Supporting information belonging to the paper "Synthesis, structure and infrared spectra of the hexa(cyanido) complexes of silicon, germanium and tin"

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Contents

General Experimental Information

All preparative operations were conducted using Schlenk and glove box techniques under the exclusion of air and moisture using argon as a protective gas. All glassware was baked out *in vacuo* prior to use, and all transfers of liquids undertaken using sealed volumetric pipettes or stainless steel cannulas. Filtrations were performed using oven-dried filter cannulas and glass-fibre filters. All solid materials were stored and handled in an argon-filled glovebox. When required, solutions or compounds were stored in a freezer with a temperature of approximately −28°C, or in a glovebox at r.t. With the exception of acetone (which was degassed only) and methanol (MeOH, which was dried over sodium), all solvents were dried over CaH_2 and then trap-to-trap condensed and degassed before use. ECl_4 (E = Si, Aldrich, 99%; Ge, Alfa Aesar, 99.9999% metals basis; Sn, Aldrich 99%) were dried over Na_2CO_3, then trap-to-trap condensed and stored in the same fashion as the solvents described above. Deutero-solvents were dried over Na_2CO_3, trap-to-trap condensed and stored in ampoules under argon in a similar fashion to the protio-solvents, with the exception to this is dmso-d_6, which was used as received (VWR, 99.80% D, <0.02% water). Trimethylsilyl cyanide was purchased from Fluorochem (98%), re-condensed into an ampoule and stored under inert atmospheres in the dark. Pyridine (Aldrich anhydrous 98%) was dried over Na_2CO_3 and re-condensed and stored under inert atmosphere in an ampoule. SnF_4 (Alfa Aesar, 99% metals basis) was dried under high vacuum at 110°C overnight and stored in a glovebox. KCN was purchased from Sigma Aldrich and dried prior to use. AgCN (Acros Organics, 99%) was dried under high vacuum at 110°C for *ca.* 3 h prior to use. PPN(Cl) was prepared by the procedure published in ref. 17**.** All solvents were stored in sealed ampoules. Paraffin oil for

IR spectroscopy and crystal mounting purposes was stored in an argon-filled glovebox over sodium.

Both $Sn(CN)_4(L)_2$ (L = MeCN, py (py =pyridine)) complexes are extremely air sensitive and must be prepared under strict exclusion of air. All IR samples were prepared in a glovebox. Solid samples were stable for brief periods of time under paraffin oil, which, for transmission IR spectroscopy purpose, acts as a mulling agent and also as a protective layer between analyte and atmosphere. Exposure of either solid to laboratory air results in a very fast colour change from white to yellow, and the release of gas, the odour of which is consistent with properties known of HCN and MeCN or py, respectively. We ascribe this observation to the formation of HCN upon hydrolysis of the material with the moisture present in air. NMR spectra of $Sn(CN)_4(py)_2$ in dmso-d_6 are affected by this extreme air sensitivity. Neither mass spectrometry nor elemental analyses returned valid data. All attempts at crystallisation were unsuccessful. The formation of $(PPN)_2Sn(CN)_6$ upon reaction of $Sn(CN)_4(MeCN)_2$ with (PPN)CN is regarded as indirect proof of the identity of the compound that is tentatively assigned to the formula $Sn(CN)_4(py)_2$.

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer run by OPUS software, with a resolution of 2 cm^{-1} and 8 scans per sample at room temperature as thin films between NaCl windows (solids) or as solutions in an air tight cell equipped with CaF_2 windows. With the exception of the cyano group CN stretches, only the most significant bands of the analyte are reported (NB: bands of mulling agent are centred at 2955, 2924, 2871, 2855, 1462, 1377, 1366, 1303(w), 1157(w), 723 cm^{-1}). Samples of solids were prepared as mulls in an argon filled glovebox, using paraffin oil stored over sodium. The spectra were recorded against the background of the clean and dry windows and are baseline-corrected. Once prepared, the sample was immediately transferred to the spectrometer for analysis. Spectra of solutions were recorded in dry, degassed MeCN under standard Schlenk conditions against a background of MeCN. Baseline correction was not applied to these spectra. Approximate concentrations for each analyte are reported in the caption under each spectrum.

NMR spectra were recorded on either Bruker Avance III HD 400 or Bruker Av I 400 spectrometers at room temperature ($\nu_0(^1H)$ = 400 MHz, $\nu_0(^{13}C)$ = 100 MHz, $\nu_0(^{19}F)$ = 377 MHz). ^1H and ^{13}C spectra are calibrated against the residual solvent signals (^1H; 1.94 ppm (MeCN-d_3) and 2.50 ppm (dmso-d_6)) or the solvent (^{13}C; 1.32 ppm or 118.26 ppm (MeCN-d_3) and 39.52 ppm dmso-d_6).[1] ^{31}P chemical shifts are externally calibrated using the resonance frequency of the solvent deuterium signal. Solid-state ^{29}Si and ^{13}C spectra were recorded using a Bruker AVANCE III HD spectrometer operating at 500.13 MHz ($\nu(^{13}C)$ = 125.76 MHz), equipped with a 4 mm HX broadband MAS probe on samples contained within a restricted rotor. All data was processed using TopSpin 3.2. Samples were either prepared in a glovebox or, in the case of samples in dmso-d_6, under inert atmosphere using standard Schlenk tube techniques. Magic-Angle Spinning (MAS) NMR spectroscopy was performed on a sample of $(PPN)_2[Sn(CN)_6]$ in a standard rotor. The sample was only exposed to air in order to pack the rotor and remained under an argon atmosphere at other times. The ^{119}Sn pulse was calibrated using a solid sample of $SnCl_2$ (99% purity, used as received from Sigma-

Aldrich). The ^{119}Sn NMR spectrum of the complex was acquired by 29,200 scans. All spectra were acquired at r.t. All spectra are uncalibrated and referenced externally.

ESI-TOF mass spectra were recorded with samples infused directly into a Micromass LCT spectrometer. Accurate mass spectra (for compound **1**) were obtained with an Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS instrument, with the sample introduced by loop injection at an approximate flow rate of 20 μL min^{-1}. Solid samples were prepared and introduced in a solution of 3 : 1 MeCN / H_2O.

C, H, N contents were determined by a Vario MICRO cube CHN/S analyser or by performing Schöniger's analysis (Cl). Care was taken to ensure that each sample was only exposed to air for a minimal duration of time before combustion. Melting points were determined in capillaries that were permanently sealed under argon. Samples were investigated using a Gallenkamp MFB595010M melting point apparatus and are uncorrected.

Single crystal X-ray diffraction studies were performed on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector cooled to −15 °C and a CuK_α microfocus X-ray source, or a Bruker SMART APEX-II diffractometer equipped with a CCD detector cooled to −50 °C using MoK_α radiation from a sealed-tube X-ray source. The mounted crystals were cooled by cryogenic nitrogen gas streams set to the reported data collection temperatures (100, 130 or 296 K). Crystals for diffraction studies were selected, placed on a glass slide in a glovebox and protected under paraffin oil before mounting on a MiTiGen microloop. Alternatively, single crystals were selected from the content of a Schlenk tube under a stream of argon and immersed straight away in paraffin oil on a glass slide before mounting. X-ray data was processed using shelxtl and Olex2-1.2 and visualised using Mercury 3.7 and Ortep3 (version 2014.1).[2-4,8] Data was corrected for absorption using empirical methods (SADABS) based on symmetry equivalent reflections combined with measurements at different azimuthal angles.[5,6] The crystal structures were solved and refined against F^2 values using shelxt for solution and shelxl for refinement accessed *via* the Olex2 or shelxtl programmes.[2,3,7,8] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with idealized geometries and then refined by employing a riding model and isotropic displacement parameters. The disorder in the solvent molecule of compound **3c** has not been modelled. All crystallographic datasets reported here have been deposited in the Cambridge Crystallographic Database (CCDC), deposition numbers 1820362 (compound **2**), 1820360 (compound **3a**), 1820145 (compound **4a**) and 1856451 (compound **3c**).

Preparative procedures and analytical data

Synthesis of PPN(CN)

It is essential for this synthesis that the solvents acetone, MeOH and diethyl ether (Et_2O) are degassed prior to use in order to prevent the oxidation of cyanide to cyanate. The preparative procedure was adapted from a method published by Martinsen *et al.*[16] MeOH (20 mL) was added to a Schlenk tube containing freshly prepared (PPN)Cl (12.137 g, 21.14 mmol) giving

a suspension. The, tube containing the suspension, was warmed by immersion in a water bath until all (PPN)Cl had dissolved. In a separate Schlenk tube, KCN (1.767 g, 27.13 mmol) was placed under vacuum for 5 mins and then suspended in MeOH. The tube was also immersed in a warm water bath (for 5 mins). The solution of (PPN)Cl was then transferred into the suspension of KCN, resulting in the immediate formation of a finely divided precipitate. After stirring this suspension at r.t. for 10 mins, the reaction vessel was cooled in an ice bath for 1 h to ensure the complete precipitation of KCl. Meanwhile, a fresh suspension of KCN (0.686 g, 10.53 mmol, placed under vacuum for 5 minutes before use) in MeOH was prepared in a separate Schlenk tube, and placed in a warm water bath for 5 mins. The supernatant solution from the previous step was then transferred by filtration onto this fresh KCN-MeOH suspension. The Schlenk tube containing the new reaction mixture was immersed in a warm water bath and kept at 50 °C for 10 min with stirring and then cooled in ice for 1 h. The resultant supernatant solution was collected by filtration and the filter residue containing KCl and excess KCN was discarded. All solvent was evaporated from the filtrate under vacuum. Acetone (30 mL) was added to the evaporation residue and the resultant suspension stirred for 5 min. A small amount of undissolved white solid remaining was filtered off and the filtrate treated with 50 mL Et_2O which resulted in the precipitation of a white solid. Crystallisation was completed at −28 ºC for approximately 17 h to afford a white, crystalline solid, which was collected by filtration and then dried at 55 °C under vacuum for 3 h. Treatment of the supernatant solution with a further portion of Et_2O (30 mL) and cooling as described above resulted in a second crop of white solid, which was dried as described above. Combined yield of (PPN)CN (6.164 g, 62%) as a white solid. Analytical data for crop 1: m.p. 231-232 ºC (lit. 212-214 ºC), anal. calcd. for $C_{37}H_{30}N_2P_2$ (546.60 g mol^{-1}): C, 78.71 H 5.35, N 4.96 %. Found: C, 77.73; H, 5.36; N, 4.84 %. IR (nujol) $\overline{\nu}$ / cm^{-1} = 3171, 3146, 3052, 2802, 2218, 2060, 2056, 2044, 1980, 1921, 1902, 1825, 1777, 1677, 1614, 1587, 1576, 1482, 1444, 1434, 1325(br), 1285, 1265, 1180, 1171, 1160, 1114, 1102, 1076, 1040, 1026, 997, 978, 928, 860, 848, 800, 765, 748, 692, 664, 616, 550, 536. IR (solution, MeCN) $\overline{\nu}$ / cm^{-1} = 2098, 2058. ^{1}H NMR (MeCN-d_3, r.t.) δ / ppm = 7.89-7.01 (m, PPN). ^{13}C NMR (MeCN-d_3, r.t.) δ / ppm = 166.46 (s, *C*N), 134.61 (s, PPN), 133.26 (m, PPN), 130.36 (d, PPN), 128.20 (d, PPN).

Attempted direct synthesis of $(PPN)_2[Ge(CN)_6]$ (**2**)

(PPN)CN (3.368 g, 5.97 mmol, 6.8 eqs.) was dissolved in MeCN (15 mL). The addition of $GeCl_4$ (ρ = 1.88 g cm^{-3}, 0.10 mL, 0.88 mmol, 1 eq.) resulted in the almost instantaneous precipitation of a white solid. The reaction mixture was stirred at r.t. for 17 h, after which time the amount of precipitate had increased. The precipitate was collected by filtration and dried under vacuum to give 0.692 g of a white solid, which was then suspended in a fresh solution of (**1**) (2.466 g, 4.37 mmol, 5.0 eqs) in MeCN (10 mL). The Schlenk tube containing the stirred suspension was immersed into an oil bath set to 60°C. Dissolution of all solids occurred after a few minutes of heating. After approximately 68 h, the Schlenk tube was allowed to cool to −20 C, upon which colourless crystals formed under a pale-orange supernatant solution. The supernatant solution was removed by filtration and the solid filter residue was dried under vacuum to afford approximately 1.86 g of a white solid. Recrystallisation from a warm saturated MeCN solution (20 mL) upon slowly cooling to

−28 °C in an insulated flask using isopropanol as immersion liquid. This produced colourless block-shaped crystals. The procedure was repeated with a further 1.647 g of (PPN)CN (2.92 mmol, 2.05 eqs w.r.t. mass of the intermediate) and heated for 96 h. This procedure finally afforded 0.845 g of large block-shaped crystals; the anal. found C, 74.87; H, 5.48; N, 5.94 ; Cl, 2.95%; fits best to $(PPN)Ge_{0.07}(CN)_{0.74}Cl_{0.52}(MeCN)_{0.89}$ C, 74.91; H, 5.33; N, 5.98; Cl, 2.98%. IR (nujol, cm^{-1}) $\overline{\nu}$ / cm^{-1} = 3175, 3157, 3146, 3077, 3064, 3055, 3037, 3023, 3013, 2992, 2799, 2293, 2248, 2215(br), 2161, 2155, 2053, [1977, 1922, 1906, 1827, 1779, 1687, 1616] (all br),1588, 1574, 1481, 1457, 1437, 1435, 1261, 1184, 1164, 1113, 1055, 1027, 998, 938, 850, 797, 759, 748, 690, 664, 616, 550, 530. ^{1}H NMR (MeCN-d_3, r.t.) δ / ppm = 7.69-7.64 (m), 7.61-7.55 (m), 7.50-7.45 (m). ^{13}C NMR (MeCN-d_3, rt) δ / ppm= 141.69 (s, CN), 140.15 (s, CN), 134.54 (s, PPN), 133.17 (m, PPN), 130.30 (m, PPN), 128.15 (dd, PPN).

Reaction of $(PPN)_2Ge(CN)_xCl_y$ with AgCN (compound **3c**)

A suspension of $(PPN)_2Ge(CN)_xCl_y$ (*ca*. 0.633g, 0.48 mmol for x = 5 and y = 1, 1 eq.) and AgCN (0.574 g, 4.29 mmol, 4.89 eqs.) in 20 mL MeCN was heated in an oil bath set to 65 °C for ca. 10 h, resulting in the white suspension becoming more finely divided. The colourless supernatant solution was isolated by filtration and the white filter residue (0.501 g) discarded. The volume of the filtrate was diminished *in vacuo* until precipitation occurred, at a solvent volume of *ca*. 5 mL. The white precipitate was re-dissolved by gentle warming in hot air and then cooled in a freezer. This resulted in a crop of colourless block crystals, which were isolated from the colourless supernatant solution by filtration. This afforded 0.448 g of $PPN_2Ag(CN)_2$·MeCN as colourless crystals. IR (nujol, cm^{-1}) $\overline{\nu}$ / cm^{-1} = 3058, 2326, 2291, 2250, 2217, 2170, 2159, 2149, 2135, 2052, 1986, 1913(br), 1824(br), 1779, 1680(br), 1617(br), 1588, 1574, 1482, 1434, 1315, 1297, 1282, 1248, 1179,1 163, 1115, 1100, 1074, 1070, 1026, 997, 977, 933, 917, 846, 840, 805, 797, 761, 750, 745, 690, 667, 616, 553, 550, 533.

Reaction of $SnCl_4$ with (PPN)CN

A solution of PPN(CN) (3.488 g, 6.17 mmol, 7.01 eq.s) was dissolved in MeCN (15 mL). $SnCl_4$ (0.1 mL, 0.88 mmol, 1 eq.) was added, and the resultant stirred solution heated in an oil bath set to 60 °C. After 133 h, the colour of the reaction solution had darkened to a pale-brown, the volume of the solvent was diminished *in vacuo* until the onset of precipitation. The tube was then gently warmed in hot air until all precipitate had dissolved, and then cooled in a freezer. This resulted in a mass of 0.706 g of colourless rectangular crystals under a pale-brown supernatant solution, which were collected by filtration. A sample of these crystals were recrystallized by the slow cooling of a saturated MeCN solution. These crystals were shown to be a mixture of $(PPN)_2[Sn(CN)_6]$ and $(PPN)_2[Sn(CN)_5Cl]$ with the effective rational formula $(PPN)_2Sn(CN)_{5.55}Cl_{0.45}$. Anal. calcd for $C_{77.55}H_{60}Cl_{0.45}N_{7.55}Sn$ (1356.21 g mol^{-1}) C, 68.68; H, 4.46; N, 7.80; Cl, 1.18%; found C, 68.52; H, 4.52; N, 7.53; Cl, 1.00%. IR (nujol) $\overline{\nu}$ / cm^{-1} 3175, 3143, 3081, 3064, 3057, 3038, 3025, 2792, 2786, 2251, 2218, 2157, 2152, 2050(br), 1985, 1915, 1898, 1833, 1806, 1694, 1615, 1588, 1575, 1483, 1439, 1318, 1308, 1294, 1276, 1260, 1253, 1186, 1181, 1171, 1165, 1114, 1069, 1028, 998, 797, 755, 692, 664, 616, 550, 531. ^{1}H NMR (MeCN-d_3, r.t.) δ / ppm = 8.05-7.11 (m, PPN^+). ^{13}C NMR

(MeCN-d_3, r.t.) δ / ppm = {134.67 (s), 133.30 (m), 130.42 (m), 128.29 (dd)} (PPN^+), 139.60 (s, CN), 138.64 (s, CN).

Synthesis of $Sn(CN)_4(py)_2$ (**4b**)

SnF_4 (0.270 g, 1.39 mmol, 1 eq.) was suspended in MeCN (15 mL). Me_3SiCN (0.72 mL, 5.69 mmol, 4.09 eqs.) was added and the suspension stirred at r.t. for 17 h, resulting in a very thick white suspension. $Sn(CN)_4(py)_2$ was obtained by filtration and drying under vacuum as as a white solid (0.434 g, 82%, M = 380.81 g mol^{-1}). IR (nujol) $\overline{\nu}$ / cm^{-1} = 3335(br), 3221, 3119, 3110, 3093, 3080, 3053, 3033, 2165, 2025, 1989, 1954, 1918, 1880, 1842, 1808, 1704, 1699, 1671, 1629, 1610, 1601, 1572, 1485, 1447, 1396, 1353, 1299, 1251, 1210, 1157, 1150, 1091, 1061, 1046, 1018, 1011, 868, 760, 705, 689, 648. ^{1}H NMR (dmso-d_6, r.t.) δ / ppm = 8.57 (m, py), 7.78(m, py), 7.38 (m, py), 6.38 (s, attributed to HCN). ^{13}C NMR (dmso-d_6, r.t.) δ / ppm = 149.62 (s, py), 136.17 (s, py), 123.95 (s, py), 113.75 (s, py). ^{19}F NMR (dmso-d_6, r.t.) no resonance found. M.p. 270 °C (dec.).

Crystallographic data

Crystallographic Summary Compounds **1** - **4**

Compound	**Space Group**	**Z**	***R*-factors**	**Cell Dimensions / Å**	**Cell Angles / °**	**Volume / Å^3**
$(PPN)_2Si(CN)_6$ (**1**) CCDC 1820362	P_{bca}	4	R_1 = 0.0300, wR_2 = 0.0799	a = 17.0534(3), b = 19.5984(3), c = 19.9350(4)	90, 90, 90	6662.7(2)
$(PPN)_2Ge(CN)_6$ (**2**) CCDC 1820360	$P2_1/c$	4	R_1 = 0.0268, wR_2 = 0.0728	a = 25.2292(8), b = 13.1356(4), c = 20.6141(7)	90, 107.5481(11), 90	6513.6(4)
$(PPN)_2Sn(CN)_6$ (**3**) CCDC 1820145	$P2_1/n$	2	R_1 = 0.0258, wR_2 = 0.0595	a = 10.4512(2), b = 24.5682(6), c = 13.2178(3)	90, 102.2838(10), 90	3316.20(13)
$(PPN)Ag(CN)_2 \cdot MeCN$ CCDC 1856451	$P2_1/n$	4	R_1 = 0.0623, wR_2 = 0.1113	a = 9.4853 (3), b = 20.0306(7), c = 19.0715(6)	90, 102.969(2), 90	3531.1(2)

Crystallographic Summary of $(PPN)_2Si(CN)_xCl_y$ mixed crystals, $x + y = 6$

In total, four $(PPN)_2Si(CN)_xCl_y$ crystal were investigated with various chlorine contents. All crystals have P_{bca} symmetry, Z =4.

Sum formula	***T* / *K***	**Cell Dimensions / Å**	**Volume / Å^3**	**Density / (g cm^{-3})**
$C_{75.34}H_{60}Cl_{2.82}N_{5.10}P_4Si$	120	16.6341(5), 19.5754(6), 19.9327(7)	6490.5(4)	1.319
$C_{77.30}H_{60}Cl_{0.70}N_{7.30}P_4Si$	296	16.920(3), 19.506(3), 19.813(3)	6539.3(18)	1.288

$C_{77.60}H_{60}Cl_{0.40}N_{7.60}P_4Si$	296	17.058(5), 19.641(6), 19.945(6)	6682.0(30)	1.257
$(PPN)_2Si(CN)_6$ (**1**)	130	17.0534(3), 19.5984(3), 19.935(4)	6662.7(2)	1.257

Crystallographic Data for $(PPN)_2Si(CN)_6$ (**1**)

Table S1. Crystal data and structure refinement for ch1ppx125_0m.

Identification code	ch1ppx125_0m	
Empirical formula	$C_{78}H_{60}N_8P_4Si$	
Formula weight	1261.31	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.0534(3) Å	α = 90°.
	b = 19.5984(3) Å	β = 90°.
	c = 19.9350(4) Å	γ = 90°.
Volume	6662.7(2) Å^3	
Z	4	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.183 mm^{-1}	
F(000)	2632	
Crystal size	0.38 x 0.35 x 0.25 mm^3	
Theta range for data collection	2.04 to 25.00°.	
Index ranges	-20<=h<=20, -23<=k<=23, -23<=l<=23	
Reflections collected	73215	
Independent reflections	5870 [R(int) = 0.0235]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9558 and 0.9339	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5870 / 0 / 412	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R_1 = 0.0300, wR_2 = 0.0799	
R indices (all data)	R_1 = 0.0336, wR_2 = 0.0844	
Largest diff. peak and hole	0.379 and -0.317 e.Å^{-3}	

Table S2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ch1ppx125_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	5000	0	10000	18(1)
P(1)	3900(1)	1925(1)	7441(1)	19(1)
P(2)	4570(1)	1208(1)	6238(1)	19(1)
N(1)	4145(1)	-1053(1)	9098(1)	34(1)
N(2)	5721(1)	630(1)	8727(1)	36(1)
N(3)	3628(1)	1015(1)	9982(1)	39(1)
N(4)	4332(1)	1774(1)	6758(1)	24(1)
C(1)	4449(1)	-657(1)	9436(1)	22(1)
C(2)	5454(1)	414(1)	9197(1)	20(1)
C(3)	4110(1)	631(1)	9966(1)	21(1)
C(4)	4615(1)	2086(1)	8088(1)	21(1)
C(5)	4406(1)	2101(1)	8766(1)	26(1)
C(6)	4975(1)	2219(1)	9249(1)	31(1)
C(7)	5743(1)	2341(1)	9062(1)	31(1)
C(8)	5950(1)	2342(1)	8390(1)	28(1)
C(9)	5393(1)	2206(1)	7903(1)	24(1)
C(10)	3312(1)	2681(1)	7325(1)	23(1)
C(11)	2744(1)	2863(1)	7797(1)	27(1)
C(12)	2290(1)	3442(1)	7699(1)	33(1)
C(13)	2407(1)	3842(1)	7135(1)	37(1)
C(14)	2969(1)	3667(1)	6669(1)	42(1)
C(15)	3422(1)	3084(1)	6760(1)	33(1)
C(16)	3246(1)	1269(1)	7731(1)	21(1)
C(17)	2509(1)	1216(1)	7429(1)	26(1)
C(18)	2003(1)	696(1)	7602(1)	30(1)
C(19)	2223(1)	228(1)	8088(1)	30(1)
C(20)	2953(1)	273(1)	8388(1)	30(1)
C(21)	3470(1)	787(1)	8209(1)	24(1)
C(22)	5522(1)	1426(1)	5911(1)	20(1)
C(23)	5774(1)	2102(1)	5942(1)	23(1)
C(24)	6510(1)	2275(1)	5697(1)	27(1)
C(25)	6991(1)	1781(1)	5423(1)	30(1)
C(26)	6740(1)	1108(1)	5386(1)	30(1)
C(27)	6008(1)	929(1)	5630(1)	26(1)
C(28)	3895(1)	1162(1)	5545(1)	23(1)
C(29)	4130(1)	1270(1)	4889(1)	28(1)
C(30)	3584(1)	1245(1)	4372(1)	34(1)
C(31)	2808(1)	1113(1)	4508(1)	31(1)
C(32)	2568(1)	998(1)	5159(1)	44(1)
C(33)	3108(1)	1020(1)	5676(1)	43(1)
C(34)	4638(1)	359(1)	6578(1)	22(1)

C(35)	4407(1)	-210(1)	6209(1)	32(1)
C(36)	4504(1)	-858(1)	6477(1)	40(1)
C(37)	4829(1)	-939(1)	7108(1)	39(1)
C(38)	5059(1)	-375(1)	7478(1)	34(1)
C(39)	4964(1)	273(1)	7214(1)	26(1)

Table S3. Bond lengths [Å] and angles [°] for ch1ppx125_0m.

Si(1)-C(1)#1	1.9501(15)	C(10)-C(15)	1.389(2)	C(25)-C(26)	1.390(2)
Si(1)-C(1)	1.9501(15)	C(10)-C(11)	1.397(2)	C(25)-H(25)	0.9500
Si(1)-C(2)#1	1.9547(15)	C(11)-C(12)	1.388(2)	C(26)-C(27)	1.385(2)
Si(1)-C(2)	1.9548(15)	C(11)-H(11)	0.9500	C(26)-H(26)	0.9500
Si(1)-C(3)	1.9588(15)	C(12)-C(13)	1.385(3)	C(27)-H(27)	0.9500
Si(1)-C(3)#1	1.9588(15)	C(12)-H(12)	0.9500	C(28)-C(29)	1.383(2)
P(1)-N(4)	1.5766(12)	C(13)-C(14)	1.378(3)	C(28)-C(33)	1.395(2)
P(1)-C(16)	1.7963(15)	C(13)-H(13)	0.9500	C(29)-C(30)	1.390(2)
P(1)-C(4)	1.8018(15)	C(14)-C(15)	1.391(2)	C(29)-H(29)	0.9500
P(1)-C(10)	1.8049(15)	C(14)-H(14)	0.9500	C(30)-C(31)	1.376(2)
P(2)-N(4)	1.5714(12)	C(15)-H(15)	0.9500	C(30)-H(30)	0.9500
P(2)-C(22)	1.8004(14)	C(16)-C(21)	1.394(2)	C(31)-C(32)	1.380(2)
P(2)-C(28)	1.8009(15)	C(16)-C(17)	1.398(2)	C(31)-H(31)	0.9500
P(2)-C(34)	1.8014(15)	C(17)-C(18)	1.379(2)	C(32)-C(33)	1.382(2)
N(1)-C(1)	1.152(2)	C(17)-H(17)	0.9500	C(32)-H(32)	0.9500
N(2)-C(2)	1.125(2)	C(18)-C(19)	1.386(2)	C(33)-H(33)	0.9500
N(3)-C(3)	1.115(2)	C(18)-H(18)	0.9500	C(34)-C(35)	1.393(2)
C(4)-C(9)	1.397(2)	C(19)-C(20)	1.384(2)	C(34)-C(39)	1.394(2)
C(4)-C(5)	1.399(2)	C(19)-H(19)	0.9500	C(35)-C(36)	1.386(3)
C(5)-C(6)	1.385(2)	C(20)-C(21)	1.386(2)	C(35)-H(35)	0.9500
C(5)-H(5)	0.9500	C(20)-H(20)	0.9500	C(36)-C(37)	1.383(3)
C(6)-C(7)	1.384(2)	C(21)-H(21)	0.9500	C(36)-H(36)	0.9500
C(6)-H(6)	0.9500	C(22)-C(23)	1.394(2)	C(37)-C(38)	1.384(3)
C(7)-C(8)	1.386(2)	C(22)-C(27)	1.397(2)	C(37)-H(37)	0.9500
C(7)-H(7)	0.9500	C(23)-C(24)	1.388(2)	C(38)-C(39)	1.384(2)
C(8)-C(9)	1.384(2)	C(23)-H(23)	0.9500	C(38)-H(38)	0.9500
C(8)-H(8)	0.9500	C(24)-C(25)	1.382(2)	C(39)-H(39)	0.9500
C(9)-H(9)	0.9500	C(24)-H(24)	0.9500		

C(1)#1-Si(1)-C(1)	180.00(7)	C(1)#1-Si(1)-C(3)	88.61(6)
C(1)#1-Si(1)-C(2)#1	89.55(6)	C(1)-Si(1)-C(3)	91.39(6)
C(1)-Si(1)-C(2)#1	90.45(6)	C(2)#1-Si(1)-C(3)	89.08(6)
C(1)#1-Si(1)-C(2)	90.45(6)	C(2)-Si(1)-C(3)	90.92(6)
C(1)-Si(1)-C(2)	89.55(6)	C(1)#1-Si(1)-C(3)#1	91.39(6)
C(2)#1-Si(1)-C(2)	180.0	C(1)-Si(1)-C(3)#1	88.61(6)

C(2)#1-Si(1)-C(3)#1	90.92(6)	C(13)-C(12)-H(12)	120.1
C(2)-Si(1)-C(3)#1	89.08(6)	C(11)-C(12)-H(12)	120.1
C(3)-Si(1)-C(3)#1	180.0	C(14)-C(13)-C(12)	120.47(15)
N(4)-P(1)-C(16)	115.73(7)	C(14)-C(13)-H(13)	119.8
N(4)-P(1)-C(4)	109.62(7)	C(12)-C(13)-H(13)	119.8
C(16)-P(1)-C(4)	108.34(7)	C(13)-C(14)-C(15)	120.16(16)
N(4)-P(1)-C(10)	107.58(7)	C(13)-C(14)-H(14)	119.9
C(16)-P(1)-C(10)	106.50(7)	C(15)-C(14)-H(14)	119.9
C(4)-P(1)-C(10)	108.86(7)	C(10)-C(15)-C(14)	119.86(16)
N(4)-P(2)-C(22)	107.69(7)	C(10)-C(15)-H(15)	120.1
N(4)-P(2)-C(28)	112.09(7)	C(14)-C(15)-H(15)	120.1
C(22)-P(2)-C(28)	108.09(7)	C(21)-C(16)-C(17)	119.30(14)
N(4)-P(2)-C(34)	114.91(7)	C(21)-C(16)-P(1)	122.33(11)
C(22)-P(2)-C(34)	107.28(7)	C(17)-C(16)-P(1)	118.21(11)
C(28)-P(2)-C(34)	106.51(7)	C(18)-C(17)-C(16)	120.62(14)
P(2)-N(4)-P(1)	145.32(9)	C(18)-C(17)-H(17)	119.7
N(1)-C(1)-Si(1)	178.01(13)	C(16)-C(17)-H(17)	119.7
N(2)-C(2)-Si(1)	177.59(14)	C(17)-C(18)-C(19)	119.71(14)
N(3)-C(3)-Si(1)	175.27(14)	C(17)-C(18)-H(18)	120.1
C(9)-C(4)-C(5)	119.52(14)	C(19)-C(18)-H(18)	120.1
C(9)-C(4)-P(1)	118.88(11)	C(20)-C(19)-C(18)	120.18(15)
C(5)-C(4)-P(1)	121.60(11)	C(20)-C(19)-H(19)	119.9
C(6)-C(5)-C(4)	119.82(15)	C(18)-C(19)-H(19)	119.9
C(6)-C(5)-H(5)	120.1	C(19)-C(20)-C(21)	120.47(15)
C(4)-C(5)-H(5)	120.1	C(19)-C(20)-H(20)	119.8
C(7)-C(6)-C(5)	120.30(15)	C(21)-C(20)-H(20)	119.8
C(7)-C(6)-H(6)	119.8	C(20)-C(21)-C(16)	119.70(14)
C(5)-C(6)-H(6)	119.8	C(20)-C(21)-H(21)	120.2
C(6)-C(7)-C(8)	120.14(15)	C(16)-C(21)-H(21)	120.2
C(6)-C(7)-H(7)	119.9	C(23)-C(22)-C(27)	119.78(13)
C(8)-C(7)-H(7)	119.9	C(23)-C(22)-P(2)	119.24(11)
C(9)-C(8)-C(7)	120.16(15)	C(27)-C(22)-P(2)	120.98(11)
C(9)-C(8)-H(8)	119.9	C(24)-C(23)-C(22)	119.81(14)
C(7)-C(8)-H(8)	119.9	C(24)-C(23)-H(23)	120.1
C(8)-C(9)-C(4)	120.01(14)	C(22)-C(23)-H(23)	120.1
C(8)-C(9)-H(9)	120.0	C(25)-C(24)-C(23)	120.22(14)
C(4)-C(9)-H(9)	120.0	C(25)-C(24)-H(24)	119.9
C(15)-C(10)-C(11)	119.68(14)	C(23)-C(24)-H(24)	119.9
C(15)-C(10)-P(1)	119.77(12)	C(24)-C(25)-C(26)	120.26(14)
C(11)-C(10)-P(1)	120.55(11)	C(24)-C(25)-H(25)	119.9
C(12)-C(11)-C(10)	120.02(15)	C(26)-C(25)-H(25)	119.9
C(12)-C(11)-H(11)	120.0	C(27)-C(26)-C(25)	119.95(15)
C(10)-C(11)-H(11)	120.0	C(27)-C(26)-H(26)	120.0
C(13)-C(12)-C(11)	119.80(15)	C(25)-C(26)-H(26)	120.0

C(26)-C(27)-C(22)	119.98(14)	C(28)-C(33)-H(33)	119.7
C(26)-C(27)-H(27)	120.0	C(35)-C(34)-C(39)	119.74(14)
C(22)-C(27)-H(27)	120.0	C(35)-C(34)-P(2)	121.52(12)
C(29)-C(28)-C(33)	119.10(14)	C(39)-C(34)-P(2)	118.68(11)
C(29)-C(28)-P(2)	122.13(11)	C(36)-C(35)-C(34)	119.70(16)
C(33)-C(28)-P(2)	118.77(12)	C(36)-C(35)-H(35)	120.2
C(28)-C(29)-C(30)	120.08(14)	C(34)-C(35)-H(35)	120.2
C(28)-C(29)-H(29)	120.0	C(37)-C(36)-C(35)	120.21(16)
C(30)-C(29)-H(29)	120.0	C(37)-C(36)-H(36)	119.9
C(31)-C(30)-C(29)	120.32(15)	C(35)-C(36)-H(36)	119.9
C(31)-C(30)-H(30)	119.8	C(36)-C(37)-C(38)	120.39(16)
C(29)-C(30)-H(30)	119.8	C(36)-C(37)-H(37)	119.8
C(30)-C(31)-C(32)	120.09(15)	C(38)-C(37)-H(37)	119.8
C(30)-C(31)-H(31)	120.0	C(39)-C(38)-C(37)	119.77(16)
C(32)-C(31)-H(31)	120.0	C(39)-C(38)-H(38)	120.1
C(31)-C(32)-C(33)	119.88(16)	C(37)-C(38)-H(38)	120.1
C(31)-C(32)-H(32)	120.1	C(38)-C(39)-C(34)	120.20(15)
C(33)-C(32)-H(32)	120.1	C(38)-C(39)-H(39)	119.9
C(32)-C(33)-C(28)	120.52(16)	C(34)-C(39)-H(39)	119.9
C(32)-C(33)-H(33)	119.7		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2

Table S4. Anisotropic displacement parameters ($Å^2x10^3$) for ch1ppx125_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	16(1)	21(1)	18(1)	2(1)	-1(1)	0(1)
P(1)	20(1)	20(1)	17(1)	-1(1)	1(1)	1(1)
P(2)	18(1)	22(1)	17(1)	-2(1)	1(1)	-2(1)
N(1)	31(1)	36(1)	35(1)	-2(1)	-1(1)	-4(1)
N(2)	40(1)	32(1)	34(1)	2(1)	4(1)	1(1)
N(3)	32(1)	51(1)	35(1)	4(1)	-1(1)	6(1)
N(4)	27(1)	22(1)	21(1)	-2(1)	4(1)	-2(1)
C(1)	18(1)	26(1)	22(1)	3(1)	1(1)	1(1)
C(2)	18(1)	21(1)	22(1)	-2(1)	-2(1)	2(1)
C(3)	25(1)	23(1)	16(1)	2(1)	1(1)	-2(1)
C(4)	25(1)	17(1)	22(1)	-1(1)	-2(1)	2(1)
C(5)	29(1)	25(1)	23(1)	-2(1)	0(1)	1(1)
C(6)	42(1)	27(1)	22(1)	-3(1)	-5(1)	1(1)

C(7)	36(1)	23(1)	34(1)	-4(1)	-14(1)	0(1)
C(8)	25(1)	22(1)	38(1)	-1(1)	-5(1)	-1(1)
C(9)	26(1)	19(1)	26(1)	0(1)	1(1)	1(1)
C(10)	25(1)	22(1)	23(1)	-2(1)	-4(1)	2(1)
C(11)	29(1)	30(1)	22(1)	-4(1)	-1(1)	5(1)
C(12)	31(1)	36(1)	31(1)	-12(1)	-6(1)	10(1)
C(13)	42(1)	28(1)	41(1)	-4(1)	-13(1)	12(1)
C(14)	57(1)	33(1)	36(1)	10(1)	-3(1)	9(1)
C(15)	38(1)	32(1)	28(1)	4(1)	3(1)	6(1)
C(16)	21(1)	23(1)	18(1)	-2(1)	2(1)	1(1)
C(17)	23(1)	32(1)	23(1)	3(1)	-2(1)	2(1)
C(18)	21(1)	39(1)	29(1)	-2(1)	-1(1)	-2(1)
C(19)	27(1)	31(1)	31(1)	-1(1)	3(1)	-6(1)
C(20)	33(1)	28(1)	30(1)	6(1)	-1(1)	-1(1)
C(21)	22(1)	26(1)	25(1)	1(1)	-2(1)	1(1)
C(22)	18(1)	26(1)	16(1)	1(1)	-2(1)	0(1)
C(23)	23(1)	26(1)	19(1)	0(1)	-1(1)	0(1)
C(24)	25(1)	29(1)	26(1)	4(1)	-4(1)	-5(1)
C(25)	18(1)	40(1)	30(1)	8(1)	-1(1)	-1(1)
C(26)	23(1)	36(1)	32(1)	2(1)	3(1)	7(1)
C(27)	24(1)	26(1)	27(1)	0(1)	1(1)	1(1)
C(28)	22(1)	27(1)	22(1)	-4(1)	-2(1)	-1(1)
C(29)	23(1)	34(1)	25(1)	4(1)	-2(1)	-5(1)
C(30)	35(1)	42(1)	23(1)	6(1)	-6(1)	-7(1)
C(31)	29(1)	31(1)	32(1)	-4(1)	-11(1)	0(1)
C(32)	22(1)	74(1)	37(1)	-10(1)	-2(1)	-7(1)
C(33)	25(1)	80(1)	24(1)	-6(1)	3(1)	-10(1)
C(34)	20(1)	22(1)	25(1)	-2(1)	6(1)	-1(1)
C(35)	40(1)	28(1)	27(1)	-5(1)	6(1)	-9(1)
C(36)	52(1)	25(1)	44(1)	-8(1)	12(1)	-11(1)
C(37)	44(1)	22(1)	51(1)	5(1)	10(1)	0(1)
C(38)	32(1)	30(1)	38(1)	5(1)	-1(1)	4(1)
C(39)	23(1)	24(1)	31(1)	-2(1)	-1(1)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for ch1ppx125_0m.

	x	y	z	U(eq)
H(5)	3876	2030	8896	31
H(6)	4836	2216	9711	37
H(7)	6130	2424	9395	37
H(8)	6476	2437	8263	34
H(9)	5539	2194	7444	28
H(11)	2669	2590	8186	32
H(12)	1899	3563	8017	39
H(13)	2099	4240	7070	44
H(14)	3047	3946	6285	50
H(15)	3805	2962	6436	39
H(17)	2355	1542	7101	31

H(18)	1507	659	7389	36
H(19)	1871	-124	8216	35
H(20)	3101	-51	8719	36
H(21)	3973	811	8410	29
H(23)	5444	2442	6129	27
H(24)	6683	2736	5719	32
H(25)	7495	1903	5259	35
H(26)	7070	770	5194	36
H(27)	5837	468	5607	31
H(29)	4665	1362	4793	33
H(30)	3748	1319	3922	40
H(31)	2437	1101	4153	37
H(32)	2032	904	5253	53
H(33)	2942	937	6123	51
H(35)	4184	-155	5776	38
H(36)	4348	-1247	6227	48
H(37)	4894	-1384	7289	47
H(38)	5282	-433	7911	40
H(39)	5120	660	7467	31

Crystallographic Data for $(PPN)_2Ge(CN)_6$ (**2**)

Table S6. Crystal data and structure refinement for ch1ppx359.

