ESI

Neutral and cationic germanium(IV) fluoride complexes with phosphine coordination – synthesis, spectroscopy and structures

Rhys P. King, William Levason and Gillian Reid

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK; email: G.Reid@soton.ac.uk

Table S1: X-ray crystallographic data[a]

Complex	$[GeF_4(PMe_3)_2]$	$[GeF_4\{CH_3C(CH_2PPh_2)_3\}]$ •CH_2Cl_2	$[GeF_3(PMe_3)_2(OTf)]$	$[GeF_2(PMe_3)_2(OTf)_2]$
Formula	$C_6H_{18}F_4GeP_2$	$C_{42}H_{41}Cl_2F_4GeP_3$	$C_7H_{18}F_6GeO_3P_2S$	$C_{24}H_{54}F_{24}Ge_3O_{18}P_6S_6$
M	300.73	858.15	430.84	1682.725
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group (no.)	$P2_1/n$ (14)	$P2_1/n$ (14)	Pbca (61)	P-1 (2)
a /Å	6.1467(2)	13.9614(2)	11.3324(1)	9.3701(3)
b /Å	10.1678(4)	12.9040(2)	11.7241(1)	15.5931(6)
c /Å	9.5754(3)	21.6728(3)	23.5687(3)	21.5703(7)
α /°	90	90	90	93.050(3)
β /°	91.210(3)	96.8620(10)	90	94.382(3)
γ /°	90	90	90	91.974(3)
U /Å^3	598.31(4)	3876.56(10)	3131.39(6)	3135.60(19)
Z	2	4	8	2
μ(Mo-$K_α$) /mm^{-1}	2.838	1.102	2.359	1.909
F(000)	305	1760	1734	1685
Total number reflns	6990	48266	80977	57396
R_{int}	0.033	0.029	0.041	0.067
Unique reflns	1509	13630	5222	19099
No. of params, restraints	64, 0	470, 0	187, 0	849, 0
GOF	1.036	1.029	1.060	1.026
R_1, wR_2 [I > 2σ(I)][b]	0.030, 0.069	0.039, 0.076	0.021, 0.049	0.071, 0.190
R_1, wR_2 (all data)	0.037, 0.074	0.055, 0.081	0.027, 0.050	0.113, 0.217

[a] Common items: T = 100 K; wavelength (Mo-$K_α$) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = Σ||F_o|-|F_c||/Σ|F_o|$;

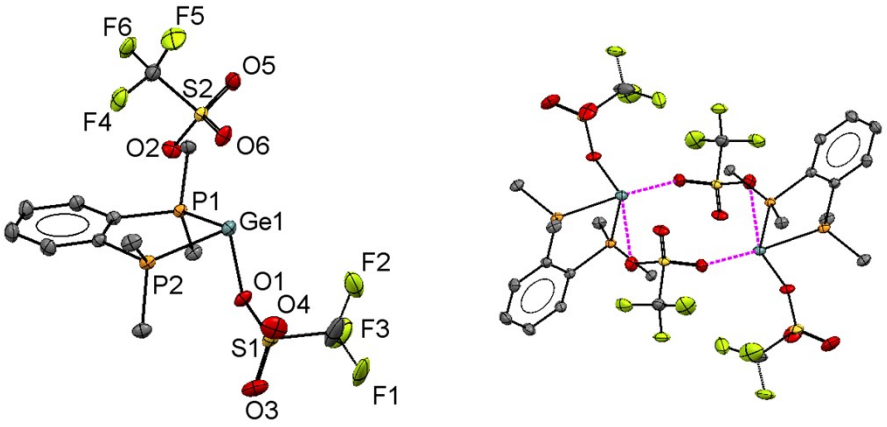
$wR_2=[Σw(F_o^2-F_c^2)_2/ΣwF_o^4]^{1/2}$

Table S1: cont.

Complex	$[GeCl_2(AsEt_3)_2][OTf]_2$	$[GeF_2(o\text{-}C_6H_4(PMe_2)_2)(OTf)_2]$	$[GeF(o\text{-}C_6H_4(PMe_2)_2)(OTf)_3]$ •$0.3CH_2Cl_2$
Formula	$C_{14}H_{30}As_2Cl_2F_6GeO_6S_2$	$C_{12}H_{16}F_8GeO_6P_2S_2$	$C_{52.6}H_{65.2}Cl_{1.2}F_{40}Ge_4O_{36}P_8S_{12}$
M	765.83	606.90	2998.82
Crystal system	triclinic	orthorhombic	monoclinic
Space group (no.)	P-1 (2)	$P2_12_12_1$ (19)	I2 (5)
a /Å	9.6136(3)	8.49904(14)	17.7401(2)
b /Å	9.7490(4)	15.8315(3)	9.08810(10)
c /Å	15.2210(5)	16.3349(4)	33.6730(3)
α /°	104.887(3)	90	90
β /°	101.440(3)	90	100.2150(13)
γ /°	97.269(3)	90	90
U /Å^3	1327.35(8)	2197.90(8)	5342.84(10)
Z	2	4	2
μ(Mo-K_α) /mm^{-1}	4.057	1.823	1.642
F(000)	760	1208	2978
Total number reflns	22109	71065	72764
R_{int}	0.060	0.071	0.039
Unique reflns	8925	6832	15790
No. of params, restraints	304, 0	284, 0	707, 1
GOF	1.029	1.131	1.037
R_1, wR_2 [I > 2σ(I)][b]	0.042, 0.081	0.061, 0.143	0.032, 0.066
R_1, wR_2 (all data)	0.059, 0.088	0.069, 0.146	0.038, 0.068

Table S1: cont.

Compound	$[GeF_3\{Ph_2P(CH_2)_2PPh_2\}(OTf)]$ $\bullet CH_2Cl_2$	$[GeF_2\{Ph_2P(CH_2)_2PPh_2\}(OTf)_2]$ $\bullet CH_2Cl_2$	$[Ge\{o\text{-}C_6H_4(PMe_2)_2\}(OTf)]$ $[OTf]\bullet 1/3CH_2Cl_2$
Formula	$C_{28}H_{26}Cl_2F_6GeO_3P_2S$	$C_{29}H_{26}Cl_2F_8GeO_6P_2S_2$	$C_{12.34}H_{16.66}Cl_{0.67}F_6GeO_6P_2S_2$
M	761.98	892.05	597.210
Crystal system	monoclinic	orthorhombic	triclinic
Space group (no.)	Pn (7)	Pccn (56)	P-1 (2)
a /Å	10.22780(19)	11.5994(2)	8.5322(2)
b /Å	12.3841(2)	20.7200(4)	12.5345(4)
c /Å	12.2598(2)	14.7520(2)	12.6057(3)
α /°	90	90	64.833(3)
β /°	94.8064(16)	90	70.313(3)
γ /°	90	90	71.230(3)
U /Å^3	1547.39(5)	3545.49(10)	1123.35(7)
Z	2	4	2
μ(Mo-K_α) /mm^{-1}	1.400	1.327	1.847
F(000)	768	1766	598
Total number reflns	21335	105333	30424
R_{int}	0.042	0.093	0.053
Unique reflns	8585	6229	7059
No. of params, restraints	388, 2	271, 0	318, 0
GOF	1.015	1.163	1.035
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.039, 0.065	0.048, 0.100	0.038, 0.084
R_1, wR_2 (all data)	0.049, 0.069	0.062, 0.105	0.049, 0.088



(a) (b)

Figure S1 (a) The structure of [Ge{*o*-$C_6H_4(PMe_2)_2$}(OTf)][OTf] showing the atom labelling scheme and (b) the weakly associated dimer arrangement. The ellipsoids are drawn at the 50% probability level and H atoms and a CH_2Cl_2 solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) are: : Ge1–P1 = 2.4321(5), Ge1–P2 = 2.4580(6), Ge1–O1 = 2.0968(15), Ge1···O2 = 2.6438(17), P1–Ge1–P2 = 81.469(18).

Figures S2 – S14 NMR and IR spectroscopic data for the complexes reported in this work

Figure S2.1-2.4 [$GeF_4(^iPr_3P)_2$]

Figure S3.1- 3.7 [$GeF_3(PMe_3)_2OTf$]

Figure S4.1-4.4 [$GeF_2(PMe_3)_2(OTf)_2$]

Figure S5.1-5.4 [$GeF(PMe_3)_2(OTf)_3$]

Figure S6.1-6.4 [$GeF_3(^iPr_3P)_2$][OTf]

Figure S7.1-7.4 [GeF_3{o-$C_6H_4(PMe_2)_2$}(OTf)]

Figure S8.1-8.4 [GeF_2{o-$C_6H_4(PMe_2)_2$}$(OTf)_2$]

Figure S9.1-9.4 [GeF{o-$C_6H_4(PMe_2)_2$}$(OTf)_3$]

Figure S10.1-10.4 [$GeF_4(\kappa^2$-triphos)]

Figure S11.1-11.4 [GeF_4(tetraphos)]

Figure S12.1-12.4 [GeF_3{$Ph_2P(CH_2)_2PPh_2$}(OTf)]

Figure S13.1-13.4 [GeF_2{$Ph_2P(CH_2)_2PPh_2$}$(OTf)_2$]

Figure S14 $GeCl_4$ + 2$AsEt_3$ + 2 TMSOTf.

Figure S2 [$GeF_4(^iPr_3P)_2$]

Figure S2.1 ^1H NMR spectrum in CD_2Cl_2, 298 K; *= [HP^iPr_3] impurity, ^= CH_2Cl_2.

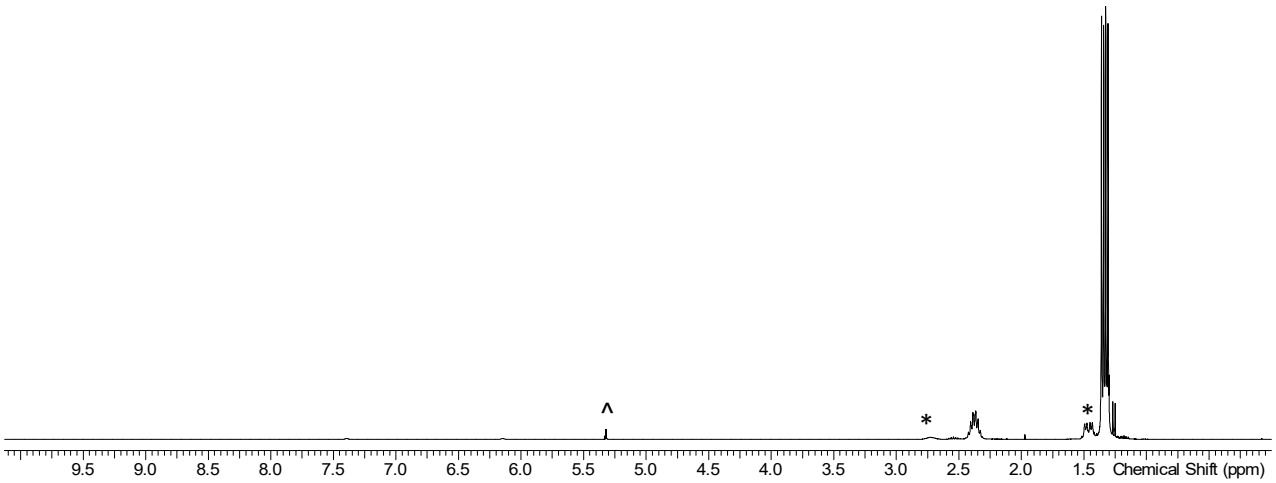


Figure S2.2 $^{19}F\{^1H\}$ NMR spectrum in CD_2Cl_2, 298 K; £= unidentified impurity.

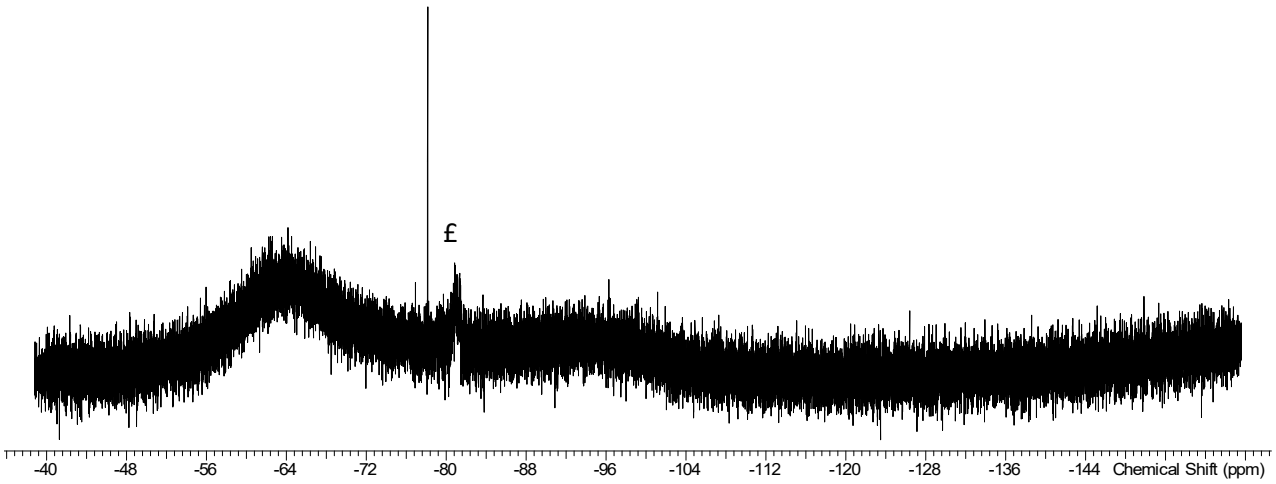


Figure S2.3 $^{19}F\{^1H\}$ NMR spectrum in CD_2Cl_2, 183 K

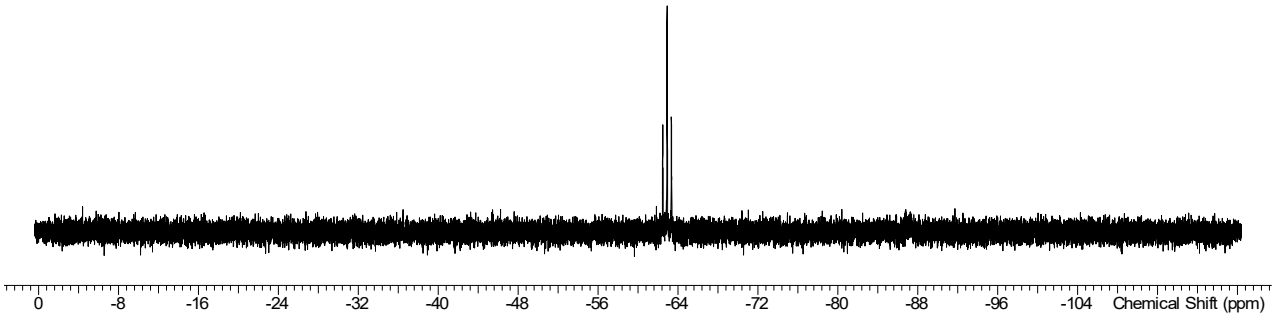


Figure S2.4 $^{31}P\{^{1}H\}$ NMR spectrum in CD_2Cl_2, 298 K; *= $[HP^iPr_3]^+$ impurity

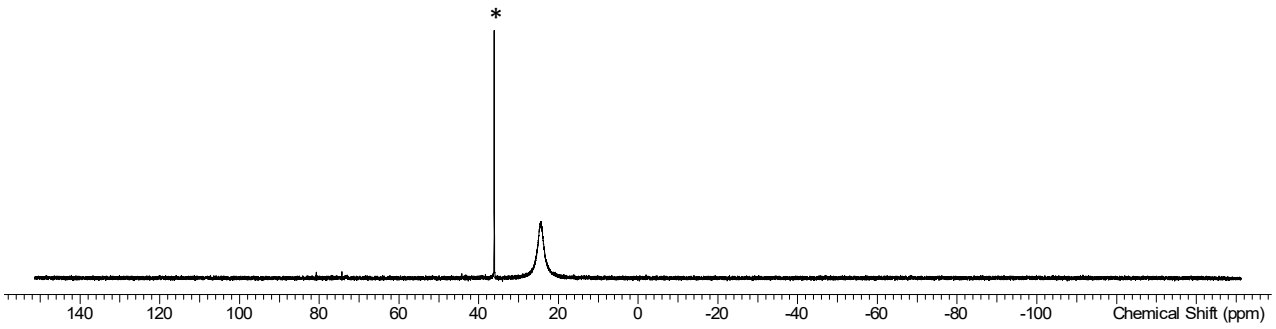


Figure S2.5 $^{31}P\{^{1}H\}$ NMR spectrum in CD_2Cl_2, 183 K.

