Electronic Supplementary Information

Self-assembly of $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$ metallocyclic Sn(II) hexamer stacks with CF_3-lined channel interiors

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Experimental details

Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000−200 cm^{-1}. ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{119}Sn NMR spectra were recorded from CD_2Cl_2 solutions using a Bruker AV400 spectrometer and referenced to $SiMe_4$ via the residual solvent resonance (^{1}H and ^{13}C), external $CFCl_3$ (^{19}F), 85% H_3PO_4 (^{31}P), and $SnMe_4$ (^{119}Sn), respectively. Microanalyses were undertaken at Medac Ltd. n-Hexane and n-pentane were dried by distillation from sodium and CH_2Cl_2 and MeCN from CaH_2, and all preparations were carried out under anhydrous conditions via a dry dinitrogen atmosphere and standard Schlenk and glovebox techniques. Tin(II) triflate, lead(II) triflate, $GeCl_2$(dioxane) and $OPMe_3$ were obtained from Sigma-Aldrich. $OPMe_3$ was sublimed freshly before use. Although formulated as "anhydrous", the IR spectra of the commercial $M(CF_3SO_3)_2$ (M = Sn or Pb) typically showed varying amounts of water, however, this could be removed effectively by prolonged drying *in vacuo.*

Powder X-ray diffraction (PXRD) was carried out using a Bruker AXS D2 Phaser with Cu Kα X-ray source (wavelength: 1.5406 Å). The scanning range analysed covered a 2θ range of 5 – 60 °. All scans were conducted with a step size of 0.00608° and a resolution of 0.2 seconds per step.

N_2 physisorption measurements on compound **(1)** were performed using a Micrometrics Gemini 2375 surface area and porosity analyser at liquid nitrogen temperature (77 K). Samples were degassed under a vacuum at a temperature of 80 °C overnight. Surface area measurements and isotherms were determined using the Brunauer, Emmett and Teller (BET) model.

Synthesis of $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$ (1)

$Sn(CF_3SO_3)_2$ (83 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (10 mL) before the addition of $OPMe_3$ (55 mg, 0.6 mmol) and stirred for 2 h. Particulates were removed by filtration and the solution was concentrated by 50% *in vacuo* before addition of Et_2O (5 mL) caused precipitation of a white solid. This was collected by filtration before being dried *in vacuo.* Yield: 101 mg, 73 %. Required for

$C_{11}H_{27}F_6O_9P_3S_2Sn$ (693.08): C, 19.06; H, 3.93. Found: 19.34; H, 4.14%. ^{1}H NMR (298 K, CD_2Cl_2): δ = 1.79 (d, $^2J_{PH}$ = 13.5 Hz). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2): δ = 16.8 (d, $^1J_{PC}$ = 70.4 Hz). $^{19}F\{^1H\}$ NMR (298 K, CD_2Cl_2): δ = –79.1 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = +60.0 (s), ^{119}Sn NMR (CH_2Cl_2, 298 K): δ = −783 (s). Single crystals suitable for single crystal X-ray analysis were grown by layering a CH_2Cl_2 solution with n-hexane.

Synthesis of $Ge(OPMe_3)_3(CF_3SO_3)_2$

$GeCl_2$(dioxane) (58 mg, 0.25 mmol) was dissolved in MeCN (2 mL) to which $Me_3SiCF_3SO_3$ (111 mg, 0.50 mmol) was added as a solution in MeCN (2 mL), the solution was stirred for 1 h yielding a colourless solution, the solution was concentrated to dryness *in vacuo* to yield a white solid. This solid was dissolved in MeCN (5 mL), to this $OPMe_3$ (100 mg, 0.75 mmol) was added as a solution in MeCN, the mixture was stirred for 1 h, the resulting colourless solution was concentrated *in vacuo* to yield an oily residue. This residue was dissolved in CH_2Cl_2 (2 mL) and pentane (15 mL) was added to deposit a waxy white solid which was isolated by filtration and dried in vacuo. Yield: 0.072 mg, 44 %. Required for $C_{11}H_{27}F_6GeO_9P_3S_2$ (646.97): C, 20.42; H, 4.21. Found: C, 20.74; H, 4.37, %. ^{1}H NMR (298 K, CD_2Cl_2): δ = 1.82 (d, $^2J_{PH}$ = 13.5 Hz). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2): δ = 17.2 (d, $^1J_{PC}$ = 69.0 Hz). $^{19}F\{^1H\}$ NMR (298 K, CD_2Cl_2): δ = –79.0 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = +62.1 (s).

Synthesis of $[\{Pb(OPMe_3)_3(CF_3SO_3)\}_2(\mu\text{-}CF_3SO_3)_2]$

$Pb(CF_3SO_3)_2$ (152 mg, 0.3 mmol) was partially dissolved in CH_2Cl_2 (10 mL) before addition of $OPMe_3$ (83 mg, 0.9 mmol) at which point the majority of solid was taken up in solution and was stirred for 2 h. Residual particulates were removed from the solution before it was concentrated by 75%. This was layered with *n*-hexane (5mL) and stored at -18°C for 24 h, yielding colourless crystals suitable for single crystal X-ray diffraction. The crystals were collected by filtration and dried *in vacuo*. Yield: 115 mg, 49%. Required for $C_{22}H_{54}F_{12}O_{18}P_6S_4Pb_2$ (1563.13): C, 16.90; H, 3.48. Found: C, 17.17; H, 3.63%. ^{1}H NMR (CD_2Cl_2, 298 K): δ = 1.66 (d, $^2J_{PH}$ = 13.7 Hz). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2): δ = 17.3 (d, $^1J_{PC}$ = 70 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = -79.4 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = +59.0 (s).

