Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Reactivity of α-Cationic Phosphines: The Effect of Imidazolinium and Amidinium Substituents

Estela Haldón, Ágnes Kozma, Hendrik Tinnermann, Lianghu Gu, Richard Goddard and Manuel Alcarazo*[a]

[a]Max-Planck-Institut für Kohlenforschung, Kaiser Wilhelm Platz 1, 45470-Mülheim an der Ruhr (Germany).
e-mail: alcarazo@kofo.mpg.de

Table of Contents:

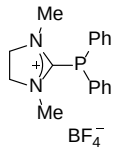
Experimental Procedures

General: All reactions were carried out in flame-dried glassware under Argon. All solvents were purified by distillation over the appropriate drying agents and were transferred under Argon. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 600, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Column chromatography was performed on Merck 60 silica gel (40-63 µm). Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by UV.

All commercially available compounds (ABCR, Acros, Aldrich) were used as received. **1a**,[1] **7(Cl)**,[2] **14**,[3] **15**,[4] **24**[5] and **27**[6] were prepared according to literature procedures.

Synthesis and Characterization of New Compounds

Compound **2**:



Ph_2PH (2.37 mL, 13.61 mmol) was added to a solution of **1a** (1.00 g, 4.54 mmol) in dry THF (18 mL) and the resulting mixture stirred at 60°C for 1 day. After cooling to room temperature, the solvent was evaporated and the residue diluted with CH_2Cl_2 (6 mL). $NaBF_4$ (2.50 g, 22.70 mmol) was then added to the suspension and stirred at room temperature for 1 hour. After filtration, the filtrate was concentrated and the crude product purified by column chromatography (CH_2Cl_2/MeOH: 97/3) to give the title compound as a transparent oil that solidified on standing (1.11 g, 66%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.85 (s, 6H), 4.05 (d, *J* = 1.1 Hz, 4H), 7.50 - 7.58 (m, 10H) ppm.

$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) δ = -14.6 ppm.

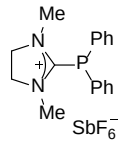
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 35.8 (d, J_{PC} = 9.2 Hz), 52.1, 126.8 (d, J_{PC} = 6.0 Hz), 130.2 (d, J_{PC} = 8.3 Hz), 131.6, 134.2 (d, J_{PC} = 21.6 Hz), 168.9 (d, J_{PC} = 53.6 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{20}N_2P]^+$: 283.135864; *found* 283.135696.

IR(solid) $\tilde{\nu}$ = 695, 747, 934, 996, 1033, 1045, 1296, 1411, 1436, 1480, 1569, 2940, 3055 cm^{-1}.

[1] S. Kitamura, N. Tashiro, S. Miyagawa, T. Okauchi, *Synthesis* 2011, 7, 1037–1044.
[2] S. Herres-Pawlis,U. Flörke, G. Henkel, *Eur. J. Inorg. Chem.* 2005, 3815-3824.
[3] J. Petuškova, H. Bruns, M. Alcarazo, *Angew. Chem. Int. Ed.* 2011, **50**, 3799-3802.
[4] H. Tinnermann, C. Wille, M. Alcarazo, *Angew. Chem. Int. Ed.* 2014, **53**, 8732-8736.
[5] S. J. Pastine, S. W. Youn, D. Sames, *Org. Lett.* 2003, **5**, 1055-1058.
[6] J. Carreras; M. Patil; W. Thiel; M. Alcarazo, *J. Am. Chem. Soc.* 2012, **134**, 16753−16758.

Compound **3**:



$NaSbF_6$ (3.10 g, 11.83 mmol) was added to a solution of compound **1(Cl)** (1.00 g, 5.91 mmol) in CH_3CN (15 mL) and the resulting mixture stirred at room temperature overnight. Evaporation of the solvent under vacuum and extraction with CH_2Cl_2 afforded 2-chloro-1,3-dimethyl-4,5-dihydro-1*H*-imidazol-3-ium hexafluoroantimonate as a white solid (1.96 g, 90%). $TMSPPh_2$ (1.36 mL, 5.31 mmol) was added to a solution of the previously prepared salt (1.96 g, 5.31 mmol) in dry CH_2Cl_2 (18 mL) and the resulting mixture stirred at 40°C overnight. After cooling to room temperature, the mixture was concentrated and the residue purified by column chromatography (CH_2Cl_2/MeOH: 97/3) to give the title compound as a white solid (2.61 g, 95%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 2.75 (s, 6H), 3.88 (d, *J* = 1.2 Hz, 4H), 7.55 - 7.35 (m, 10H) ppm.

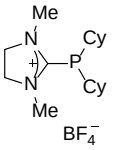
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ = -14.32 ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 36.1 (d, J_{PC} = 9.2 Hz), 52.3, 126.7 (dd, J_{PC} = 6.0, 2.5 Hz), 130.5 (d, J_{PC} = 8.3 Hz), 132.2, 134.5 (d, J_{PC} = 21.7 Hz), 169.8 (d, J_{PC} = 56.3 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{20}N_2P]^+$: 283.135862; *found*: 283.135680.

IR(solid) $\tilde{\nu}$ = 435, 444, 493, 505, 652, 694, 745, 846, 938, 999, 1096, 1295, 1335, 1408, 1440, 1479, 1572, 2943, 3076 cm^{-1}.

Compound **4**:



Cy_2PH (2.20 mL, 10.89 mmol) was added to a solution of **1a** (800 mg, 3.63 mmol) in dry THF (15 mL) and the resulting mixture stirred at 60°C for 1 day. After cooling to room temperature, the solvent was evaporated, the residue washed with Et_2O (3 x 8 mL) and diluted with CH_3CN (5 mL). $NaBF_4$ (2.00 g, 18.15 mmol) was then added to the suspension and stirred at room temperature for 12 hours. The solvent was then evaporated and the product extracted with CH_2Cl_2. Evaporation of the solvent and purification of the crude product by column chromatography (CH_2Cl_2/acetone: 90/10) gave the title compound as a white solid (819 mg, 59%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.67 - 1.43 (m, 10H), 1.46 - 1.56 (m, 2H), 1.65 - 1.74 (m, 2H), 1.74 - 1.85 (m, 4H), 1.85 - 1.94 (m, 2H), 2.27 - 2.39 (m, 2H), 3.31 (s, 6H), 3.98 (s, 4H) ppm.

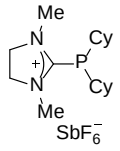
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = -10.4 ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 25.9, 26.5 (d, J_{PC} = 25.3 Hz), 26.6 (d, J_{PC} = 19.3 Hz), 30.6 (d, J_{PC} = 8.0 Hz), 32.0 (d, J_{PC} = 24.2 Hz), 33.9 (d, J_{PC} = 14.9 Hz), 36.4 (d, J_{PC} = 11.9 Hz), 51.8, 171.3 (d, J_{PC} = 63.8 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{32}N_2P]^+$: 295.229762; *found* 295.229690.

IR(solid) $\tilde{\nu}$ = 483, 517, 633, 852, 890, 933, 1032, 1046, 1093, 1203, 1300, 1341, 1411, 1447, 1525, 1579, 2846, 2932 cm^{-1}.

Compound **5**:



$NaSbF_6$ (699 mg, 2.70 mmol) was added to a solution of compound **4** (516 mg, 1.35 mmol) in CH_3CN (5 mL) and the resulting mixture stirred at room temperature for 12 hours. The solvent was then evaporated and the crude extracted with CH_2Cl_2. Evaporation of the solvent under vacuum afforded the desired product as a white solid (524 mg, 73%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.39 - 1.21 (m, 10H), 1.59 - 1.50 (m, 2H), 1.75 - 1.66 (m, 2H), 1.90 - 1.77 (m, 6H), 2.37 - 2.26 (m, 2H), 3.32 (s, 6H), 4.00 (s, 4H) ppm.

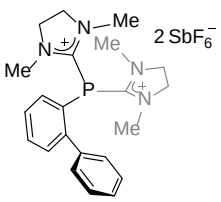
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ = -9.5 ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 25.9 (d, J_{PC} = 1.3 Hz), 26.5 (d, J_{PC} = 14.8 Hz), 26.7 (d, J_{PC} = 8.6 Hz), 30.6 (d, J_{PC} = 7.9 Hz), 32.1 (d, J_{PC} = 24.1 Hz), 33.9 (d, J_{PC} = 14.7 Hz), 36.5 (d, J_{PC} = 11.7 Hz), 51.8 (d, J_{PC} = 0.8 Hz), 171.7 (d, J_{PC} = 65.7 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{32}N_2P]^+$: 295.229762; *found*: 295.229620.

IR(solid) $\tilde{\nu}$ = 482, 653, 851, 936, 1003, 1112, 1299, 1339, 1448, 1575, 2854, 2933 cm^{-1}.

Compound **6**:



1a (133 mg, 0.60 mmol) and Et_3N (0.088 mL, 0.63 mmol) were added to a solution of diphenyl(2-phosphinophenyl)phosphine (56 mg, 0.34 mmol) in THF (5 mL) and the mixture stirred at 60^{o}C overnight. After cooling to room temperature, the solvent was evaporated under vacuum. The resulting white solid was dissolved in CH_2Cl_2, washed with saturated aq. solution of $NaSbF_6$ (2 x 5 mL) and dried with Na_2SO_4. After filtration, the solvent was evaporated under vacuum to give the crude product, which could be recrystallized from CH_3CN/Et_2O yielding the title compound as white solid (61 mg, 24%).

^{1}H NMR (400 MHz, CD_3CN) δ = 2.88 (s, 12H), 3.96 - 3.82 (m, 8H), 7.43 - 7.41 (m, 2H), 7.66 - 7.57 (m, 6H), 7.84 - 7.79 (m, 1H) ppm.

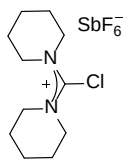
^{31}P{^{1}H} NMR (121 MHz, CD_3CN) δ = -43.1 ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ = 36.9 (d, J_{PC} = 9.0 Hz), 53.4, 128.6, 128.9 (d, J_{PC} = 24.1 Hz), 130.3 (d, J_{PC} = 4.0 Hz), 130.5 (d, J_{PC} = 13.8 Hz), 130.8 (d, J_{PC} = 1.4 Hz), 133.0 (d, J_{PC} = 6.0 Hz), 135.0, 135.7, 139.7 (d, J_{PC} = 8.0 Hz), 150.1 (d, J_{PC} = 34.1 Hz), 164.1 (d, J_{PC} = 47.1 Hz) ppm.

HRMS *calcd.* for $[C_{22}H_{29}N_4F_6PSb]^+$: 615.106410; *found* 615.106603.

IR(solid) $\tilde{\nu}$ = 435, 455, 468, 554, 653, 707, 761, 779, 935, 1206, 1301, 1337, 1413, 1447, 1526, 1583 cm^{-1}.

Compound **7**:



$NaSbF_6$ (2.40 g, 9.26 mmol) was added under argon to a solution of known **7(Cl)** (1.16 g, 4.63 mmol) in CH_3CN (10 mL). The resulting mixture was stirred at room temperature overnight. The solvent was then removed and extracted with CH_2Cl_2. Evaporation of the solvent afforded **7** as a white solid (1.70 g, 84%).

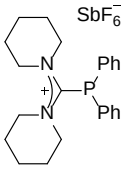
^{1}H NMR (300 MHz, CD_2Cl_2) δ = 1.89 - 1.73 (m, 12H), 3.74 (t, J = 5.1 Hz, 8H) ppm.

$^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ = 23.2, 26.2, 55.1, 156.8 ppm.

HRMS *calcd.* for $[C_{11}H_{20}N_2Cl]^+$:215.130950; *found*: 215.130780.

IR(solid) $\tilde{\nu}$ = 421, 445, 502, 521, 568, 650, 696, 746, 782, 854, 903, 928, 949, 1003, 1093, 1132, 1160, 1252, 1272, 1362, 1434, 1480, 1547, 1676, 2856, 2942 cm^{-1}.

Compound **8**:



Ph_2PH (2.16 mL, 11.64 mmol) was added to a solution of compound **7** (1.70 g, 3.88 mmol) in dry THF (6 mL) and the resulting mixture was stirred at 65°C for 3 days. After cooling to room temperature, the solvent was evaporated and the residue washed with Et_2O (3 x 10 mL) to yield the title compound as a white solid (1.20 g, 52%).

^1H NMR (300 MHz, CD_3CN) δ = 1.40 - 1.19 (m, 8H), 1.53 (p, *J* = 6.0 Hz, 4H), 3.72 - 3.64 (t, *J* = 5.5 Hz, 8H), 7.52 - 7.42 (m, 4H), 7.62 - 7.53 (m, 6H) ppm.

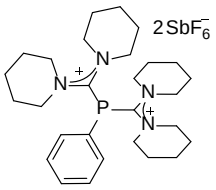
$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ = -4.1 ppm.

$^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ = 23.2, 26.0, 55.0 (d, J_{PC} = 8.0 Hz), 128.6 (d, J_{PC} = 7.1 Hz), 130.4 (d, J_{PC} = 7.9 Hz), 131.5, 134.1 (d, J_{PC} = 20.6 Hz), 179.9 (d, J_{PC} = 38.3 Hz) ppm.

HRMS *calcd.* for $[C_{23}H_{30}N_2P]^+$: 365.214112 ; *found* 365.214320.

IR(solid) $\tilde{\nu}$ = 446, 502, 521, 568, 650, 696, 746, 781, 854, 903, 928, 949, 1003, 1093, 1131, 1160, 1251, 1362, 1434, 1480, 1547, 1676, 2856, 2941 cm^{-1}.

Compound **9**:



A solution of phenylphosphine (50 mg, 0.45 mmol) in THF (5 mL) was added to a mixture of compound **7** (410 mg, 0.91 mmol) and KHDMS (181 mg, 0.91 mmol) at -78°C. The resulting suspension was warmed up to room temperature overnight. After evaporation of the solvents under vacuum, the residue was disolved with CH_3CN (5 mL) and $NaSbF_6$ (352 mg, 1.36 mmol) was added and the resulting suspension stirred at room temperature overnight. After evaporation of the solvent under vacuum, the solid was extracted twice with CH_2Cl_2. After evaporation of the combined organic phases, the solid obtained was washed with Et_2O to afford the title compound as a white solid (155 mg, 41%).

^1H NMR (400 MHz, CD_3CN) δ =1.82 - 1.37 (m, 24H), 4.22 - 3.21 (m, 16H), 7.91 - 7.36 (m, 5H) ppm.

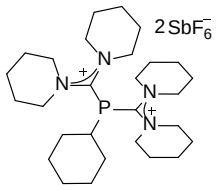
$^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN) δ = -15.3 ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ = 23.3, 26.3, 56.0, 122.8, 132.1 (d, J_{PC} = 10.3 Hz), 134.8, 137.5 (d, J_{PC} = 23.6 Hz), 173.9 (d, J_{PC} = 25.0 Hz) ppm.

HRMS *calcd.* for $[C_{28}H_{45}N_4SbF_6P]^+$: 703.231110; *found* 703.231803.

IR(solid) $\tilde{\nu}$ = 460, 496, 586, 654, 752, 859, 1013, 1132, 1255, 1290, 1362, 1441, 1538, 1557, 2864, 2945 cm^{-1}.

Compound **10**:



A solution of cyclohexylphosphine (50 mg, 0.43 mmol) in THF (5 mL) was added to a mixture of compound **7** (389 mg, 0.86 mmol) and KHDMS (172 mg, 0.86 mmol) at -78°C. The resulting suspension was warmed up to room temperature overnight. The solvent was then evaporated under vacuum and the residue disolved with CH_3CN (5 mL). $NaSbF_6$ (352 mg, 1.36 mmol) was added to the previous suspension and stirred at room temperature overnight. After evaporation of the solvent under vacuum, the solid obtained was extracted twice with CH_2Cl_2. Removal of the solvents under vacuum afforded a solid that was further washed with Et_2O. The title compound was obtained as a white solid (297 mg, 73%).

