Electronic Supplementary Material (ESI) for Dalton Transactions.

Neutral and cationic phosphine and arsine complexes of tin(IV) halides: synthesis, properties, structures and anion influence

ESI

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Supporting Information

Figure S1 [$SnCl_4(AsEt_3)_2$]

Figure S1.1 [$SnCl_4(AsEt_3)_2$]: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.31 (q, [12H], $^3J_{H-H}$ = 7.6 Hz, CH_2), 1.39 (t, [18H], $^3J_{H-H}$ = 7.6 Hz, CH_3). * *impurity due to decomposition/oxidation*

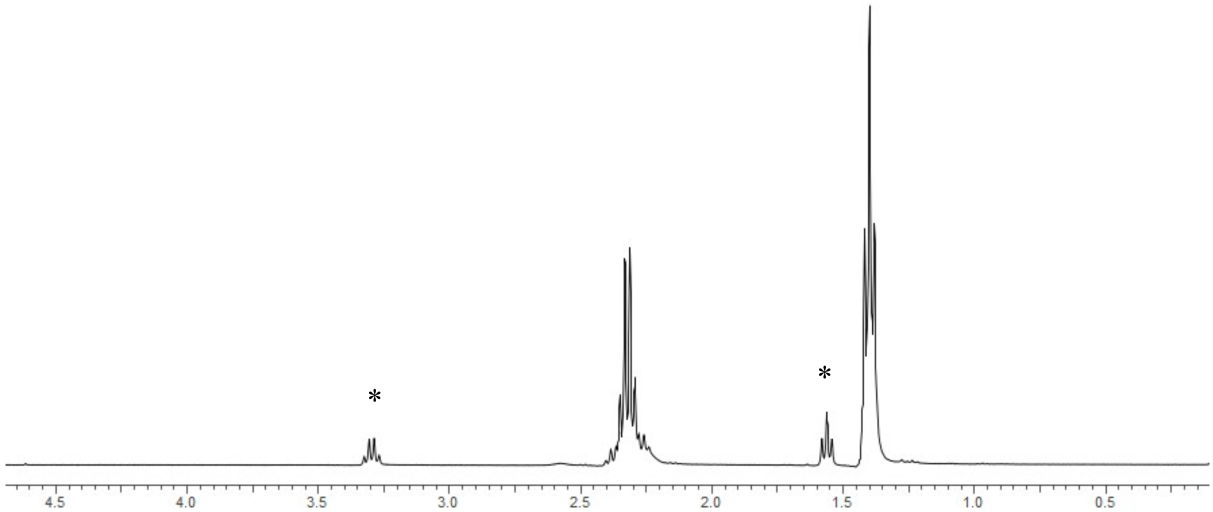


Figure S1.2 [$SnCl_4(AsEt_3)_2$]: ^{1}H NMR ($CDCl_3$, 295 K): δ = 2.34 (q, [12H], $^3J_{H-H}$ = 7.6 Hz, CH_2), 1.42 (t, [18H], $^3J_{H-H}$ = 7.6 Hz, CH_3). * *impurity due to decomposition/oxidation.*

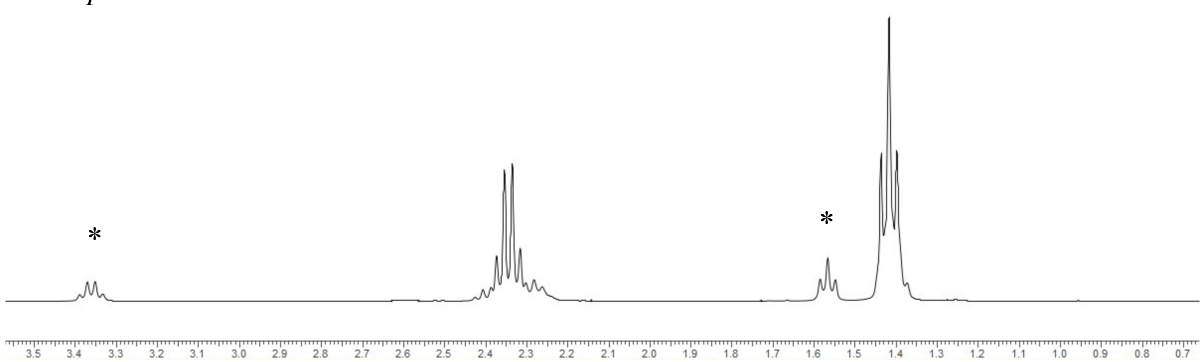


Figure S1.3 [$SnCl_4(AsEt_3)_2$]: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 8.62 (CH_2), 15.04 (CH_3).

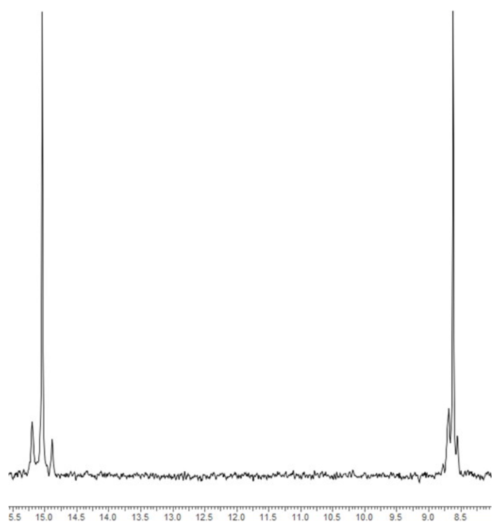


Figure S1.4 $[SnCl_4(AsEt_3)_2]$: ^{119}Sn NMR (CD_2Cl_2, 193K): $\delta = -657.4$.

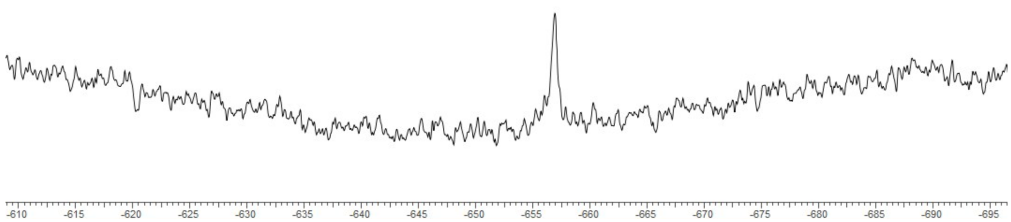


Figure S1.5 $[SnCl_4(AsEt_3)_2]$: IR (Nujol/cm^{-1}) = 288 (Sn-Cl).

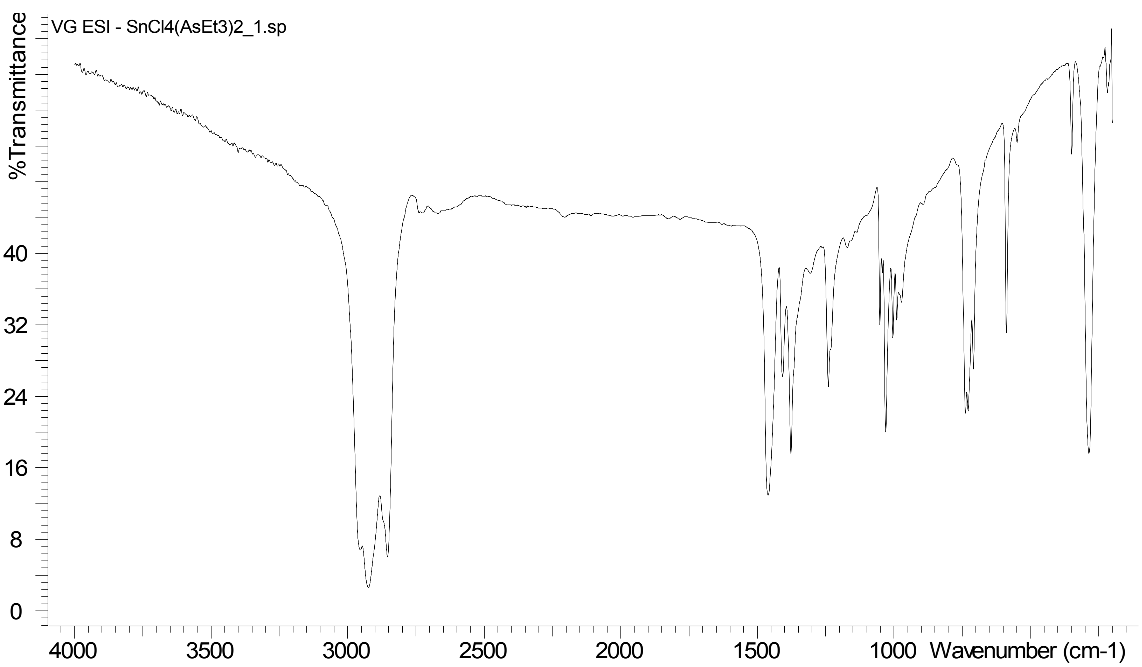


Figure S2 [$SnBr_4(AsEt_3)_2$]

Figure S2.1 [$SnBr_4(AsEt_3)_2$]: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.35 (q, [12H], $^{3}J_{H-H}$ = 7.6 Hz, CH_2), 1.43 (t, [18H], $^{3}J_{H-H}$ = 7.6 Hz, CH_3).

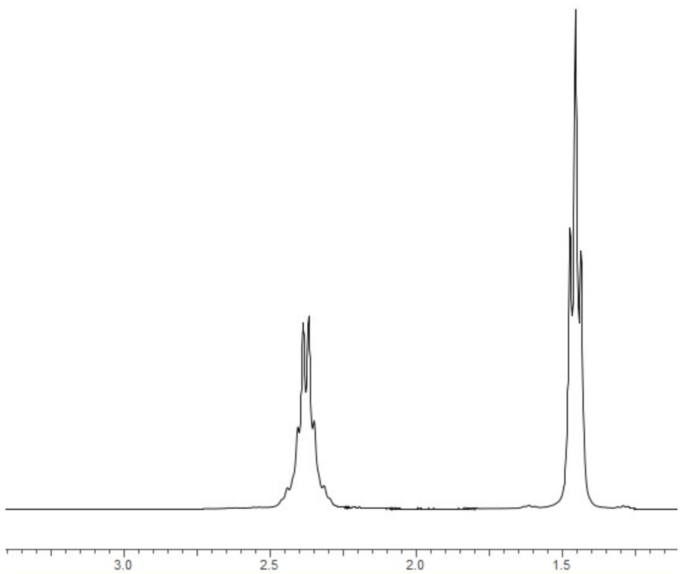


Figure S2.2 [$SnBr_4(AsEt_3)_2$]: $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): δ = 8.5 (CH_2), 14.8 (CH_3).

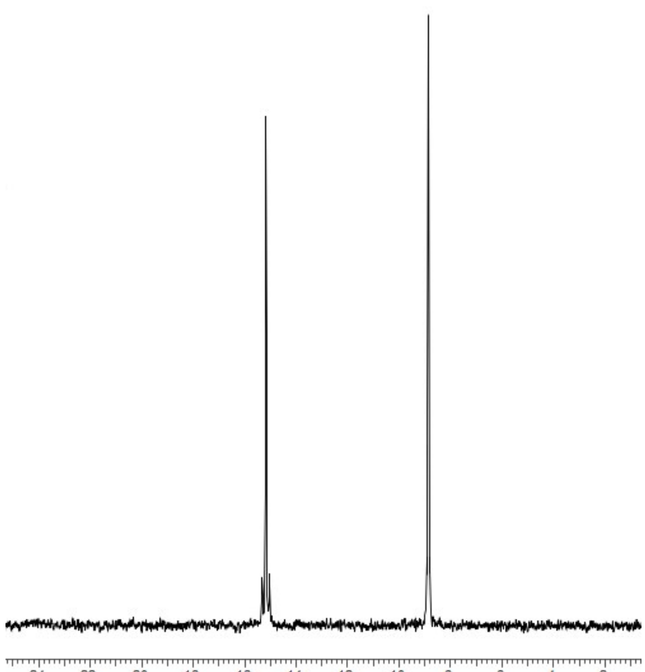


Figure S2.3 $[SnBr_4(AsEt_3)_2]$: ^{119}Sn NMR (CD_2Cl_2, 295 K): δ = –1173.4.

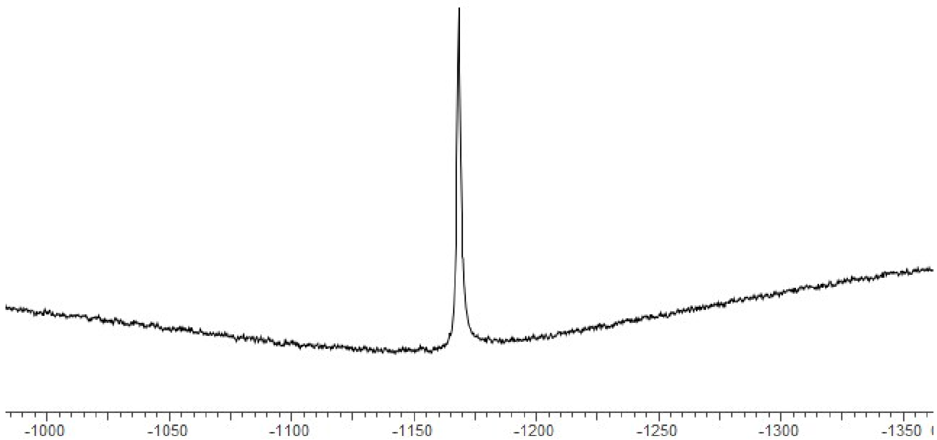


Figure S2.4 $[SnBr_4(AsEt_3)_2]$: ^{119}Sn NMR (CD_2Cl_2, 193 K): δ –1125.3.

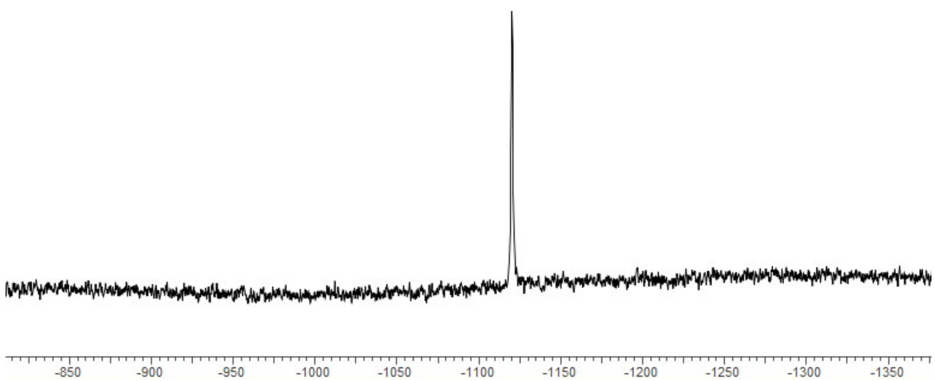


Figure S2.5 [$SnBr_4(AsEt_3)_2$]: IR (Nujol/cm^{-1}) = 210s (Sn-Br).

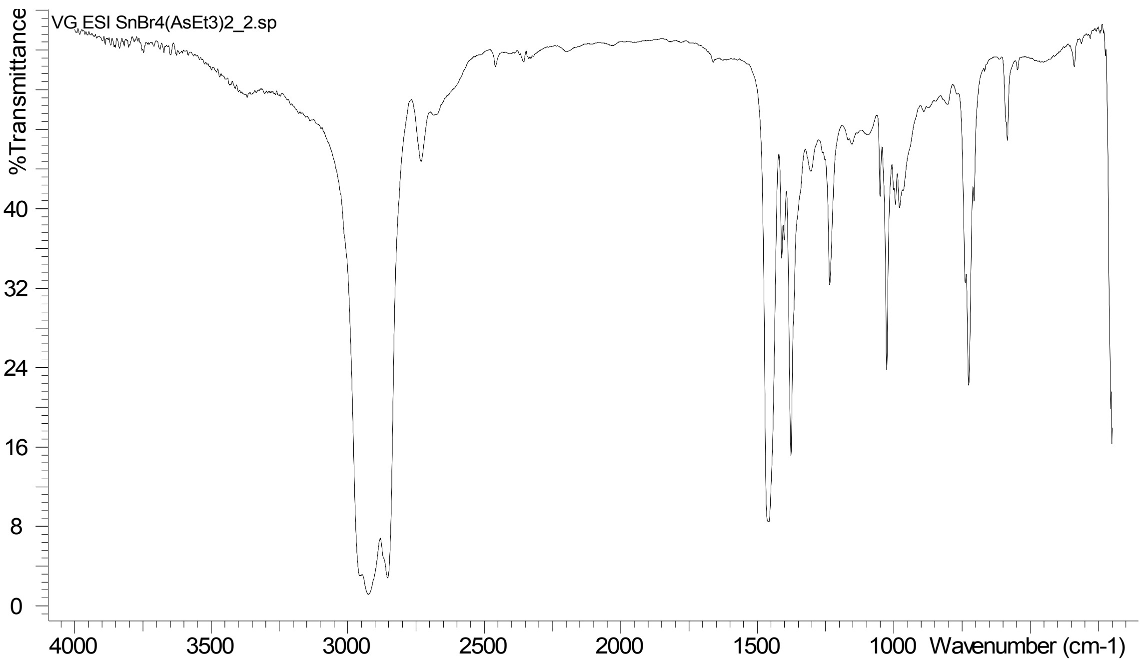


Figure S3 $[SnCl_3(AsEt_3)_2OTf]$

Figure S3.1 $[SnCl_3(AsEt_3)_2OTf]$: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.38 (q, [12H], $^{3}J_{H\text{-}H}$ = 7.8 Hz, CH_2), 1.39 (t, [18H], $^{3}J_{H\text{-}H}$ = 7.8 Hz, CH_3). * *impurity due to ligand chlorination.*

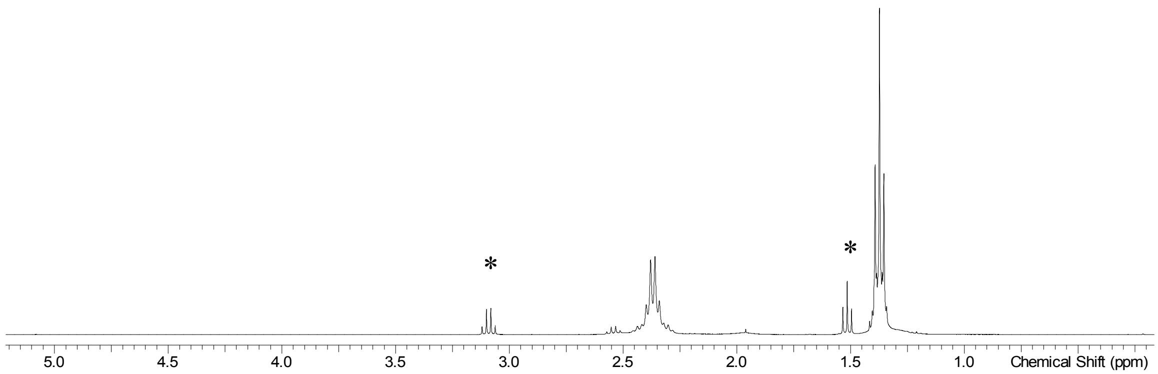


Figure S3.2 $[SnCl_3(AsEt_3)_2OTf]$: $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): δ = 9.0 (CH_2), 16.0 (CH_3). * *impurity due to ligand chlorination.*

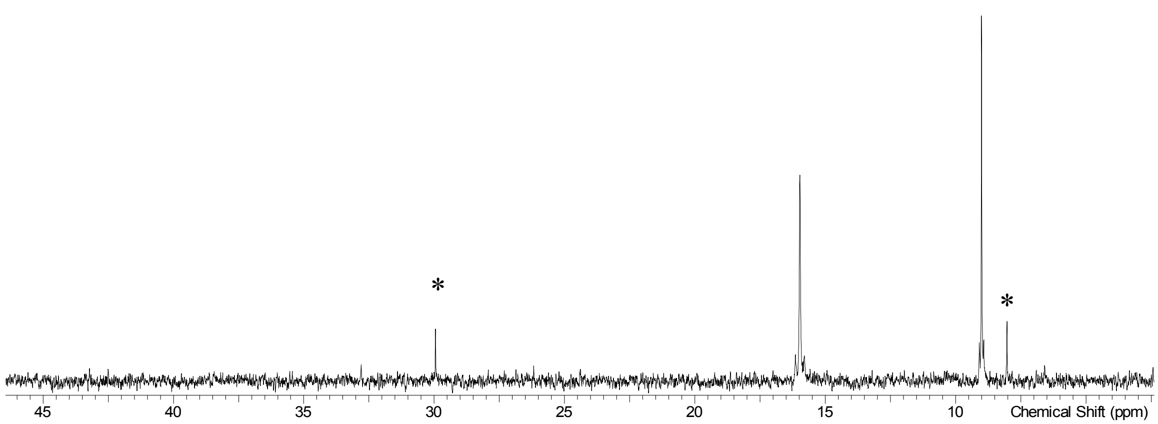


Figure S3.3 $[SnCl_3(AsEt_3)_2OTf]$: $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): δ = -78.2 (-OTf).