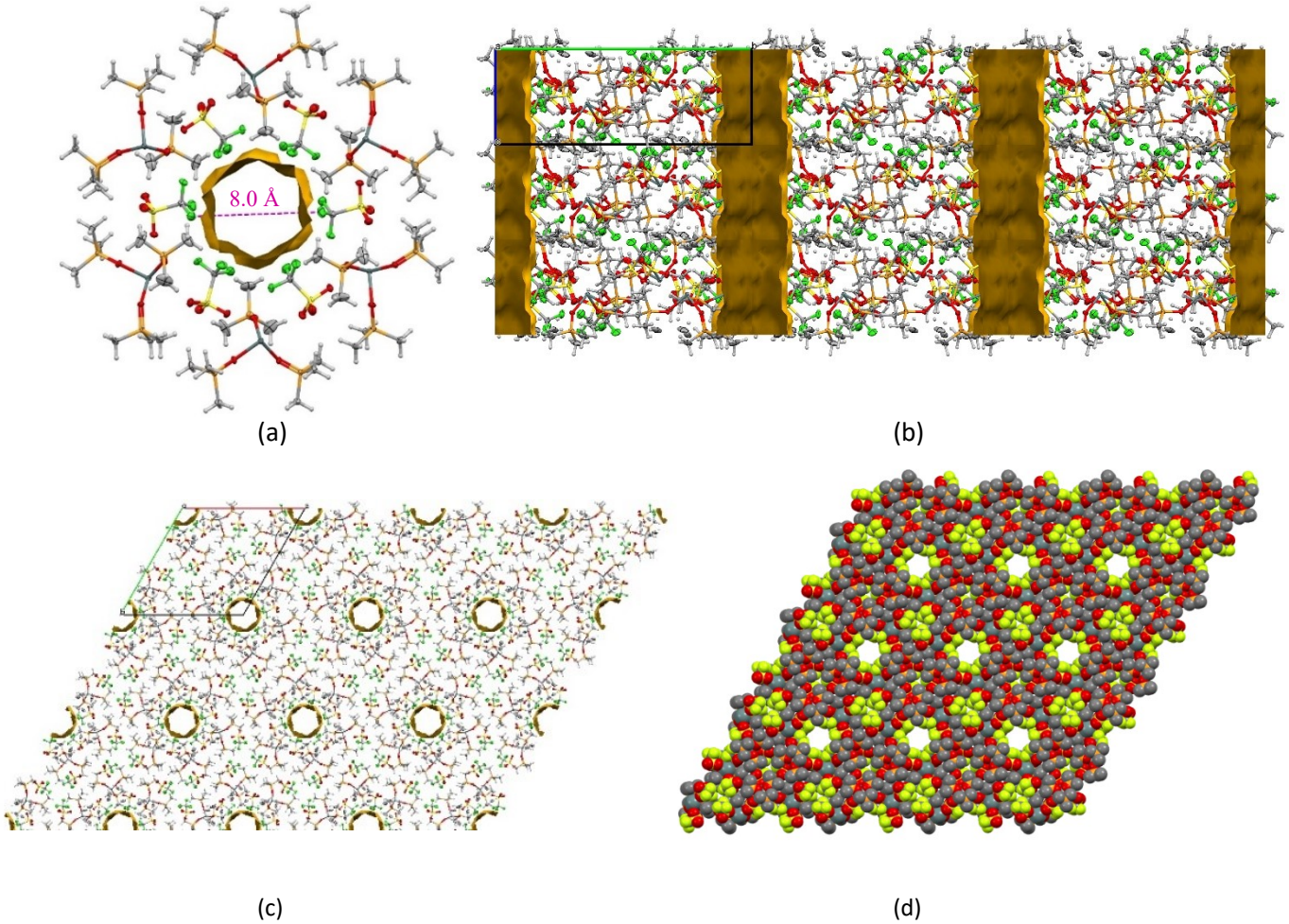


Figure S1 (a) View of a discrete $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$ hexamer showing the pore diameter; (b) view along the *a*-axis showing the hydrophobic channels (brown); (c) the extended lattice viewed down the *c*-direction; (d) space filling vesion of the lattice viewed down the c-direction.