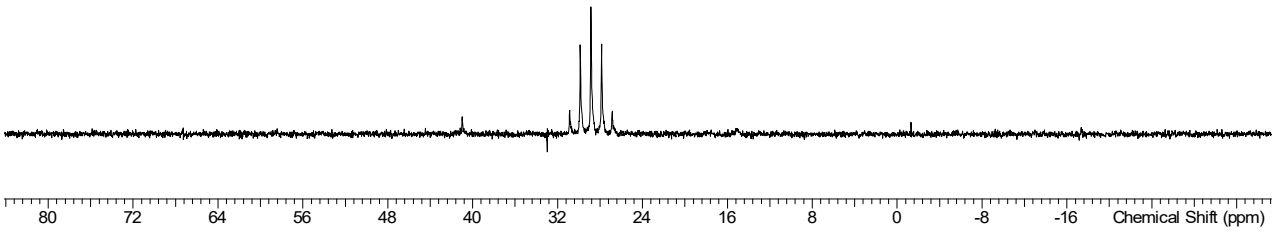


Figure S2.6 IR (Nujol/cm^{-1})

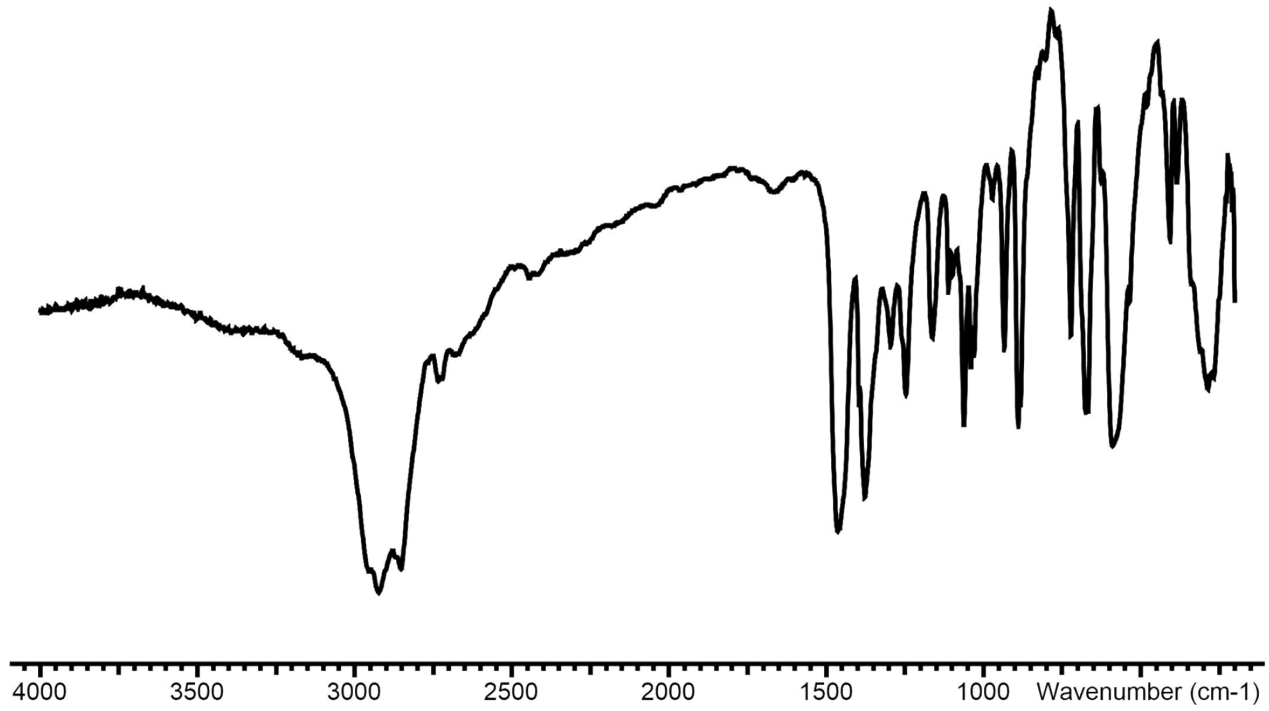


Figure S3 [$GeF_3(PMe_3)_2OTf$]

Figure S3.1 ^1H NMR spectrum in CD_2Cl_2, 298 K; *= $[HPMe_3]^+$.

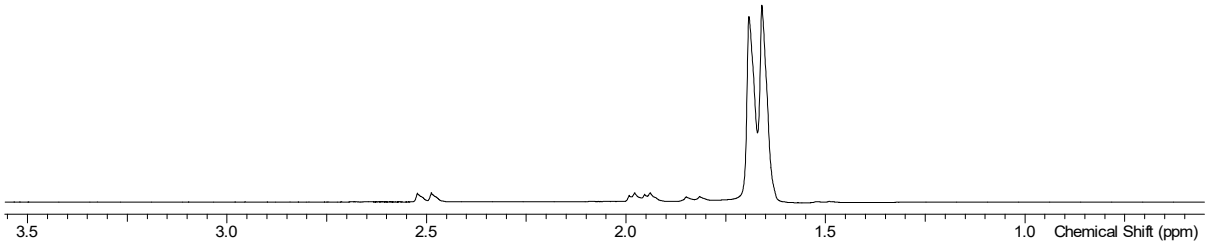


Figure S3.2.1 $^{19}F\{^{1}H\}$ NMR spectrum in CD_2Cl_2, 298 K.

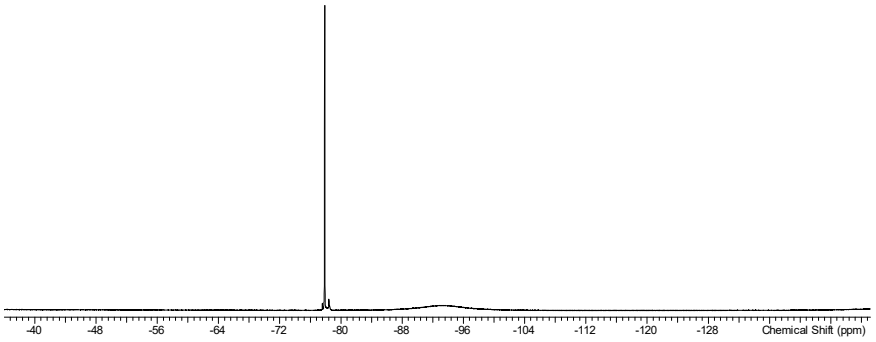


Figure S3.2.2 $^{19}F\{^{1}H\}$ NMR spectrum in CD_2Cl_2, 183 K.

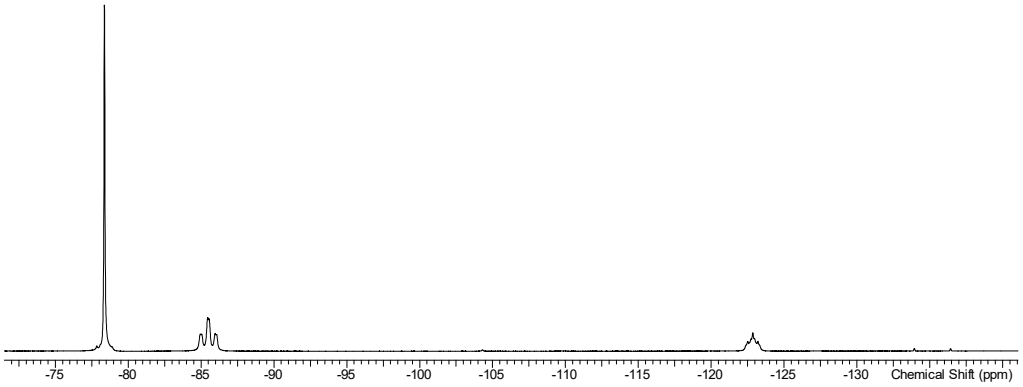


Figure S3.2.3 Expansion of the spectrum

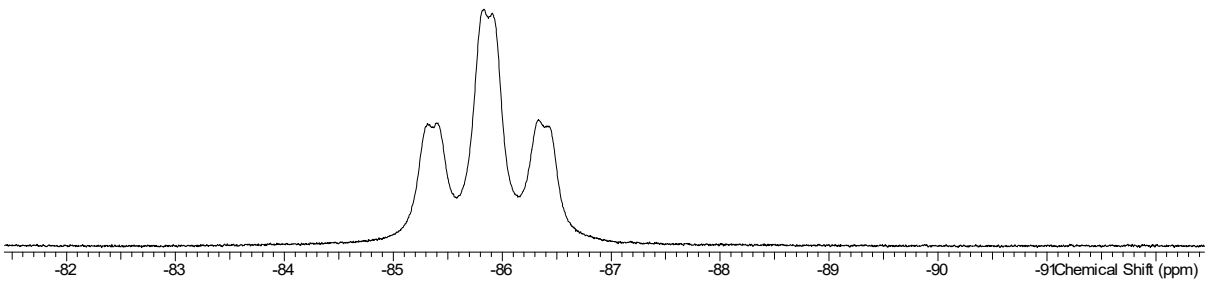


Figure S3.2.4 Expansion of the spectrum

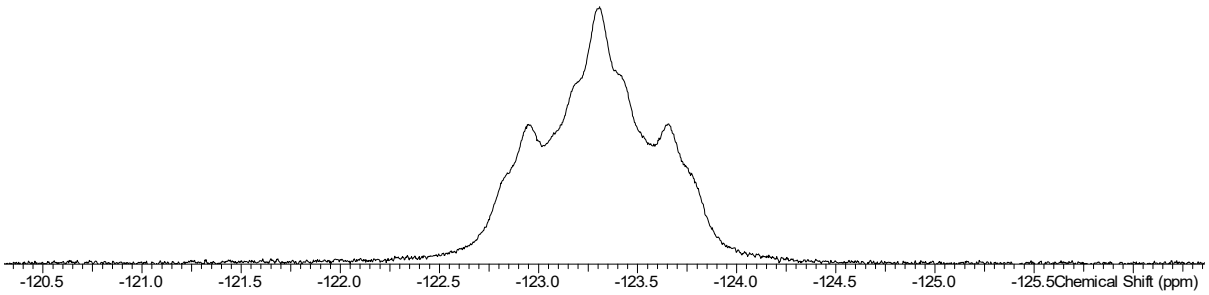


Figure S3.2.5 Expansion of the spectrum showing the doublet corresponding to the $[FPMe_3]^+$ by-product from reductive defluorination of the complex.

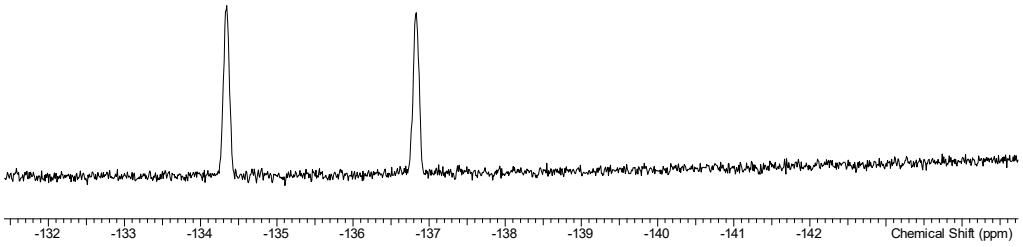


Figure S3.4.1 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K; *= $[HPMe_3]^+$.

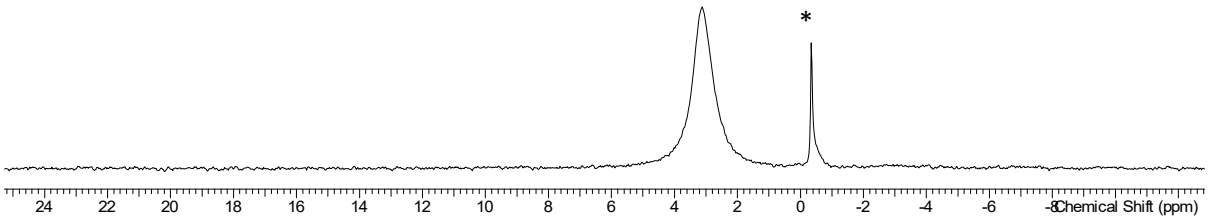


Figure S3.4.2 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 183 K; *= $[HPMe_3]^+$.

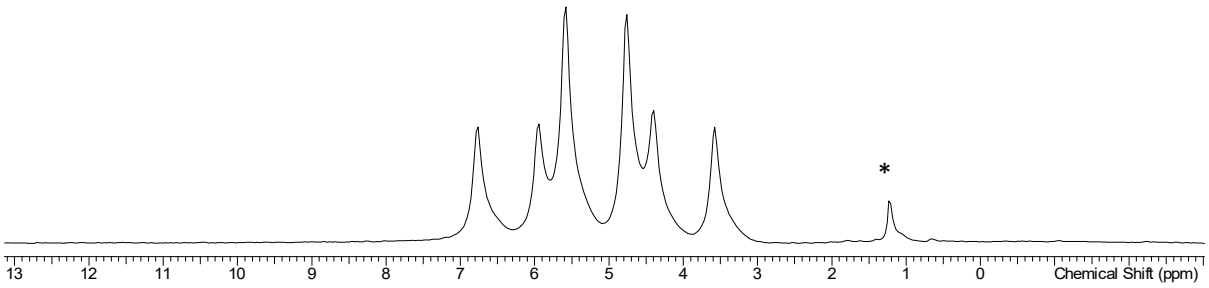


Figure S3.5 Stacked plot variable temperature $^{19}F\{^{1}H\}$ NMR spectra.

