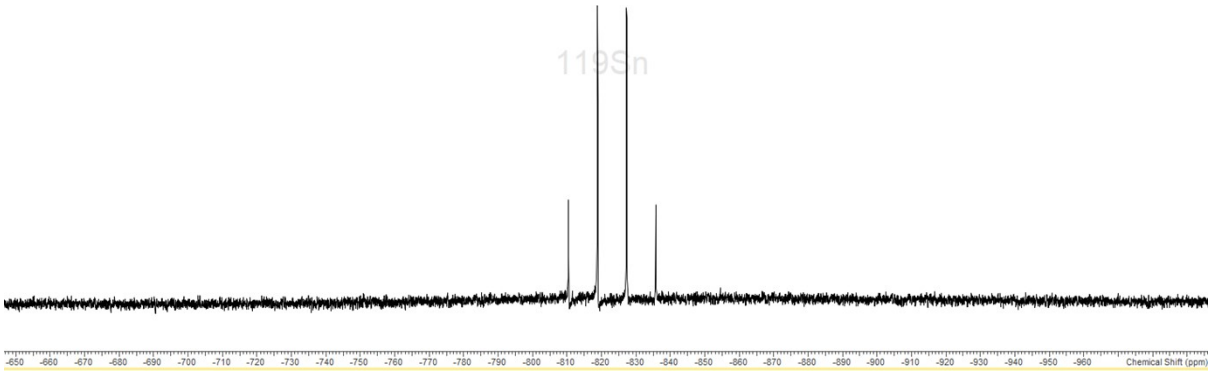
S4.3 – $^{31}P\{^1H\}$ NMR spectrum (298 K, CD_3CN)



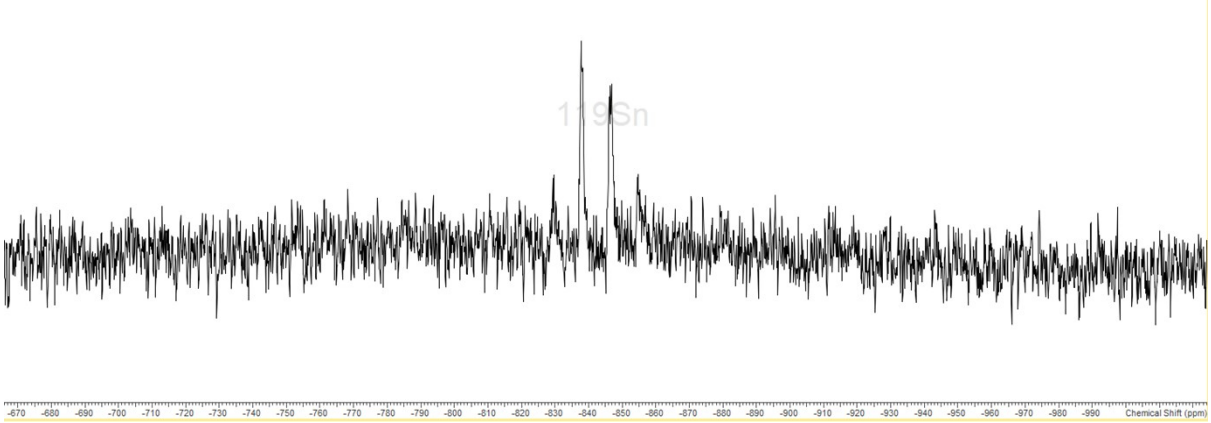


S4.4 - $^{31}P\{^{1}H\}$ NMR spectrum (258 K, CD_3CN) * = unidentified impurity

S4.5 – ^{119}Sn NMR spectrum (298 K, CD_3CN)



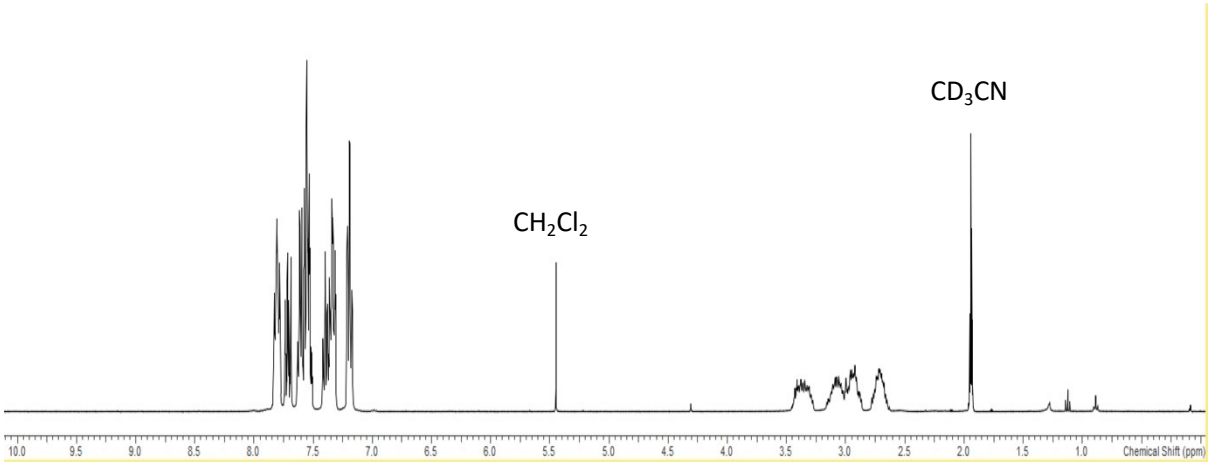
S4.6 - ^{119}Sn NMR spectrum (258 K, CD_3CN)



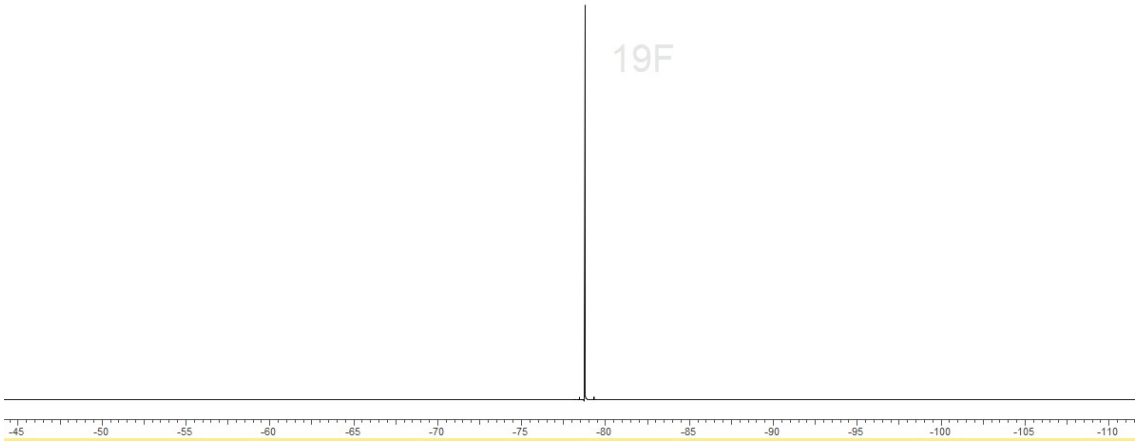
S4.7 – IR spectrum (Nujol)

Figure S5 – [Sn(OTf){PhP($CH_2CH_2PPh_2$)$_2$}][OTf]

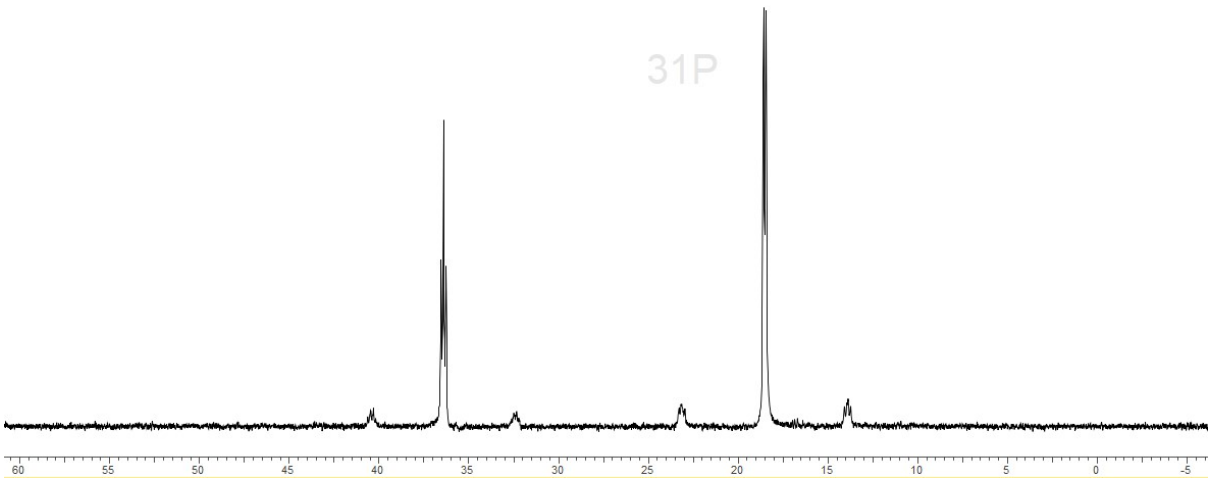
S5.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



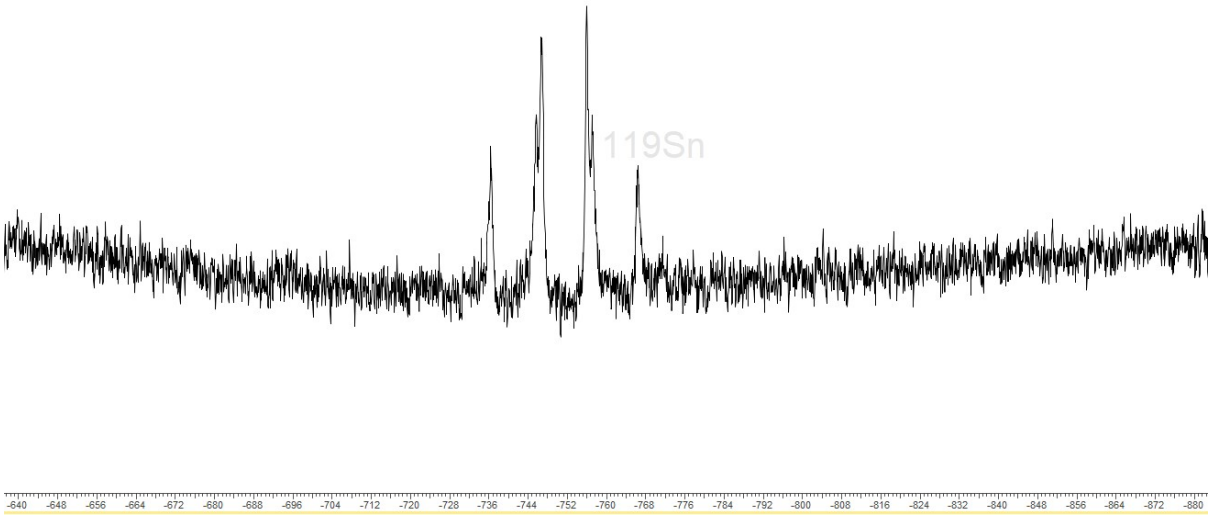
S5.2 – ^{19}F{^{1}H} NMR spectrum (298 K, CD_3CN)



S5.3 – ^{31}P{^{1}H} NMR spectrum (298 K, CD_3CN)



S5.4 – ^{119}Sn NMR spectrum (298 K, CD_3CN)



S5.5 – IR spectrum (Nujol)