^{1}H NMR (400 MHz, CD_3CN) δ = 1.84 - 1.26 (m, 30H), 1.92 - 1.84 (m, 4H), 3.32 - 3.13 (m, 1H), 3.68 (m, 16H) ppm.

^{31}P{^{1}H} NMR (121 MHz, CD_3CN) δ = -3.7 ppm.

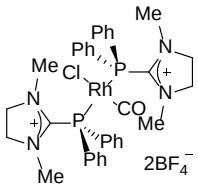
^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ = 23.3, 25.7 (d, J_{PC} = 2.1 Hz), 26.5, 27.1 (d, J_{PC} = 15.9 Hz), 32.8 (d, J_{PC} = 17.8 Hz), 38.9 (d, J_{PC} = 23.2 Hz), 55.9 (d, J_{PC} = 5.1 Hz), 174.5 (d, J_{PC} = 34.7 Hz) ppm.

HRMS *calcd.* for $[C_{28}H_{51}N_4SbF_6P]^+$: 709.278630; *found* 709.278753.

Anal.Calcd. for $C_{28}H_{51}F_{12}N_4PSb_2$: C, 35.54; H, 5.43; N, 5.92; *found*: C, 35.62; H, 5.39; N, 5.94.

IR(solid) $\tilde{\nu}$ = 483, 578, 653, 780, 860, 1012, 1130, 1255, 1354, 1445, 1533, 2862, 2943 cm^{-1}.

Compound **11**:



$[RhCl(CO)_2]_2$ (13 mg, 0.03 mmol) was added to a solution of compound **2** (48 mg, 0.13 mmol) in CH_2Cl_2 (1 mL) and the resulting mixture stirred at room temperature for 1 hour. Evaporation of the solvent afforded the desired product as a pale yellow solid (56 mg, 95%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 2.89 (s, 12H), 4.14 (s, 8H), 7.62 - 7.76 (m, 12H), 8.00 - 8.11 (m, 8H) ppm.

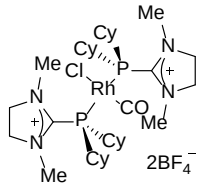
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ = 35.8 (d, J_{RhP} = 132.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 37.6, 52.9, 124.7 (t, J_{PC} = 24.7 Hz), 130.7 (t, J_{PC} = 5.8 Hz), 134.0, 135.5 (t, J_{PC} = 7.5 Hz), 164.1 (t, J_{PC} = 13.0 Hz), 185.3 (dt, J_{RhC} = 70.4 Hz, J_{PC} = 16.4 Hz) ppm.

HRMS *calcd.* for $[C_{35}H_{40}BClF_4N_4OP_2Rh]^+$: 819.145939; *found* 819.145265.

IR(solid) $\tilde{\nu}$ = 691, 731, 750, 931, 997, 1034, 1047, 1296, 1410, 1437, 1481, 1580, 1993, 2941 cm^{-1}.

Compound **12**:



$[RhCl(CO)_2]_2$ (25 mg, 0.07 mmol) was added to a solution of compound **4** (100 mg, 0.26 mmol) in CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a pale yellow solid (115 mg, 94%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.28 - 1.50 (m, 12H), 1.59 - 1.72 (m, 4H), 1.73 - 1.86

(m, 8H), 1.92 - 2.10 (m, 16H), 2.62 - 2.73 (m, 4H), 3.58 (s, 12H), 4.10 (s, 8H) ppm.

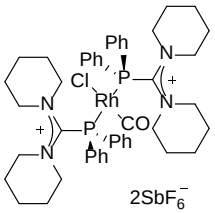
$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ = 50.1 (d, J_{RhP} = 127.8 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) δ = 25.4, 25.9 (br), 26.3 (br), 29.2 (br), 30.0 (br), 34.6 (br), 38.6 (br), 52.5, 161.4, 184.0 (dt, J_{RhC} = 72.1 Hz, J_{PC} = 16.2 Hz) ppm.

HRMS *calcd.* for $[C_{35}H_{64}N_4OBClF_4P_2Rh]^+$: 843.331561; *found* 843.332700.

IR(solid) $\tilde{\nu}$ = 480, 519, 571, 640, 743, 848, 931, 1019, 1040, 1292, 1448, 1557, 1962, 1971, 2854, 2930 cm^{-1}.

Compound **13**:



$[RhCl(CO)_2]_2$ (15 mg, 0.04 mmol) was added to a solution of compound **8** (95 mg, 0.16 mmol) in CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a pale yellow solid (135 mg, 94%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.44 - 1.20 (m, 16H), 1.55 - 1.46 (m, 8H), 3.72 - 3.41 (m, 16H), 7.62 (q, *J* = 7.6, 6.4 Hz, 12H), 7.86 (q, *J* = 6.1 Hz, 8H) ppm.

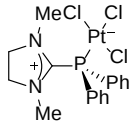
$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ = 45.4 (d, J_{RhP} = 127.9 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ = 21.5, 24.8, 54.2, 124.5 (t, J_{PC} = 23.4 Hz), 129.6 (t, J_{PC} = 5.5 Hz), 132.8, 134.6 (t, J_{PC} = 7.2 Hz), 174.2 (t, J_{RhC} = 19.4 Hz) ppm.

HRMS *calcd.* for $[C_{47}H_{60}ClN_4OF_6P_2RhSb]^+$:1131.191511; *found*: 1131.192190.

IR(solid) $\tilde{\nu}$ = 433, 469, 499, 533, 564, 653, 695, 749, 857, 1010, 1089, 1252, 1363, 1437, 1544, 1986, 2089, 2943 cm^{-1}.

Compound **16**:



K_2PtCl_4 (112 mg, 0.27 mmol) was added to a solution of compound **2** (100 mg, 0.27 mmol) in dry CH_3CN (4 mL) and the mixture was stirred at room temperature overnight. The solvent was then evaporated and the residue recrystallized from DMSO/CH_2Cl_2 affording the desired product as a yellow solid (122 mg, 77%).

^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ = 2.62 (s, 6H), 3.95 (s, 4H), 7.56 - 7.76 (m, 6H), 8.26 - 8.43 (m, 4H) ppm.

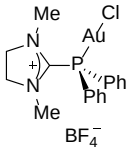
$^{31}P\{^{1}H\}$ NMR (121 MHz, $(CD_3)_2SO$) δ = 4.4 (J_{PtP} = 3941.6 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) δ = 36.6 (d, J_{PC} = 2.4 Hz), 52.0 (d, J_{PC} = 2.5 Hz), 124.0 (d, J_{PC} = 62.7 Hz), 129.1 (d, J_{PC} = 12.0 Hz), 132.9 (d, J_{PC} = 2.8 Hz), 135.5 (d, J_{PC} = 12.2 Hz), 162.6 (d, J_{PC} = 42.5 Hz) ppm.

HRMS *calcd.* for $[C_{19}H_{26}Cl_2N_2OPPtS]^+$: 626.051010; *found* 626.052329.

IR(solid) $\tilde{\nu}$ = 494, 516, 625, 694, 707, 748, 766, 847, 934, 996, 1089, 1121, 1191, 1285, 1414, 1433, 1522, 1578, 2944 cm^{-1}.

Compound **17**:



[AuCl(SMe$_2$)] (81 mg, 0.27 mmol) was added to a solution of compound **2** (100 mg, 0.27 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a white solid (156 mg, 96%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 2.78 (s, 6H), 4.11 (s, 4H), 7.64 - 7.77 (m, 6H), 8.04 (dd, *J* = 14.8, 7.5 Hz, 4H) ppm.

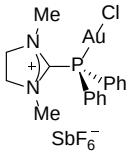
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 23.3 ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 37.2 (d, J_{PC} = 4.1 Hz), 53.4 (d, J_{PC} = 2.5 Hz), 122.5 (d, J_{PC} = 61.5 Hz), 131.2 (d, J_{PC} = 13.2 Hz), 135.0 (d, J_{PC} = 2.7 Hz), 135.8 (d, J_{PC} = 17.0 Hz), 161.0 (d, J_{PC} = 34.0 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{20}N_2AuClP]^+$: 515.071269; *found* 515.071361.

IR(solid) $\tilde{\nu}$ =689, 750, 931, 996, 1034, 1047, 1095, 1296, 1410, 1438, 1482, 1524, 1585, 2941, 3060 cm^{-1}.

Compound **18**:



[AuCl(SMe$_2$)] (57 mg, 0.19 mmol) was added to a solution of compound **3** (100 mg, 0.19 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a white solid (137 mg, 96%).

^{1}H NMR (300 MHz, CD_3CN) δ = 2.72 (s, 6H), 3.94 (s, 4H), 7.74 - 7.63 (m, 4H), 7.84 - 7.74 (m, 2H), 7.99 - 7.85 (m, 4H) ppm.

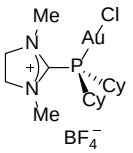
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ = 24.3 ppm.

^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ = 36.3 (d, J_{PC} = 1.6 Hz), 52.7 (d, J_{PC} = 2.4 Hz), 121.9 (d, J_{PC} = 61.5 Hz), 130.5 (d, J_{PC} = 13.2 Hz), 134.4 (d, J_{PC} = 2.8 Hz), 135.1 (d, J_{PC} = 16.3 Hz), 160.1 (d, J_{PC} = 35.8 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{20}AuClN_2P]^+$: 515.071268; *found:* 515.071580.

IR(solid) $\tilde{\nu}$ = 480, 512, 651, 691, 751, 802, 932, 998, 1097, 1297, 1439, 1583, 2962 cm^{-1}.

Compound **19**:



[AuCl(SMe$_2$)] (62 mg, 0.21 mmol) was added to a solution of compound **4** (80 mg, 0.21 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a white solid (121 mg, 94 %).

^{1}H NMR (400 MHz, CD_3CN) δ = 1.25 - 1.37 (m, 2H), 1.39 - 1.54 (m, 6H), 1.56 - 1.65 (m, 2H), 1.68 - 1.79 (m, 4H), 1.80 - 1.92 (m, 4H), 2.10 - 2.19 (m, 2H), 2.74 - 2.86 (m, 2H), 3.51 (s, 6H), 3.95 (s, 4H) ppm.

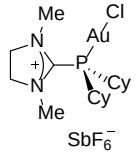
^{31}P{^{1}H} NMR (162 MHz, CD_3CN) δ = 42.4 ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ = 25.7 (d, J_{PC} = 1.5 Hz), 26.3 (d, J_{PC} = 16.9 Hz), 26.6 (d, J_{PC} = 13.4 Hz), 30.8, 33.4 (d, J_{PC} = 6.5 Hz), 36.5 (d, J_{PC} = 27.4 Hz), 38.6 (d, J_{PC} = 3.3 Hz), 53.7, 160.5 (d, J_{PC} = 23.9 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{32}N_2AuClP]^+$: 527.165167; *found:* 527.165410.

IR(solid) $\tilde{\nu}$ = 506, 519, 711, 755, 801, 930, 958, 1036, 1051, 1092, 1263, 1304, 1448, 1577, 2854, 2931 cm^{-1}.

Compound **20**:



$[AuCl(SMe_2)]$ (55 mg, 0.19 mmol) was added to a solution of compound **5** (100 mg, 0.19 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a white solid (140 mg, 97%).

^1H NMR (300 MHz, CD_3CN) δ = 1.59 - 1.14 (m, 10H), 1.84 - 1.59 (m, 8H), 2.13 - 2.00 (m, 2H), 2.80 - 2.65 (m, 2H), 3.43 (s, 6H), 3.88 (s, 4H) ppm.

$^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN) δ = 42.7 ppm.

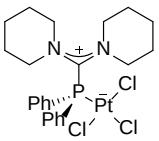
$^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN) δ = 25.8 (d, J_{PC} = 2.0 Hz), 26.5 (d, J_{PC} = 16.9 Hz), 26.7 (d, J_{PC} = 13.6 Hz), 30.9, 33.5 (d, J_{PC} = 6.6 Hz), 36.7 (d, J_{PC} = 27.1 Hz), 38.7 (d, J_{PC} = 3.7 Hz), 53.8 (d, J_{PC} = 2.0 Hz), 160.7 (d, J_{PC} = 23.6 Hz) ppm.

HRMS *calcd.* for $[C_{17}H_{32}AuClN_2P]^+$: 527.165167; *found*: 527.165410.

Anal.Calcd. for $C_{17}H_{32}AuClF_6N_2PSb$: C, 26.74; H, 4.22; N, 3.67; *found*: C, 27.03; H, 3.95; N, 4.08.

IR(solid) $\tilde{\nu}$ = 459, 516, 652, 751, 847, 890, 931, 1003, 1117, 1204, 1301, 1339, 1448, 1578, 2855, 2931 cm^{-1}.

Compound **21**:



K_2PtCl_4 (100 mg, 0.24 mmol) was added to a solution of compound **8** (145 mg, 0.24 mmol) in dry CH_3CN (5 mL) and the mixture was stirred overnight at room temperature. The solvent was then evaporated and the residue recrystallized from CH_2Cl_2/Et_2O affording the desired product as a pale pink solid (145 mg, 90%).

^1H NMR (300 MHz, $(CD_3)_2SO$) δ = 2.62 (br, 8H), 3.95 (br, 4H), 5.57 (br, 8H), 7.56 - 7.76 (m, 6H), 8.26 - 8.43 (m, 4H) ppm.

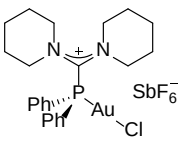
$^{31}P\{^1H\}$ NMR (121 MHz, $(CD_3)_2SO$) δ = 16.4 (J_{PtP} = 3914.6 Hz) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $(CD_3)_2SO$) δ = 21.8, 24.9, 53.9 (d, J_{PC} = 2.3 Hz), 125.7, 129.0 (d, J_{PC} = 11.4 Hz), 132.6 (d, J_{PC} = 3.0 Hz), 136.0 (d, J_{PC} = 11.0 Hz), 222.5 (d, J_{PC} = 1.4 Hz) ppm.

HRMS *calcd.* for $[C_{25}H_{36}Cl_2N_2OPPtS]^+$: 708.130568; *found*: 708.130310.

IR(solid) $\tilde{\nu}$ = 427, 499, 525, 573, 640, 699, 757, 778, 856, 908, 927, 1008, 1089, 1129, 1156, 1251, 1359, 1436, 1478, 1540, 2855, 2950 cm^{-1}.

Compound **22**:



[AuCl(SMe$_2$)] (505 mg, 1.71 mmol) was added to a solution of compound **8** (1.03 g, 1.71 mmol) in dry CH_2Cl_2 (10 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated and the residue recrystallized from CH_3CN/Et_2O affording the desired product as a white solid (898 mg, 63%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.44 -1.30 (m, 8H), 1.51 (m, 4H), 3.68 - 3.55 (t, *J* = 5.4 Hz, 8H), 7.72 - 7.55 (m, 6H), 7.87 - 7.75 (m, 4H) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 34.8 ppm.

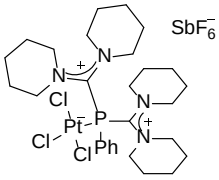
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 22.6, 26.1, 56.2 (d, J_{PC} = 3.8 Hz), 123.5 (d, J_{PC} = 62.0 Hz), 131.2 (d, J_{PC} = 12.8 Hz), 134.9 (d, J_{PC} = 2.7 Hz), 135.9 (d, J_{PC} = 15.5 Hz), 169.5 (d, J_{PC} = 52.0 Hz) ppm.

HRMS *calcd.* for $[C_{23}H_{30}AuClN_2P]^+$: 597.149518; *found* 597.149810.

Anal.Calcd. for $C_{23}H_{30}AuClF_6N_2PSb$: C, 33.14; H, 3.63; N, 3.36; *found*: C, 33.07; H, 3.64; N, 3.38.