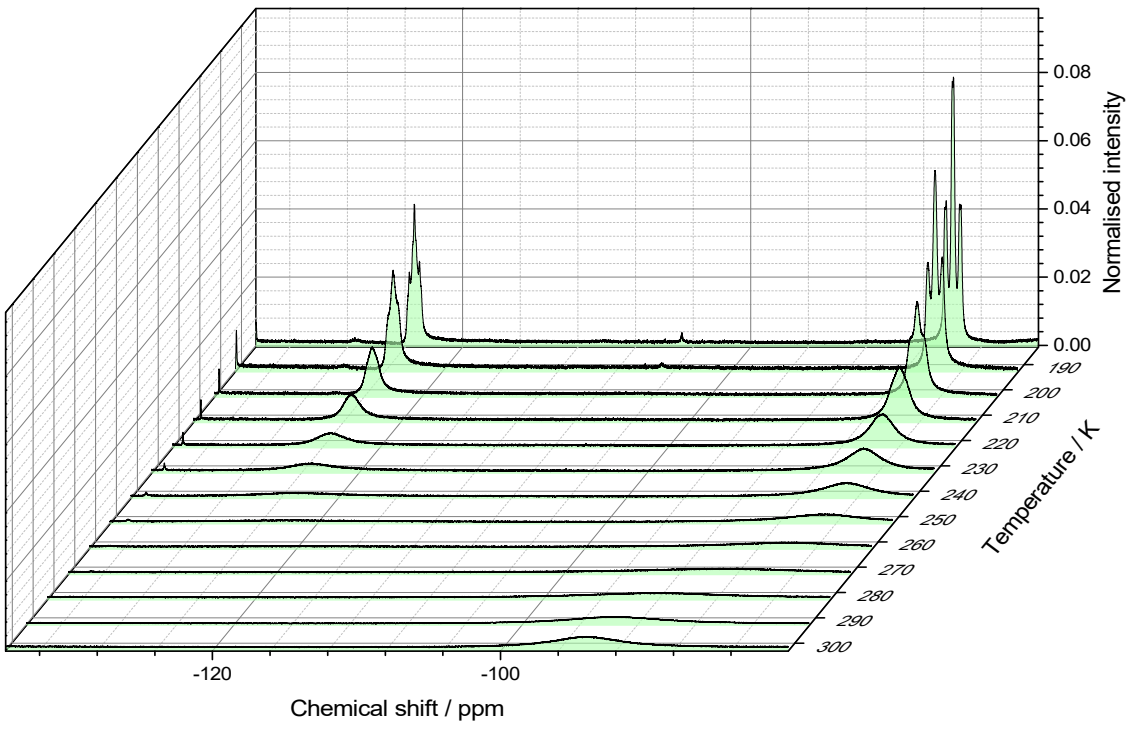


Figure S3.6 Stacked plot variable temperature $^{31}P\{^{1}H\}$ NMR spectra.

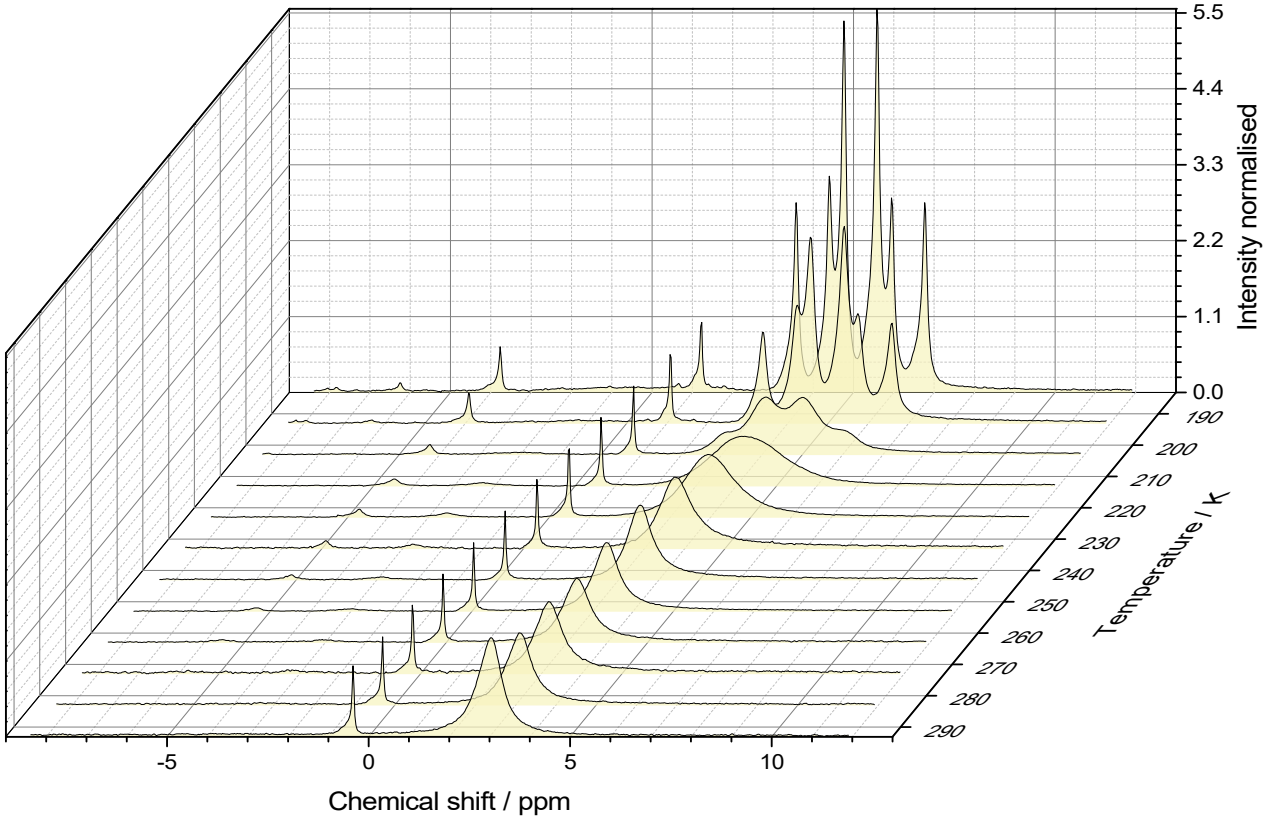


Figure S3.7: IR (Nujol/cm^{-1})

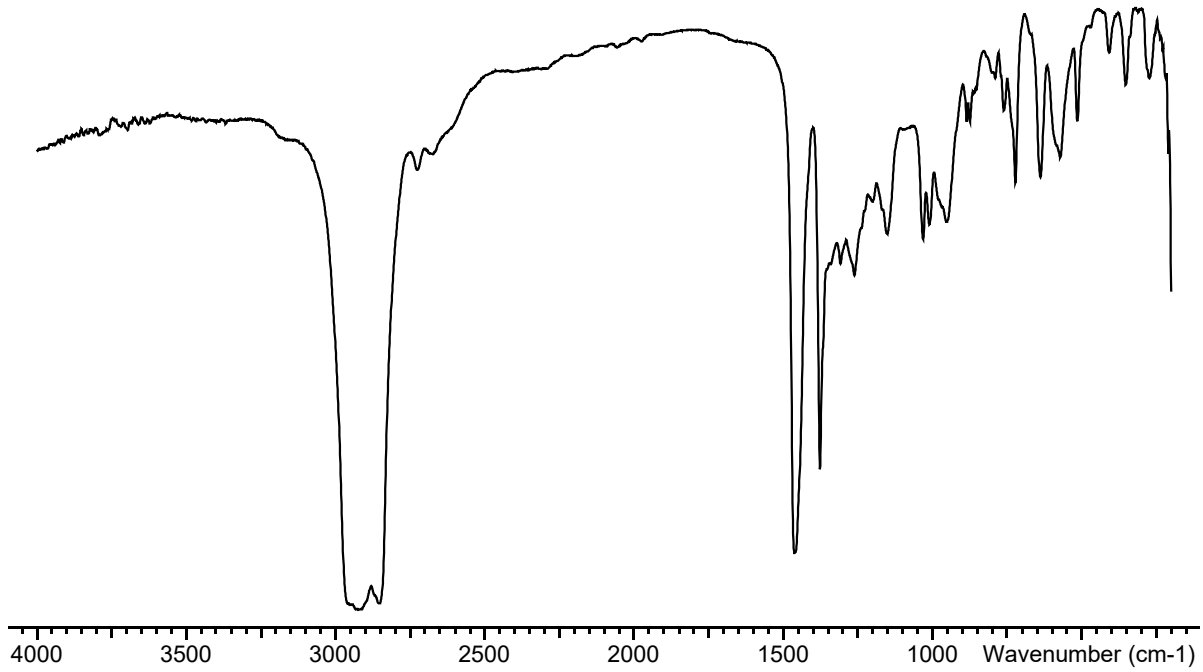


Figure S4 [$GeF_2(PMe_3)_2(OTf)_2$]

Figure S4.1.1 ^{1}H NMR spectrum CD_2Cl_2, 298 K; *= unidentified impurity, ^= CH_2Cl_2.

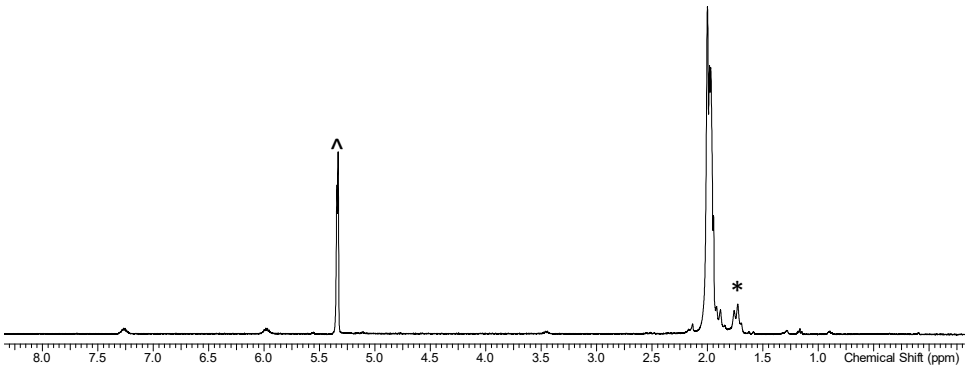


Figure S4.1.2 ^{1}H NMR spectrum CD_2Cl_2, 233 K.

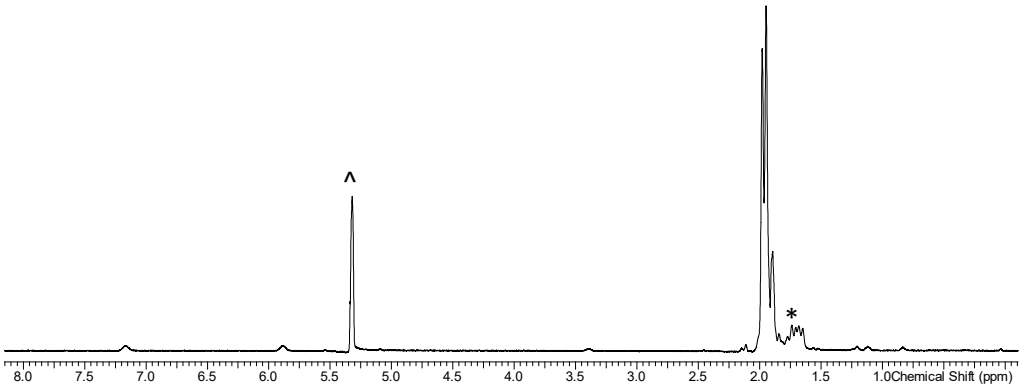


Figure S4.2.1 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K.

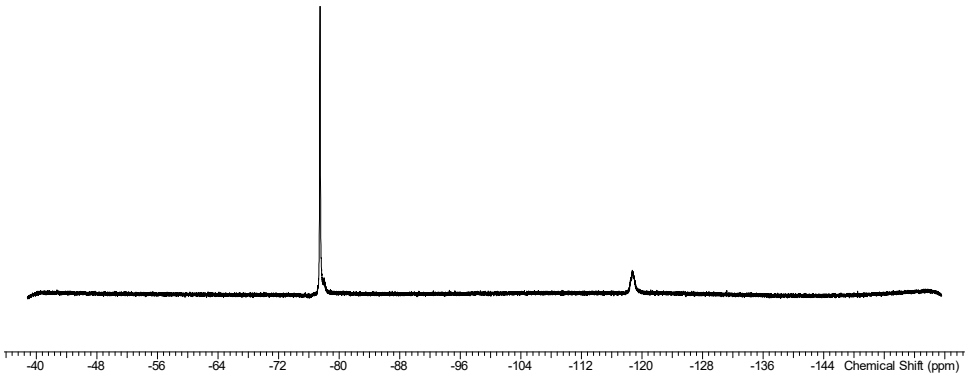


Figure S4.2.2 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2, 233 K.

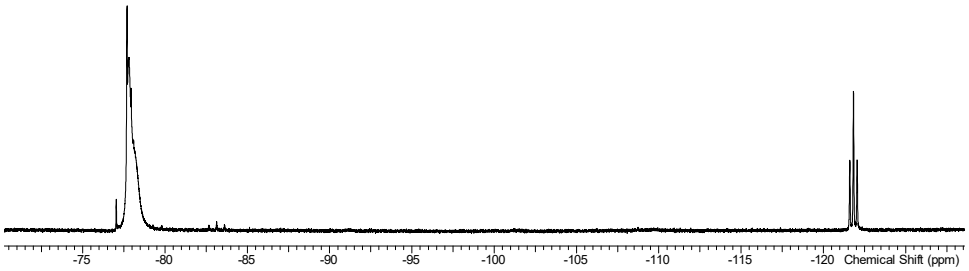


Figure S4.3.1 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2 298 K; *= $[HPMe_3]^+$

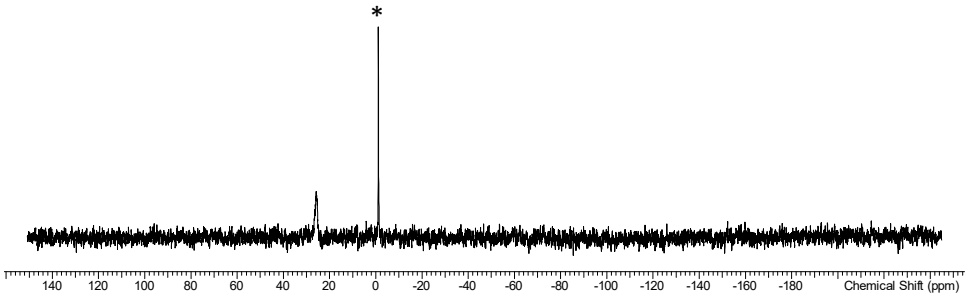


Figure S4.3.2 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2 233 K; *= $[HPMe_3]^+$.