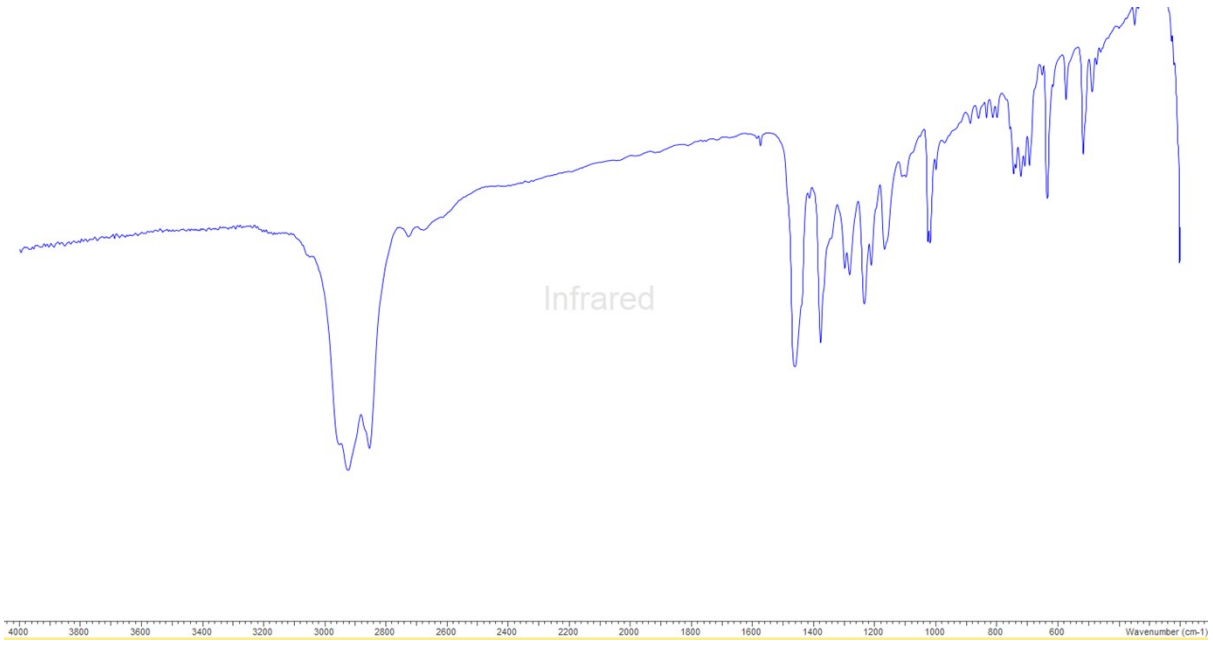
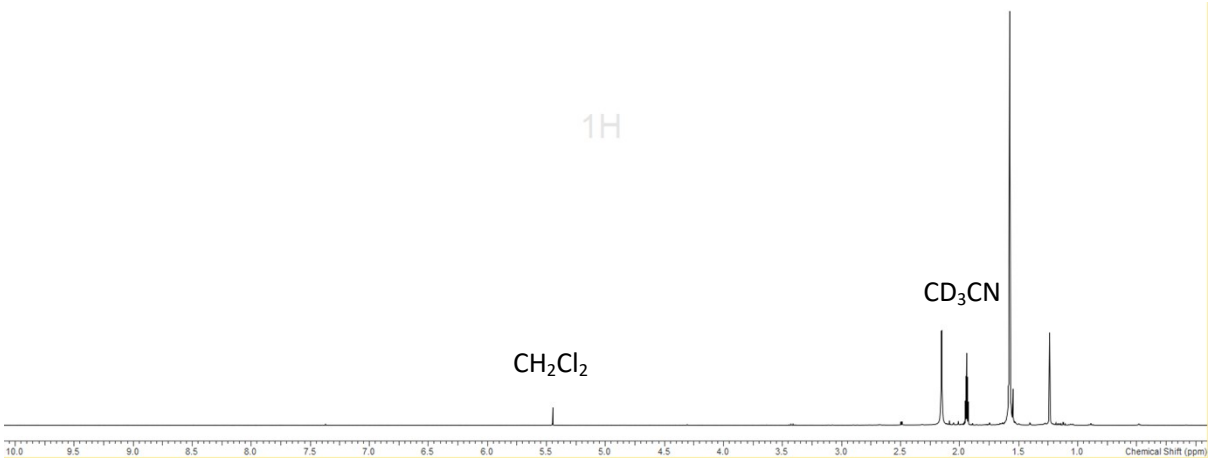
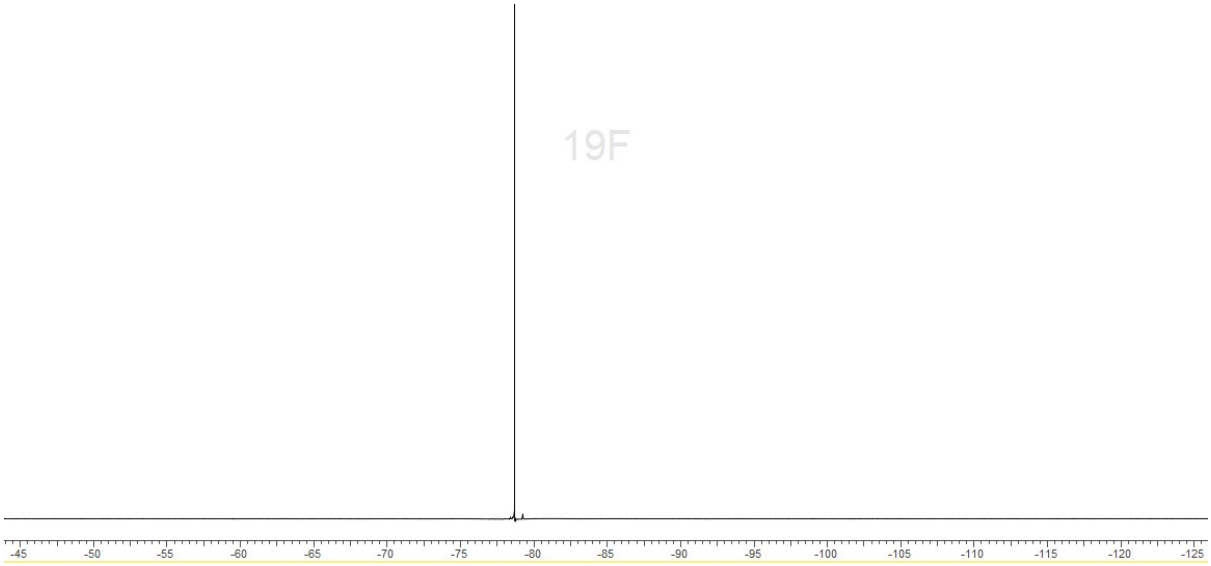


Figure S6 – $[Sn(OTf)_2\{MeC(CH_2AsMe_2)_3\}]$

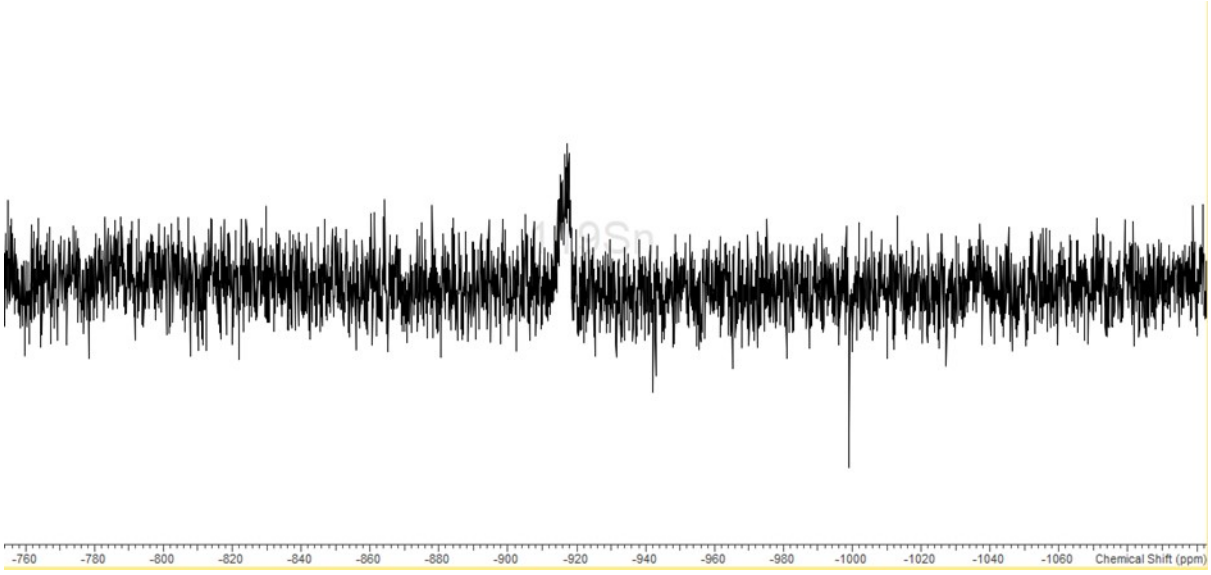
S6.1 – ^1H NMR spectrum (298 K, CD_3CN)



S6.2 – $^{19}F\{^1H\}$ NMR spectrum (298 K, CD_3CN)



S6.3 – ^{119}Sn NMR spectrum (258 K, CD_3CN)



S6.4 – IR spectrum (Nujol)

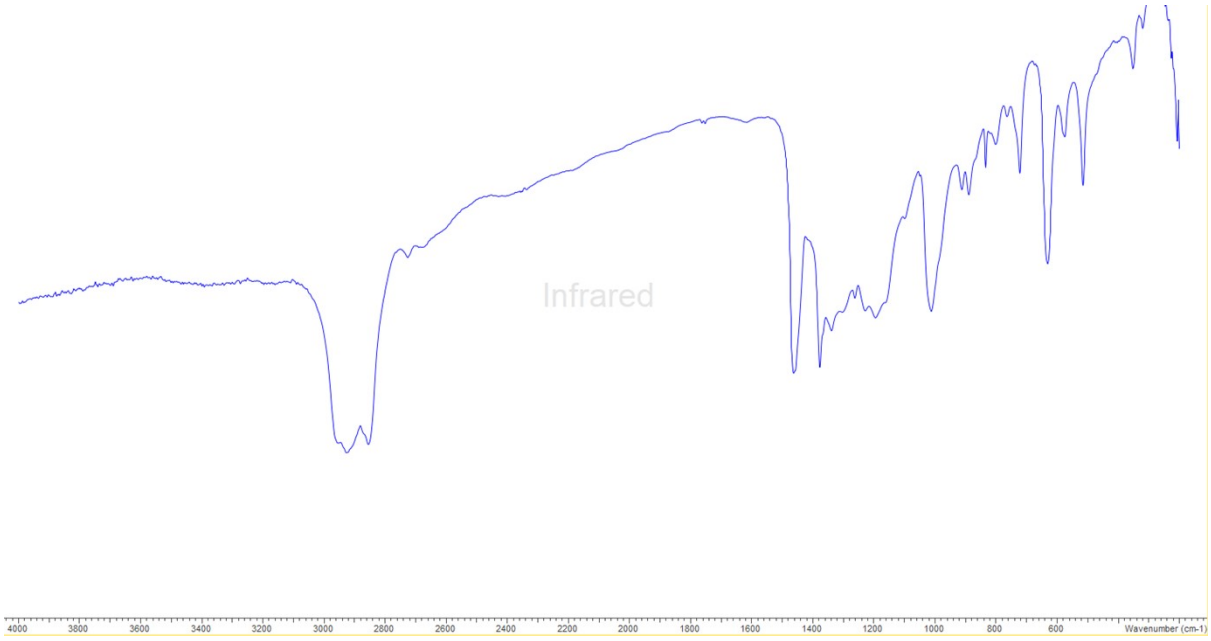
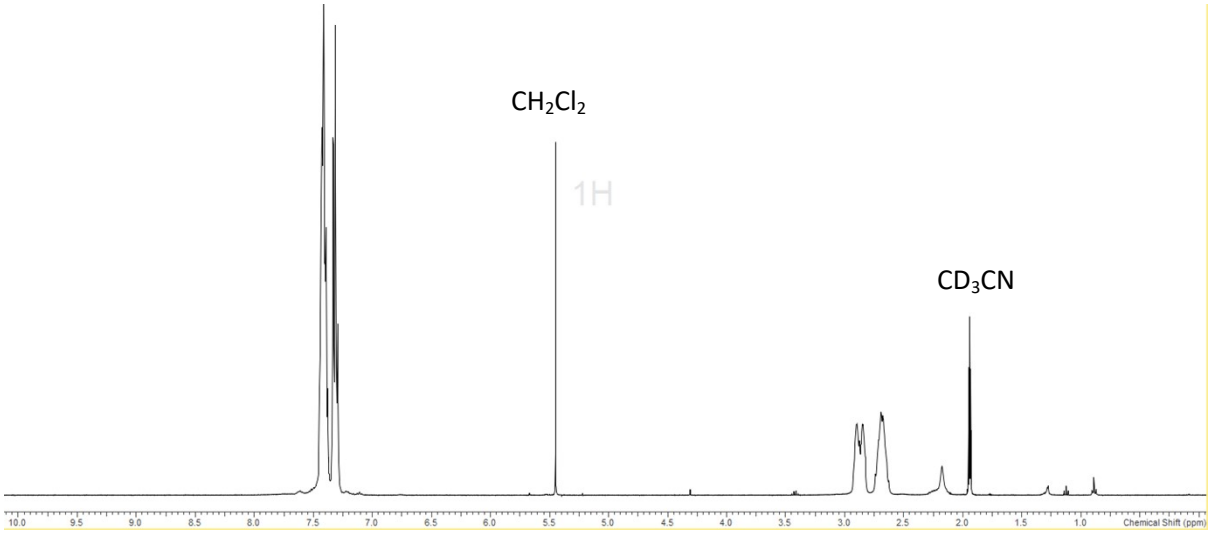
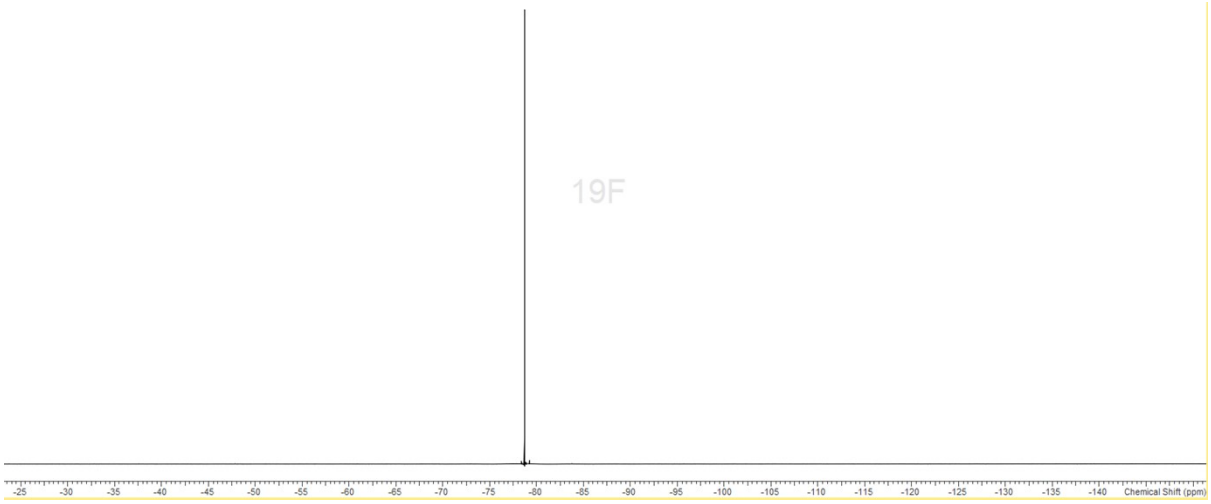


Figure S7 - [Sn(OTf){P($CH_2CH_2PPh_2$)$_3$}][OTf]