Identification code	ch1ppx359	
Empirical formula	$C_{78}H_{60}GeN_8P_4$	
Formula weight	1305.81	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 25.2314(8) Å	α = 90°.
	b = 13.1344(4) Å	β = 107.5545(11) °.
	c = 20.6130(6) Å	γ = 90°.
Volume	6513.0(3) $Å^3$	
Z	4	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	1.974 mm^{-1}	
F(000)	2704	
Crystal size	0.3 x 0.29 x 0.11 mm^3	
Theta range for data collection	1.836 to 66.747°.	
Index ranges	-29<=h<=30, -15<=k<=15, -24<=l<=24	
Reflections collected	88733	
Independent reflections	11500 [R(int) = 0.028]	
Completeness to theta = 66.747°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6076	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11500 / 0 / 820	
Goodness-of-fit on F^2	1.06	

Final R indices [I>2sigma(I)]	$R_1 = 0.0261$, $wR_2 = 0.0693$
R indices (all data)	$R_1 = 0.0283$, $wR_2 = 0.0708$
Extinction coefficient	n/a
Largest diff. peak and hole	0.35 and -0.51 e.Å^{-3}

Table S7. Final Coordinates and Equiv. Isotropic Displacement Params. of the non-H atoms for ch1ppx359. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq) [Ang^2]
P1	0.04068(2)	0.41415(3)	0.86597(2)	0.0123(1)
P2	0.11316(2)	0.40169(3)	0.77658(2)	0.0123(1)
N7	0.06245(5)	0.37904(9)	0.80498(6)	0.0155(3)
C7	0.04448(6)	0.54961(11)	0.88145(7)	0.0147(4)
C8	-0.00100(7)	0.61095(12)	0.85106(8)	0.0260(5)
C9	0.00241(7)	0.71575(12)	0.86054(9)	0.0321(5)
C10	0.05155(7)	0.75990(12)	0.89970(8)	0.0239(5)
C11	0.09705(6)	0.69955(12)	0.92951(8)	0.0238(5)
C12	0.09384(6)	0.59481(12)	0.92072(8)	0.0216(4)
C13	0.07558(6)	0.35504(11)	0.94627(7)	0.0157(4)
C14	0.09573(7)	0.25642(12)	0.94727(8)	0.0240(4)
C15	0.11889(8)	0.20724(13)	1.00856(8)	0.0318(5)
C16	0.12336(7)	0.25581(13)	1.06915(8)	0.0287(5)
C17	0.10430(7)	0.35413(14)	1.06914(8)	0.0302(5)
C18	0.07992(7)	0.40374(13)	1.00792(8)	0.0266(5)
C19	-0.03119(6)	0.37572(10)	0.84417(7)	0.0161(4)
C20	-0.06089(6)	0.35697(11)	0.77646(8)	0.0221(4)
C21	-0.11694(7)	0.33123(12)	0.75893(9)	0.0282(5)
C22	-0.14293(7)	0.32238(12)	0.80893(10)	0.0317(5)
C23	-0.11318(7)	0.33817(13)	0.87678(10)	0.0318(5)
C24	-0.05739(6)	0.36465(12)	0.89449(8)	0.0238(5)
C25	0.14432(6)	0.28185(11)	0.76561(7)	0.0147(4)
C26	0.12075(6)	0.19088(11)	0.77782(7)	0.0180(4)
C27	0.14661(7)	0.09869(12)	0.77336(8)	0.0231(4)
C28	0.19553(7)	0.09734(12)	0.75615(8)	0.0245(5)
C29	0.21908(6)	0.18777(12)	0.74363(7)	0.0229(4)
C30	0.19398(6)	0.28007(12)	0.74876(7)	0.0185(4)
C31	0.09003(6)	0.46882(10)	0.69673(7)	0.0154(4)
C32	0.12830(7)	0.49850(12)	0.66339(8)	0.0228(5)
C33	0.11062(7)	0.55060(13)	0.60240(8)	0.0274(5)
C34	0.05479(7)	0.57344(13)	0.57393(8)	0.0289(5)

C35	0.01677(7)	0.54474(13)	0.60648(9)	0.0308(5)
C36	0.03415(6)	0.49286(12)	0.66798(8)	0.0226(5)
C37	0.16891(6)	0.47474(11)	0.83156(7)	0.0157(4)
C38	0.17222(6)	0.57999(12)	0.82501(8)	0.0224(5)
C39	0.21282(7)	0.63404(13)	0.87307(9)	0.0298(5)
C40	0.24982(7)	0.58350(14)	0.92651(9)	0.0317(5)
C41	0.24765(6)	0.47884(14)	0.93232(8)	0.0268(5)
C42	0.20689(6)	0.42393(12)	0.88510(7)	0.0196(4)
P3	0.39853(2)	0.58874(3)	0.22633(2)	0.0128(1)
P4	0.46996(2)	0.57014(3)	0.13628(2)	0.0120(1)
N8	0.45181(5)	0.60076(9)	0.20092(6)	0.0155(3)
C43	0.41738(6)	0.52362(10)	0.30714(7)	0.0151(4)
C44	0.47283(6)	0.50360(11)	0.34236(8)	0.0187(4)
C45	0.48620(6)	0.45250(12)	0.40434(8)	0.0244(4)
C46	0.44441(7)	0.42228(12)	0.43107(8)	0.0247(4)
C47	0.38916(6)	0.44105(12)	0.39601(8)	0.0218(4)
C48	0.37545(6)	0.49096(11)	0.33408(8)	0.0186(4)
C49	0.37127(6)	0.71340(11)	0.23392(7)	0.0169(4)
C50	0.32720(6)	0.72531(12)	0.26098(8)	0.0236(5)
C51	0.30280(7)	0.82022(14)	0.25984(8)	0.0310(5)
C52	0.32201(8)	0.90299(13)	0.23202(8)	0.0313(5)
C53	0.36646(7)	0.89254(12)	0.20683(8)	0.0283(5)
C54	0.39121(6)	0.79750(11)	0.20730(7)	0.0214(4)
C55	0.34115(6)	0.51476(11)	0.17362(7)	0.0162(4)
C56	0.34711(6)	0.40864(11)	0.17242(8)	0.0202(4)
C57	0.30426(7)	0.34913(13)	0.13219(8)	0.0272(5)
C58	0.25531(7)	0.39471(15)	0.09413(8)	0.0326(5)
C59	0.24897(7)	0.49921(14)	0.09554(8)	0.0304(5)
C60	0.29181(6)	0.55983(13)	0.13479(7)	0.0215(4)
C61	0.45416(6)	0.43920(11)	0.11266(7)	0.0147(4)
C62	0.41523(6)	0.41151(11)	0.05156(7)	0.0189(4)
C63	0.40013(6)	0.30960(12)	0.03935(8)	0.0250(5)
C64	0.42385(7)	0.23644(12)	0.08769(9)	0.0271(5)
C65	0.46312(7)	0.26369(12)	0.14831(8)	0.0246(5)
C66	0.47838(6)	0.36490(11)	0.16106(8)	0.0193(4)
C67	0.43957(6)	0.64953(10)	0.06307(7)	0.0141(4)
C68	0.46977(6)	0.67587(11)	0.01879(7)	0.0199(4)
C69	0.44601(6)	0.73819(12)	-0.03672(8)	0.0234(4)
C70	0.39261(6)	0.77531(11)	-0.04839(7)	0.0205(4)
C71	0.36277(6)	0.75010(11)	-0.00433(7)	0.0197(4)
C72	0.38573(6)	0.68754(11)	0.05086(7)	0.0175(4)
C73	0.54360(6)	0.58744(11)	0.15393(7)	0.0147(4)
C74	0.57444(6)	0.52118(11)	0.12654(7)	0.0185(4)
C75	0.62894(6)	0.54478(12)	0.13068(8)	0.0221(4)

C76	0.65286(6)	0.63384(13)	0.16153(8)	0.0254(5)
C77	0.62268(7)	0.69921(13)	0.18991(9)	0.0281(5)
C78	0.56814(6)	0.67651(12)	0.18616(8)	0.0223(4)
Ge1	0.24768(2)	0.50922(2)	0.49185(2)	0.0138(1)
N1	0.25810(5)	0.61394(10)	0.35591(6)	0.0224(4)
N2	0.26811(6)	0.29175(10)	0.43525(7)	0.0285(4)
N3	0.11783(5)	0.51073(10)	0.41214(7)	0.0259(4)
N4	0.23986(5)	0.40381(10)	0.62810(7)	0.0242(4)
N5	0.23062(6)	0.72785(10)	0.55138(7)	0.0267(4)
N6	0.37858(5)	0.50979(10)	0.56277(7)	0.0248(4)
C1	0.25618(6)	0.57692(11)	0.40547(7)	0.0163(4)
C2	0.25772(6)	0.36930(11)	0.45374(7)	0.0184(4)
C3	0.16387(6)	0.50768(11)	0.44320(8)	0.0181(4)
C4	0.23996(6)	0.44168(11)	0.57809(7)	0.0181(4)
C5	0.23818(6)	0.64990(11)	0.53080(7)	0.0181(4)
C6	0.33163(6)	0.51326(11)	0.53684(7)	0.0174(4)

Table S8. Bond lengths [Å] and angles [°] for ch1ppx359.

Ge1	-C2	2.0442(15)	C7	-C8	1.387(2)
Ge1	-C3	2.0490(17)	C7	-C12	1.397(2)
Ge1	-C4	2.0479(15)	C8	-C9	1.389(2)
Ge1	-C5	2.0573(15)	C9	-C10	1.386(2)
Ge1	-C6	2.0407(16)	C10	-C11	1.378(2)
Ge1	-C1	2.0585(15)	C11	-C12	1.387(2)
P1	-C7	1.8050(15)	C13	-C14	1.389(2)
P1	-N7	1.5848(13)	C13	-C18	1.397(2)
P1	-C13	1.7996(15)	C14	-C15	1.382(2)
P1	-C19	1.8038(16)	C15	-C16	1.376(2)
P2	-C25	1.8039(15)	C16	-C17	1.378(3)
P2	-N7	1.5875(14)	C17	-C18	1.388(2)
P2	-C37	1.7950(15)	C19	-C20	1.393(2)
P2	-C31	1.8021(14)	C19	-C24	1.396(2)
P3	-C49	1.8009(15)	C20	-C21	1.392(2)
P3	-C43	1.8040(14)	C21	-C22	1.383(3)
P3	-N8	1.5910(14)	C22	-C23	1.389(3)
P3	-C55	1.8088(15)	C23	-C24	1.388(2)
P4	-C67	1.8040(14)	C25	-C26	1.391(2)
P4	-C61	1.7991(15)	C25	-C30	1.398(2)
P4	-C73	1.7968(16)	C26	-C27	1.392(2)

P4	-N8	1.5858(13)	C27	-C28	1.383(3)
N1	-C1	1.1455(19)	C28	-C29	1.387(2)
N2	-C2	1.145(2)	C29	-C30	1.387(2)
N3	-C3	1.146(2)	C31	-C36	1.391(2)
N4	-C4	1.145(2)	C31	-C32	1.399(2)
N5	-C5	1.146(2)	C32	-C33	1.382(2)
N6	-C6	1.144(2)	C33	-C34	1.386(3)
C34	-C35	1.379(3)	C32	-H32	0.9500
C35	-C36	1.389(2)	C33	-H33	0.9500
C37	-C38	1.394(2)	C34	-H34	0.9500
C37	-C42	1.394(2)	C35	-H35	0.9500
C38	-C39	1.387(2)	C36	-H36	0.9500
C39	-C40	1.380(3)	C38	-H38	0.9500
C40	-C41	1.382(3)	C39	-H39	0.9500
C41	-C42	1.386(2)	C40	-H40	0.9500
C8	-H8	0.9500	C41	-H41	0.9500
C9	-H9	0.9500	C42	-H42	0.9500
C10	-H10	0.9500	C43	-C48	1.402(2)
C11	-H11	0.9500	C43	-C44	1.393(2)
C12	-H12	0.9500	C44	-C45	1.392(2)
C14	-H14	0.9500	C45	-C46	1.387(2)
C15	-H15	0.9500	C46	-C47	1.385(2)
C16	-H16	0.9500	C47	-C48	1.383(2)
C17	-H17	0.9500	C49	-C50	1.395(2)
C18	-H18	0.9500	C49	-C54	1.393(2)
C20	-H20	0.9500	C50	-C51	1.387(2)
C21	-H21	0.9500	C51	-C52	1.383(3)
C22	-H22	0.9500	C52	-C53	1.378(3)
C23	-H23	0.9500	C53	-C54	1.395(2)
C24	-H24	0.9500	C55	-C56	1.403(2)
C26	-H26	0.9500	C55	-C60	1.393(2)
C27	-H27	0.9500	C56	-C57	1.388(2)
C28	-H28	0.9500	C57	-C58	1.384(2)
C29	-H29	0.9500	C58	-C59	1.383(3)
C30	-H30	0.9500	C59	-C60	1.389(2)
C61	-C66	1.398(2)	C51	-H51	0.9500
C61	-C62	1.392(2)	C52	-H52	0.9500
C62	-C63	1.394(2)	C53	-H53	0.9500
C63	-C64	1.384(2)	C54	-H54	0.9500
C64	-C65	1.387(2)	C56	-H56	0.9500
C65	-C66	1.387(2)	C57	-H57	0.9500
C67	-C72	1.397(2)	C58	-H58	0.9500
C67	-C68	1.398(2)	C59	-H59	0.9500

C68	-C69	1.387(2)	C60	-H60	0.9500
C69	-C70	1.384(2)	C62	-H62	0.9500
C70	-C71	1.383(2)	C63	-H63	0.9500
C71	-C72	1.381(2)	C64	-H64	0.9500
C73	-C78	1.395(2)	C65	-H65	0.9500
C73	-C74	1.395(2)	C66	-H66	0.9500
C74	-C75	1.387(2)	C68	-H68	0.9500
C75	-C76	1.380(2)	C69	-H69	0.9500
C76	-C77	1.389(2)	C70	-H70	0.9500
C77	-C78	1.387(2)	C71	-H71	0.9500
C44	-H44	0.9500	C72	-H72	0.9500
C45	-H45	0.9500	C74	-H74	0.9500
C46	-H46	0.9500	C75	-H75	0.9500
C47	-H47	0.9500	C76	-H76	0.9500
C48	-H48	0.9500	C77	-H77	0.9500
C50	-H50	0.9500	C78	-H78	0.9500

C4	-Ge1	-C6	88.52(6)	C49	-P3	-C55	106.45(7)
C5	-Ge1	-C6	91.52(6)	N8	-P3	-C55	117.28(7)
C4	-Ge1	-C5	89.86(6)	N8	-P3	-C43	109.72(7)
C1	-Ge1	-C6	90.99(6)	N8	-P3	-C49	108.73(7)
C2	-Ge1	-C3	91.85(6)	C43	-P3	-C49	110.61(7)
C2	-Ge1	-C4	89.97(6)	C61	-P4	-C67	108.82(7)
C1	-Ge1	-C2	89.92(6)	C61	-P4	-C73	107.87(7)
C1	-Ge1	-C3	86.69(6)	C67	-P4	-C73	104.42(7)
C1	-Ge1	-C4	179.50(7)	N8	-P4	-C73	109.93(7)
C1	-Ge1	-C5	90.25(6)	N8	-P4	-C61	111.92(7)
C3	-Ge1	-C6	177.68(6)	N8	-P4	-C67	113.49(7)
C2	-Ge1	-C6	88.06(6)	P1	-N7	-P2	138.48(8)
C3	-Ge1	-C4	93.80(6)	P3	-N8	-P4	137.58(9)
C2	-Ge1	-C5	179.54(6)	P1	-C7	-C8	120.00(12)
C3	-Ge1	-C5	88.59(6)	P1	-C7	-C12	120.80(12)
C7	-P1	-C19	108.40(7)	C8	-C7	-C12	119.10(14)
C13	-P1	-C19	106.54(7)	C7	-C8	-C9	120.28(16)
C7	-P1	-C13	106.11(7)	C8	-C9	-C10	120.20(16)
N7	-P1	-C19	106.49(7)	C9	-C10	-C11	119.85(15)
N7	-P1	-C7	114.48(7)	C10	-C11	-C12	120.30(15)
N7	-P1	-C13	114.43(7)	C7	-C12	-C11	120.27(14)
N7	-P2	-C25	108.24(7)	P1	-C13	-C18	121.43(12)
N7	-P2	-C31	110.70(7)	C14	-C13	-C18	119.04(14)
N7	-P2	-C37	115.64(7)	P1	-C13	-C14	119.42(11)
C25	-P2	-C31	110.23(7)	C13	-C14	-C15	120.09(15)
C25	-P2	-C37	104.91(7)	C14	-C15	-C16	120.61(16)

C31	-P2	-C37	106.94(7)	C15	-C16	-C17	120.07(15)
C43	-P3	-C55	103.90(7)	C16	-C17	-C18	119.93(15)
C13	-C18	-C17	120.24(15)	C37	-C38	-C39	119.44(15)
C20	-C19	-C24	119.61(14)	C38	-C39	-C40	120.00(16)
P1	-C19	-C24	120.66(11)	C39	-C40	-C41	120.83(16)
P1	-C19	-C20	119.72(12)	C40	-C41	-C42	119.80(15)
C19	-C20	-C21	120.05(15)	C37	-C42	-C41	119.61(15)
C20	-C21	-C22	120.00(16)	C7	-C8	-H8	120.00
C21	-C22	-C23	120.27(17)	C9	-C8	-H8	120.00
C22	-C23	-C24	119.97(17)	C8	-C9	-H9	120.00
C19	-C24	-C23	120.06(15)	C10	-C9	-H9	120.00
P2	-C25	-C30	120.20(11)	C11	-C10	-H10	120.00
P2	-C25	-C26	120.04(12)	C9	-C10	-H10	120.00
C26	-C25	-C30	119.66(14)	C10	-C11	-H11	120.00
C25	-C26	-C27	120.06(15)	C12	-C11	-H11	120.00
C26	-C27	-C28	120.03(15)	C7	-C12	-H12	120.00
C27	-C28	-C29	120.15(15)	C11	-C12	-H12	120.00
C28	-C29	-C30	120.23(15)	C13	-C14	-H14	120.00
C25	-C30	-C29	119.86(14)	C15	-C14	-H14	120.00
P2	-C31	-C32	120.24(12)	C14	-C15	-H15	120.00
P2	-C31	-C36	120.50(12)	C16	-C15	-H15	120.00
C32	-C31	-C36	119.25(13)	C15	-C16	-H16	120.00
C31	-C32	-C33	120.25(16)	C17	-C16	-H16	120.00
C32	-C33	-C34	120.03(16)	C16	-C17	-H17	120.00
C33	-C34	-C35	120.16(15)	C18	-C17	-H17	120.00
C34	-C35	-C36	120.26(16)	C13	-C18	-H18	120.00
C31	-C36	-C35	120.05(15)	C17	-C18	-H18	120.00
C38	-C37	-C42	120.29(14)	C21	-C20	-H20	120.00
P2	-C37	-C42	117.68(11)	C19	-C20	-H20	120.00
P2	-C37	-C38	121.83(11)	C22	-C21	-H21	120.00
C20	-C21	-H21	120.00	C39	-C38	-H38	120.00
C23	-C22	-H22	120.00	C38	-C39	-H39	120.00
C21	-C22	-H22	120.00	C40	-C39	-H39	120.00
C22	-C23	-H23	120.00	C39	-C40	-H40	120.00
C24	-C23	-H23	120.00	C41	-C40	-H40	120.00
C23	-C24	-H24	120.00	C40	-C41	-H41	120.00
C19	-C24	-H24	120.00	C42	-C41	-H41	120.00
C27	-C26	-H26	120.00	C37	-C42	-H42	120.00
C25	-C26	-H26	120.00	C41	-C42	-H42	120.00
C26	-C27	-H27	120.00	P3	-C43	-C44	120.95(12)
C28	-C27	-H27	120.00	P3	-C43	-C48	119.37(12)
C27	-C28	-H28	120.00	C44	-C43	-C48	119.67(13)
C29	-C28	-H28	120.00	C43	-C44	-C45	119.78(14)

C28	-C29	-H29	120.00	C44	-C45	-C46	120.00(15)
C30	-C29	-H29	120.00	C45	-C46	-C47	120.52(15)
C29	-C30	-H30	120.00	C46	-C47	-C48	119.88(15)
C25	-C30	-H30	120.00	C43	-C48	-C47	120.14(14)
C33	-C32	-H32	120.00	P3	-C49	-C50	120.53(11)
C31	-C32	-H32	120.00	P3	-C49	-C54	119.60(12)
C34	-C33	-H33	120.00	C50	-C49	-C54	119.65(14)
C32	-C33	-H33	120.00	C49	-C50	-C51	119.81(15)
C33	-C34	-H34	120.00	C50	-C51	-C52	120.27(17)
C35	-C34	-H34	120.00	C51	-C52	-C53	120.32(16)
C34	-C35	-H35	120.00	C52	-C53	-C54	120.03(15)
C36	-C35	-H35	120.00	C49	-C54	-C53	119.89(15)
C31	-C36	-H36	120.00	P3	-C55	-C56	118.27(11)
C35	-C36	-H36	120.00	P3	-C55	-C60	122.12(12)
C37	-C38	-H38	120.00	C56	-C55	-C60	119.61(14)
C55	-C56	-C57	120.11(15)	C73	-C78	-C77	119.82(15)
C56	-C57	-C58	119.75(16)	C45	-C44	-H44	120.00
C57	-C58	-C59	120.43(16)	C43	-C44	-H44	120.00
C58	-C59	-C60	120.43(16)	C46	-C45	-H45	120.00
C55	-C60	-C59	119.65(15)	C44	-C45	-H45	120.00
C62	-C61	-C66	120.05(13)	C47	-C46	-H46	120.00
P4	-C61	-C62	122.21(11)	C45	-C46	-H46	120.00
P4	-C61	-C66	117.44(11)	C46	-C47	-H47	120.00
C61	-C62	-C63	119.62(13)	C48	-C47	-H47	120.00
C62	-C63	-C64	120.11(14)	C47	-C48	-H48	120.00
C63	-C64	-C65	120.38(15)	C43	-C48	-H48	120.00
C64	-C65	-C66	120.00(15)	C49	-C50	-H50	120.00
C61	-C66	-C65	119.83(14)	C51	-C50	-H50	120.00
P4	-C67	-C68	120.77(12)	C52	-C51	-H51	120.00
P4	-C67	-C72	120.14(11)	C50	-C51	-H51	120.00
C68	-C67	-C72	119.08(13)	C51	-C52	-H52	120.00
C67	-C68	-C69	119.98(14)	C53	-C52	-H52	120.00
C68	-C69	-C70	120.47(14)	C52	-C53	-H53	120.00
C69	-C70	-C71	119.71(13)	C54	-C53	-H53	120.00
C70	-C71	-C72	120.47(14)	C49	-C54	-H54	120.00
C67	-C72	-C71	120.30(14)	C53	-C54	-H54	120.00
P4	-C73	-C74	120.53(11)	C55	-C56	-H56	120.00
P4	-C73	-C78	119.07(12)	C57	-C56	-H56	120.00
C74	-C73	-C78	119.62(14)	C56	-C57	-H57	120.00
C73	-C74	-C75	119.96(14)	C58	-C57	-H57	120.00
C74	-C75	-C76	120.36(14)	C57	-C58	-H58	120.00
C75	-C76	-C77	119.93(15)	C59	-C58	-H58	120.00
C76	-C77	-C78	120.30(16)	C58	-C59	-H59	120.00

C60	-C59	-H59	120.00	C72	-C71	-H71	120.00
C55	-C60	-H60	120.00	C67	-C72	-H72	120.00
C59	-C60	-H60	120.00	C71	-C72	-H72	120.00
C63	-C62	-H62	120.00	C73	-C74	-H74	120.00
C61	-C62	-H62	120.00	C75	-C74	-H74	120.00
C62	-C63	-H63	120.00	C74	-C75	-H75	120.00
C64	-C63	-H63	120.00	C76	-C75	-H75	120.00
C65	-C64	-H64	120.00	C75	-C76	-H76	120.00
C63	-C64	-H64	120.00	C77	-C76	-H76	120.00
C64	-C65	-H65	120.00	C76	-C77	-H77	120.00
C66	-C65	-H65	120.00	C78	-C77	-H77	120.00
C61	-C66	-H66	120.00	C73	-C78	-H78	120.00
C65	-C66	-H66	120.00	C77	-C78	-H78	120.00
C69	-C68	-H68	120.00	Ge1	-C1	-N1	176.56(14)
C67	-C68	-H68	120.00	Ge1	-C2	-N2	174.13(14)
C70	-C69	-H69	120.00	Ge1	-C3	-N3	174.90(14)
C68	-C69	-H69	120.00	Ge1	-C4	-N4	174.92(14)
C69	-C70	-H70	120.00	Ge1	-C5	-N5	177.24(14)
C71	-C70	-H70	120.00	Ge1	-C6	-N6	176.15(13)
C70	-C71	-H71	120.00				

Symmetry transformations used to generate equivalent atoms: -

Table S9. Anisotropic displacement parameters ($Å^2x10^3$) for ch1ppx359. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P1	0.0124(2)	0.0124(2)	0.0124(2)	-0.0006(1)	0.0044(1)	0.0005(1)
P2	0.0137(2)	0.0119(2)	0.0116(2)	-0.0003(1)	0.0044(1)	0.0002(1)
N7	0.0163(6)	0.0164(6)	0.0145(6)	-0.0015(5)	0.0058(5)	-0.0007(5)
C7	0.0172(7)	0.0137(7)	0.0151(7)	-0.0014(5)	0.0076(5)	-0.0007(5)
C8	0.0225(8)	0.0175(8)	0.0310(9)	-0.0006(6)	-0.0023(7)	-0.0020(6)
C9	0.0294(9)	0.0173(8)	0.0410(10)	0.0032(7)	-0.0021(7)	0.0030(7)
C10	0.0328(9)	0.0147(7)	0.0255(8)	-0.0020(6)	0.0109(7)	-0.0048(6)
C11	0.0216(8)	0.0235(8)	0.0261(8)	-0.0084(6)	0.0067(6)	-0.0067(6)
C12	0.0168(7)	0.0225(8)	0.0239(8)	-0.0052(6)	0.0039(6)	0.0010(6)
C13	0.0141(7)	0.0182(7)	0.0153(7)	0.0006(5)	0.0052(5)	0.0010(5)
C14	0.0316(8)	0.0212(8)	0.0168(7)	-0.0032(6)	0.0038(6)	0.0056(6)
C15	0.0435(10)	0.0227(8)	0.0240(8)	0.0012(7)	0.0023(7)	0.0113(7)
C16	0.0324(9)	0.0318(9)	0.0182(8)	0.0068(7)	0.0021(7)	0.0048(7)
C17	0.0400(10)	0.0355(9)	0.0149(7)	-0.0022(7)	0.0078(7)	0.0066(8)
C18	0.0355(9)	0.0248(8)	0.0204(8)	-0.0006(6)	0.0100(7)	0.0098(7)

C19	0.0149(7)	0.0099(6)	0.0242(7)	-0.0008(5)	0.0072(6)	-0.0005(5)
C20	0.0209(7)	0.0192(7)	0.0247(8)	0.0010(6)	0.0046(6)	-0.0035(6)
C21	0.0216(8)	0.0210(8)	0.0353(9)	-0.0008(7)	-0.0014(7)	-0.0042(6)
C22	0.0163(8)	0.0213(8)	0.0568(12)	-0.0041(8)	0.0098(8)	-0.0045(6)
C23	0.0262(8)	0.0281(9)	0.0488(11)	-0.0063(8)	0.0229(8)	-0.0043(7)
C24	0.0236(8)	0.0214(8)	0.0295(8)	-0.0046(6)	0.0128(7)	-0.0025(6)
C25	0.0177(7)	0.0158(7)	0.0095(6)	-0.0006(5)	0.0026(5)	0.0023(5)
C26	0.0220(7)	0.0164(7)	0.0155(7)	0.0000(6)	0.0054(6)	-0.0005(6)
C27	0.0325(8)	0.0157(7)	0.0184(7)	-0.0007(6)	0.0038(6)	0.0009(6)
C28	0.0316(9)	0.0215(8)	0.0171(7)	-0.0040(6)	0.0025(6)	0.0103(6)
C29	0.0216(7)	0.0311(9)	0.0162(7)	-0.0027(6)	0.0058(6)	0.0077(6)
C30	0.0201(7)	0.0216(7)	0.0141(7)	0.0004(6)	0.0057(6)	0.0016(6)
C31	0.0202(7)	0.0126(6)	0.0134(7)	-0.0003(5)	0.0049(6)	0.0001(5)
C32	0.0213(8)	0.0272(8)	0.0216(8)	0.0056(6)	0.0091(6)	0.0055(6)
C33	0.0333(9)	0.0286(9)	0.0243(8)	0.0084(7)	0.0146(7)	0.0041(7)
C34	0.0339(9)	0.0280(9)	0.0211(8)	0.0105(7)	0.0026(7)	-0.0004(7)
C35	0.0211(8)	0.0324(9)	0.0326(9)	0.0135(7)	-0.0012(7)	-0.0003(7)
C36	0.0194(8)	0.0214(8)	0.0265(8)	0.0061(6)	0.0062(6)	-0.0015(6)
C37	0.0150(7)	0.0180(7)	0.0155(7)	-0.0029(5)	0.0069(5)	-0.0015(5)
C38	0.0251(8)	0.0190(8)	0.0239(8)	-0.0013(6)	0.0088(6)	-0.0041(6)
C39	0.0323(9)	0.0236(8)	0.0361(9)	-0.0090(7)	0.0141(8)	-0.0116(7)
C40	0.0220(8)	0.0426(10)	0.0300(9)	-0.0158(8)	0.0072(7)	-0.0129(7)
C41	0.0181(7)	0.0423(10)	0.0187(8)	-0.0062(7)	0.0034(6)	0.0009(7)
C42	0.0184(7)	0.0242(8)	0.0169(7)	-0.0029(6)	0.0065(6)	0.0017(6)
P3	0.0142(2)	0.0135(2)	0.0121(2)	0.0002(1)	0.0059(1)	-0.0001(1)
P4	0.0120(2)	0.0128(2)	0.0121(2)	-0.0001(1)	0.0047(1)	-0.0010(1)
N8	0.0161(6)	0.0174(6)	0.0140(6)	-0.0011(5)	0.0061(5)	-0.0025(5)
C43	0.0184(7)	0.0137(7)	0.0144(7)	-0.0002(5)	0.0067(6)	0.0001(5)
C44	0.0180(7)	0.0186(7)	0.0203(7)	0.0013(6)	0.0070(6)	-0.0031(6)
C45	0.0195(7)	0.0278(8)	0.0219(8)	0.0051(6)	0.0004(6)	-0.0009(6)
C46	0.0297(8)	0.0264(8)	0.0169(7)	0.0063(6)	0.0056(6)	-0.0006(7)
C47	0.0249(8)	0.0230(8)	0.0212(7)	0.0030(6)	0.0126(6)	-0.0009(6)
C48	0.0178(7)	0.0207(7)	0.0193(7)	0.0008(6)	0.0085(6)	0.0021(6)
C49	0.0212(7)	0.0158(7)	0.0125(6)	-0.0013(5)	0.0033(5)	0.0022(6)
C50	0.0276(8)	0.0251(8)	0.0207(8)	0.0007(6)	0.0110(6)	0.0051(6)
C51	0.0331(9)	0.0346(9)	0.0259(8)	-0.0040(7)	0.0097(7)	0.0137(7)
C52	0.0445(10)	0.0228(8)	0.0194(8)	-0.0057(6)	-0.0011(7)	0.0139(7)
C53	0.0450(10)	0.0163(8)	0.0186(8)	-0.0005(6)	0.0020(7)	-0.0002(7)
C54	0.0280(8)	0.0186(7)	0.0172(7)	-0.0015(6)	0.0061(6)	-0.0021(6)
C55	0.0164(7)	0.0207(7)	0.0137(7)	-0.0010(5)	0.0079(6)	-0.0037(6)
C56	0.0220(7)	0.0206(8)	0.0224(7)	-0.0023(6)	0.0135(6)	-0.0042(6)
C57	0.0327(9)	0.0267(8)	0.0292(8)	-0.0083(7)	0.0199(7)	-0.0136(7)
C58	0.0274(9)	0.0486(11)	0.0232(8)	-0.0093(8)	0.0098(7)	-0.0194(8)
C59	0.0199(8)	0.0483(11)	0.0213(8)	-0.0003(7)	0.0036(6)	-0.0056(7)
C60	0.0203(7)	0.0290(8)	0.0162(7)	0.0015(6)	0.0069(6)	-0.0011(6)
C61	0.0146(7)	0.0144(7)	0.0180(7)	-0.0018(5)	0.0094(5)	-0.0016(5)
C62	0.0185(7)	0.0212(8)	0.0190(7)	-0.0023(6)	0.0086(6)	-0.0027(6)
C63	0.0242(8)	0.0273(8)	0.0269(8)	-0.0116(7)	0.0128(7)	-0.0090(6)
C64	0.0341(9)	0.0162(8)	0.0400(10)	-0.0067(7)	0.0247(8)	-0.0064(6)
C65	0.0313(8)	0.0168(7)	0.0323(9)	0.0030(6)	0.0195(7)	0.0025(6)

C66	0.0206(7)	0.0186(7)	0.0207(7)	0.0003(6)	0.0093(6)	0.0014(6)
C67	0.0167(7)	0.0119(6)	0.0134(6)	-0.0011(5)	0.0042(5)	-0.0016(5)
C68	0.0194(7)	0.0235(8)	0.0194(7)	0.0017(6)	0.0099(6)	0.0025(6)
C69	0.0278(8)	0.0265(8)	0.0197(7)	0.0037(6)	0.0131(6)	0.0004(6)
C70	0.0272(8)	0.0160(7)	0.0165(7)	0.0021(6)	0.0040(6)	-0.0001(6)
C71	0.0176(7)	0.0178(7)	0.0218(7)	-0.0004(6)	0.0033(6)	0.0012(6)
C72	0.0166(7)	0.0186(7)	0.0186(7)	0.0004(6)	0.0072(6)	-0.0016(6)
C73	0.0128(6)	0.0187(7)	0.0129(6)	0.0028(5)	0.0042(5)	-0.0004(5)
C74	0.0171(7)	0.0199(7)	0.0182(7)	0.0000(6)	0.0049(6)	0.0007(6)
C75	0.0168(7)	0.0303(8)	0.0204(7)	0.0040(6)	0.0075(6)	0.0055(6)
C76	0.0137(7)	0.0354(9)	0.0266(8)	0.0041(7)	0.0053(6)	-0.0035(6)
C77	0.0218(8)	0.0292(9)	0.0328(9)	-0.0064(7)	0.0073(7)	-0.0097(7)
C78	0.0200(7)	0.0238(8)	0.0241(8)	-0.0051(6)	0.0082(6)	-0.0034(6)
Ge1	0.0133(1)	0.0131(1)	0.0159(1)	0.0009(1)	0.0057(1)	0.0005(1)
N1	0.0237(7)	0.0227(7)	0.0224(7)	-0.0002(5)	0.0095(5)	-0.0025(5)
N2	0.0272(7)	0.0213(7)	0.0350(8)	-0.0060(6)	0.0065(6)	0.0000(6)
N3	0.0195(7)	0.0266(7)	0.0314(7)	0.0019(6)	0.0073(6)	0.0014(5)
N4	0.0238(7)	0.0263(7)	0.0238(7)	0.0025(6)	0.0092(5)	-0.0014(5)
N5	0.0280(7)	0.0226(7)	0.0292(7)	-0.0039(6)	0.0080(6)	0.0014(6)
N6	0.0193(7)	0.0229(7)	0.0320(7)	-0.0007(6)	0.0075(6)	0.0013(5)
C1	0.0142(7)	0.0149(7)	0.0200(7)	-0.0021(6)	0.0054(6)	-0.0007(5)
C2	0.0162(7)	0.0185(8)	0.0203(7)	0.0012(6)	0.0051(6)	-0.0016(6)
C3	0.0187(8)	0.0161(7)	0.0213(7)	0.0016(6)	0.0087(6)	0.0005(6)
C4	0.0159(7)	0.0182(7)	0.0204(8)	-0.0007(6)	0.0060(6)	-0.0004(6)
C5	0.0161(7)	0.0193(8)	0.0189(7)	0.0019(6)	0.0054(6)	0.0002(6)
C6	0.0193(8)	0.0146(7)	0.0200(7)	0.0001(6)	0.0085(6)	0.0006(5)

Table S10. Hydrogen coordinates and isotropic displacement parameters (Å^2) for ch1ppx359.