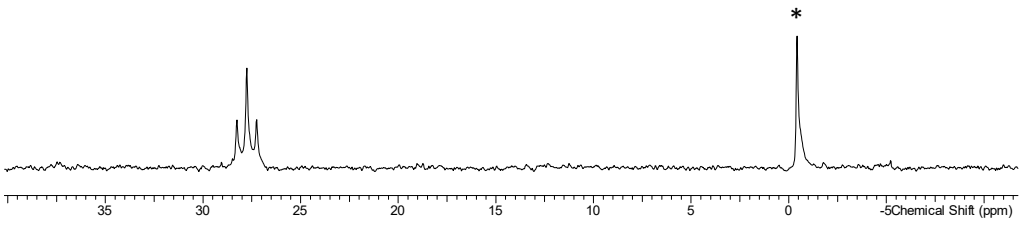


Figure S4.4 IR (Nujol/cm^{-1}):

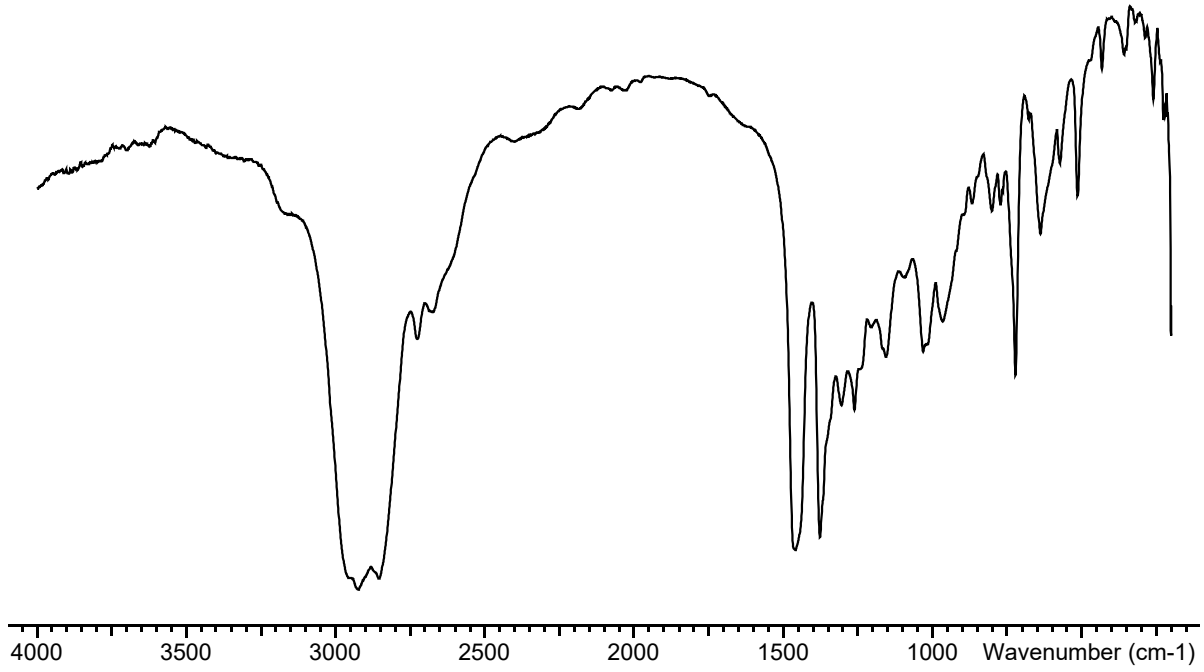


Figure S5 [GeF(PMe$_3$)$_2$(OTf)$_3$]

Figure S5.1 ^{1}H NMR spectrum CD_2Cl_2 298 K; *= $[HPMe_3]^+$, ^= CH_2Cl_2

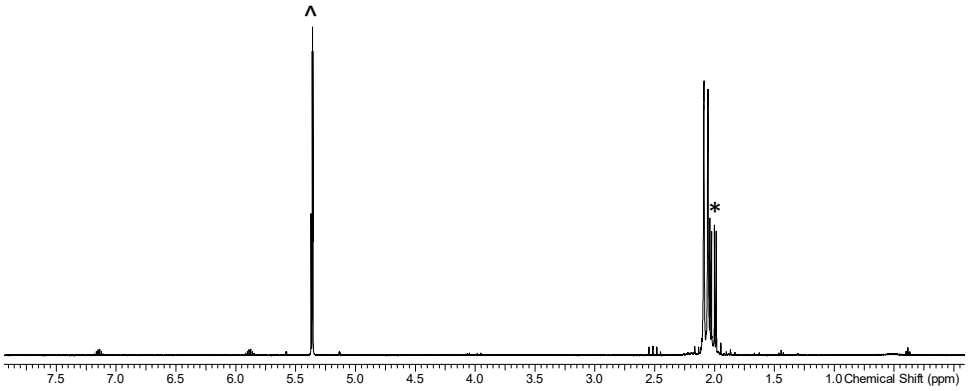


Figure S5.2 $^{19}F\{^1H\}$ NMR spectrum CD_2Cl_2 298 K.

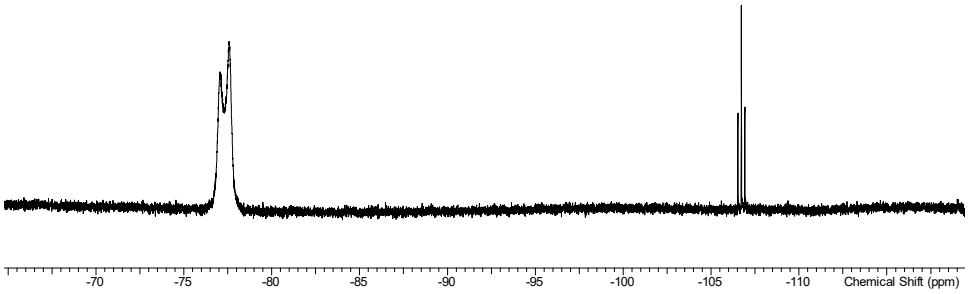


Figure S5.3 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2 298 K.

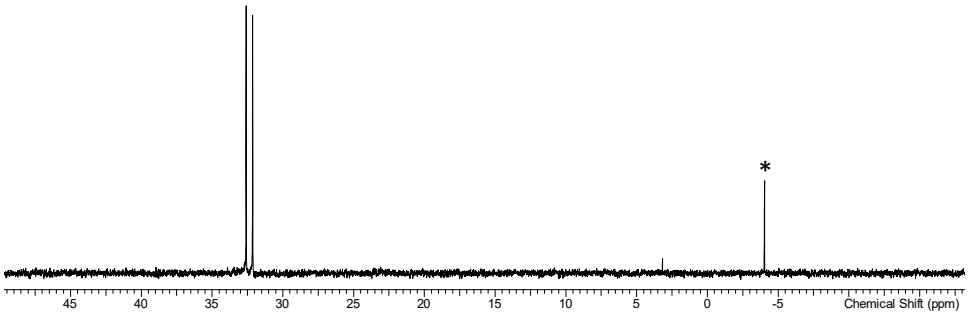


Figure S5.4 IR (Nujol/cm^{-1})

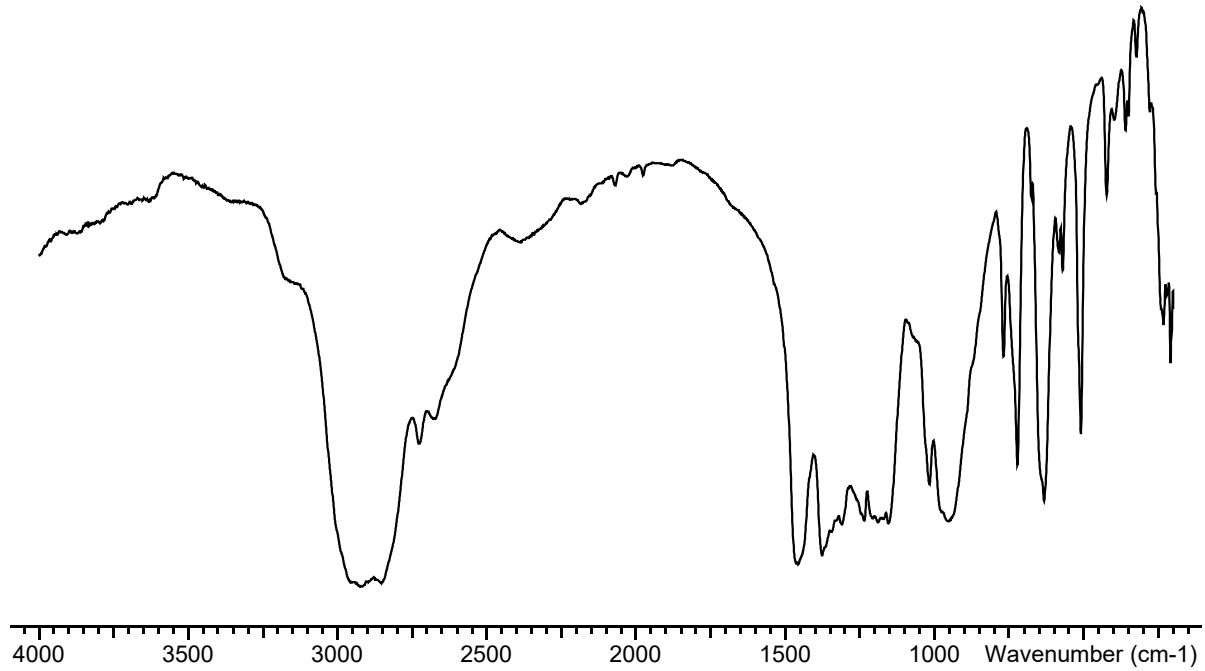


Figure S6 $[GeF_3(^{i}Pr_3P)_2][OTf]$

Figure S6.1 ^{1}H NMR spectrum CD_2Cl_2, 298 K; *= CH_2Cl_2

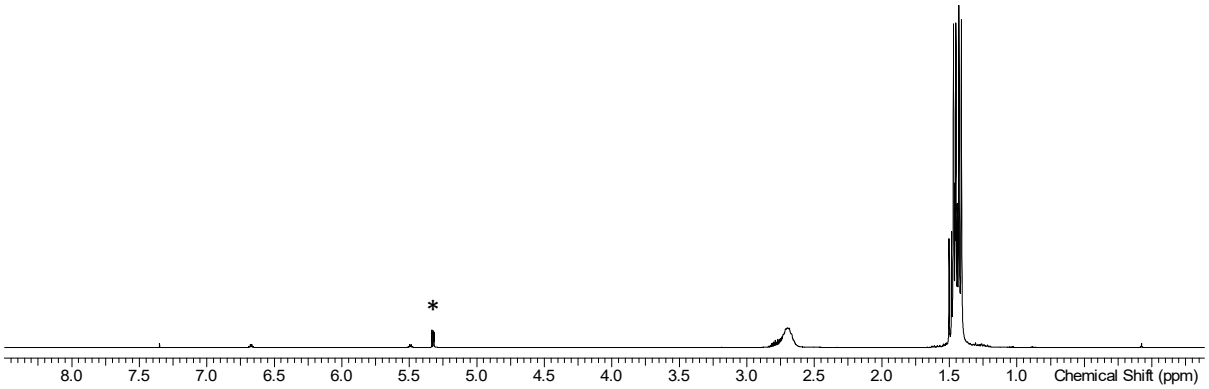


Figure S6.2 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2. 298 K.

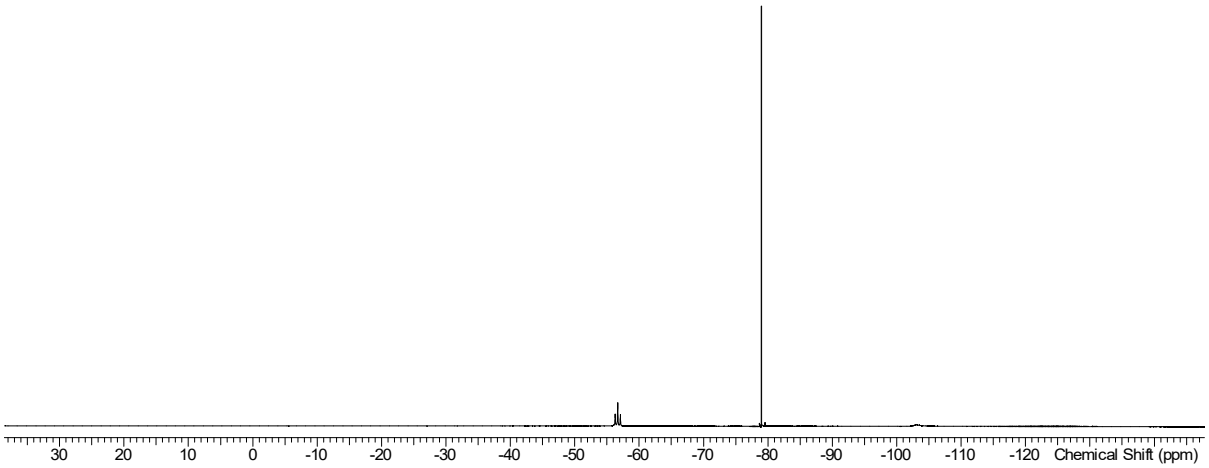


Figure S6.3 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K; *= $[HP^{i}Pr_3]^{+}$

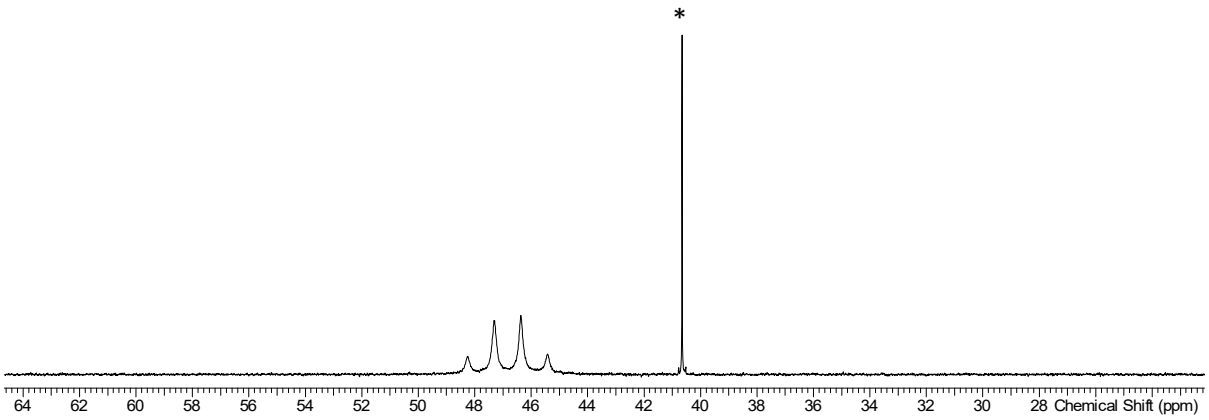


Figure S6.3.2 $^{31}P\{^{1}H\}$ spectrum CD_2Cl_2, 183 K; *= $[HP^{i}Pr_3]^{+}$

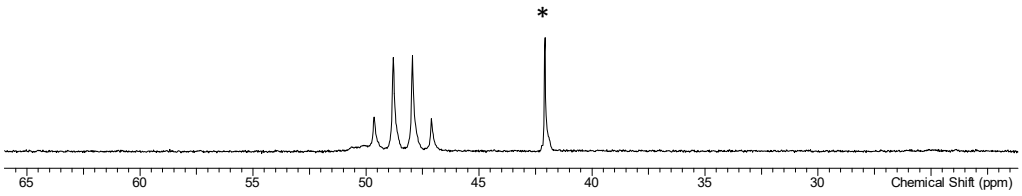


Figure S6.4 IR (Nujol/cm^{-1})