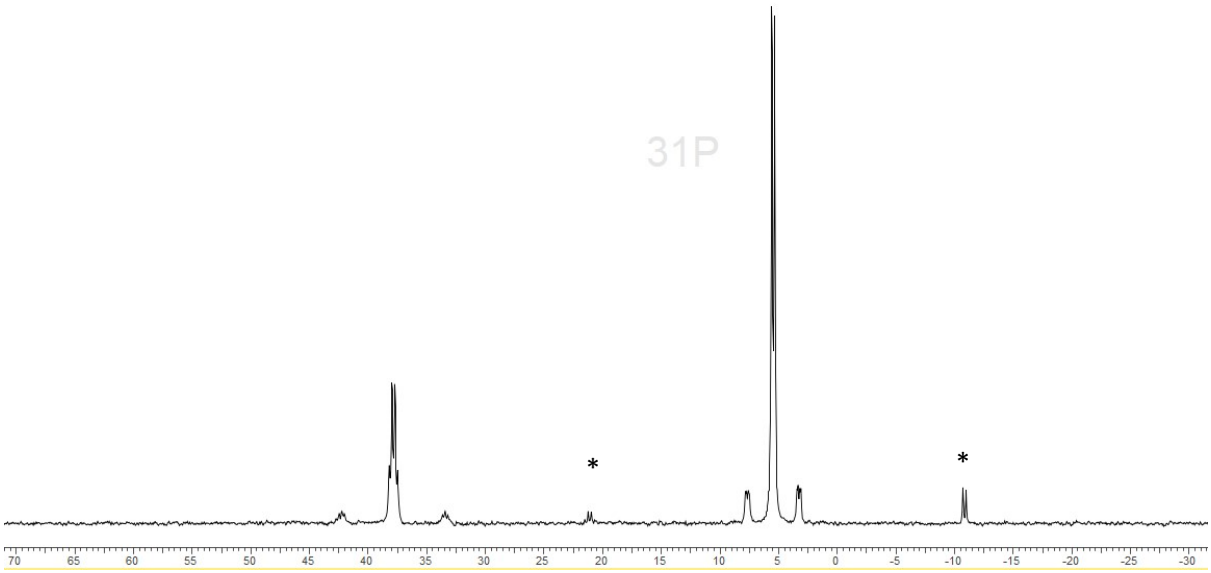
S7.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



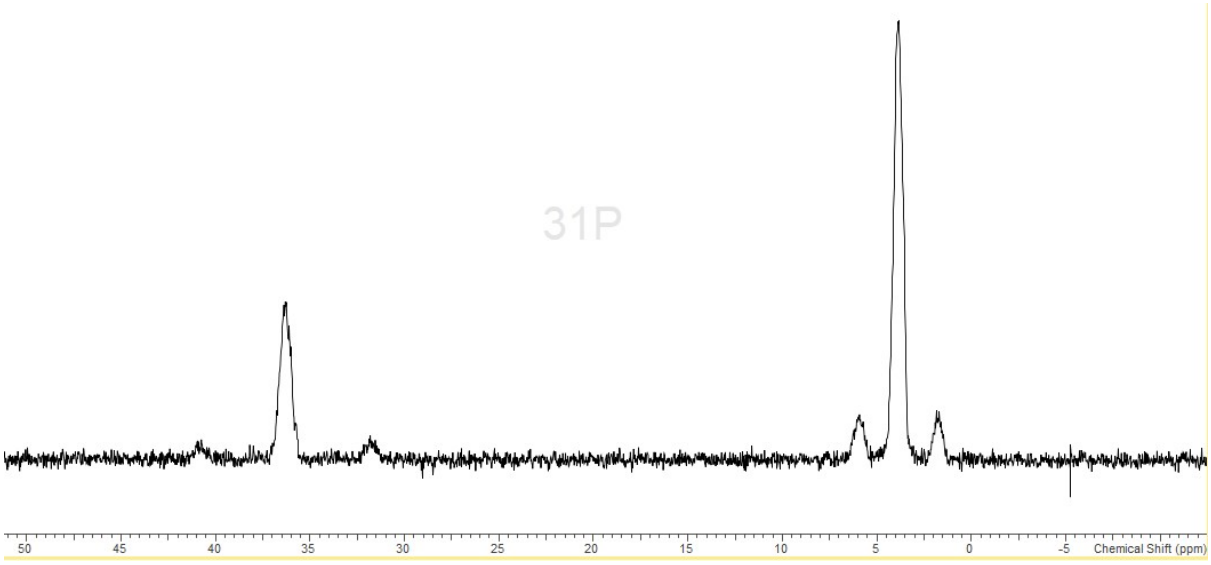
S7.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



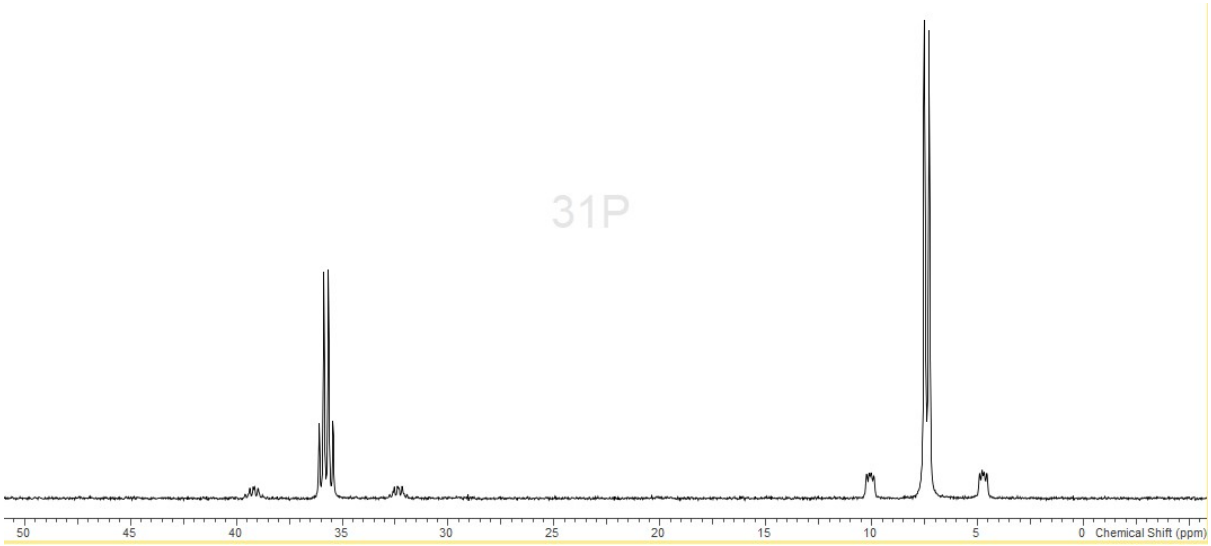
S7.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN) * = minor hydrolysis product



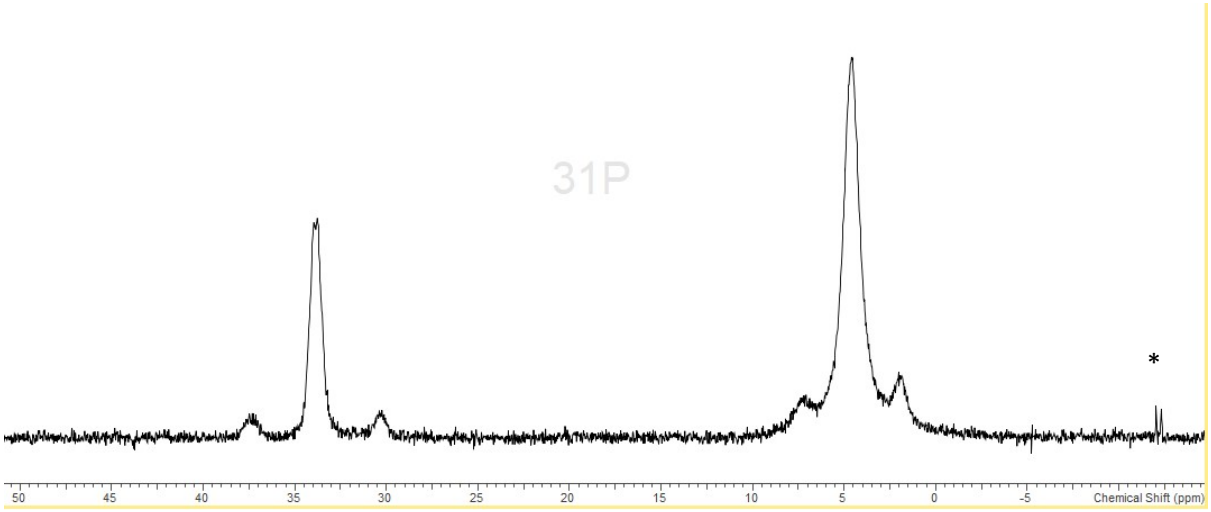
S7.4 – $^{31}P\{^{1}H\}$ NMR spectrum (258 K, CD_3CN)



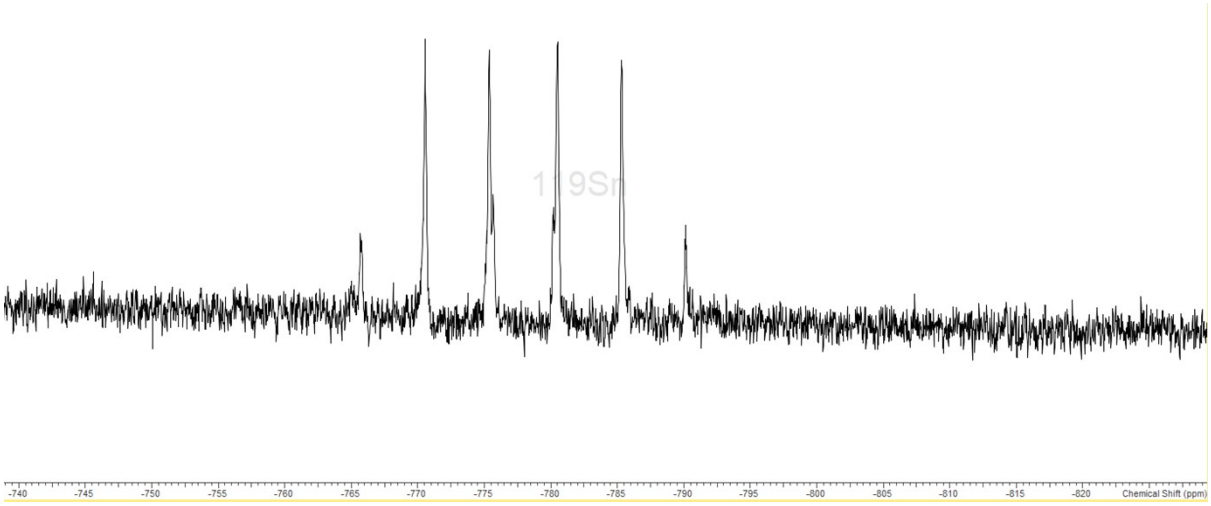
S7.5 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)



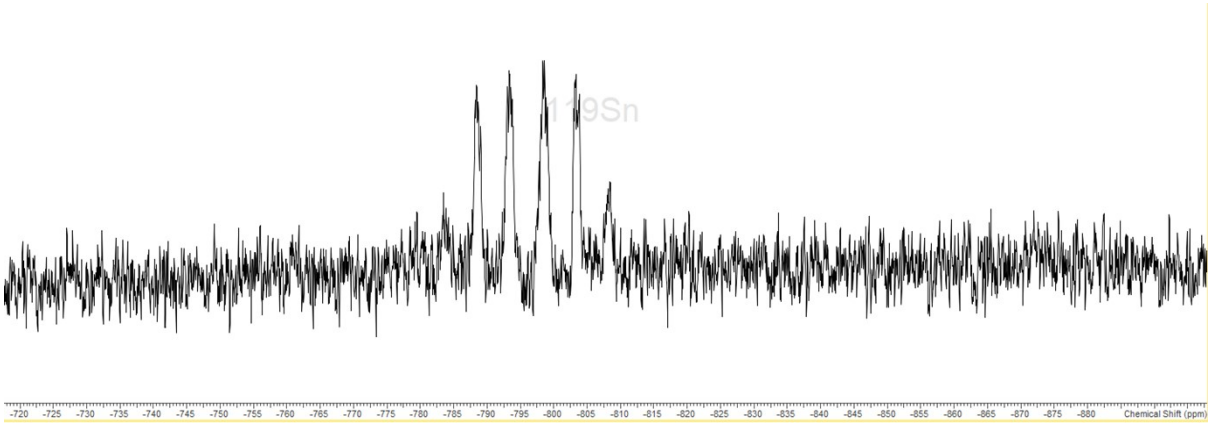
S7.6 – $^{31}P\{^{1}H\}$ NMR spectrum (208 K, CD_2Cl_2) * = minor hydrolysis product



S7.7 – ^{119}Sn NMR spectrum (298 K, CD_3CN)



S7.8 – ^{119}Sn NMR spectrum (258 K, CD_3CN)



S7.9 – IR spectrum (Nujol)