IR(solid) $\tilde{\nu}$ = 425, 468, 500, 517, 571, 654, 700, 755, 780, 856, 906, 927, 999, 1090, 1160, 1252, 1364, 1437, 1551, 2863, 2932, 2959 cm^{-1}.

Compound **23**:



K_2PtCl_4 (44 mg, 0.11 mmol) was added to a solution of bis(piperidin-1-ylmethanylylidene)phenylphosphine (100 mg, 0.11 mmol) in dry CH_3CN (5 mL) and the mixture was stirred overnight at 60°C. After cooling to room temperature, the solvent evaporated under vacuum and the resulting solid washed with CH_2Cl_2. Extraction with CH_3CN and evaporation of the solvent under vacuum gave the crude product, which was recrystallized from CH_3CN/Et_2O to afford the title compound as a yellow solid (24 mg, 21%).

^{1}H NMR (400 MHz, CD_3CN) δ = 1. 67 (br, 24H), 3.63 (br, 16H), 7.77 - 7.66 (m, 1H), 7.86 - 7.82 (m, 3H), 8.78 (br, 1H) ppm.

^{31}P{^{1}H} NMR (121 MHz, CD_3CN) δ = 26.0 (d, J_{PtP} = 3818.7 Hz) ppm.

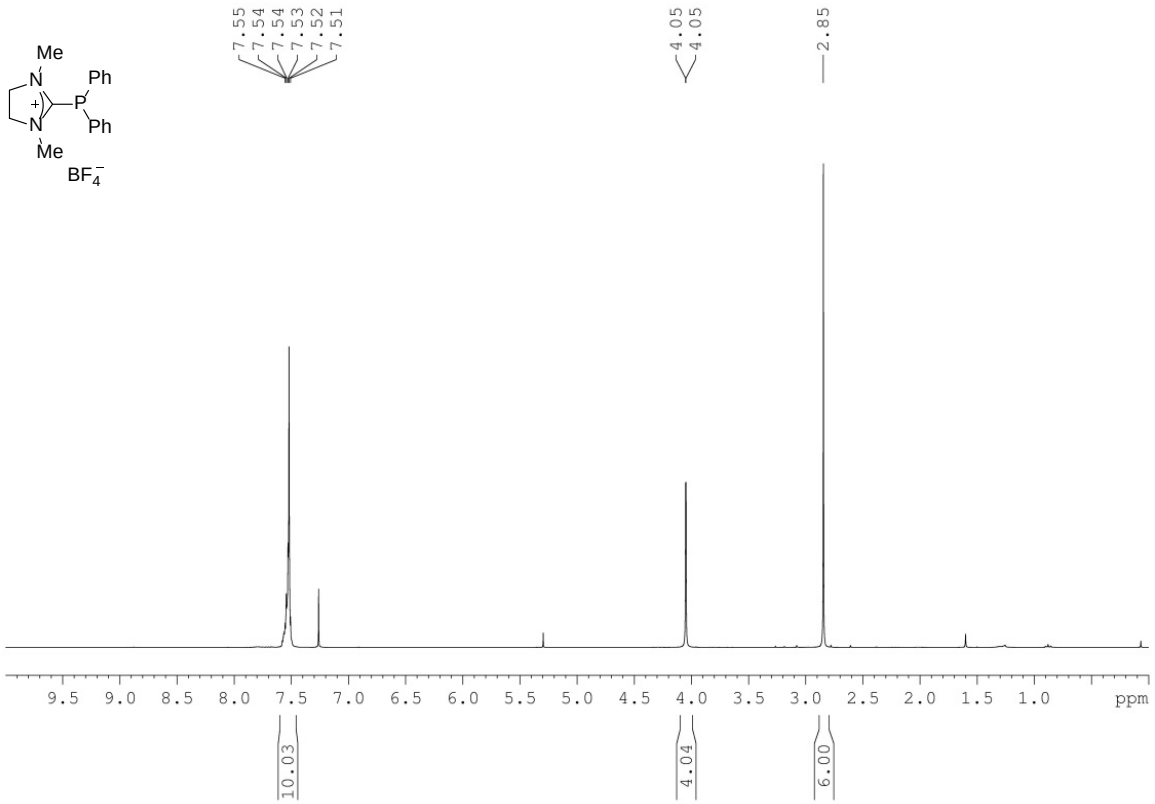
^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ = 22.6, 26.0 (br), 55.9 (br), 122.5 (d, J_{PC} = 60.2 Hz), 131.9 (d), 136.0 (d, J_{PC} = 2.8 Hz), 138.7 (dm, J_{PC} = 122.1 Hz), 171.0 (br) ppm.

HRMS *calcd.* for $[C_{28}H_{45}N_4Cl_3PPt]^+$: 768.209320; *found* 768.209006.

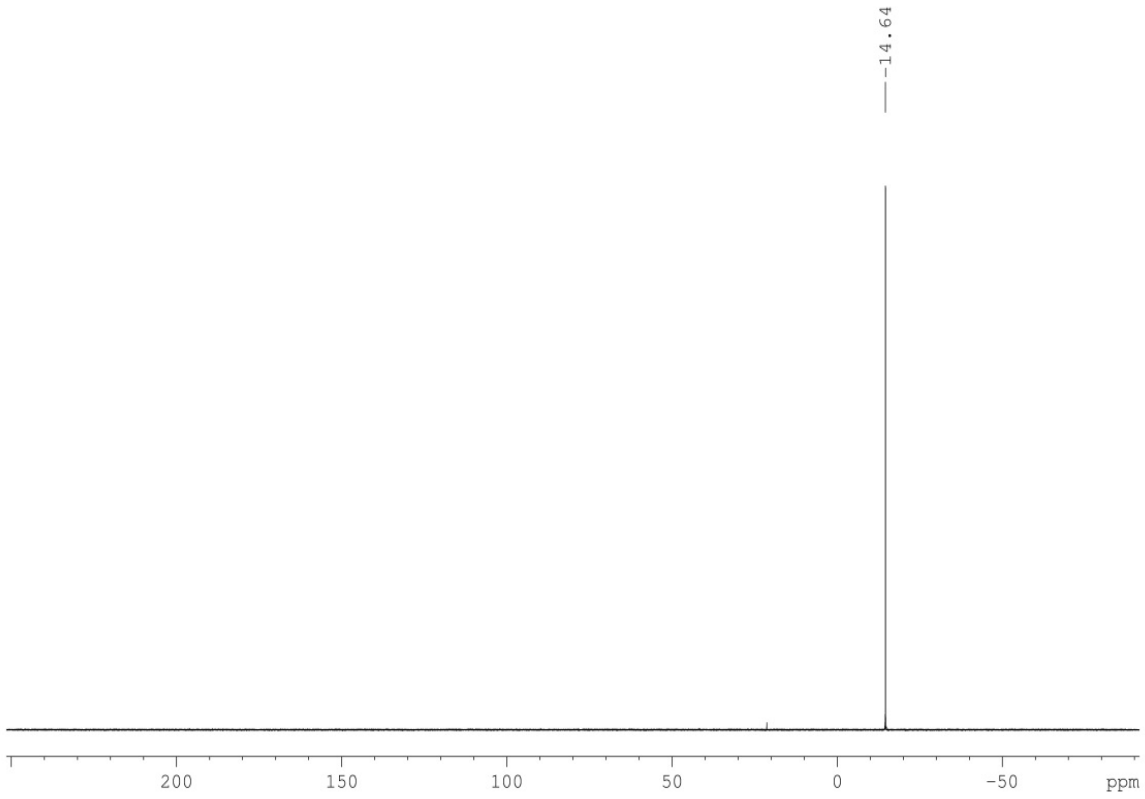
IR(solid) $\tilde{\nu}$ = 425, 467, 495, 505, 583, 654, 751, 778, 858, 925, 952, 1010, 952, 1089, 1130, 1159, 1255, 1358, 1440, 1548, 2862, 2946 cm^{-1}.

NMR Spectra

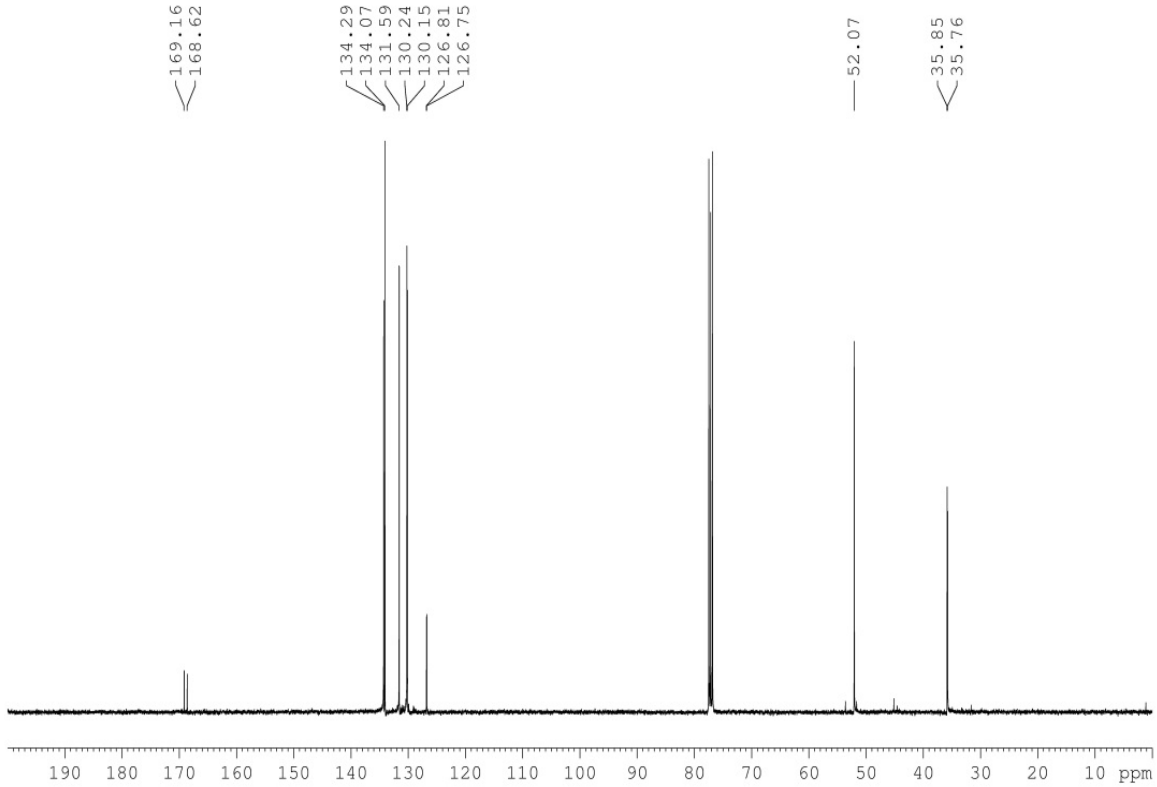
^{1}H NMR (300 MHz, $CDCl_3$) **2**



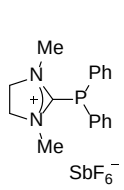
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) **2**

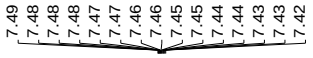


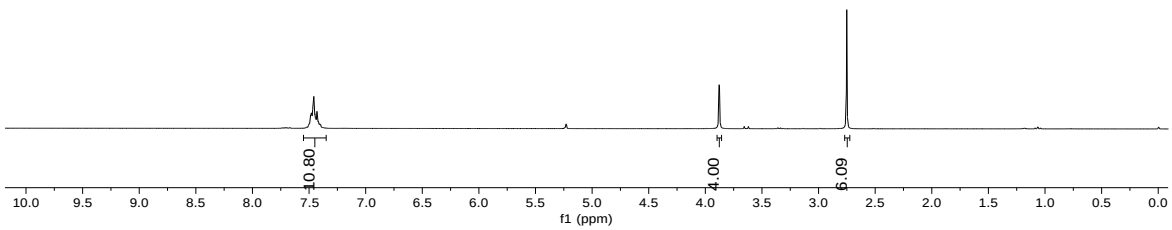
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) **2**