Atom	x	y	z	U(iso) [Ang^2]
H8	-0.03460	0.58120	0.82370	0.0310
H9	-0.02900	0.75730	0.84010	0.0380
H10	0.05390	0.83160	0.90600	0.0290
H11	0.13080	0.72980	0.95620	0.0290
H12	0.12530	0.55360	0.94150	0.0260
H14	0.09360	0.22280	0.90580	0.0290
H15	0.13180	0.13930	1.00890	0.0380
H16	0.13960	0.22150	1.11100	0.0340
H17	0.10780	0.38790	1.11100	0.0360
H18	0.06610	0.47100	1.00790	0.0320
H20	-0.04290	0.36180	0.74220	0.0270
H21	-0.13740	0.31970	0.71260	0.0340
H22	-0.18130	0.30540	0.79680	0.0380

H23	-0.13100	0.33080	0.91110	0.0380
H24	-0.03700	0.37520	0.94090	0.0290
H26	0.08700	0.19170	0.78920	0.0220
H27	0.13070	0.03660	0.78210	0.0280
H28	0.21300	0.03430	0.75290	0.0290
H29	0.25250	0.18650	0.73150	0.0280
H30	0.21050	0.34200	0.74080	0.0220
H32	0.16660	0.48280	0.68270	0.0270
H33	0.13680	0.57080	0.58000	0.0330
H34	0.04270	0.60890	0.53190	0.0350
H35	-0.02150	0.56050	0.58680	0.0370
H36	0.00790	0.47380	0.69040	0.0270
H38	0.14690	0.61440	0.78790	0.0270
H39	0.21520	0.70590	0.86920	0.0360
H40	0.27710	0.62110	0.95970	0.0380
H41	0.27400	0.44460	0.96860	0.0320
H42	0.20480	0.35210	0.88920	0.0230
H44	0.50140	0.52480	0.32410	0.0220
H45	0.52400	0.43830	0.42830	0.0290
H46	0.45380	0.38840	0.47380	0.0300
H47	0.36070	0.41970	0.41450	0.0260
H48	0.33750	0.50310	0.30970	0.0220
H50	0.31390	0.66860	0.28010	0.0280
H51	0.27280	0.82840	0.27820	0.0370
H52	0.30450	0.96740	0.23030	0.0380
H53	0.38030	0.95010	0.18910	0.0340
H54	0.42160	0.79010	0.18950	0.0260
H56	0.38050	0.37750	0.19920	0.0240
H57	0.30850	0.27740	0.13080	0.0330
H58	0.22590	0.35400	0.06680	0.0390
H59	0.21510	0.52970	0.06950	0.0370
H60	0.28750	0.63170	0.13510	0.0260
H62	0.39910	0.46180	0.01840	0.0230
H63	0.37350	0.29030	-0.00220	0.0300
H64	0.41320	0.16710	0.07930	0.0330
H65	0.47960	0.21300	0.18110	0.0300
H66	0.50520	0.38370	0.20260	0.0230
H68	0.50660	0.65110	0.02670	0.0240
H69	0.46650	0.75550	-0.06690	0.0280
H70	0.37650	0.81790	-0.08650	0.0250
H71	0.32620	0.77600	-0.01210	0.0240
H72	0.36480	0.67030	0.08070	0.0210
H74	0.55810	0.45990	0.10510	0.0220

H75	0.64990	0.49940	0.11220	0.0260
H76	0.68990	0.65040	0.16330	0.0310
H77	0.63950	0.75980	0.21200	0.0340
H78	0.54760	0.72150	0.20550	0.0270

Crystallographic Data for $(PPN)_2Sn(CN)_6$ (**3**)

Table S11. Crystal data and structure refinement for ch1ppx330_0m.

Identification code	ch1ppx330_0m	
Empirical formula	$C_{78}H_{60}N_8P_4Sn$	
Formula weight	1351.91	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.4512(2) Å	α = 90°.
	b = 24.5682(6) Å	β = 102.2838(10)°.
	c = 13.2178(3) Å	γ = 90°.
Volume	3316.20(13) $Å^3$	
Z	2	
Density (calculated)	1.354 Mg/m^3	
Absorption coefficient	4.376 mm^{-1}	
F(000)	1388	
Crystal size	0.300 x 0.250 x 0.200 mm^3	
Theta range for data collection	3.598 to 66.685°.	
Index ranges	-12<=h<=12, -29<=k<=29, -15<=l<=15	
Reflections collected	46511	
Independent reflections	5872 [R(int) = 0.0425]	
Completeness to theta	= 66.685°	99.9 %
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5872 / 0 / 412	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R_1 = 0.0258, wR_2 = 0.0595	
R indices (all data)	R_1 = 0.0300, wR_2 = 0.0612	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.559 and -0.425 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for ch1ppx330_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	0	0	0	20(1)
P(1)	3882(1)	2917(1)	410(1)	14(1)
P(2)	1505(1)	3574(1)	387(1)	14(1)
N(1)	1325(2)	216(1)	2511(2)	38(1)
N(2)	2934(2)	75(1)	-670(2)	34(1)
N(3)	-489(2)	1352(1)	-203(2)	39(1)
N(4)	2489(2)	3075(1)	615(1)	17(1)
C(1)	917(2)	122(1)	1665(2)	26(1)
C(2)	1942(2)	72(1)	-432(2)	26(1)
C(3)	-309(2)	886(1)	-133(2)	25(1)
C(4)	4147(2)	2208(1)	723(1)	16(1)
C(5)	5406(2)	1991(1)	863(2)	22(1)
C(6)	5600(2)	1436(1)	1006(2)	24(1)
C(7)	4544(2)	1096(1)	1012(2)	25(1)
C(8)	3298(2)	1310(1)	898(2)	27(1)
C(9)	3093(2)	1865(1)	752(2)	23(1)
C(10)	4043(2)	2992(1)	-918(1)	16(1)
C(11)	3813(2)	2545(1)	-1586(2)	22(1)
C(12)	3867(2)	2606(1)	-2618(2)	26(1)
C(13)	4137(2)	3110(1)	-2996(2)	26(1)
C(14)	4359(2)	3555(1)	-2338(2)	22(1)
C(15)	4318(2)	3499(1)	-1302(2)	19(1)
C(16)	5214(2)	3286(1)	1206(2)	16(1)
C(17)	6152(2)	3687(1)	2862(2)	28(1)
C(18)	5102(2)	3438(1)	2201(2)	24(1)
C(19)	7299(2)	3789(1)	2535(2)	24(1)
C(20)	7411(2)	3644(1)	1548(2)	23(1)
C(21)	6381(2)	3389(1)	887(2)	19(1)
C(22)	2030(2)	4139(1)	-280(2)	18(1)
C(23)	1734(2)	4160(1)	-1359(2)	23(1)
C(24)	2266(2)	4565(1)	-1871(2)	30(1)
C(25)	3084(2)	4951(1)	-1307(2)	36(1)
C(26)	3352(2)	4943(1)	-237(2)	36(1)
C(27)	2845(2)	4533(1)	288(2)	26(1)
C(28)	1197(2)	3827(1)	1591(2)	17(1)
C(29)	700(2)	4346(1)	1678(2)	22(1)

C(30)	469(2)	4522(1)	2619(2)	27(1)
C(31)	717(2)	4183(1)	3468(2)	29(1)
C(32)	1186(2)	3662(1)	3383(2)	32(1)
C(33)	1428(2)	3484(1)	2448(2)	25(1)
C(34)	-39(2)	3346(1)	-381(1)	16(1)
C(35)	-993(2)	3724(1)	-828(2)	19(1)
C(36)	-2184(2)	3544(1)	-1404(2)	22(1)
C(37)	-2435(2)	2989(1)	-1521(2)	24(1)
C(38)	-1498(2)	2614(1)	-1057(2)	27(1)
C(39)	-295(2)	2793(1)	-494(2)	22(1)

Table S13. Bond lengths [Å] and angles [°] for ch1ppx330_0m.

Sn(1)-C(3)	2.203(2)	C(4)-C(5)	1.394(3)	C(22)-C(27)	1.397(3)
Sn(1)-C(3)#1	2.203(2)	C(5)-C(6)	1.387(3)	C(23)-C(24)	1.385(3)
Sn(1)-C(1)	2.225(2)	C(6)-C(7)	1.386(3)	C(24)-C(25)	1.384(4)
Sn(1)-C(1)#1	2.225(2)	C(7)-C(8)	1.383(3)	C(25)-C(26)	1.382(4)
Sn(1)-C(2)#1	2.229(2)	C(8)-C(9)	1.388(3)	C(26)-C(27)	1.390(3)
Sn(1)-C(2)	2.229(2)	C(10)-C(11)	1.396(3)	C(28)-C(29)	1.390(3)
P(1)-N(4)	1.5850(16)	C(10)-C(15)	1.399(3)	C(28)-C(33)	1.390(3)
P(1)-C(16)	1.7993(19)	C(11)-C(12)	1.385(3)	C(29)-C(30)	1.386(3)
P(1)-C(4)	1.7998(19)	C(12)-C(13)	1.386(3)	C(30)-C(31)	1.378(3)
P(1)-C(10)	1.8085(19)	C(13)-C(14)	1.386(3)	C(31)-C(32)	1.383(3)
P(2)-N(4)	1.5869(16)	C(14)-C(15)	1.386(3)	C(32)-C(33)	1.384(3)
P(2)-C(22)	1.7930(19)	C(16)-C(21)	1.396(3)	C(34)-C(39)	1.388(3)
P(2)-C(28)	1.8003(19)	C(16)-C(18)	1.396(3)	C(34)-C(35)	1.397(3)
P(2)-C(34)	1.8026(19)	C(17)-C(19)	1.381(3)	C(35)-C(36)	1.385(3)
N(1)-C(1)	1.134(3)	C(17)-C(18)	1.390(3)	C(36)-C(37)	1.390(3)
N(2)-C(2)	1.146(3)	C(19)-C(20)	1.380(3)	C(37)-C(38)	1.388(3)
N(3)-C(3)	1.159(3)	C(20)-C(21)	1.384(3)	C(38)-C(39)	1.389(3)
C(4)-C(9)	1.393(3)	C(22)-C(23)	1.395(3)		

		C(3)-Sn(1)-C(2)	91.58(8)
		C(3)#1-Sn(1)-C(2)	88.42(8)
C(3)-Sn(1)-C(3)#1	180.0	C(1)-Sn(1)-C(2)	91.08(8)
C(3)-Sn(1)-C(1)	88.35(8)	C(1)#1-Sn(1)-C(2)	88.92(8)
C(3)#1-Sn(1)-C(1)	91.65(8)	C(2)#1-Sn(1)-C(2)	180.0
C(3)-Sn(1)-C(1)#1	91.65(8)	N(4)-P(1)-C(16)	113.70(9)
C(3)#1-Sn(1)-C(1)#1	88.35(8)	N(4)-P(1)-C(4)	107.41(9)
C(1)-Sn(1)-C(1)#1	180.0	C(16)-P(1)-C(4)	106.94(9)
C(3)-Sn(1)-C(2)#1	88.43(8)	N(4)-P(1)-C(10)	114.83(8)
C(3)#1-Sn(1)-C(2)#1	91.57(8)	C(16)-P(1)-C(10)	107.24(9)
C(1)-Sn(1)-C(2)#1	88.92(8)	C(4)-P(1)-C(10)	106.20(9)
C(1)#1-Sn(1)-C(2)#1	91.08(8)	N(4)-P(2)-C(22)	116.00(9)

N(4)-P(2)-C(28)	109.20(9)	C(17)-C(18)-C(16)	119.88(19)
C(22)-P(2)-C(28)	107.33(9)	C(20)-C(19)-C(17)	120.20(19)
N(4)-P(2)-C(34)	109.50(9)	C(19)-C(20)-C(21)	120.16(19)
C(22)-P(2)-C(34)	107.12(9)	C(20)-C(21)-C(16)	120.25(19)
C(28)-P(2)-C(34)	107.36(9)	C(23)-C(22)-C(27)	120.11(18)
P(1)-N(4)-P(2)137.54(11)		C(23)-C(22)-P(2)	120.38(15)
N(1)-C(1)-Sn(1)	174.89(19)	C(27)-C(22)-P(2)	119.22(16)
N(2)-C(2)-Sn(1)	175.73(19)	C(24)-C(23)-C(22)	120.0(2)
N(3)-C(3)-Sn(1)	179.1(2)	C(25)-C(24)-C(23)	119.7(2)
C(9)-C(4)-C(5)	119.70(18)	C(26)-C(25)-C(24)	120.6(2)
C(9)-C(4)-P(1)	120.52(15)	C(25)-C(26)-C(27)	120.4(2)
C(5)-C(4)-P(1)	119.61(15)	C(26)-C(27)-C(22)	119.1(2)
C(6)-C(5)-C(4)	119.99(19)	C(29)-C(28)-C(33)	119.37(18)
C(7)-C(6)-C(5)	120.06(19)	C(29)-C(28)-P(2)	121.99(15)
C(8)-C(7)-C(6)	120.14(19)	C(33)-C(28)-P(2)	118.61(15)
C(7)-C(8)-C(9)	120.21(19)	C(30)-C(29)-C(28)	120.03(19)
C(8)-C(9)-C(4)	119.87(19)	C(31)-C(30)-C(29)	120.2(2)
C(11)-C(10)-C(15)	119.46(18)	C(30)-C(31)-C(32)	120.2(2)
C(11)-C(10)-P(1)	119.72(15)	C(31)-C(32)-C(33)	119.9(2)
C(15)-C(10)-P(1)	120.70(15)	C(32)-C(33)-C(28)	120.3(2)
C(12)-C(11)-C(10)	120.01(19)	C(39)-C(34)-C(35)	120.06(18)
C(11)-C(12)-C(13)	120.42(19)	C(39)-C(34)-P(2)	119.54(15)
C(14)-C(13)-C(12)	119.81(19)	C(35)-C(34)-P(2)	120.35(14)
C(13)-C(14)-C(15)	120.41(19)	C(36)-C(35)-C(34)	119.88(18)
C(14)-C(15)-C(10)	119.88(19)	C(35)-C(36)-C(37)	119.93(19)
C(21)-C(16)-C(18)	119.25(18)	C(38)-C(37)-C(36)	120.19(19)
C(21)-C(16)-P(1)	122.15(15)	C(37)-C(38)-C(39)	120.02(19)
C(18)-C(16)-P(1)	118.46(15)	C(34)-C(39)-C(38)	119.88(19)
C(19)-C(17)-C(18)	120.3(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z

Table S14. Anisotropic displacement parameters ($Å^2x10^3$) for ch1ppx330_0m. The anisotropic displacement factor exponent takes the form:$-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	26(1)	15(1)	19(1)	0(1)	7(1)	2(1)
P(1)	13(1)	14(1)	17(1)	0(1)	3(1)	0(1)
P(2)	13(1)	14(1)	16(1)	0(1)	3(1)	-1(1)
N(1)	52(1)	29(1)	31(1)	1(1)	3(1)	7(1)

N(2)	38(1)	35(1)	29(1)	-2(1)	9(1)	1(1)
N(3)	55(1)	34(1)	33(1)	1(1)	18(1)	6(1)
N(4)	14(1)	16(1)	21(1)	2(1)	4(1)	0(1)
C(1)	32(1)	21(1)	25(1)	-1(1)	8(1)	4(1)
C(2)	34(1)	22(1)	22(1)	0(1)	7(1)	-2(1)
C(3)	39(1)	19(1)	21(1)	-2(1)	14(1)	-4(1)
C(4)	20(1)	15(1)	14(1)	1(1)	2(1)	-1(1)
C(5)	20(1)	21(1)	24(1)	1(1)	4(1)	0(1)
C(6)	26(1)	21(1)	25(1)	2(1)	1(1)	7(1)
C(7)	35(1)	16(1)	21(1)	3(1)	0(1)	3(1)
C(8)	30(1)	19(1)	33(1)	3(1)	5(1)	-6(1)
C(9)	19(1)	20(1)	29(1)	1(1)	5(1)	-1(1)
C(10)	12(1)	20(1)	16(1)	2(1)	2(1)	1(1)
C(11)	21(1)	21(1)	22(1)	0(1)	2(1)	-5(1)
C(12)	26(1)	28(1)	22(1)	-6(1)	0(1)	-4(1)
C(13)	20(1)	39(1)	17(1)	4(1)	1(1)	3(1)
C(14)	17(1)	26(1)	25(1)	8(1)	5(1)	3(1)
C(15)	14(1)	20(1)	22(1)	1(1)	4(1)	2(1)
C(16)	15(1)	12(1)	21(1)	1(1)	1(1)	0(1)
C(17)	30(1)	33(1)	21(1)	-6(1)	3(1)	-4(1)
C(18)	20(1)	29(1)	23(1)	-1(1)	7(1)	-5(1)
C(19)	21(1)	20(1)	29(1)	-2(1)	-2(1)	-2(1)
C(20)	16(1)	19(1)	32(1)	-1(1)	6(1)	-2(1)
C(21)	18(1)	18(1)	23(1)	-2(1)	6(1)	0(1)
C(22)	14(1)	16(1)	25(1)	3(1)	6(1)	1(1)
C(23)	19(1)	24(1)	26(1)	6(1)	6(1)	4(1)
C(24)	29(1)	31(1)	34(1)	16(1)	12(1)	11(1)
C(25)	38(1)	22(1)	56(2)	16(1)	25(1)	5(1)
C(26)	34(1)	20(1)	56(2)	-2(1)	17(1)	-10(1)
C(27)	24(1)	22(1)	33(1)	-3(1)	9(1)	-5(1)
C(28)	11(1)	21(1)	17(1)	-3(1)	2(1)	-2(1)
C(29)	21(1)	20(1)	24(1)	-2(1)	4(1)	0(1)
C(30)	24(1)	25(1)	32(1)	-10(1)	5(1)	1(1)
C(31)	23(1)	43(1)	22(1)	-10(1)	5(1)	2(1)
C(32)	31(1)	44(1)	20(1)	5(1)	6(1)	9(1)
C(33)	25(1)	26(1)	23(1)	3(1)	6(1)	6(1)
C(34)	14(1)	20(1)	15(1)	-2(1)	3(1)	-1(1)
C(35)	16(1)	18(1)	24(1)	1(1)	5(1)	0(1)
C(36)	17(1)	26(1)	22(1)	2(1)	2(1)	3(1)
C(37)	17(1)	30(1)	24(1)	-6(1)	-1(1)	-2(1)
C(38)	22(1)	22(1)	34(1)	-7(1)	0(1)	-2(1)
C(39)	18(1)	19(1)	26(1)	-2(1)	1(1)	1(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3)
for ch1ppx330_0m.

	x	y	z	U(eq)
H(5)	6130	2225	860	26
H(6)	6458	1289	1101	29
H(7)	4677	714	1093	30
H(8)	2580	1076	921	33
H(9)	2236	2011	673	28
H(11)	3620	2200	-1333	26
H(12)	3717	2301	-3069	31
H(13)	4171	3150	-3705	31
H(14)	4539	3901	-2599	27
H(15)	4477	3805	-853	23
H(17)	6080	3786	3543	34
H(18)	4311	3373	2425	28
H(19)	8012	3959	2990	29
H(20)	8197	3720	1323	27
H(21)	6468	3284	213	23
H(23)	1167	3895	-1743	27
H(24)	2071	4578	-2606	37
H(25)	3464	5224	-1658	44
H(26)	3886	5219	141	43
H(27)	3050	4521	1023	31
H(29)	519	4579	1092	26
H(30)	139	4878	2679	32
H(31)	566	4307	4113	35
H(32)	1342	3426	3967	38
H(33)	1752	3127	2391	30
H(35)	-826	4102	-736	23
H(36)	-2827	3800	-1720	26
H(37)	-3250	2867	-1918	29
H(38)	-1680	2236	-1126	32
H(39)	352	2536	-186	26

Crystallographic Data for (PPN)Ag(CN)$_2$

Table S16. Crystal data and structure refinement for ch1ppx350_0m.

Identification code	ch1ppx350_0m	
Empirical formula	C40 H33 Ag N4 P2	
Formula weight	739.51	
Temperature	99.98 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 2_1/n 1	
Unit cell dimensions	a = 9.4853(3) Å	α= 90°.
	b = 20.0306(7) Å	β= 102.969(2)°.
	c = 19.0715(6) Å	γ = 90°.
Volume	3531.1(2) Å^3	
Z	4	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	5.695 mm^{-1}	
F(000)	1512	
Crystal size	0.21 x 0.19 x 0.13 mm^3	
Theta range for data collection	3.244 to 66.859°.	

Index ranges	-11<=h<=11, -23<=k<=23, -22<=l<=22
Reflections collected	46631
Independent reflections	6255 [R(int) = 0.1787]
Completeness to theta = 66.859°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.5533
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6255 / 0 / 425
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R_1 = 0.0623, wR_2 = 0.1113
R indices (all data)	R_1 = 0.1067, wR_2 = 0.1261
Extinction coefficient	n/a
Largest diff. peak and hole	0.545 and -0.627 e.Å^{-3}

Table S17. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for ch1ppx350_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag(1)	4803(1)	1843(1)	3427(1)	32(1)
P(2)	765(2)	6816(1)	5508(1)	16(1)
P(1)	1982(2)	6959(1)	4244(1)	17(1)
N(3)	1995(5)	6897(2)	5072(2)	18(1)
C(33)	1376(6)	6251(3)	6243(3)	16(1)
C(26)	-2160(6)	6835(3)	4773(3)	22(1)
C(3)	2516(6)	6181(3)	3910(3)	17(1)
C(27)	403(6)	7613(3)	5888(3)	18(1)
C(38)	2850(6)	6162(3)	6512(3)	20(1)
C(25)	-3350(6)	6551(3)	4315(3)	26(1)
C(15)	3235(6)	7597(3)	4134(3)	20(1)
C(22)	-824(6)	5827(3)	4727(3)	20(1)
C(14)	-201(6)	7846(3)	3754(3)	26(1)
C(28)	1126(6)	8181(3)	5752(3)	22(1)
C(4)	2902(6)	5641(3)	4377(3)	22(1)
C(16)	3120(7)	7913(3)	3464(3)	26(2)
C(21)	-894(6)	6475(3)	4983(3)	18(1)
C(34)	371(7)	5918(3)	6560(3)	23(1)
C(23)	-2020(6)	5543(3)	4274(3)	25(1)
N(2)	5623(7)	325(3)	3651(3)	45(2)
C(35)	864(6)	5500(3)	7144(3)	23(1)
C(12)	-2432(7)	7611(4)	2921(3)	35(2)
C(5)	3233(7)	5031(3)	4112(4)	31(2)

N(1)	3487(6)	3299(3)	3341(3)	44(2)
C(13)	-1542(7)	8054(3)	3379(3)	34(2)
C(29)	881(7)	8784(3)	6055(3)	26(2)
C(8)	2501(7)	6101(3)	3186(3)	27(2)
C(24)	-3287(6)	5906(3)	4067(3)	25(1)
C(9)	265(6)	7194(3)	3679(3)	21(1)
C(30)	-98(7)	8812(3)	6495(3)	29(2)
C(37)	3334(7)	5746(3)	7108(3)	25(1)
C(36)	2329(7)	5413(3)	7416(3)	22(1)
C(32)	-596(6)	7644(3)	6329(3)	25(1)
C(10)	-625(6)	6751(3)	3218(3)	23(1)
C(2)	5363(8)	848(4)	3564(3)	32(2)
C(6)	3170(7)	4947(3)	3388(4)	32(2)
C(31)	-830(6)	8246(3)	6633(3)	29(2)
C(20)	4314(7)	7788(3)	4718(3)	27(2)
C(19)	5295(7)	8295(3)	4629(4)	33(2)
C(17)	4100(7)	8410(3)	3389(4)	34(2)
C(7)	2826(6)	5488(3)	2928(3)	29(2)
C(11)	-1969(7)	6969(3)	2835(3)	33(2)
C(1)	4008(7)	2806(4)	3359(4)	32(2)
C(18)	5168(8)	8603(3)	3972(4)	39(2)
C(39)	7257(10)	29(5)	5391(5)	80(3)
N(4)	9729(13)	514(4)	5943(6)	146(5)
C(40)	8631(13)	306(4)	5694(5)	83(4)

Table S18. Bond lengths [Å] and angles [°] for ch1ppx350_0m.

Ag(1)-C(2)	2.064(8)	C(26)-C(21)	1.381(8)
Ag(1)-C(1)	2.064(8)	C(3)-C(4)	1.396(8)
P(2)-N(3)	1.585(4)	C(3)-C(8)	1.387(8)
P(2)-C(33)	1.795(6)	C(27)-C(28)	1.383(8)
P(2)-C(27)	1.816(6)	C(27)-C(32)	1.402(8)
P(2)-C(21)	1.800(6)	C(38)-H(38)	0.9500
P(1)-N(3)	1.582(4)	C(38)-C(37)	1.401(8)
P(1)-C(3)	1.799(6)	C(25)-H(25)	0.9500
P(1)-C(15)	1.790(6)	C(25)-C(24)	1.381(8)
P(1)-C(9)	1.801(6)	C(15)-C(16)	1.407(8)
C(33)-C(38)	1.388(7)	C(15)-C(20)	1.387(8)
C(33)-C(34)	1.406(8)	C(22)-H(22)	0.9500
C(26)-H(26)	0.9500	C(22)-C(21)	1.394(7)
C(26)-C(25)	1.385(8)	C(22)-C(23)	1.385(8)

C(14)-H(14)	0.9500	C(9)-C(10)	1.393(8)
C(14)-C(13)	1.376(8)	C(30)-H(30)	0.9500
C(14)-C(9)	1.397(8)	C(30)-C(31)	1.384(8)
C(28)-H(28)	0.9500	C(37)-H(37)	0.9500
C(28)-C(29)	1.381(8)	C(37)-C(36)	1.396(8)
C(4)-H(4)	0.9500	C(36)-H(36)	0.9500
C(4)-C(5)	1.384(8)	C(32)-H(32)	0.9500
C(16)-H(16)	0.9500	C(32)-C(31)	1.377(8)
C(16)-C(17)	1.390(8)	C(10)-H(10)	0.9500
C(34)-H(34)	0.9500	C(10)-C(11)	1.390(8)
C(34)-C(35)	1.388(8)	C(6)-H(6)	0.9500
C(23)-H(23)	0.9500	C(6)-C(7)	1.387(9)
C(23)-C(24)	1.385(8)	C(31)-H(31)	0.9500
N(2)-C(2)	1.082(8)	C(20)-H(20)	0.9500
C(35)-H(35)	0.9500	C(20)-C(19)	1.413(8)
C(35)-C(36)	1.381(8)	C(19)-H(19)	0.9500
C(12)-H(12)	0.9500	C(19)-C(18)	1.376(9)
C(12)-C(13)	1.389(9)	C(17)-H(17)	0.9500
C(12)-C(11)	1.381(9)	C(17)-C(18)	1.381(9)
C(5)-H(5)	0.9500	C(7)-H(7)	0.9500
C(5)-C(6)	1.380(9)	C(11)-H(11)	0.9500
N(1)-C(1)	1.101(8)	C(18)-H(18)	0.9500
C(13)-H(13)	0.9500	C(39)-H(39A)	0.9800
C(29)-H(29)	0.9500	C(39)-H(39B)	0.9800
C(29)-C(30)	1.386(8)	C(39)-H(39C)	0.9800
C(8)-H(8)	0.9500	C(39)-C(40)	1.416(13)
C(8)-C(7)	1.384(8)	N(4)-C(40)	1.123(13)
C(24)-H(24)	0.9500		

		C(38)-C(33)-C(34)	120.3(5)
C(2)-Ag(1)-C(1)	172.0(3)	C(34)-C(33)-P(2)	120.3(4)
N(3)-P(2)-C(33)	109.1(3)	C(25)-C(26)-H(26)	120.0
N(3)-P(2)-C(27)	110.3(3)	C(21)-C(26)-H(26)	120.0
N(3)-P(2)-C(21)	113.7(2)	C(21)-C(26)-C(25)	120.0(6)
C(33)-P(2)-C(27)	107.4(3)	C(4)-C(3)-P(1)	120.0(4)
C(33)-P(2)-C(21)	106.5(3)	C(8)-C(3)-P(1)	120.7(5)
C(21)-P(2)-C(27)	109.6(3)	C(8)-C(3)-C(4)	119.2(5)
N(3)-P(1)-C(3)	110.2(3)	C(28)-C(27)-P(2)	120.1(4)
N(3)-P(1)-C(15)	108.5(3)	C(28)-C(27)-C(32)	120.4(5)
N(3)-P(1)-C(9)	114.9(3)	C(32)-C(27)-P(2)	119.5(4)
C(3)-P(1)-C(9)	107.7(3)	C(33)-C(38)-H(38)	120.2
C(15)-P(1)-C(3)	109.3(3)	C(33)-C(38)-C(37)	119.7(6)
C(15)-P(1)-C(9)	106.2(3)	C(37)-C(38)-H(38)	120.2
P(1)-N(3)-P(2)	133.6(3)	C(26)-C(25)-H(25)	119.7
C(38)-C(33)-P(2)	119.4(4)	C(24)-C(25)-C(26)	120.6(6)

C(24)-C(25)-H(25)	119.7	C(7)-C(8)-C(3)	120.2(6)
C(16)-C(15)-P(1)	120.6(5)	C(7)-C(8)-H(8)	119.9
C(20)-C(15)-P(1)	119.5(5)	C(25)-C(24)-C(23)	119.7(6)
C(20)-C(15)-C(16)	119.9(6)	C(25)-C(24)-H(24)	120.1
C(21)-C(22)-H(22)	119.8	C(23)-C(24)-H(24)	120.1
C(23)-C(22)-H(22)	119.8	C(14)-C(9)-P(1)	116.6(5)
C(23)-C(22)-C(21)	120.3(6)	C(10)-C(9)-P(1)	123.4(5)
C(13)-C(14)-H(14)	119.8	C(10)-C(9)-C(14)	119.9(5)
C(13)-C(14)-C(9)	120.4(6)	C(29)-C(30)-H(30)	119.5
C(9)-C(14)-H(14)	119.8	C(31)-C(30)-C(29)	121.0(6)
C(27)-C(28)-H(28)	119.8	C(31)-C(30)-H(30)	119.5
C(29)-C(28)-C(27)	120.3(5)	C(38)-C(37)-H(37)	120.2
C(29)-C(28)-H(28)	119.8	C(36)-C(37)-C(38)	119.6(6)
C(3)-C(4)-H(4)	120.0	C(36)-C(37)-H(37)	120.2
C(5)-C(4)-C(3)	120.0(6)	C(35)-C(36)-C(37)	120.5(6)
C(5)-C(4)-H(4)	120.0	C(35)-C(36)-H(36)	119.8
C(15)-C(16)-H(16)	120.1	C(37)-C(36)-H(36)	119.8
C(17)-C(16)-C(15)	119.9(6)	C(27)-C(32)-H(32)	120.5
C(17)-C(16)-H(16)	120.1	C(31)-C(32)-C(27)	119.1(6)
C(26)-C(21)-P(2)	123.9(4)	C(31)-C(32)-H(32)	120.5
C(26)-C(21)-C(22)	119.5(5)	C(9)-C(10)-H(10)	120.4
C(22)-C(21)-P(2)	116.4(4)	C(11)-C(10)-C(9)	119.1(6)
C(33)-C(34)-H(34)	120.3	C(11)-C(10)-H(10)	120.4
C(35)-C(34)-C(33)	119.5(6)	N(2)-C(2)-Ag(1)	177.4(7)
C(35)-C(34)-H(34)	120.3	C(5)-C(6)-H(6)	120.4
C(22)-C(23)-H(23)	120.1	C(5)-C(6)-C(7)	119.3(6)
C(22)-C(23)-C(24)	119.9(6)	C(7)-C(6)-H(6)	120.4
C(24)-C(23)-H(23)	120.1	C(30)-C(31)-H(31)	119.9
C(34)-C(35)-H(35)	119.8	C(32)-C(31)-C(30)	120.1(6)
C(36)-C(35)-C(34)	120.4(6)	C(32)-C(31)-H(31)	119.9
C(36)-C(35)-H(35)	119.8	C(15)-C(20)-H(20)	120.4
C(13)-C(12)-H(12)	119.8	C(15)-C(20)-C(19)	119.2(6)
C(11)-C(12)-H(12)	119.8	C(19)-C(20)-H(20)	120.4
C(11)-C(12)-C(13)	120.3(6)	C(20)-C(19)-H(19)	119.8
C(4)-C(5)-H(5)	119.6	C(18)-C(19)-C(20)	120.4(6)
C(6)-C(5)-C(4)	120.7(6)	C(18)-C(19)-H(19)	119.8
C(6)-C(5)-H(5)	119.6	C(16)-C(17)-H(17)	119.9
C(14)-C(13)-C(12)	119.6(6)	C(18)-C(17)-C(16)	120.2(6)
C(14)-C(13)-H(13)	120.2	C(18)-C(17)-H(17)	119.9
C(12)-C(13)-H(13)	120.2	C(8)-C(7)-C(6)	120.5(6)
C(28)-C(29)-H(29)	120.5	C(8)-C(7)-H(7)	119.7
C(28)-C(29)-C(30)	119.1(6)	C(6)-C(7)-H(7)	119.7
C(30)-C(29)-H(29)	120.5	C(12)-C(11)-C(10)	120.6(6)
C(3)-C(8)-H(8)	119.9	C(12)-C(11)-H(11)	119.7

C(10)-C(11)-H(11)	119.7	H(39A)-C(39)-H(39C)	109.5
N(1)-C(1)-Ag(1)	174.1(6)	H(39B)-C(39)-H(39C)	109.5
C(19)-C(18)-C(17)	120.4(6)	C(40)-C(39)-H(39A)	109.5
C(19)-C(18)-H(18)	119.8	C(40)-C(39)-H(39B)	109.5
C(17)-C(18)-H(18)	119.8	C(40)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39B)	109.5	N(4)-C(40)-C(39)	178.5(11)

Symmetry transformations used to generate equivalent atoms: -

Table S19. Anisotropic displacement parameters ($Å^2x10^3$) for ch1ppx350_0m. The anisotropic displacement factor exponent takes the form:$-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	32(1)	34(1)	27(1)	-2(1)	3(1)	-4(1)
P(2)	14(1)	16(1)	17(1)	1(1)	4(1)	-1(1)
P(1)	18(1)	16(1)	17(1)	0(1)	7(1)	0(1)
N(3)	15(2)	24(3)	17(2)	0(2)	8(2)	-1(2)
C(33)	16(3)	16(3)	14(3)	-5(2)	1(2)	0(2)
C(26)	22(3)	23(3)	21(3)	-5(3)	4(2)	0(3)
C(3)	8(3)	20(3)	26(3)	-4(3)	7(2)	1(2)
C(27)	16(3)	19(3)	18(3)	-3(3)	2(2)	3(2)
C(38)	20(3)	21(3)	20(3)	-8(3)	6(3)	0(3)
C(25)	16(3)	35(4)	25(3)	-2(3)	3(3)	2(3)
C(15)	23(3)	18(3)	21(3)	0(3)	10(3)	2(3)
C(22)	26(3)	14(3)	20(3)	6(2)	5(3)	6(2)
C(14)	24(4)	25(3)	26(3)	4(3)	2(3)	-3(3)
C(28)	18(3)	24(3)	25(3)	1(3)	7(2)	-1(3)
C(4)	16(3)	28(3)	26(3)	-3(3)	10(3)	0(3)
C(16)	27(4)	29(4)	25(3)	2(3)	12(3)	-2(3)
C(21)	21(3)	17(3)	21(3)	-2(3)	10(3)	0(2)
C(34)	23(3)	25(3)	20(3)	-8(3)	6(3)	0(3)
C(23)	29(4)	25(3)	21(3)	-4(3)	5(3)	-8(3)
N(2)	57(5)	48(4)	33(4)	-10(3)	15(3)	-14(4)
C(35)	25(3)	24(3)	23(3)	2(3)	12(3)	-3(3)
C(12)	24(4)	56(5)	23(4)	12(3)	-2(3)	11(3)
C(5)	35(4)	13(3)	47(4)	-2(3)	17(3)	4(3)
N(1)	33(4)	39(4)	57(4)	-5(3)	5(3)	-8(3)
C(13)	25(4)	39(4)	38(4)	16(3)	9(3)	8(3)
C(29)	28(4)	21(3)	29(4)	-1(3)	8(3)	-3(3)
C(8)	25(4)	28(4)	30(4)	-2(3)	12(3)	1(3)
C(24)	17(3)	28(3)	28(4)	3(3)	-2(3)	-4(3)