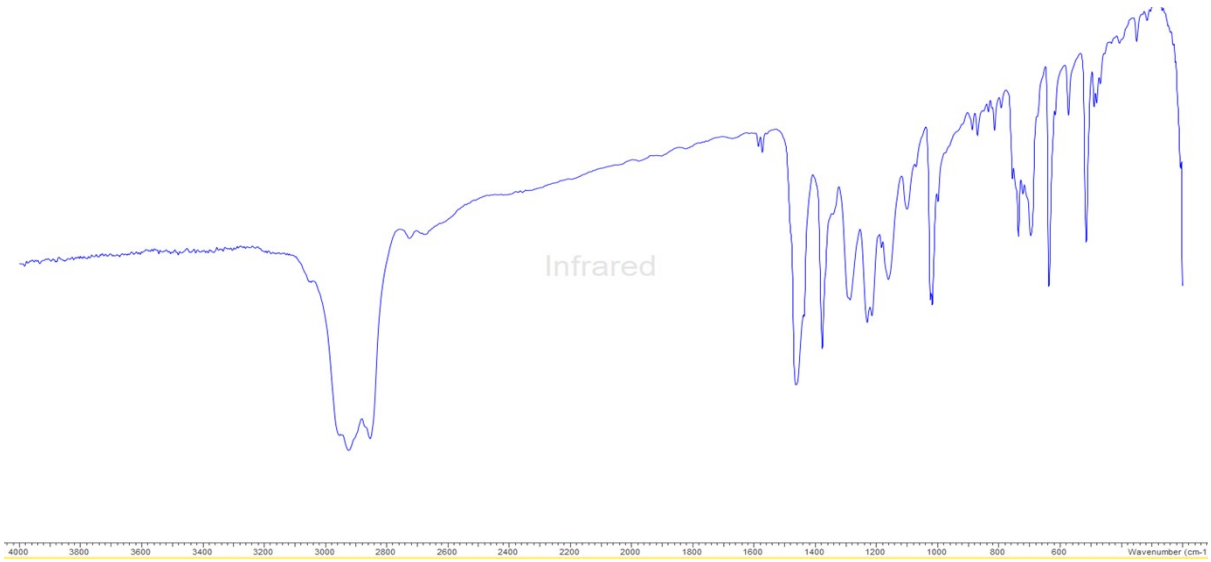
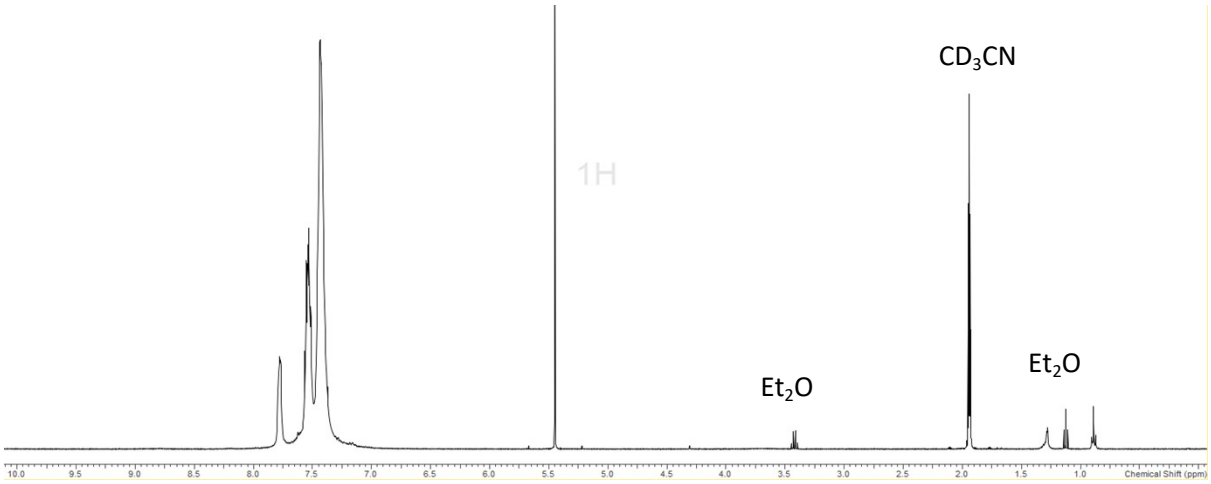
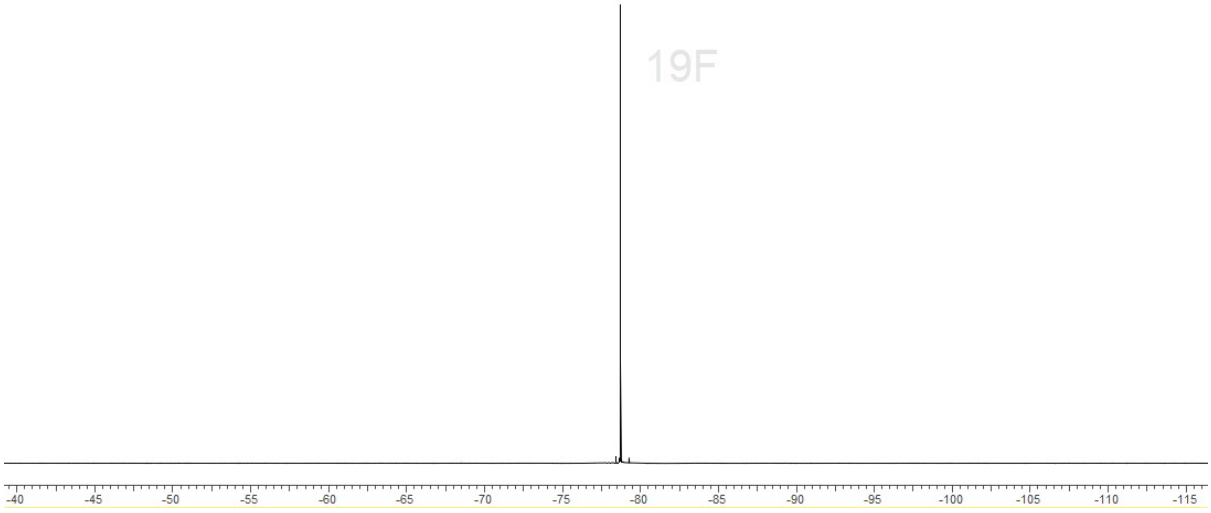


Figure S8 – [Sn(OTf)$_2${*o*-C$_6$H$_4$(PPh$_2$)$_2$}]

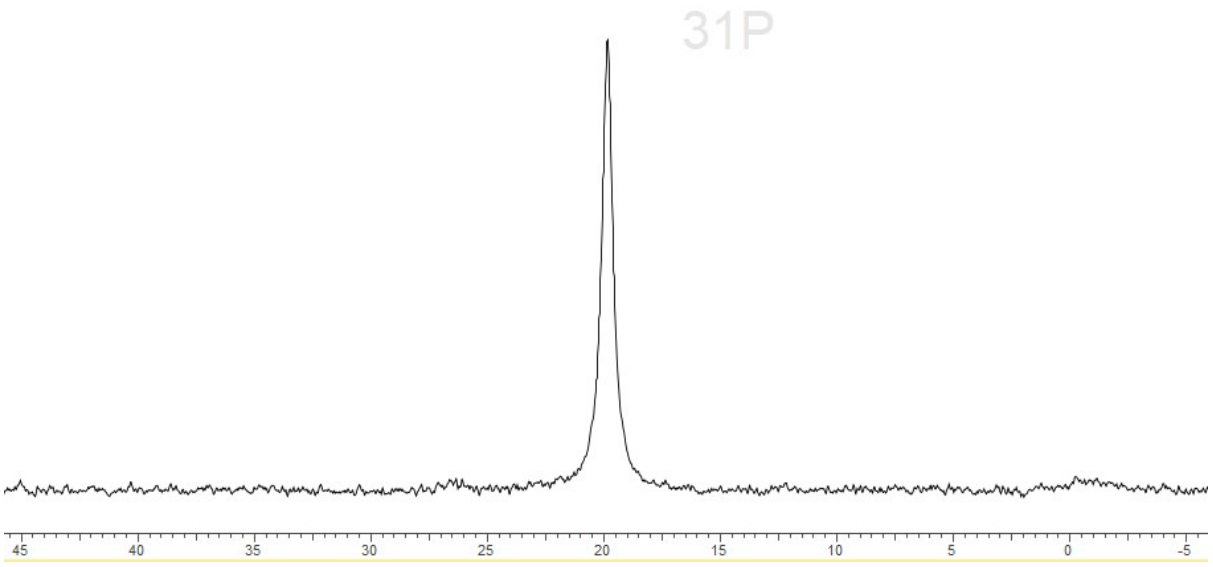
S8.1 – ^{1}H NMR spectrum (298 K, CD_3CN) CH_2Cl_2



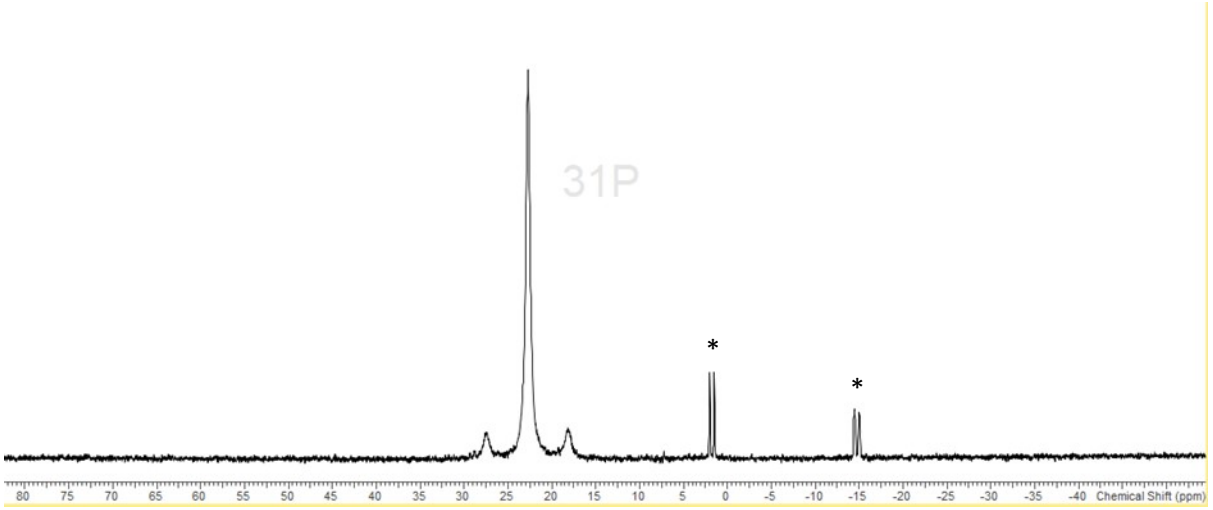
S8.2 – ^{19}F{^{1}H} NMR spectrum (298 K, CD_3CN)



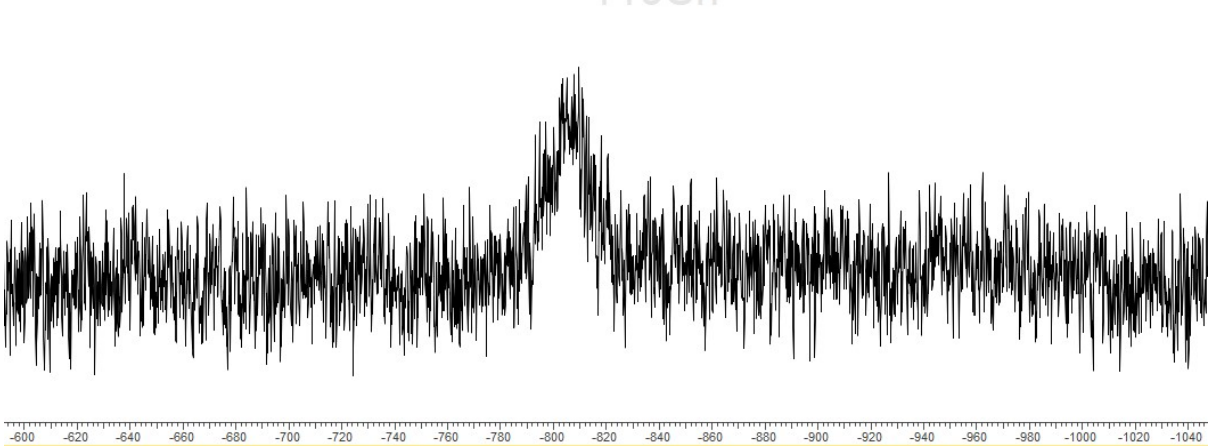
S8.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



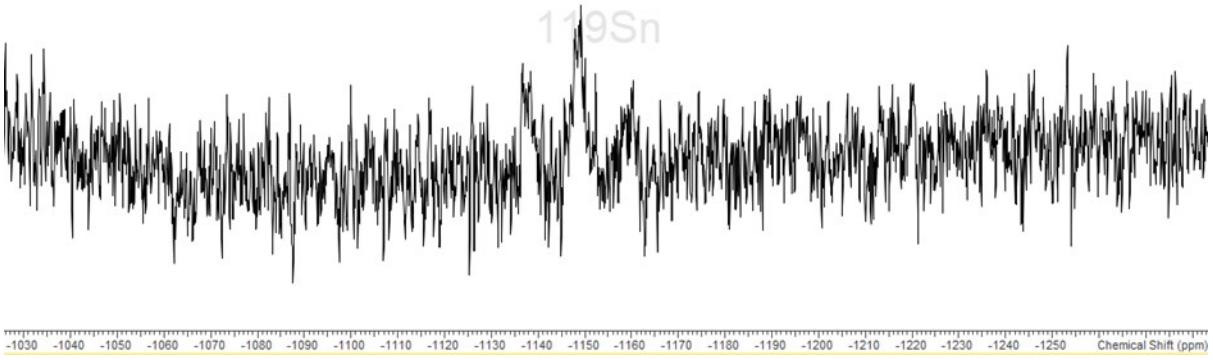
S8.4 $^{31}P\{^{1}H\}$ NMR spectrum (258 K, CD_3CN) * = *o*-$C_6H_4(PPh_2H)(PPh_2)]^+$ hydrolysis product



S8.5 – ^{119}Sn NMR spectrum (298 K, CD_3CN)



S8.6 – ^{119}Sn NMR spectrum (258 K, CD_3CN) (poorly soluble)



S8.7 – IR spectrum (Nujol)