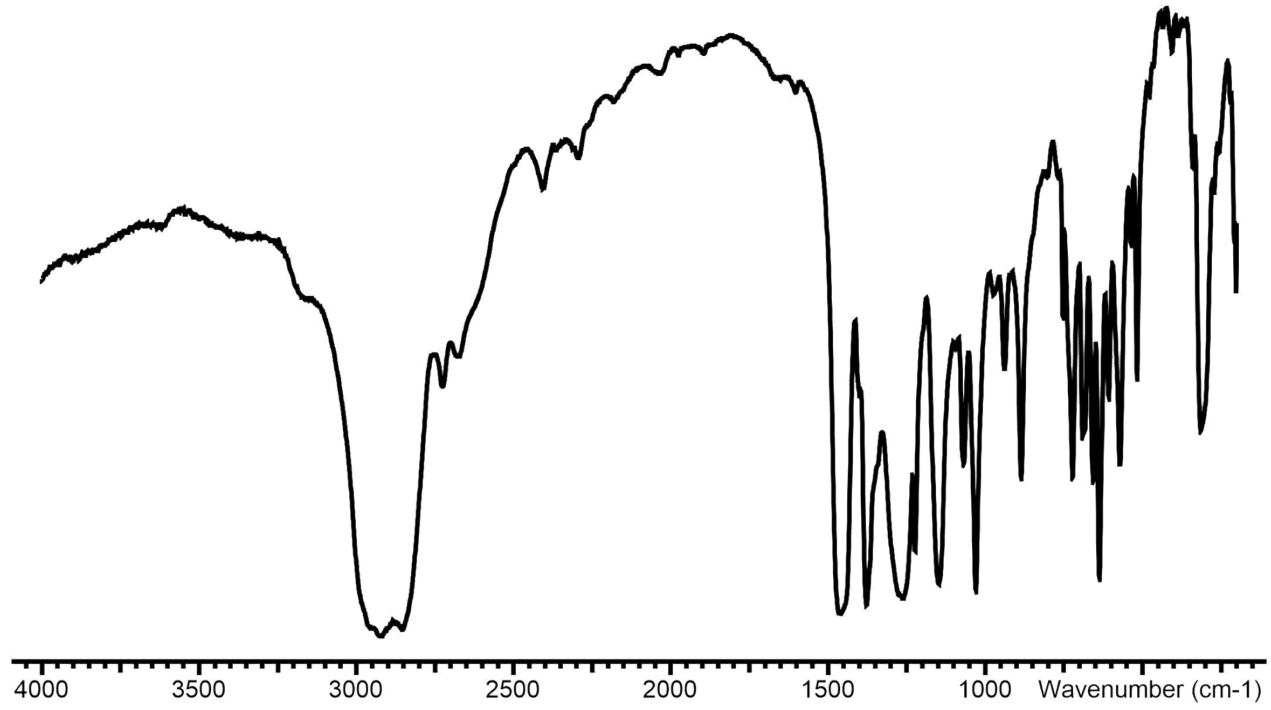


Figure S7 [GeF_3{o-$C_6H_4(PMe_2)_2$}(OTf)]

Figure S7.1 ^{1}H NMR spectrum CD_2Cl_2, 298 K; *= impurity/decomposition; ^= CH_2Cl_2

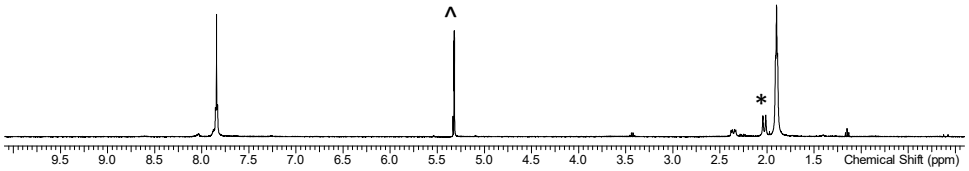


Figure S7.2.1 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K.

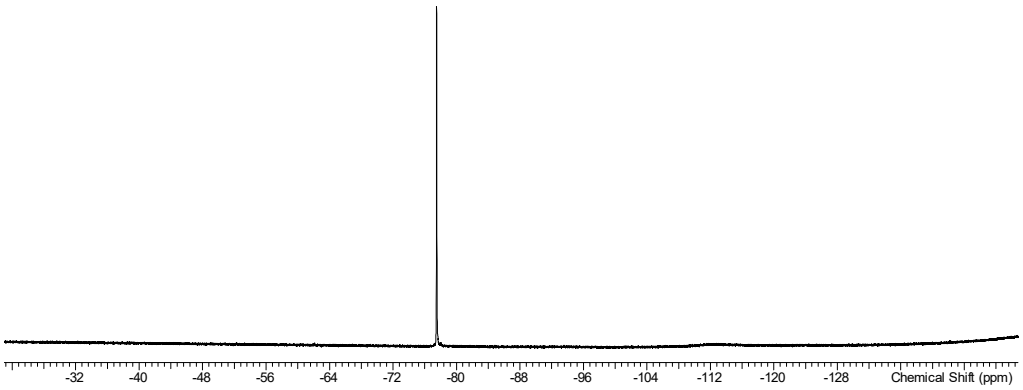


Figure S7.2.2 $^{19}F\{^{1}H\}$ NMR spectrum (183 K)

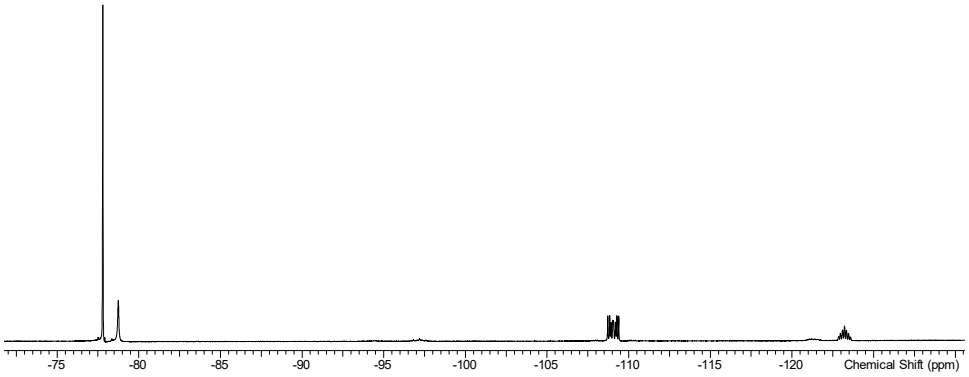


Figure S7.2.3 Expansion of the spectrum (*= $[GeF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ impurity)

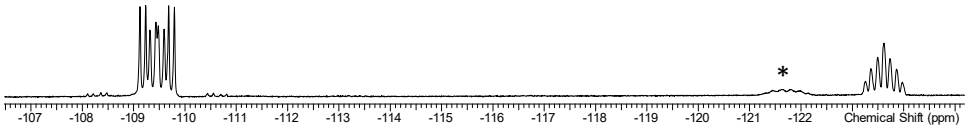


Figure S7.3.1 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K; £= unidentified impurities

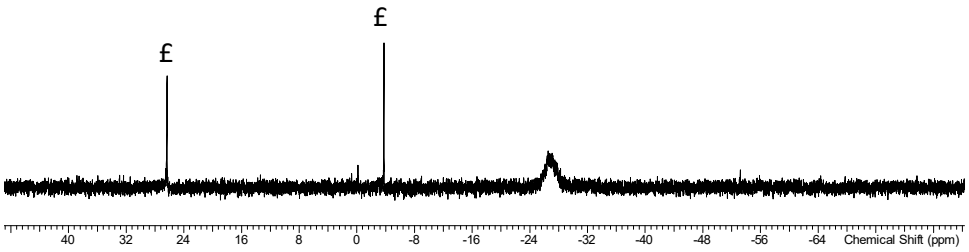


Figure S7.3.2 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 183 K; *= $[GeF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$

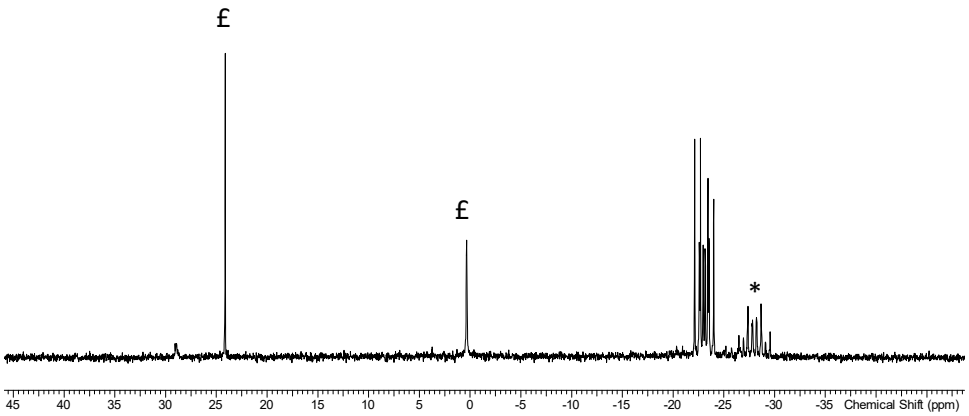


Figure S7.3.3 Expansion of the spectrum

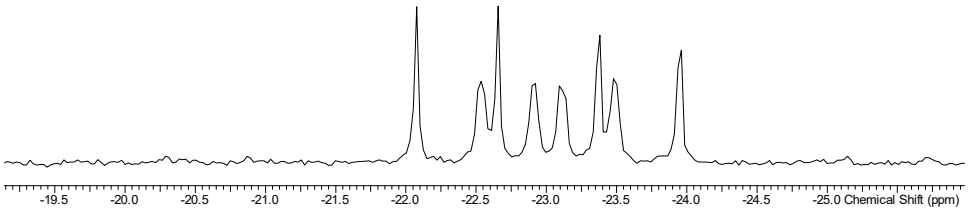


Figure S7.4 IR (Nujol/cm^{-1})

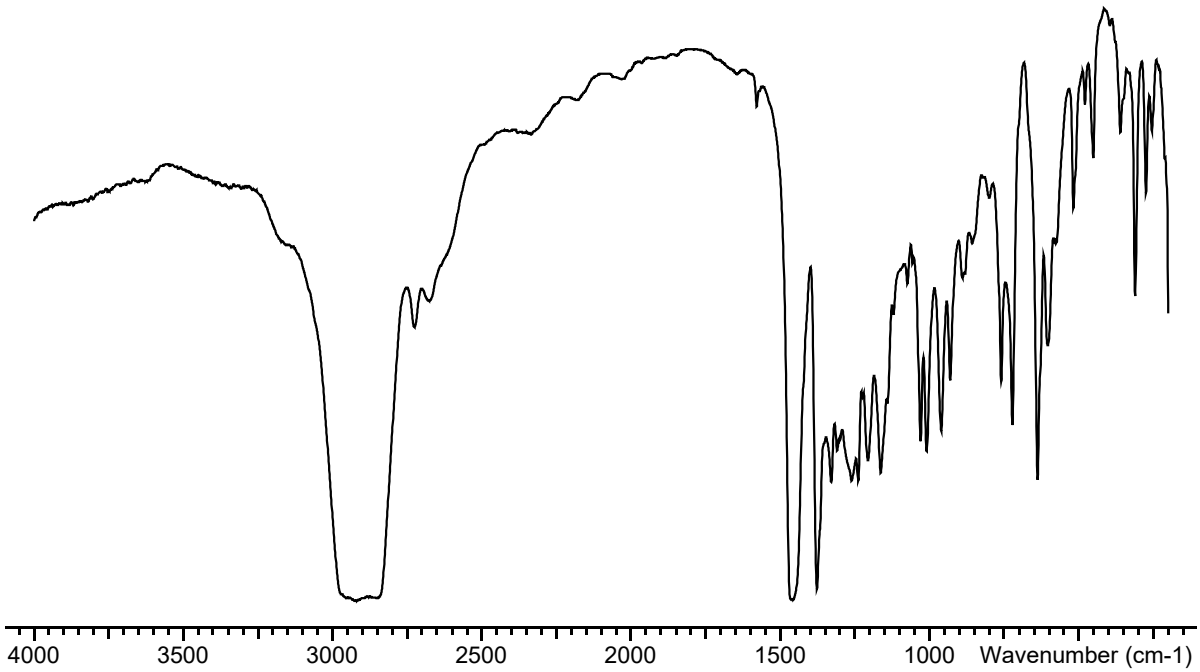


Figure S8 [GeF_2{o-$C_6H_4(PMe_2)_2$}$(OTf)_2$]

Figure S8.1 ^1H NMR CD_2Cl_2, 298 K; *= unidentified impurity/decomposition, ^= CH_2Cl_2

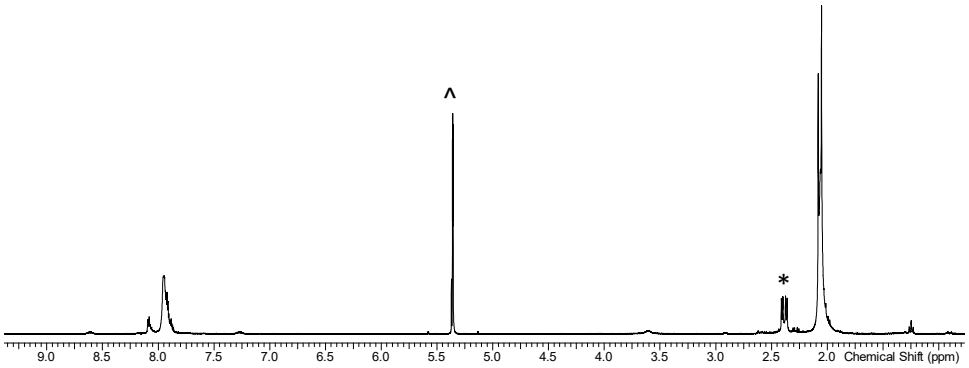


Figure S8.2.1 $^{19}F\{^1H\}$ NMR spectrum CD_2Cl_2, 298 K.