C(9)	22(3)	22(3)	17(3)	7(3)	2(2)	2(3)
C(30)	33(4)	18(3)	31(4)	-7(3)	-4(3)	4(3)
C(37)	25(3)	25(3)	20(3)	1(3)	-5(3)	1(3)
C(36)	30(4)	15(3)	21(3)	1(3)	2(3)	2(3)
C(32)	21(3)	27(3)	29(4)	-3(3)	10(3)	-2(3)
C(10)	22(3)	30(4)	17(3)	2(3)	6(2)	0(3)
C(2)	32(4)	47(5)	17(3)	-9(3)	6(3)	-11(4)
C(6)	26(4)	24(4)	49(4)	-13(3)	18(3)	-9(3)
C(31)	26(3)	27(4)	39(4)	-11(3)	18(3)	3(3)
C(20)	27(4)	24(3)	30(4)	-7(3)	7(3)	-5(3)
C(19)	32(4)	34(4)	38(4)	-19(3)	17(3)	-11(3)
C(17)	42(4)	25(3)	41(4)	4(3)	23(4)	-6(3)
C(7)	17(3)	44(4)	27(4)	-8(3)	6(3)	-7(3)
C(11)	26(4)	44(5)	27(3)	-4(3)	3(3)	-8(3)
C(1)	18(4)	47(5)	32(4)	-3(4)	7(3)	-15(3)
C(18)	46(5)	24(4)	56(5)	-4(4)	29(4)	-11(3)
C(39)	67(7)	101(8)	64(6)	14(6)	-5(5)	-18(6)
N(4)	173(11)	30(5)	170(11)	4(6)	-97(9)	-16(6)
C(40)	119(10)	27(5)	73(7)	-8(5)	-40(7)	10(5)

Table S20. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for ch1ppx350_0m.

	x	y	z	U(eq)		x	y	z	U(eq)
H(26)	-2214	7278	4943	27	H(35)	189	5271	7357	28
H(38)	3527	6383	6293	24	H(12)	-3363	7751	2666	42
H(25)	-4217	6801	4171	31	H(5)	3505	4667	4433	37
H(22)	48	5579	4865	24	H(13)	-1857	8497	3433	40
H(14)	411	8148	4066	31	H(29)	1377	9175	5962	31
H(28)	1795	8156	5450	26	H(8)	2267	6469	2866	32
H(4)	2938	5692	4876	27	H(24)	-4109	5713	3756	30
H(16)	2374	7788	3065	31	H(30)	-269	9225	6706	35
H(34)	-637	5979	6377	27	H(37)	4341	5690	7302	30
H(23)	-1971	5099	4105	30	H(36)	2655	5126	7815	27
					H(32)	-1103	7256	6417	30

H(10)	-318	6306	3166	27
H(6)	3360	4522	3206	38
H(31)	-1495	8273	6937	35
H(20)	4392	7581	5173	33
H(19)	6047	8424	5024	40
H(17)	4035	8617	2934	41
H(7)	2814	5437	2431	35

H(11)	-2575	6673	2511	40
H(18)	5818	8950	3920	47
H(39A)		6805	278	4956	120
H(39B)		6643	57	5740	120
H(39C)		7370	-439	5266	120

Infrared spectra

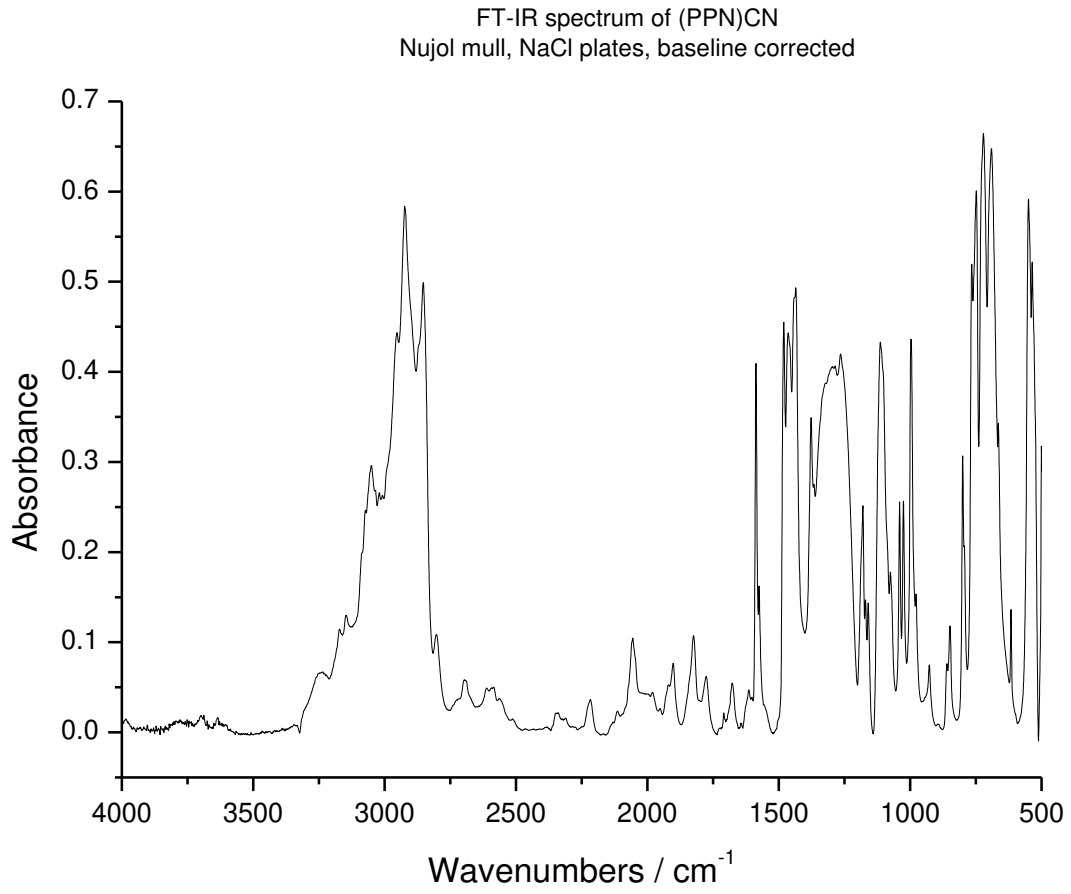

Fig. SI1a. IR spectrum (PPN)CN as nujol mulls in the range 4000 to 500 cm^{-1}.

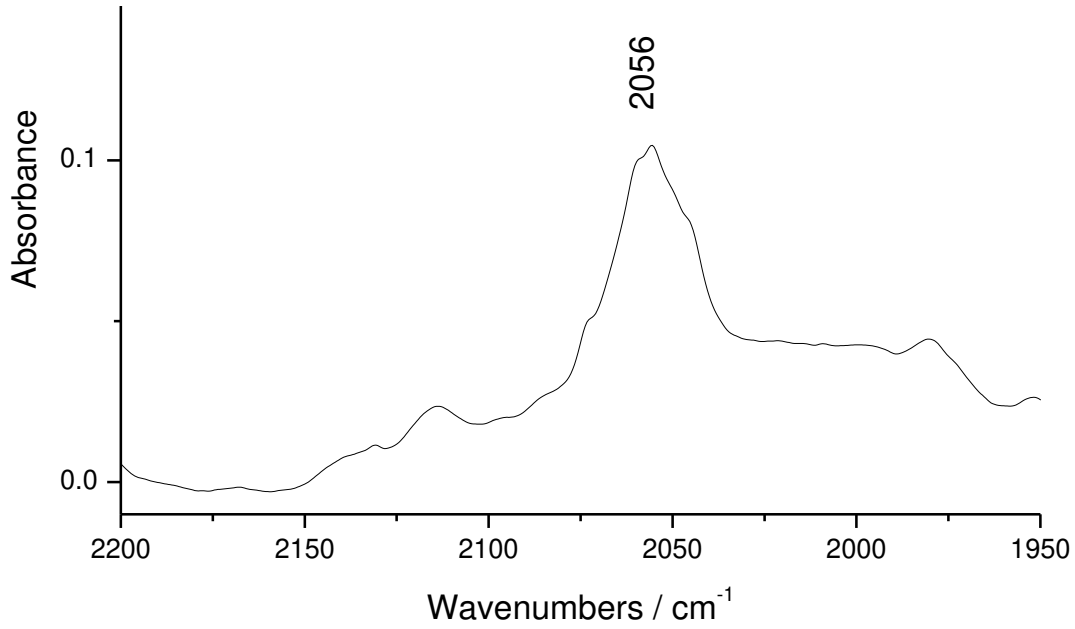

Fig. SI1b. IR spectrum (PPN)CN as nujol mulls in the range 2200 to 1950 cm^{-1}; expansion of spectrum shown in Fig.S1a.

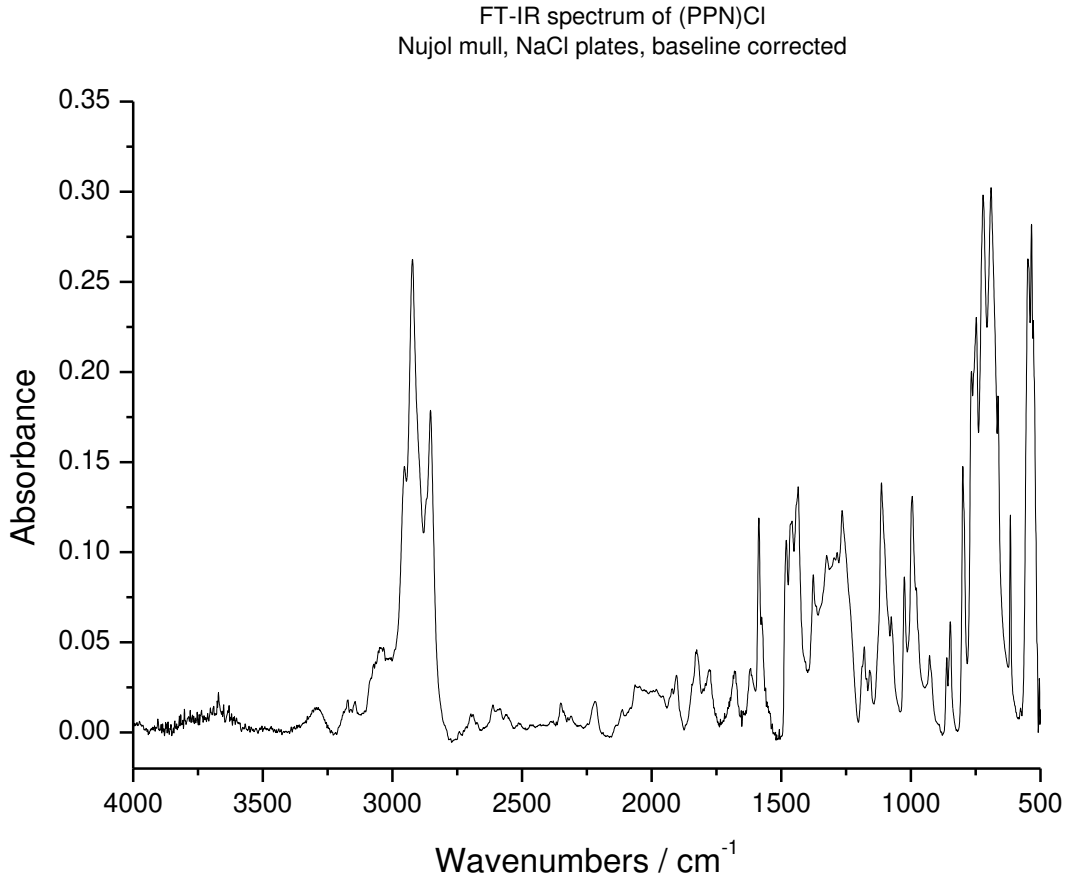

Fig. SI1c. IR spectrum (PPN)Cl as nujol mull in the range 4000 to 500 cm^{-1}.

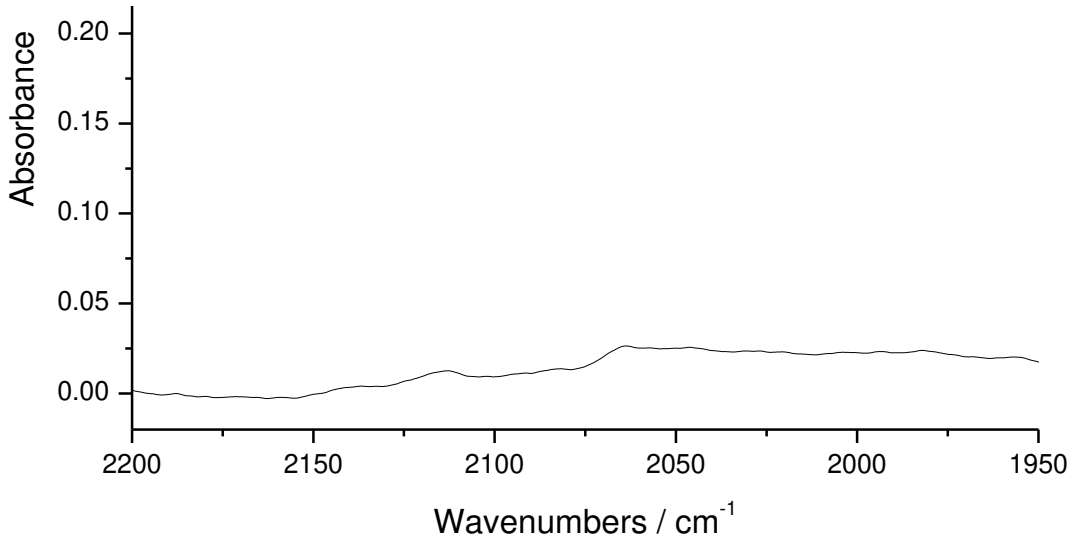

Fig. SI1d. IR spectrum (PPN)Cl as nujol mull, expanded range 2200 to 1950 cm^{-1} of spectrum shown in Fig.SI1c for comparison with spectrum shown in Fig. SI1b.

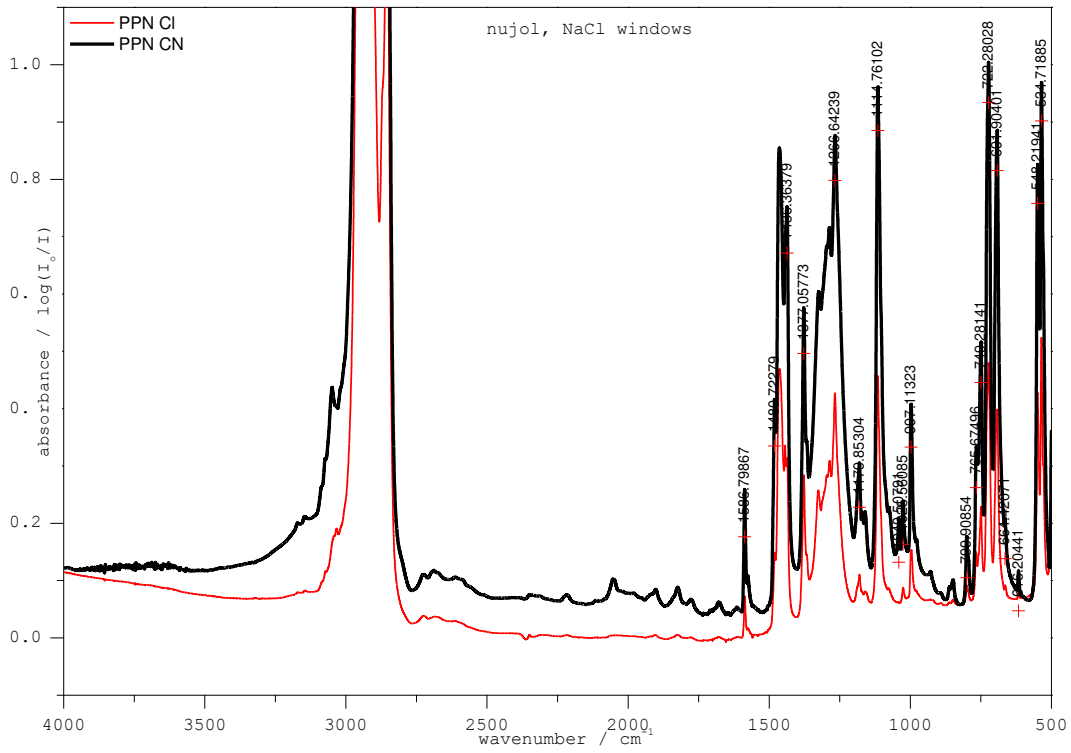

Fig. SI1. IR spectral series of (PPN)Cl & (PPN)CN nujol mulls in the range 4000 to 500 cm^{-1}.

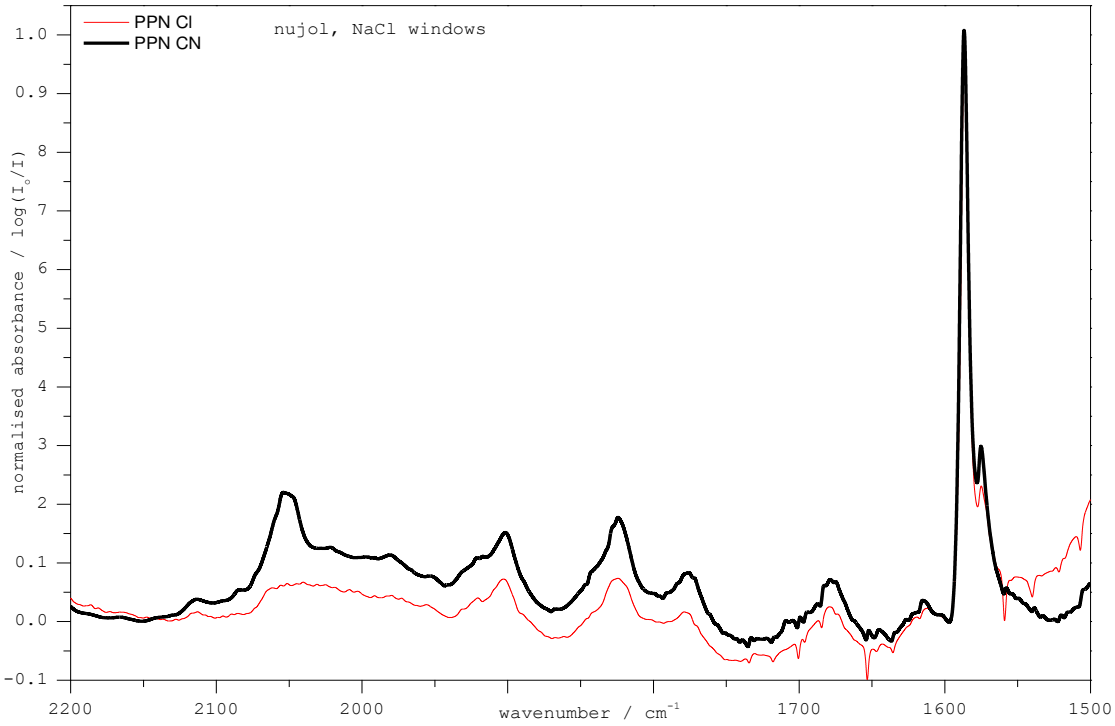

Fig. SI2. 2200 to 1500 cm^{-1} range of spectral series shown in Fig. SI1, normalised to the band at 1587 cm^{-1} showing the CN stretch at 2052 cm^{-1}.

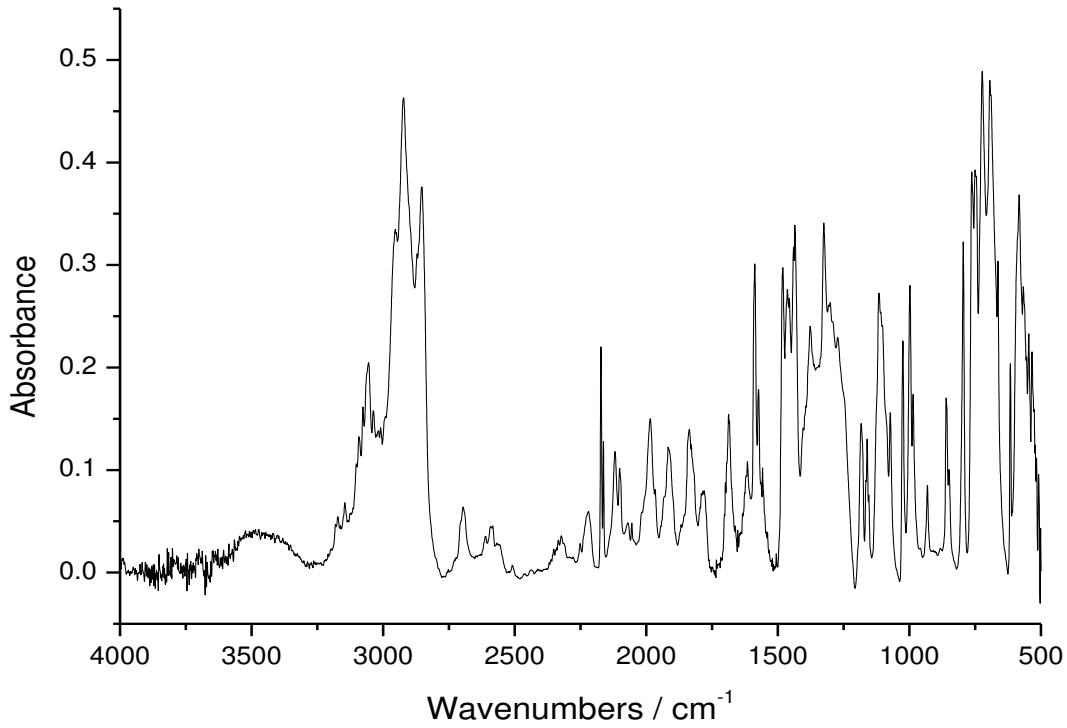

Fig. SI3. FTIR spectrum of $(PPN)_2Si(CN)_6$ as nujol mull in the range 4000 to 500 cm^{-1}.

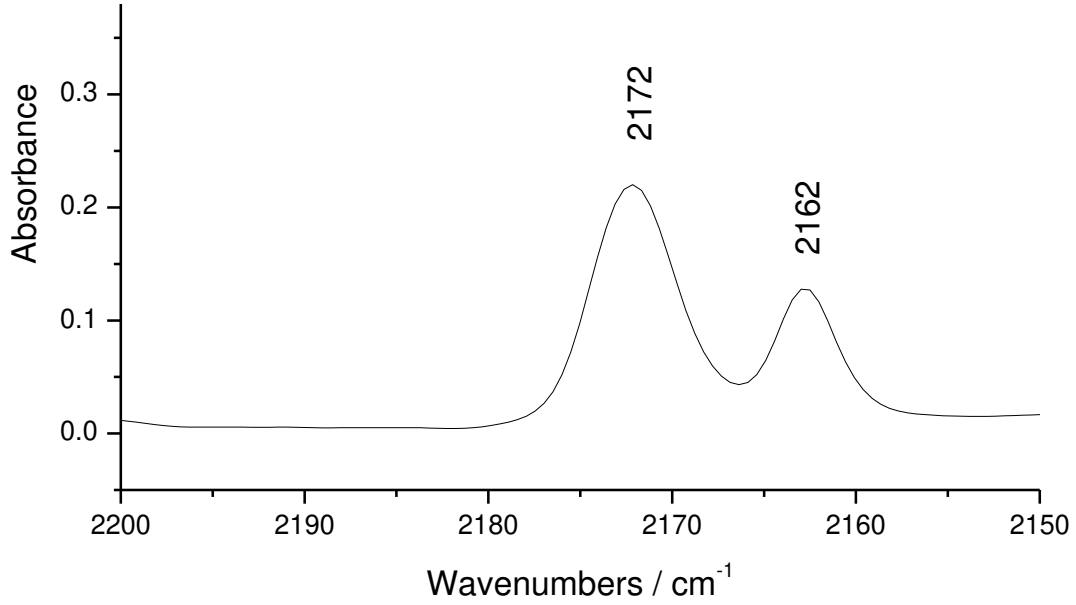

Fig. SI4. 2200-2150 cm^{-1} range of spectrum shown in Fig. SI3.

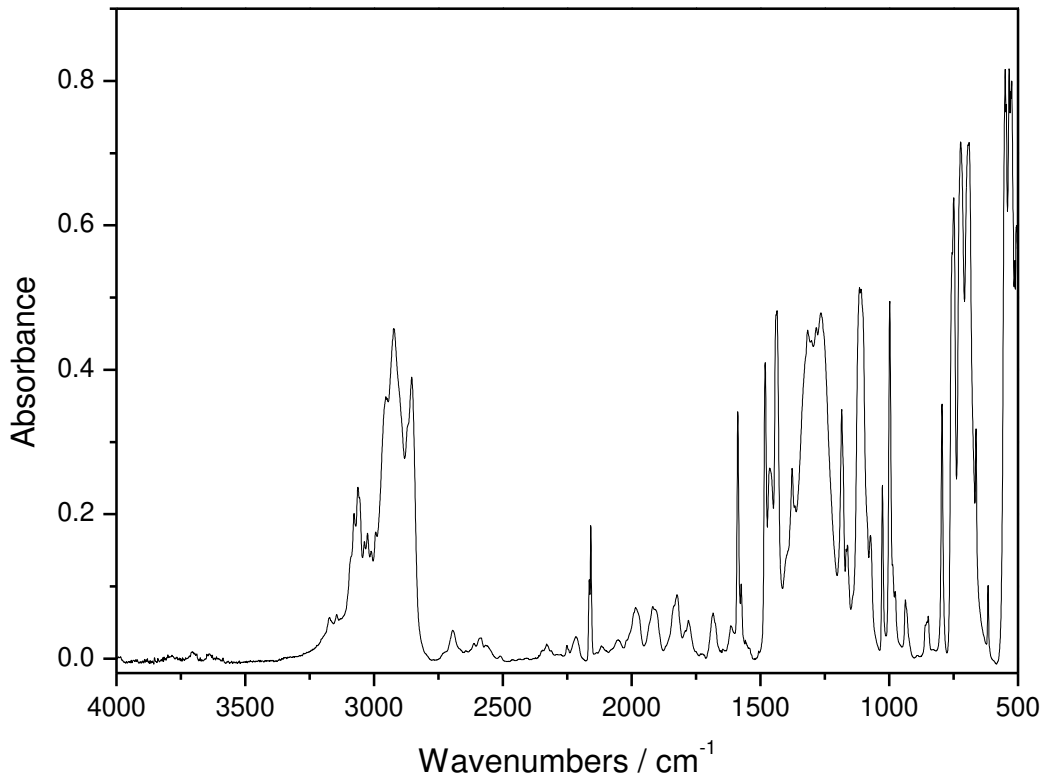

Fig. SI5. FTIR spectrum of $(PPN)_2Ge(CN)_6$ as nujol mull in the range 4000 to 500 cm^{-1}.

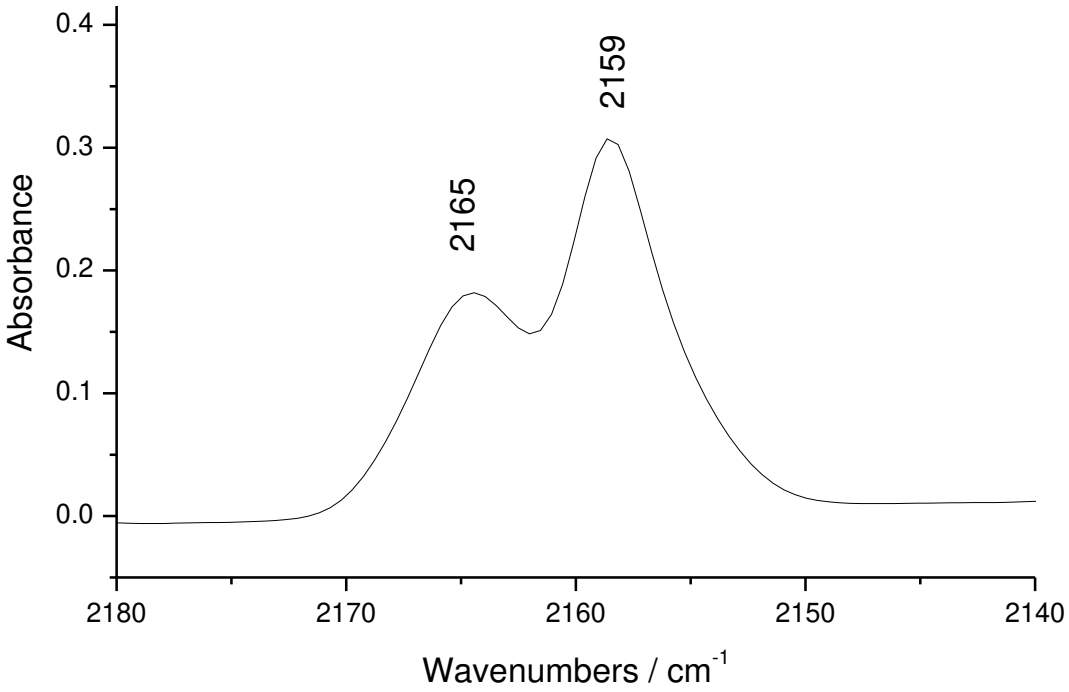

Fig. SI6. 2180 to 2140 cm^{-1} range of spectrum shown in Fig. SI5.

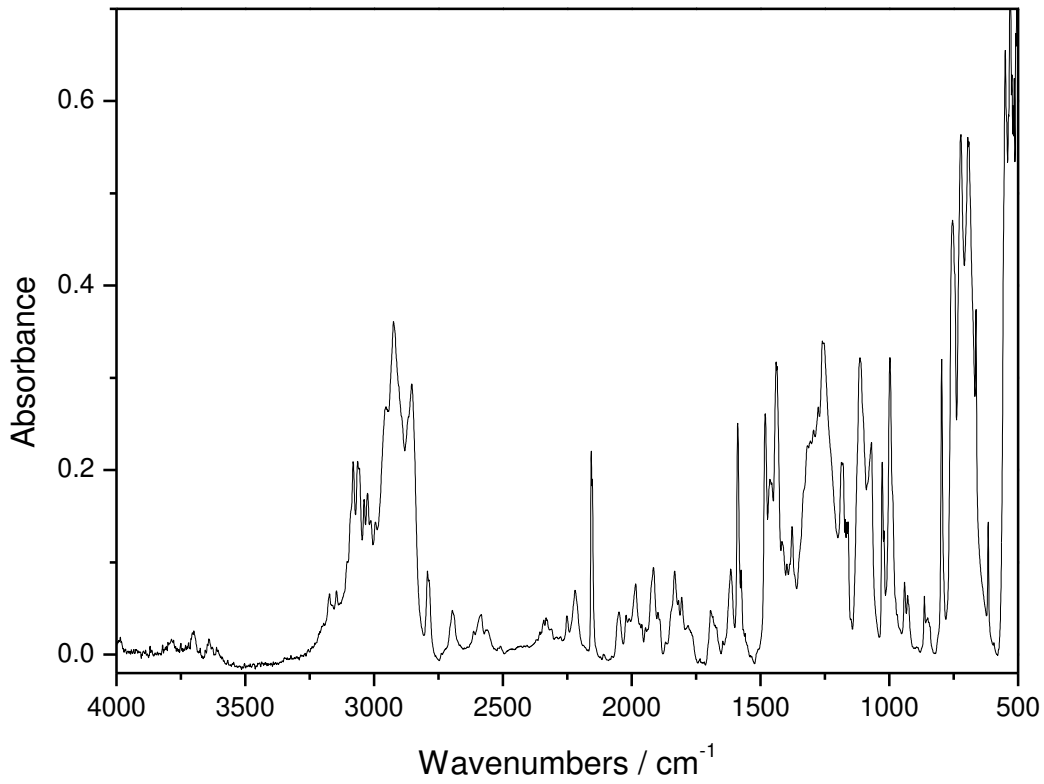

Fig. SI7. FTIR spectrum of $(PPN)_2Sn(CN)_6$ as nujol mull in the range 4000 to 500 cm^{-1}.

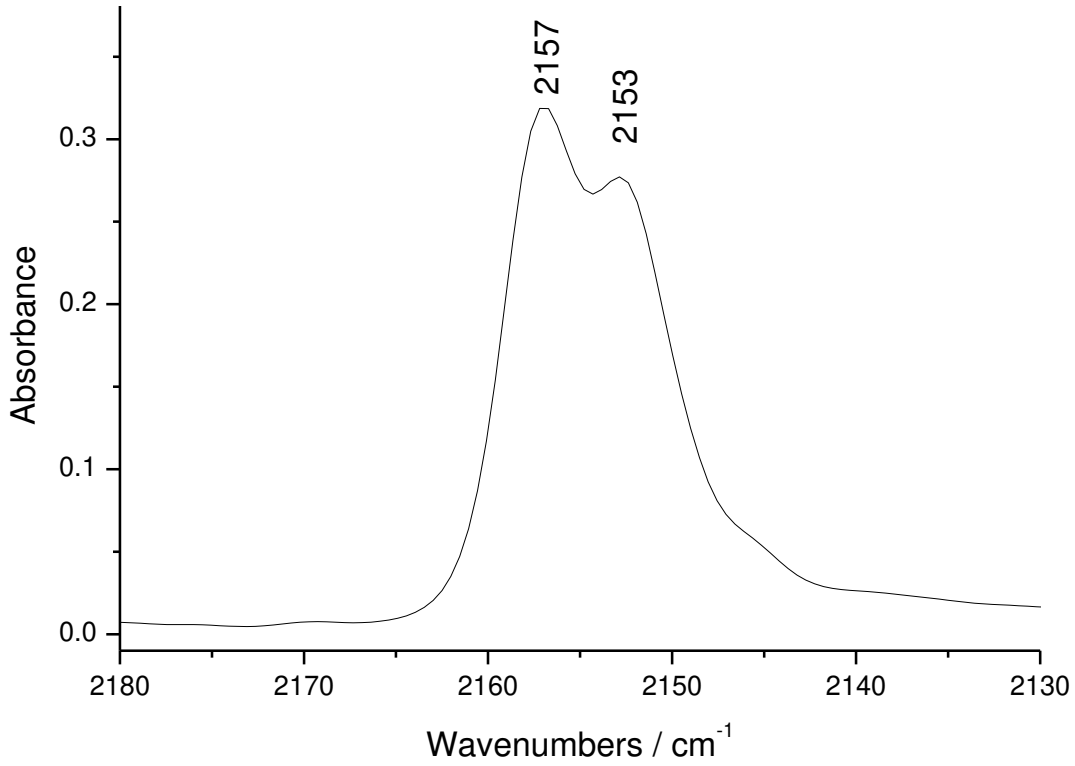

Fig. SI8. 2180 to 2130 cm^{-1} range of spectrum shown in Fig. S7

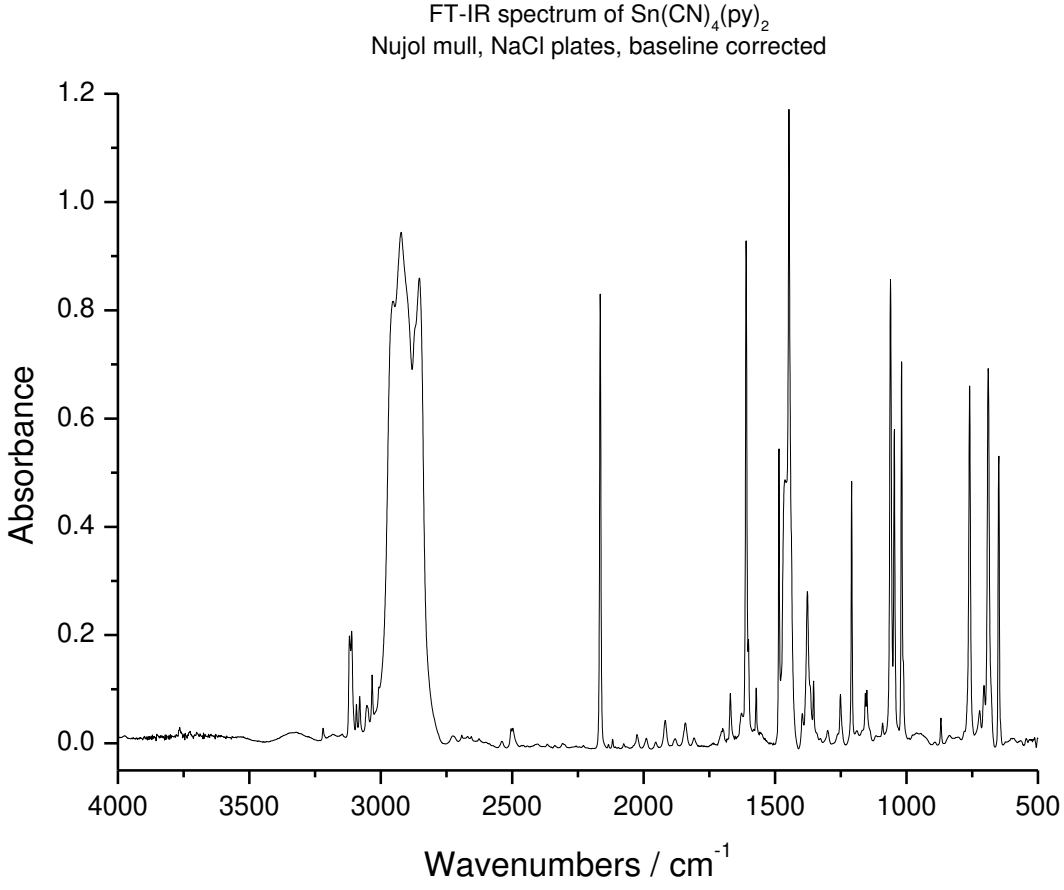

Fig. SI9a. FTIR spectrum of $Sn(CN)_4(py)_2$ as nujol mull in the range 4000 to 500 cm^{-1}.