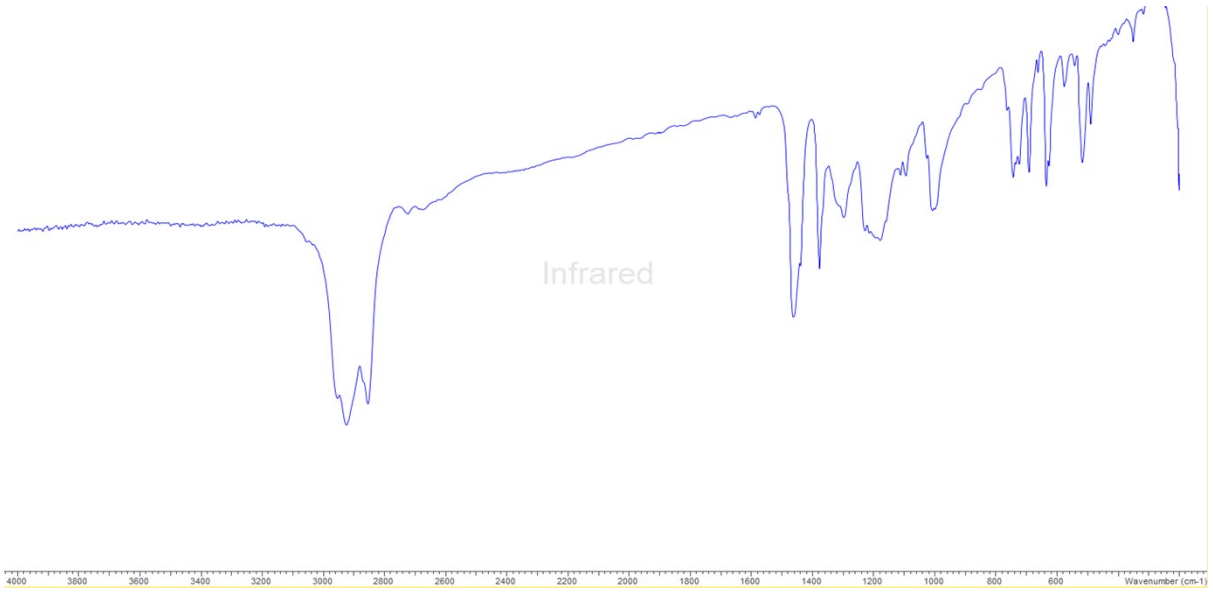
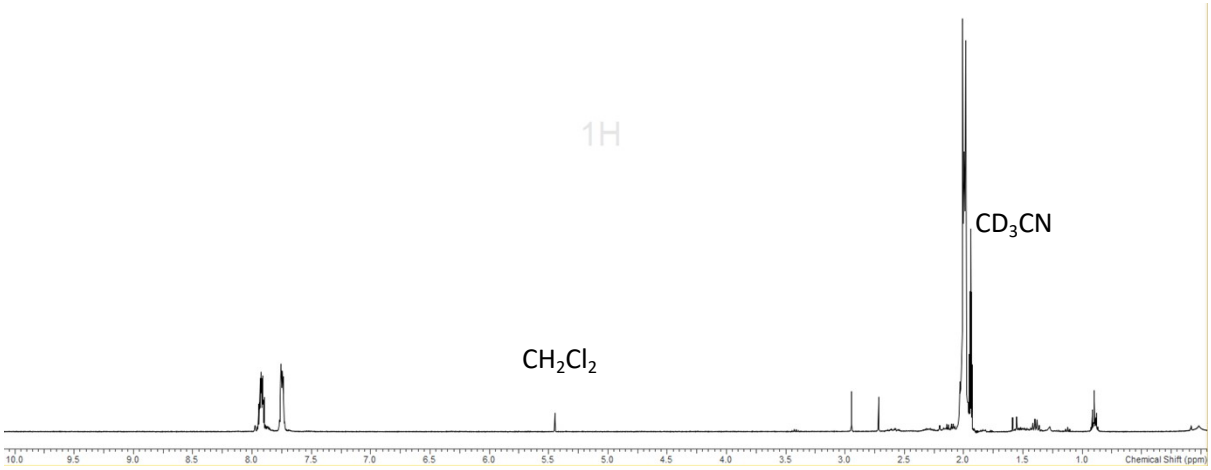
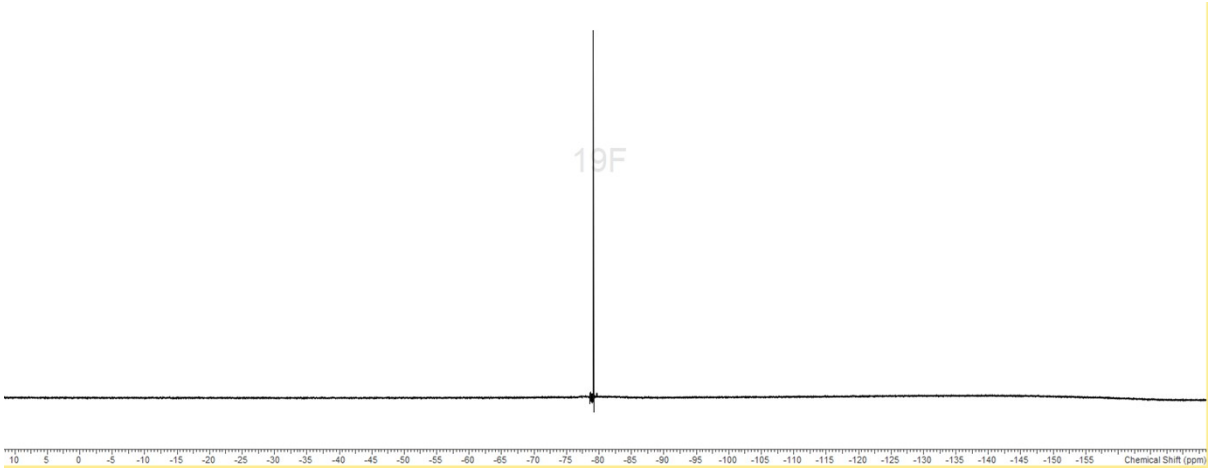


Figure S9 – $[Pb(OTf)_2\{o\text{-}C_6H_4(PMe_2)_2\}]$

S9.1 – ^1H NMR spectrum (298 K, CD_3CN)



S9.2 – $^{19}F\{^1H\}$ NMR spectrum (298 K, CD_3CN)



S9.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN) * = unidentified impurity

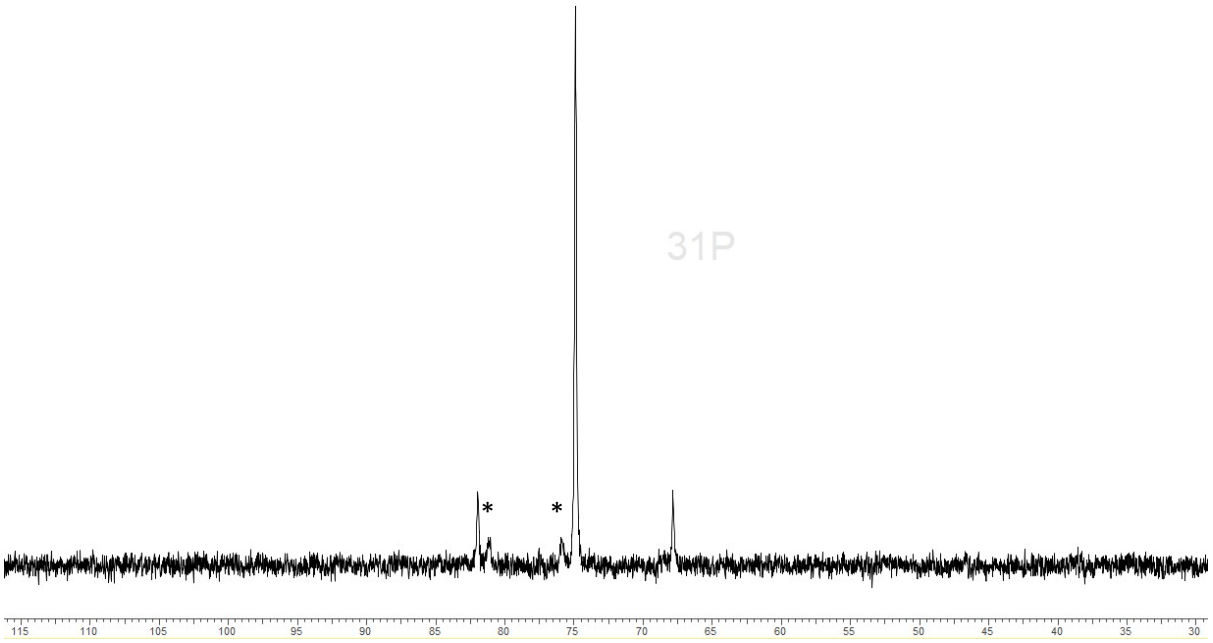
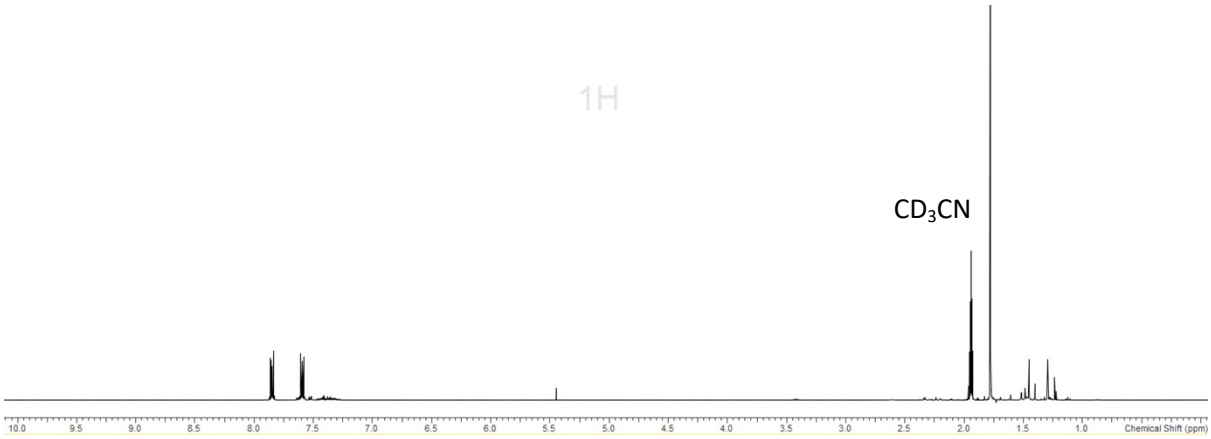
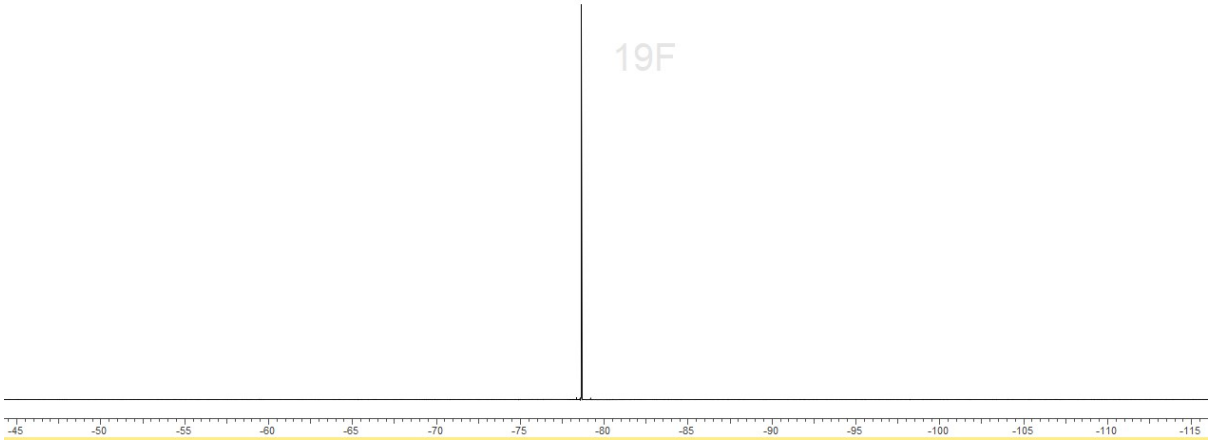


Figure S10 – [Pb(OTf)$_2${*o*-C$_6$H$_4$(AsMe$_2$)$_2$}]

S10.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



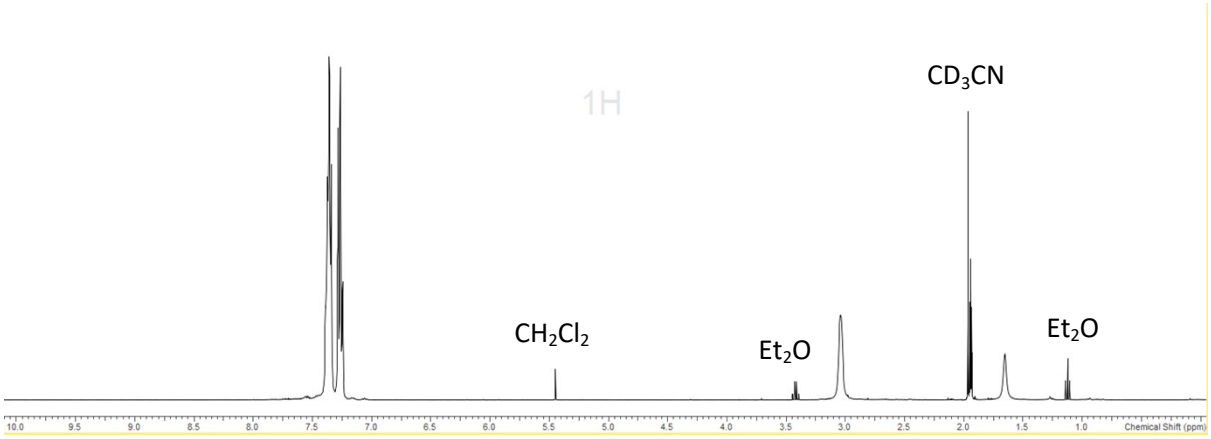
S10.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