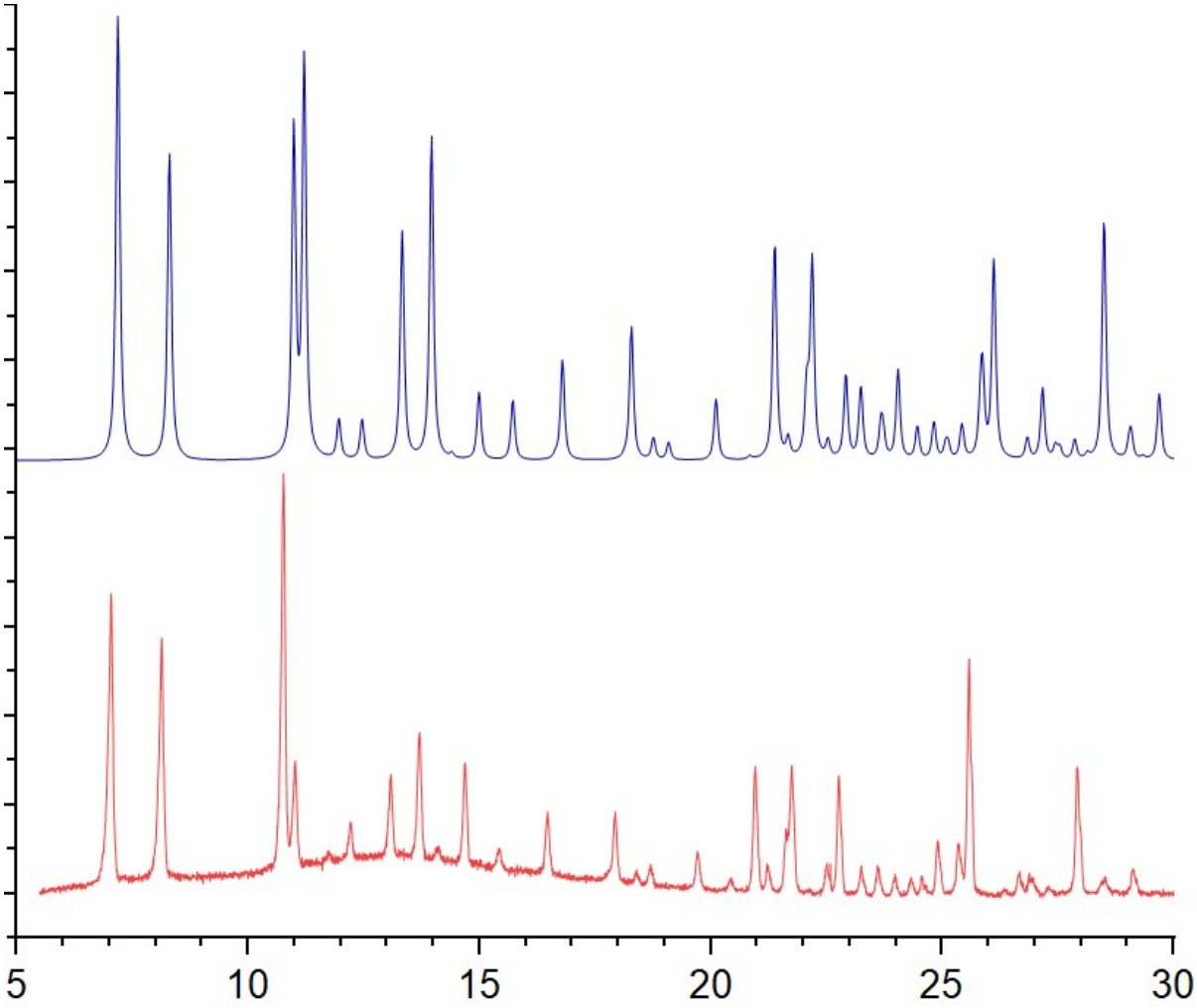


Figure S2 Top: PXRD pattern for $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$ simulated from the single crystal structure data; collected at 100 K; bottom: PXRD pattern recorded from the bulk powder isolated from the preparation of $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$ (298 K). The variations in intensity between some of the peaks suggests some preferred orientation.

X-ray Experimental

Crystals of the complexes were grown as described in the Experimental section. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K, or an Agilent Xcalibur Gemini S diffractometer with a CCD plate detector using Mo Kα (λ = 0.71073 Å) radiation with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX2013, or SHELX-2014/7 using Olex.[1-3] Details of the crystallographic parameters are given in Table S1. In the structure of $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$, some rotational disorder of the C atoms associated with the Me groups was evident. This was resolved satisfactorily by refining split C atom occupancies for these, leading to an 80%:20% split; the discussion and figures refer to the major component. Applying a solvent mask indicates one disordered C_6H_{14} molecule per hexamer unit.

Table S1 Crystallographic data[a]

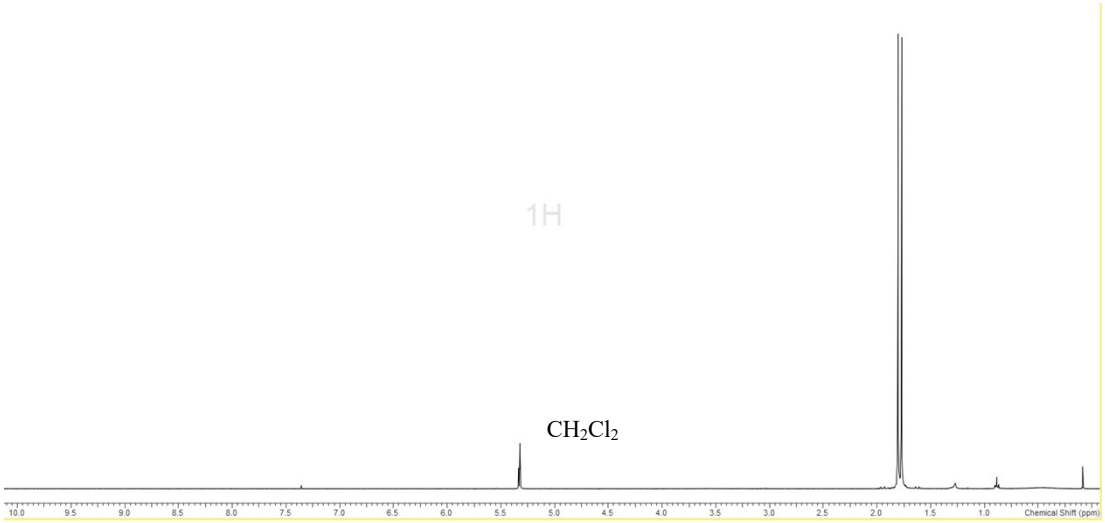
Compound	$[Sn(OPMe_3)_3(CF_3SO_3)_2]_6{\cdot}C_6H_{14}$	$[\{Pb(OPMe_3)_3(CF_3SO_3)\}_2(\mu\text{-}CF_3SO_3)_2]$
Formula	$C_{11}H_{27}F_6O_9P_3S_2Sn{\cdot}0.167C_6H_{14}$	$C_{11}H_{27}F_6O_9P_3PbS_2$
M	707.40	781.54
Crystal system	Trigonal	Monoclinic
Space group (no.)	P−3 (147)	$P2_1/c$ (14)
a /Å	24.5947(4)	9.7633(3)
b /Å	24.5947(4)	14.2131(4)
c /Å	7.88970(10)	18.8859(5)
α /°	90	90
β /°	90	98.257(2)
γ/°	120	90
U /Å^3	4133.08(14)	2593.57(13)
Z	6	4
μ(Mo-k_α) /mm^{-1}	1.330	6.931
F(000)	2126	1512
Total no. reflns	23416	30244
R_{int}	0.023	0.041
Unique reflns	6587	6662
No. of params, restraints	311, 3	298, 0
GOF	1.043	1.026
R_1, wR_2 [I > 2σ(I)][b]	0.019, 0.048	0.022, 0.043
R_1, wR_2 (all data)	0.022, 0.047	0.022, 0.045