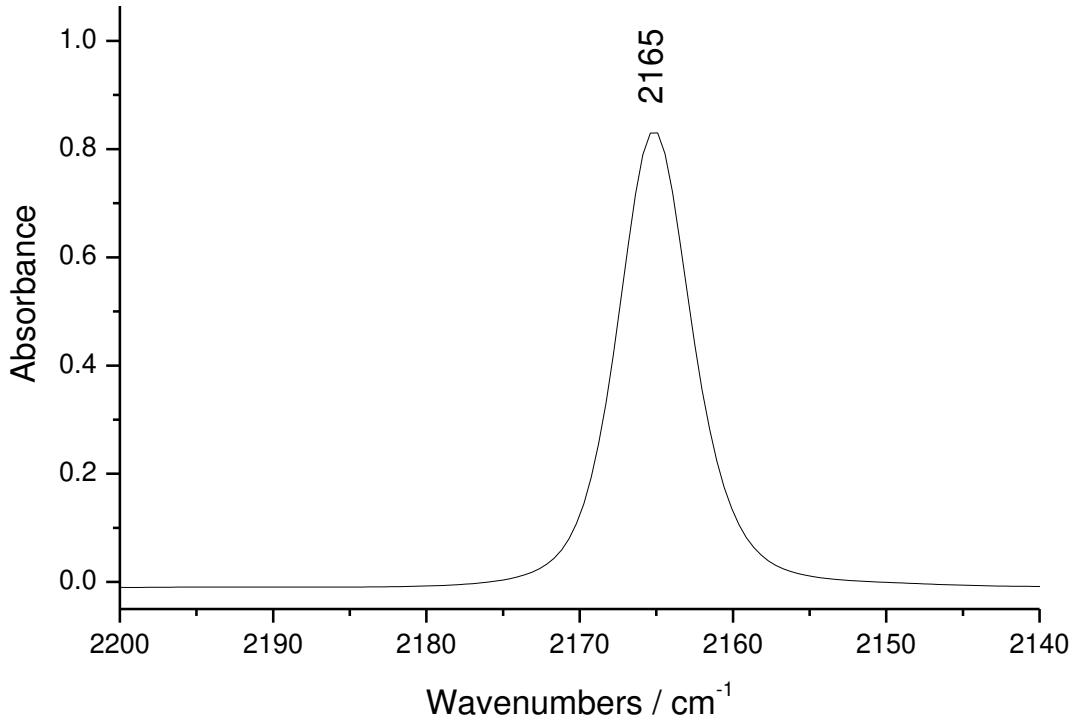

Fig. SI9b. 2200 to 2140 cm^{-1} range of spectrum shown in Fig.SI9a.

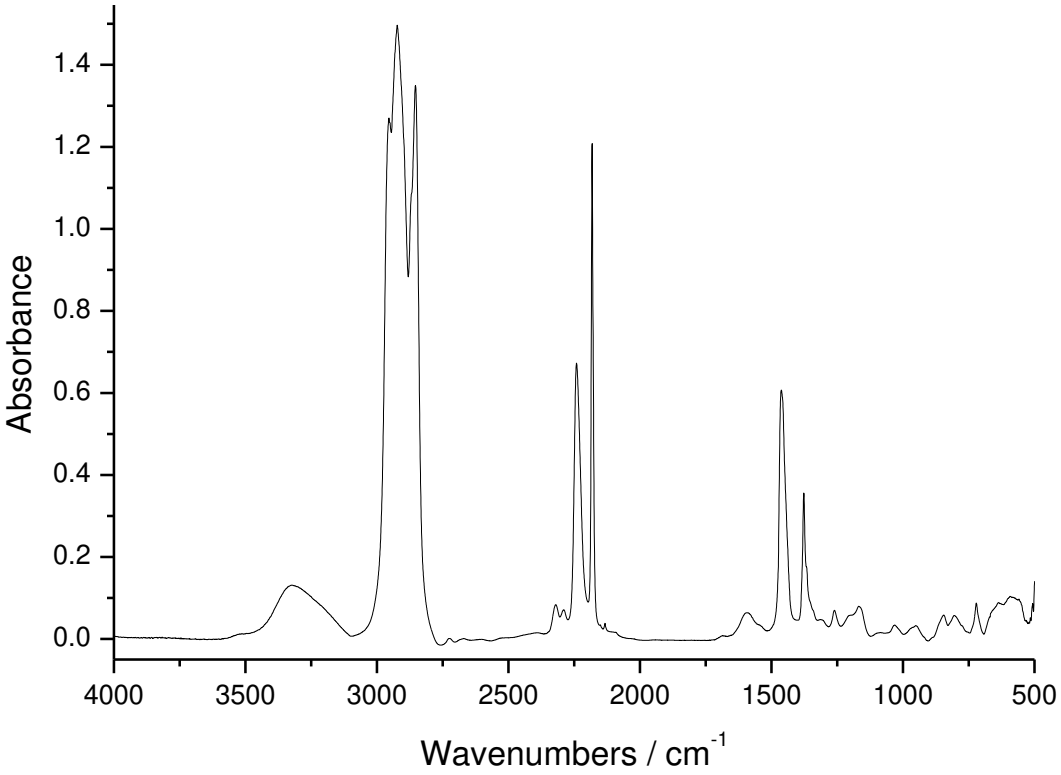

Fig. S10a. FTIR spectrum of a mull of $Sn(CN)_4(MeCN)_2$ in the range 4000 to 500 cm^{-1}.

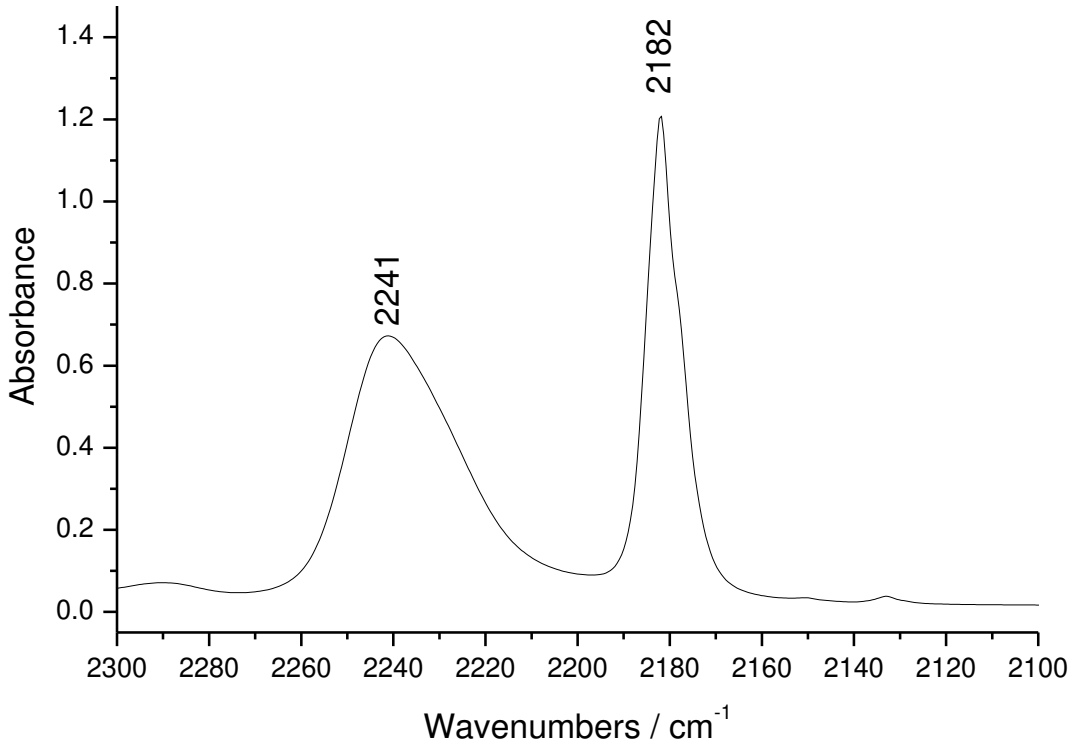

Fig. S10b. 2300 to 2100 cm^{-1} range of spectrum shown in Fig.SI10a.

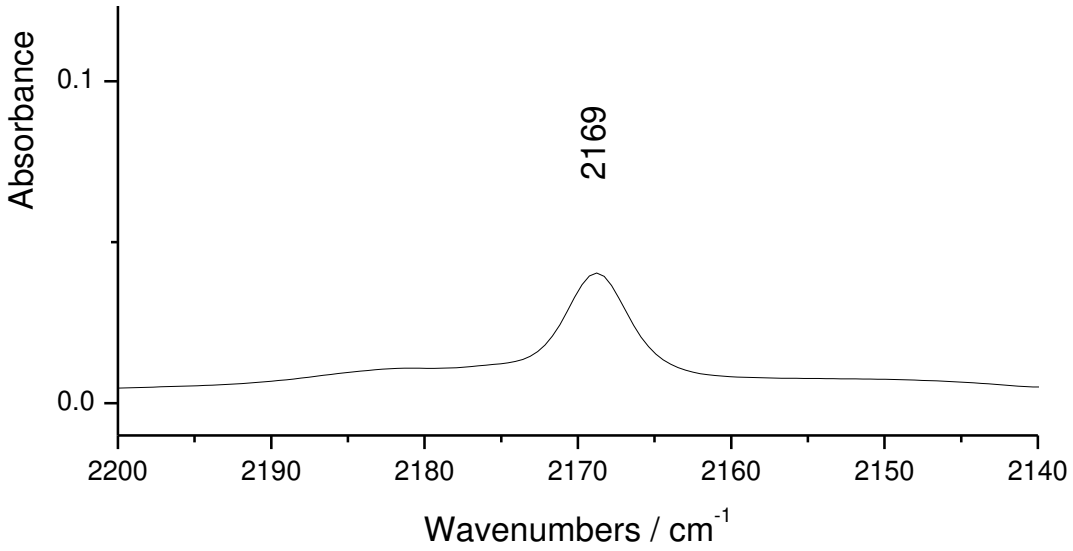

Fig. S11a. 2200 to 2140 cm^{-1} range of FTIR spectrum of $(PPN)_2Si(CN)_6$ in MeCN.

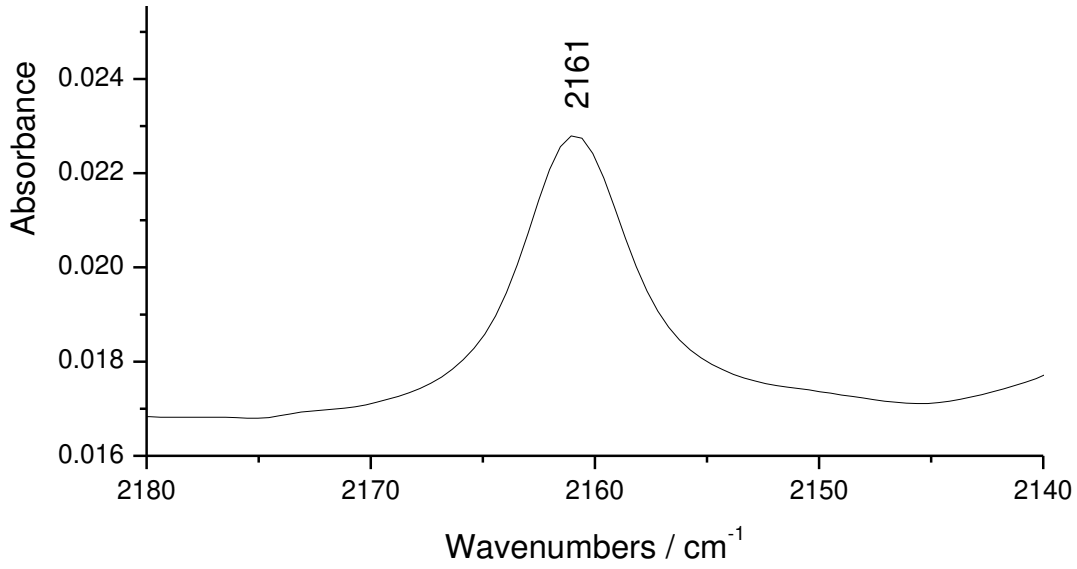

Fig. S11b. 2180 to 2140 cm^{-1} range of FTIR spectrum of $(PPN)_2Ge(CN)_6$ in MeCN.

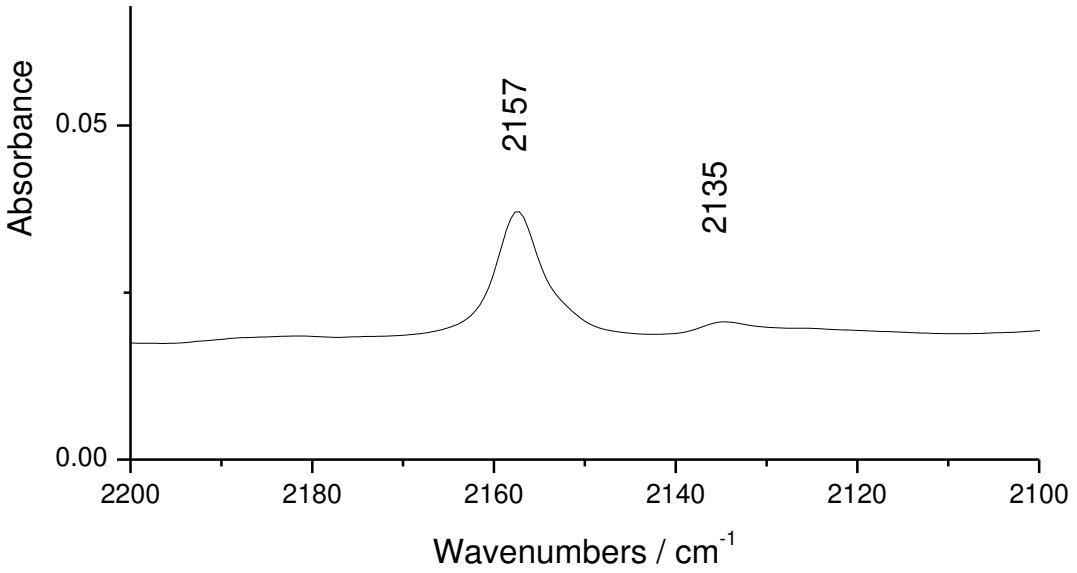

Fig. S12. 2180 to 2100 cm^{-1} range of FTIR spectrum of $(PPN)_2Sn(CN)_6$ in MeCN.

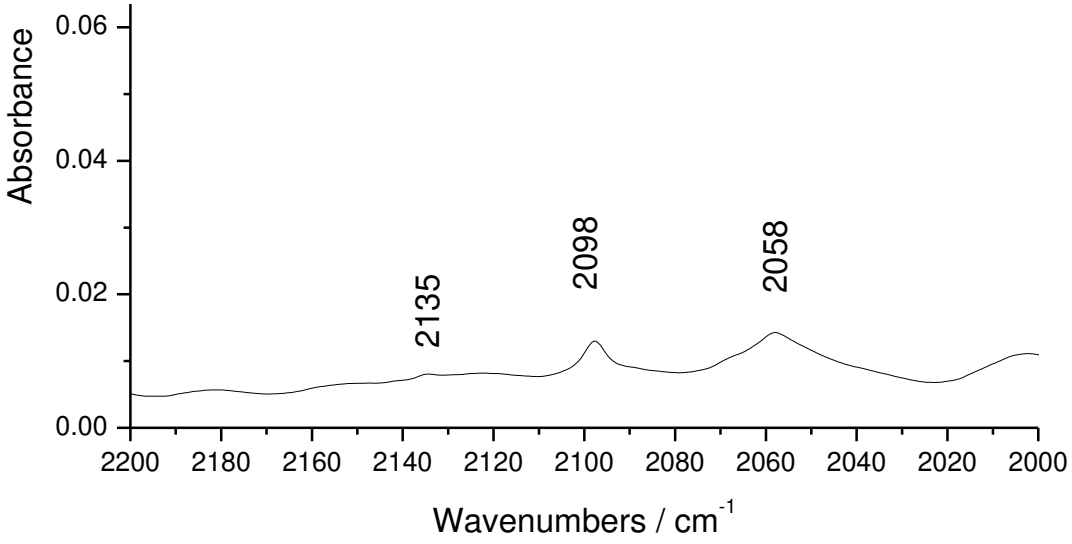

Fig. S13. 2200 to 2000 cm^{-1} range of FTIR spectrum of (PPN)CN in MeCN.

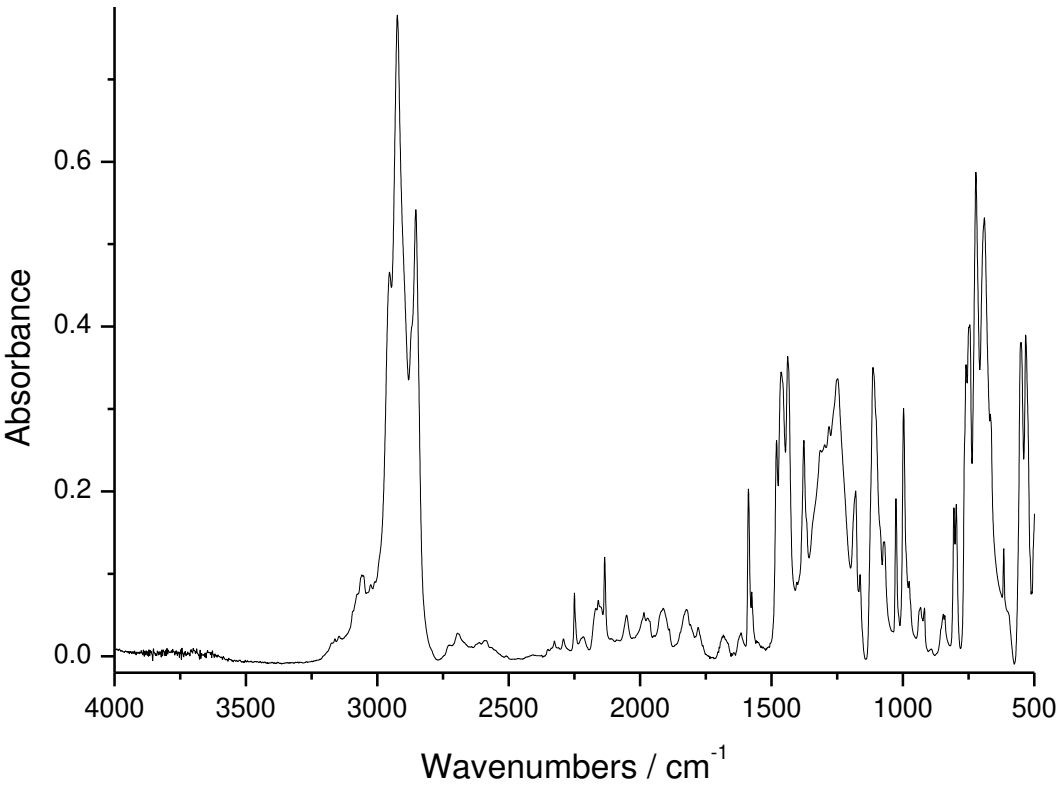

Fig. S13A. FTIR spectrum of $(PPN)Ag(CN)_2$.MeCN nujol mull.

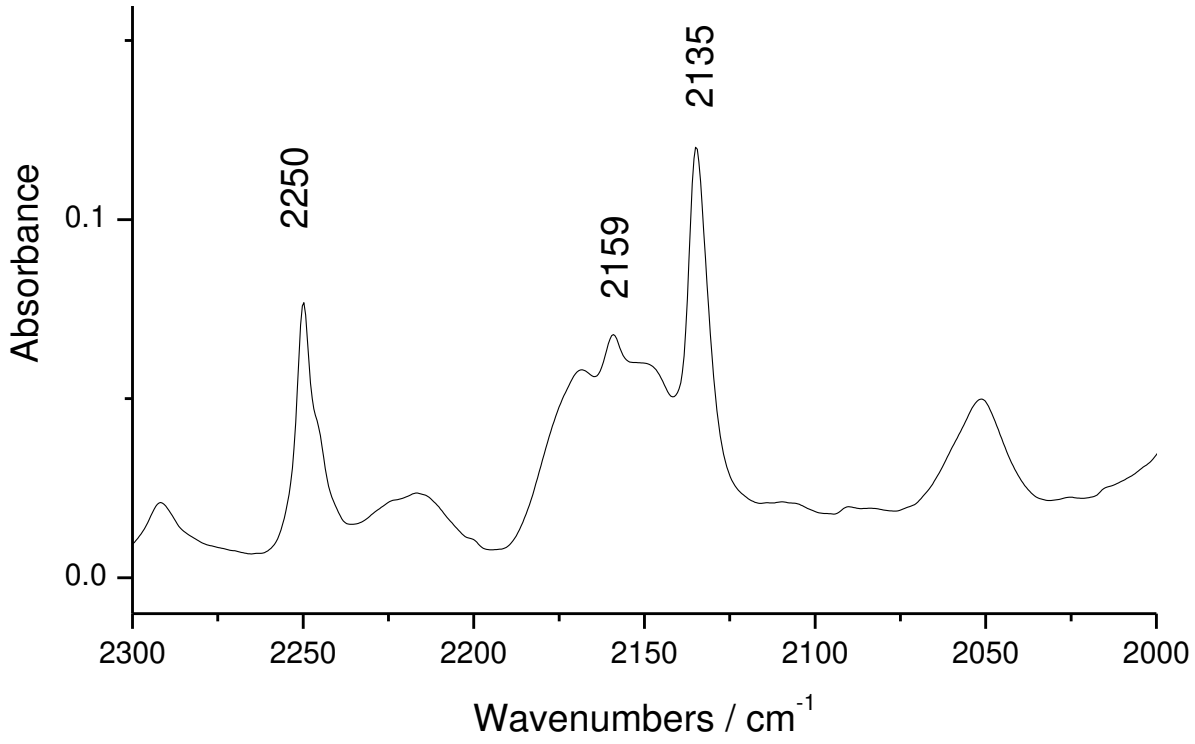

Fig. S13B. 2300-2000 cm^{-1} range of spectrum shown in Fig.S13A.

NMR spectra of solutions

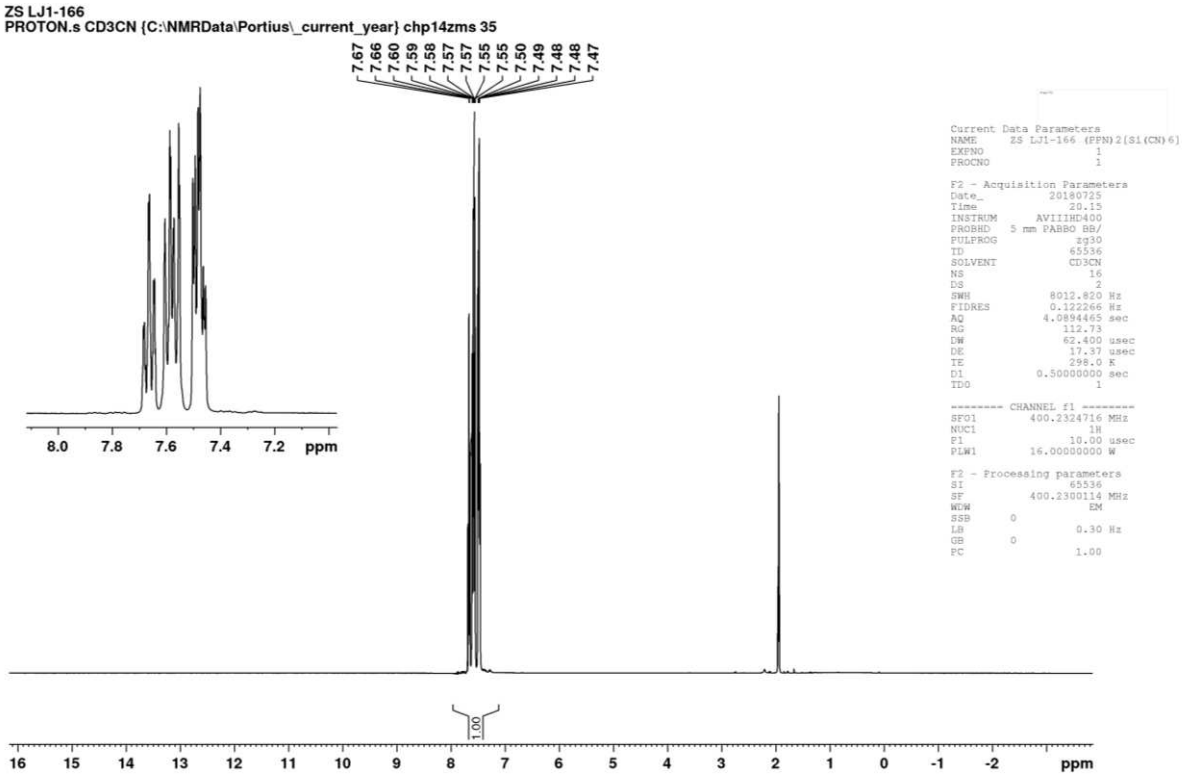

Fig. S14a. ^{1}H NMR spectrum of $(PPN)_2Si(CN)_6$ in CD_3CN.

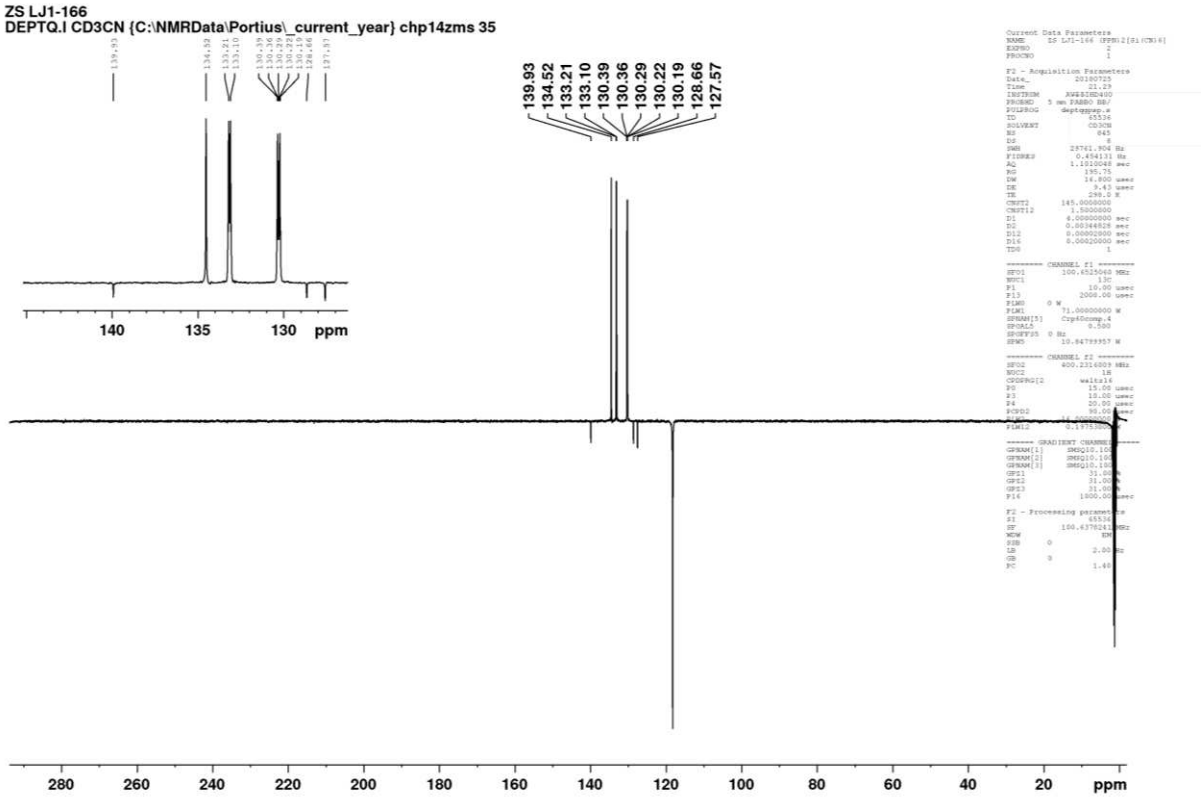

Fig. S14b. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum of $(PPN)_2Si(CN)_6$ in CD_3CN.

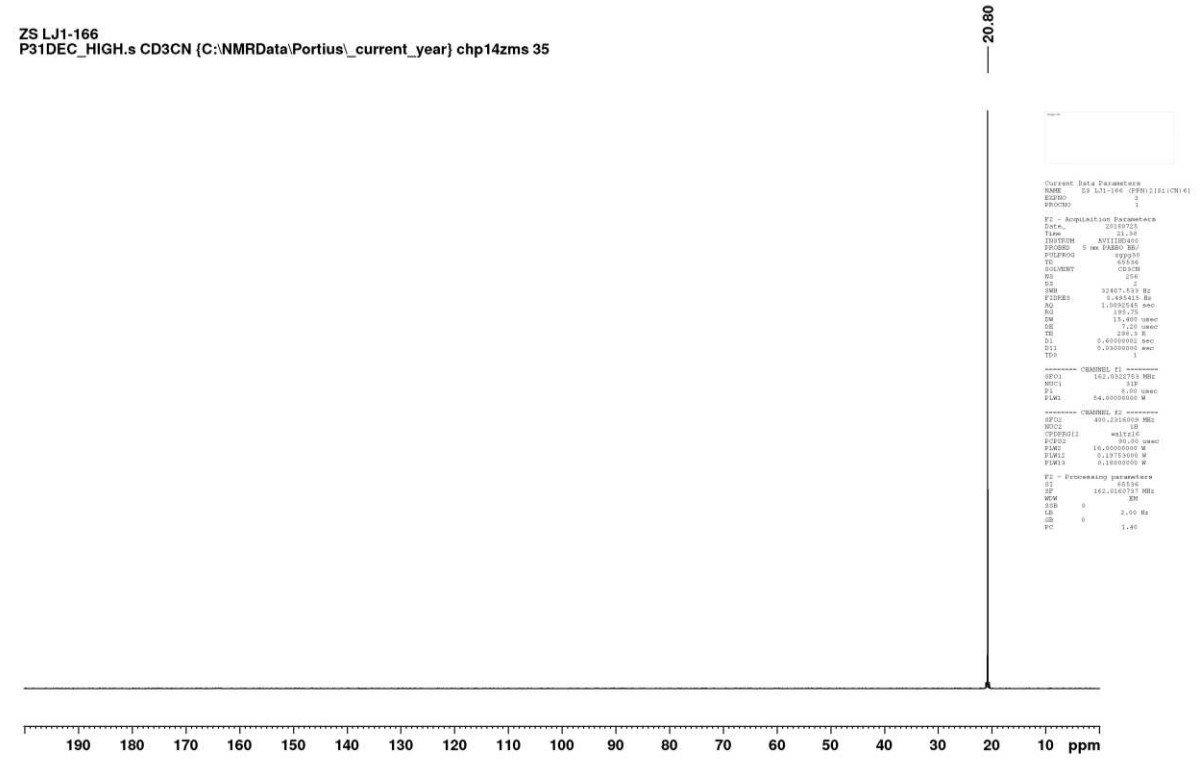

Fig. S14c. $^{31}P\{^{1}H\}$ NMR spectrum of $(PPN)_2Si(CN)_6$ in CD_3CN.

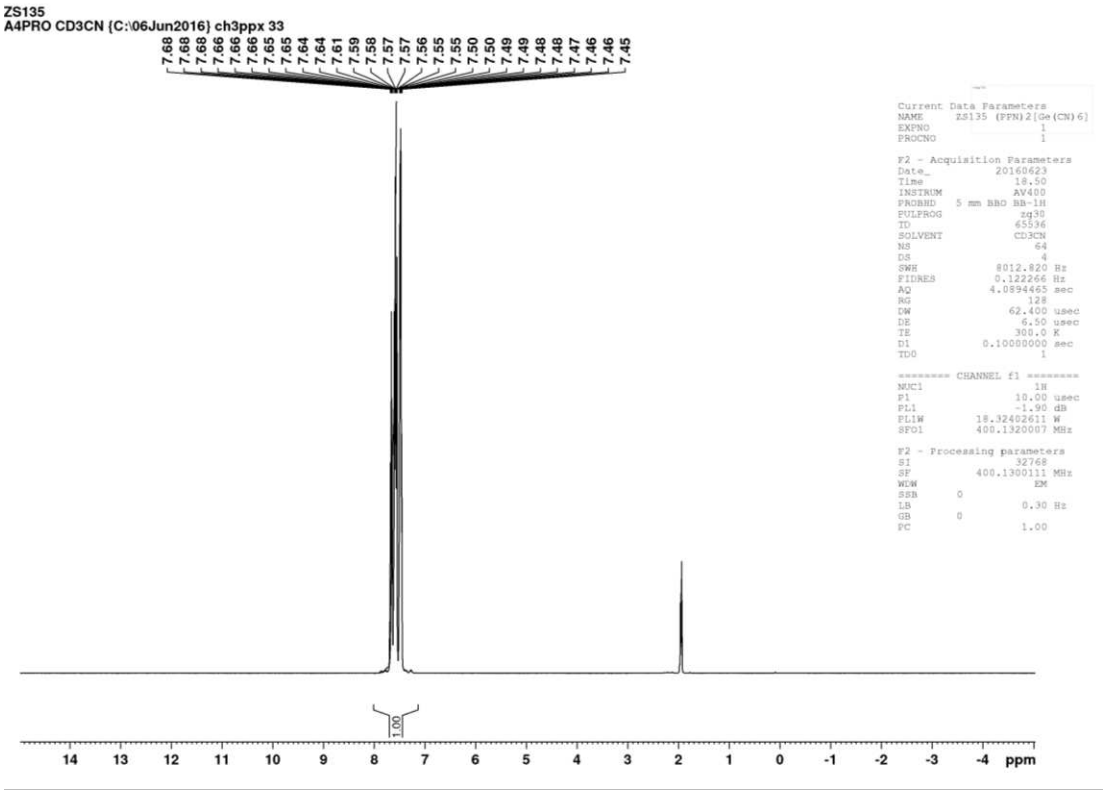

Fig. S15a. ^{1}H NMR spectrum of $(PPN)_2Ge(CN)_6$ in CD_3CN.

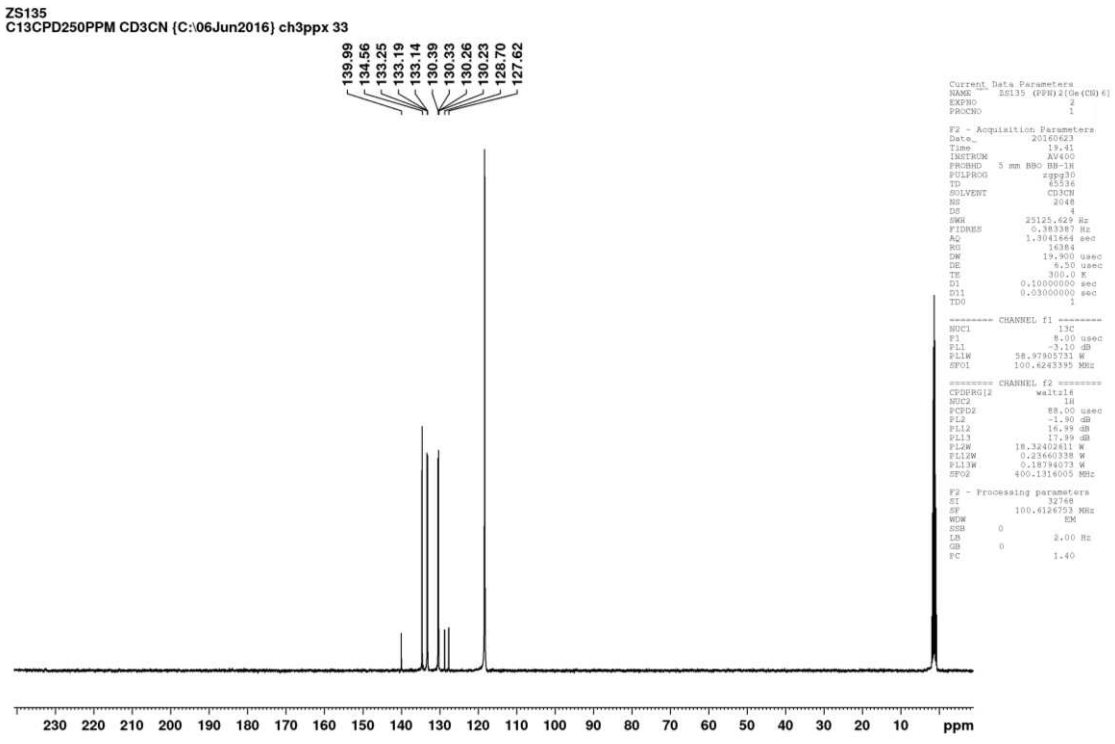

Fig. S15b. $^{13}C\{^{1}H\}$ NMR spectrum of $(PPN)_2Ge(CN)_6$ in CD_3CN.

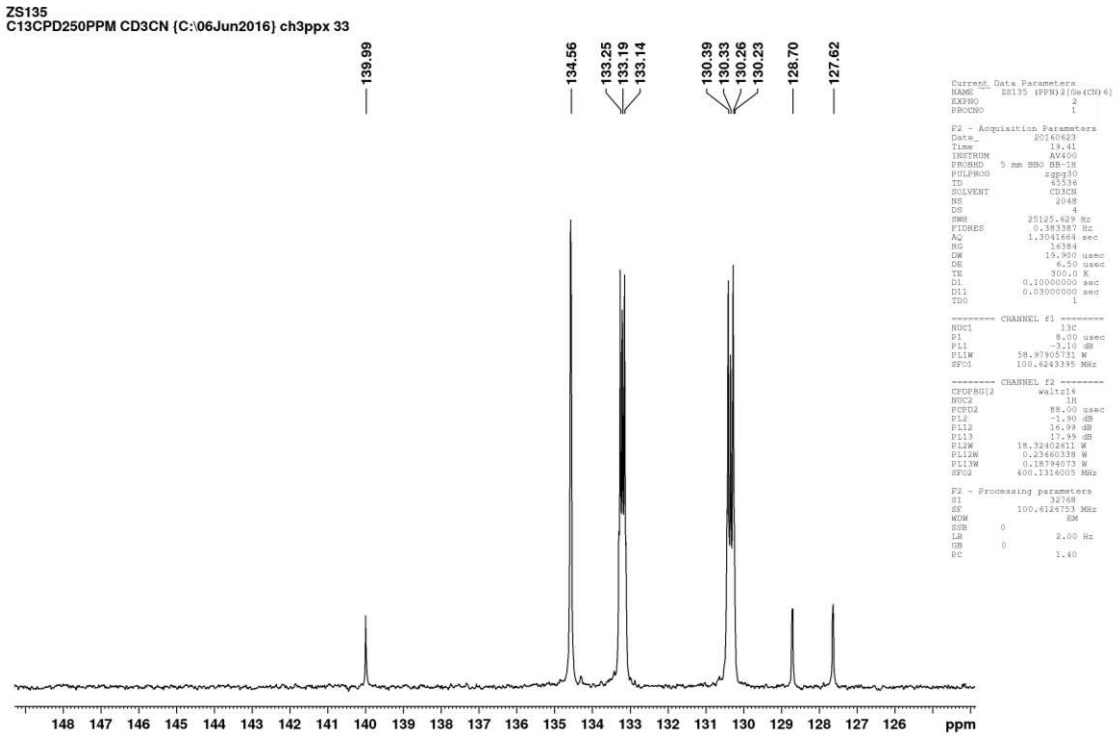

Fig. S15c. Expanded of spectrum shown in Fig.SI15b.