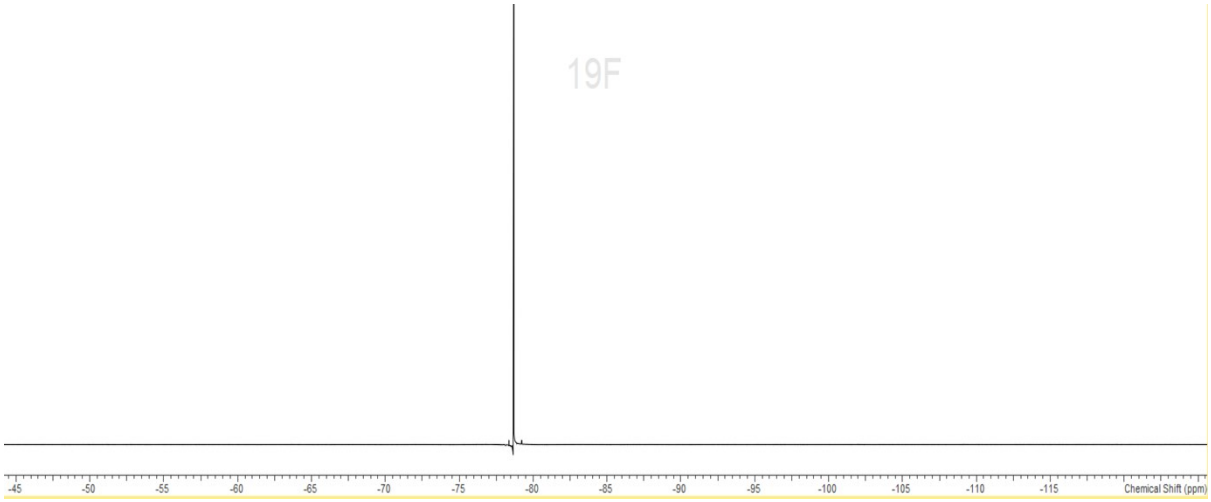
S10.3 – IR spectrum (Nujol)

Figure S11 – $[Pb(OTf)_2\{MeC(CH_2PPh_2)_3\}]$

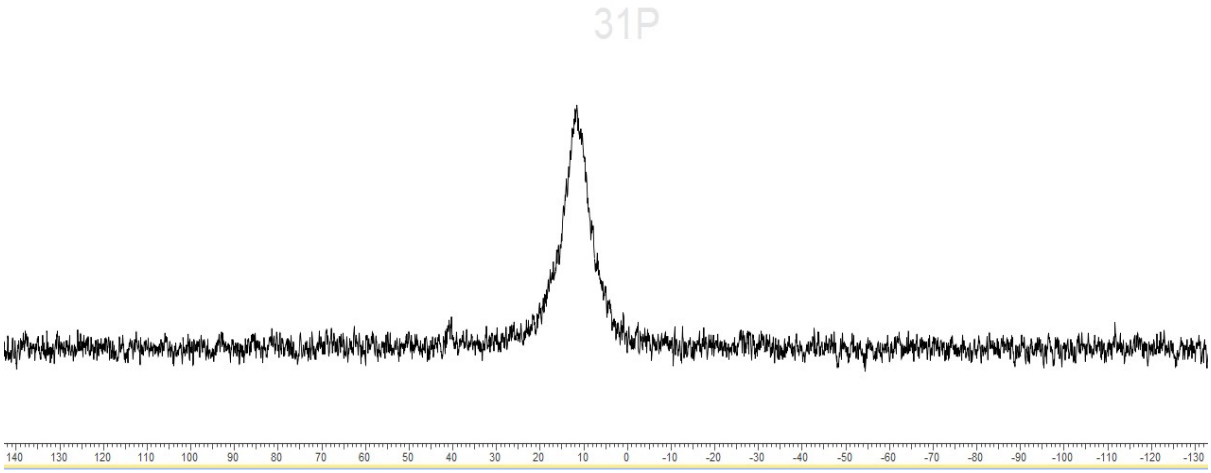
S11.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



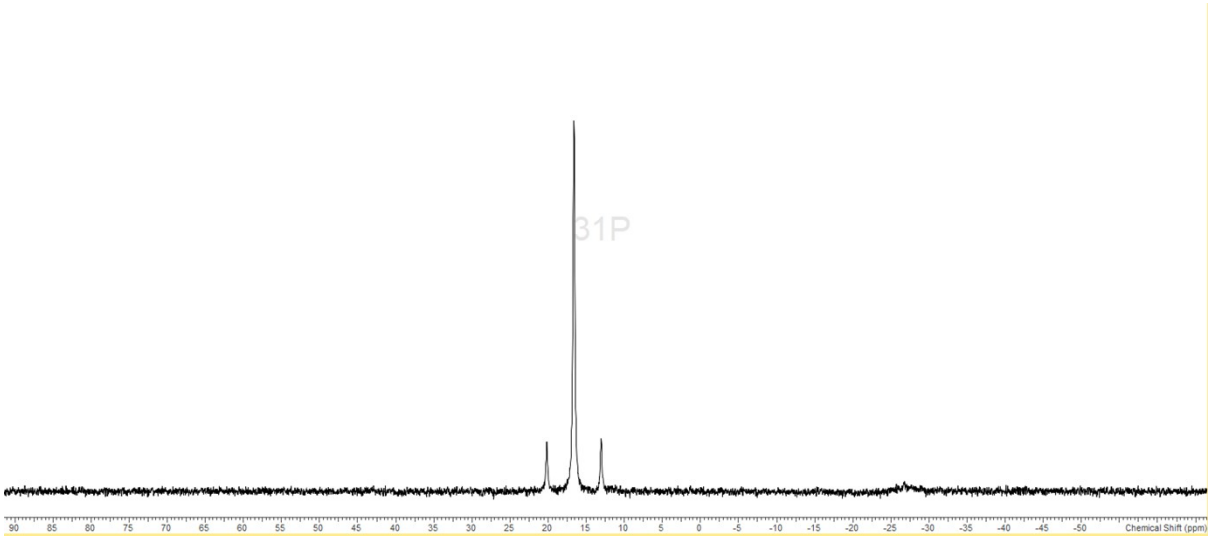
S11.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



S11.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



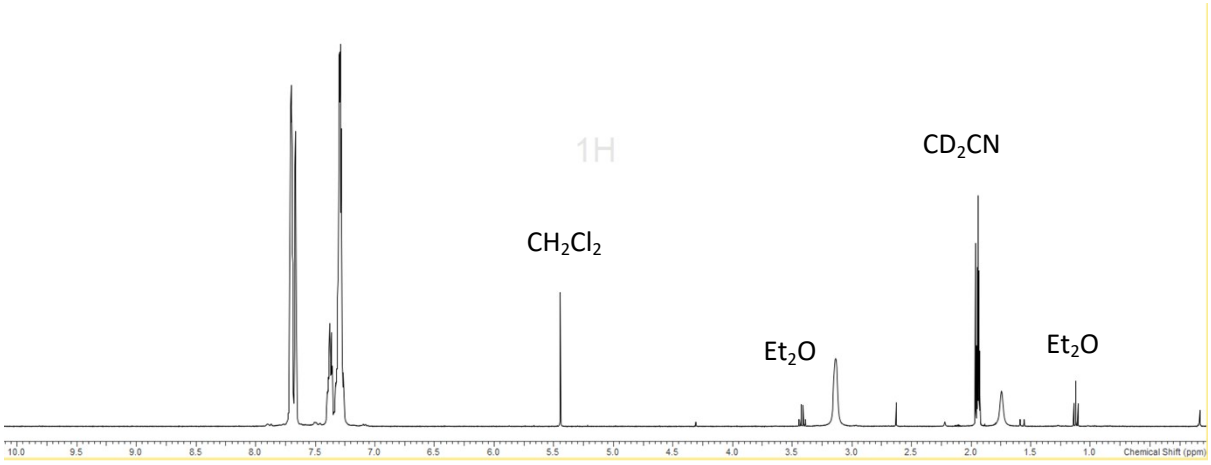
S11.4 $^{31}P\{^{1}H\}$ NMR spectrum (258 K, CD_3CN)



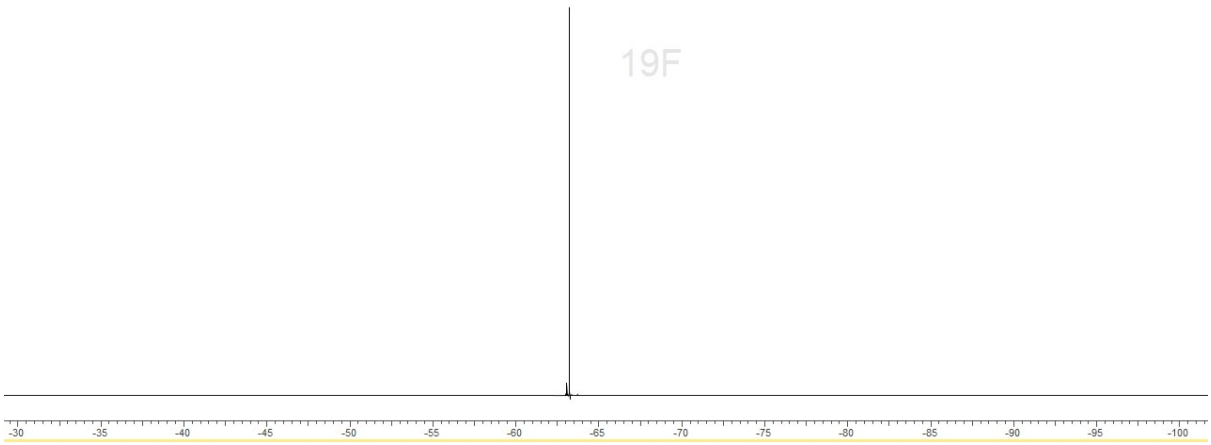
S11.5 – IR spectrum (Nujol)

Figure S12 – [Pb{MeC(CH_2PPh_2)$_3$}][BAr^F]$_2$

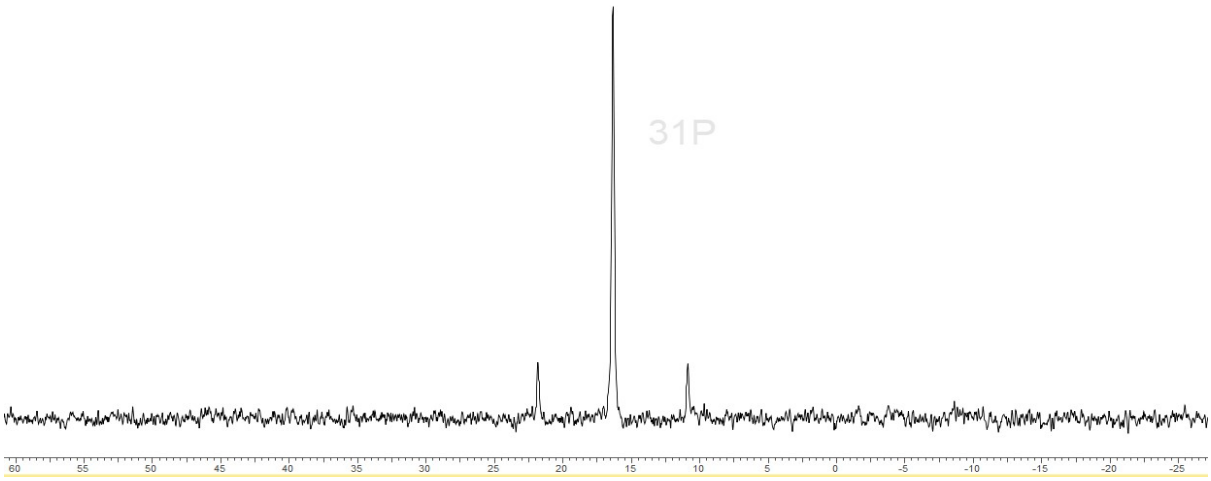
S12.1– ^{1}H NMR spectrum (298 K, CD_3CN)



S12.2 – ^{19}F{^{1}H} NMR spectrum (298 K, CD_3CN)



S12.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



S12.4 IR spectrum (Nujol)