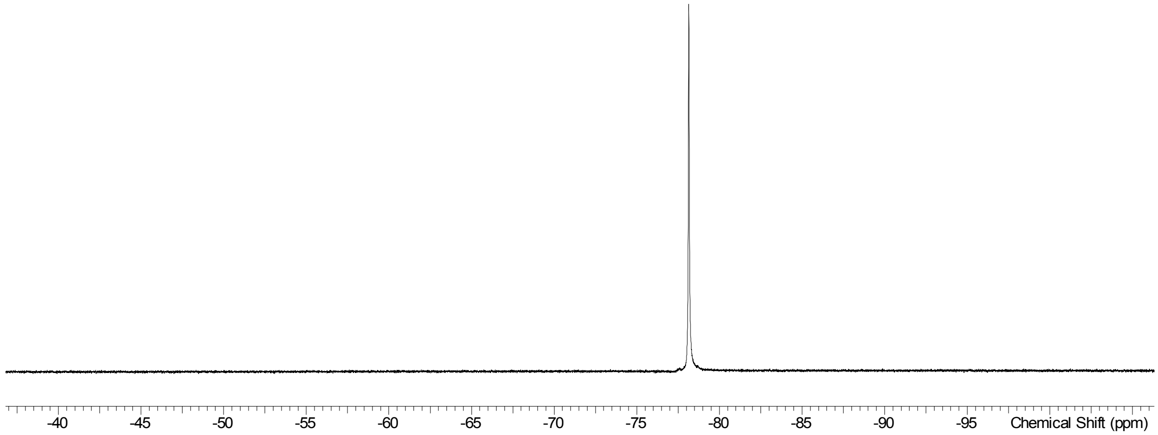


Figure S3.4 [$SnCl_3(AsEt_3)_2OTf$]: $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 183 K): δ = -620
* *[$SnCl_4(AsEt_3)_2$] impurity.*

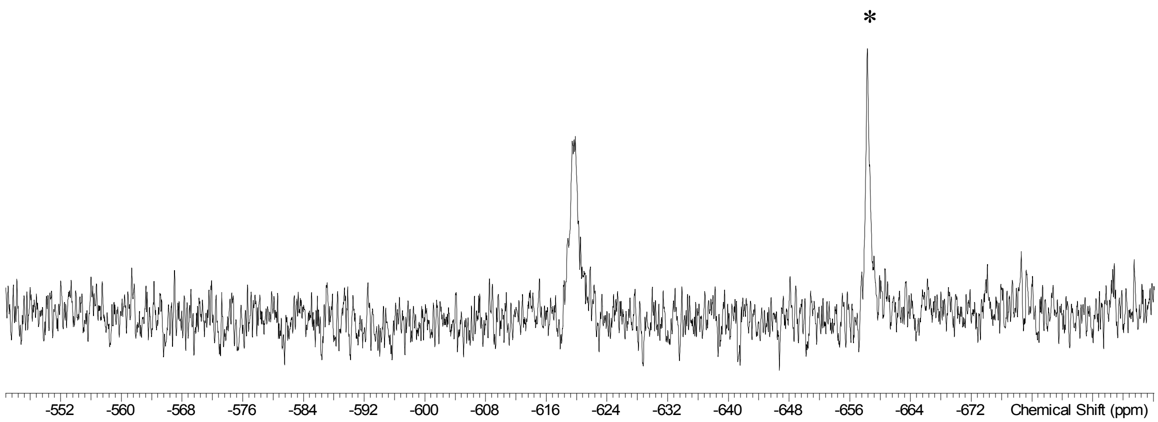


Figure S3.5 [$SnCl_3(AsEt_3)_2OTf$]: IR (Nujol/cm^{-1}) = 294s, 378w (Sn-Cl), 1156m (-OSO_2), 1231m, 1200m (CF_3).

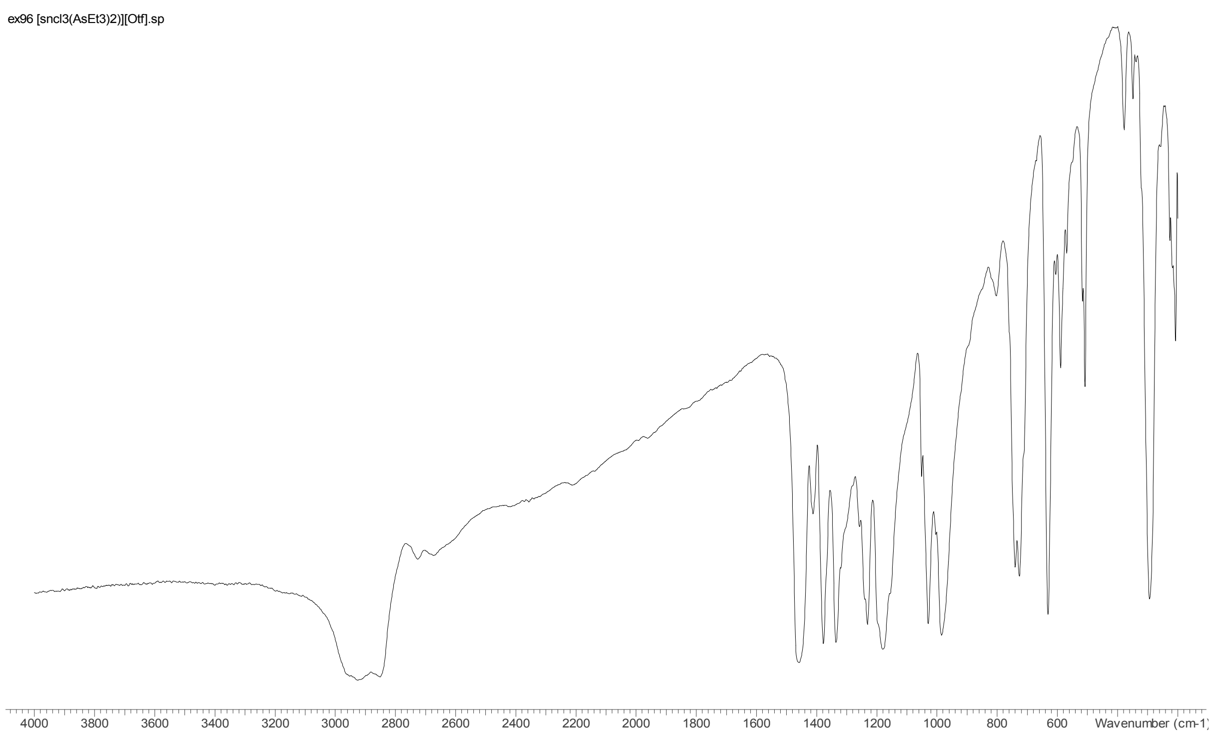


Figure S4 [$SnCl_3(PMe_3)_2OTf$]

Figure S4.1 [$SnCl_3(PMe_3)_2OTf$]: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.84 (m)

* *Hydrolysis/decomposition.*

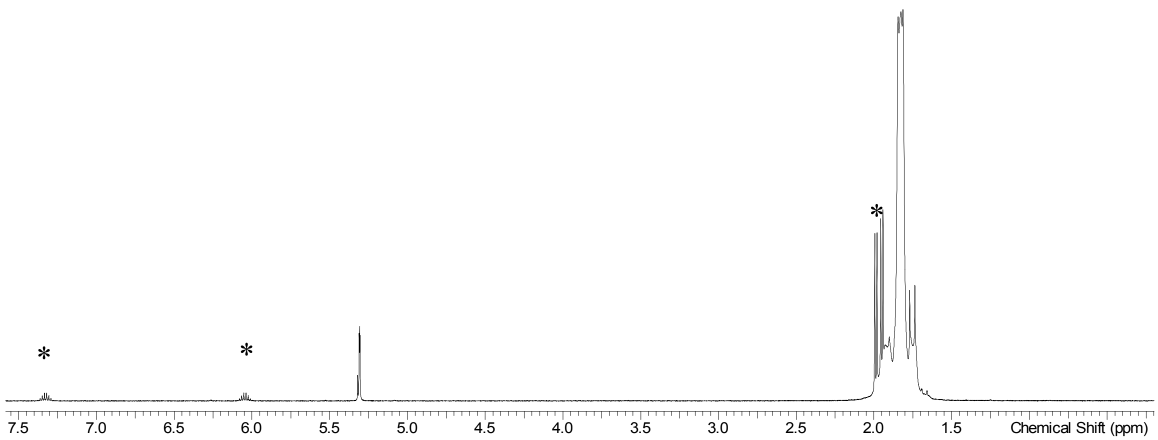


Figure S4.2 [$SnCl_3(PMe_3)_2OTf$]: $^{13}C\{^{1}H\}$ (CD_2Cl_2, 295 K): δ = 10.09 (t, $^{1}J + ^{3}J_{31P-13C}$ = 19.4 Hz, CH_3). * *Hydrolysis/decomposition.*

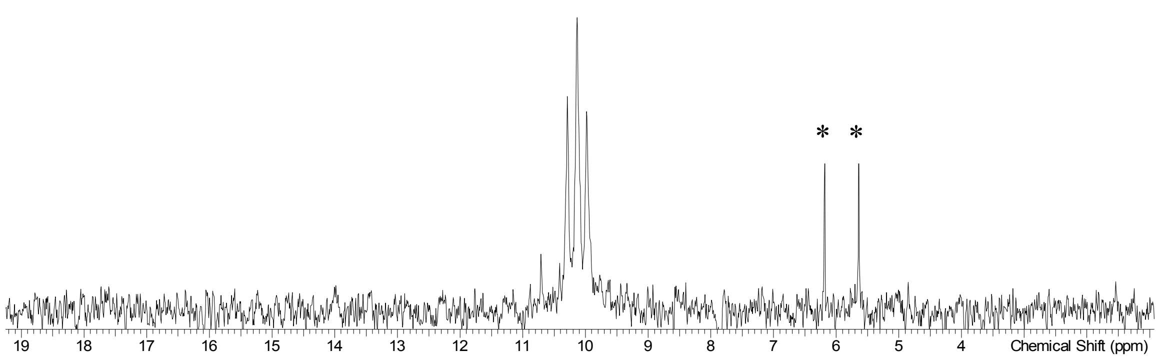


Figure S4.3 [$SnCl_3(PMe_3)_2OTf$]: $^{19}F\{^{1}H\}$ (CD_2Cl_2, 295 K): δ = -78.6.

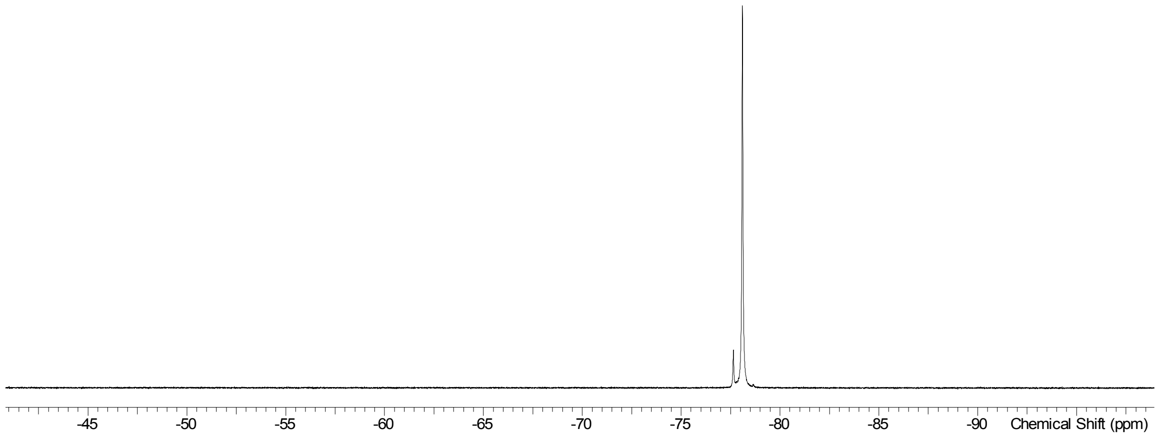


Figure S4.4 $[SnCl_3(PMe_3)_2OTf]$: $^{31}P\{^1H\}$ (CD_2Cl_2, 298 K): δ = 8.74 (s, $^1J_{31P\text{-}117Sn}$= 2814, $^1J_{31P\text{-}119Sn}$ = 2963 Hz). * *Hydrolysis/decomposition*; $^+$ $[SnCl_4(PMe_3)_2]$.

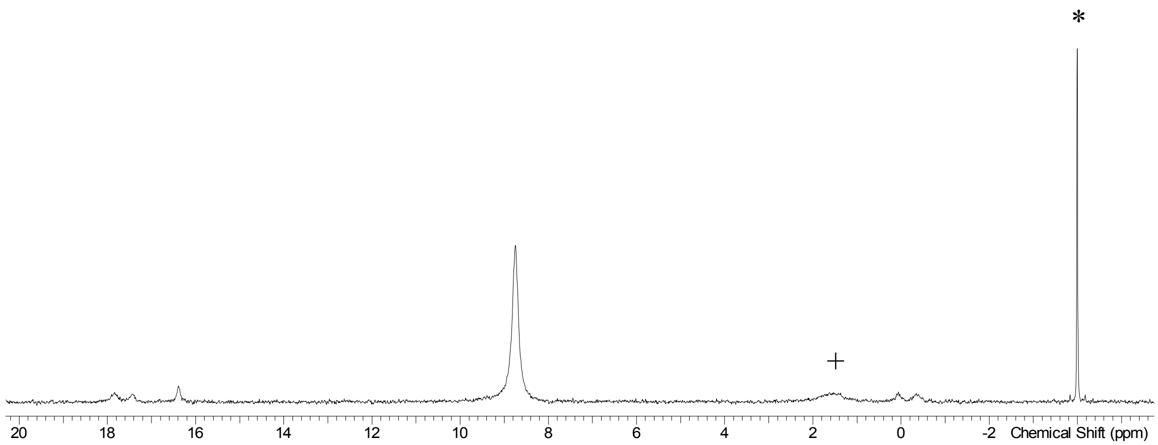


Figure S4.5 $[SnCl_3(PMe_3)_2OTf]$: ^{119}Sn (CD_2Cl_2, 298 K): δ = –516 (t, $^1J_{P\text{-}119Sn}$ = 2963 Hz).

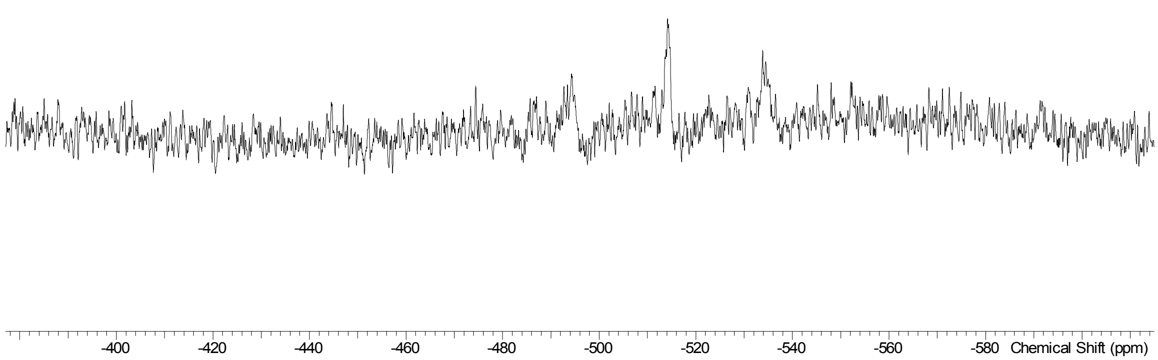


Figure 4.6 [$SnCl_3(PMe_3)_2OTf$]: IR (Nujol/cm^{-1}) = 296m, 306m, 377w (Sn-Cl), 1173m (-OSO_2), 1200m, 1235m (CF_3).