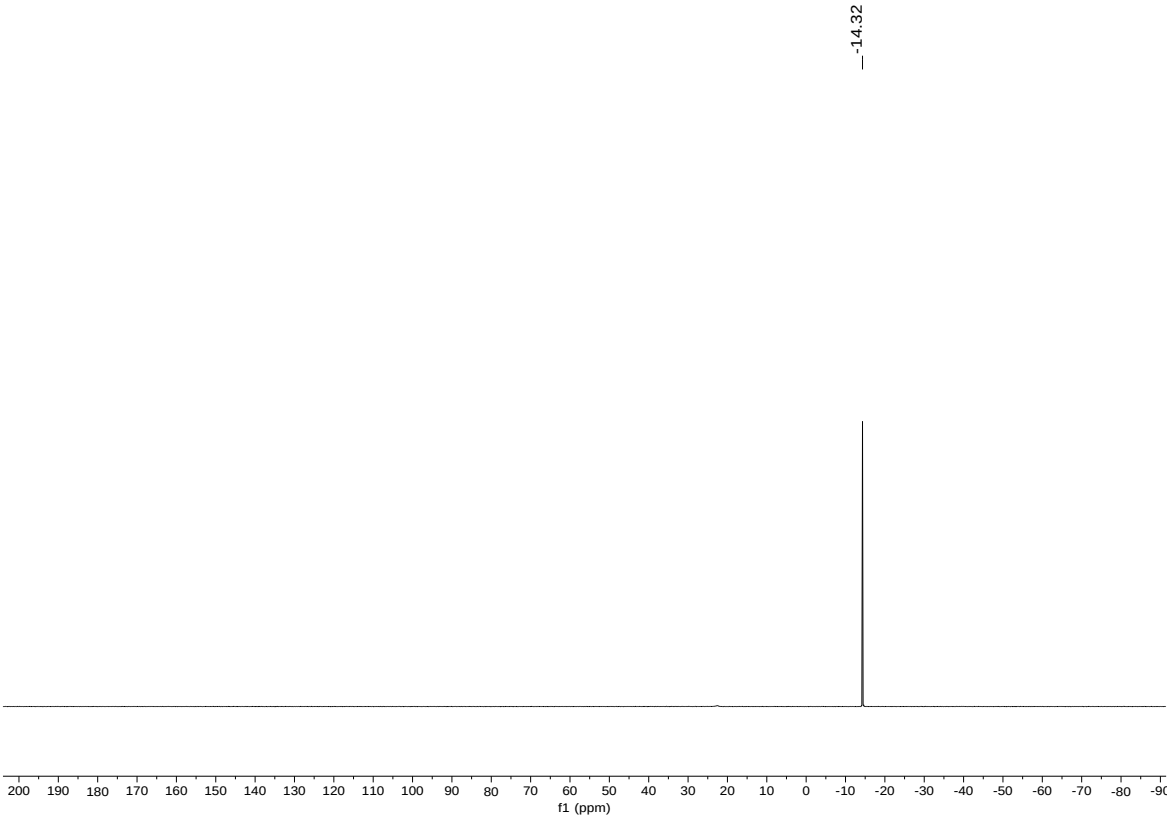
^{1}H NMR (300 MHz, CD_2Cl_2) **3**



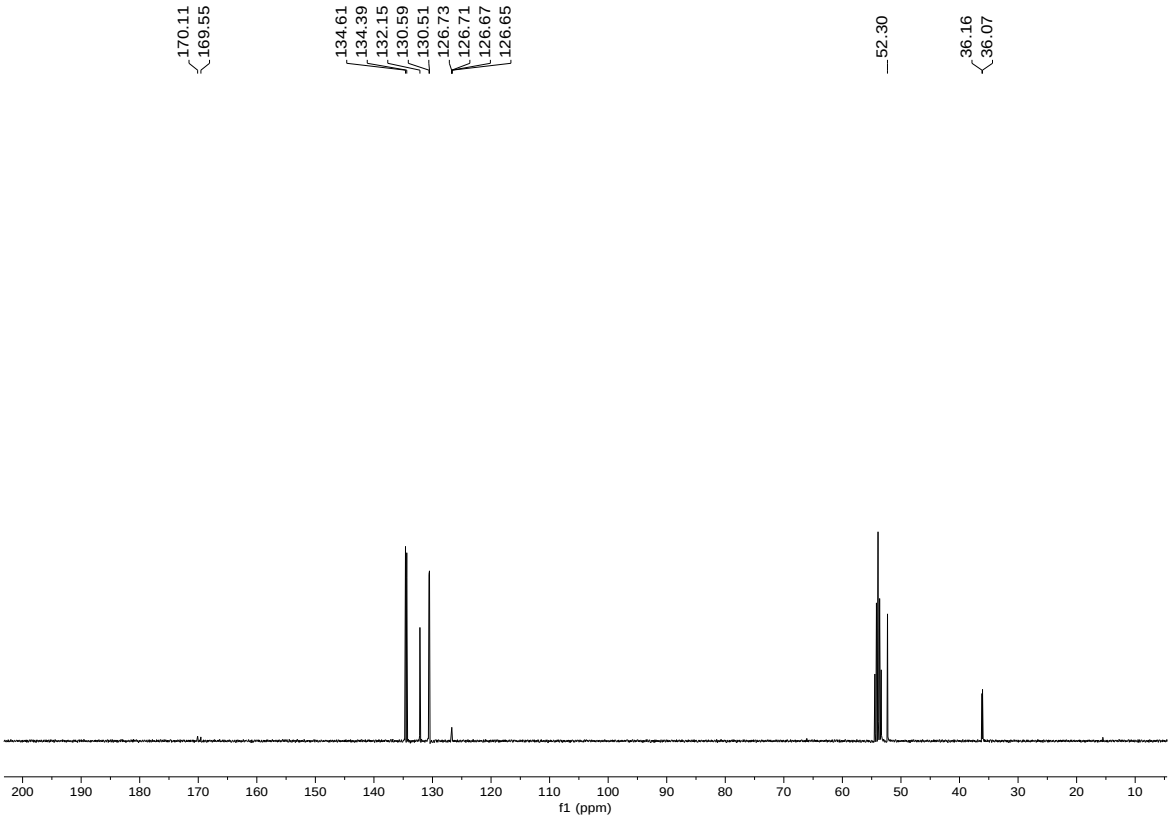




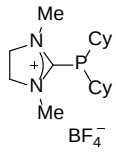
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) **3**



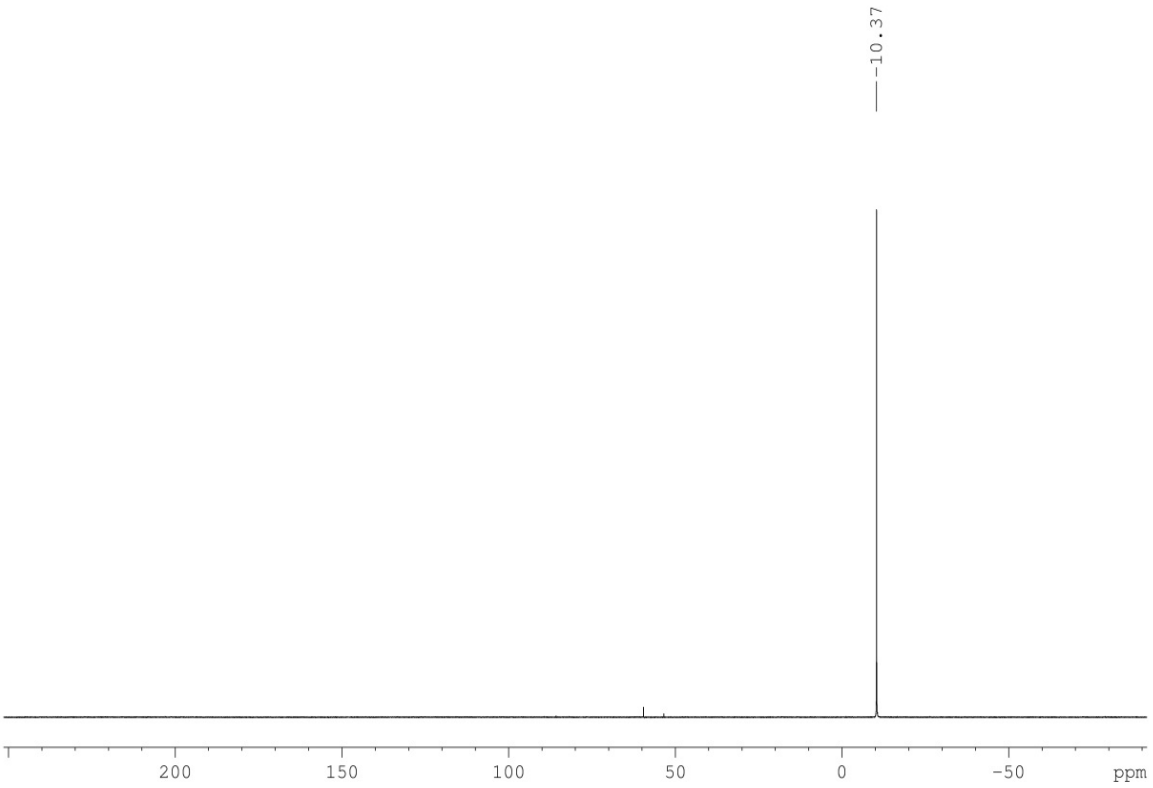
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **3**



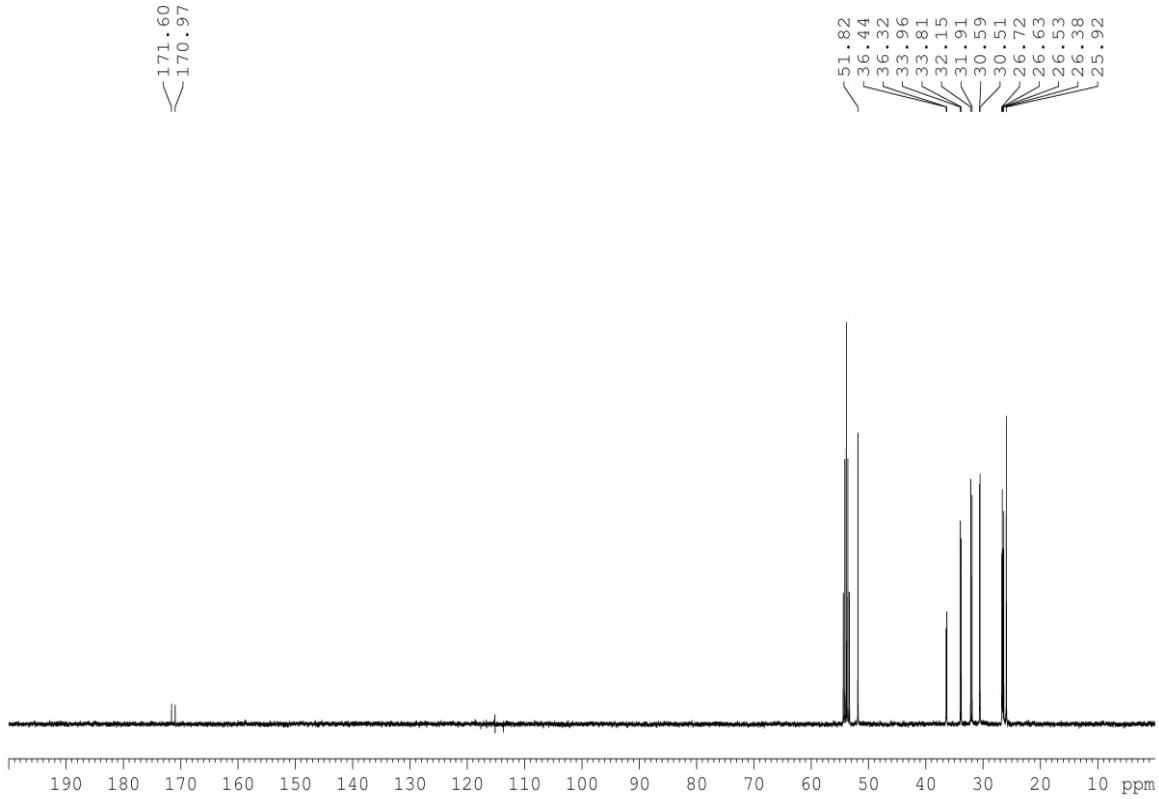
^{1}H NMR (400 MHz, CD_2Cl_2) **4**



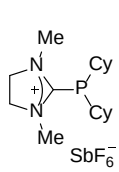
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) **4**



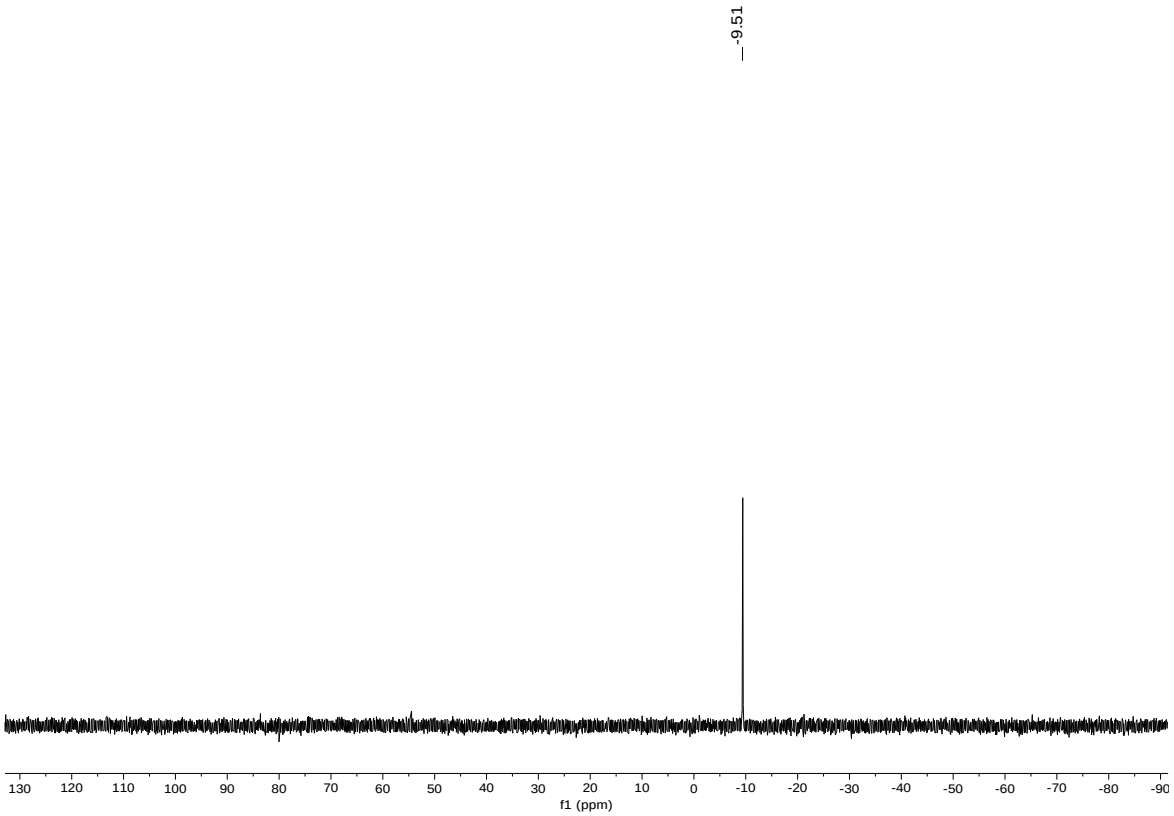
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **4**



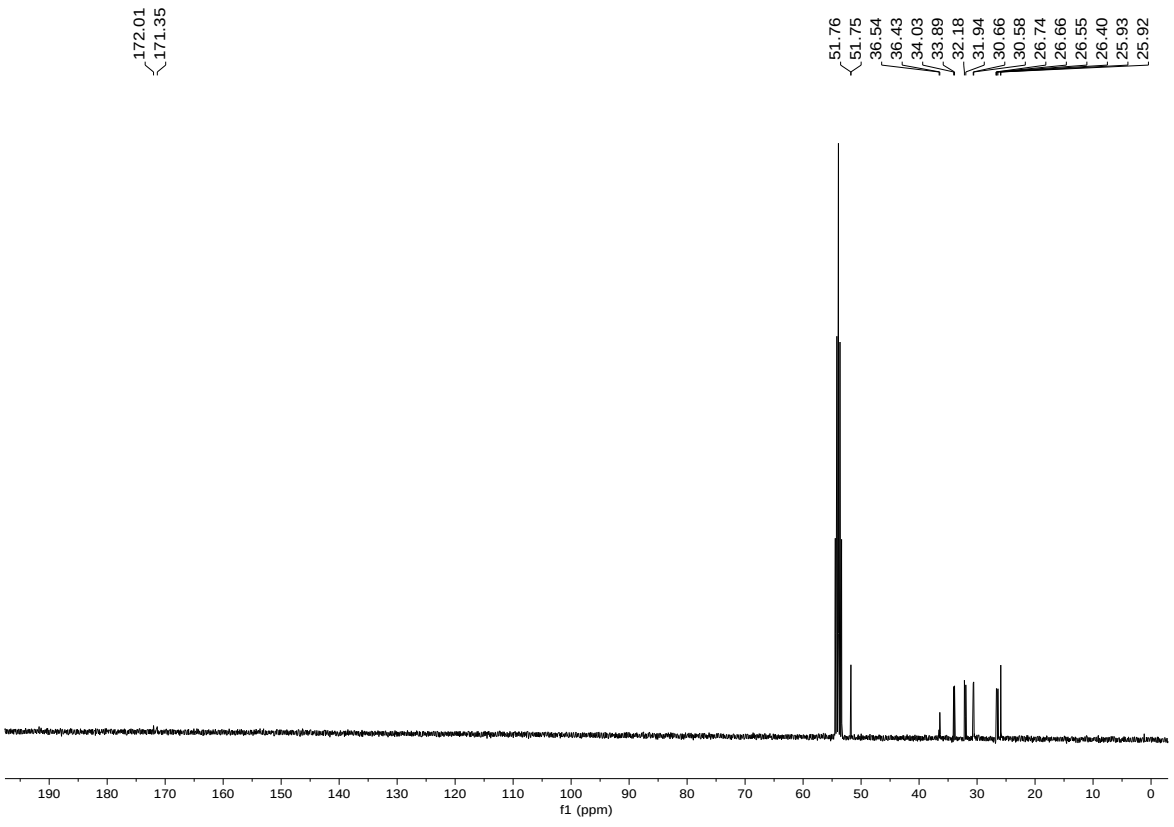
^{1}H NMR (300 MHz, $CDCl_3$) **5**



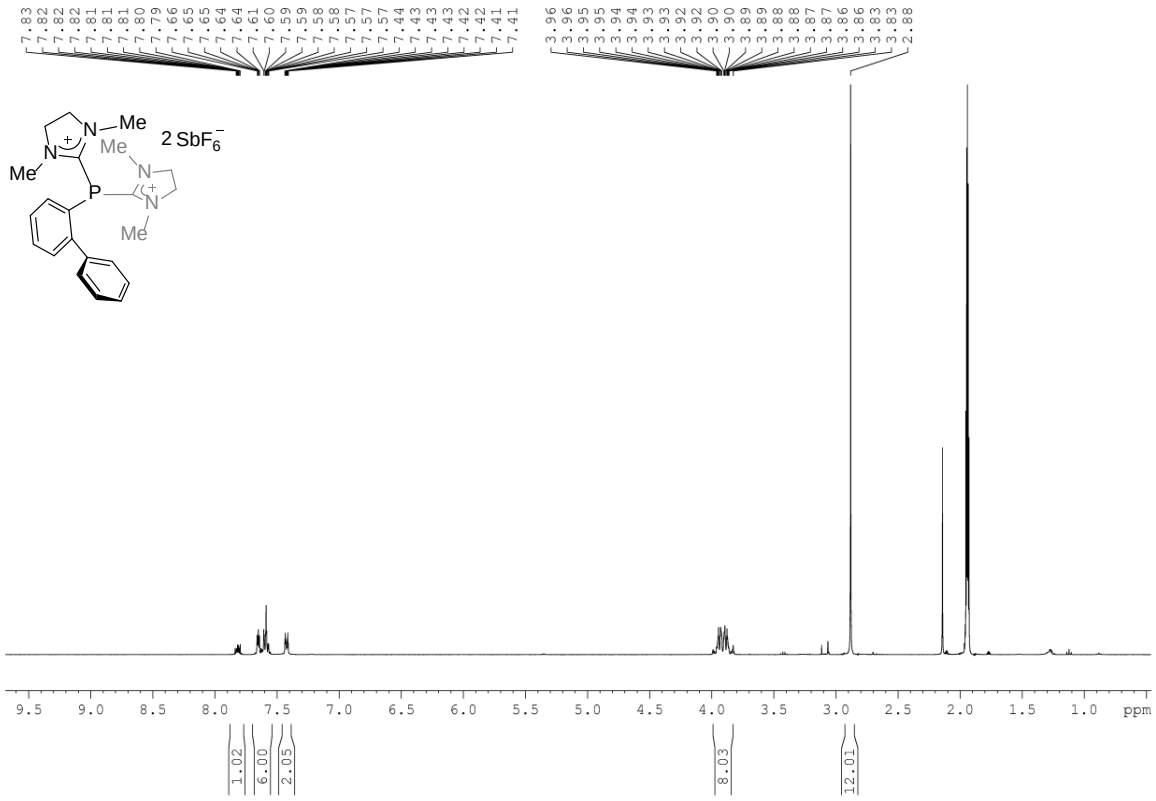
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) **5**