[a] common data: wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$

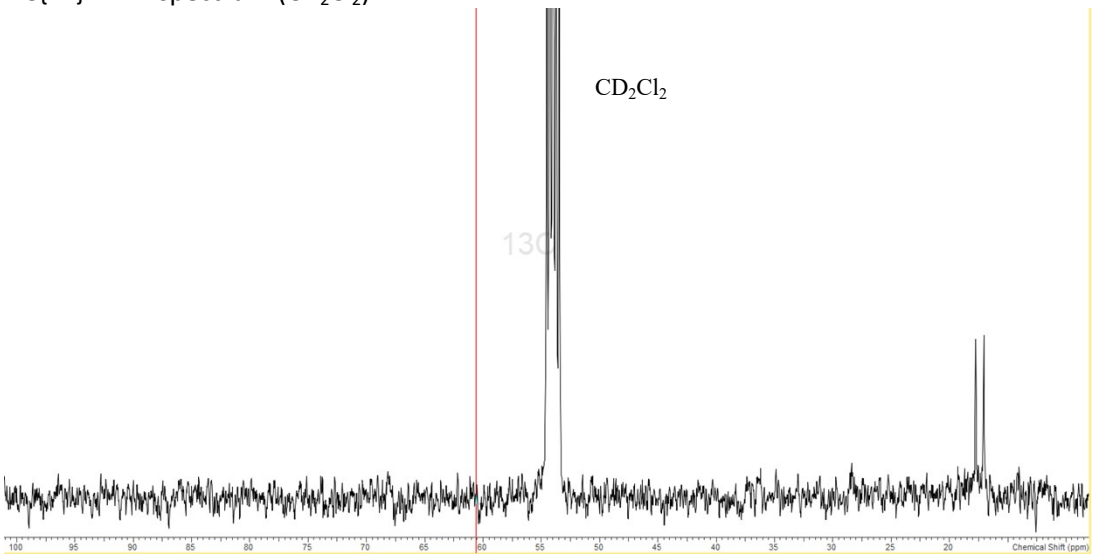
1. G. M. Sheldrick, *Acta Crystallog. Sect. C*, 2015, *71*, 3.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*., 2008, *64*, 112.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*., 2009, *42*, 339.

Figure S3: Spectroscopic data for $[Sn(OPMe_3)_3(CF_3SO_3)_2]_6$ (**1**)

^1H NMR spectrum (CD_2Cl_2)

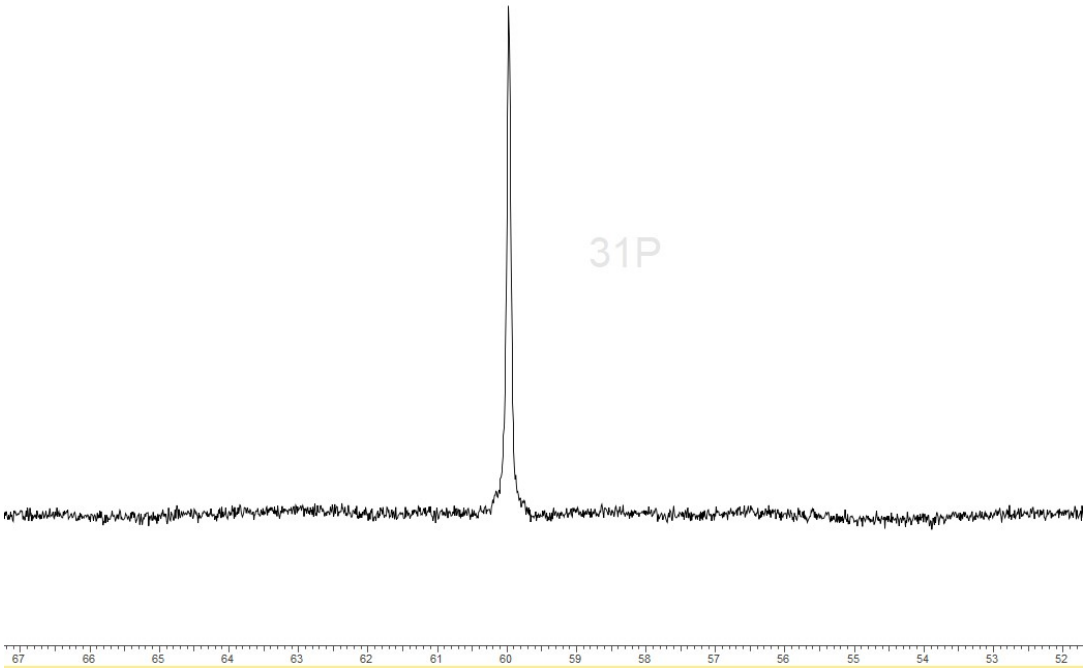


$^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2)