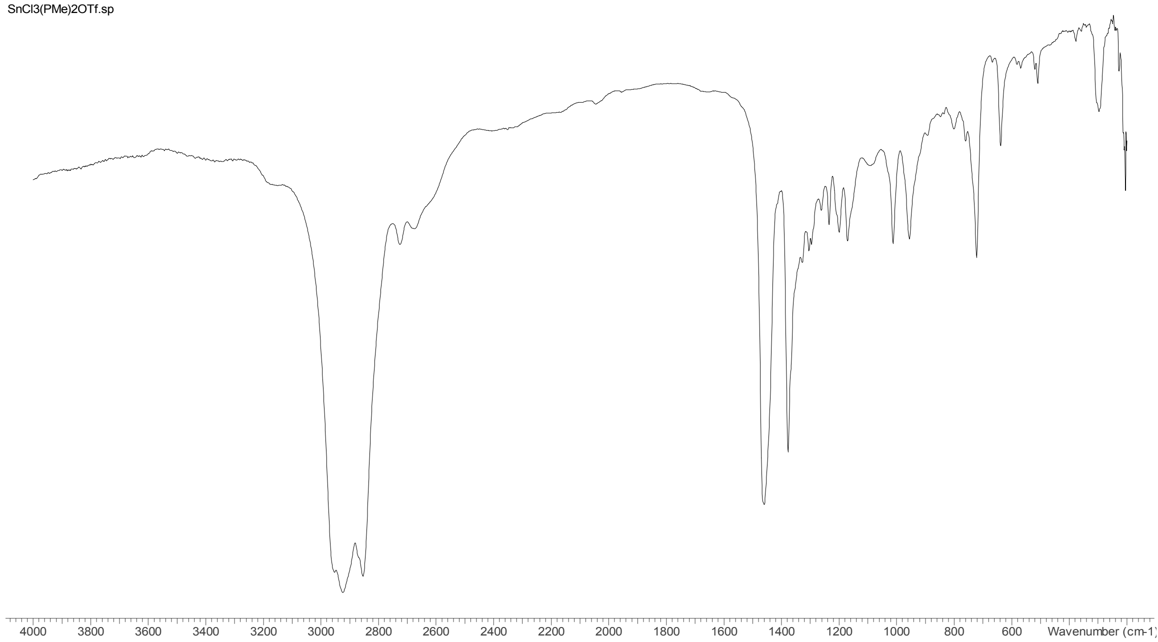


Figure S5 [$SnCl_3(PEt_3)_2OTf$]

Figure S5.1 [$SnCl_3(PEt_3)_2OTf$]: ^1H NMR (CD_2Cl_2, 295 K): δ = 1.30 (m, [18H], CH_3), 2.33 (m, [12H], CH_2) * *Hydrolysis/decomposition.*

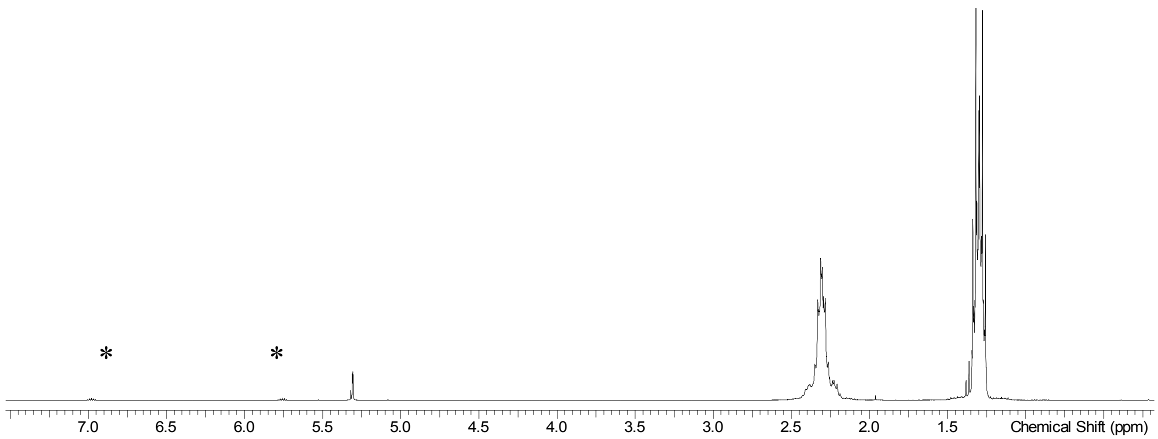


Figure S5.2 [$SnCl_3(PEt_3)_2OTf$]: $^{13}C\{^1H\}$ (CD_2Cl_2, 295 K): δ = 7.59 (t, $^1J + ^3J_{31P\text{-}13C}$ = 2.93 Hz, CH_2), 13.95 (t, $^1J + ^3J_{31P\text{-}13C}$ = 11 Hz, CH_3).

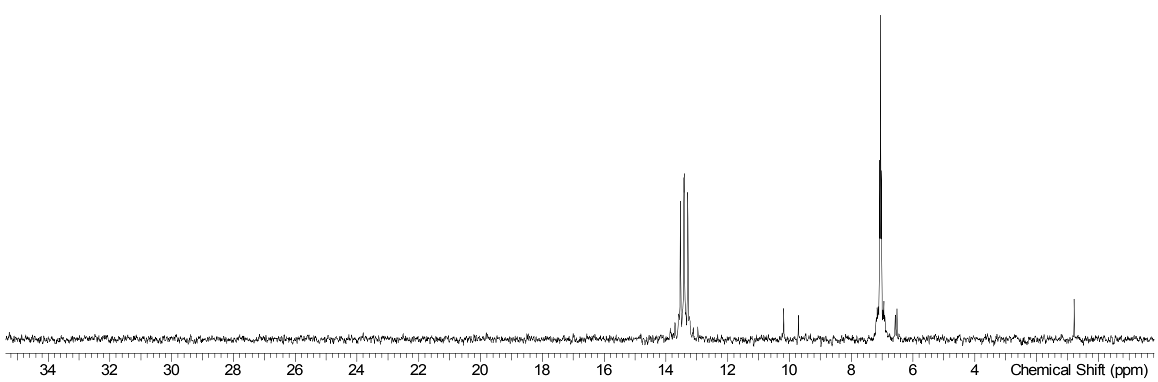


Figure S5.3 [$SnCl_3(PEt_3)_2OTf$]: $^{19}F\{^1H\}$ (CD_2Cl_2, 295 K): δ = –78.6.

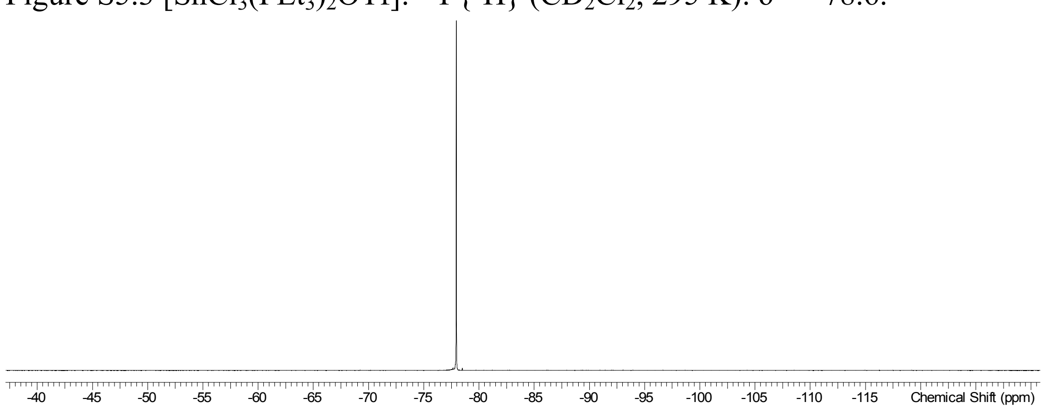


Figure S5.4 [$SnCl_3(PEt_3)_2OTf$]: $^{31}P\{^1H\}$ (CD_2Cl_2, 298 K): δ = 28.45
* *Hydrolysis/decomposition.*

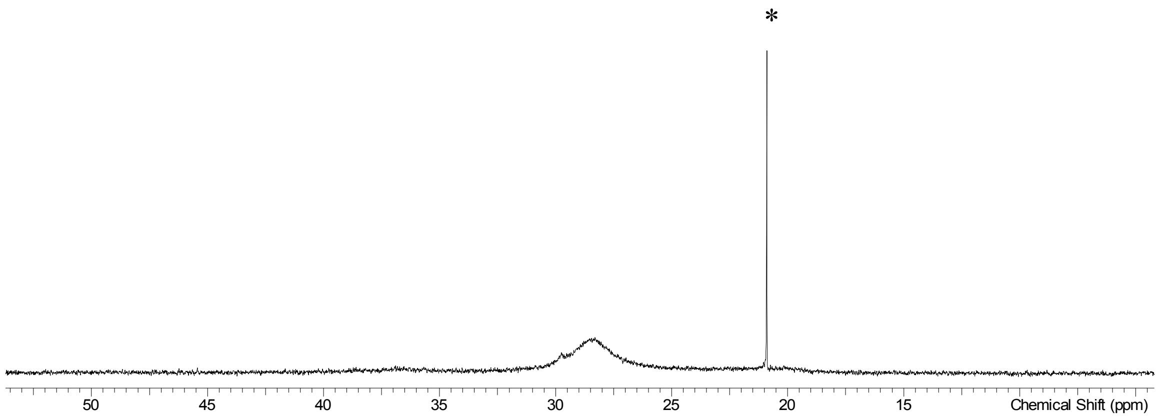


Figure S5.5 [$SnCl_3(PEt_3)_2OTf$]: $^{31}P\{^1H\}$ (CD_2Cl_2, 183 K): δ = 33.58 (s, $^1J_{31P\text{-}117Sn}$ = 2617 Hz, $^1J_{31P\text{-}119Sn}$ = 2734 Hz) * *Hydrolysis/decomposition.*

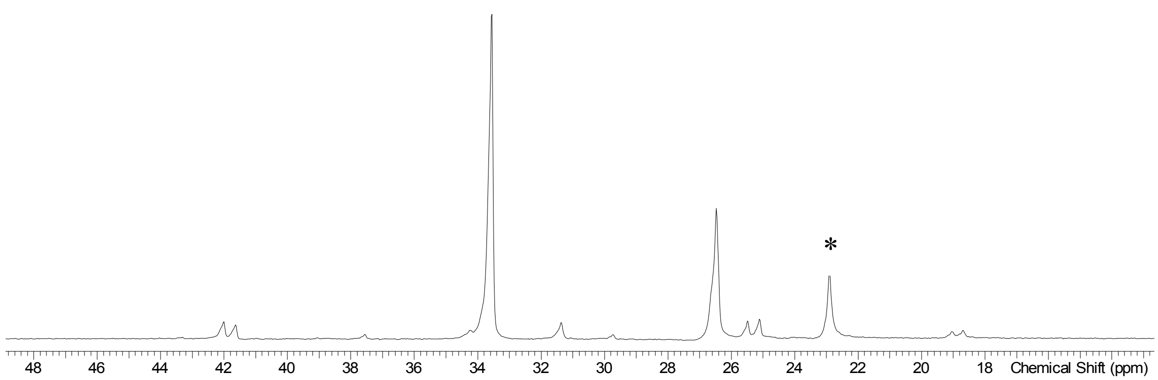


Figure S5.5 [$SnCl_3(PEt_3)_2OTf$]: ^{119}Sn (CD_2Cl_2, 298K): δ = 535.

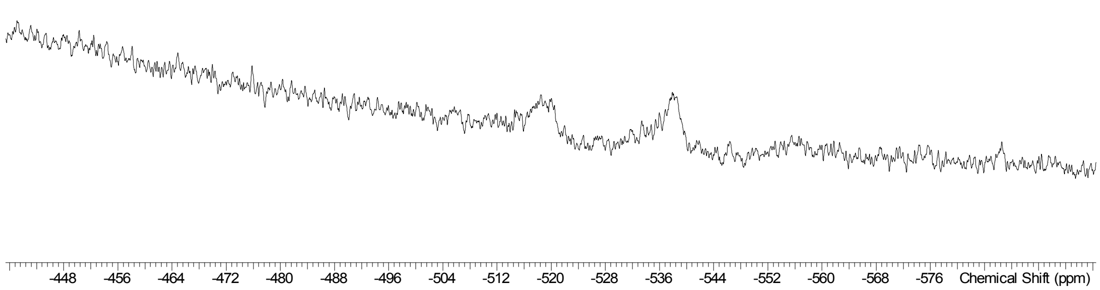


Figure S5.6 [$SnCl_3(PEt_3)_2OTf$]: ^{119}Sn (CD_2Cl_2, 183K): δ = –535 (t, $^{1}J_{31P\text{-}119Sn}$ = 2737 Hz).

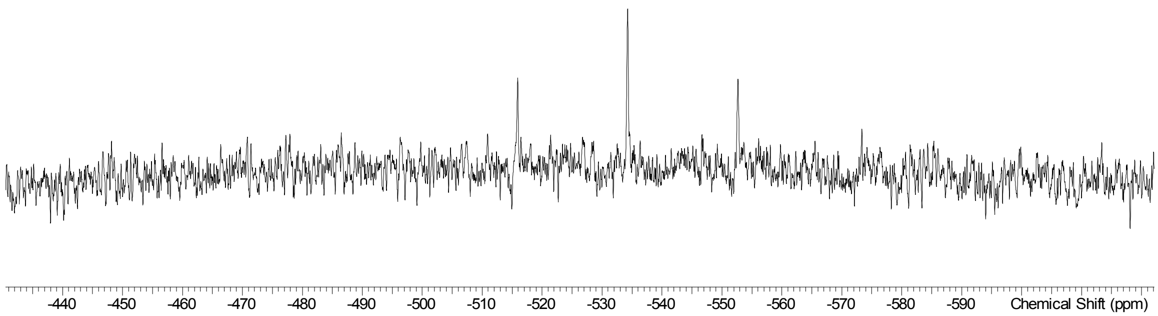


Figure S5.7 [$SnCl_3(PEt_3)_2OTf$]: IR (Nujol/cm^{-1}): ν = 289m, 301w, 374w (Sn-Cl), 1187m (-OSO_2), 1235m (CF_3).

Figure S6 [$SbEt_3Cl(OTf)$]

Figure S6.1 [$SbEt_3Cl(OTf)$]: ^1H NMR (CD_2Cl_2, 295 K): δ = 1.62 (t, [9H], $^3J_{HH}$ = 7.7 Hz, CH_3), 2.80 (q, [6H], $^3J_{HH}$ = 7.7 Hz, CH_2).

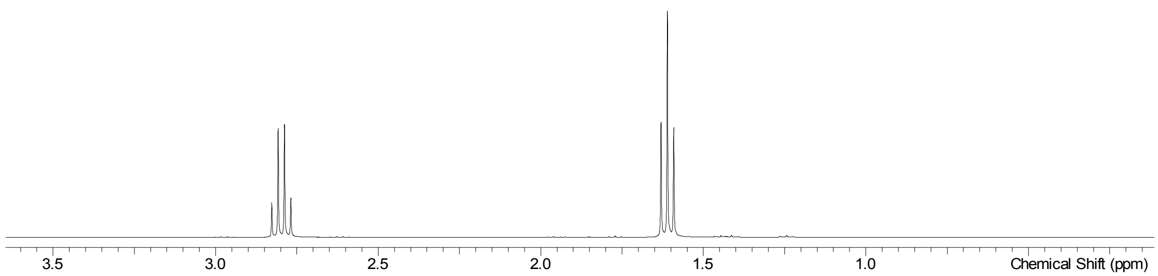


Figure S6.2 [$SbEt_3Cl(OTf)$]: $^{13}C\{^1H\}$ (CD_2Cl_2, 295 K): δ = 9.68 (CH_2), 28.55 (CH_3).

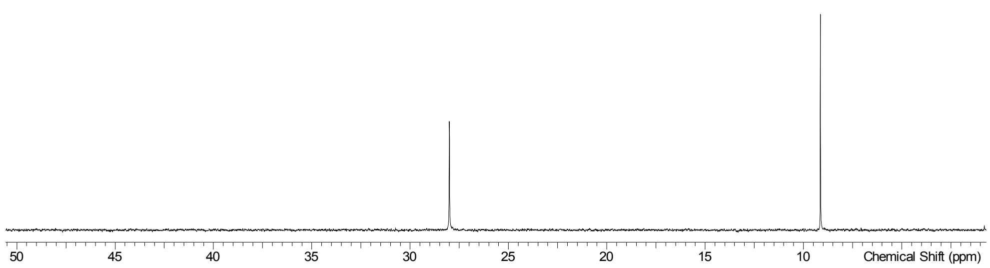


Figure S6.3 [$SbEt_3Cl(OTf)$]: IR (Nujol/cm^{-1}): ν = 329m (Sb-Cl), 1167w ($-OSO_2$), 1198w, 1235w (CF_3).

Figure S7 [$SnCl_3${*o*-$C_6H_4(PMe_2)_2$}][$AlCl_4$]

Figure S7.1 [$SnCl_3${*o*-$C_6H_4(PMe_2)_2$}][$AlCl_4$]: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.06 (t, $^2J + ^5J_{P-H}$ = 4.5 Hz, [12H], CH_3), 7.86-7.92 (m, [4H], Ar-*H*).

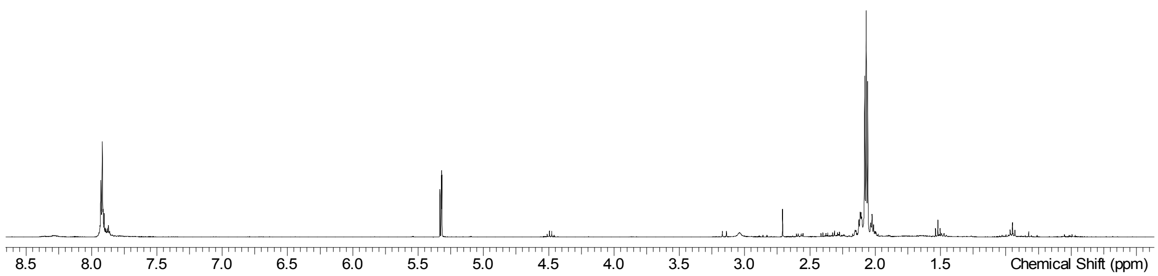
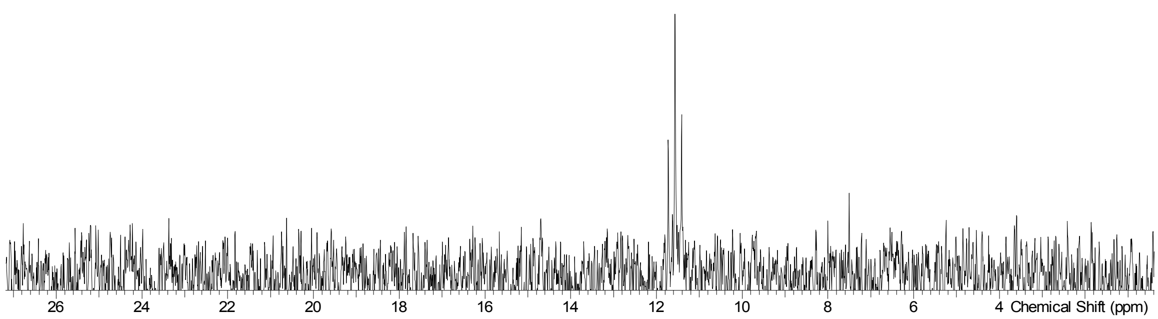


Figure S7.2 [$SnCl_3${*o*-$C_6H_4(PMe_2)_2$}][$AlCl_4$]: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 11.52 (t, $^1J + ^3J_{31P-13C}$ = 16.4 Hz, CH_3), 130.7-131.3, 134.2, 135.3 (Ar).