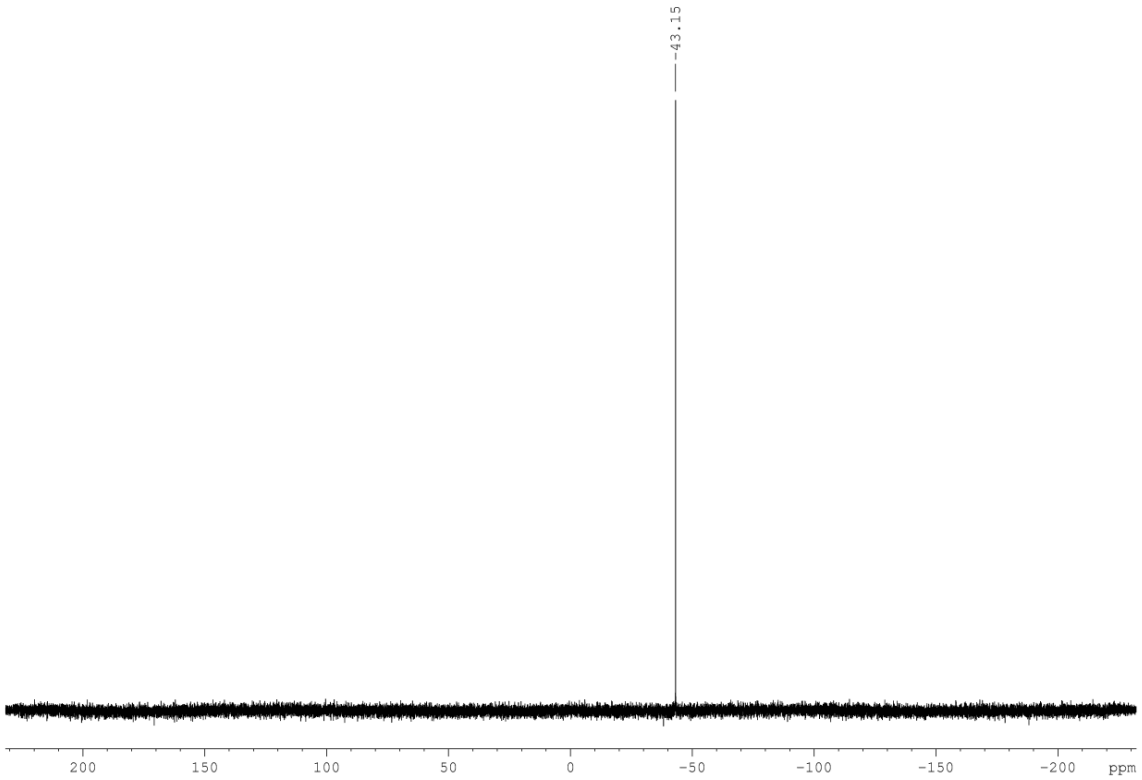
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **5**



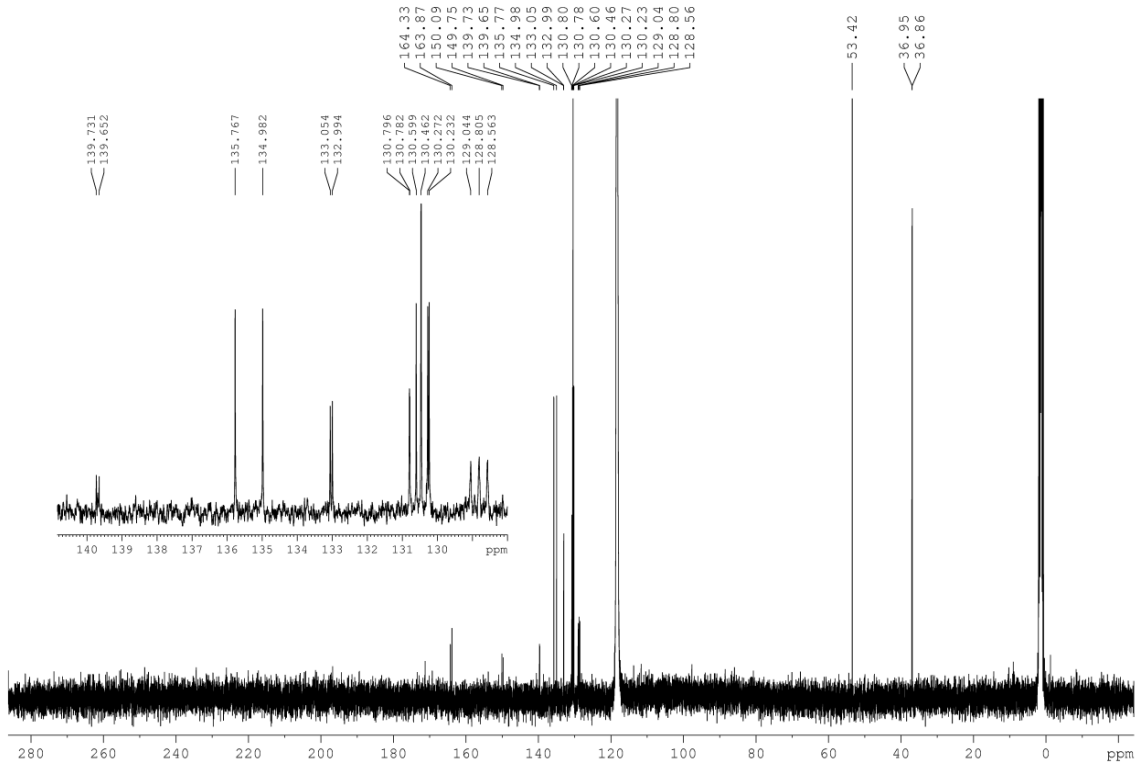
^{1}H NMR (400 MHz, CD_3CN) **6**



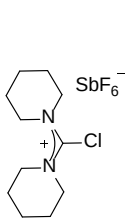
^{31}P{^{1}H} NMR (121 MHz, CD_3CN) **6**



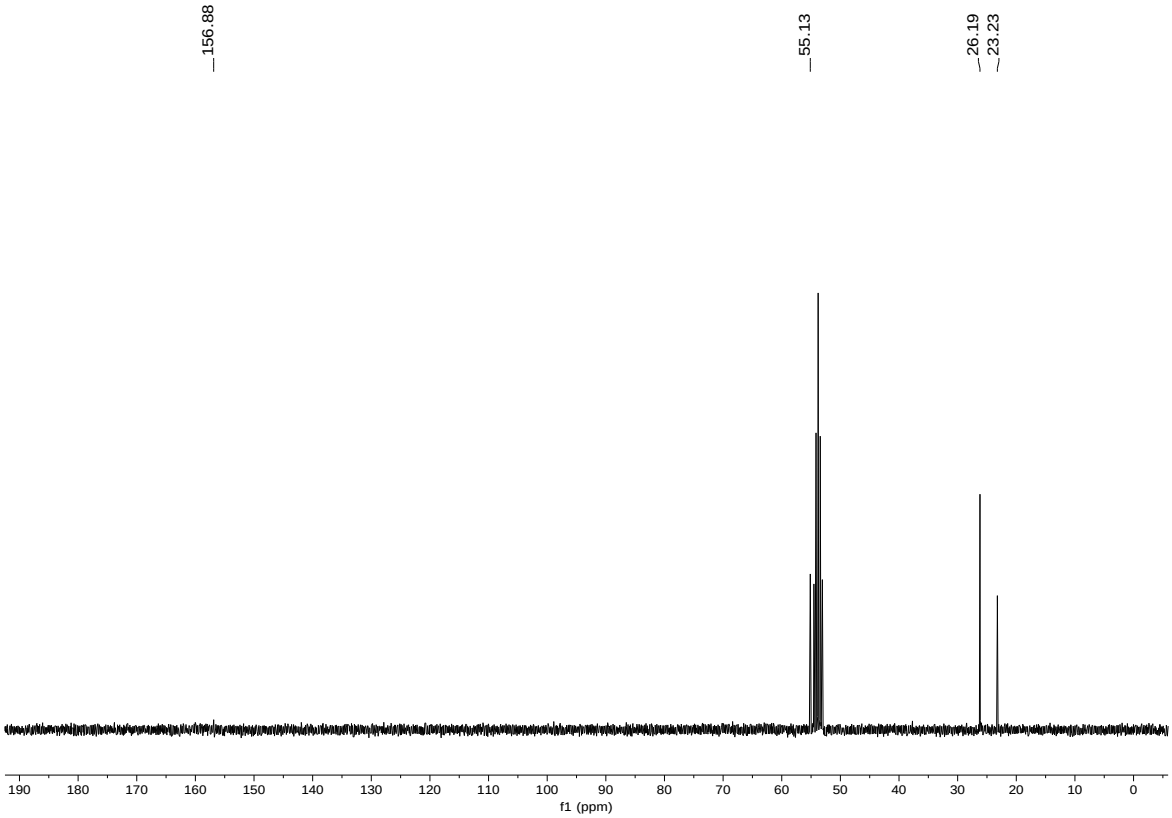
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) **6**



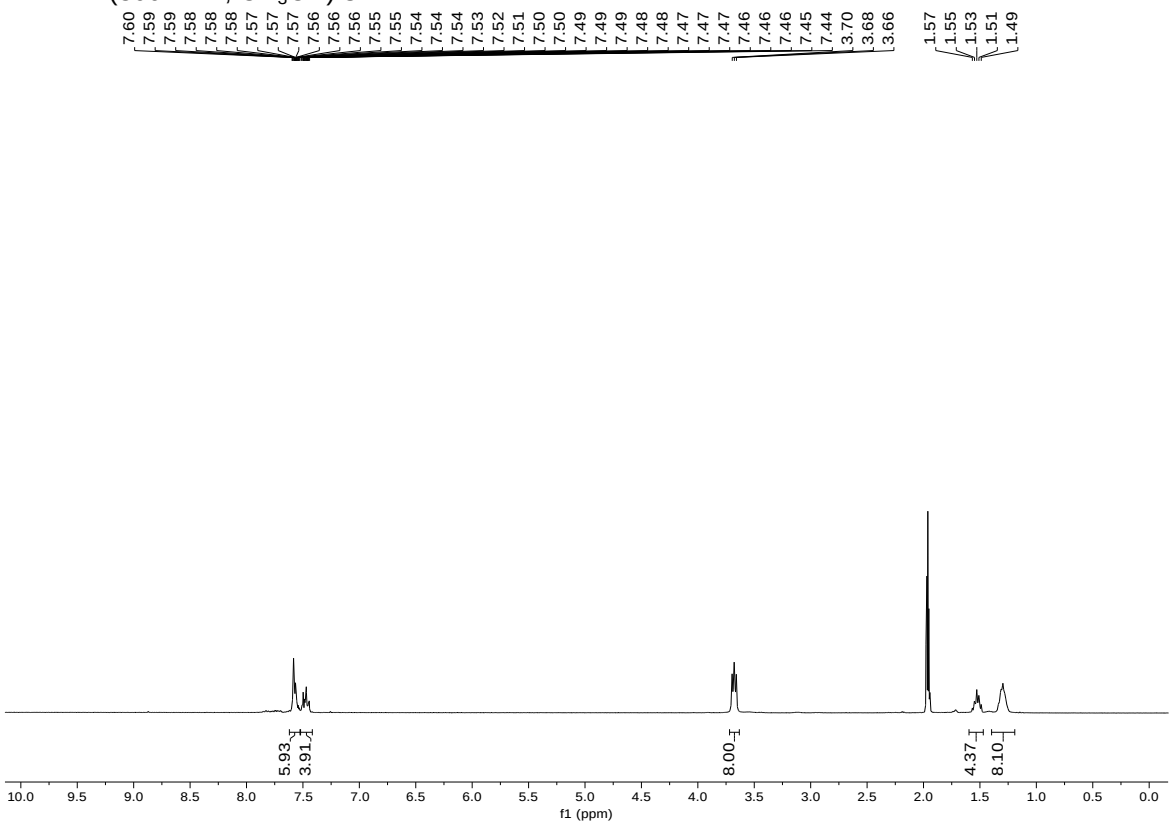
^{1}H NMR (300 MHz, CD_2Cl_2) **7**



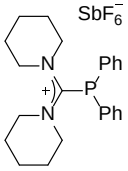
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2) **7**