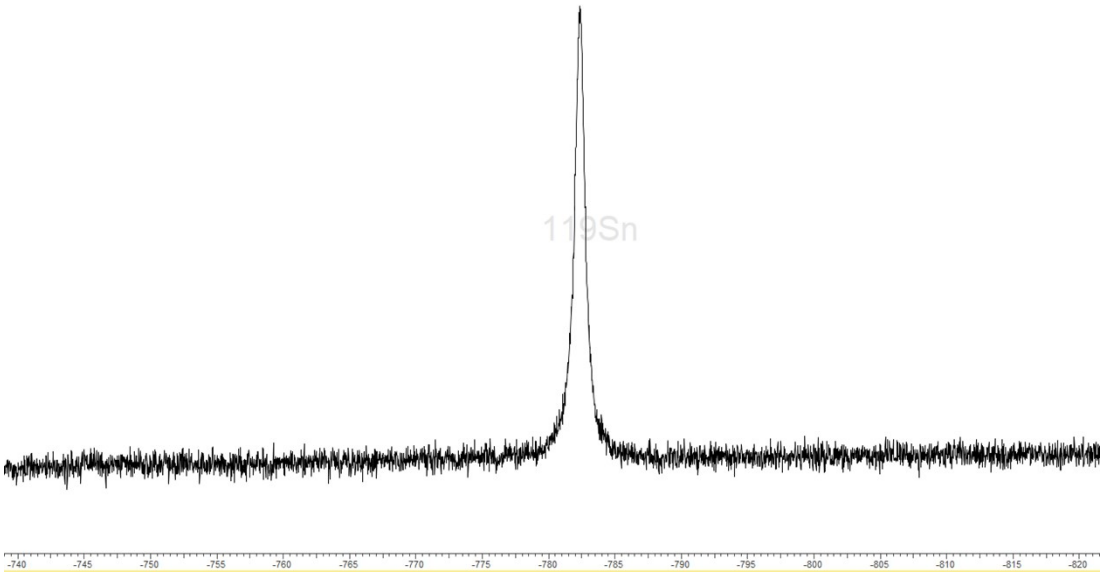


$^{19}F\{^{1}H\}$ NMR spectrum (CH_2Cl_2)

$^{31}P\{^{1}H\}$ NMR spectrum (CH_2Cl_2)



^{119}Sn NMR spectrum (CH_2Cl_2)



IR spectrum (Nujol)

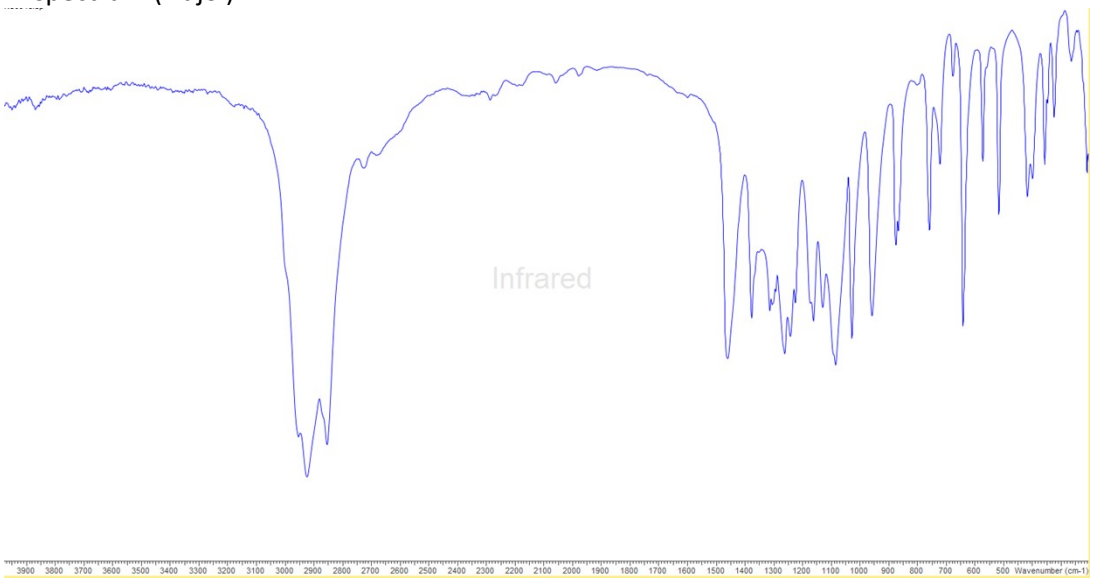
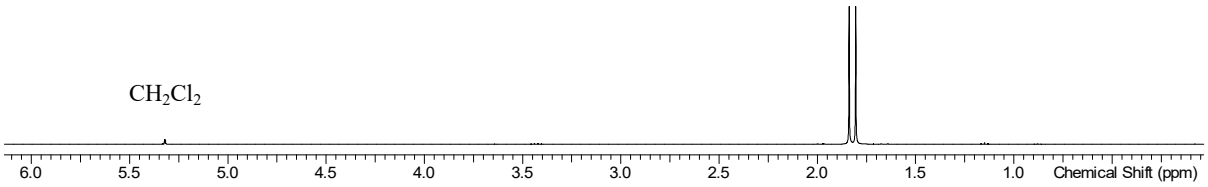
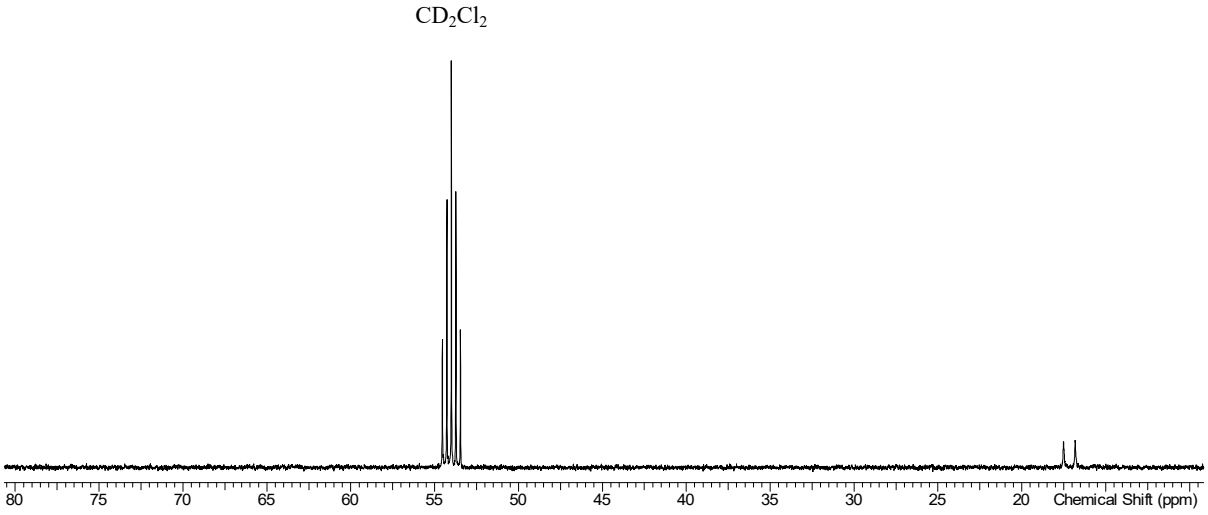