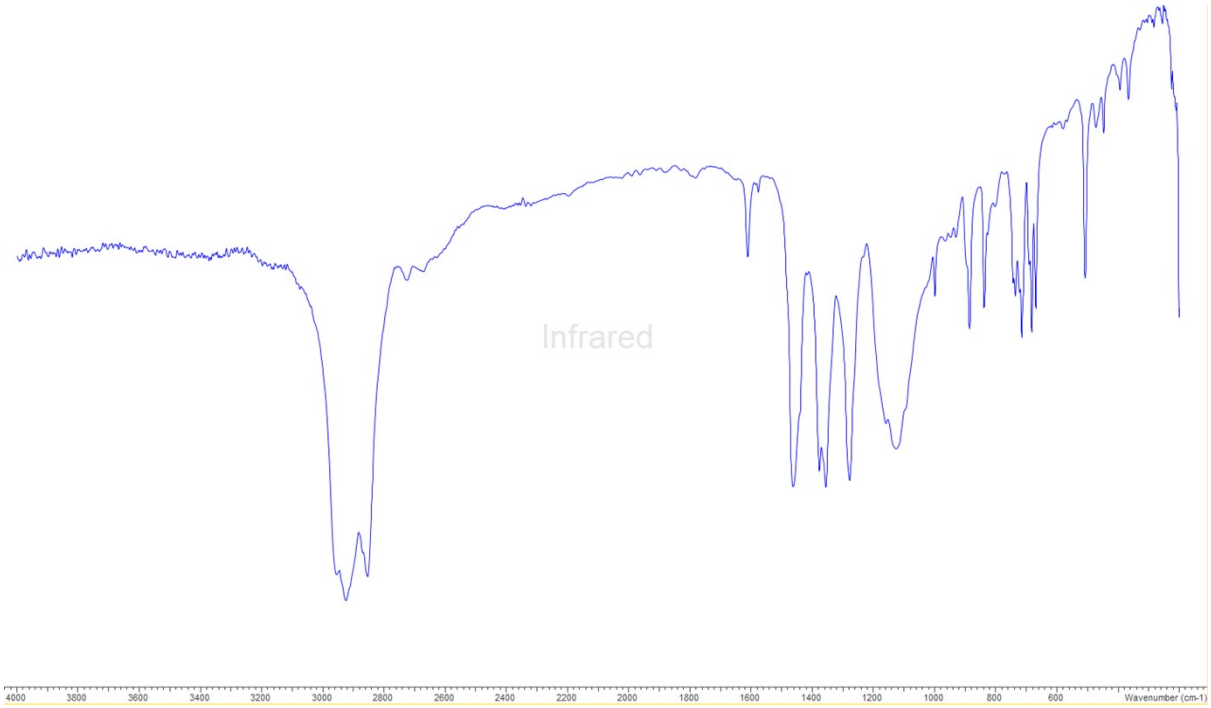
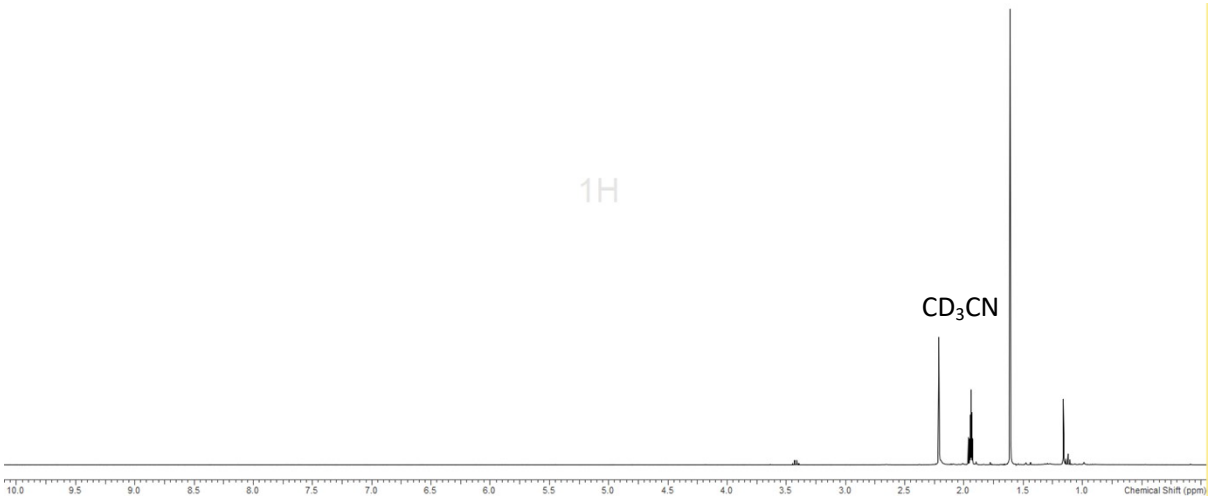


Figure S13 – $[Pb(OTf)_2\{MeC(CH_2AsMe_2)_3\}]$

S13.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



S13.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)

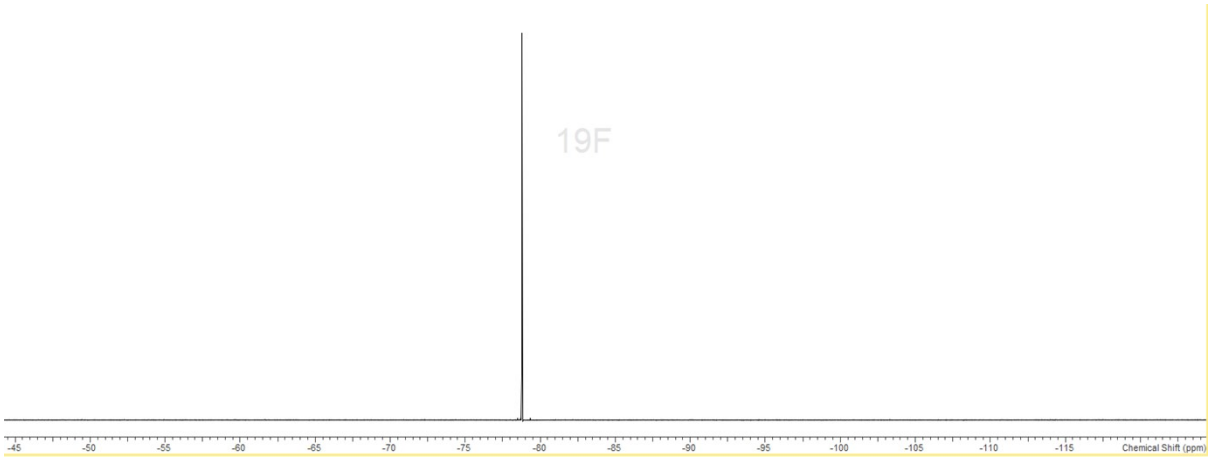
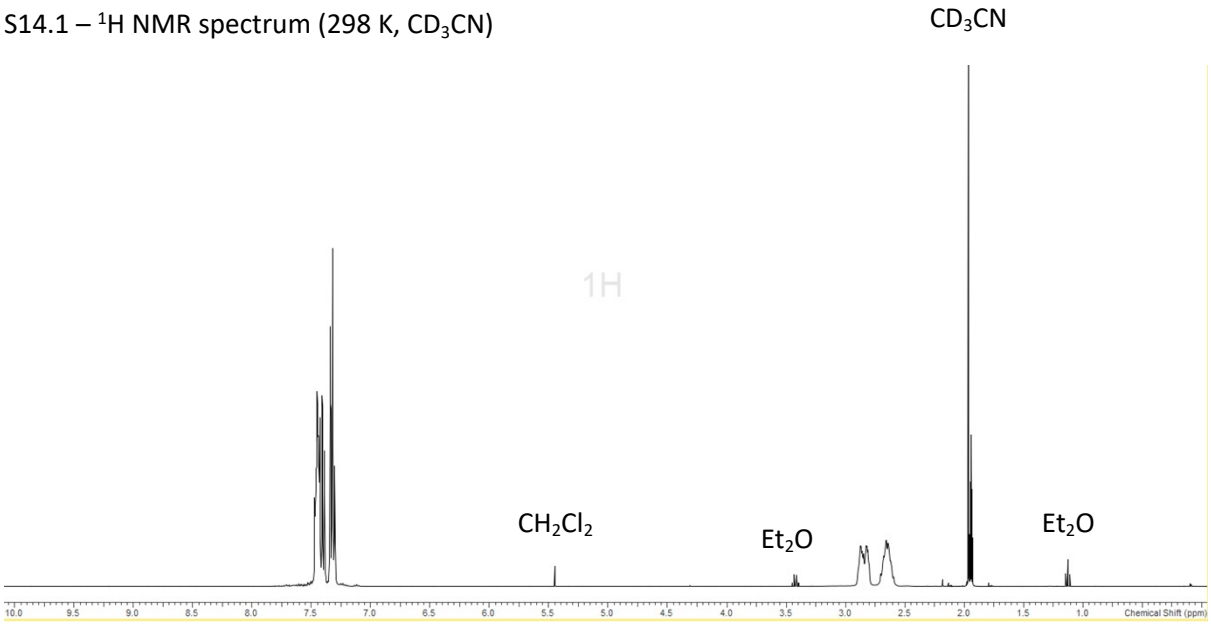
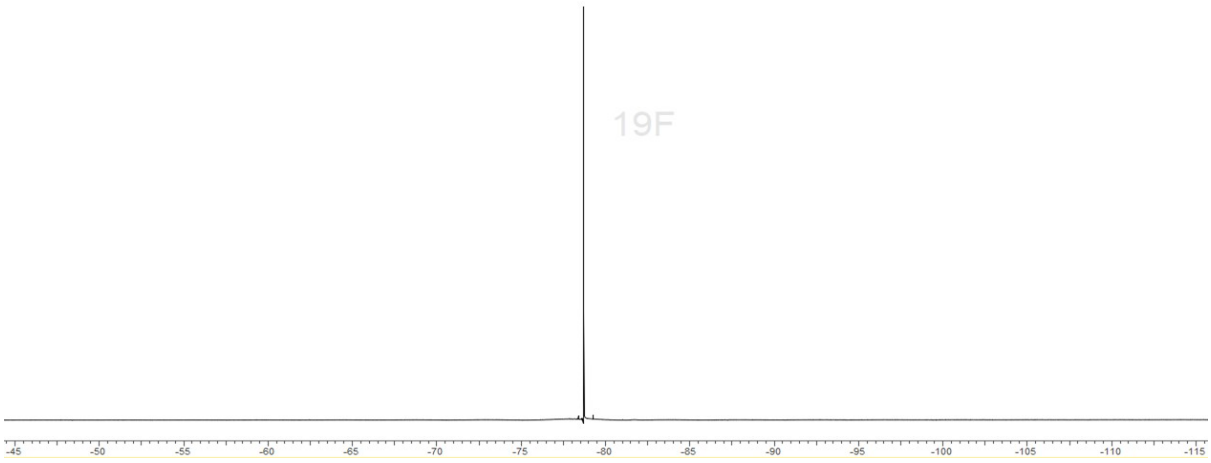


Figure S14 – [Pb(OTf){P($CH_2CH_2PPh_2$)$_3$}][OTf]

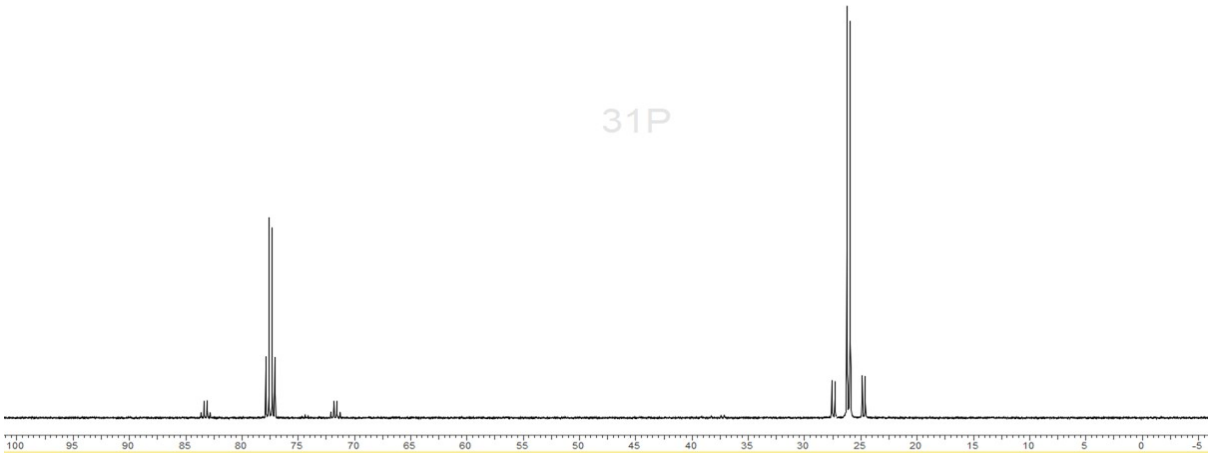
S14.1 – ^{1}H NMR spectrum (298 K, CD_3CN)



S14.2 – $^{19}F\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



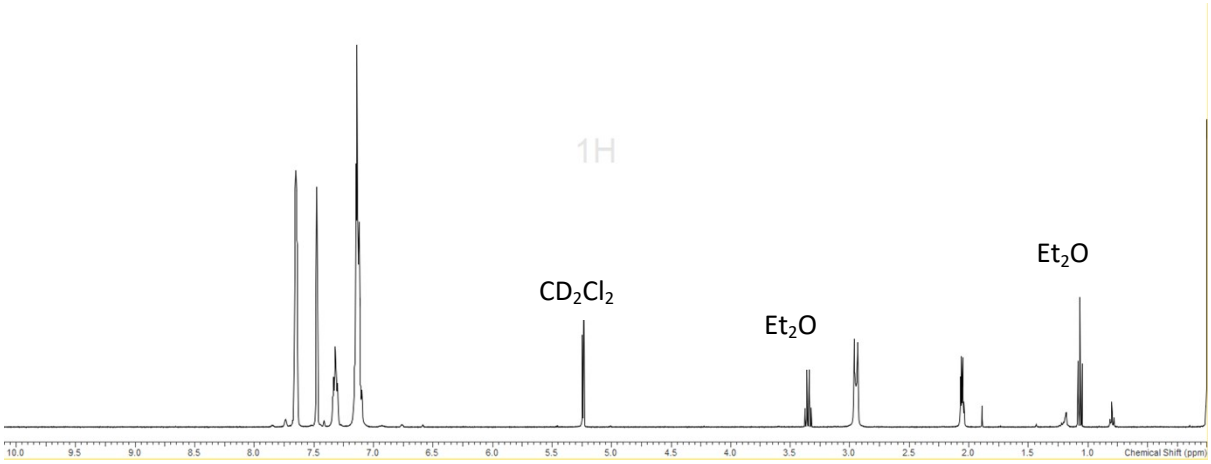
S14.3 – $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_3CN)



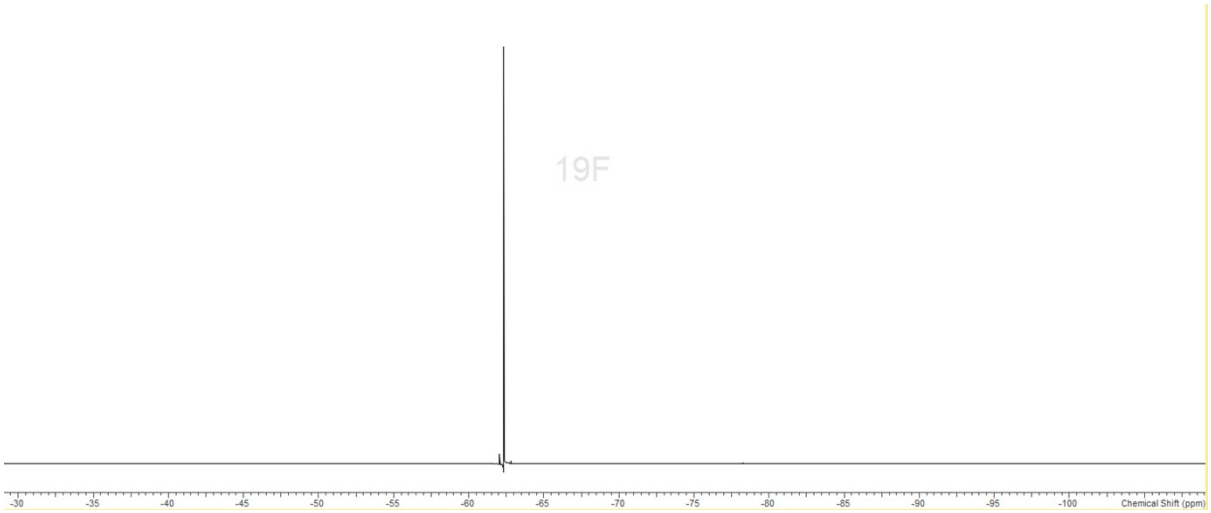
S14.4 – IR spectrum (Nujol)