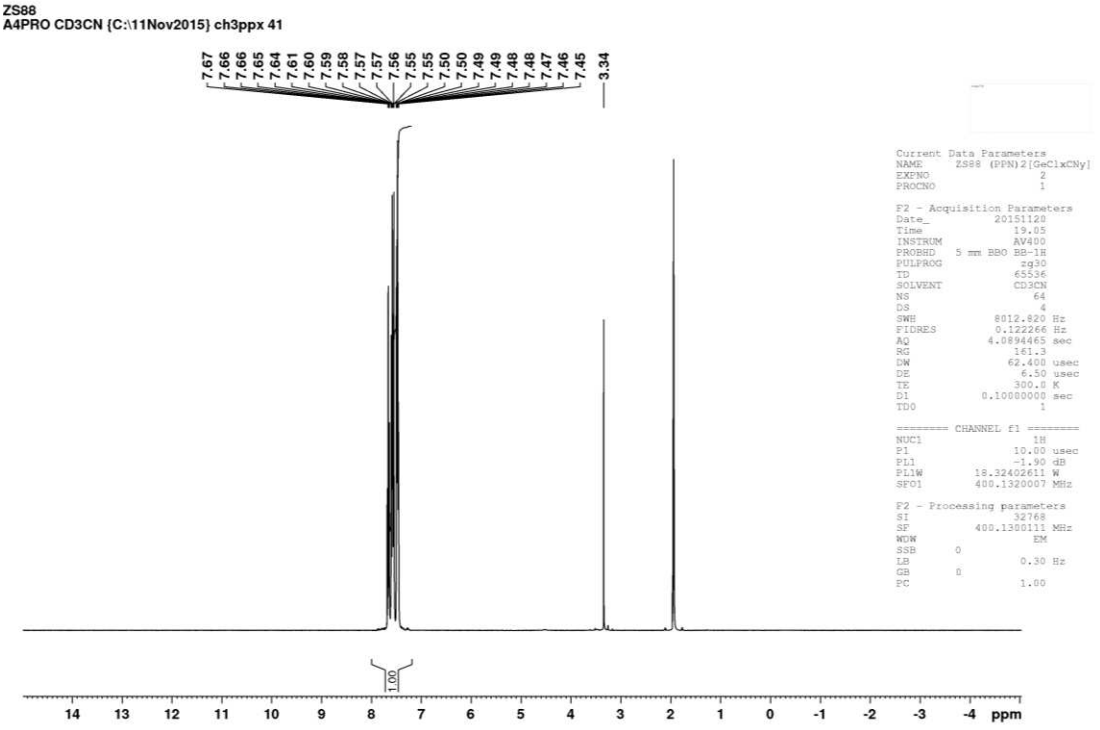

Fig. S16a. ^{1}H NMR spectrum of $(PPN)_2Ge(CN)_xCl_y$, x + y = 6, in CD_3CN.
Note: The signal at 3.34 ppm is attributed to a trace of MeOH.

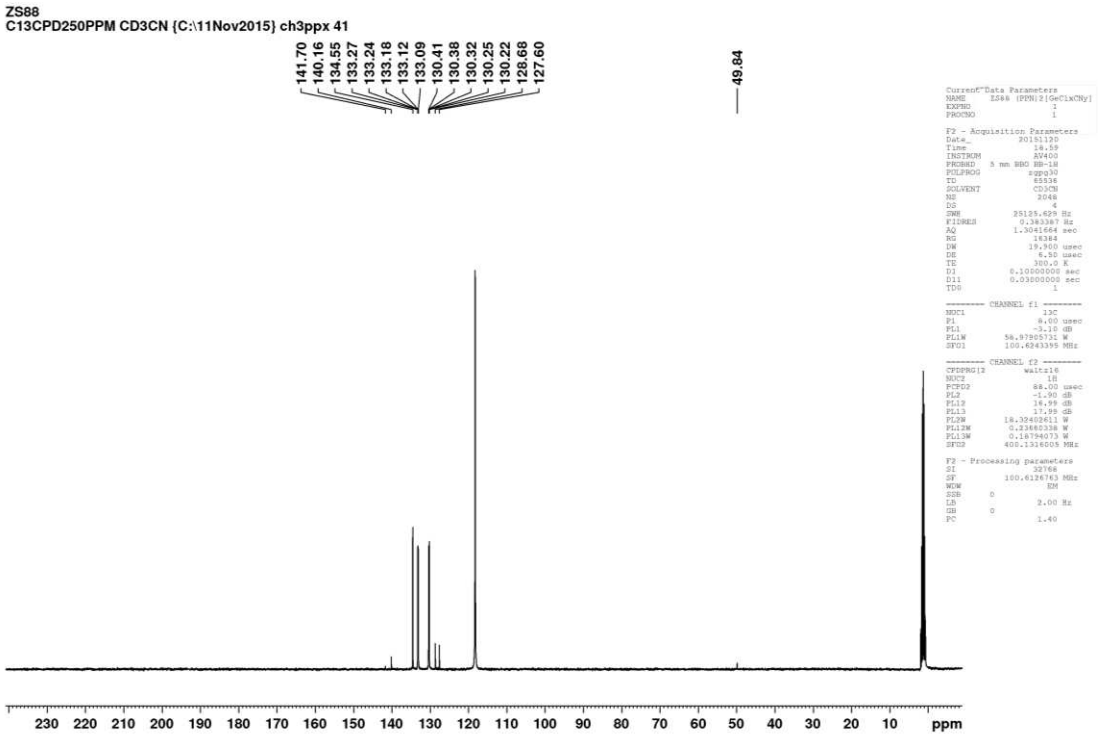

Fig. S16b. $^{13}C\{^{1}H\}$ NMR spectrum of $(PPN)_2Ge(CN)_xCl_y$, x + y = 6, in CD_3CN.
Note: The signal at 49.9 ppm is attributed to a trace of MeOH.

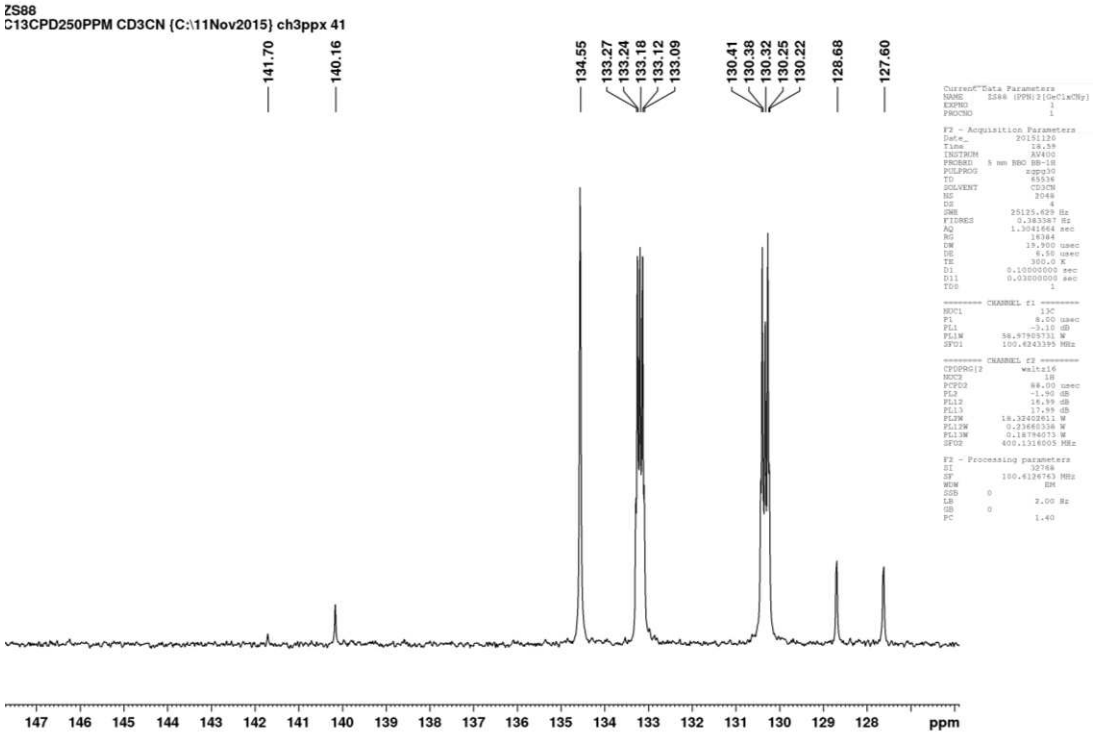

Fig. S16c. Expanded range of spectrum shown in Fig.SI16b.

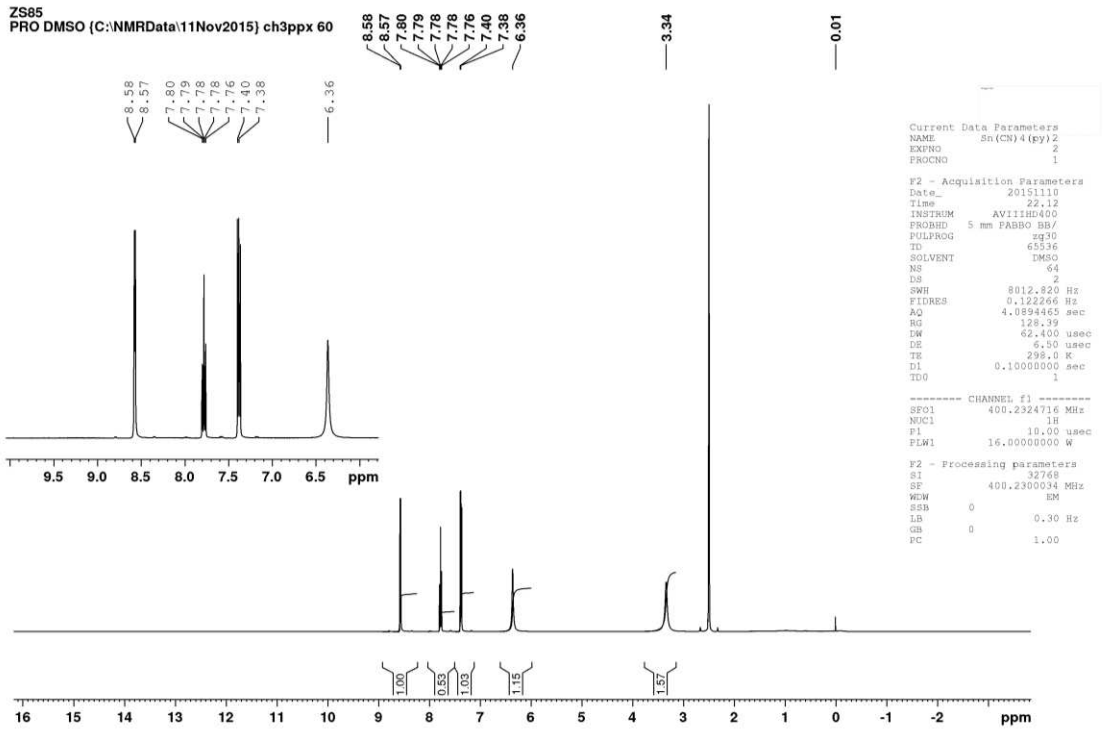

Fig. S17a. ^{1}H NMR spectrum of $Sn(CN)_4(py)_2$ in dmso-d_6.

Note: the multiplets at δ / ppm = 8.59, 7.38 and 7.79 are assigned to uncoordinated pyridine, the broad singlets at δ / ppm = 6.37 and 3.34 to HCN and H_2O, respectively.

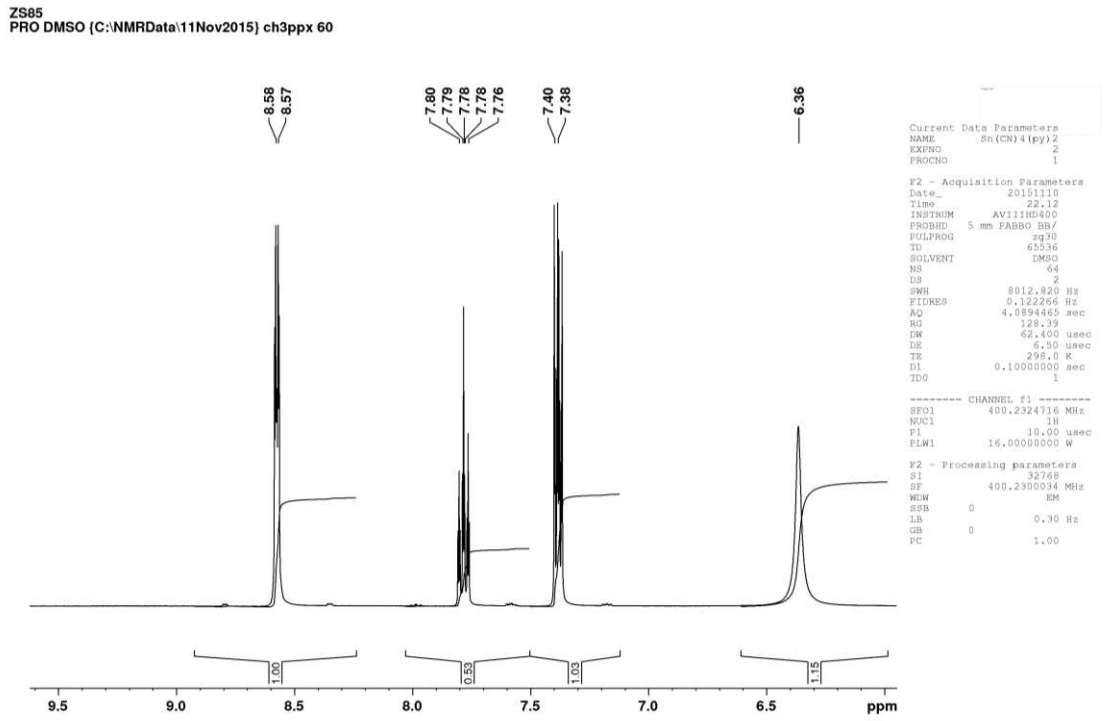

Fig. SI17b. 9.5 to 6 ppm range of spectrum shown in Fig. SI17a.

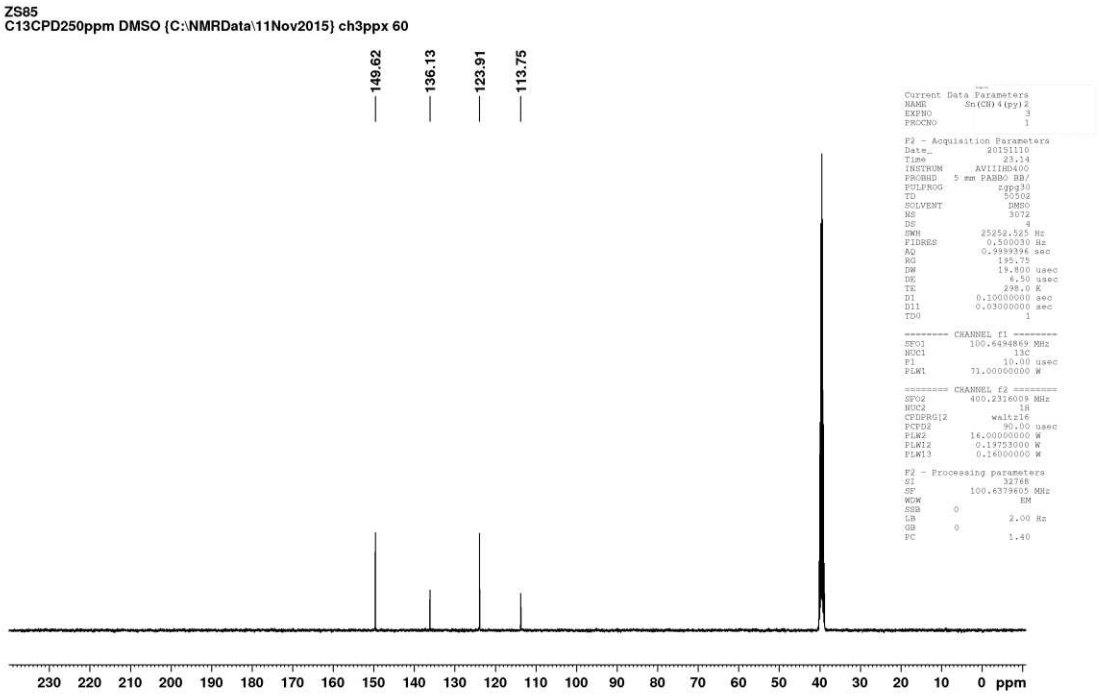

Fig. SI17c. $^{13}C\{^{1}H\}$ NMR spectrum of $Sn(CN)_4(py)_2$ in dmso-d_6.

Note: the observed peaks at δ / ppm = 149.62, 123.91, 136.13 ppm are assigned to uncoordinated pyridine (pyridine in dmso-d_6 at 149.58(*o*), 123.84(*m*), 136.05(*p*), Gottlieb *et al.*, *J. Org. Chem.*, **1997**, 62, 7512-7515). Using data on $\sigma(^{13}C)$ shielding constants obtained for the gas phase (H*C*N, 82.1 ppm; Me*C*N, 73.8 ppm; $SiMe_4$, 188.1 ppm)[10] $\delta(^{13}C)$ / ppm chemcial shifts can be predicted (106, 114.3 and 0) related to the observed $\delta(^{13}C)$ for Me*C*N at 117.9 ppm in dmso (ref. 10). From this data we estimate $\delta(^{13}C)$ / ppm = 109.6 for HCN in dmso-d_6; The calculated shift according to ref. 11: is 110.9 ppm in $CDCl_3$. We therefore assign tentatively the peak at 113.8 ppm to H*C*N.

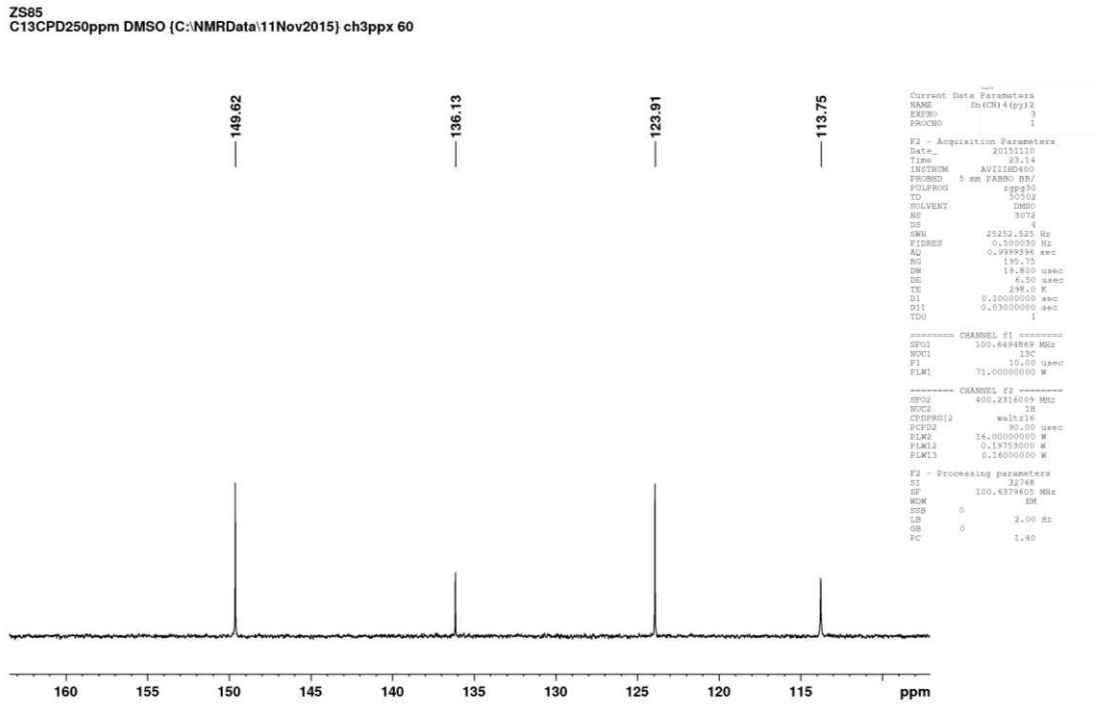

Fig. SI17d. $^{13}C\{^{1}H\}$ NMR shown in Fig.SI16c, expanded range 110 to 165 ppm.

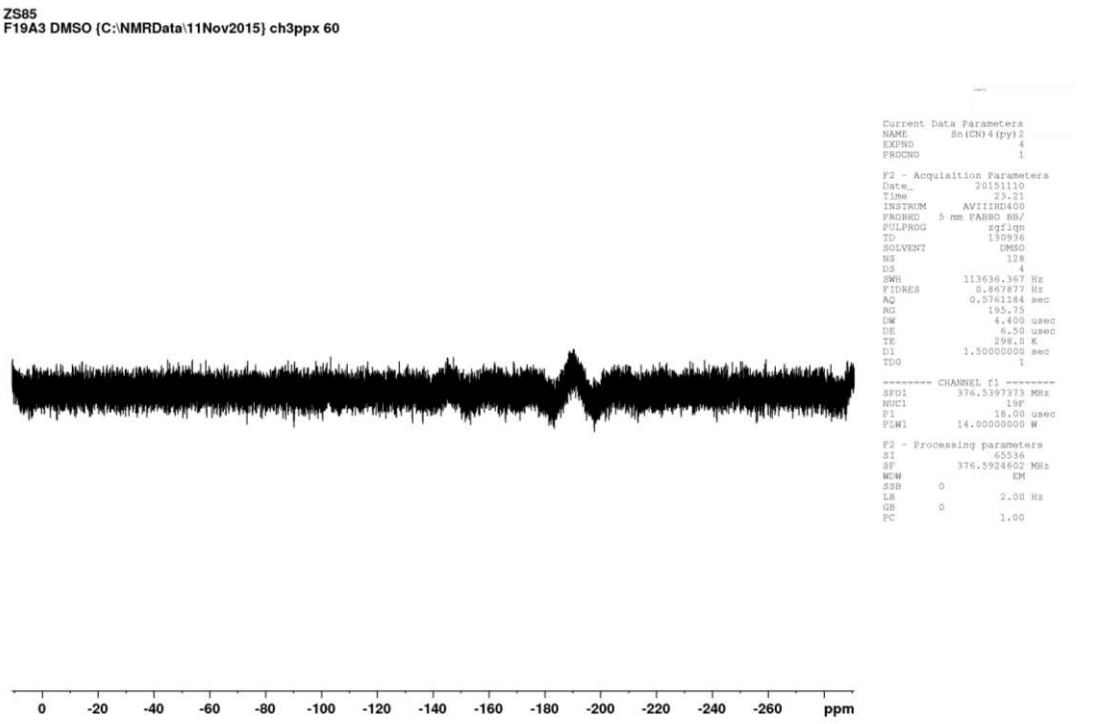

Fig. SI17e. $^{19}F\{^{1}H\}$ NMR shown of $Sn(CN)_4(py)_2$ in dmso-d_6.

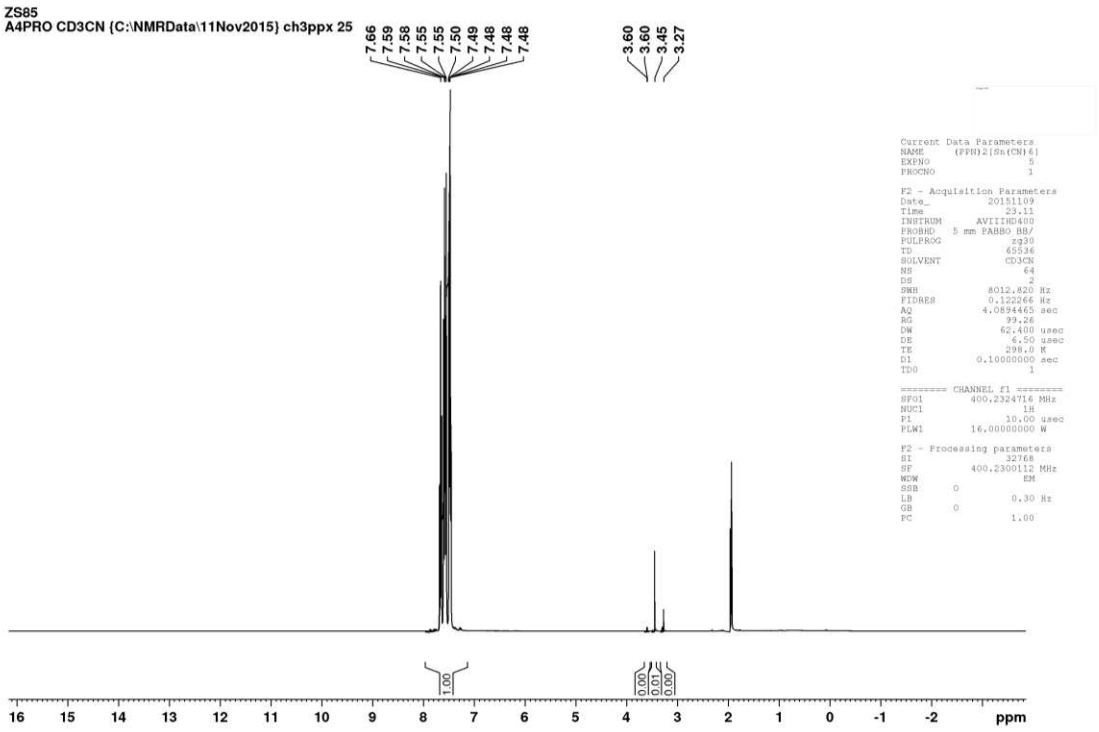

Fig. SI18a. ^{1}H NMR spectrum of $(PPN)_2Sn(CN)_6$ in CD_3CN.

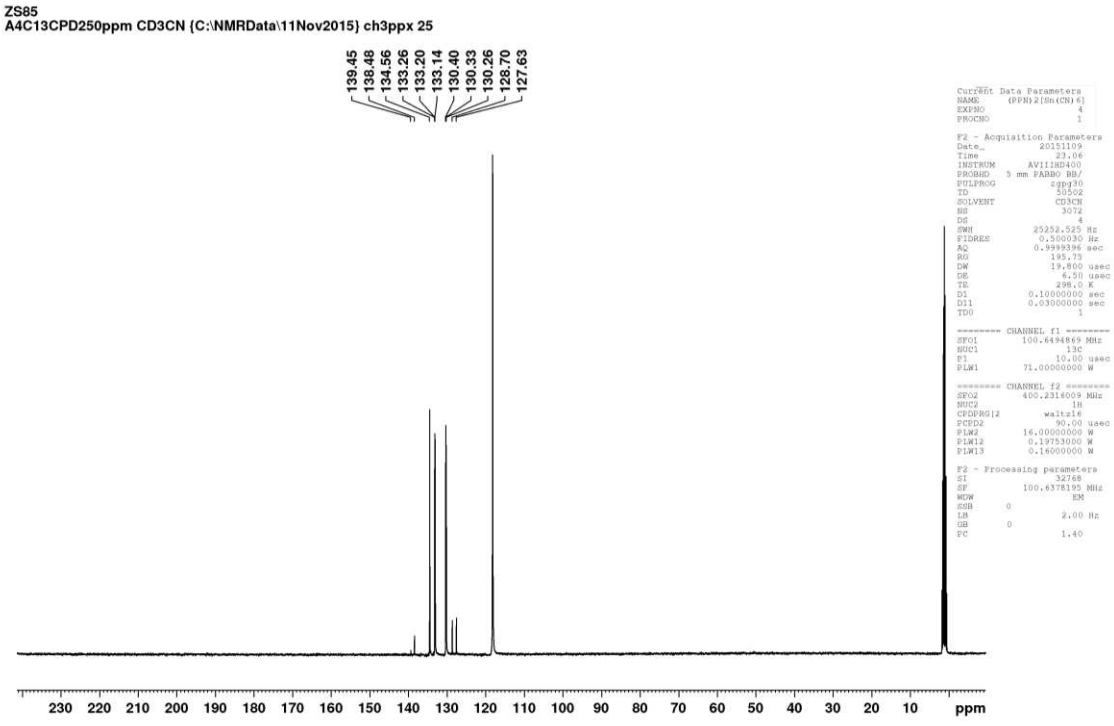

Fig. SI18b. $^{13}C\{^{1}H\}$ NMR spectrum of $(PPN)_2Sn(CN)_6$ in CD_3CN.

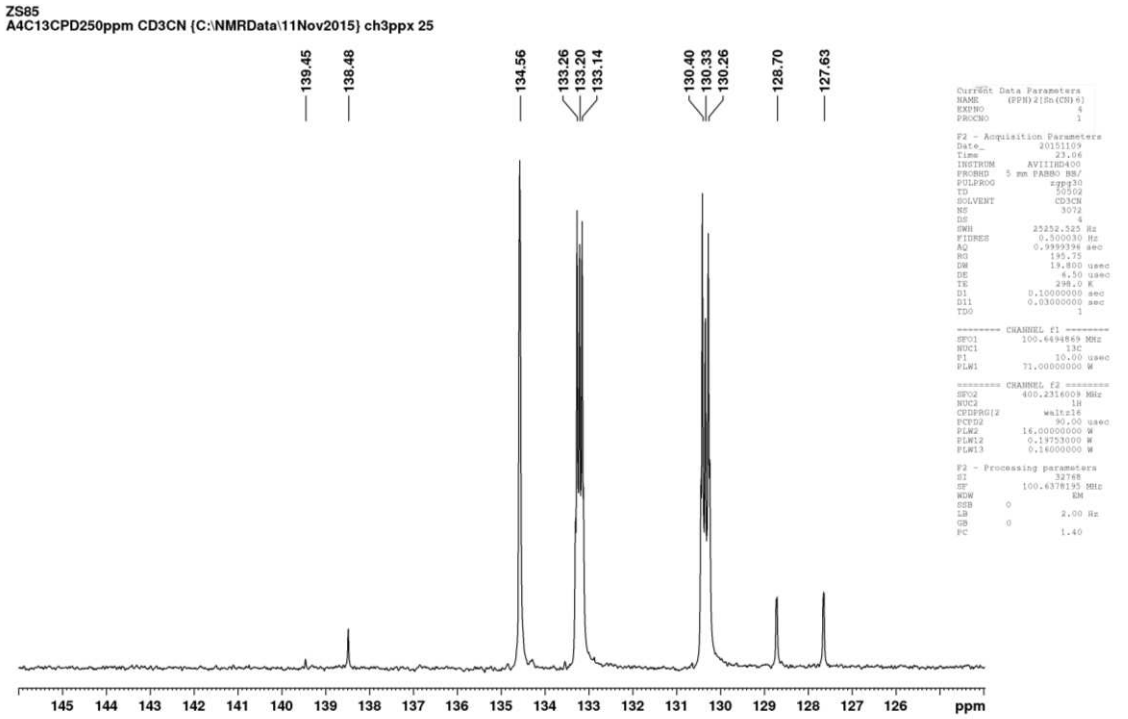

Fig. SI18c. $^{13}C\{^{1}H\}$ NMR spectrum shown in Fig.SI18b, expanded range.

MAS NMR spectra

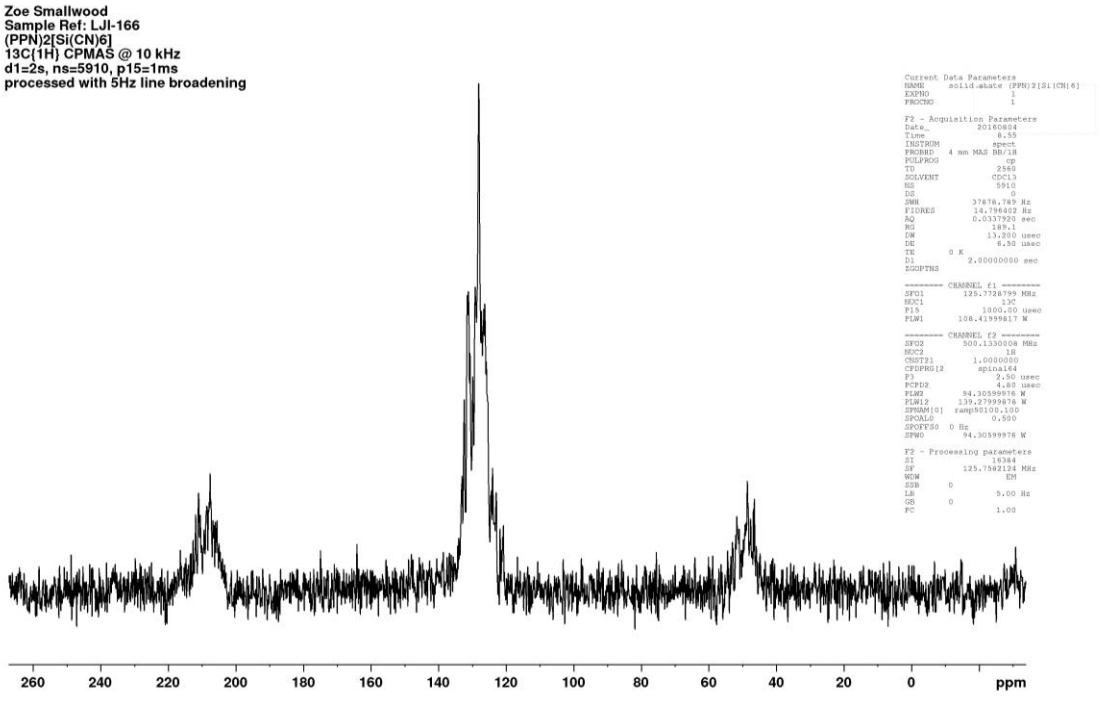

Fig. SI19a. ^{13}C NMR spectrum of solid $(PPN)_2Si(CN)_6$ in the range +260 to -20 ppm.

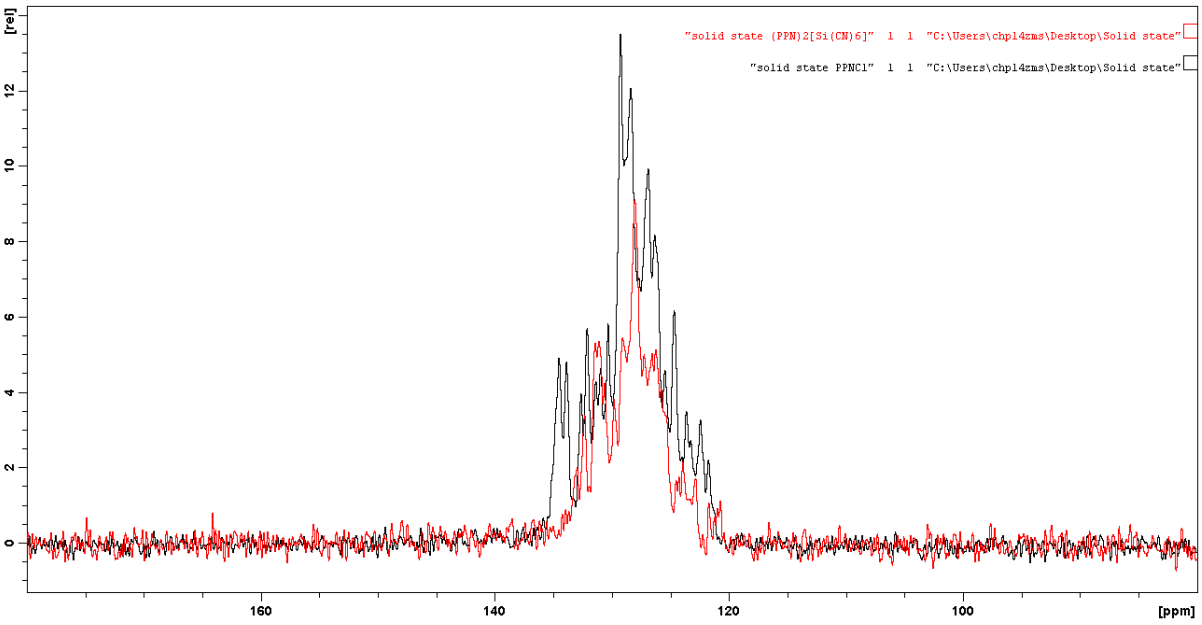

Fig. SI19b. Series of ^{13}C NMR spectra of solid $(PPN)_2Si(CN)_6$ (red, expanded from Fig.SI18a) and (PPN)Cl (black) in the range +180 to 80 ppm.