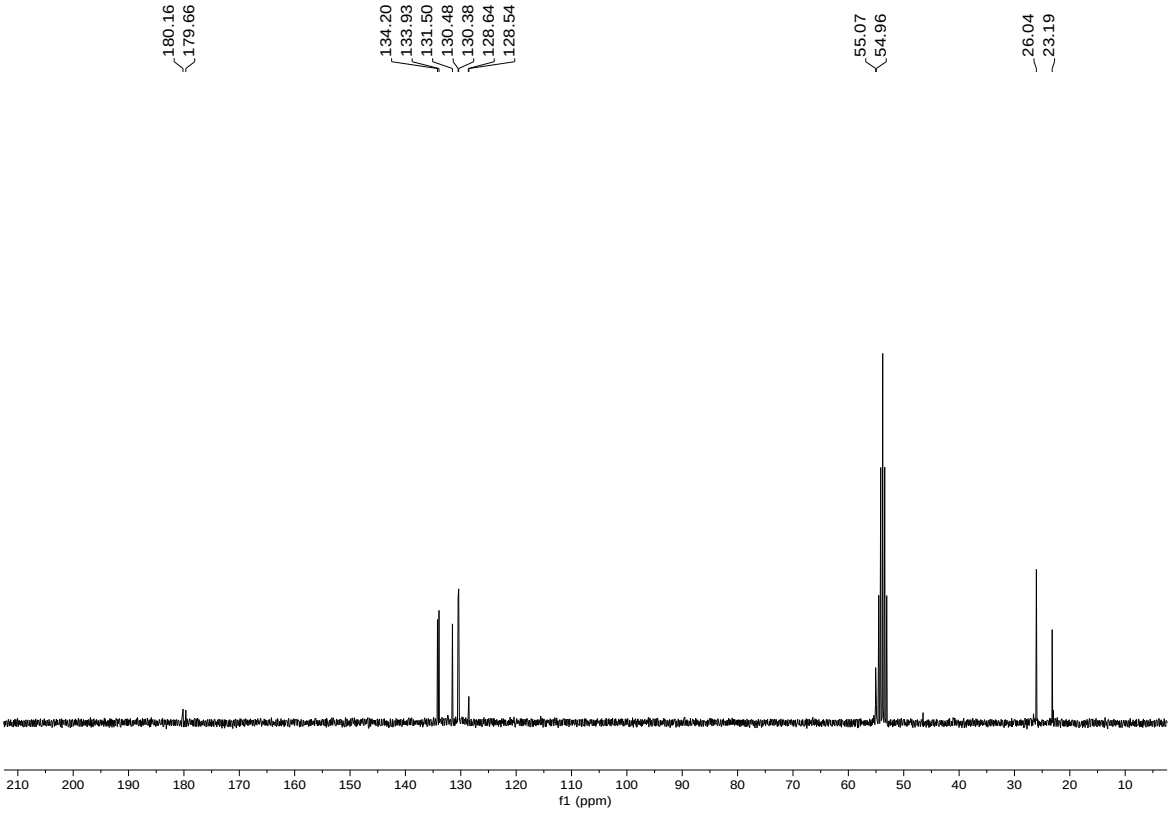
^{1}H NMR (300 MHz, CD_3CN) **8**



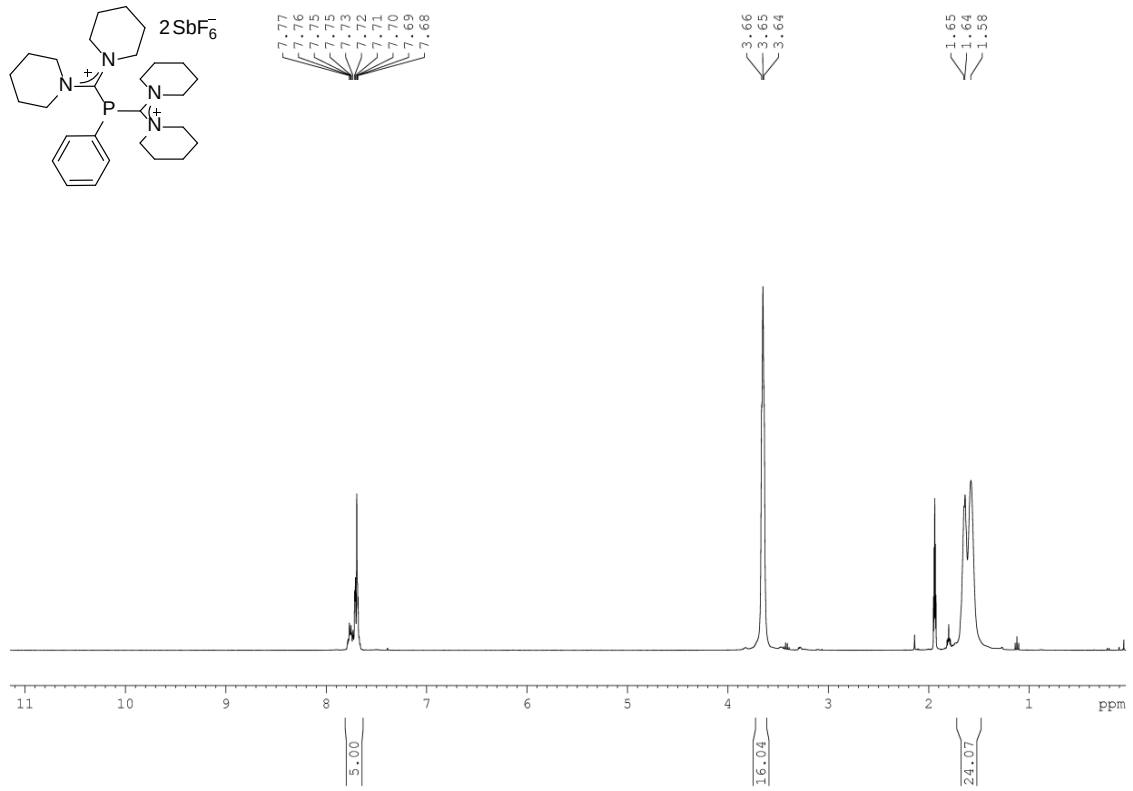
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) **8**



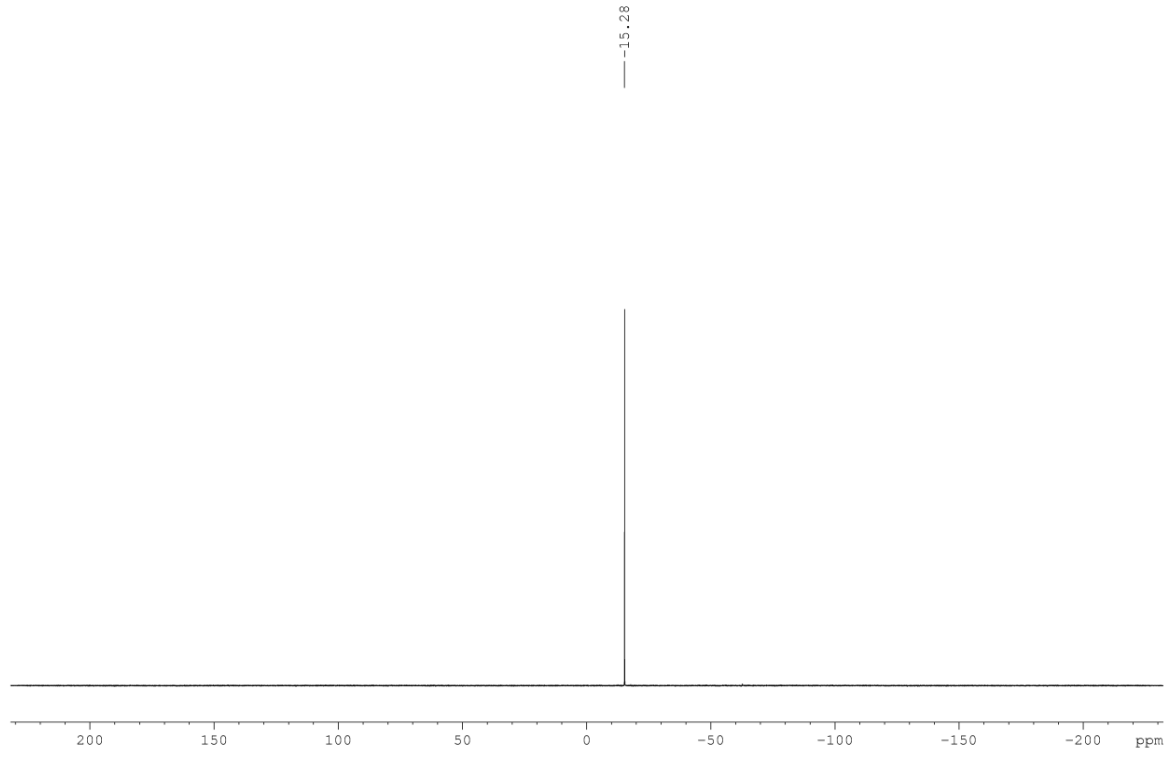
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2) **8**



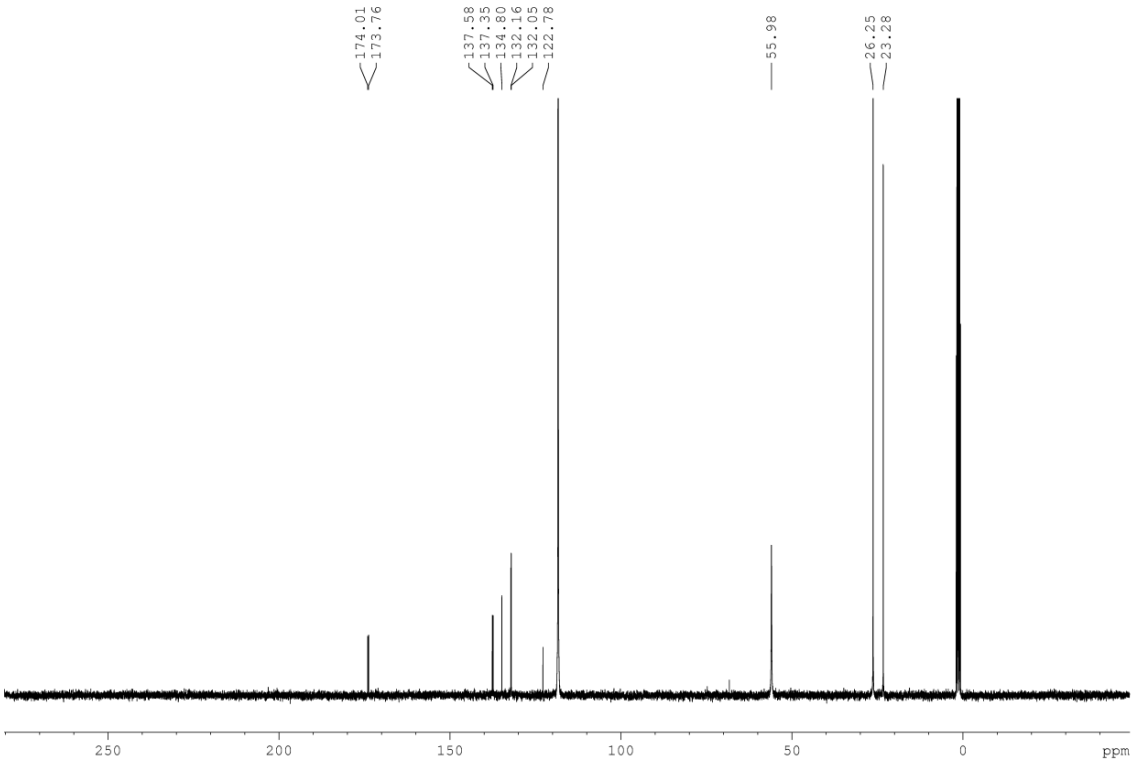
^{1}H NMR (400 MHz, CD_3CN) **9**



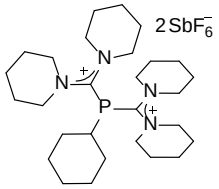
^{31}P{^{1}H} NMR (121 MHz, CD_3CN) **9**



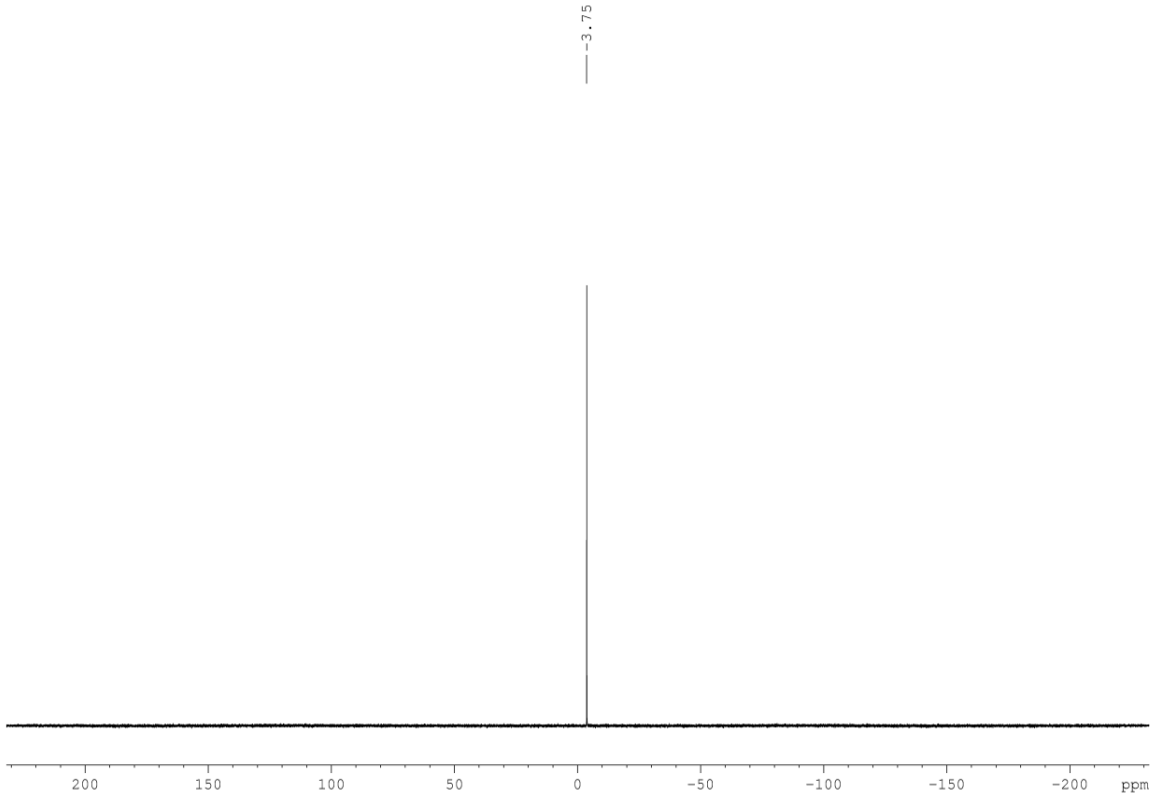
^{13}C{^{1}H} NMR (100 MHz, CD_3CN) **9**