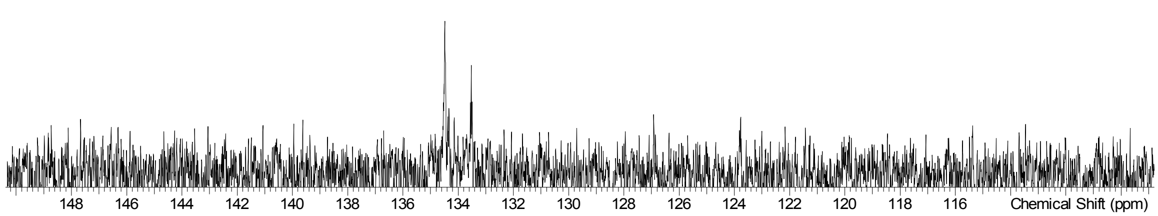


Figure S7.3 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]$: ^{27}Al NMR ($CD_2Cl_2$, 295 K): δ = 102.8 (s, $[AlCl_4]^-$); the broad feature is due to Al in the probe.

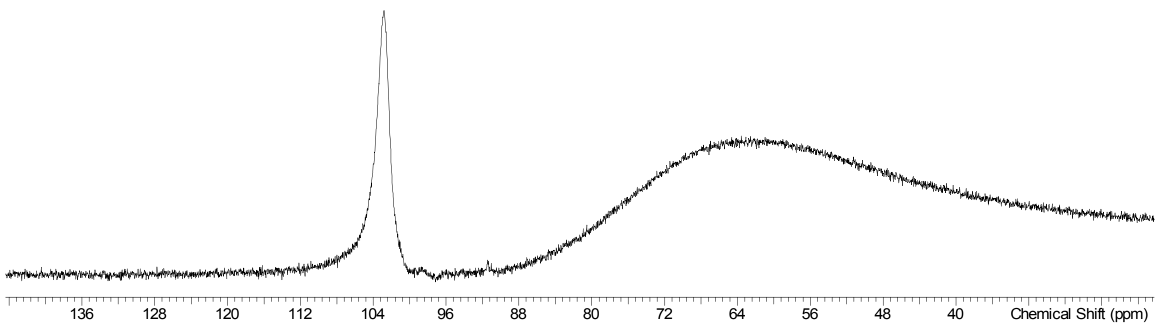


Figure S7.4 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = –24.7 (s, $^1J_{31p\text{-}117Sn}$ = 892 Hz, $^1J_{31P\text{-}119Sn}$ = 972 Hz).

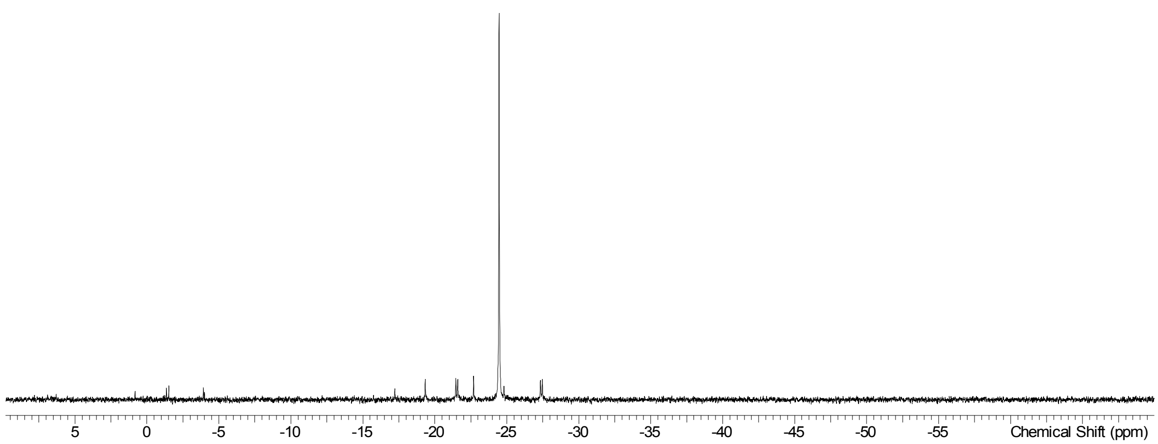


Figure S7.5 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]$: ^{119}Sn ($CD_2Cl_2$, 298 K): δ = –469 ($^1J_{31P\text{-}119Sn}$ = 972 Hz).

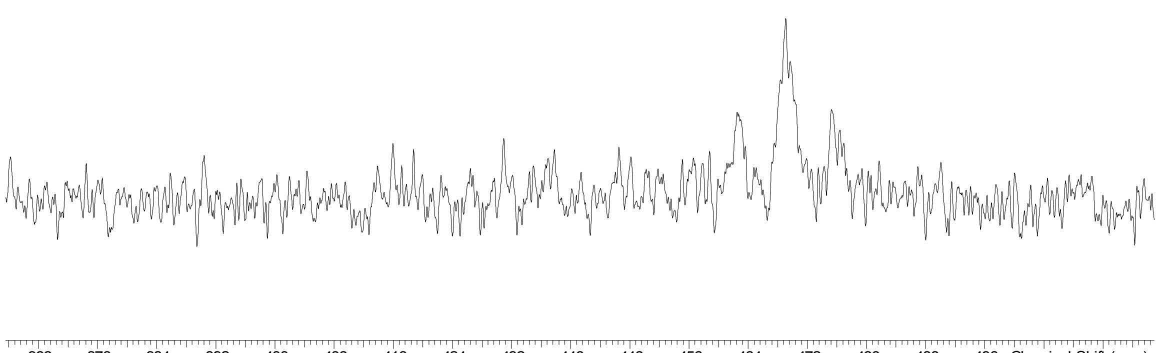


Figure S7.6 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]$: IR (Nujol/cm^{-1}): ν = 322m, 342m (Sn-Cl), 451m, 497br ($[AlCl_4]^-$).

Figure S8 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$

Figure S8.1 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.18 (t, ^{2}J $+^{5}J_{PH}$ = 4.5 Hz, [12H], CH_3), 7.94-8.30 (m, [4H], Ar-*H*.)

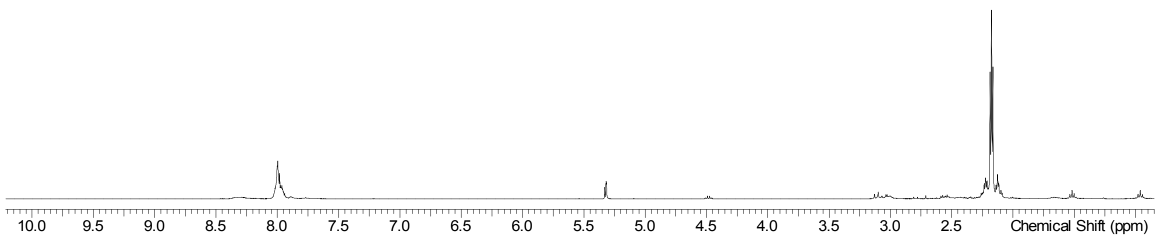
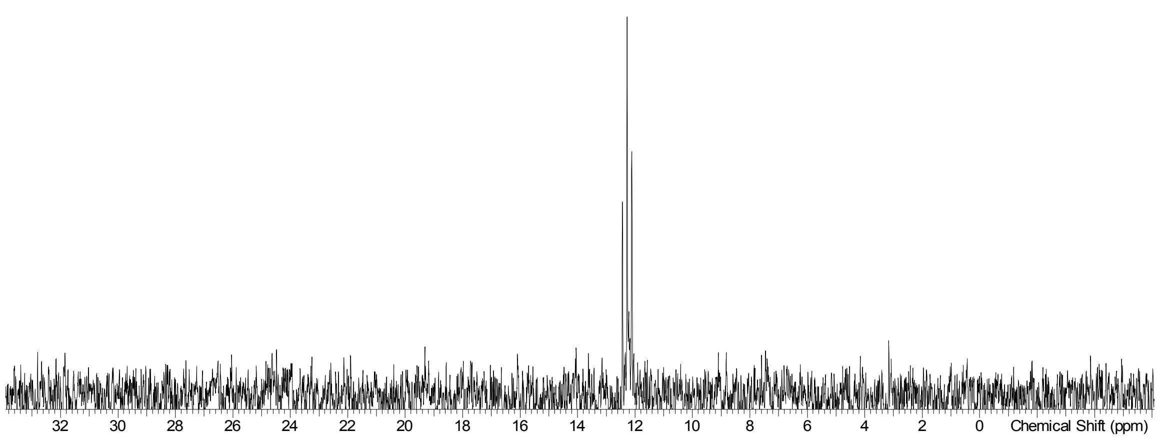


Figure S8.2 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$: $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): δ = 12.28 (t,^{1}J $+^{3}J_{31P\text{-}13C}$ = 16.1 Hz, CH_3), 129.8-130.1, 134.4, 135.9 (Ar-H).



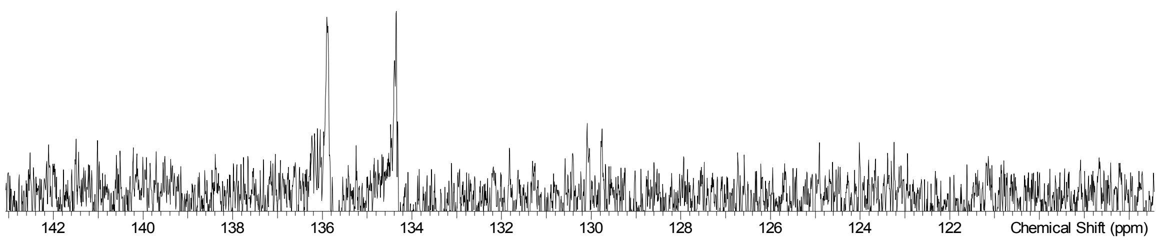


Figure S8.3 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$: ^{27}Al NMR ($CD_2Cl_2$, 295 K): δ 102.9 (s, $[AlCl_4]^-$) ; the broad feature is due to Al in the probe.

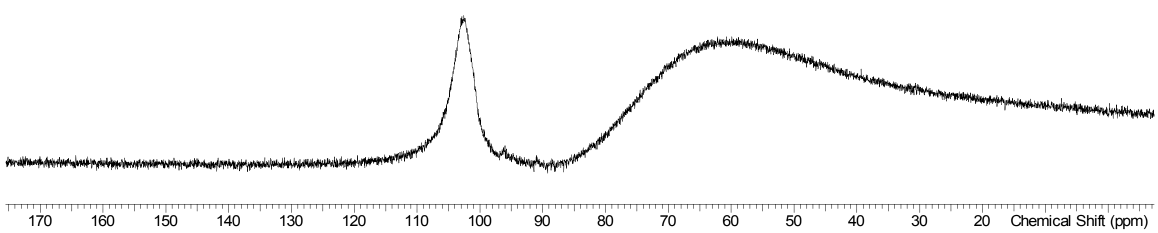


Figure S8.4 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = –23.7 ($^1J_{31P\text{-}117Sn}$ = 835 Hz, $^1J_{31P\text{-}119Sn}$ = 875 Hz).

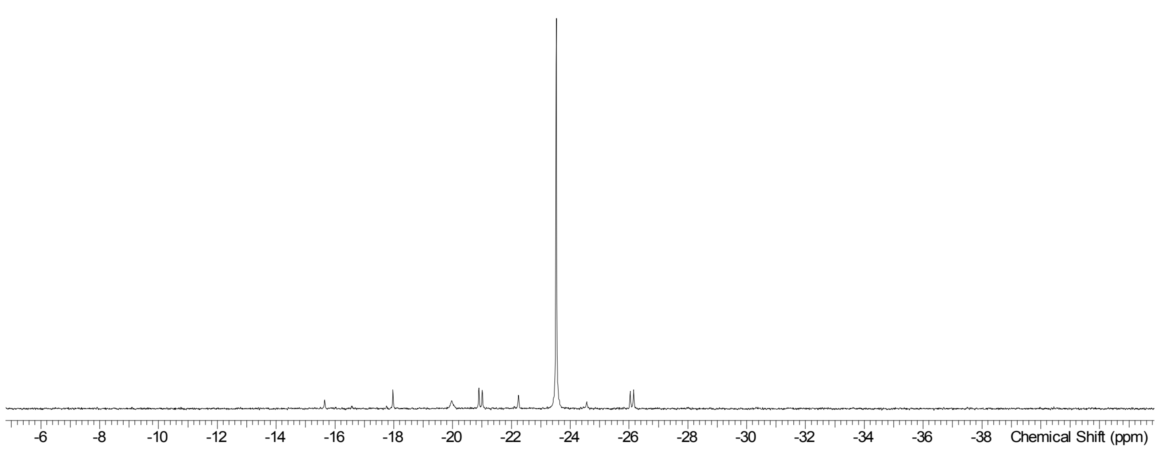


Figure S8.5 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$: ^{119}Sn NMR (CD_2Cl_2, 298 K): δ = -429 (br, t, $^1J_{31P\text{-}119Sn}$ = 880 Hz).

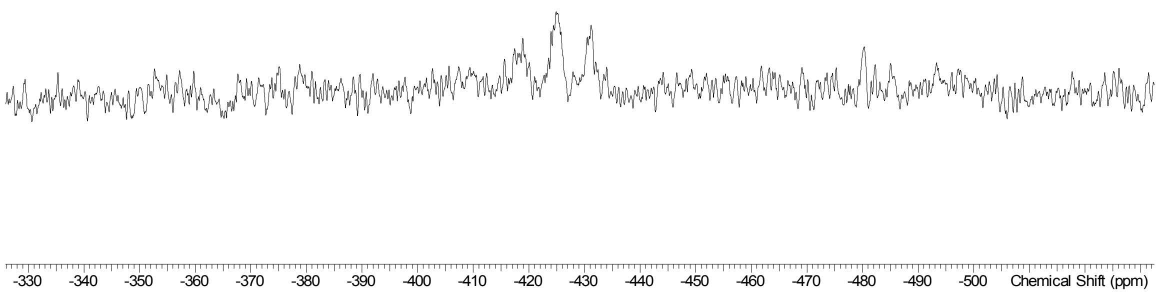


Figure S8.6 $[SnCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][AlCl_4]_2$: IR (Nujol/$cm^{-1}$): ν = 294m, 310m (Sn-Cl), 452sh, 487s ($[AlCl_4]^-$).

Figure S9 $[SnCl_3(PEt_3)_2][AlCl_4]$

Figure S9.1 $[SnCl_3(PEt_3)_2][AlCl_4]$: ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.36 (m, [18H], CH_3), 2.32 (m, [12H], CH_2).

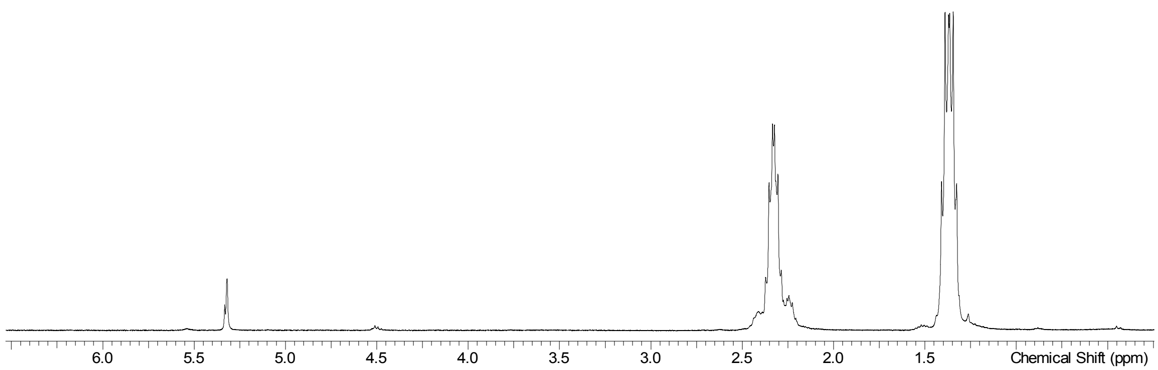


Figure S9.2 $[SnCl_3(PEt_3)_2][AlCl_4]$: $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): δ = 7.34 (t, $^{2}J + ^{4}J_{31P\text{-}13C}$ = 2.93 Hz, -CH_3), 14.12 (t, $^{1}J + ^{3}J_{31P\text{-}13C}$ = 22.45 Hz).

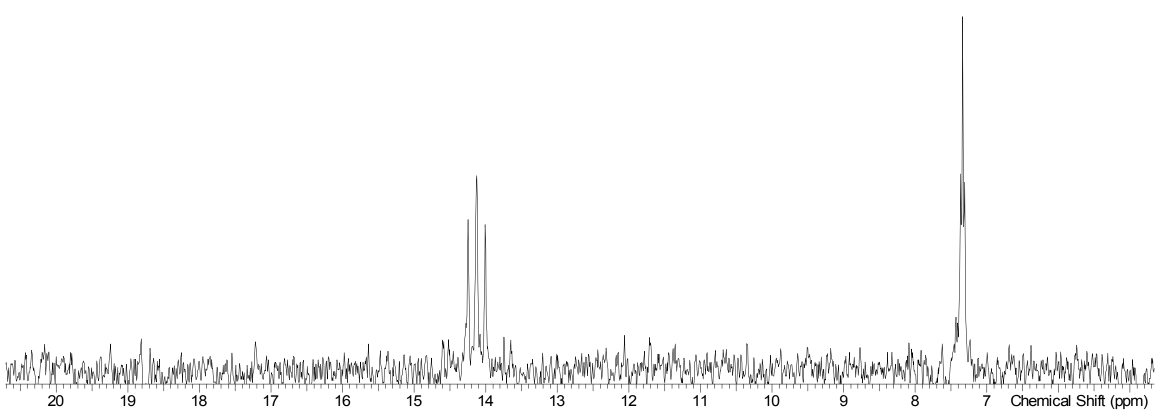


Figure S9.3 $[SnCl_3(PEt_3)_2][AlCl_4]$: ^{27}Al NMR (CD_2Cl_2, 295 K): δ = 103.2 (s, $[AlCl_4]^-$).