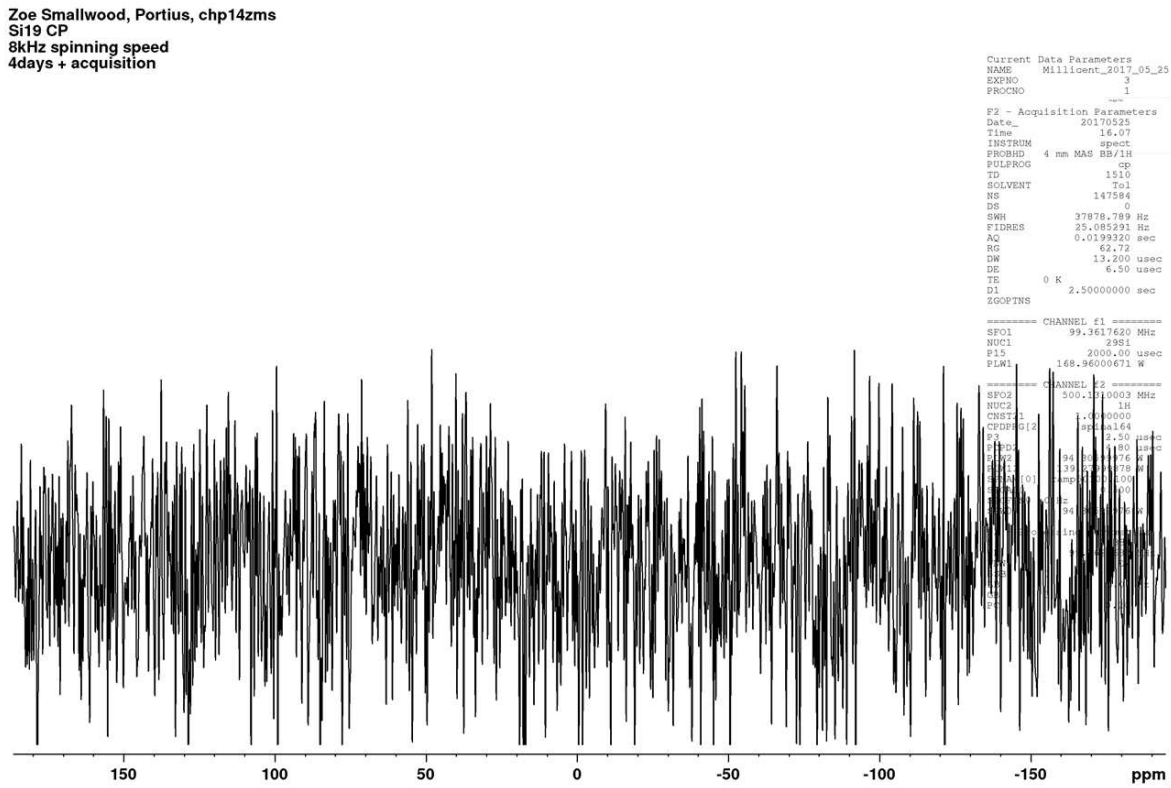

Fig. SI19c. ^{29}Si NMR spectra of solid $(PPN)_2Si(CN)_6$ in the range +180 to −190 ppm.

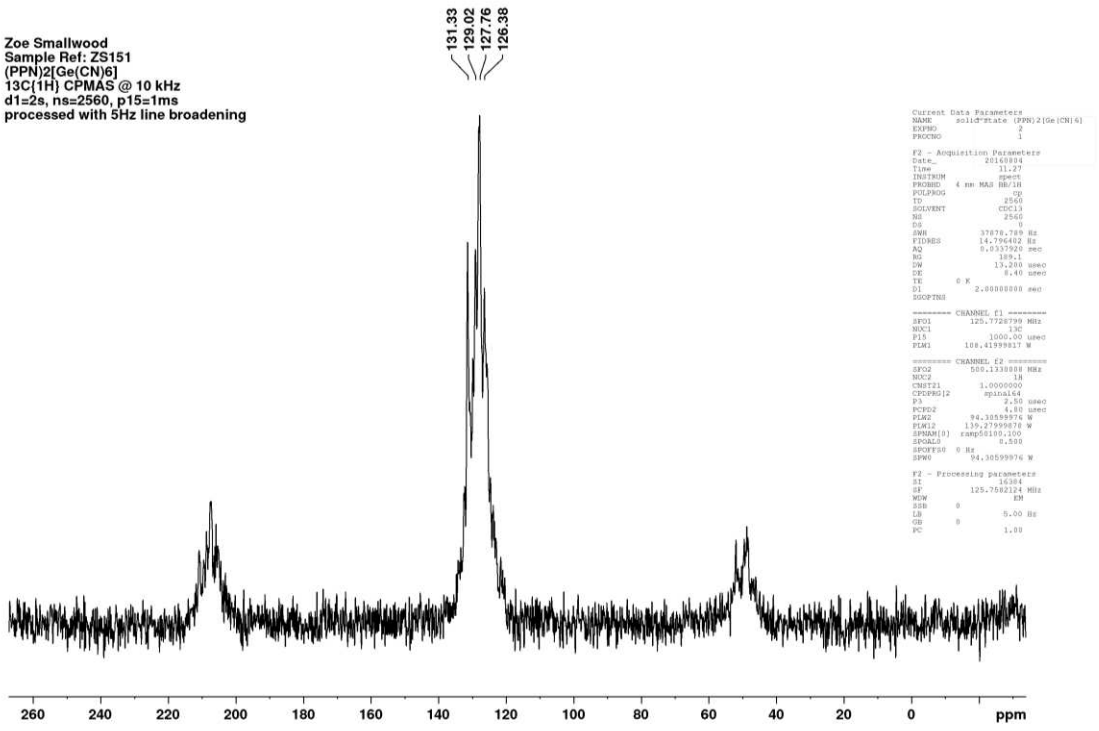

Fig. SI19d. ^{13}C NMR spectrum of solid $(PPN)_2Ge(CN)_6$ in the range +260 to -20 ppm.

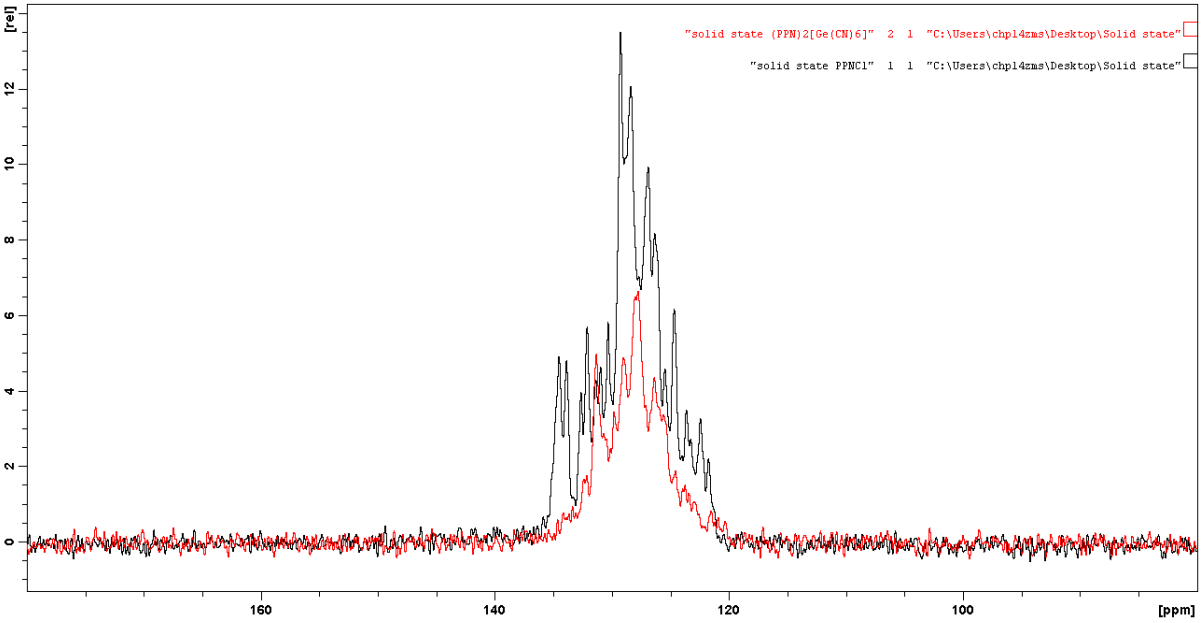

Fig. SI19e. Series of ^{13}C NMR spectra of solid $(PPN)_2Ge(CN)_6$ (red expanded from Fig.SI19a) and (PPN)Cl (black) in the range +180 to 80 ppm.

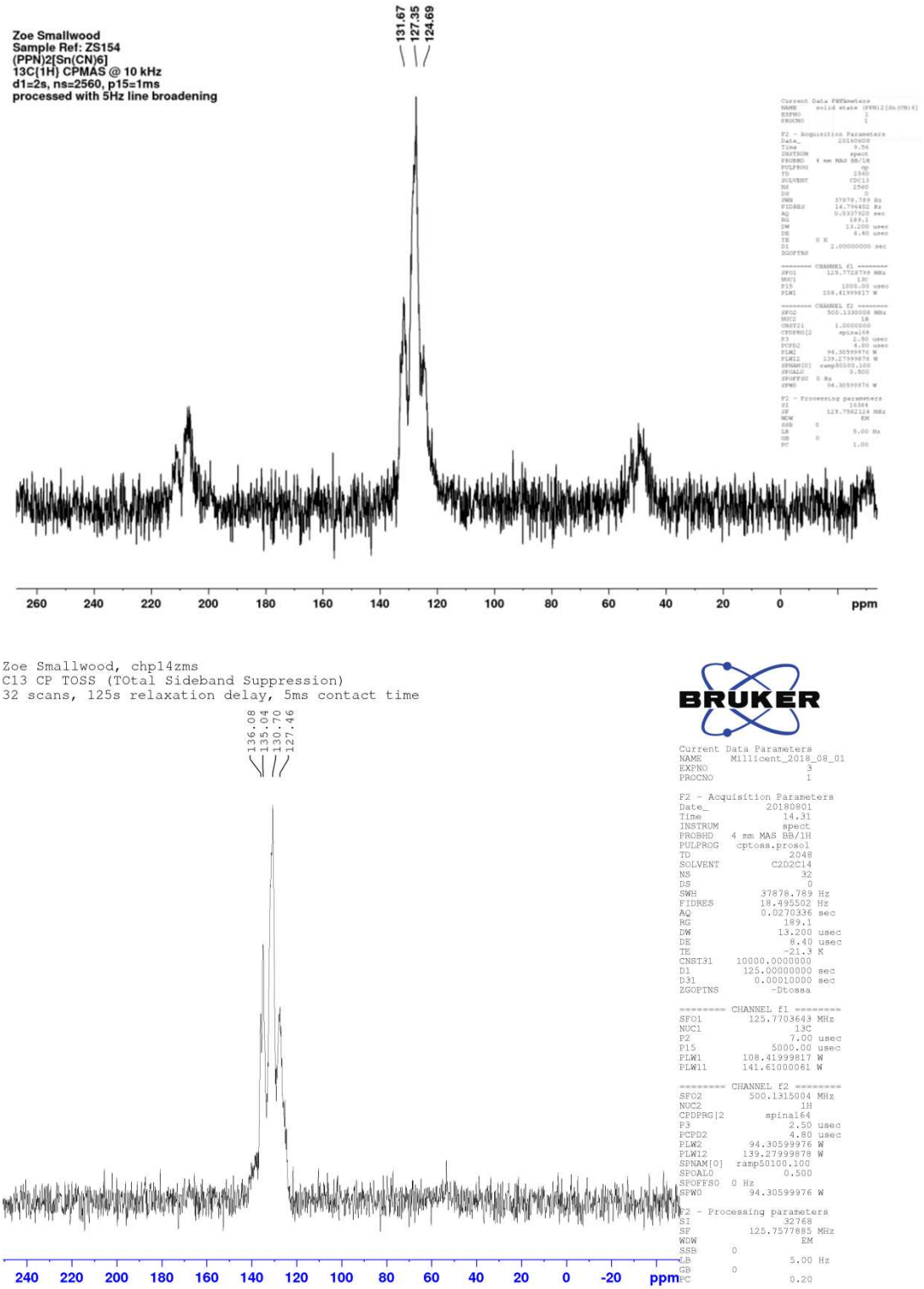

Fig. SI20a. ^{13}C NMR spectra of solid $(PPN)_2Sn(CN)_6$ in the range +260 to -20 ppm.

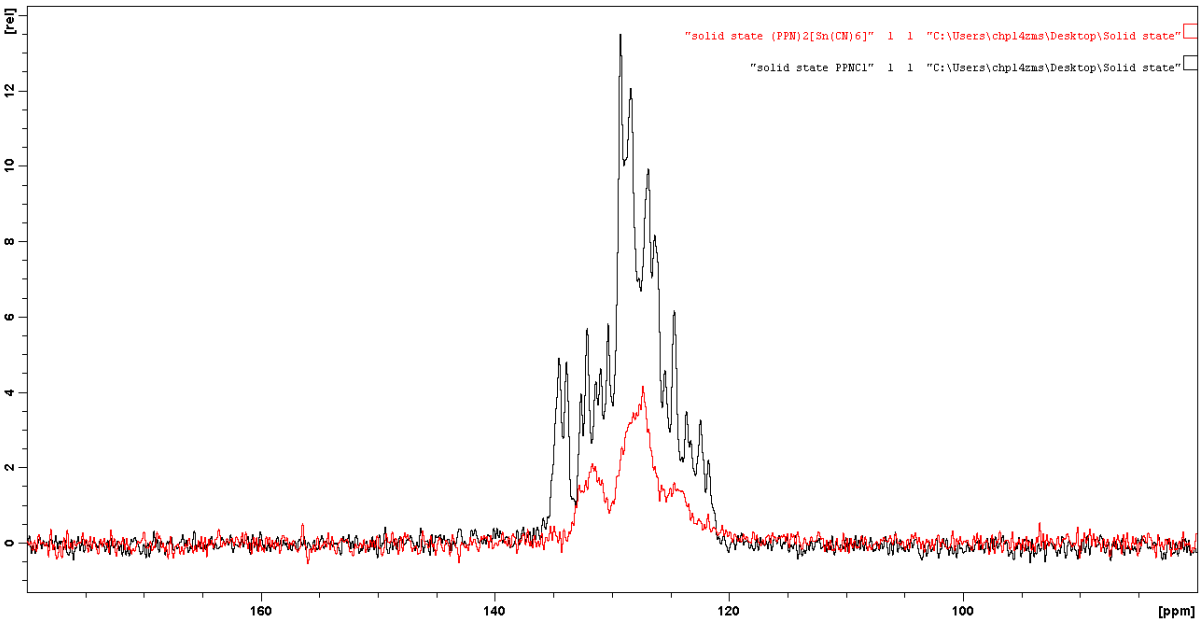

Fig. SI20b. Series of ^{13}C NMR spectra of solid $(PPN)_2Ge(CN)_6$ (red expanded from Fig.SI20a) and (PPN)Cl (black) in the range +180 to 80 ppm.

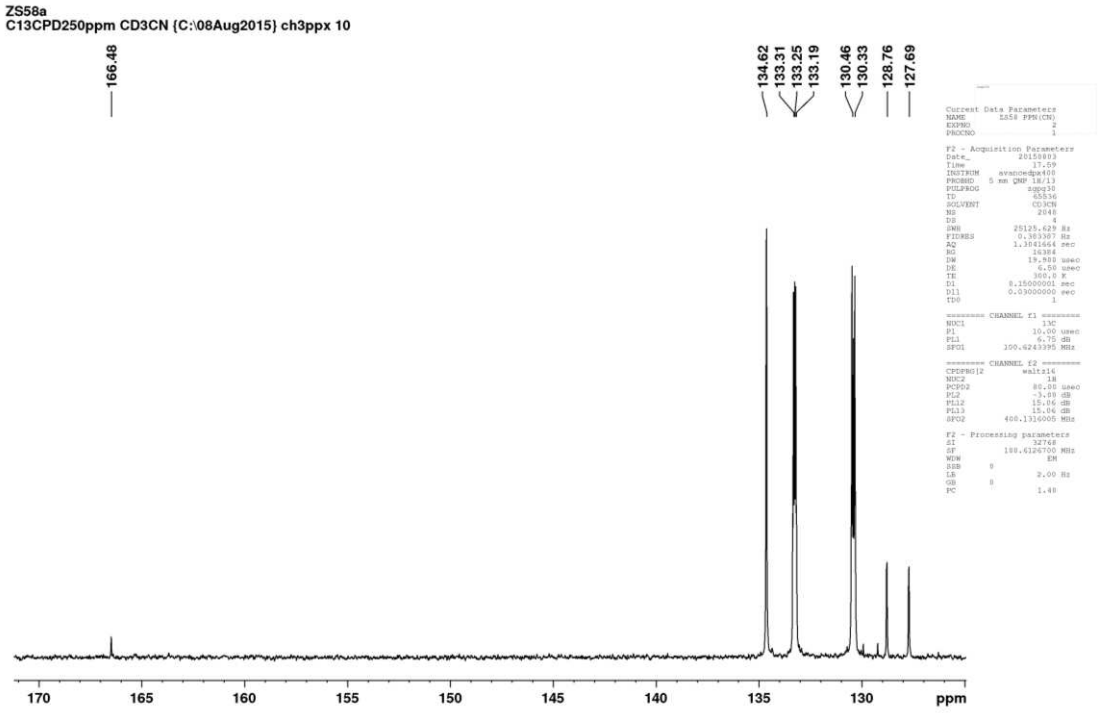

Fig. SI21. Expansion of $^{13}C\{^1H\}$ NMR spectrum of (PPN)CN in CD_3CN 171 to 125 ppm.

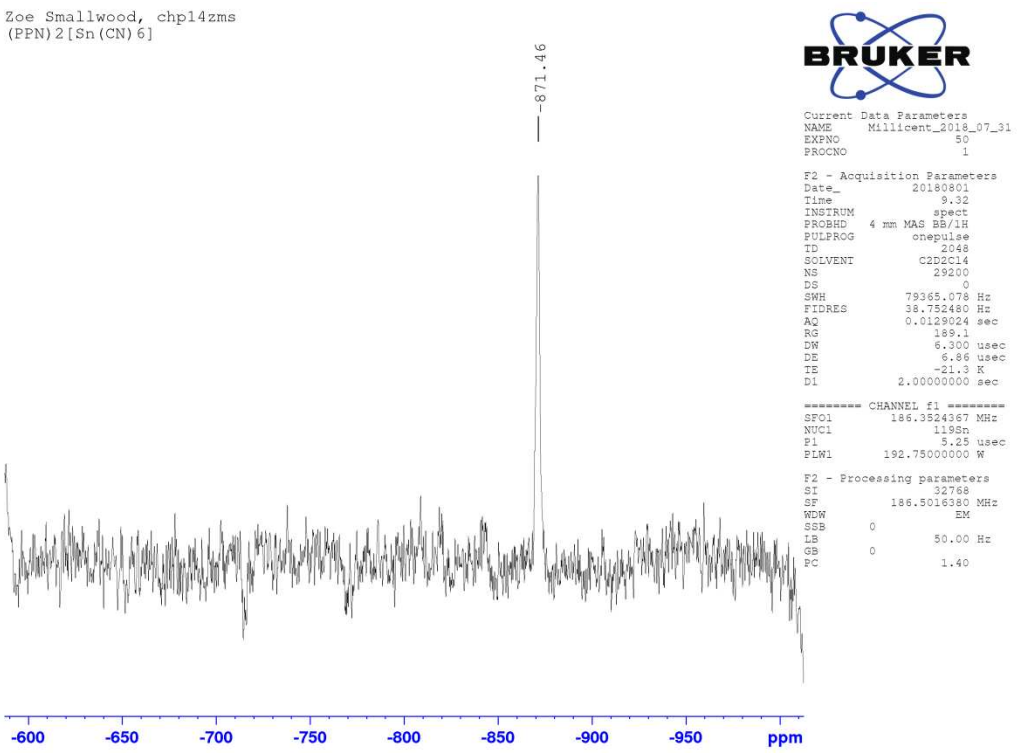

Fig. SI22a. ^{119}Sn MAS NMR spectrum of $(PPN)_2Sn(CN)_6$, -600 to -1000 ppm range.
Note: The expected spinning side-bands are weak and indistinguishable from the noise of the baseline, presumably due to the comparably low concentration 119Sn in the sample volume.

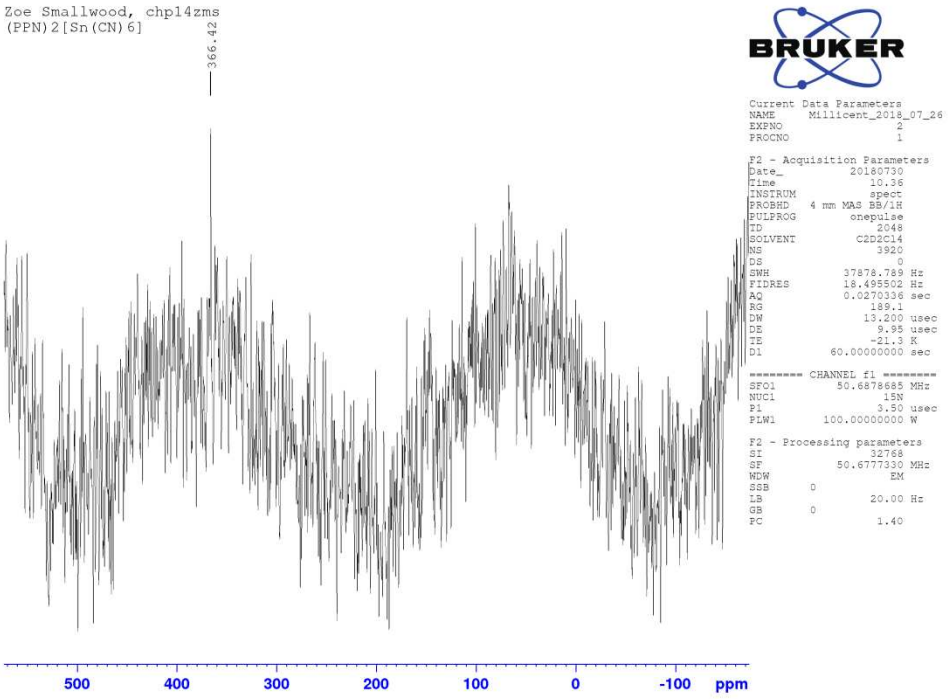

Fig. SI22b. ^{14}N MAS NMR spectrum of $(PPN)_2Sn(CN)_6$, 600 to -200 ppm range.

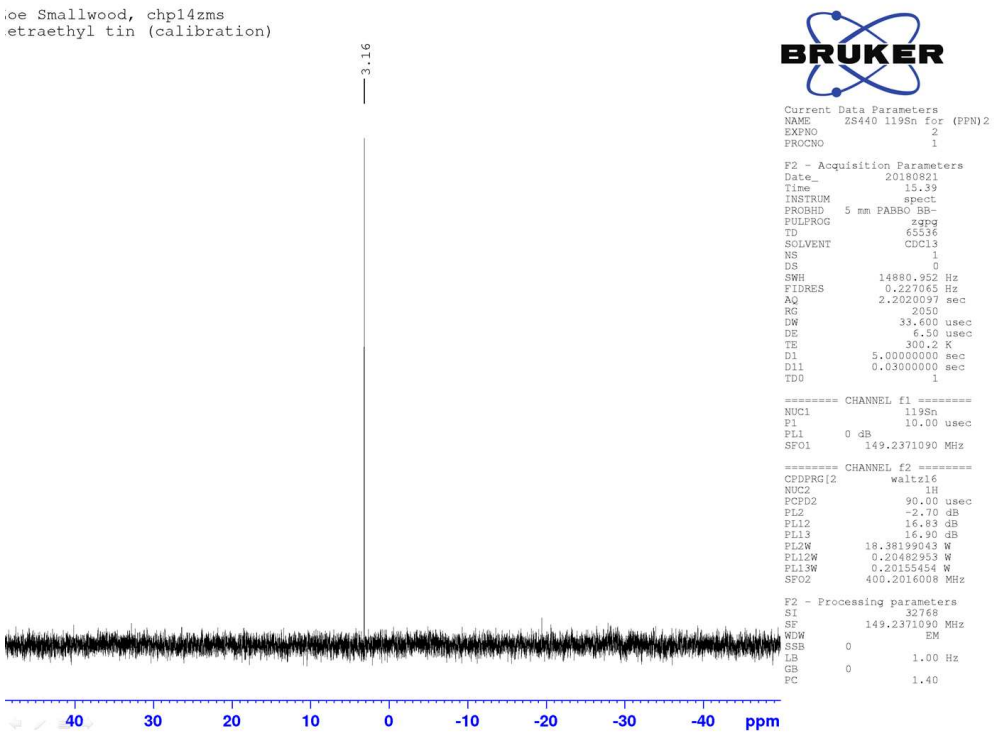

Fig. SI22c. ^{119}Sn NMR spectrum of $(PPN)_2Sn(CN)_6$, in $CDCl_3$, -830 to -970 ppm range, $\delta(Et_4Sn)$ = 3.16 ppm reference).

Mass spectra

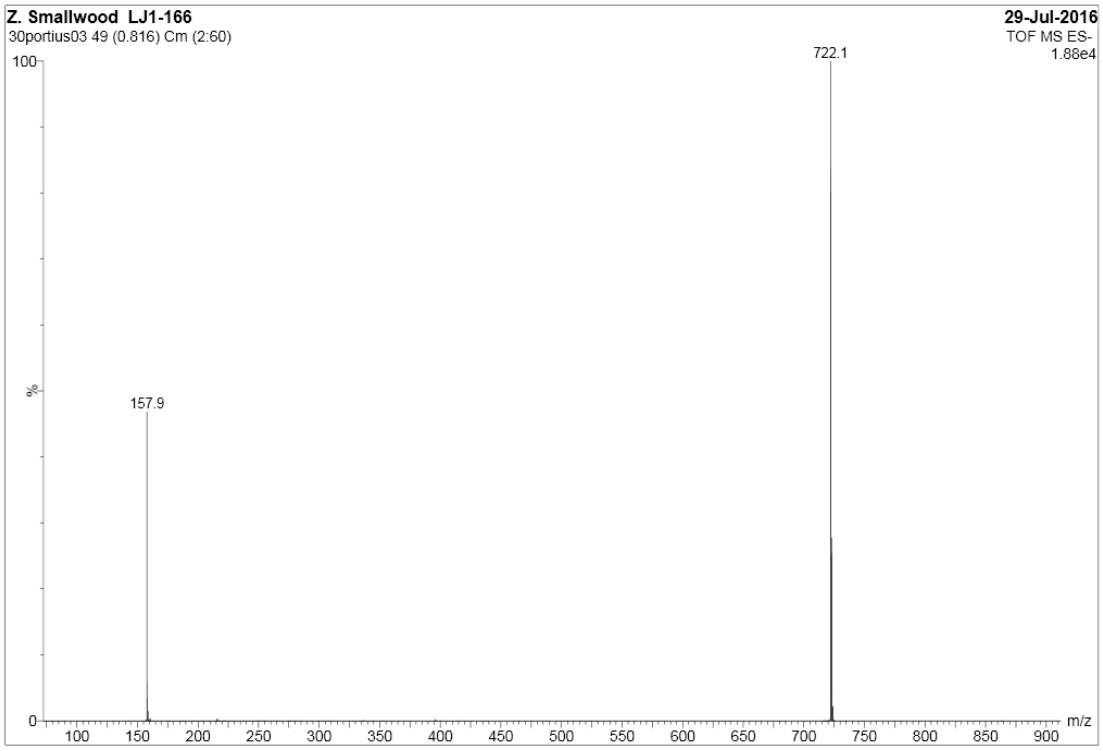

Fig. SI23a. ESI(−) TOF mass spectrum of $PPN_2Si(CN)_6$ between m/z = 75 to 900.

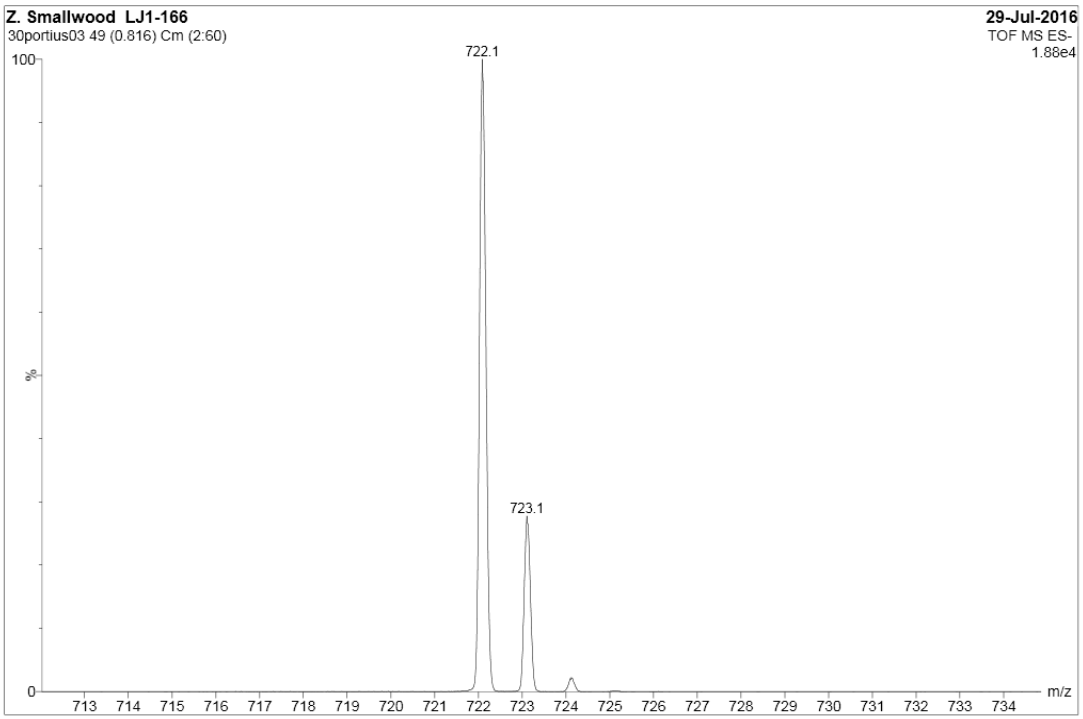

Fig. SI23b. Mass spectrum shown in Fig. SI23a, range m/z = 712 to 735 expanded.

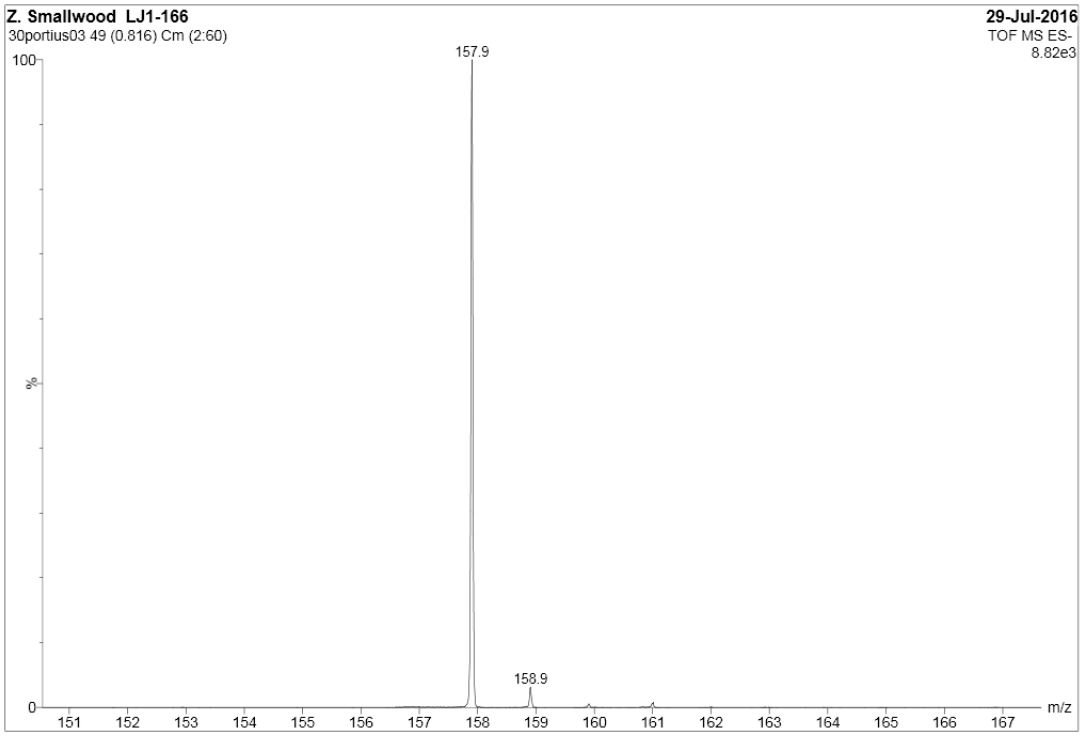

Fig. SI23c. Mass spectrum shown in Fig. SI23a, range *m*/*z* = 150 to 168 expanded.

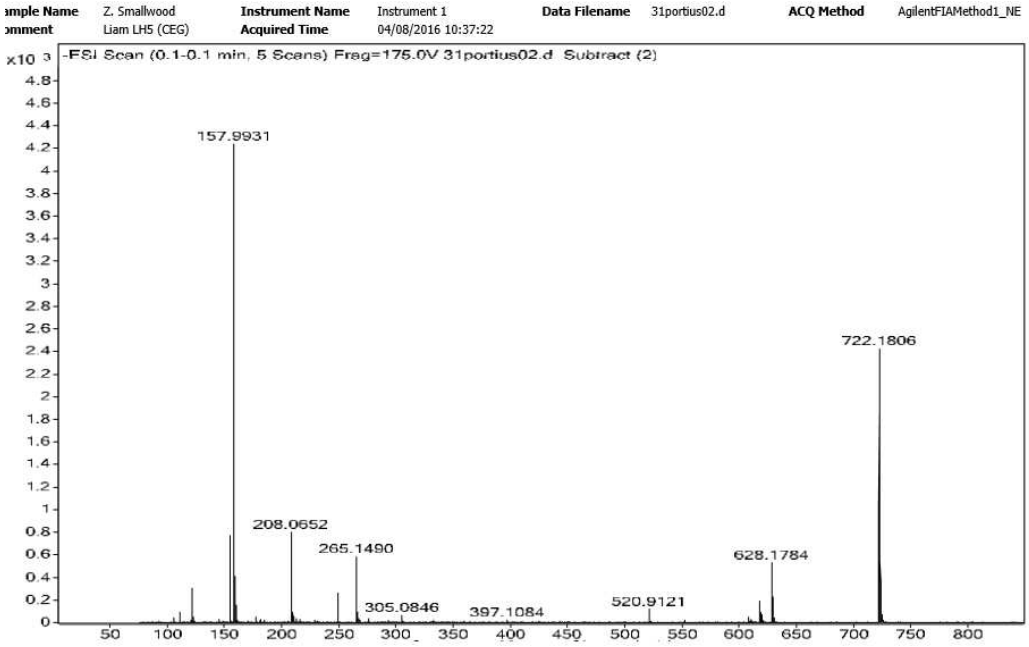

Fig. SI23c. Negative ion accurate mass measurement involving $PPN_2Si(CN)_6$.

m/*z*	Abundance	Formula	Ion	ppm diff.	Calculated mass / a.m.u.
157.9931	4249.25	C_5N_5Si	M^-	1.61	157.9928
208.0652	815.51	-	-	-	-
722.1806	2433.78	$C_{42}H_{30}N_7P_2Si$	M^-	0.92	722.1813
723.1837	1192.47	$C_{42}H_{30}N_7P_2Si$	M^-	1.28	723.1846
955.9674	1015.85	-	-	-	-

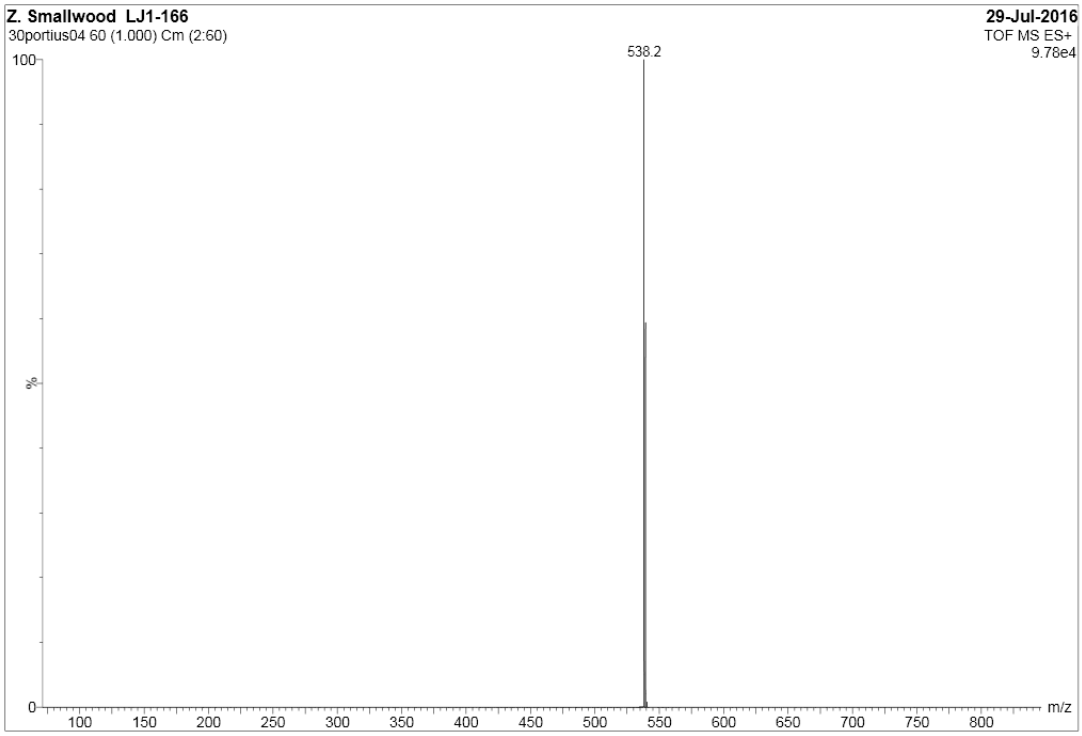

Fig. SI23e. ESI(+) TOF mass spectrum of $PPN_2Si(CN)_6$ between m/z = 75 and 840.