Figure S4 Spectroscopic data for $[Ge(OPMe_3)_3][OTf]_2$ (**2**)

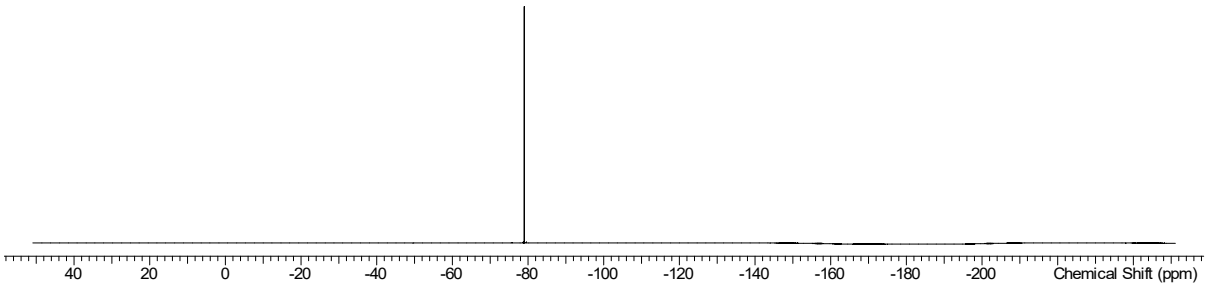
^1H NMR spectrum (CD_2Cl_2, 298 K)



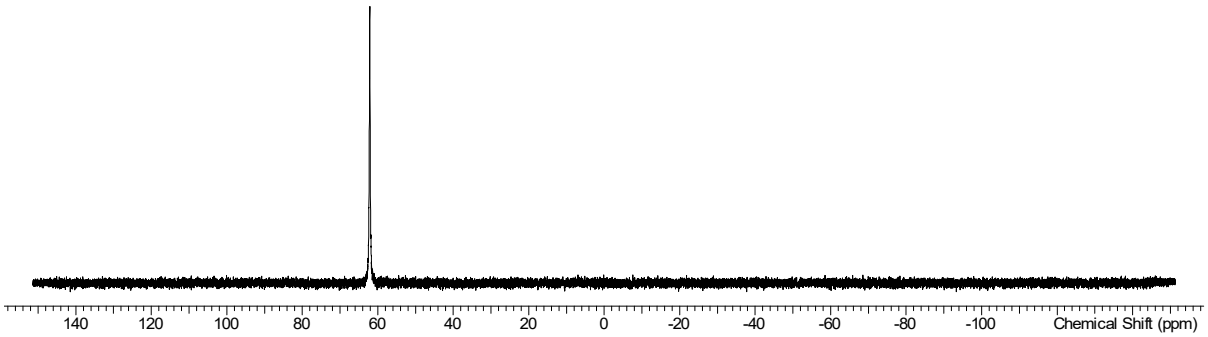
$^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 298 K)