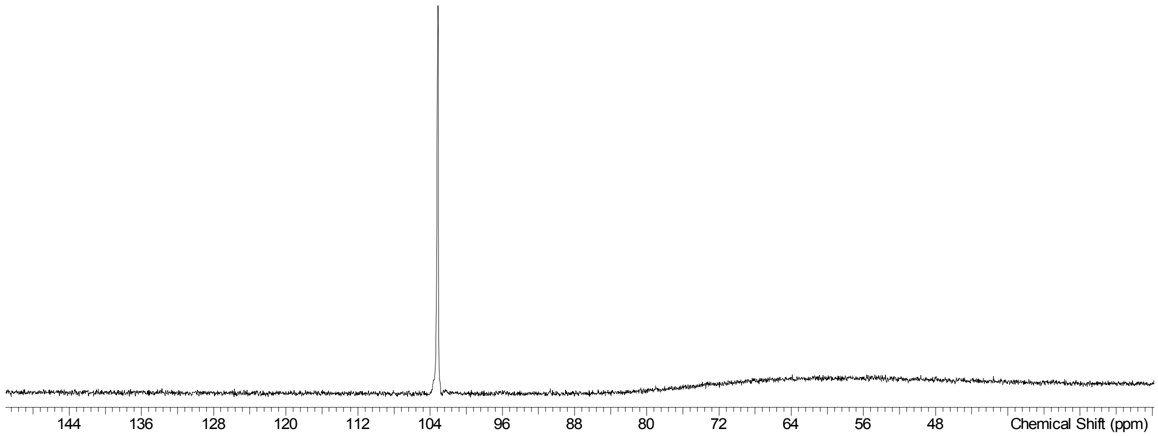


Figure S9.4 $[SnCl_3(PEt_3)_2][AlCl_4]$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): $\delta = 35.22$ ($^1J_{31P\text{-}117Sn} = 2208$ Hz, $^1J_{31P\text{-}119Sn} = 2317$ Hz) * *impurity due hydrolysis.*

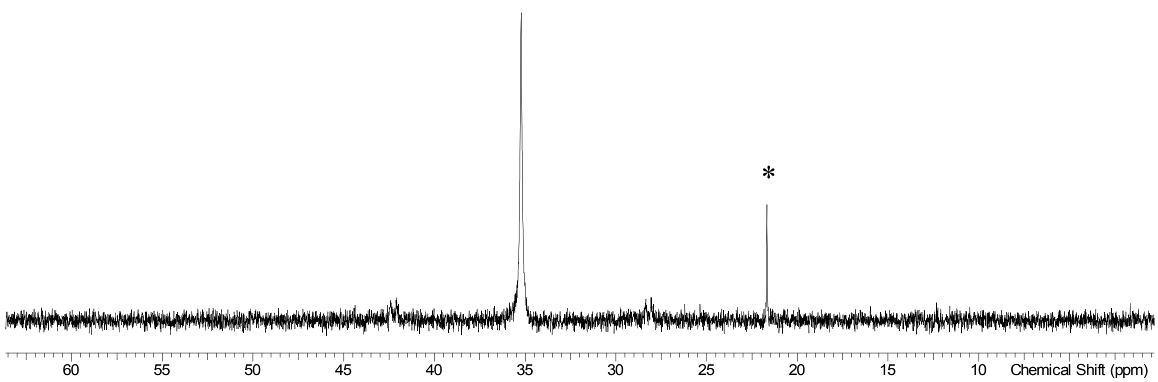


Figure S9.5 $[SnCl_3(PEt_3)_2][AlCl_4]$: ^{119}Sn NMR (CD_2Cl_2, 298 K): $\delta = -350.2$ (br t, $^1J_{31P\text{-}119Sn} = 2307$ Hz).

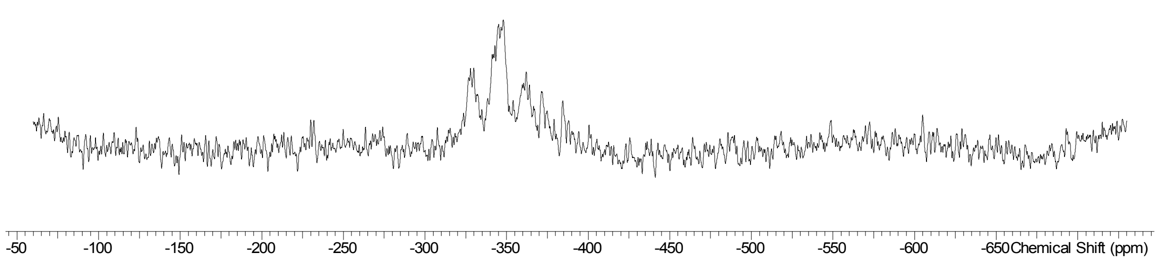


Figure S9.6 $[SnCl_3(PEt_3)_2][AlCl_4]$: IR (Nujol/$cm^{-1}$): ν = 280m, 289m (Sn-Cl), 484s, 503sh ($[AlCl_4]^-$).

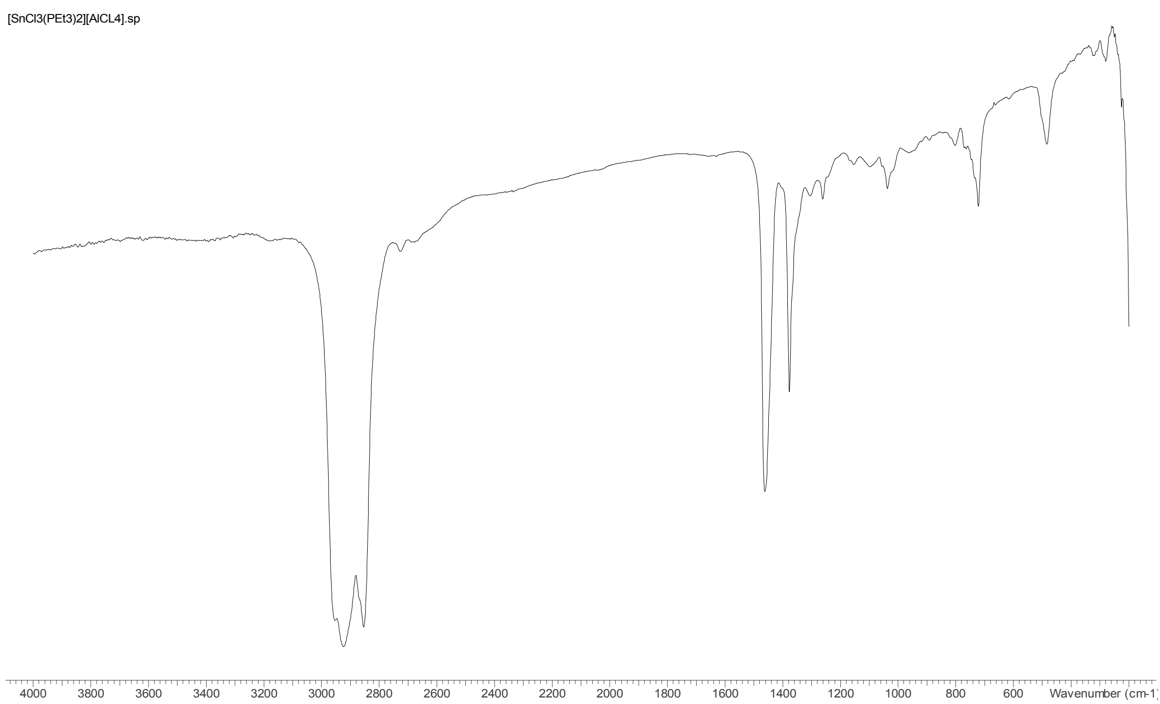


Figure S10 $[SnCl_2(PEt_3)_2][AlCl_4]_2$

Figure S10.1 $[SnCl_2(PEt_3)_2][AlCl_4]_2$: ^{1}H NMR ($CD_2Cl_2$, 295K): δ = 1.39 (m, [18H], CH_3), 2.38 (m, [12H], CH_2).

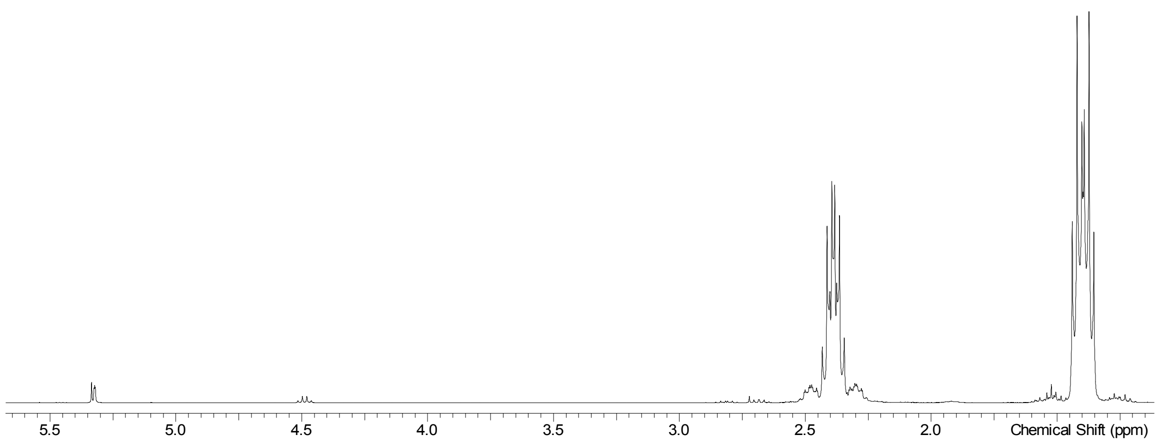


Figure S10.2 $[SnCl_2(PEt_3)_2][AlCl_4]_2$: $^{13}C\{^1H\}$NMR (CD_2Cl_2, 295 K): δ = 7.50 (t, $^2J + ^4J_{31P\text{-}13C}$ = 2.93 Hz, $-CH_3$), 14.51 (t, $^1J + ^3J_{31P\text{-}13C}$ = 13.2 Hz).

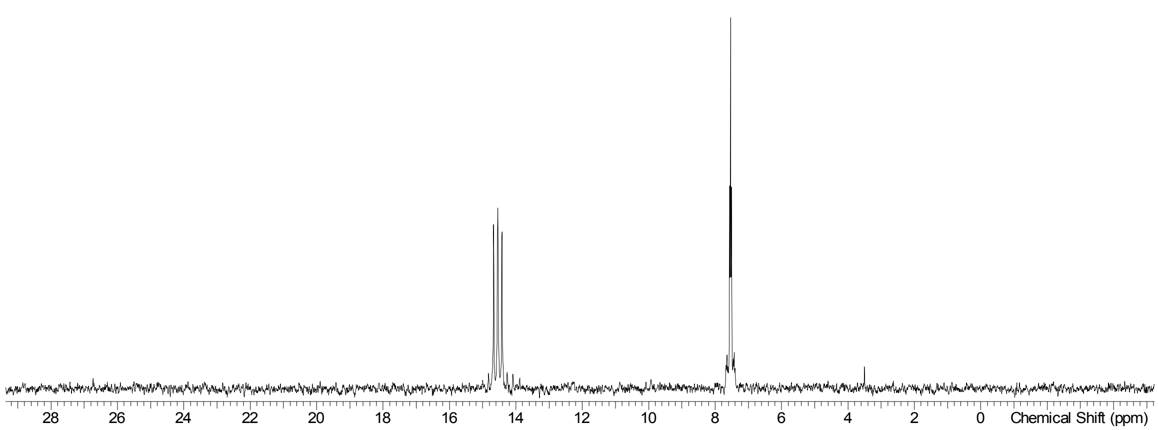


Figure S10.3 $[SnCl_2(PEt_3)_2][AlCl_4]_2$: ^{27}Al NMR (CD_2Cl_2, 295 K): δ = 103.0 * *impurity of* *$[AlCl_3(PEt_3)]$*.

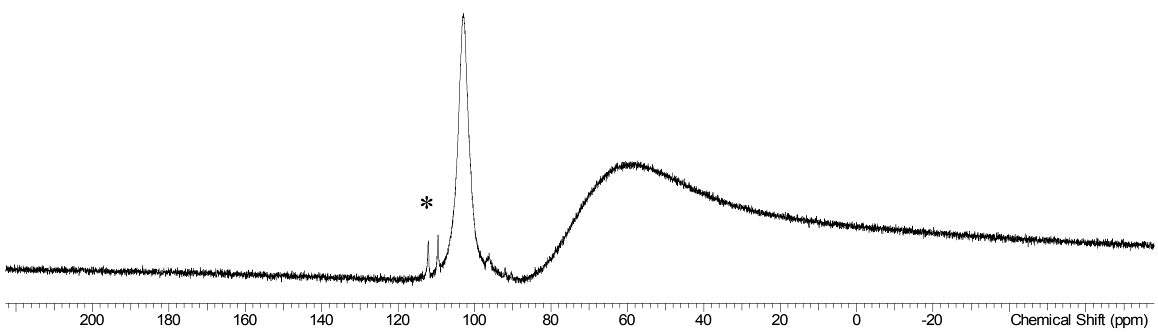


Figure S10.4 $[SnCl_2(PEt_3)_2][AlCl_4]_2$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 40.78 ($^1J_{31P\text{-}117Sn}$ = 2172 Hz, $^1J_{31P\text{-}119Sn}$ = 2274 Hz).

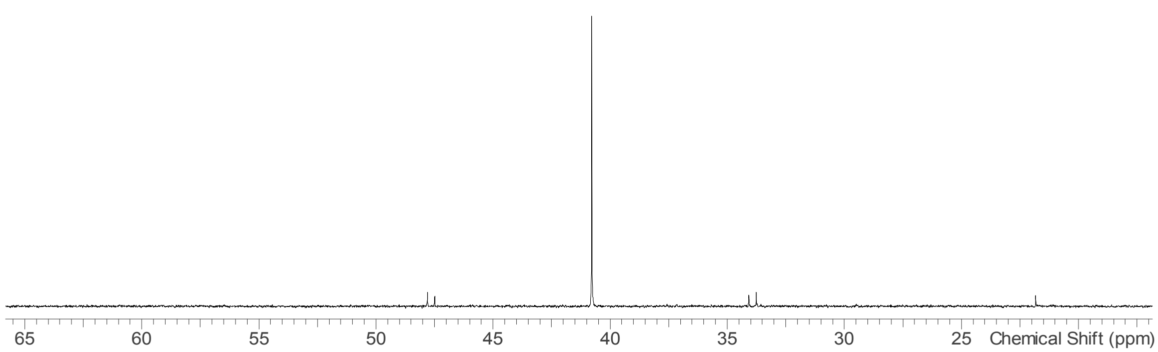


Figure S10.5 $[SnCl_2(PEt_3)_2][AlCl_4]_2$: ^{119}Sn NMR (CD_2Cl_2, 298 K): δ = −301.4 (br, t, $^1J_{31P\text{-}119Sn}$ = 2291).

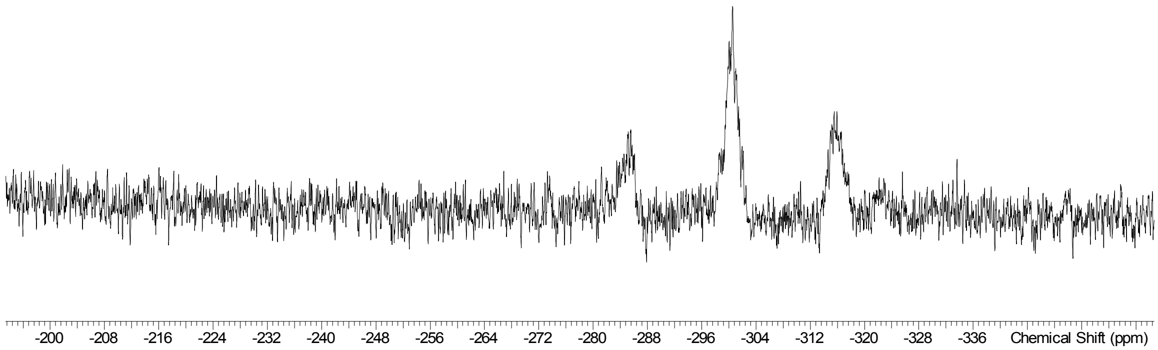


Figure S10.6 $[SnCl_2(PEt_3)_2][AlCl_4]_2$: IR (Nujol/$cm^{-1}$) = 289m, (Sn-Cl), 484s, ($[AlCl_4]^-$).

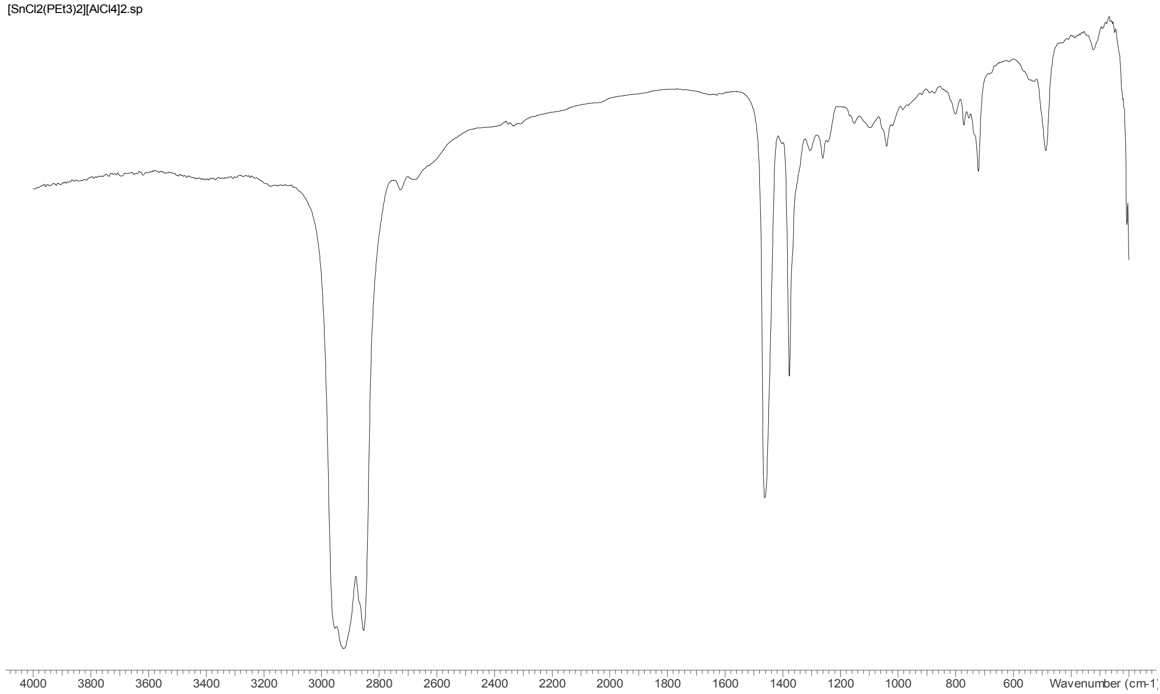


Figure S11 $[SnCl_3(PEt_3)_2][BAr^F]$

Figure S11.1 $[SnCl_2(PEt_3)_2][BAr^F]$: ^1H NMR (CD_2Cl_2, 295 K): δ = 1.35 (m, [18H], CH_3), 2.29 (m, [12H], CH_2), 7.57 (s, [4H], $[Bar^F]$), 7.72 (m, [8H], $[Bar^F]$)