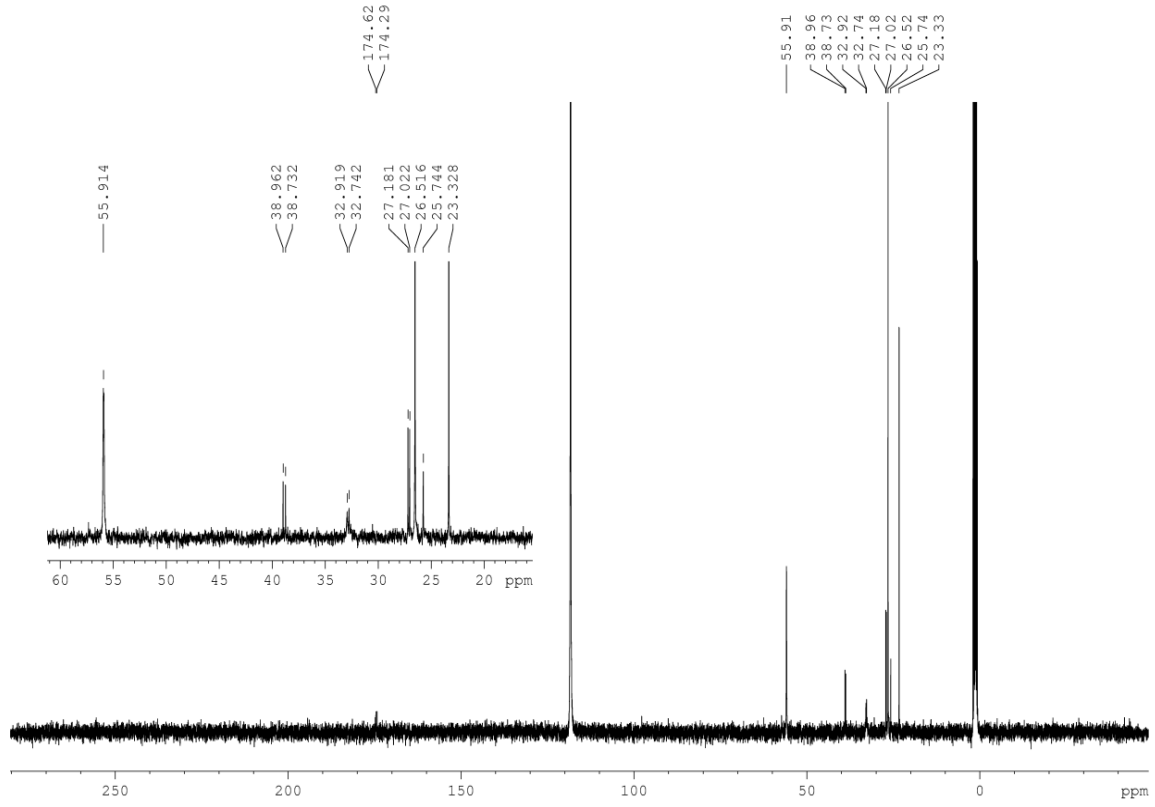
^{1}H NMR (400 MHz, CD_3CN) **10**



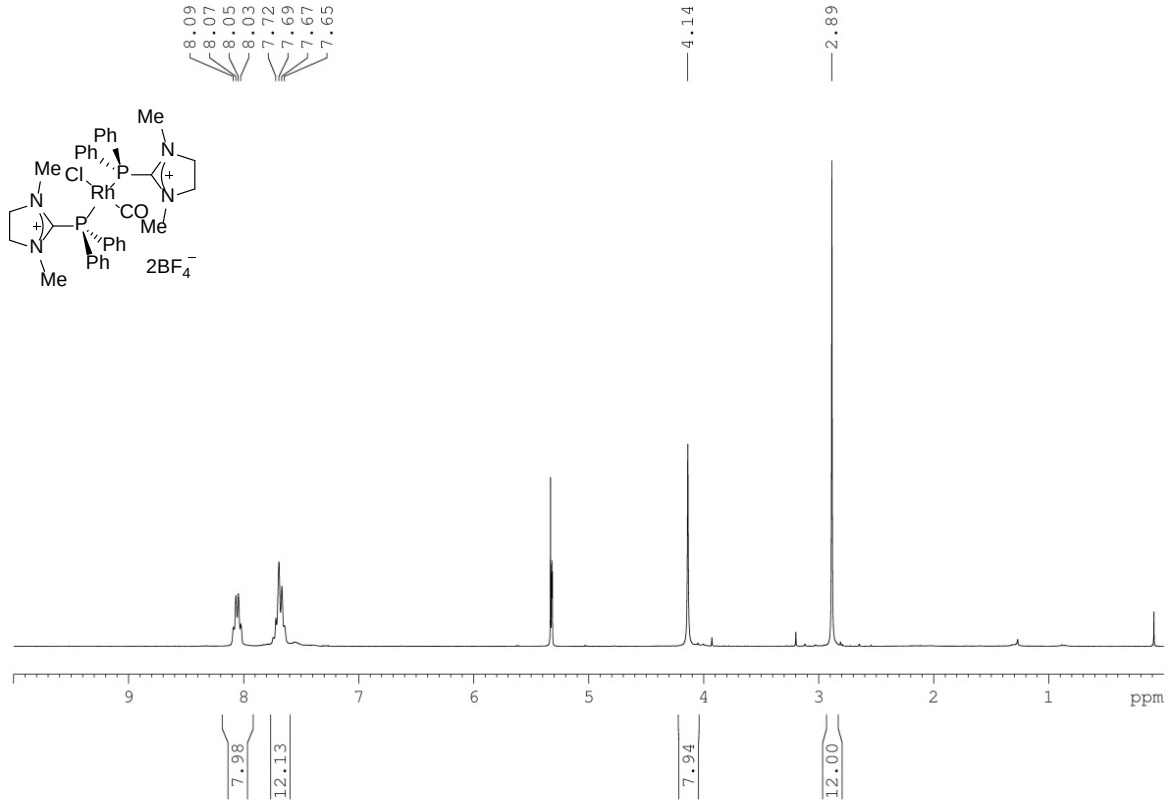
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_3CN) **10**



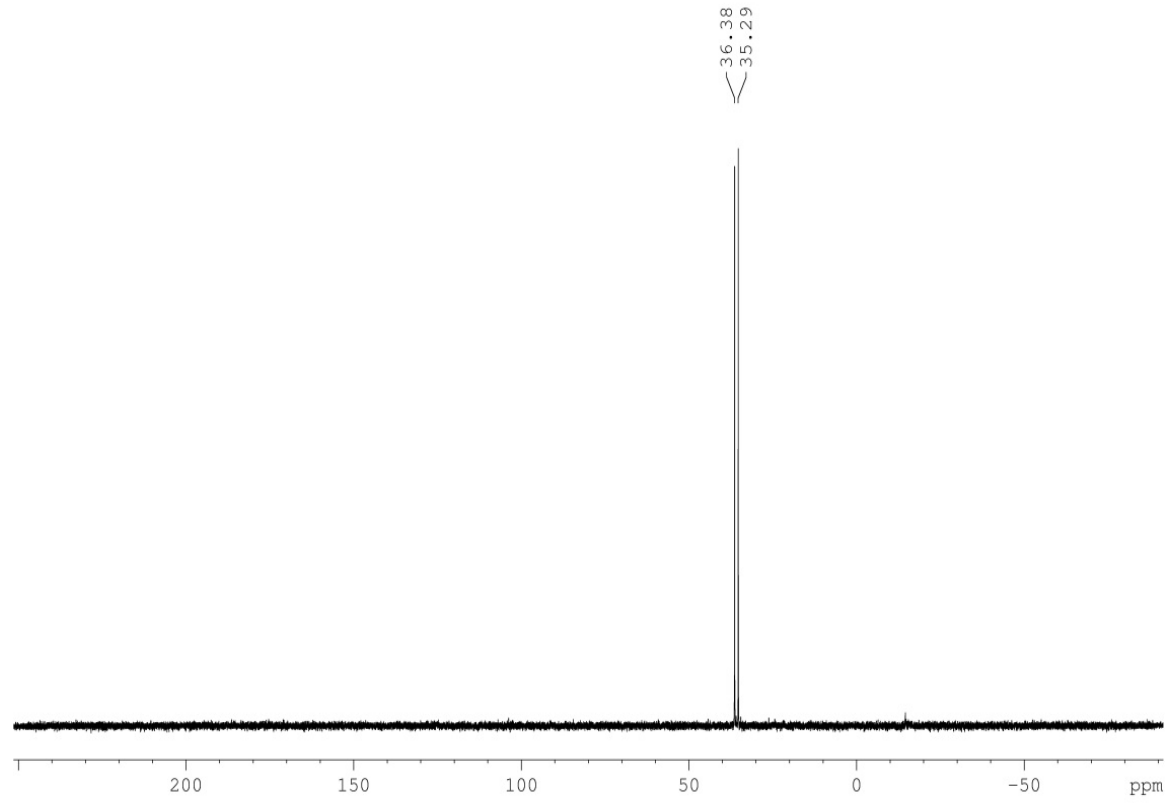
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) **10**



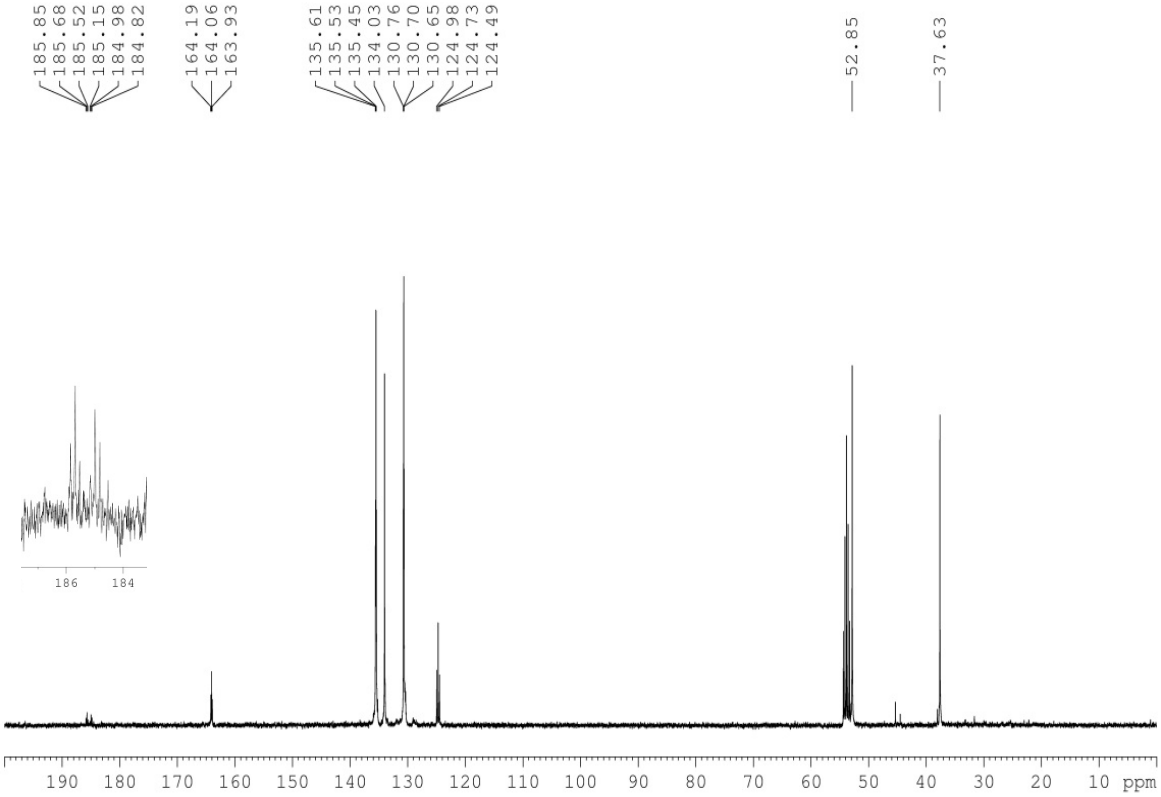
^{1}H NMR (300 MHz, CD_2Cl_2) **11**



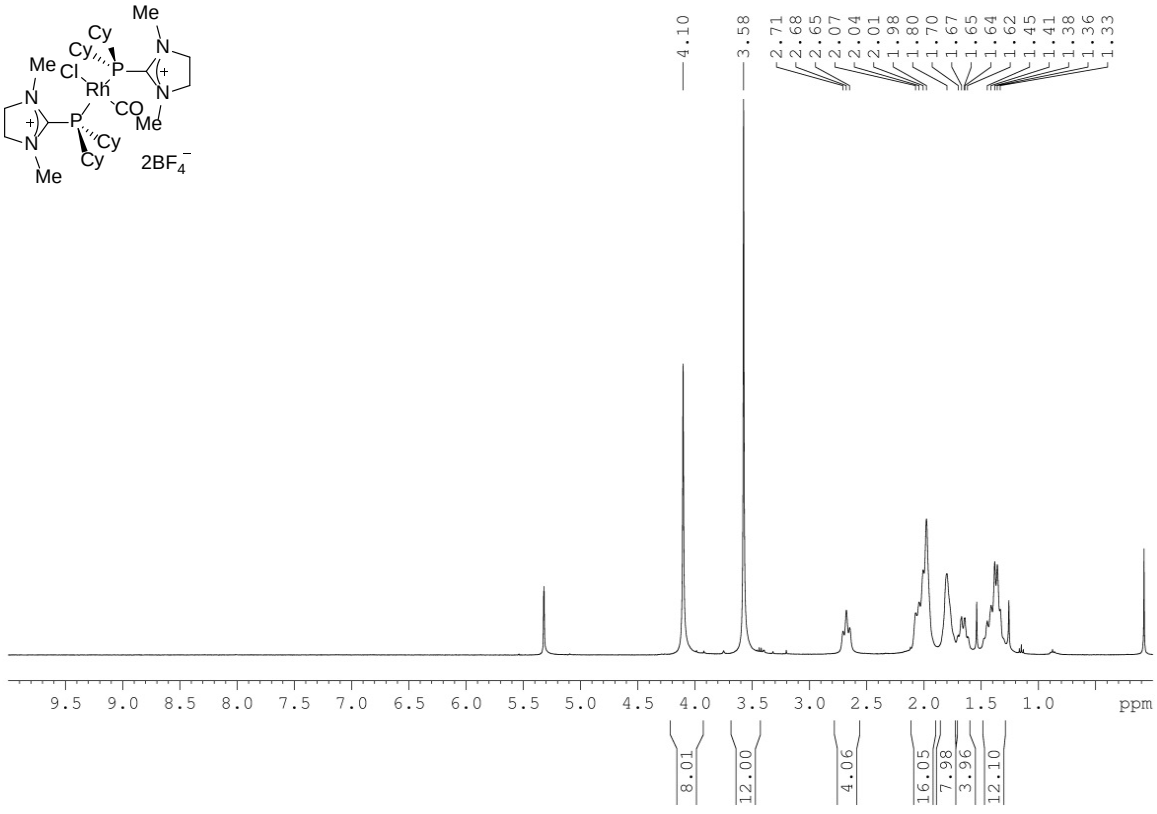
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) **11**



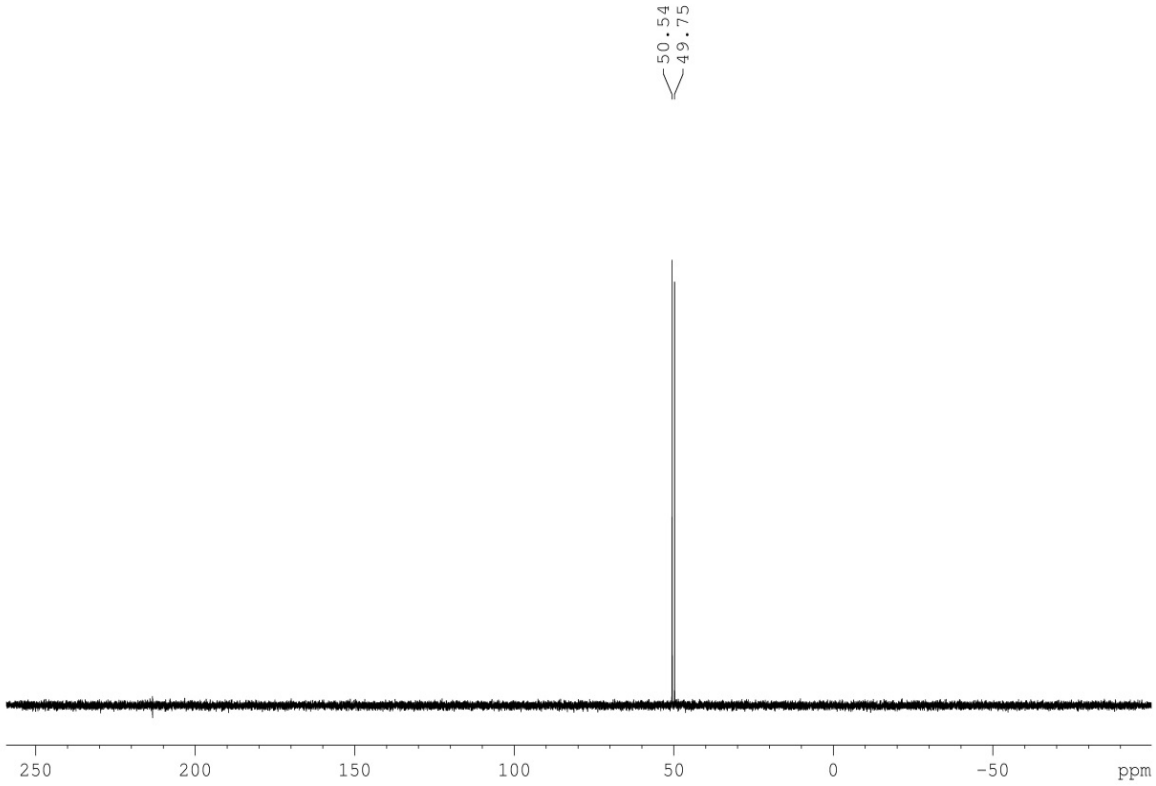
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **11**