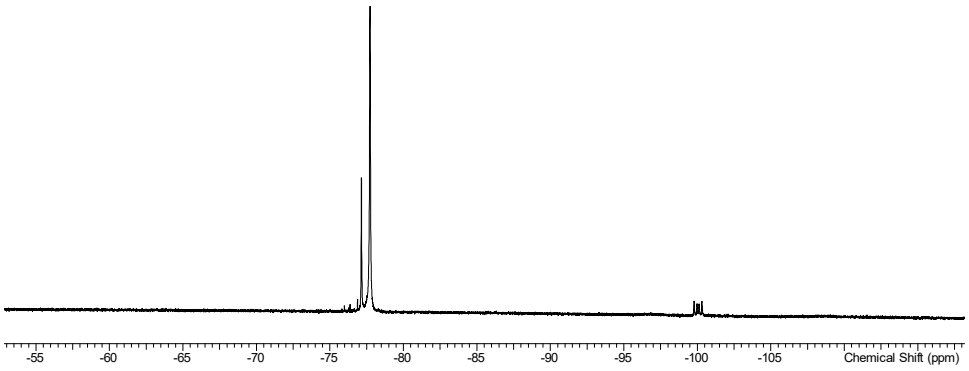


Figure S8.2.2 Expansion of the spectrum

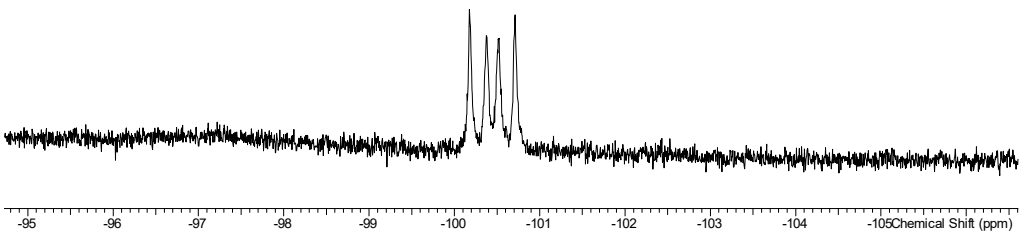


Figure S8.2.3 $^{19}F\{^{1}H\}$ NMR spectrum (*trans* triflate isomer [%], possibly one triflate *trans* P one *trans* F isomer[£], $[GeF_3\{o\text{-}C_6H_4(PMe_2)_2\}(OTf)]$ impurity*

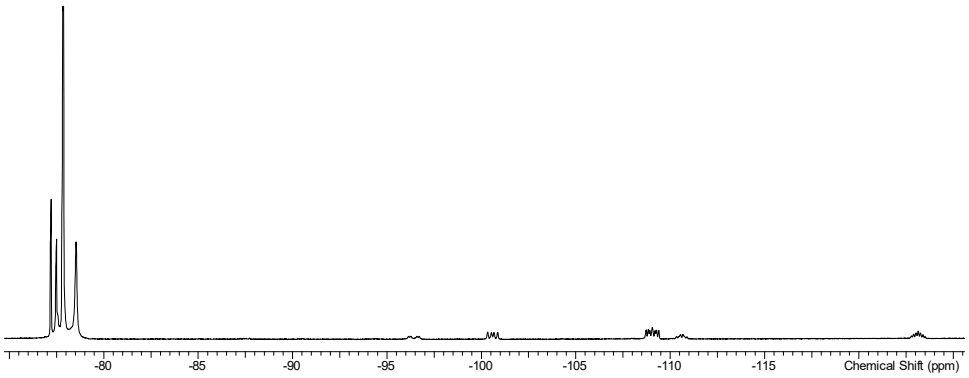


Figure S8.2.4 Expansion of the spectrum

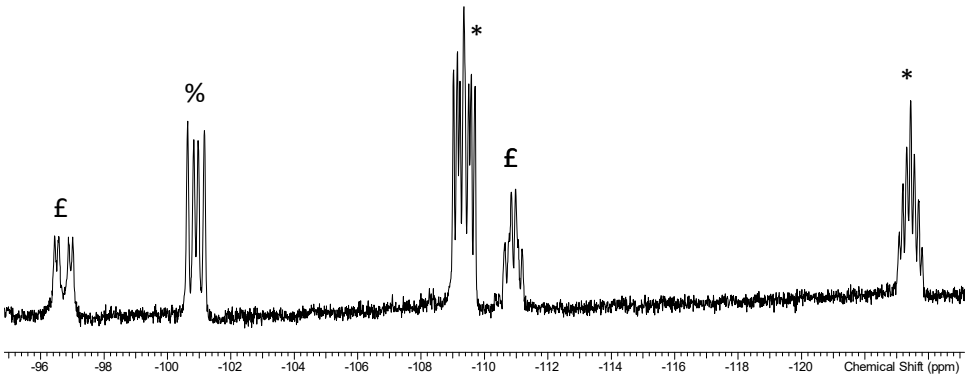


Figure S8.3.1 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2 298 K; [&]= unidentified impurities

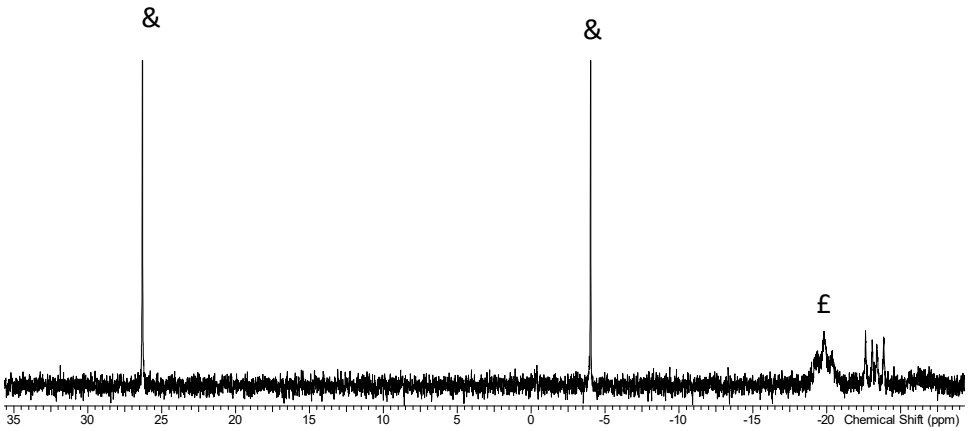


Figure S8.3.2 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 183 K

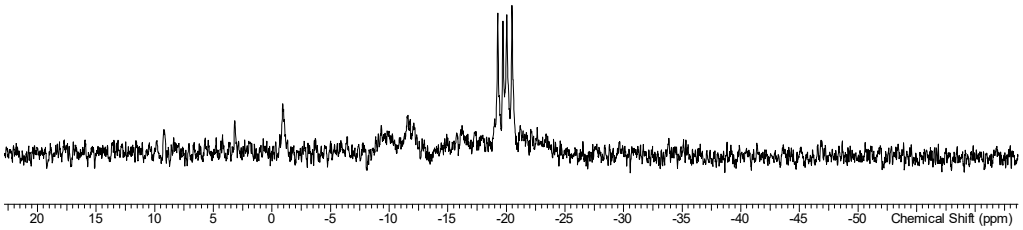


Figure S8.4 IR (Nujol/cm^{-1})

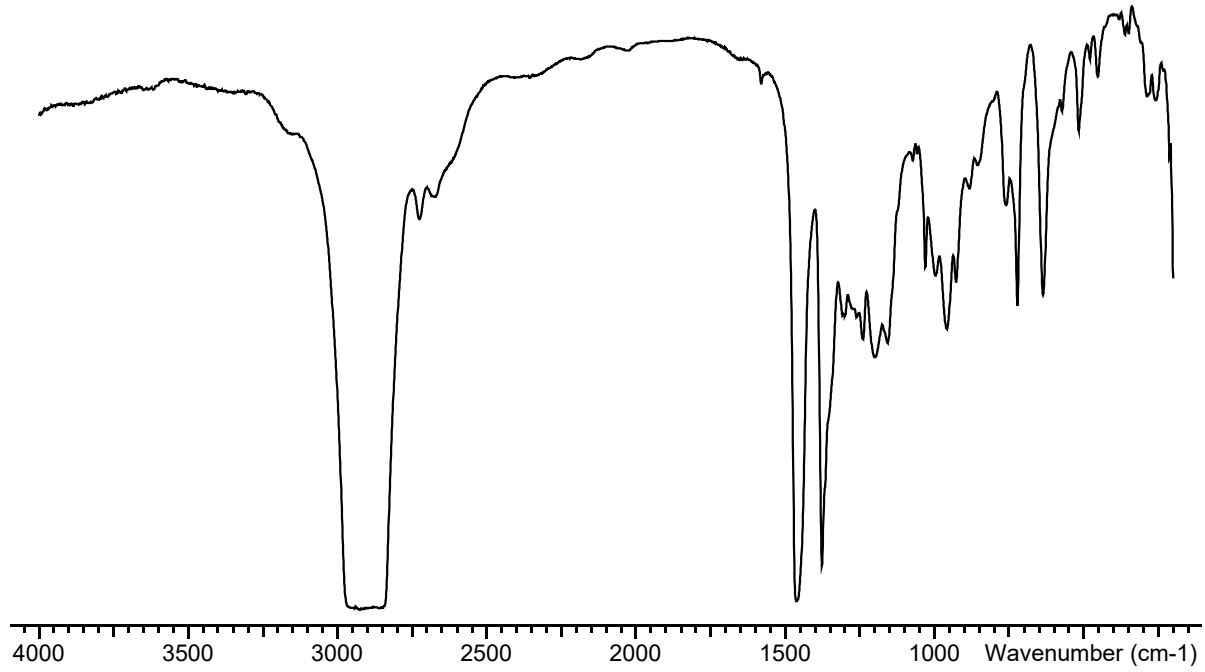


Figure S9 [GeF{o-$C_6H_4(PMe_2)_2$}$(OTf)_3$]

Figure S9.1 ^1H NMR spectrum CD_2Cl_2, 298 K; *= CH_2Cl_2

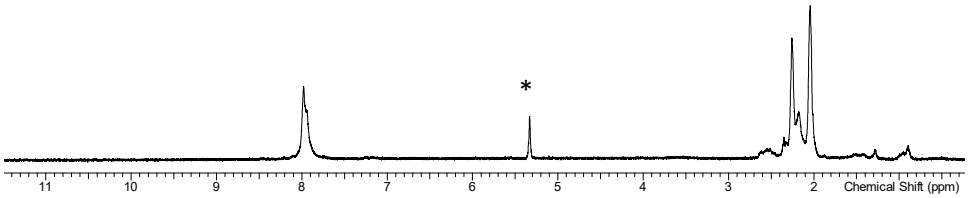


Figure S9.2.1 $^{19}F\{^1H\}$ NMR spectrum CD_2Cl_2, 298 K.

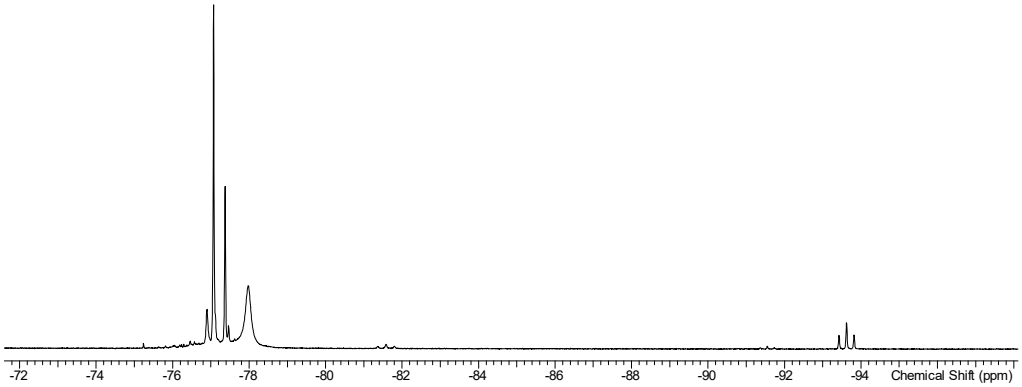


Figure S9.2.2 Expansion of the spectrum

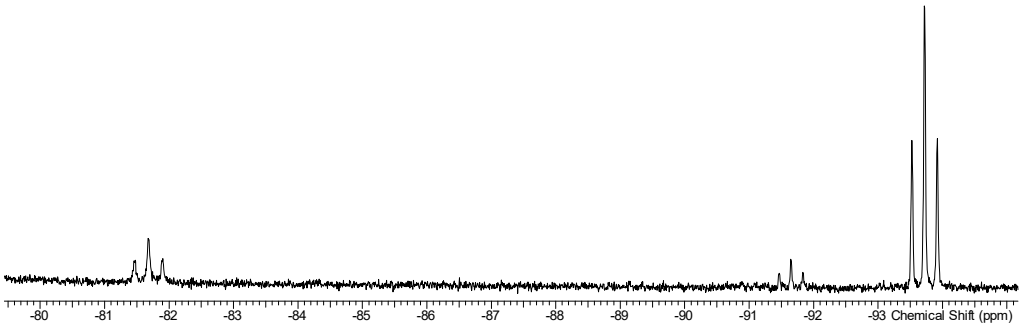


Figure S9.3 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2 298 K; *= unidentified impurities/decomposition

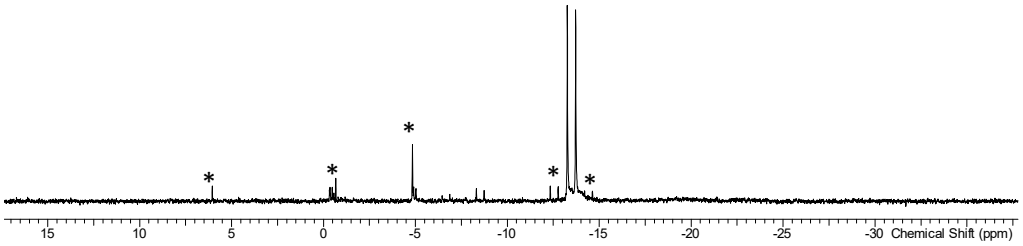


Figure S9.4 IR (Nujol/cm^{-1})

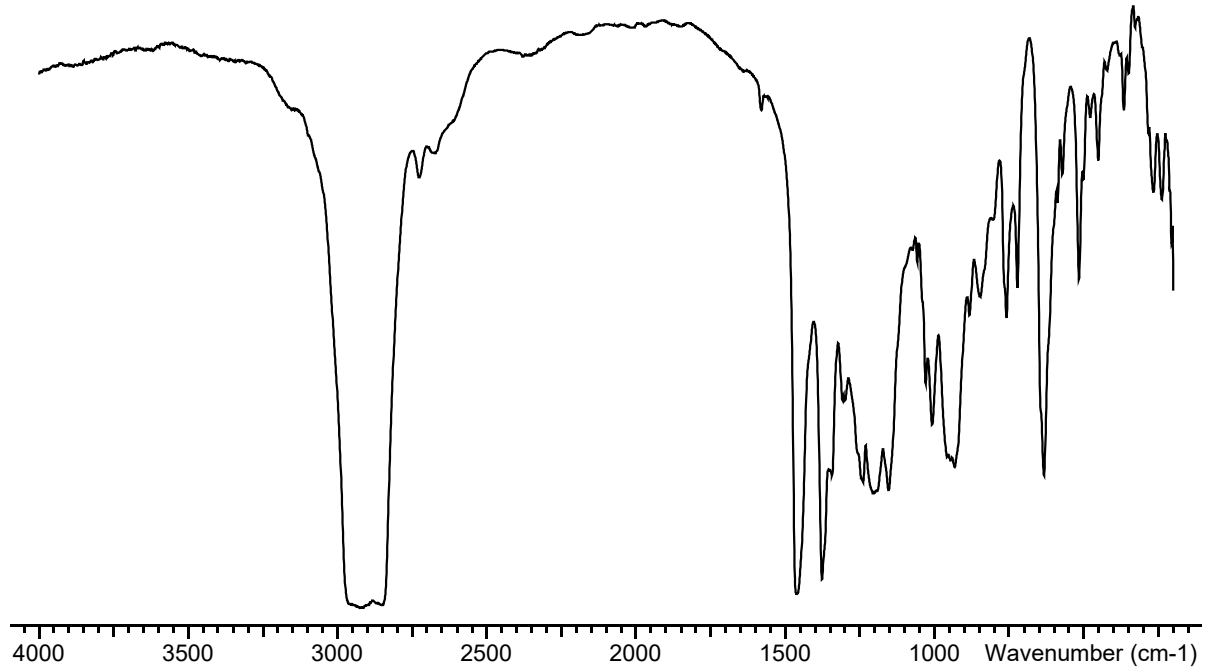


Figure S10 [$GeF_4\{\kappa^2\text{-}CH_3C(CH_2PPh_2)_3\}$]

Figure S10.1.1 ^1H NMR spectrum CD_2Cl_2, 298 K; *= uncoordinated triphosphine, ^= MeCN, "= CH_2Cl_2

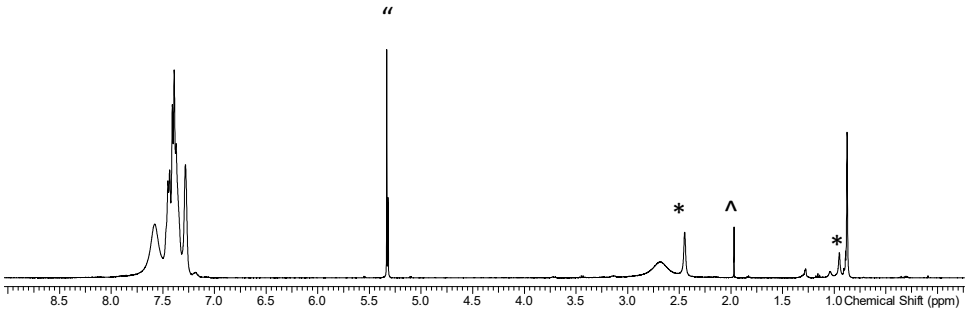


Figure S10.1.2 ^1H NMR spectrum CD_2Cl_2 183 K.