Figure S15 – [Ge{MeC(CH_2PPh_2)$_3$}][BAr^F]$_2$

S15.1 – ^{1}H NMR spectrum (298 K, CD_2Cl_2)



S15.2 – ^{19}F{^{1}H} NMR spectrum (298 K, CD_2Cl_2)



S15.3 - $^{31}P\{^{1}H\}$ NMR spectrum (298 K, CD_2Cl_2)

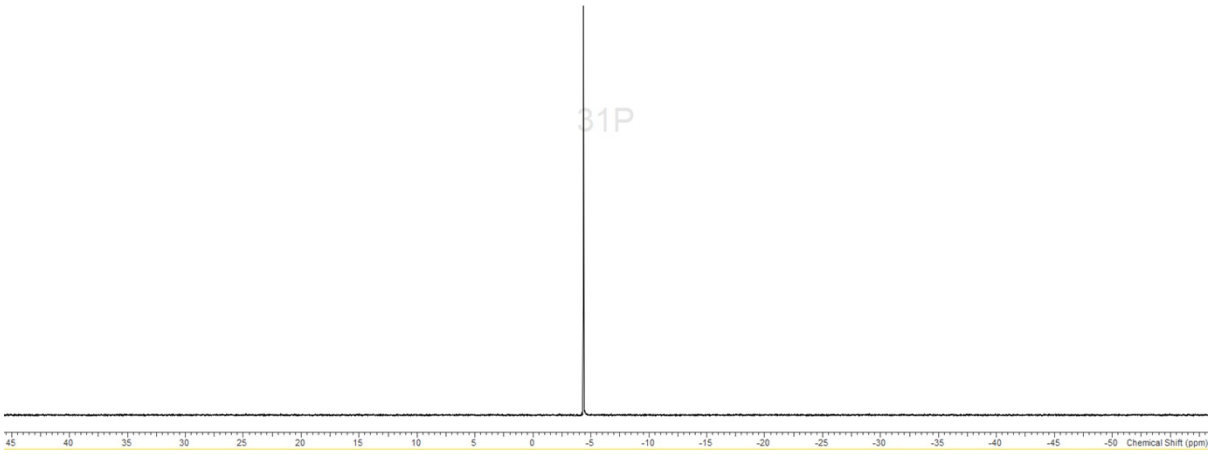


Figure S16 – $Sn(OTf)_2$

S16.1 – IR spectrum (Nujol)

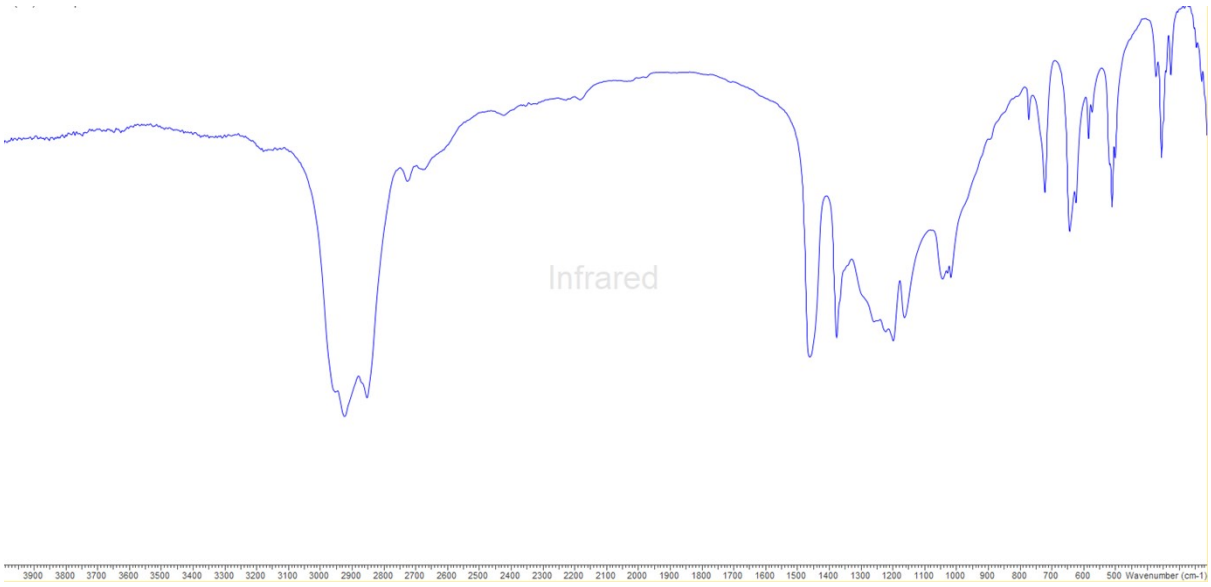


Figure S17 – $Pb(OTf)_2$

S17.1 - IR spectrum (Nujol)

Table S1 - X-ray crystallographic parameters[a]

Complex	$[Sn(OTf)_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	$[Sn(OTf)_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$	$[Sn(OTf)\{PhP(CH_2CH_2PPh_2)_2\}][OTf]\cdot Et_2O$ *
Formula	$C_{36}H_{48}F_{18}O_{18}P_6S_6Sn_3$	$C_{12}H_{16}As_2F_6O_6S_2Sn$	$C_{40}H_{43}F_6O_7P_3S_2Sn$
M	2215.59	702.92	1025.46
Crystal system	orthorhombic	monoclinic	monoclinic
Space group (no.)	Pnna (52)	C2/c (15)	$P2_1/n$ (14)
a /Å	16.2539(3)	15.8316(5)	15.8064(5)
b /Å	24.0871(5)	14.0437(4)	10.1469(2)
c /Å	20.0157(5)	9.7168(3)	27.2193(6)
α /°	90	90	90
β /°	90	95.863(3)	91.081(2)
γ /°	90	90	90
U /Å^3	7836.3(3)	2149.06(11)	4364.82(19)
Z	4	4	4
μ(Mo-K_α) /mm^{-1}	1.346	4.517	7.232
F(000)	4464	1352	2080
Total number reflns	74108	14822	78496
R_{int}	0.0774	0.0346	0.0791
Unique reflns	10118	3237	8919
No. of params, restraints	490, 468	134, 0	534, 9
GOF	1.042	1.054	1.085
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.0602, 0.1519	0.0203, 0.0453	0.0624, 0.1642
R_1, wR_2 (all data)	0.0959, 0.1674	0.0246, 0.0464	0.0671, 0.1681

Complex	$[Sn(OTf)_2\{o\text{-}C_6H_4(PPh_2)_2\}]\cdot CH_2Cl_2$	$[Sn(OTf)\{P(CH_2CH_2PPh_2)_3\}][OTf]\cdot CH_2Cl_2$ *	$[Ge\{MeC(CH_2PPh_2)_3\}][BAr^F]_2\cdot 0.5\ CH_2Cl_2$
Formula	$C_{33}H_{26}Cl_2F_6O_6P_2S_2Sn$	$C_{45}H_{44}Cl_2F_6O_6P_4S_2Sn$	$C_{105.5}H_{64}B_2ClF_{48}GeP_3$
M	948.19	1172.39	2466.13
Crystal system	monoclinic	monoclinic	triclinic
Space group (no.)	$I1_2/a$ (15)	$P2_1/c$ (14)	P-1 (2)
a /Å	26.1551(8)	16.1811(2)	12.73530(10)
b /Å	8.8030(2)	14.49840(10)	16.7939(2)
c /Å	33.6112(9)	21.3672(2)	26.6298(3)
α /°	90	90	79.1070(10)
β /°	107.604(3)	97.9480(10)	89.4620(10)
γ /°	90	90	69.1300(10)
U /Å^3	7376.3(4)	4964.59(9)	5215.47(10)
Z	8	4	2
μ(Mo-K_α) /mm^{-1}	1.112	7.689	0.500
F(000)	3776	2368	2466
Total number reflns	49013	118476	134869
R_{int}	0.0506	0.0657	0.0290
Unique reflns	9513	8946	26892
No. of params, restraints	469, 0	595, 0	1600, 1546
GOF	1.138	1.050	1.016
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.0497, 0.1084	0.0379, 0.1045	0.0440, 0.1048
R_1, wR_2 (all data)	0.0646, 0.1126	0.0391, 0.1054	0.0508, 0.1091

Complex	$[Pb(OTf)_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	$[Pb(OTf)_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$ *	$[\{Pb_2(OTf)_3\{MeC(CH_2PPh_2)_3\}_2]OTf \cdot MeCN$
Formula	$C_{12}H_{16}F_6O_6P_2PbS_2$	$C_{12}H_{16}As_2F_6O_6PbS_2$	$C_{88}H_{81}F_{12}NO_{12}P_6Pb_2S_4$
M	703.50	791.40	2300.97
Crystal system	triclinic	monoclinic	orthorhombic
Space group (no.)	P-1 (2)	$P2_1/c$ (14)	Pbca (61)
a /Å	10.4025(2)	10.58200(10)	20.7298(2)
b /Å	10.4520(2)	21.4899(2)	29.4124(2)
c /Å	11.9474(3)	9.72860(10)	29.6444(2)
α /°	105.687(2)	90	90
β /°	106.932(2)	95.1510(10)	90
γ /°	110.441(2)	90	90
U /Å^3	1059.39(4)	2203.41(4)	18074.6(2)
Z	2	4	8
μ(Mo-K_α) /mm^{-1}	8.389	20.735	4.005
F(000)	668	1480	9104
Total number reflns	15069	21504	274211
R_{int}	0.0230	0.0280	0.0381
Unique reflns	6025	3966	23338
No. of params, restraints	266, 0	266, 218	1157, 603
GOF	1.035	1.053	1.017
R_1, wR_2 $[I > 2\sigma(I)]^b$	0.0192, 0.0419	0.0289, 0.0675	0.0191, 0.426
R_1, wR_2 (all data)	0.0219, 0.0430	0.0294, 0.0678	0.0244, 0.0448

Complex	[Pb(OTf){P($CH_2CH_2PPh_2$)$_3$}]OTf ·MeCN	[Sn{MeC(CH_2PPh_2)$_3$}][BAr^F]$_2$ ·0.5CH_2Cl_2	[Pb{MeC(CH_2PPh_2)$_3$}][BAr^F]$_2$ ·0.5CH_2Cl_2
Formula	$C_{46}H_{45}F_6NO_6P_4PbS_2$	$C_{105.5}H_{64}B_2ClF_{48}P_3Sn$	$C_{105.5}H_{64}B_2ClF_{48}P_3Pb$
M	1217.02	2512.23	2600.73
Crystal system	monoclinic	triclinic	triclinic
Space group (no.)	$P2_1/c$ (14)	P-1 (2)	P-1 (2)
a /Å	16.3354(5)	12.7643(2)	12.7607(2)
b /Å	14.2959(3)	16.7092(2)	16.7182(2)
c /Å	21.6774(5)	26.6628(3)	26.6413(3)
α /°	90	78.5010(10)	78.0880(10)
β /°	102.940(2)	89.4220(10)	89.0490(10)
γ /°	90	69.6880(10)	69.7810(10)
U /Å^3	4933.7(2)	5215.19(12)	5208.49(12)
Z	4	2	2
μ(Mo-K_α) /mm^{-1}	3.704	0.451	1.826
F(000)	2416	2502	2566
Total number reflns	44954	141657	134409
R_{int}	0.0373	0.0332	0.0408
Unique reflns	11554	31821	26898
No. of params, restraints	604, 0	1572, 1784	1544, 1392
GOF	1.019	1.036	1.028
R_1, wR_2 [I > 2σ(I)][b]	0.0314, 0.0515	0.0443, 0.0987	0.0343, 0.0794
R_1, wR_2 (all data)	0.0470, 0.0546	0.0536, 0.1032	0.0383, 0.0815

[a] Common items: T = 100 K; θ(max) = 27.5°; wavelength (Mo-K_α) = 0.71073 Å, except for those marked * which used (Cu- K_α) radiation. λ = 1.54184 Å; [b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)_2/\Sigma wF_o^4]^{1/2}$

Table S2 Experimental (X-ray) *vs.* calculated (DFT, B3LYP-D3) metrics for $[M\{MeC(CH_2PPh_2)_3\}]^{2+}$ (M = Ge, Sn, Pb)

$[Ge\{MeC(CH_2PPh_2)_3\}]^{2+}$	X-ray	DFT
d(Ge-P) / Å	2.4070(4) 2.4239(4) 2.4110(5)	2.42947 2.42978 2.42966
<(P-Ge-P) / °	86.609(14) 85.412(15) 85.912(15)	86.13757 86.17999 86.15668
$[Sn\{MeC(CH_2PPh_2)_3\}]^{2+}$	X-ray	DFT
d(Sn-P) / Å	2.6194(4) 2.6438(4) 2.6249(4)	2.64552 2.64663 2.64198
<(P-Sn-P) / °	82.120(13) 80.160(14) 80.761(14)	80.81234 81.57846 80.70846
$[Pb\{MeC(CH_2PPh_2)_3\}]^{2+}$	X-ray	DFT
d(Pb-P) / Å	2.7092(6) 2.7184(7) 2.7360(5)	2.71964 2.72140 2.72068
<(P-Pb-P) / °	77.868(17) 80.594(17) 78.676(17)	79.51974 79.61498 79.72607