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



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



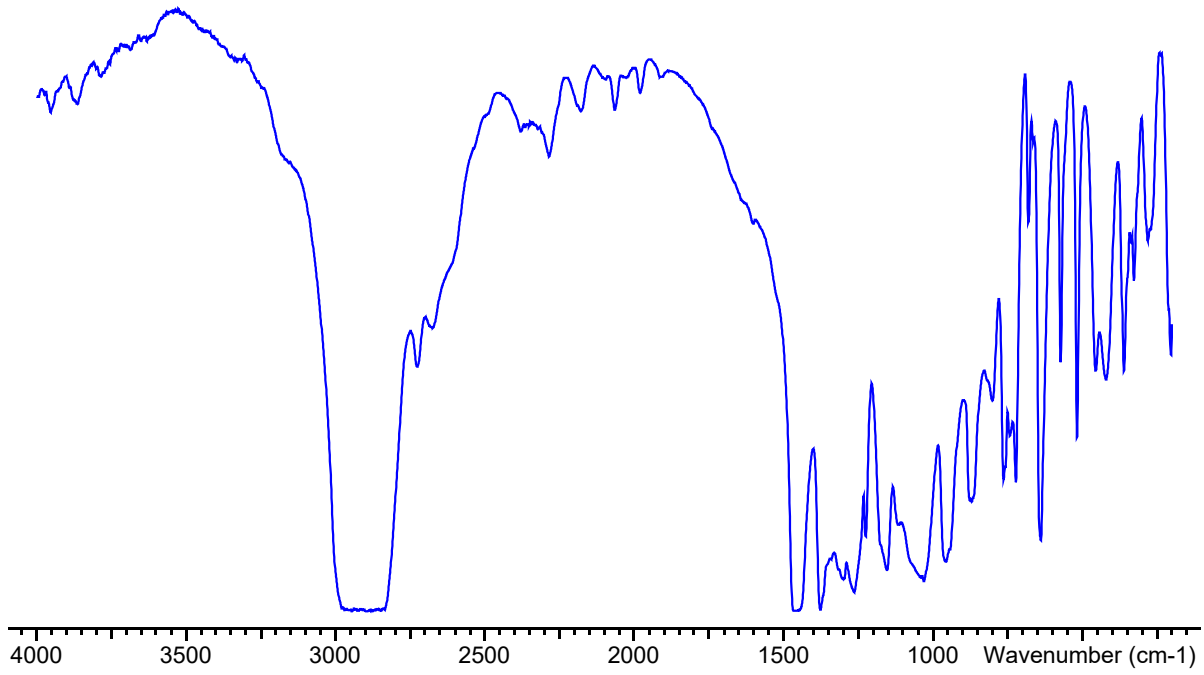
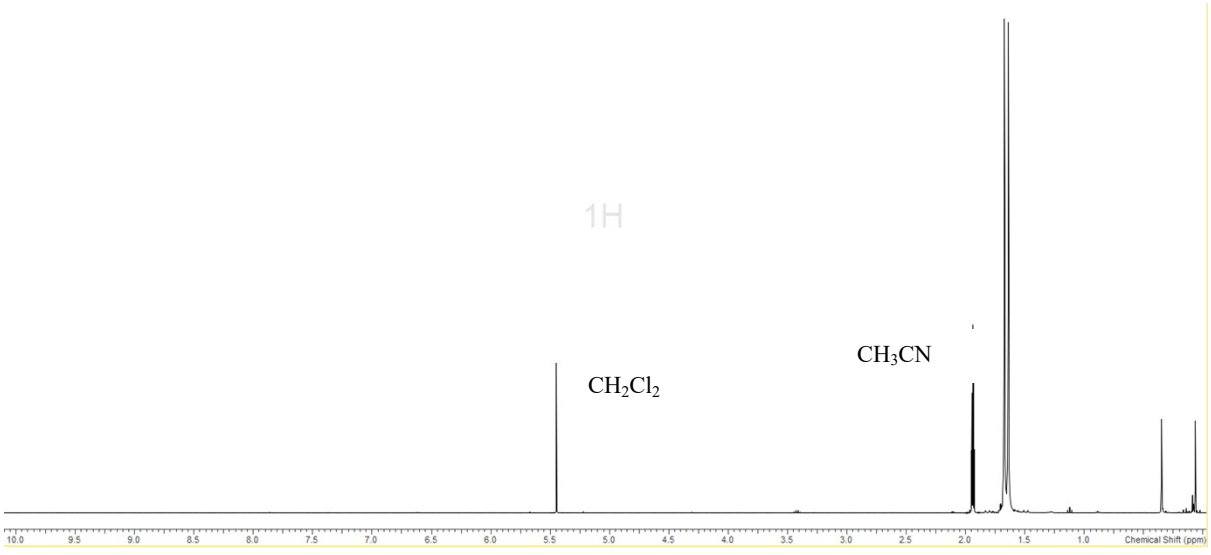
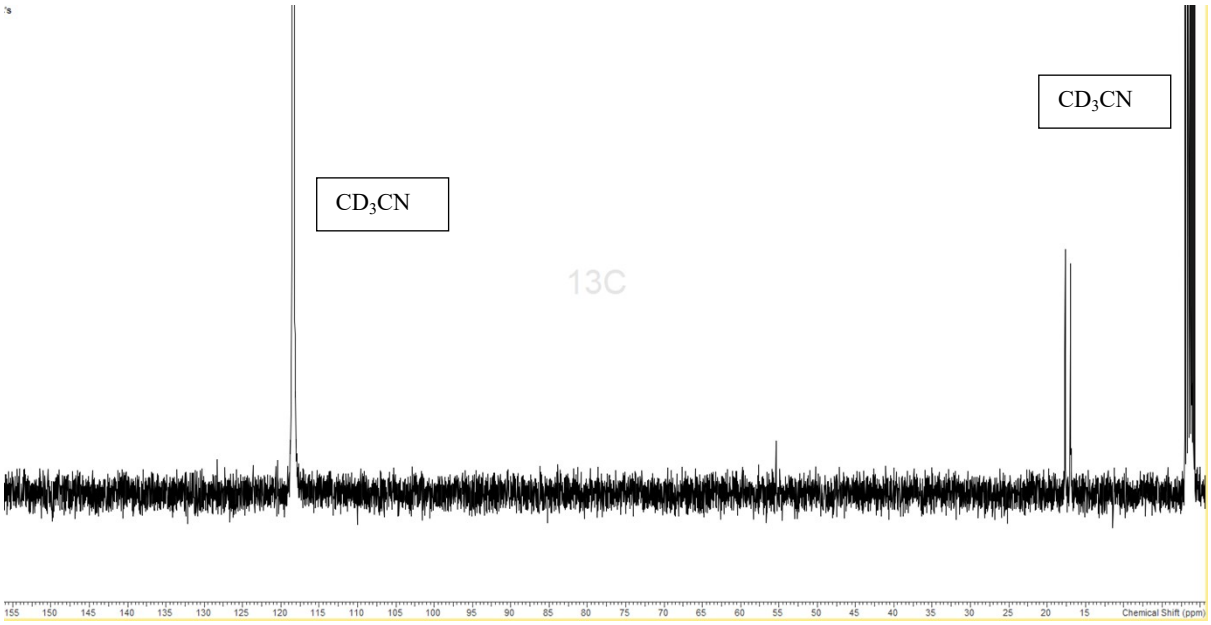