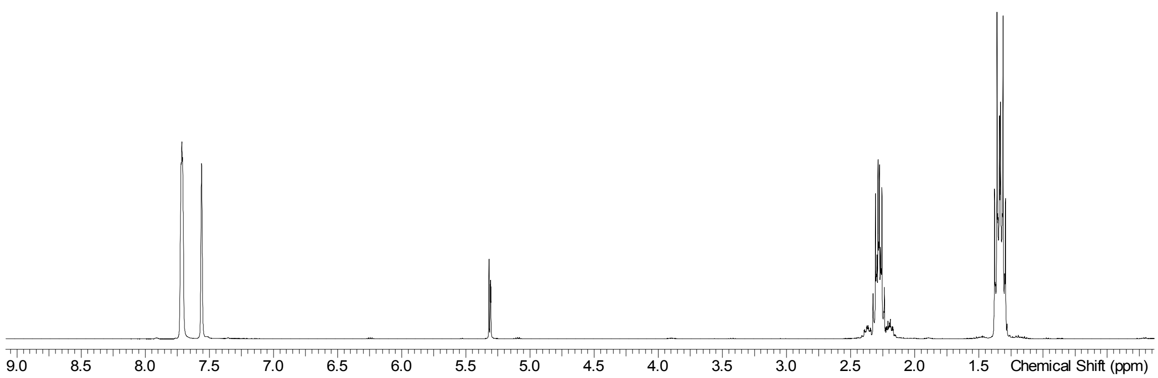


Figure S11.2 $[SnCl_3(PEt_3)_2][BAr^F]$: $^{13}C\{^1H\}$NMR (CD_2Cl_2, 295 K): δ = 7.84 (t, $^2J + ^4J_{31P\text{-}13C}$ = 2.9 Hz, $-CH_3$), 14.51 (t, $^1J + ^3J_{31P\text{-}13C}$ = 11.7 Hz), 118.1(s), 123.8(s), 126.5(s), 129.3(m), 135.4(s), 162.3(q, $^1J_{11B\text{-}13C}$ = 49.9)

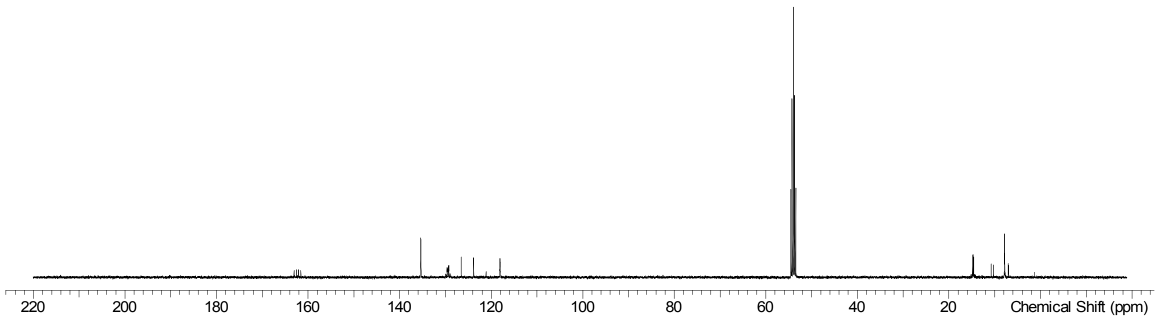


Figure S11.3 $[SnCl_3(PEt_3)_2][BAr^F]$: $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = -63.0 (s, $-CF_3$)

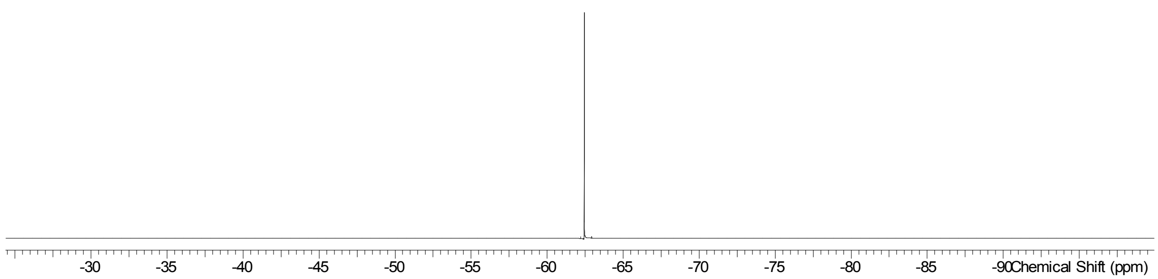


Figure S11.4 $[SnCl_3(PEt_3)_2][BAr^F]$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 37.1 ($^1J_{31P\text{-}117Sn}$ = 2226 Hz, $^1J_{31P\text{-}119Sn}$ = 2296 Hz)

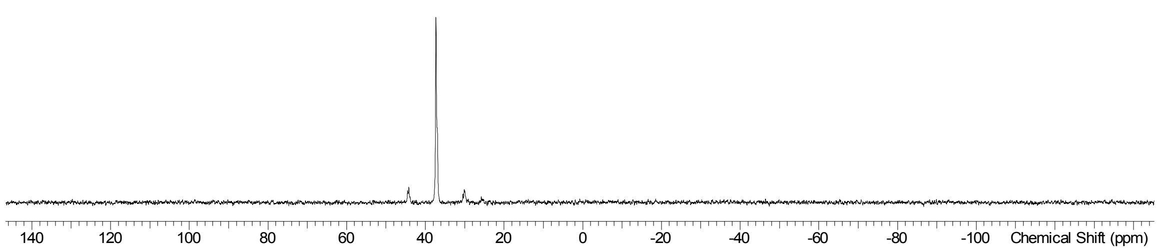


Figure S11.5 $[SnCl_3(PEt_3)_2][BAr^F]$: ^{119}Sn NMR (CD_2Cl_2, 298 K): δ = -379 (t, $^1J_{31P\text{-}119Sn}$ = 2311 Hz)

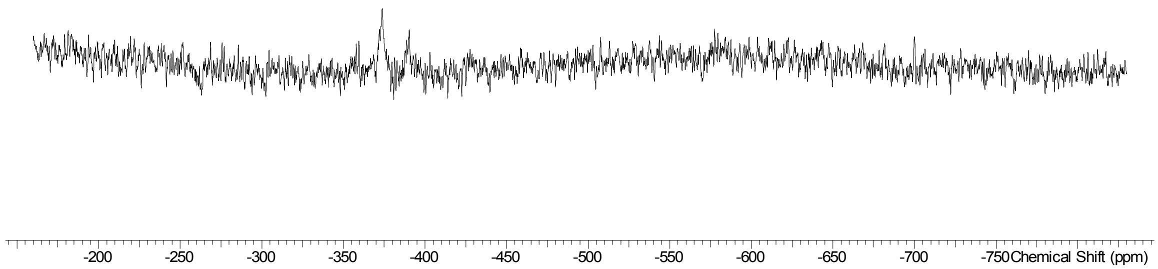


Figure S11.6 $[SnCl_3(PEt_3)_2][BAr^F]$: IR (Nujol/cm^{-1}) = 286 (Sn-Cl)

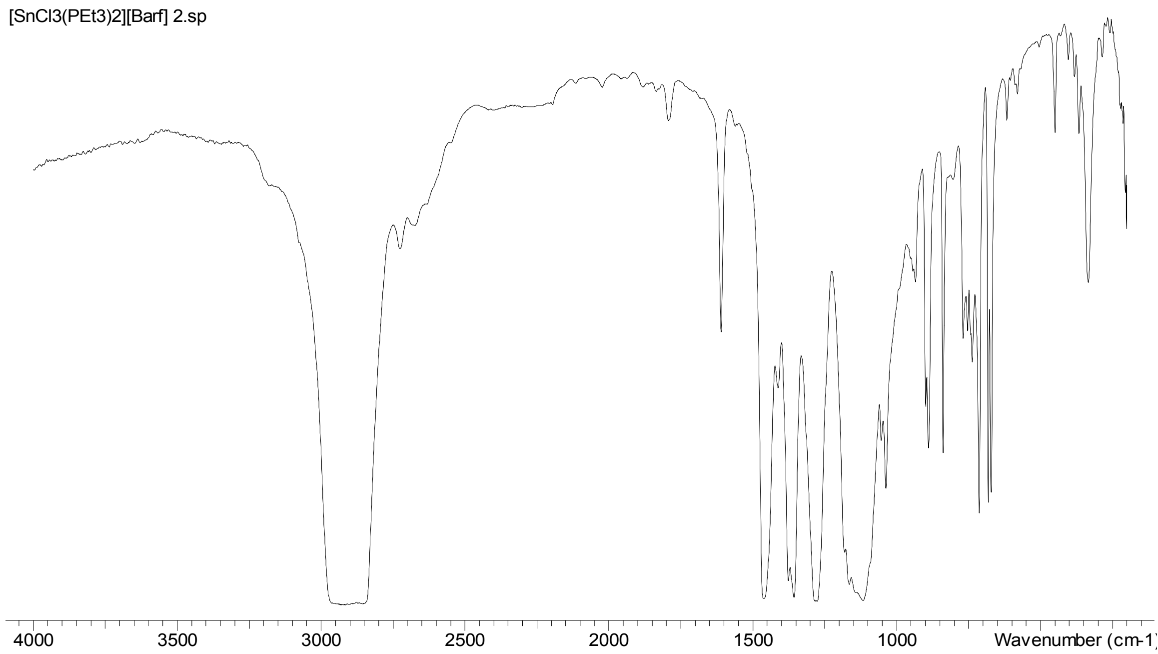


Figure S12 $[SnCl_3(AsEt_3)_2][BAr^F]$

Figure S12.1 $[SnCl_3(AsEt_3)_2][BAr^F]$: ^{1}H NMR ($CD_2Cl_2$, 295 K): δ = 1.44 (t, $^3J_{HH}$ = 7.7 Hz, [18H], CH_3), 2.42 (q, ^3J = 7.7 Hz, [12H], CH_2), 7.57 (s, [4H], $[BAr^F]$), 7.72 (m, [8H], $[BAr^F]$)

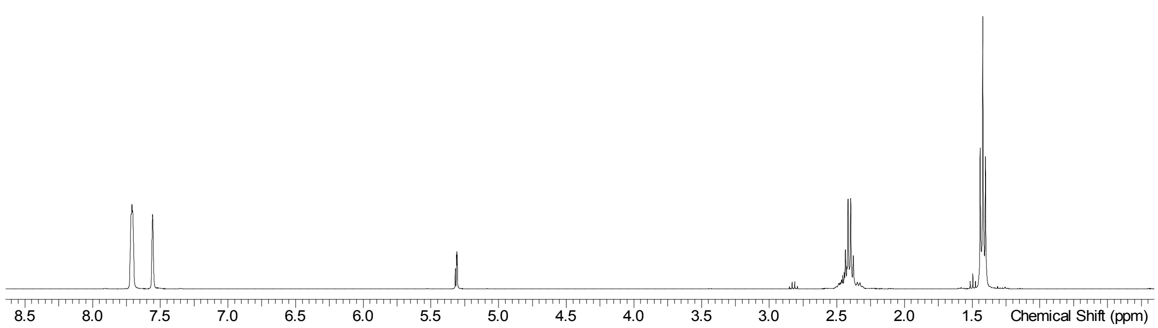


Figure S12.2 $[SnCl_3(AsEt_3)_2][BAr^F]$: $^{13}C\{^1H\}$NMR (CD_2Cl_2, 295 K): δ = 9.00 (s, $-CH_3$), 14.3 (br s, $-CH_2$), 118.1(s), 123.8(s), 126.5(s), 129.3(m), 135.4(s), 162.3(q, $^1J_{11B\text{-}13C}$ = 49.9)

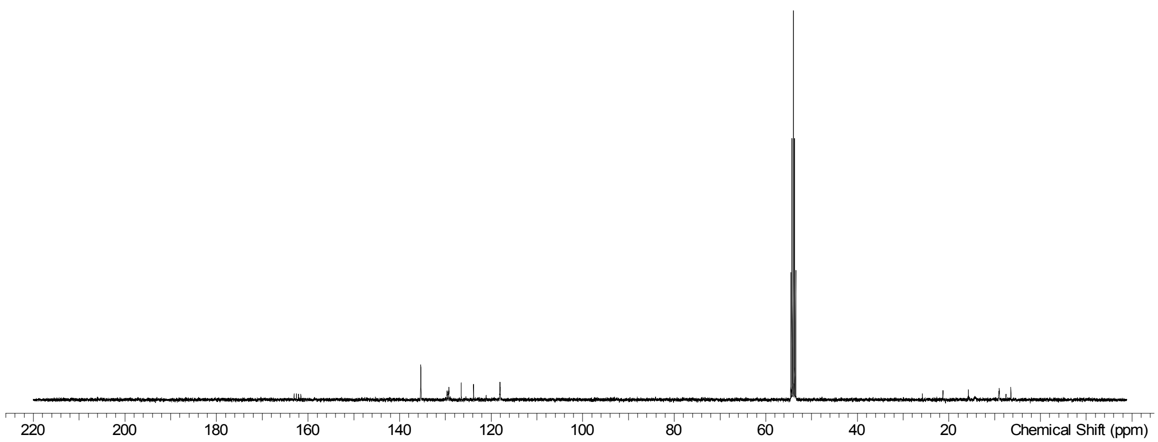


Figure S12.3 $[SnCl_3(AsEt_3)_2][BAr^F]$: $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = -63.0 (s, $-CF_3$)

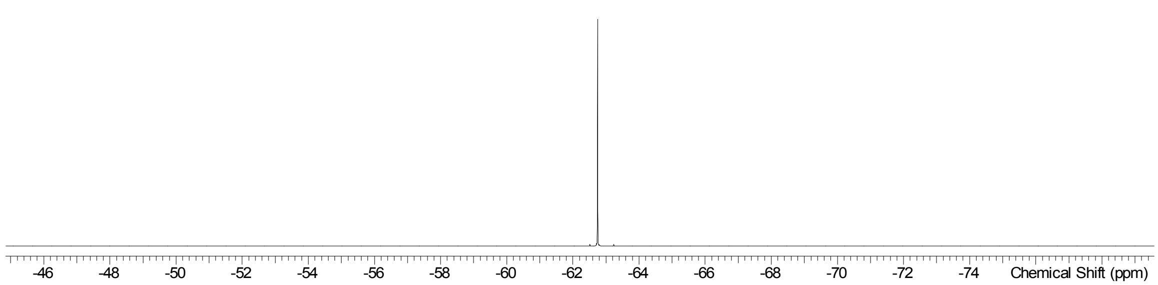


Figure S12.4 $[SnCl_3(AsEt_3)_2][BAr^F]$: ^{119}Sn NMR (CD_2Cl_2, 183 K): δ = -388 (br s)

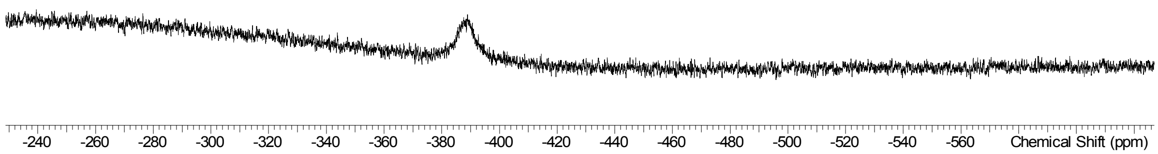


Figure S12.5 : IR (Nujol/cm^{-1}) = 285 (Sn-Cl)

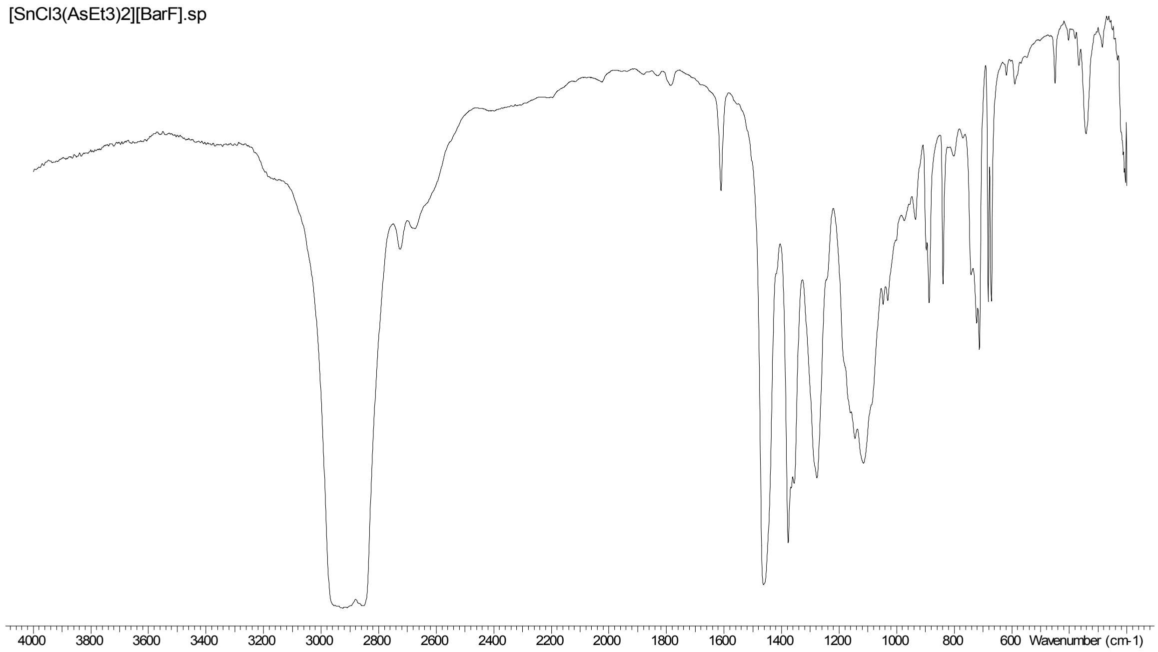


Figure S13 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][BAr^F]$

Figure S13.1 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][BAr^F]$: ^1H NMR (CD_2Cl_2, 295 K): δ = 2.01 (t, $^2J + ^5J_{PH}$ = 4.7 Hz, [12H], CH_3), 7.57 (s, [4H], $[BAr^F]$), 7.72 (m, [8H], $[BAr^F]$), 7.82 (m, [4H], $[BAr^F]$)

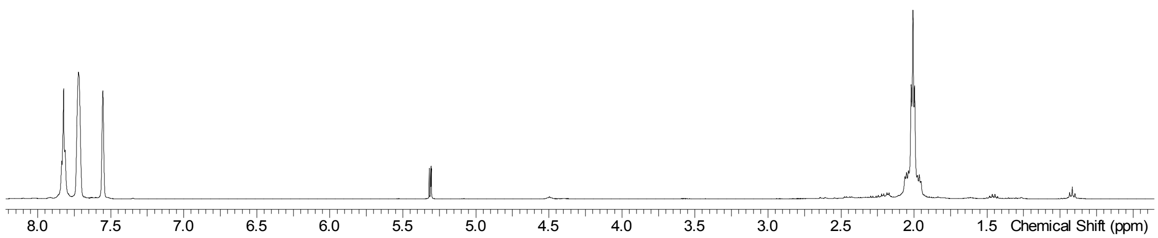


Figure S13.2 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][BAr^F]$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = -24.50 ($^1J_{31P\text{-}Sn}$ = 1007 Hz)