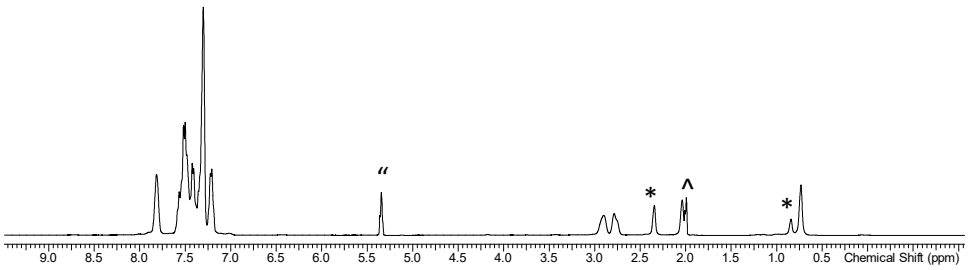


Figure S10.2.1 $^{19}F\{^1H\}$ NMR spectrum CD_2Cl_2 298 K; *= GeF_4

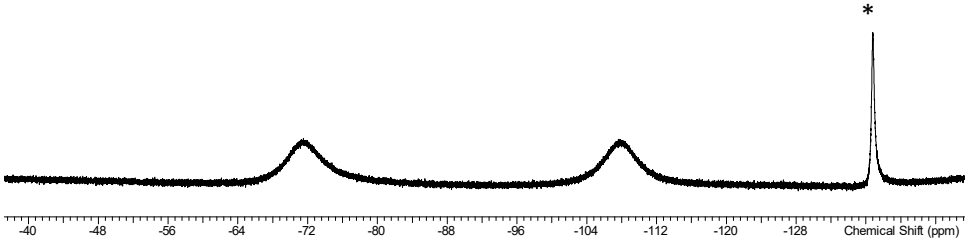


Figure S10.2.2 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2, 243 K.

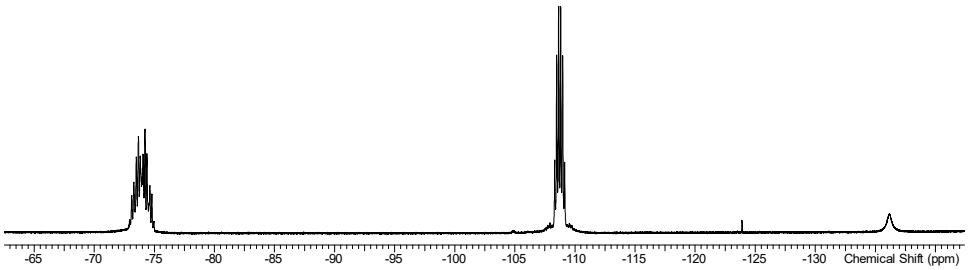


Figure S10.2.3 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2, 183 K.

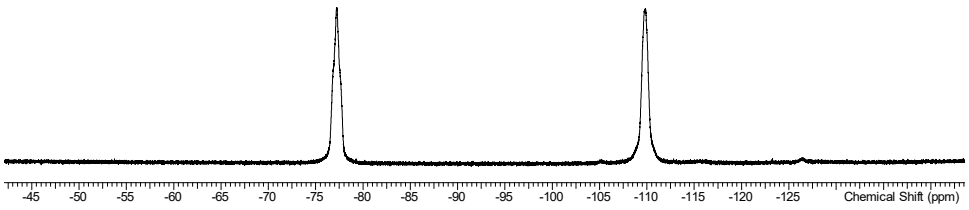


Figure S10.3.1 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K.

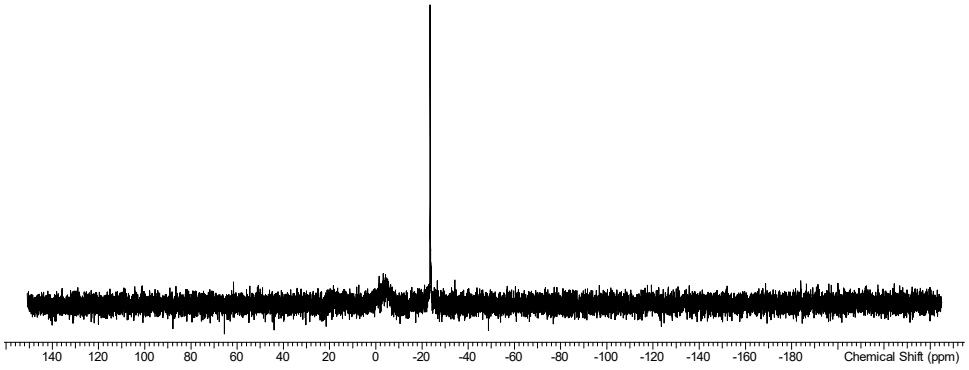


Figure S10.3.2 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 183 K; *= uncoordinated triphosphine

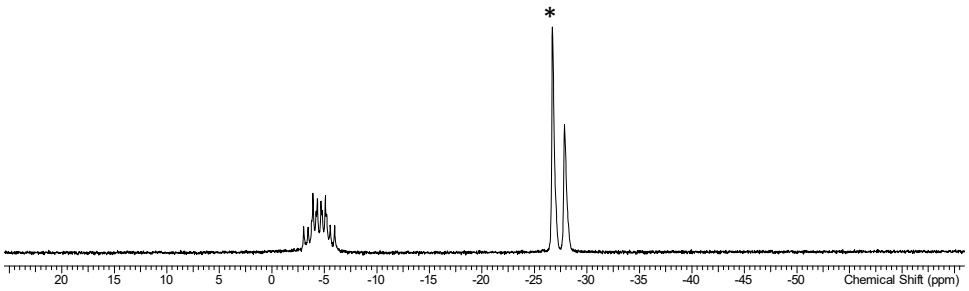


Figure S10.4 IR (Nujol/cm^{-1})

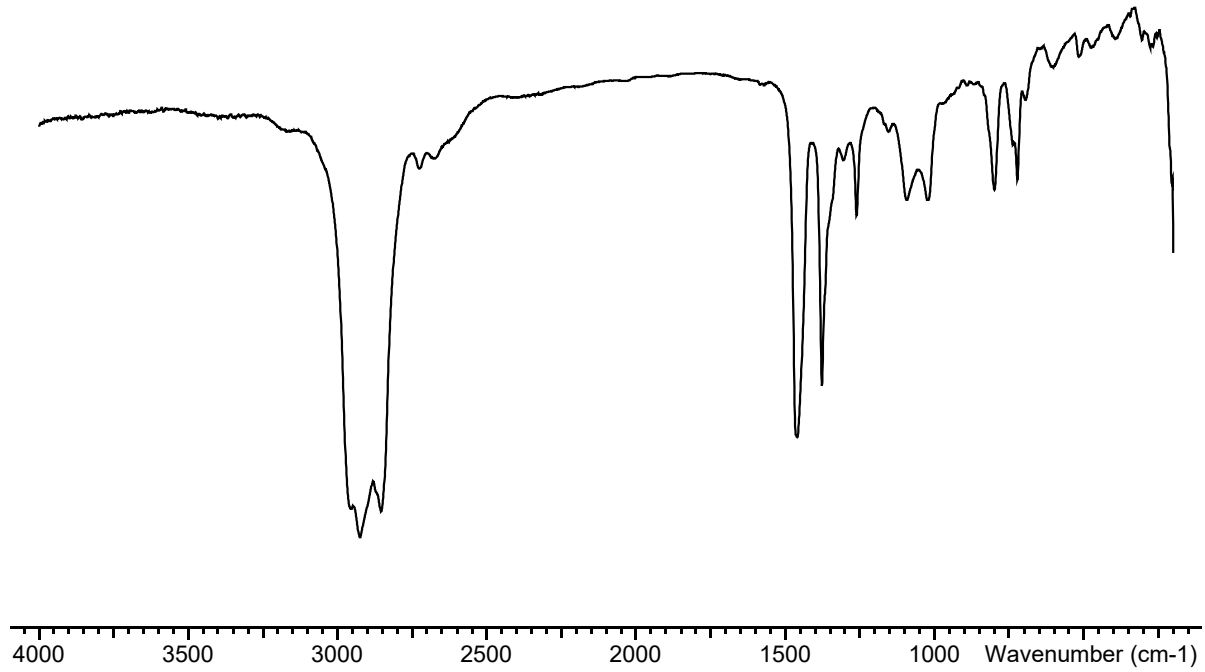


Figure S11 [GeF_4{$P(CH_2CH_2PPh_2)_3$}]

Figure S11.1.1 ^1H NMR spectrum CD_2Cl_2, 298 K.

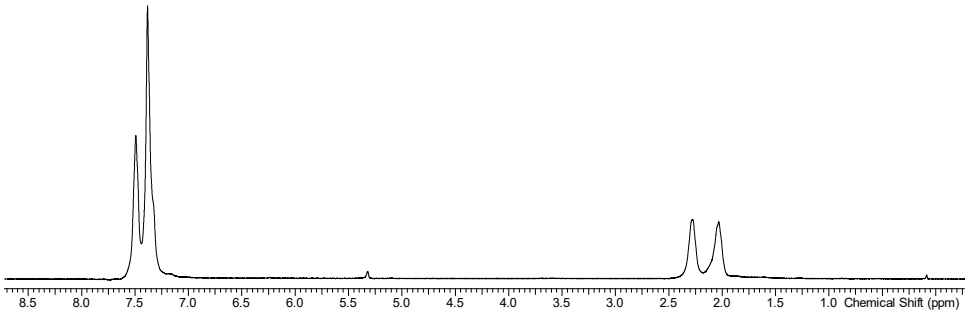


Figure S11.1.2 ^1H NMR spectrum CD_2Cl_2, 183 K; *= CH_2Cl_2

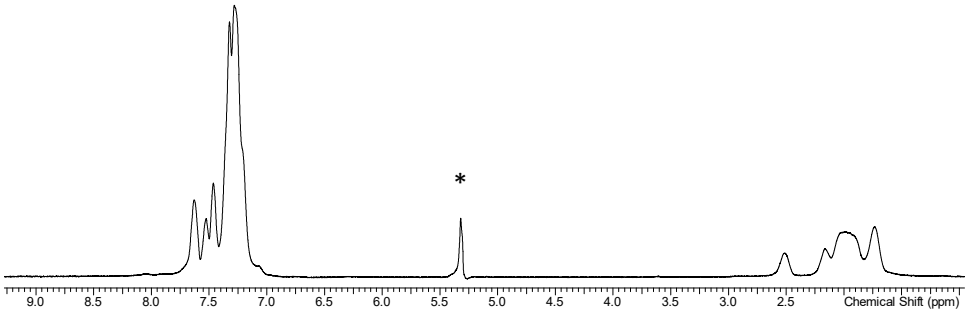


Figure S11.2.1 $^{19}F\{^1H\}$ NMR spectrum CD_2Cl_2, 298 K.

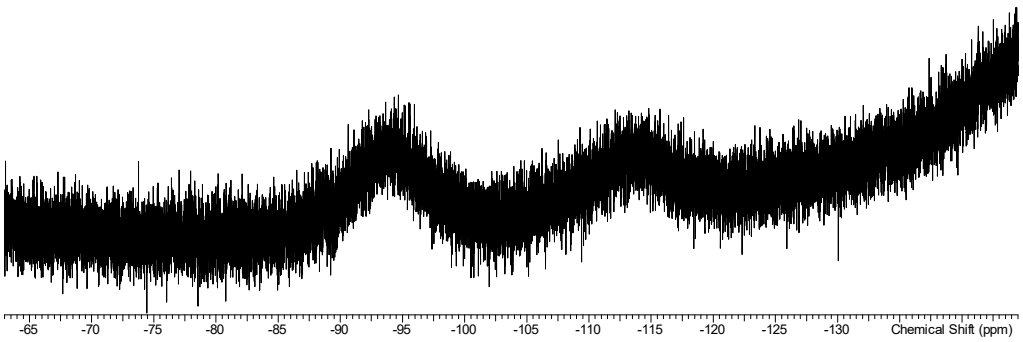


Figure S11.2.2 $^{19}F\{^{1}H\}$ NMR spectrum CD_2Cl_2, 213 K; *= $[GeF_4\{\kappa^1\text{-}P(CH_2CH_2PPh_2)_3\}_2]$, ^= unidentified impurity

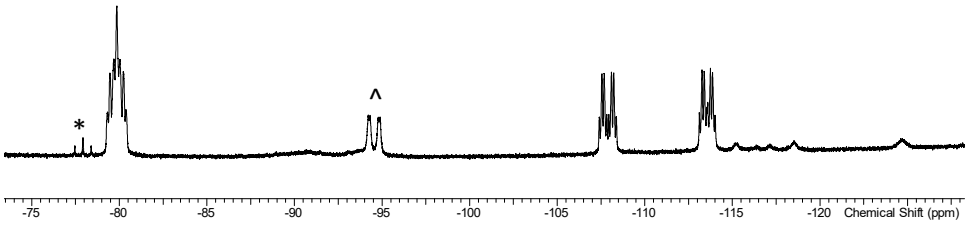


Figure S11.2.3 Expansion of the spectrum (*= $[GeF_4\{\kappa^1\text{-}P(CH_2CH_2PPh_2)_3\}_2]$)

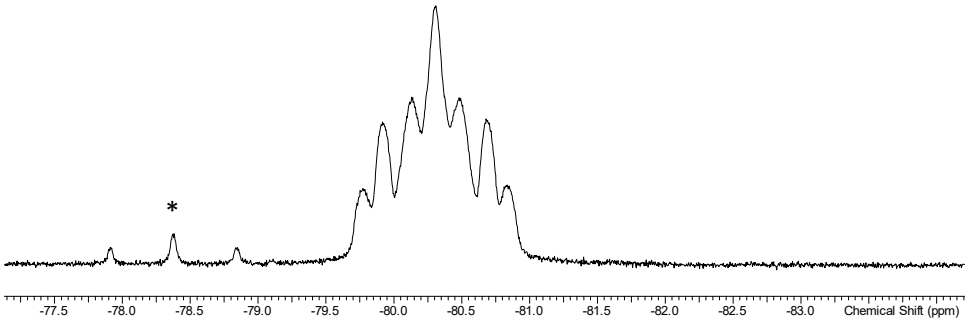


Figure S11.2.4 Expansion of the spectrum.