Figure S5 Spectroscopic data for [{Pb(OPMe$_3$)$_3$(CF$_3$SO$_3$)}$_2$(μ-CF$_3$SO$_3$)$_2$] (**3**)

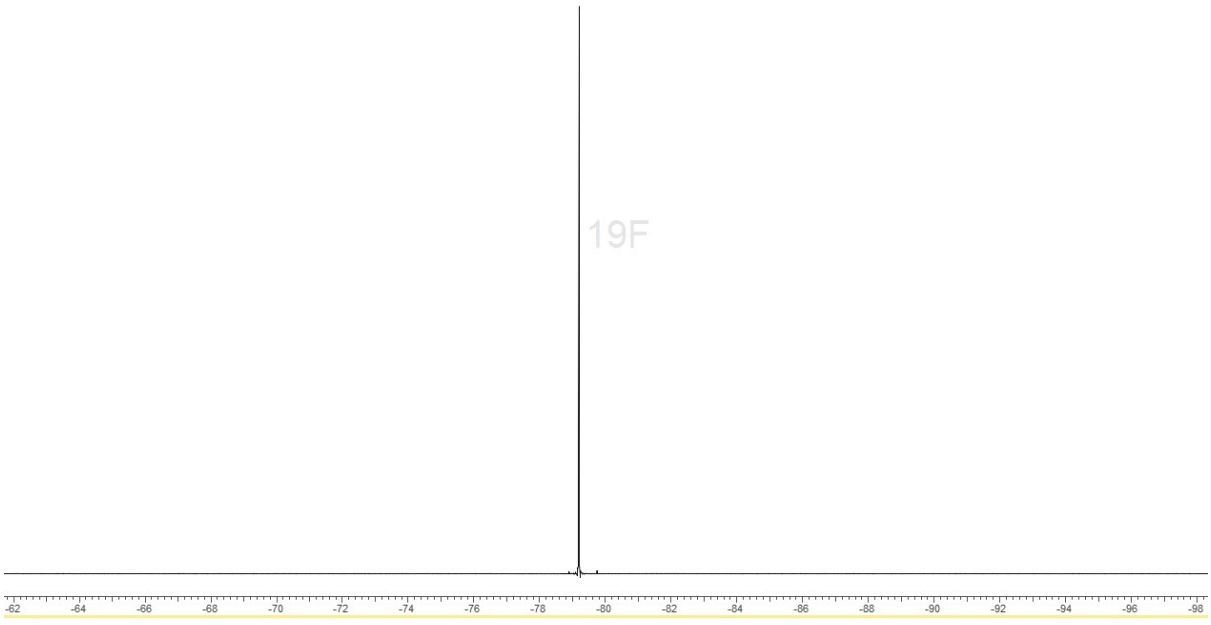
^{1}H NMR spectrum (CD$_3$CN)



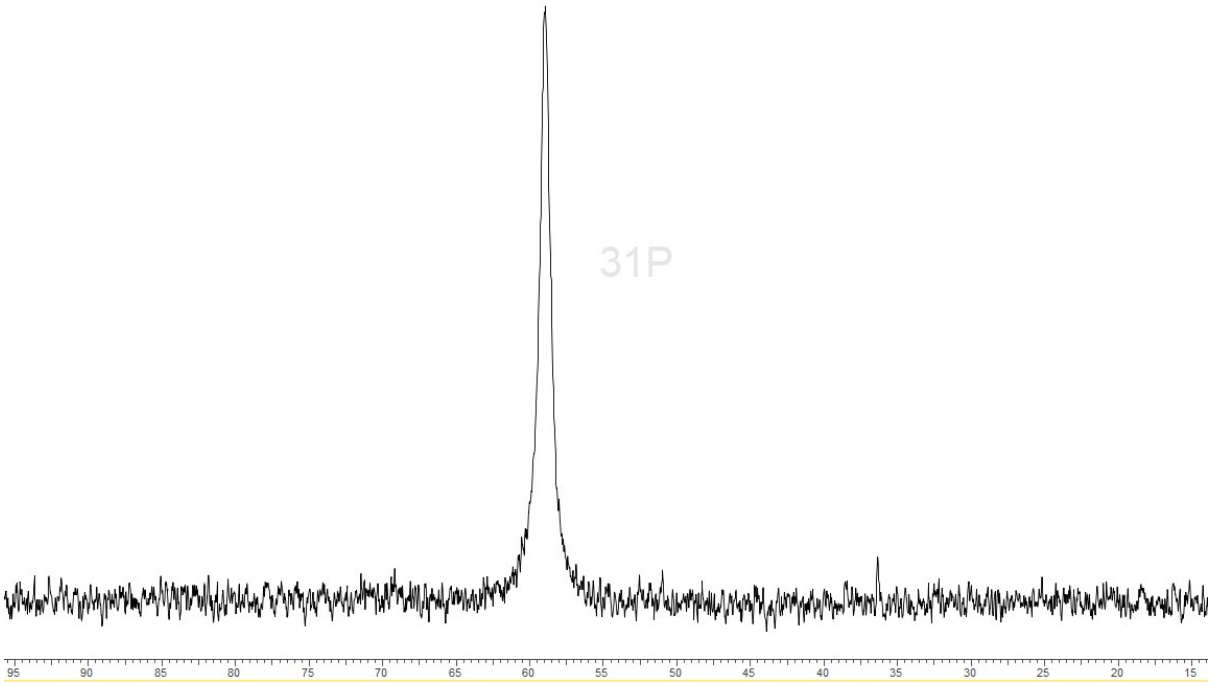
$^{13}C\{^{1}H\}$ NMR spectrum (CD_3CN)



$^{19}F\{^{1}H\}$ NMR spectrum (CD_3CN)



$^{31}P\{^{1}H\}$ NMR spectrum (CD_3CN)



IR spectrum (Nujol)