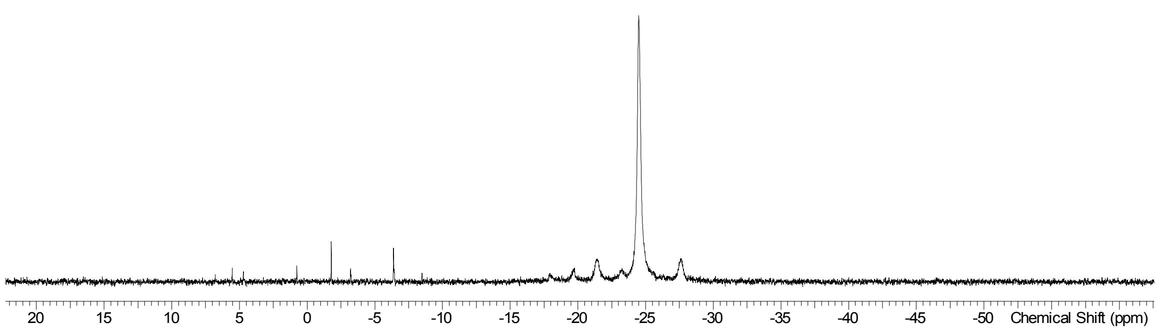


Figure S13.3 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][BAr^F]$: $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = -63.0 (s, $-CF_3$)

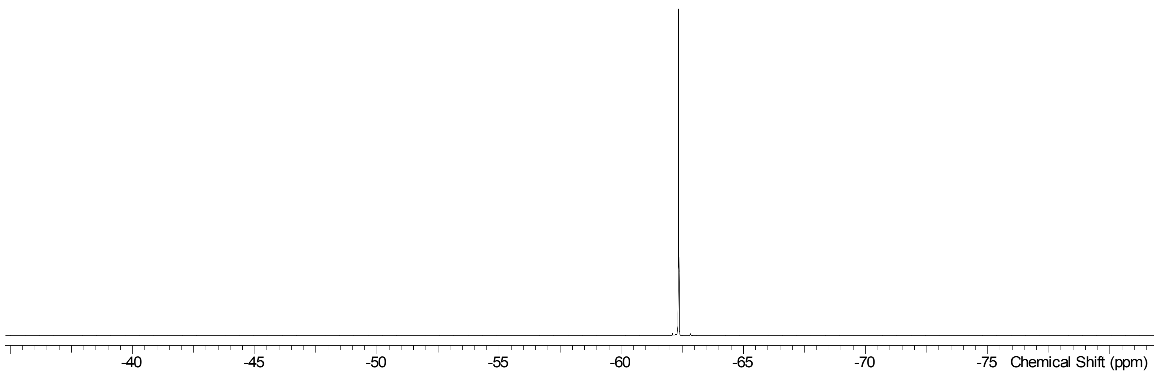


Figure S13.4 $[SnCl_3\{o\text{-}C_6H_4(PMe_2)_2\}][BAr^F]$: IR (Nujol/cm^{-1}) = 281 (Sn-Cl)

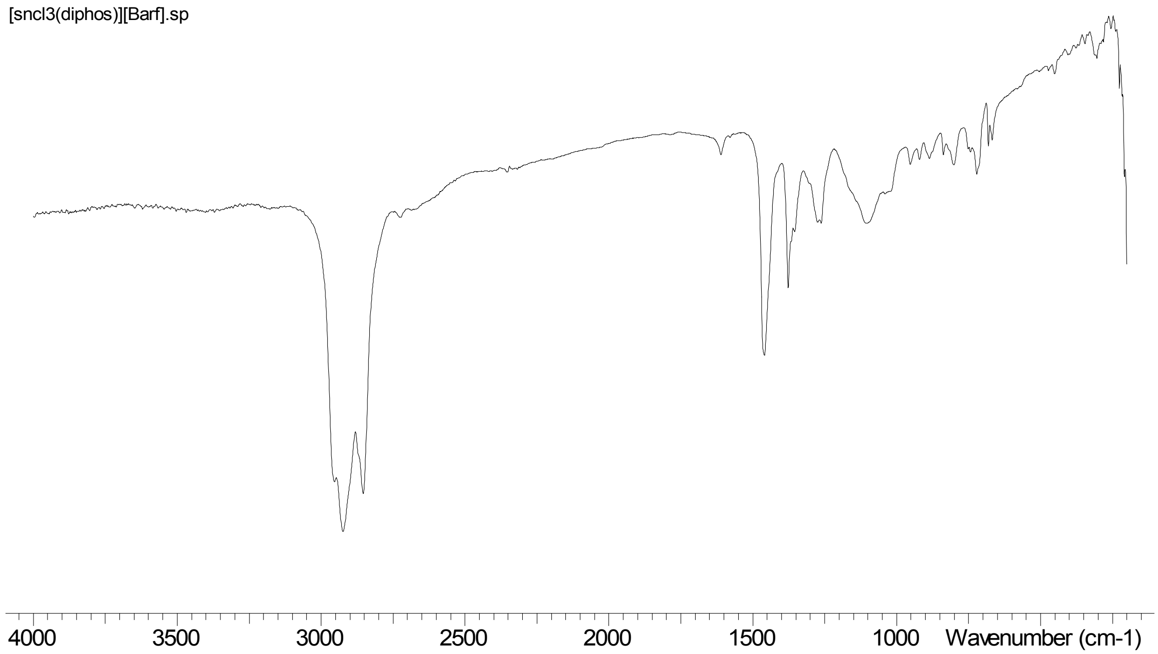


Figure S14 $[SnBr_3(AsEt_3)_2\}][BAr^F]$

Figure S14.1 $[SnBr_3(AsEt_3)_2][BAr^F]$: ^1H NMR (CD_2Cl_2, 295 K): δ = 1.39 (t, $^3J_{HH}$ = 7.6 Hz, [18H], CH_3), 2.42 (br, [12H], CH_2), 7.58 (s, [4H], [Bar^F]), 7.73 (m, [8H], [Bar^F])

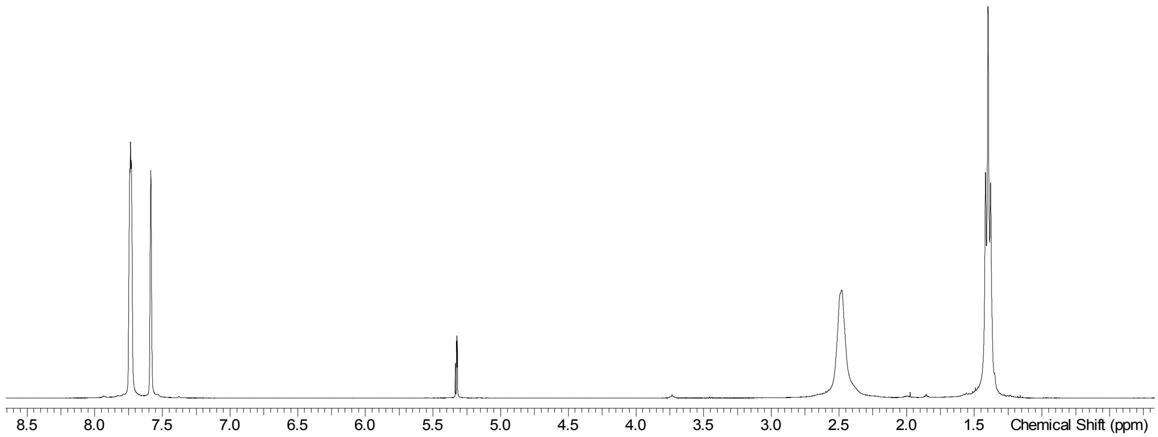


Figure S14.2 $[SnBr_3(AsEt_3)_2][BAr^F]$: $^{13}C\{^1H\}$NMR (CD_2Cl_2, 295 K): δ = 9.1 (s, $-CH_3$), 15.9 (s, $-CH_2$), 118.1(s), 123.8(s), 126.5(s), 129.3(m), 135.4(s), 162.3(q, $^1J_{11B\text{-}13C}$ = 49.9 Hz)

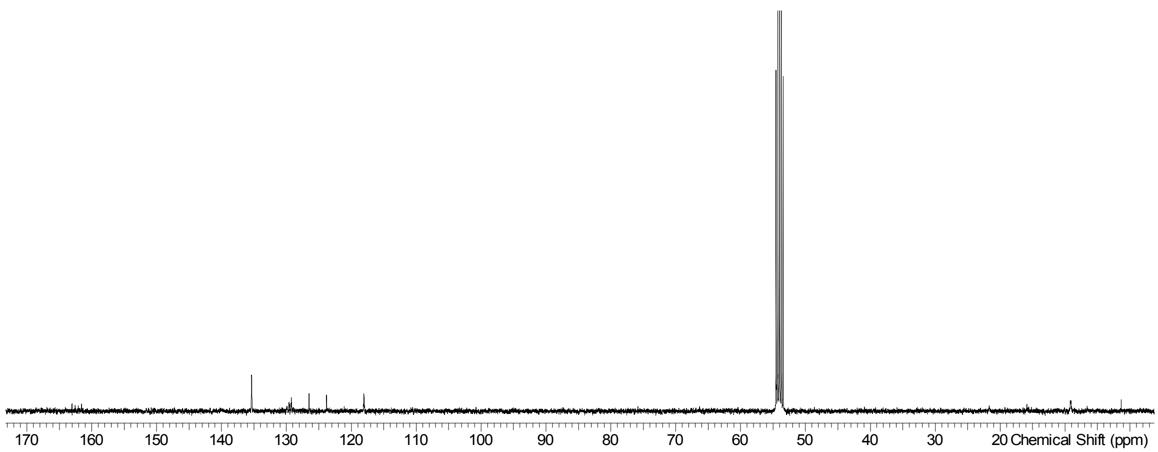


Figure S14.3 $[SnBr_3(AsEt_3)_2][BAr^F]$: $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = -62.9

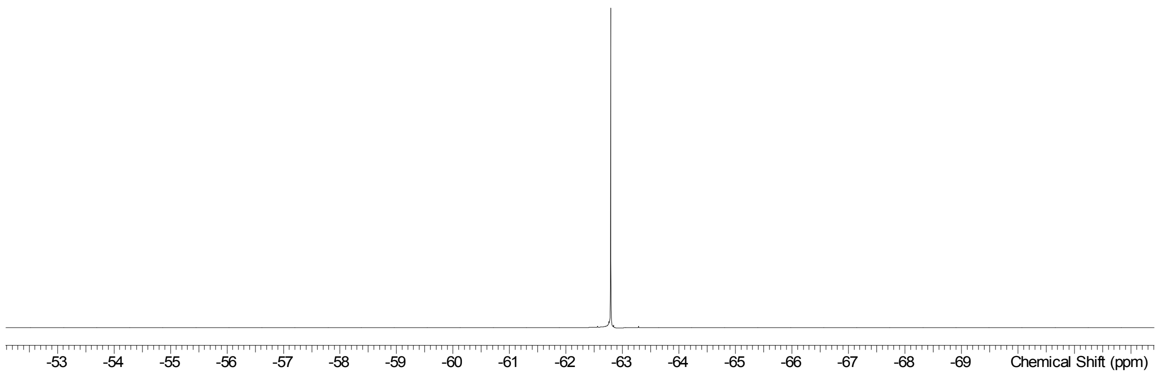


Figure S14.4 $[SnBr_3(AsEt_3)_2][BAr^F]$: IR (Nujol/cm^{-1}) = 210 (Sn-Br)

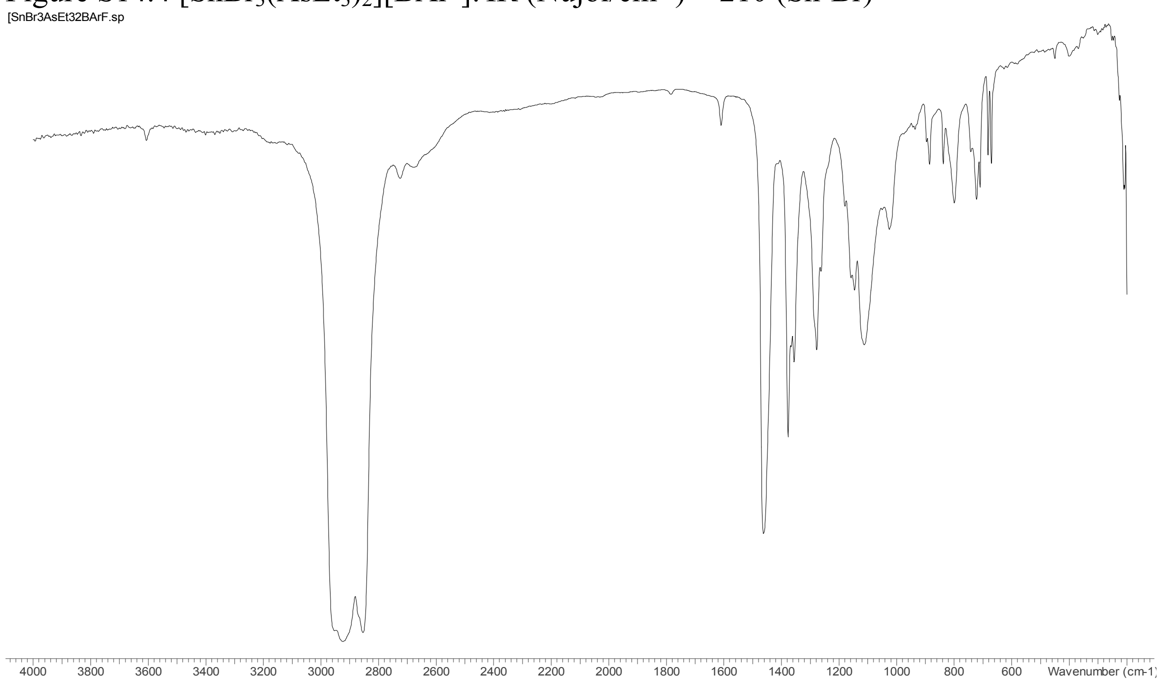


Table S1. X-Ray crystallographic data[a]

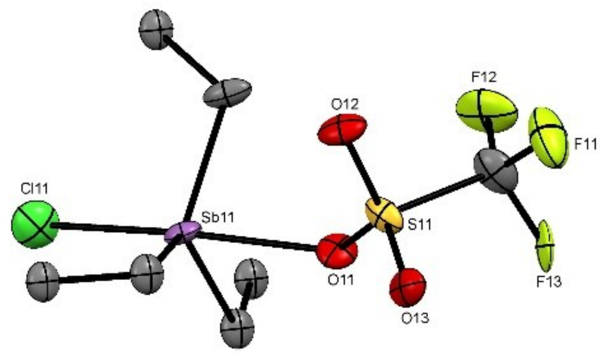
Compound	**$[SnCl_4(AsEt_3)_2]$**	**$[SnBr_4(AsEt_3)_2]$**	**$[SnCl_3(AsEt_3)_2(OTf)]$**
Formula	$C_6H_{15}AsCl_2Sn_{0.5}$	$C_{12}H_{30}As_2Br_4Sn$	$C_{13}H_{30}As_2Cl_3F_3O_3SSn$
M	292.34	762.53	698.31
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group (no.)	$P\ 2_1/n$ (14)	P b c a (61)	$P\ c\ a\ 2_1$ (29)
a /Å	7.1388(2)	13.8250(2)	13.21000(10)
b /Å	12.1065(2)	11.0254(2)	13.77830(10)
c /Å	11.9952(3)	14.4329(2)	13.2995(2)
α /°	90	90	90
β /°	91.301(2)	90	90
γ /°	90	90	90
U /$Å^3$	1036.43(4)	2199.95(6)	2420.66(4)
Z	4	4	4
μ(Mo-K_α) /mm^{-1}	4.905	11.401	4.220
F(000)	572	1432	1368
Total number reflns	27819	55967	66478
R_{int}	0.036	0.059	0.026
Unique reflns	3286	3615	7702
No. of params, restraints	91, 0	91, 0	242, 1
GOF	1.019	0.938	1.059
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.020, 0.036	0.036, 0.110	0.020, 0.042
R_1, wR_2 (all data)	0.030, 0.038	0.044, 0.116	0.022, 0.042

[a] Common items: T = 293 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°; [b] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)_2/\Sigma wF_o^4]^{1/2}$

Compound	**[$SnCl_3(PMe_3)_2(OTf)$]**	**[$SnCl_5(AsEt_3)$][$ClAsEt_3$]**	**[$SnCl_2(PEt_3)_3$][$AlCl_4$]$_2$**
Formula	$C_7H_{18}Cl_3F_3O_3P_2SSn$	$C_{12}H_{30}As_2Cl_6Sn$	$C_{18}H_{45}Al_2Cl_{10}P_3Sn$
M	526.25	655.59	881.60
Crystal system	monoclinic	monoclinic	monoclinic
Space group (no.)	P 2_1/n (14)	P 2_1/n (14)	P 2_1/n (14)
a /Å	12.0116(4)	11.6759(3)	14.9000(3)
b /Å	12.9896(5)	10.3481(2)	25.4564(3)
c /Å	12.1849(3)	19.4678(5)	20.3339(4)
α /°	90	90	90
β /°	101.720(3)	92.168(3)	99.560(2)
γ /°	90	90	90
U /Å^3	1861.52(11)	2350.48(10)	7605.5(2)
Z	4	4	8
μ(Mo-K_α) /mm^{-1}	2.114	4.556	1.558
F(000)	1032	1280	3552
Total number reflns	38860	14864	83974
R_{int}	0.095	0.031	0.062
Unique reflns	5809	5392	14932
No. of params, restraints	187, 0	196, 0	631, 0
GOF	0.966	0.922	1.043
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.051, 0.131	0.034, 0.119	0.057, 0.136
R_1, wR_2 (all data)	0.076, 0.152	0.041, 0.125	0.089, 0.154

[a] Common items: T = 293 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°; [b] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)_2/\Sigma wF_o^4]^{1/2}$

Figure S15 Structure of [$Et_3SbCl(OTf)$]



The crystal structure of [$Et_3SbCl(OTf)$] was of low quality, however, it does confirm the geometry, and further suggests that the reaction of $SnCl_4$, $SbEt_3$ and TMSOTf results in redox chemistry.

Crystal Data. $C_7H_{15}ClF_3O_3SSb$, M_r = 393.46, monoclinic, $P2_1/c$ (No. 14), a = 29.6795(9) Å, b = 8.4762(3) Å, c = 21.7447(10) Å, b = 91.258(3) °, a = g = 90°, V = 5469.0(4) Å^3, T = 100(2) K, Z = 4, μ(Mo-K_α) /mm^{-1} = 2.391, 77854 reflections measured, 15757 unique (R_{int} = 0.163) which were used in all calculations. The final wR_2 was 0.408 (all data) and R_1 was 0.208 (I > 2(I)).

NMR data for R_3SbX_2

The oil resulting from the addition of $SnCl_4$ to $^iPr_3Sb$ matched the spectroscopic and IR data of $^iPr_3SbCl_2$, reported by Breunig and Kanig.[1]

In order to prove the formation of Et_3SbX_2 (X = Cl or Br) from the addition of $SbEt_3$ to SnX_4, Et_3SbX_2 was made directly from the addition of an ethereal solution of two equivalents of $SbEt_3$ to an ethereal solution of three equivalents of SbX_3 at 0 °C. After warming to room temperature, the product was extracted in either CD_2Cl_2 or $CDCl_3$ for the purposes of NMR spectroscopy.

Et_3SbCl_2

^{1}H NMR ($CDCl_3$, 295K): δ = 1.63 (t, [9H], $^3J_{H\text{-}H}$ = 7.8 Hz, CH_3), 2.72 (q, [6H], $^3J_{H\text{-}H}$ = 7.8 Hz, CH_2).