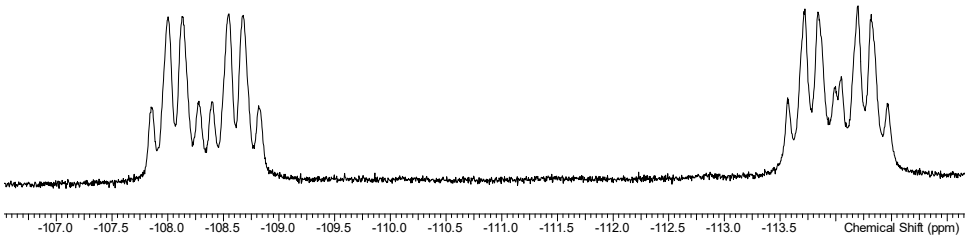


Figure S11.2.5 simulated $^{19}F\{^{1}H\}$ spectrum

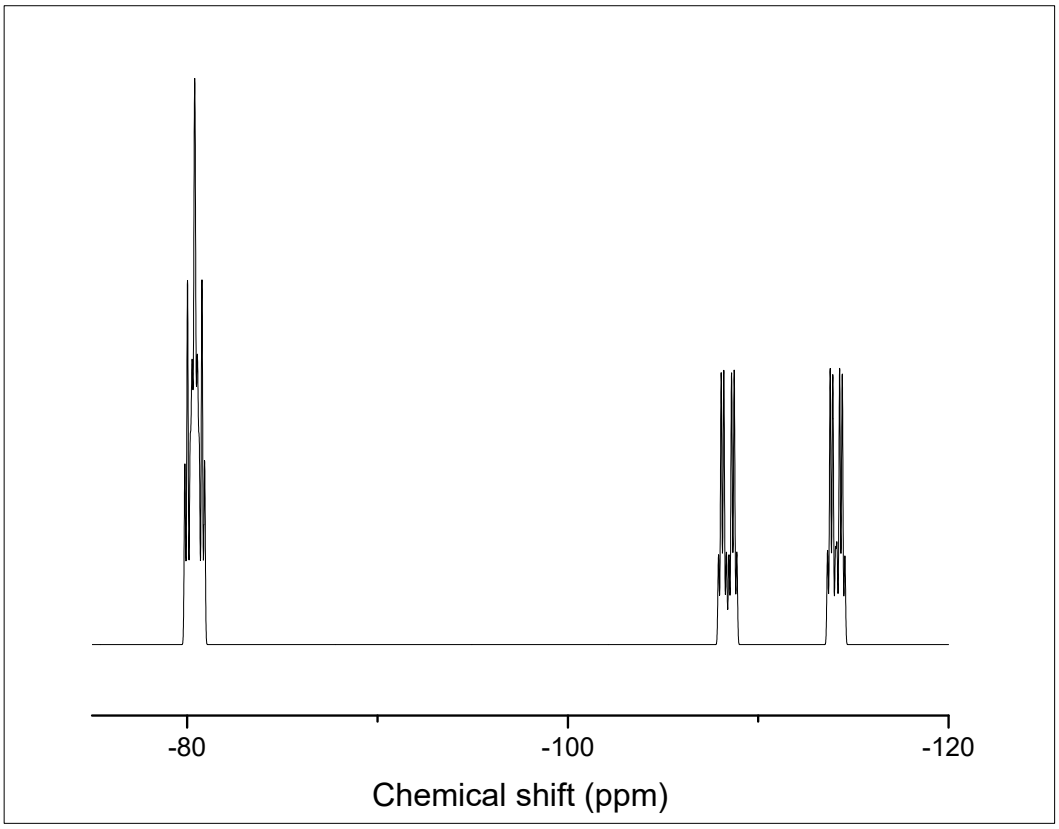


Figure S11.3.1 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 298 K.

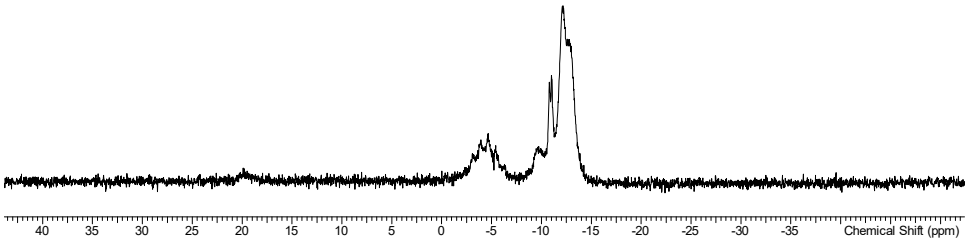


Figure S11.3.2 $^{31}P\{^{1}H\}$ NMR spectrum CD_2Cl_2, 183 K.

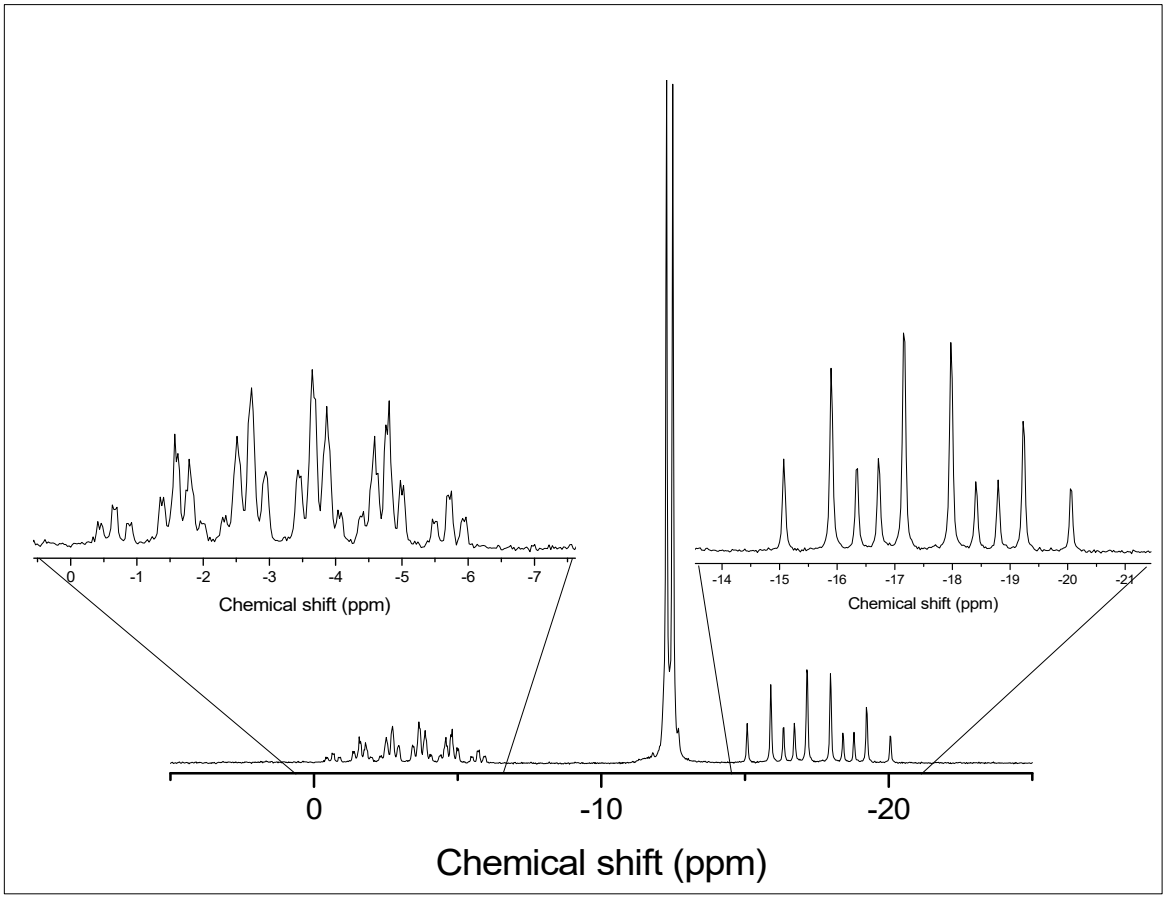


Figure S11.4 IR (Nujol/cm^{-1})

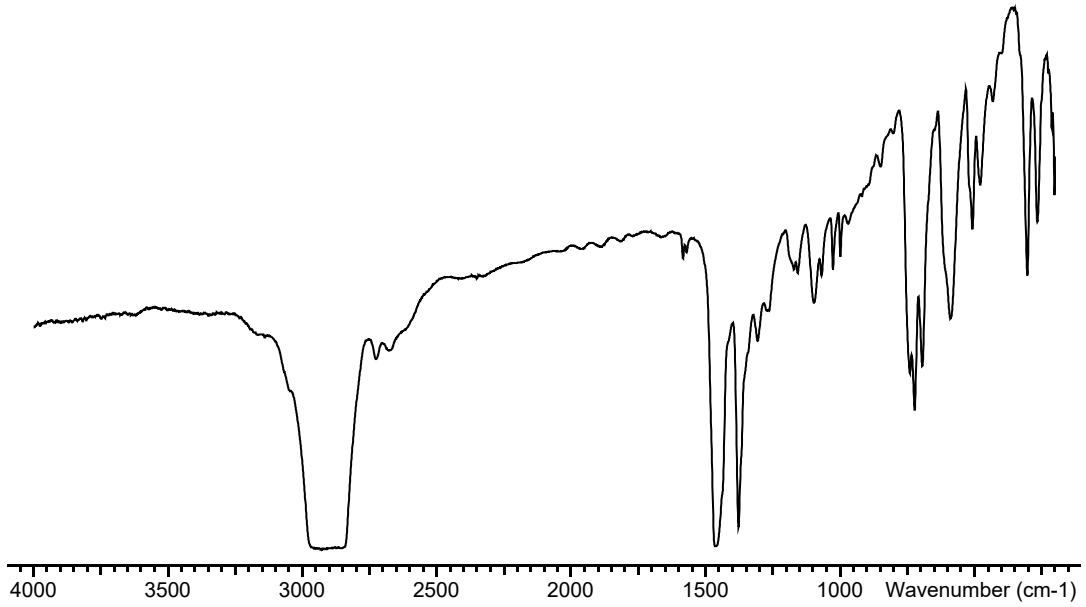


Figure S12 [GeF_3{$Ph_2P(CH_2)_2PPh_2$}(OTf)]

Figure S12.1.1 IR (Nujol/cm^{-1})

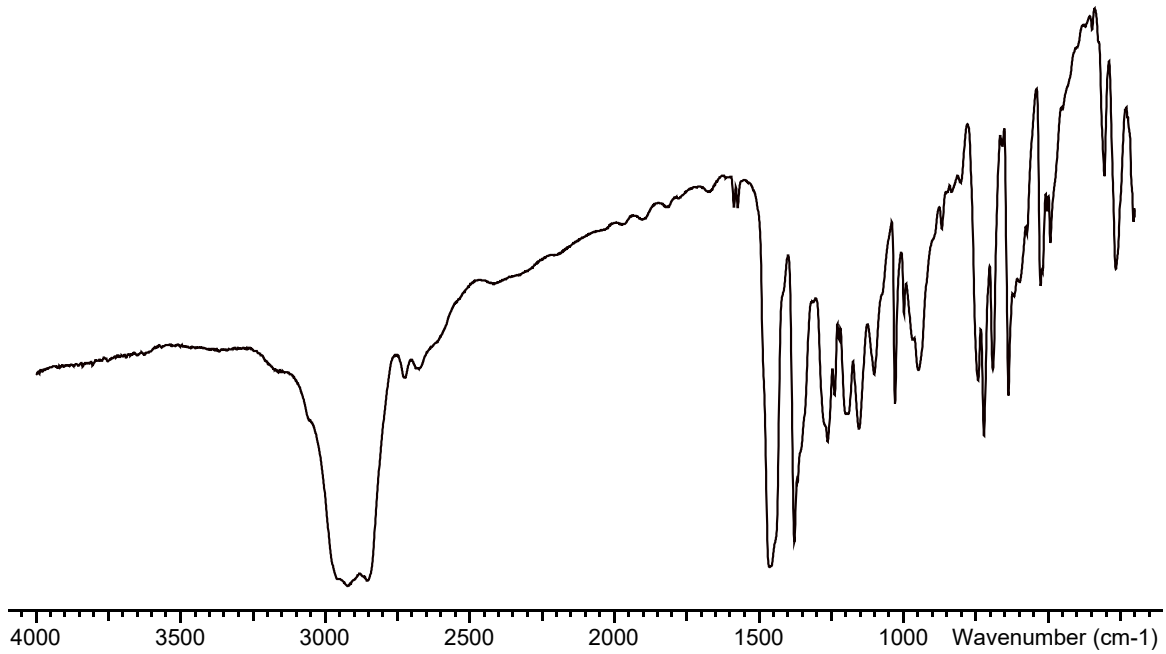


Figure S13 [$GeF_2\{Ph_2P(CH_2)_2PPh_2\}(OTf)_2$]

Figure S13.1 IR (Nujol/cm^{-1})

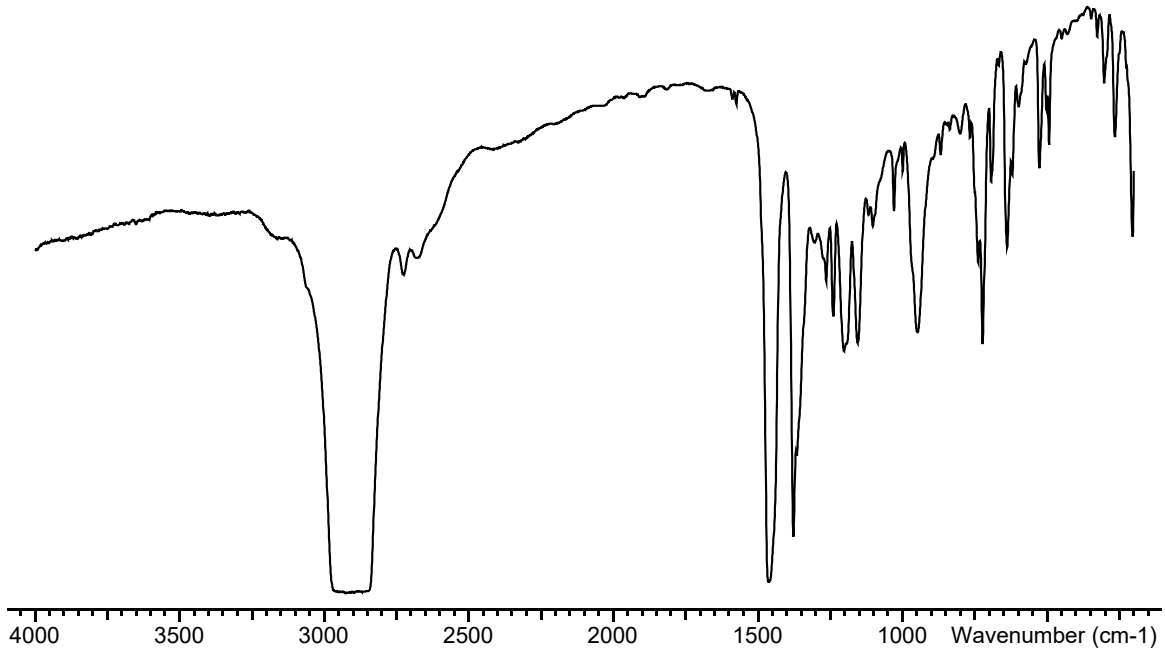


Figure S14 $GeCl_4$ + $2AsEt_3$ + 2 TMSOTf.

Figure S14.1 ^1H NMR spectrum in CD_2Cl_2 (mixture of products)