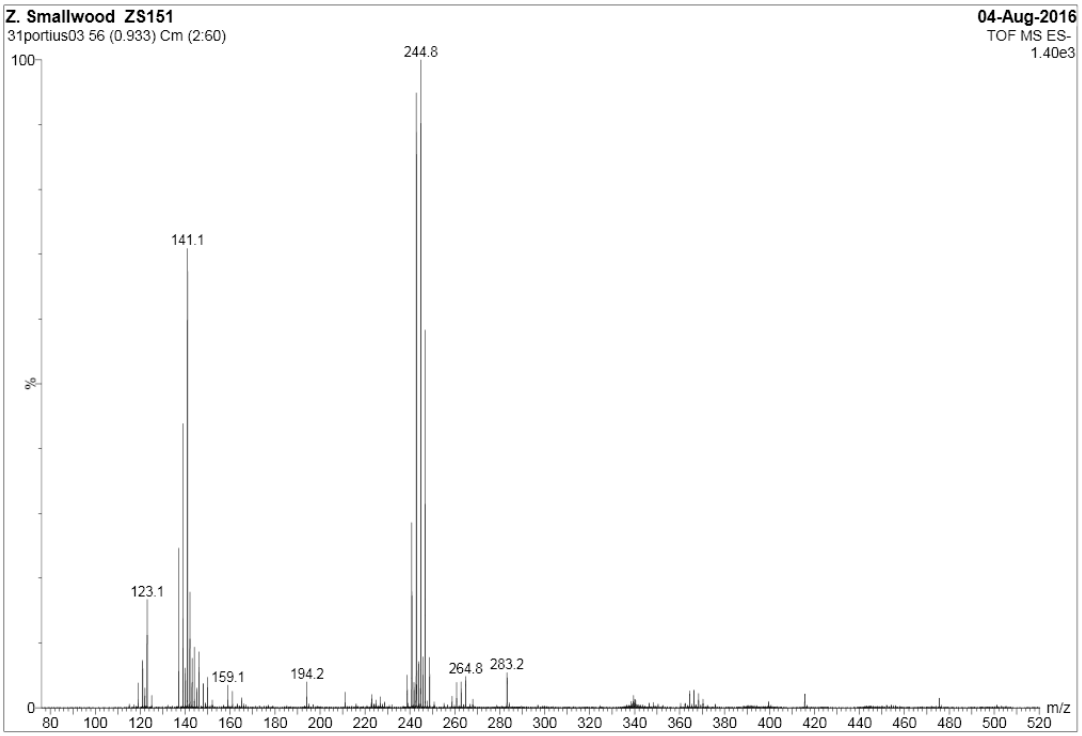

Fig. SI24a. ESI(−) TOF mass spectrum of $PPN_2Ge(CN)_6$ between m/z = 78 and 520.

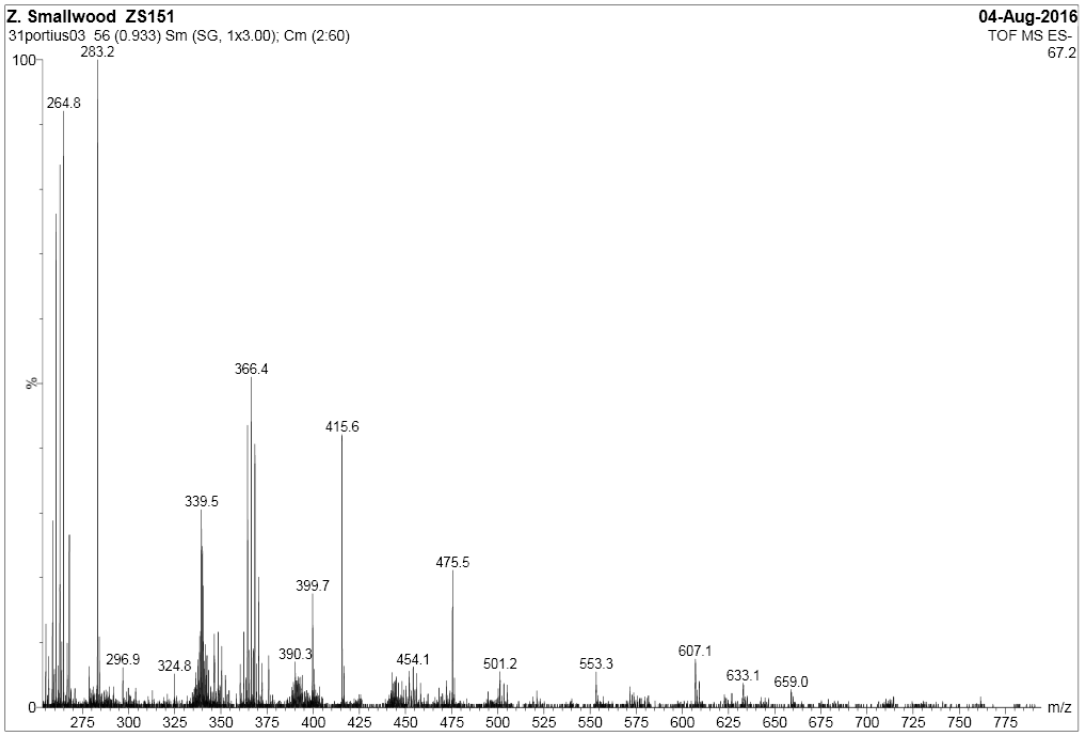

Fig. SI24b. ESI(−) TOF mass spectrum of $PPN_2Ge(CN)_6$ between m/z = 250 and 800.

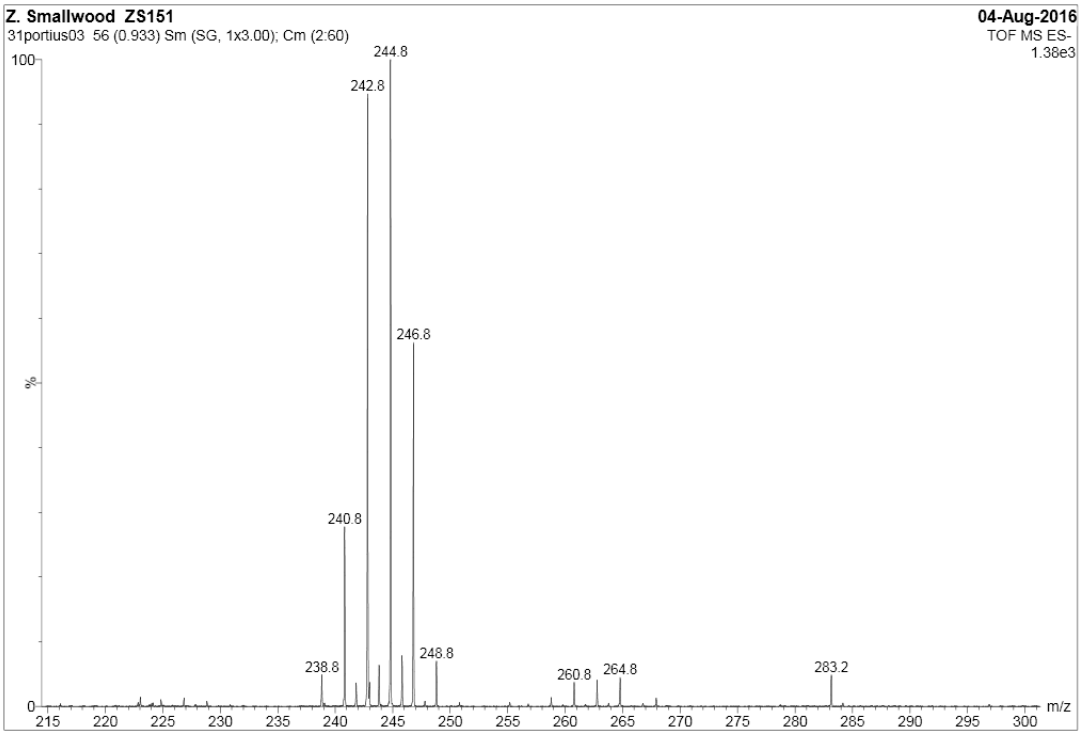

Fig. SI24c. ESI(−) TOF mass spectrum of $PPN_2Ge(CN)_6$ between m/z = 215 and 201.

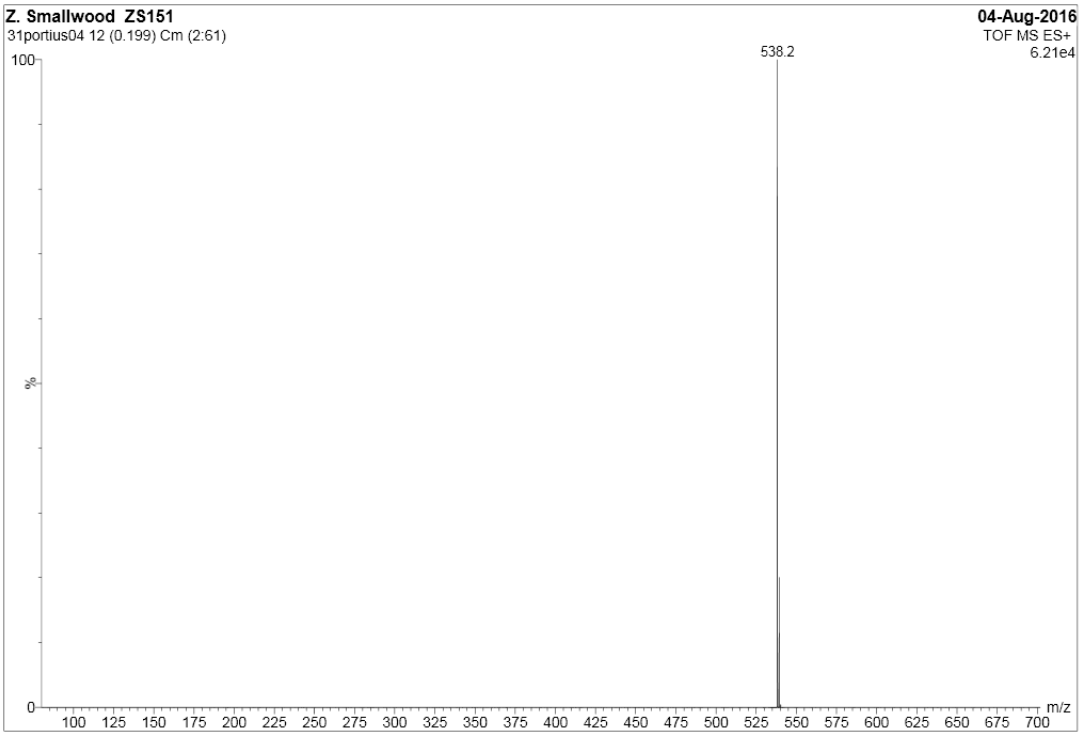

Fig. SI24c. ESI(+) TOF mass spectrum of $PPN_2Ge(CN)_6$ between m/z = 75 and 700.

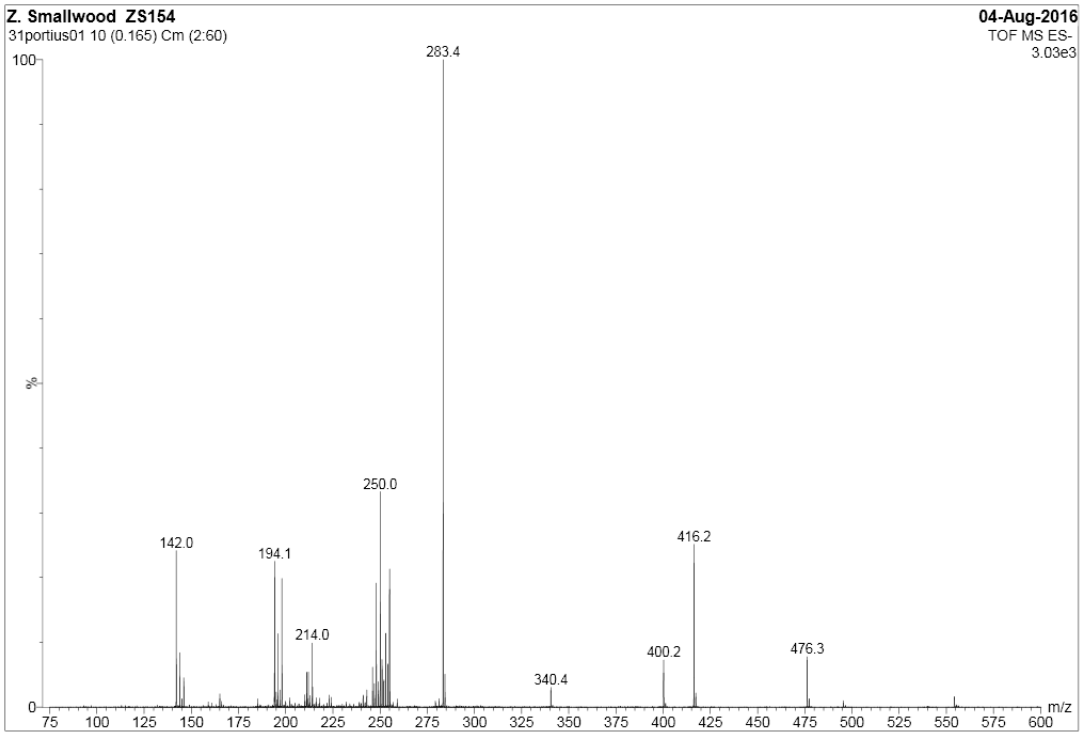

Fig. SI25a. ESI(−) TOF mass spectrum of $PPN_2Sn(CN)_6$ between m/z = 75 and 600.

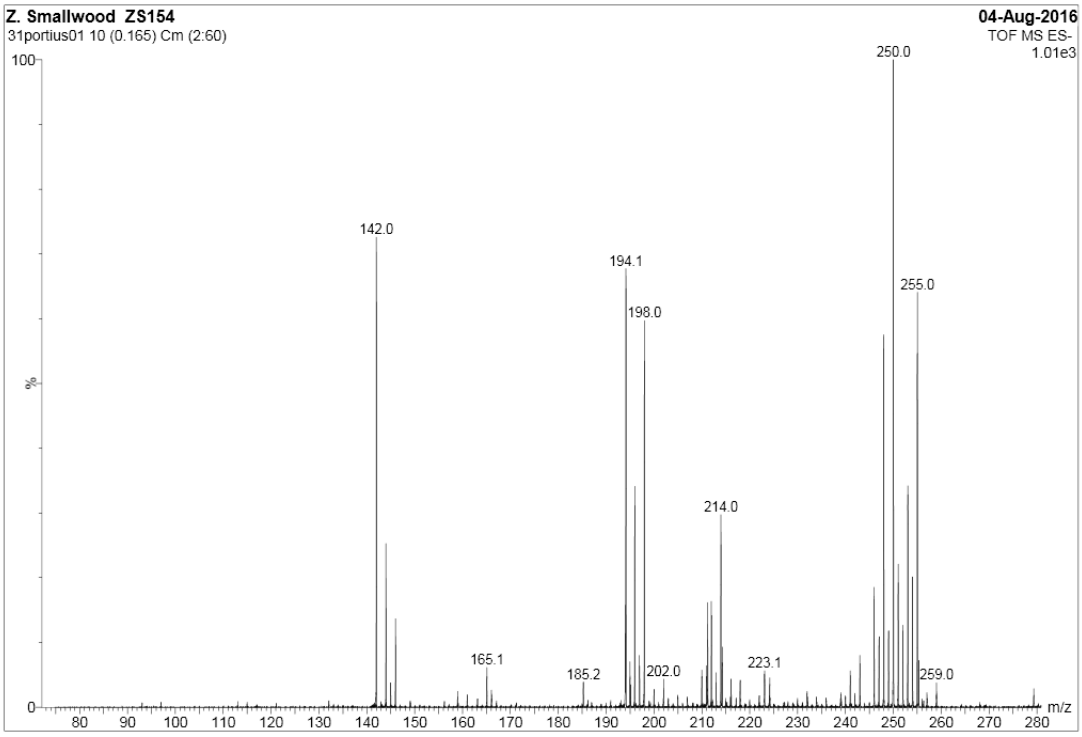

Fig. SI25b. ESI(−) TOF mass spectrum of $PPN_2Sn(CN)_6$ between m/z = 73 and 280.

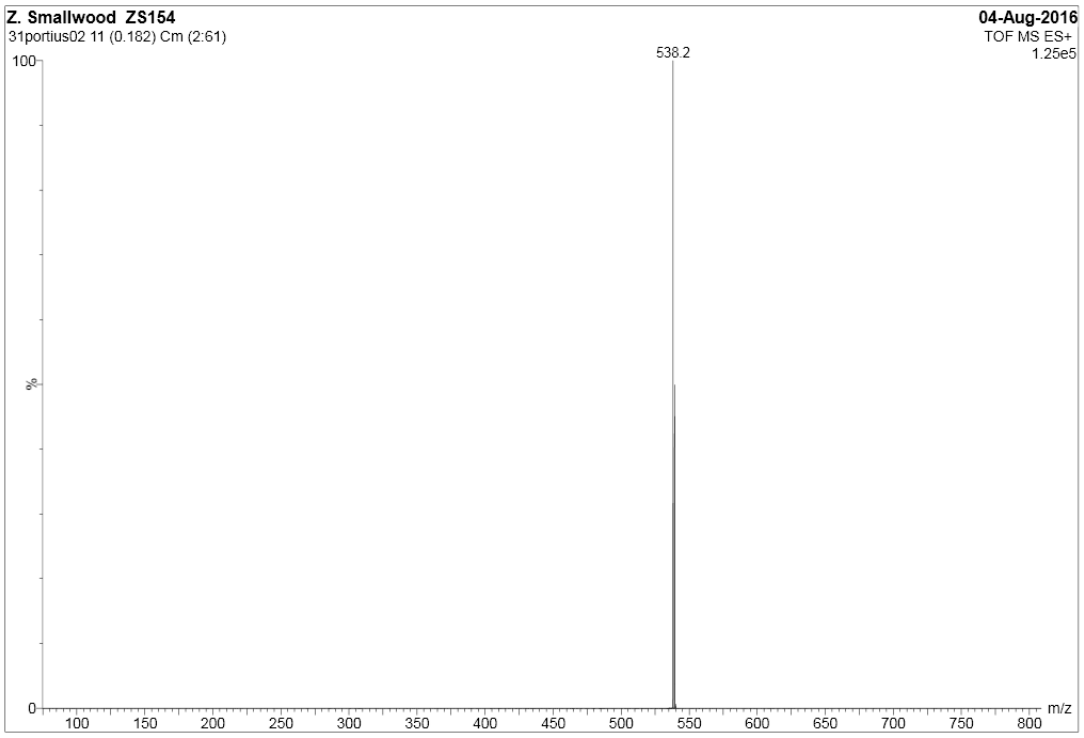

Fig. SI25c. ESI(+) TOF mass spectrum of $PPN_2Sn(CN)_6$ between m/z = 75 and 809.

Results of computational chemistry

Density functional theory was used to optimise gas phase geometries and calculate vibrational frequencies for the complexes $E(CN)_6^{2-}$ present in compounds **1**, **2** and **3**, using the PBE0 hybrid functional in the Gaussian 09 software package.[12,13,14] The basis set selected was aug-cc-pV(T+d)Z for carbon, nitrogen and silicon,[15,16] where the "+d" denotes additional tight *d* functions for second row atoms,[17] and the aug-cc-pVTZ-PP basis for heavier elements.[18] The latter is matched to small-core relativistic pseudopotentials replacing 10, 28 and 60 electrons for germanium, tin and lead, respectively.[19] Tight convergence criteria were used in geometry optimisation, along with an UltraFine integration grid (99 radial shells and 590 angular points per shell). The optimised geometries belong to the O_h point group and frequency calculations indicate that the geometries are true minima.

Solution phase reaction energies (ΔG_{sol}) were calculated in a composite fashion, using explicitly correlated coupled cluster [CCSD(T)-F12b][20,21] single point gas phase calculations on the PBE0 optimised geometries. The CCSD(T)-F12b calculations were carried out in the MOLPRO package of *ab initio* programs,[22,23] using the aug-cc-pVTZ-F12 basis set for lighter elements and cc-pVTZ-PP-F12 for Ge, Sn and Pb.[24,25,26] This basis set for the heavier elements was augmented with additional diffuse *d* and *f* functions, with the exponents created as an even-tempered extension. Matching auxiliary basis sets were used,[25, 27,28,29,30] along with a geminal Slater exponent of 1.0 a_0^{-1}. The outer *d* electrons, for the Ge, Sn and Pb cases, were included in the correlation treatment. The thermal corrections and entropies at the PBE0

level of theory were used for the CCSD(T)-F12b energies. Gibbs free energies of solvation were calculated in the Gaussian 09 program at the PBE0 level of theory using the Solvation Model based on Density (SMD)[31] with the parameters for acetonitrile.

Cartesian coordinates for minimum structure of $Si(CN)_6^{2-}$

```
13
PBE0/aug-cc-pV(T+d)Z Energy = -846.103256503
Si     0.000000    0.000000    0.000000
C      0.000000    0.000000    1.960603
C      0.000000    1.960603    0.000000
C      0.000000   -1.960603    0.000000
C     -1.960603    0.000000    0.000000
C      0.000000    0.000000   -1.960603
C      1.960603    0.000000    0.000000
N      0.000000    0.000000    3.116990
N     -3.116990    0.000000    0.000000
N      0.000000    0.000000   -3.116990
N      0.000000   -3.116990    0.000000
N      3.116990    0.000000    0.000000
N      0.000000    3.116990    0.000000
```

Vibrational frequencies for $Si(CN)_6^{2-}$

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	t2u	89.62	0.00000	NO	NO
8	t2u	89.62	0.00000	NO	NO
9	t2u	89.62	0.00000	NO	NO
10	t2g	110.07	0.00000	NO	YES
11	t2g	110.07	0.00000	NO	YES
12	t2g	110.07	0.00000	NO	YES
13	t1u	136.44	17.3318	YES	NO
14	t1u	136.44	17.3318	YES	NO
15	t1u	136.44	17.3318	YES	NO
16	t1g	293.01	0.00000	NO	NO
17	t1g	293.01	0.00000	NO	NO
18	t1g	293.01	0.00000	NO	NO
19	eg	313.25	0.00000	NO	YES
20	eg	313.25	0.00000	NO	YES
21	a1g	397.46	0.00000	NO	YES
22	t2u	424.52	0.00000	NO	NO
23	t2u	424.52	0.00000	NO	NO
24	t2u	424.52	0.00000	NO	NO
25	t1u	433.90	24.4522	YES	NO
26	t1u	433.90	24.4522	YES	NO
27	t1u	433.90	24.4522	YES	NO
28	t2g	477.01	0.00000	NO	YES
29	t2g	477.01	0.00000	NO	YES
30	t2g	477.01	0.00000	NO	YES

31	t1u	593.86	247.024	YES	NO
32	t1u	593.86	247.024	YES	NO
33	t1u	593.86	247.024	YES	NO
34	eg	2277.35	0.00000	NO	YES
35	eg	2277.35	0.00000	NO	YES
36	t1u	2281.78	0.0259	YES	NO
37	t1u	2281.78	0.0259	YES	NO
38	t1u	2281.78	0.0259	YES	NO
39	a1g	2282.42	0.00000	NO	YES

Cartesian coordinates for minimum structure of $Ge(CN)_6^{2-}$

```
13
PBE0/aug-cc-pV(T+d)Z-PP Energy = -851.229046534
Ge    0.000000    0.000000    0.000000
C     0.000000    0.000000    2.059096
C     0.000000    2.059096    0.000000
C     0.000000   -2.059096    0.000000
C    -2.059096    0.000000    0.000000
C     0.000000    0.000000   -2.059096
C     2.059096    0.000000    0.000000
N     0.000000    0.000000    3.215457
N    -3.215457    0.000000    0.000000
N     0.000000    0.000000   -3.215457
N     0.000000   -3.215457    0.000000
N     3.215457    0.000000    0.000000
N     0.000000    3.215457    0.000000
```

Vibrational frequencies for $Ge(CN)_6^{2-}$

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	t2u	80.39	0.00000	NO	NO
8	t2u	80.39	0.00000	NO	NO
9	t2u	80.39	0.00000	NO	NO
10	t2g	99.85	0.00000	NO	YES
11	t2g	99.85	0.00000	NO	YES
12	t2g	99.85	0.00000	NO	YES
13	t1u	115.63	25.8037	YES	NO
14	t1u	115.63	25.8037	YES	NO
15	t1u	115.63	25.8037	YES	NO
16	t1g	263.80	0.00000	NO	NO
17	t1g	263.80	0.00000	NO	NO
18	t1g	263.80	0.00000	NO	NO
19	eg	275.60	0.00000	NO	YES
20	eg	275.60	0.00000	NO	YES
21	t1u	370.79	157.830	YES	NO
22	t1u	370.79	157.830	YES	NO
23	t1u	370.79	157.830	YES	NO
24	a1g	377.41	0.00000	NO	YES
25	t2u	380.15	0.00000	NO	NO

26	t2u	380.15	0.00000	NO	NO
27	t2u	380.15	0.00000	NO	NO
28	t1u	417.35	37.3168	YES	NO
29	t1u	417.35	37.3168	YES	NO
30	t1u	417.35	37.3168	YES	NO
31	t2g	437.32	0.00000	NO	YES
32	t2g	437.32	0.00000	NO	YES
33	t2g	437.32	0.00000	NO	YES
34	eg	2273.87	0.00000	NO	YES
35	eg	2273.87	0.00000	NO	YES
36	t1u	2277.23	0.0076	YES	NO
37	t1u	2277.23	0.0076	YES	NO
38	t1u	2277.23	0.0076	YES	NO
39	a1g	2281.94	0.00000	NO	YES

Cartesian coordinates for minimum structure of $Sn(CN)_6^{2-}$

```
13
PBE0/aug-cc-pV(T+d)Z-PP Energy = -770.983203854
Sn    0.000000    0.000000    0.000000
C     0.000000    0.000000    2.238116
C     0.000000    2.238116    0.000000
C     0.000000   -2.238116    0.000000
C    -2.238116    0.000000    0.000000
C     0.000000    0.000000   -2.238116
C     2.238116    0.000000    0.000000
N     0.000000    0.000000    3.394619
N    -3.394619    0.000000    0.000000
N     0.000000    0.000000   -3.394619
N     0.000000   -3.394619    0.000000
N     3.394619    0.000000    0.000000
N     0.000000    3.394619    0.000000
```

Vibrational frequencies for $Sn(CN)_6^{2-}$

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	t2u	67.98	0.00000	NO	NO
8	t2u	67.98	0.00000	NO	NO
9	t2u	67.98	0.00000	NO	NO
10	t2g	87.71	0.00000	NO	YES
11	t2g	87.71	0.00000	NO	YES
12	t2g	87.71	0.00000	NO	YES
13	t1u	98.87	31.8319	YES	NO
14	t1u	98.87	31.8319	YES	NO
15	t1u	98.87	31.8319	YES	NO
16	t1g	236.70	0.00000	NO	NO
17	t1g	236.70	0.00000	NO	NO
18	t1g	236.70	0.00000	NO	NO
19	eg	272.90	0.00000	NO	YES
20	eg	272.90	0.00000	NO	YES

21	t2u	313.07	0.00000	NO	NO
22	t2u	313.07	0.00000	NO	NO
23	t2u	313.07	0.00000	NO	NO
24	t1u	334.91	170.721	YES	NO
25	t1u	334.91	170.721	YES	NO
26	t1u	334.91	170.721	YES	NO
27	t1u	353.05	10.0734	YES	NO
28	t1u	353.05	10.0734	YES	NO
29	t1u	353.05	10.0734	YES	NO
30	a1g	355.51	0.00000	NO	YES
31	t2g	371.60	0.00000	NO	YES
32	t2g	371.60	0.00000	NO	YES
33	t2g	371.60	0.00000	NO	YES
34	eg	2273.83	0.00000	NO	YES
35	eg	2273.83	0.00000	NO	YES
36	t1u	2275.96	0.5296	YES	NO
37	t1u	2275.96	0.5296	YES	NO
38	t1u	2275.96	0.5296	YES	NO
39	a1g	2279.35	0.00000	NO	YES

Cartesian coordinates for minimum structure of $Pb(CN)_6^{2-}$

```
13
PBE0/aug-cc-pV(T+d)Z-PP Energy = -749.464340747
Pb    0.000000    0.000000    0.000000
C     0.000000    0.000000    2.329288
C     0.000000    2.329288    0.000000
C     0.000000   -2.329288    0.000000
C    -2.329288    0.000000    0.000000
C     0.000000    0.000000   -2.329288
C     2.329288    0.000000    0.000000
N     0.000000    0.000000    3.486484
N    -3.486484    0.000000    0.000000
N     0.000000    0.000000   -3.486484
N     0.000000   -3.486484    0.000000
N     3.486484    0.000000    0.000000
N     0.000000    3.486484    0.000000
```

Vibrational frequencies for $Pb(CN)_6^{2-}$

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	t2u	60.39	0.00000	NO	NO
8	t2u	60.39	0.00000	NO	NO
9	t2u	60.39	0.00000	NO	NO
10	t2g	80.17	0.00000	NO	YES
11	t2g	80.17	0.00000	NO	YES
12	t2g	80.17	0.00000	NO	YES
13	t1u	85.74	36.9009	YES	NO
14	t1u	85.74	36.9009	YES	NO
15	t1u	85.74	36.9009	YES	NO

16	t1g	213.86	0.00000	NO	NO
17	t1g	213.86	0.00000	NO	NO
18	t1g	213.86	0.00000	NO	NO
19	eg	234.80	0.00000	NO	YES
20	eg	234.80	0.00000	NO	YES
21	t1u	274.31	159.546	YES	NO
22	t1u	274.31	159.546	YES	NO
23	t1u	274.31	159.546	YES	NO
24	t2u	275.56	0.00000	NO	NO
25	t2u	275.56	0.00000	NO	NO
26	t2u	275.56	0.00000	NO	NO
27	t1u	320.07	6.8779	YES	NO
28	t1u	320.07	6.8779	YES	NO
29	t1u	320.07	6.8779	YES	NO
30	a1g	326.43	0.00000	NO	YES
31	t2g	337.01	0.00000	NO	YES
32	t2g	337.01	0.00000	NO	YES
33	t2g	337.01	0.00000	NO	YES
34	eg	2263.18	0.00000	NO	YES
35	eg	2263.18	0.00000	NO	YES
36	t1u	2265.34	0.8160	YES	NO
37	t1u	2265.34	0.8160	YES	NO
38	t1u	2265.34	0.8160	YES	NO
39	a1g	2268.94	0.00000	NO	YES

Cartesian coordinates for minimum structure of CN^-

```
 2
PBE0/aug-cc-pVTZ Energy = -92.7744916685
C    0.000000    0.000000    -0.630582
N    0.000000    0.000000     0.540499
```

Energy of Cl^-

```
 1
PBE0/aug-cc-pV(T+d)Z Energy = -460.137055441
Cl   0.000000    0.000000     0.000000
```

Cartesian coordinates for minimum structure of $Si(CN)_5^-$

```
11
PBE0/aug-cc-pV(T+d)Z Energy = -753.340694467
Si   0.000000    0.000000    0.000000
C    0.000000    0.000000    1.948047
N    0.000000    0.000000    3.102778
C    0.000000    1.872530    0.000000
N    0.000000    3.025328    0.000000
C    0.000000    0.000000   -1.948047
N    0.000000    0.000000   -3.102778
C   -1.621659   -0.936265    0.000000
N   -2.620011   -1.512664    0.000000
C    1.621659   -0.936265    0.000000
N    2.620011   -1.512664    0.000000
```

Cartesian coordinates for minimum structure of $Si(CN)_4$

```
 9
PBE0/aug-cc-pV(T+d)Z Energy = -660.452912621
```

```
Si    0.000000    0.000000    0.000000
C     1.053140    1.053140    1.053140
C    -1.053140   -1.053140    1.053140
C     1.053140   -1.053140   -1.053140
C    -1.053140    1.053140   -1.053140
N     1.717687    1.717687    1.717687
N    -1.717687   -1.717687    1.717687
N    -1.717687    1.717687   -1.717687
N     1.717687   -1.717687   -1.717687
```

Cartesian coordinates for minimum structure of Si(CN)5Cl2-

```
12
PBE0/aug-cc-pV(T+d)Z Energy = -1213.44441103
Si    0.000000    0.000000   -0.047073
C     0.000000    1.952935   -0.043495
C     0.000000    0.000000   -2.002254
C     1.952935    0.000000   -0.043495
C     0.000000   -1.952935   -0.043495
C    -1.952935    0.000000   -0.043495
N     0.000000    3.109430   -0.054672
N     3.109430    0.000000   -0.054672
N     0.000000   -3.109430   -0.054672
N     0.000000    0.000000   -3.158457
N    -3.109430    0.000000   -0.054672
Cl    0.000000    0.000000    2.197438
```

Cartesian coordinates for minimum structure of $Ge(CN)_5^-$

```
11
PBE0/aug-cc-pV(T+d)Z-PP Energy = -758.478575730
Ge    0.000000    0.000000    0.000000
C     0.000000    0.000000    2.056614
N     0.000000    0.000000    3.211526
C     0.000000    1.944992    0.000000
N     0.000000    3.097052    0.000000
C     0.000000    0.000000   -2.056614
N     0.000000    0.000000   -3.211526
C    -1.684413   -0.972496    0.000000
N    -2.682125   -1.548526    0.000000
C     1.684413   -0.972496    0.000000
N     2.682125   -1.548526    0.000000
```

Cartesian coordinates for minimum structure of $Ge(CN)_4$

```
 9
PBE0/aug-cc-pV(T+d)Z-PP Energy = -665.606127187
Ge    0.000000    0.000000    0.000000
C     1.093368    1.093368    1.093368
C    -1.093368   -1.093368    1.093368
C     1.093368   -1.093368   -1.093368
C    -1.093368    1.093368   -1.093368
N     1.757397    1.757397    1.757397
N    -1.757397   -1.757397    1.757397
N    -1.757397    1.757397   -1.757397
N     1.757397   -1.757397   -1.757397
```

Cartesian coordinates for minimum structure of $Ge(CN)_5Cl^{2-}$

```
12
PBE0/aug-cc-pV(T+d)Z-PP Energy = -1218.57517226
Ge    0.000000    0.000000    0.053554
C     0.000000    2.048179    0.035260
```

```
C    0.000000    0.000000    2.100533
C   -2.048179    0.000000    0.035260
C    0.000000   -2.048179    0.035260
C    2.048179    0.000000    0.035260
N    0.000000    3.204582    0.040352
N   -3.204582    0.000000    0.040352
N    0.000000   -3.204582    0.040352
N    0.000000    0.000000    3.256517
N    3.204582    0.000000    0.040352
Cl   0.000000    0.000000   -2.299332
```

Cartesian coordinates for minimum structure of $Sn(CN)_5^-$

```
11
PBE0/aug-cc-pV(T+d)Z-PP Energy = -678.219416893
Sn   0.000000    0.000000    0.000000
C    0.000000    0.000000    2.211336
N    0.000000    0.000000    3.366116
C    2.137686   -0.000005    0.000000
N    3.290478    0.000003    0.000000
C    0.000000    0.000000   -2.211336
N    0.000000    0.000000   -3.366116
C   -1.068839    1.851293    0.000000
N   -1.645242    2.849636    0.000000
C   -1.068848   -1.851288    0.000000
N   -1.645236   -2.849639    0.000000
```

Cartesian coordinates for minimum structure of $Sn(CN)_4$

```
 9
PBE0/aug-cc-pV(T+d)Z-PP Energy = -585.330932132
Sn   0.000000    0.000000    0.000000
C    1.198994    1.198994    1.198994
C   -1.198994   -1.198994    1.198994
C    1.198994   -1.198994   -1.198994
C   -1.198994    1.198994   -1.198994
N    1.863469    1.863469    1.863469
N   -1.863469   -1.863469    1.863469
N   -1.863469    1.863469   -1.863469
N    1.863469   -1.863469   -1.863469
```

Cartesian coordinates for minimum structure of $Sn(CN)_5Cl^{2-}$

```
12
PBE0/aug-cc-pV(T+d)Z-PP Energy = -1138.33405358
Sn   0.000000    0.000000    0.037230
C    0.000000    2.232609    0.034943
C    0.000000    0.000000    2.271947
C   -2.232609    0.000000    0.034943
C    0.000000   -2.232609    0.034943
C    2.232609    0.000000    0.034943
N    0.000000    3.389212    0.040129
N   -3.389212    0.000000    0.040129
N    0.000000   -3.389212    0.040129
N    0.000000    0.000000    3.428375
N    3.389212    0.000000    0.040129
Cl   0.000000    0.000000   -2.438474
```

Cartesian coordinates for minimum structure of $Pb(CN)_5^-$

```
11
PBE0/aug-cc-pV(T+d)Z-PP Energy = -656.709980672
Pb   0.000000    0.000000    0.000000
```

```
C     0.000000    0.000000    2.297870
N     0.000000    0.000000    3.453279
C     2.211485   -0.000004    0.000000
N     3.364680    0.000003    0.000000
C     0.000000    0.000000   -2.297870
N     0.000000    0.000000   -3.453279
C    -1.105739    1.915205    0.000000
N    -1.682342    2.913897    0.000000
C    -1.105746   -1.915201    0.000000
N    -1.682338   -2.913900    0.000000
```

Cartesian coordinates for minimum structure of $Pb(CN)_4$

```
 9
PBE0/aug-cc-pV(T+d)Z-PP Energy = -563.832495366
Pb    0.000000    0.000000    0.000000
C     1.236473    1.236473    1.236473
C    -1.236473   -1.236473    1.236473
C     1.236473   -1.236473   -1.236473
C    -1.236473    1.236473   -1.236473
N     1.901026    1.901026    1.901026
N    -1.901026   -1.901026    1.901026
N    -1.901026    1.901026   -1.901026
N     1.901026   -1.901026   -1.901026
```

Cartesian coordinates for minimum structure of $Pb(CN)_5Cl^{2-}$

```
12
PBE0/aug-cc-pV(T+d)Z-PP Energy = -1116.81866423
Pb    0.000000    0.000000    0.034817
C     0.000000    2.323050    0.026114
C     0.000000    0.000000    2.359516
C    -2.323050    0.000000    0.026114
C     0.000000   -2.323050    0.026114
C     2.323050    0.000000    0.026114
N     0.000000    3.480301    0.030081
N    -3.480301    0.000000    0.030081
N     0.000000   -3.480301    0.030081
N     0.000000    0.000000    3.516612
N     3.480301    0.000000    0.030081
Cl    0.000000    0.000000   -2.535138
```

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