^{1}H NMR (CD_2Cl_2, 295K): δ = 1.58 (t, [9H], $^3J_{H\text{-}H}$ = 7.8 Hz, CH_3), 2.67 (q, [6H], $^3J_{H\text{-}H}$ = 7.8 Hz, CH_2).

Et_3SbBr_2
^{1}H NMR ($CDCl_3$, 295K): δ = 1.64 (t, [9H], $^3J_{H\text{-}H}$ = 7.8 Hz, CH_3), 2.93 (q, [6H], $^3J_{H\text{-}H}$ = 7.8 Hz, CH_2).

Computational details

Calculations were performed using Gaussian 09W, Revision C.01,39 running on an Intel Core i5-2500 (quad, 3.3 GHz), equipped with 4 GB RAM; results were visualized using GaussView 5.0. Geometry optimisation and frequency calculations were performed on the isolated molecules, and using the B3LYP hybrid density functional, using a basis set with a Stuttgart-Dresden effective core potential on Sn and As atoms, and an all-electron double-ζ basis set on all electrons in H, C, O, F, P, Al, S, and Cl atoms. Minima were characterized by frequency calculations at the same level of theory. NBO calculations were performed at the same level of theory.

In addition, the structures of two uncoordinated ligands ($AsEt_3$ and PEt_3) have been calculated. The optimized structures of PEt_3 and $AsEt_3$ were calculated on the basis of experimental data for PMe_3, and $AsMe_3$, available from X-ray diffraction[2] or electron diffraction[3] respectively, and compare well (Table S3 in the Supporting Information).

While some DFT studies of $[SnCl_4(PMe_3)_2]$ and $[SnCl_3(PMe_3)_2]^+$ have been previously reported,[3] this was using a different basis set, and therefore new DFT studies were carried out for the purposes of this study. When compared, the geometry data for these complexes in this report, compare well to the geometries reported by MacDonald *et al.*.[4]

The supplemental file tin(IV) halides complexes.xyz contains the computed Cartesian coordinates of all complexes. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modelling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

Table S2 Bond lengths and angles for optimised structures:

[$SnCl_4(AsEt_3)_2$]	X-ray	DFT
Sn-Cl	2.4544(4) 2.4544(4) 2.4498(4) 2.4498(4)	2.54275 2.54843 2.54275 2.54842
Sn-As	2.65962(16) 2.65964(16)	2.75346 2.75346
As-C (av)	1.94	1.98
As-Sn-As	180.0	179.999
Cl-Sn-Cl	180.0 90.367(15) 89.633(15) 89.633(15) 90.367(15) 180.0	180.0 90.295 89.705 90.295 89.705 179.999
Cl-Sn-As	90.354(10) 89.646(10) 90.354(10) 89.647(10) 90.991(10) 89.010(10) 90.991(10) 89.008(10)	88.078 88.128 91.872 91.921 91.922 91.872 88.128 88.079
C-As-C (av)	105.89	105.85

[$SnCl_3(AsEt_3)_2(OTf)$]	X-ray	DFT
Sn-Cl	2.4168(8) 2.4480(7) 2.4533(7)	2.532 2.527 2.528
Sn-O_{OTf}	2.259(2)	2.189
Sn-As	2.6530(4) 2.6451(4)	2.740 2.738
As-C (av)	1.941	1.979
As-Sn-As	172.239(12)	177.913
Cl-Sn-Cl(trans)	173.76(3)	171.519
Cl2-As-O1	178.65(6)	176.576
Cl-Sn-As	93.32(2) 94.44(2) 89.64(2) 90.182(19) 88.319(19) 91.05(2)	89.241 91.947 89.138 91.086 90.085 90.238
C-As-C (av)	106.01	106.20

[$SnCl_3(AsEt_3)_2$]$^+$	DFT

Sn-Cl	2.476 2.495 2.489
Sn-As	2.741 2.737
As-C (av)	1.982
As-Sn-As	176.158
Cl-Sn-Cl	120.200 116.631 123.169
Cl-Sn-As	92.472 87.502 90.303 90.107 91.330 88.487
C-As-C (av)	107.33

[$SnCl_4(PMe_3)_2$]	X-ray	DFT
Sn-Cl	2.4565(7) 2.4762(6)	2.531 2.532 2.531 2.533
Sn-P	2.5654(7)	2.689 2.689
P-C (av)	1.80	1.870
P-Sn-P	180.000(17)	179.707
Cl-Sn-Cl	180.0 89.47(2) 90.53(2)	89.995 179.975 89.939 90.002 179.930 90.064
Cl-Sn-P	92.00(2) 88.00(2) 87.22(2) 92.78(2)	92.881 90.181 87.096 89.844 87.161 89.529 92.863 90.446
C-P-C (av)	107.46	106.61

[$SnCl_3(PMe_3)_2(OTf)$]	X-ray	DFT
Sn-Cl	2.4457(9) 2.4558(9) 2.4085(10)	2.530 2.520 2.528

Sn-O_{OTf}	2.266(3)	2.181
Sn-P	2.5496(9) 2.5506(9)	2.691 2.694
P-C (av)	1.797	1.891
P-Sn-P	164.16(3)	176.075
Cl-Sn-Cl(trans)	174.66(3) 92.67(3) 92.68(4)	171.769 95.225 92.998
Cl2-Sn-O1	178.03(7)	176.836
Cl-Sn-P	92.14(3) 91.66(3) 87.16(3) 87.62(3) 97.28(3) 97.89(3)	87.714 91.618 91.687 88.362 88.671 92.207
C-P-C (av)	107.84	106.90

$[SnCl_3(PMe_3)_2]^+$	DFT
Sn-Cl	2.463 2.461 2.462
Sn-P	2.665 2.665
P-C (av)	1.868
P-Sn-P	179.619
Cl-Sn-Cl	120.117 119.758 120.125
Cl-Sn-P	89.805 90.105 90.093 89.814 90.099 90.084
C-P-C (av)	108.350

$[SnCl_4(PEt_3)_2]$	X-ray	DFT
Sn-Cl	2.445(5) 2.465(5)	2.541 2.547 2.541 2.547
Sn-P	2.615(5)	2.699 2.699
P-C (av)	1.81	1.891
P-Sn-P	180	180.000
Cl-Sn-Cl	89.90(18)	89.633

	90.10(18)	90.367 89.633 90.367 180.000 180.000
Cl-Sn-P	91.18(18) 88.82(18) 91.29(15) 88.71(15)	88.032 92.062 91.968 87.938 91.968 87.938 88.032 92.062
C-P-C (av)	107.133	106.7810

[$SnCl_3(PEt_3)_2(OTf)$]	DFT
Sn-Cl	2.530 2.520 2.528
Sn-O_{OTf}	2.181
Sn-P	2.691 2.694
P-C (av)	1.891
P-Sn-P	176.075
Cl-Sn-Cl	171.769 92.998 95.225
Cl2-Sn-O1	176.836
Cl-Sn-P	91.618 91.687 87.714 88.671 92.207 88.362
C-P-C (av)	106.90

Table S3 Bond lengths and angles for optimised free ligands

PR_3	Structural data PEt_3*	DFT – PEt_3	DFT – PMe_3
P-C	1.840 1.843 1.841	1.91622 1.92055 1.91479	1.90404 1.90385 1.90390
C-P-C	100.2 99.39	101.400 100.299	98.788 98.765

	98.81	99.380	98.800

*Structural data from ref[2]

	Structural data $AsMe_3$	DFT $AsMe_3$	DFT of $AsEt_3$
As-C (Å)	1.98 ± 0.02*	2.01427 2.01998 2.01233	2.01233 2.01427 2.01998
C-As-C (°)	96 ± 5*	96.965 96.934 96.971	97.615 98.596 99.281

*Structural data from ref[3]

Table S4 Average E-C bond distances and C-E-C angles *(to ~ 3dp)*

	DFT		X-ray	
	E-C	**C-E-C**	**E-C**	**C-E-C**
PMe_3	1.904	98.784	1.841[2]	99.467[2]
PEt_3	1.917	100.360	-	-
$AsEt_3$	2.016	98.497	-	-
$[SnCl_4(AsEt_3)_2]$	1.981	105.847	1.940	105.897
$[SnCl_3(AsEt_3)_2(OTf)]$	1.979	106.205	1.941	106.008
$[SnCl_3(AsEt_3)_2]^+$	1.982	107.330	-	-
$[SnCl_4(PMe_3)_2]$	1.870	106.613	1.800[4]	107.463[4]
$[SnCl_3(PMe_3)_2(OTf)]$	1.891	106.906	1.797	107.837

$[SnCl_3(PMe_3)_2]^+$	1.868	108.350	(1.790)[*4]	(109.073) [*4]
$[SnCl_4(PEt_3)_2]$	1.891	106.781	1.790[5]	107.110[5]
$[SnCl_3(PEt_3)_2(OTf)]$	1.891	106.906	-	-

*values from crystal structure of $[SnCl_3(PMe_3)_2][AlCl_4]$ [4]

Table S5 NBO data for optimised coordination complexes.

Table of averaged E-C bonds, E = As/P

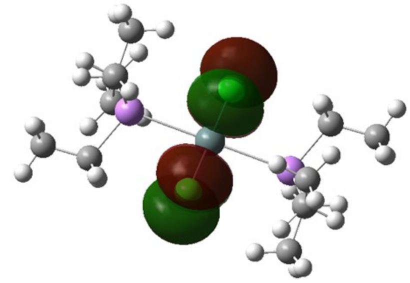
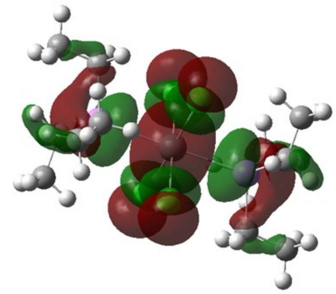
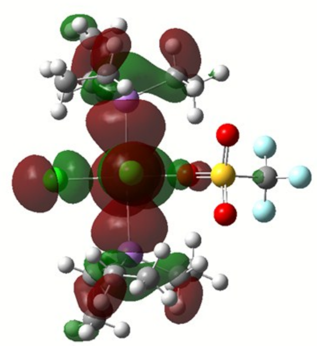
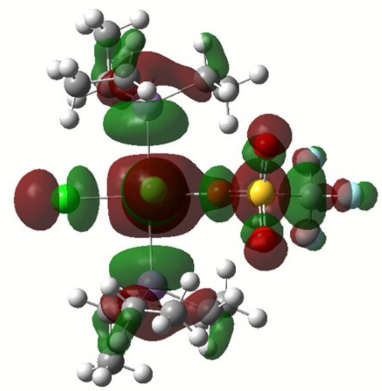
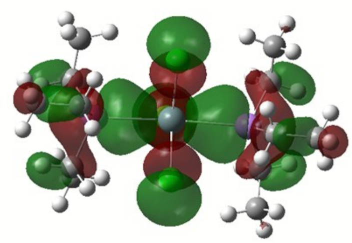
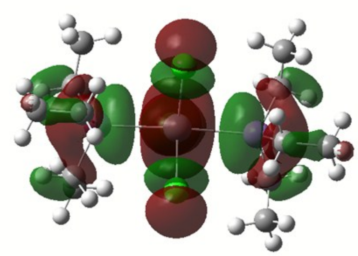
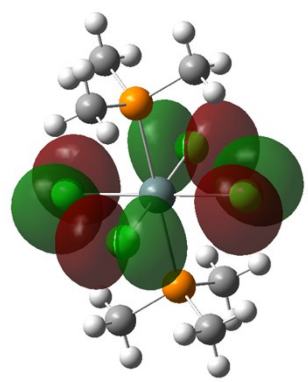
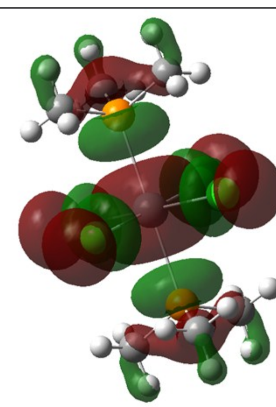
	Contribution (%)		Breakdown of E contributions (%)		Breakdown of C contributions (%)	
	E	C	*s*	*p*	*s*	*p*
Me_3P	39.46	60.54	15.08	84.92	24.13	75.87
Et_3P	39.85	60.15	15.57	84.43	22.65	77.35
Et_3As	35.72	64.28	12.20	87.80	21.65	78.35
$[SnCl_4(AsEt_3)_2]$	40.70	59.30	25.29	74.71	20.48	79.52
$[SnCl_3(AsEt_3)_2(OTf)]$	41.24	58.76	25.62	74.38	20.17	79.83
$[SnCl_3(AsEt_3)_2]^+$	42.50	57.50	26.76	73.24	19.61	80.39
$[SnCl_4(PMe)_2]$	44.42	55.58	25.33	74.67	23.03	76.97
$[SnCl_3(PMe_3)_2(OTf)]$	44.83	55.17	25.53	74.47	22.85	77.15
$[SnCl_3(PMe_3)_2]^+$	46.04	53.96	26.72	73.28	22.46	77.54
$[SnCl_4(PEt_3)_2]$	44.97	55.03	25.76	74.24	21.05	78.95
$[SnCl_3(PEt_3)_2(OTf)]$	45.23	54.77	25.89	74.11	20.93	79.07

(~ +5% contribution from As/P, for each complex compared to the free ligands. Significant amount of s-character from E in complexes compared to free ligands.)

Table of averaged E-Sn bonds, E = As/P

	Contribution (%)		Breakdown of Sb/As/P contributions (%)		Breakdown of Sn contributions (%)	
	P/As	M	*s*	*p*	*s*	*p*
$[SnCl_4(AsEt_3)_2]$	70.77	29.23	24.21	75.79	35.56	64.44
$[SnCl_3(AsEt_3)_2(OTf)]$	77.14	22.86	23.34	76.66	47.20	52.80
$[SnCl_3(AsEt_3)_2]^+$	80.94	19.06	22.21	77.79	49.68	50.32
$[SnCl_4(PMe_3)_2]$	76.24	23.76	24.25	75.75	35.37	64.63
$[SnCl_3(PMe_3)_2(OTf)]$	81.44	18.56	23.30	76.70	45.88	54.12
$[SnCl_3(PMe_3)_2]^+$	79.80	20.20	19.96	80.04	50.00	50.00
$[SnCl_4(PEt_3)_2]$	75.11	24.89	22.87	77.13	35.72	64.28
$[SnCl_3(PEt_3)_2(OTf)]$	80.98	19.02	22.14	77.86	47.28	52.72

Table S6 Frontier Molecular Orbitals for tin complexes

	HOMO	LUMO
[$SnCl_4(AsEt_3)_2$]		
[$SnCl_3(AsEt_3)_2(OTf)$]		
[$SnCl_3(AsEt_3)_2]^+$		
[$SnCl_4(PMe_3)_2$]		

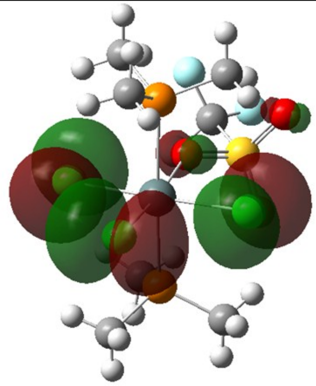
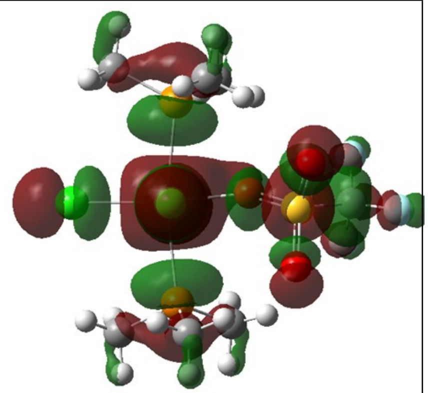
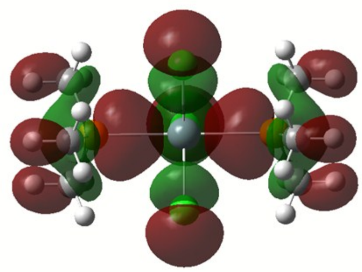
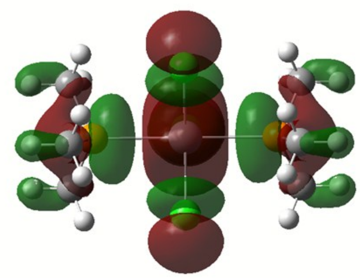
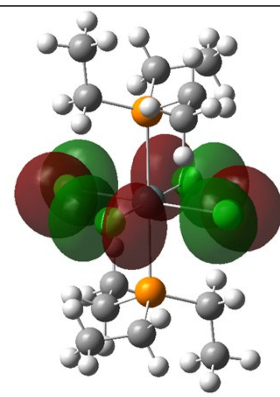
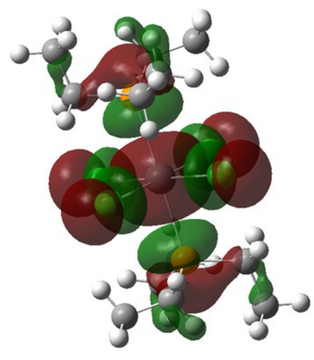
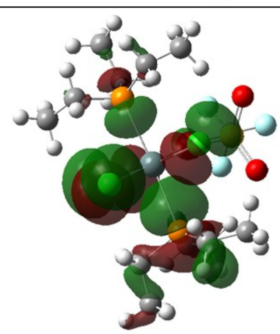
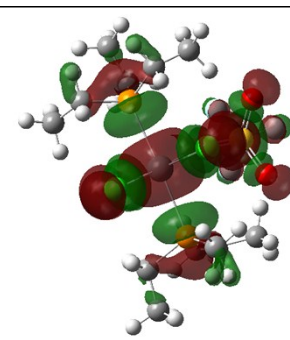
$[SnCl_3(PMe_3)_2(OTf)]$		
$[SnCl_3(PMe_3)_2]^+$		
$[SnCl_4(PEt_3)_2]$		
$[SnCl_3(PEt_3)_2(OTf)]$		

Table S7 Relative Orbital Energies

Orbital energies are given in eV and are for comparative purposes only

	HOMO	LUMO	Difference
$[SnCl_4(AsEt_3)_2]$	-6.92	-2.73	4.19
$[SnCl_3(AsEt_3)_2(OTf)]$	-7.41	-3.11	4.30
$[SnCl_3(AsEt_3)_2]^+$	-10.60	-6.53	4.07
$[SnCl_4(PMe_3)_2]$	-6.99	-2.69	4.30
$[SnCl_3(PMe_3)_2(OTf)]$	-7.61	-3.16	4.45
$[SnCl_3(PMe_3)_2]^+$	-11.27	-6.78	4.49
$[SnCl_4(PEt_3)_2]$	-6.93	-2.63	4.30
$[SnCl_3(PEt_3)_2(OTf)]$	-7.54	-3.10	4.44

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