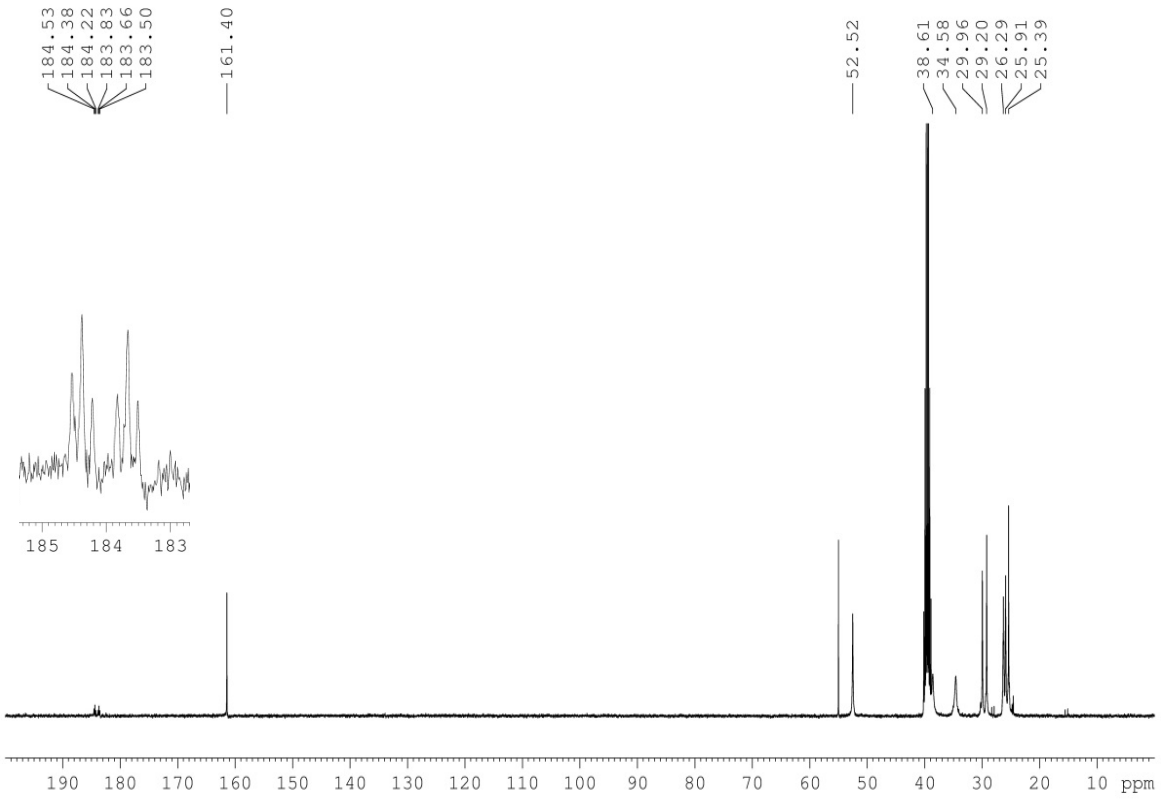
^{1}H NMR (400 MHz, CD_2Cl_2) **12**



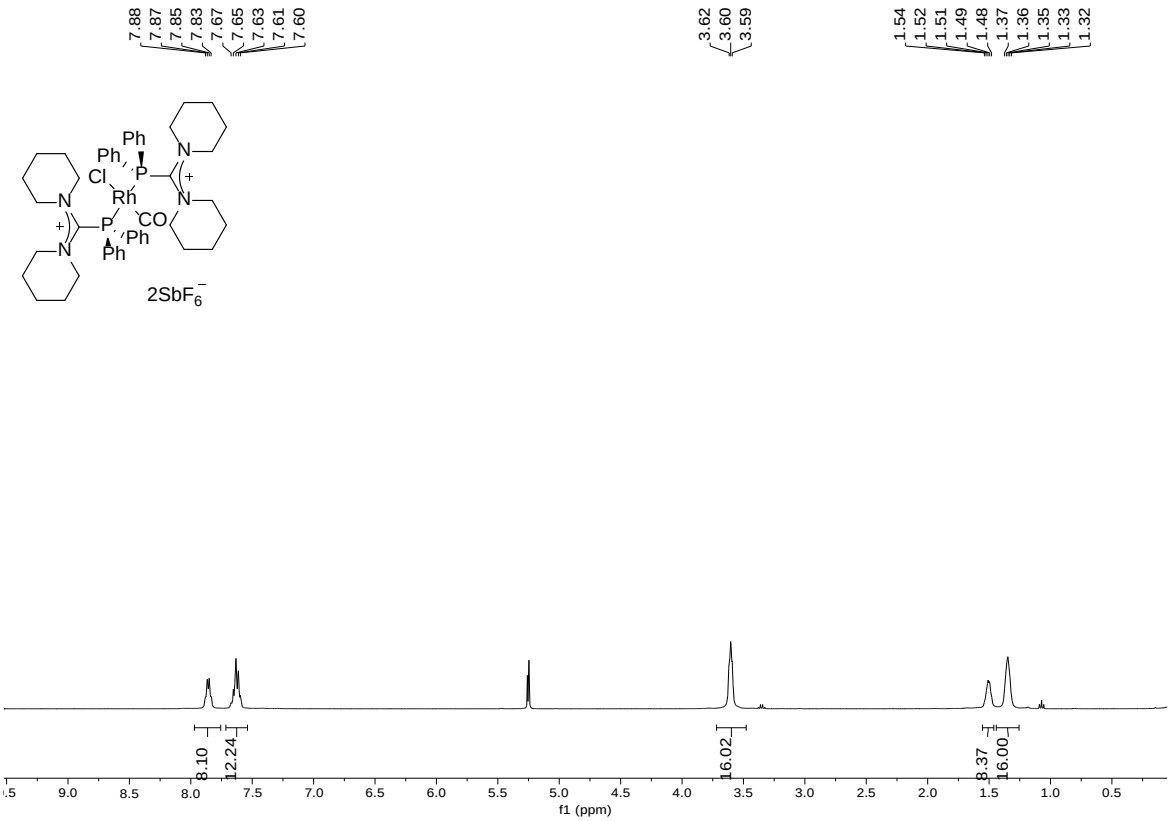
$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) **12**



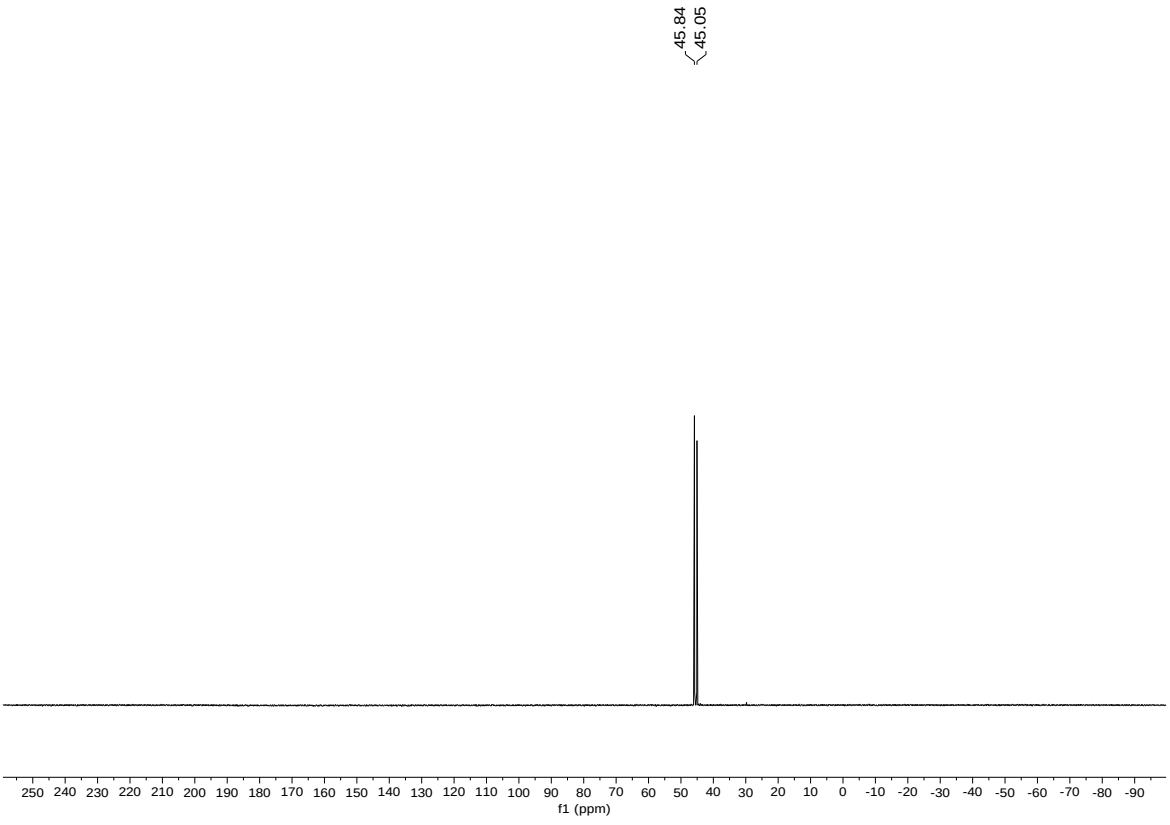
$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) **12**



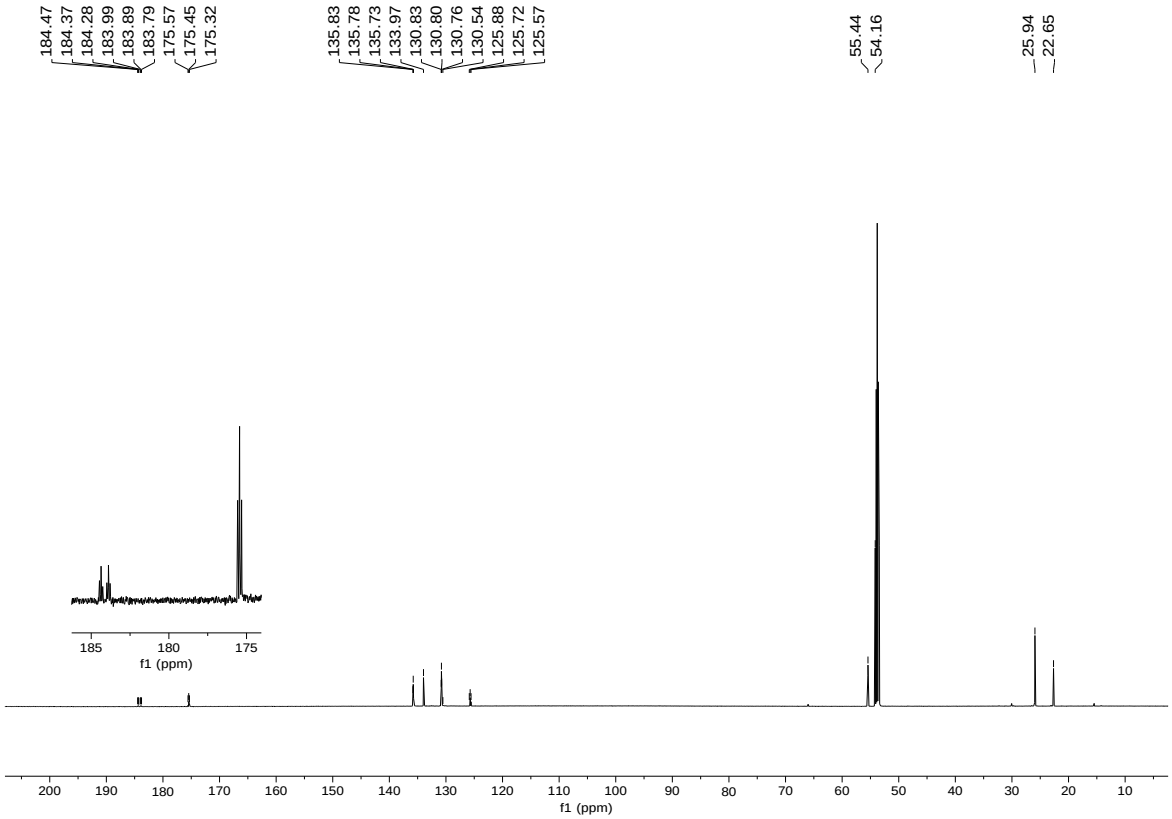
^{1}H NMR (400 MHz, CD_2Cl_2) **13**



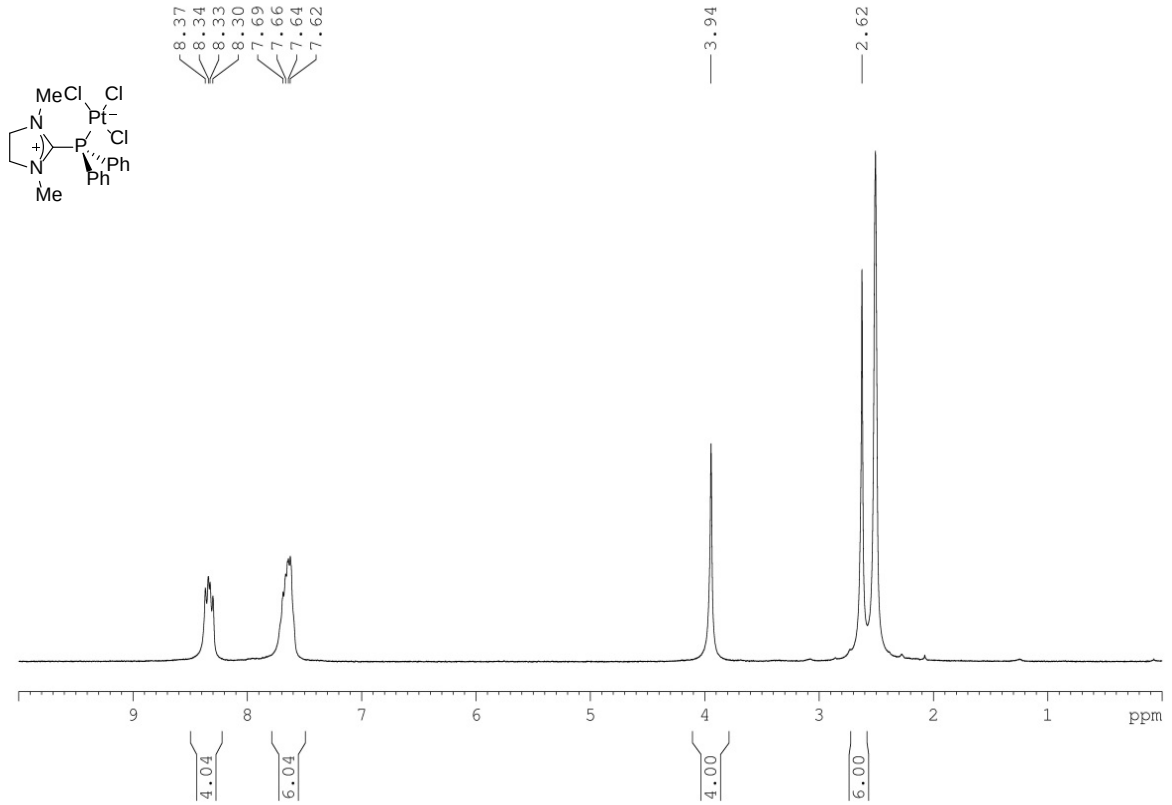
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) **13**



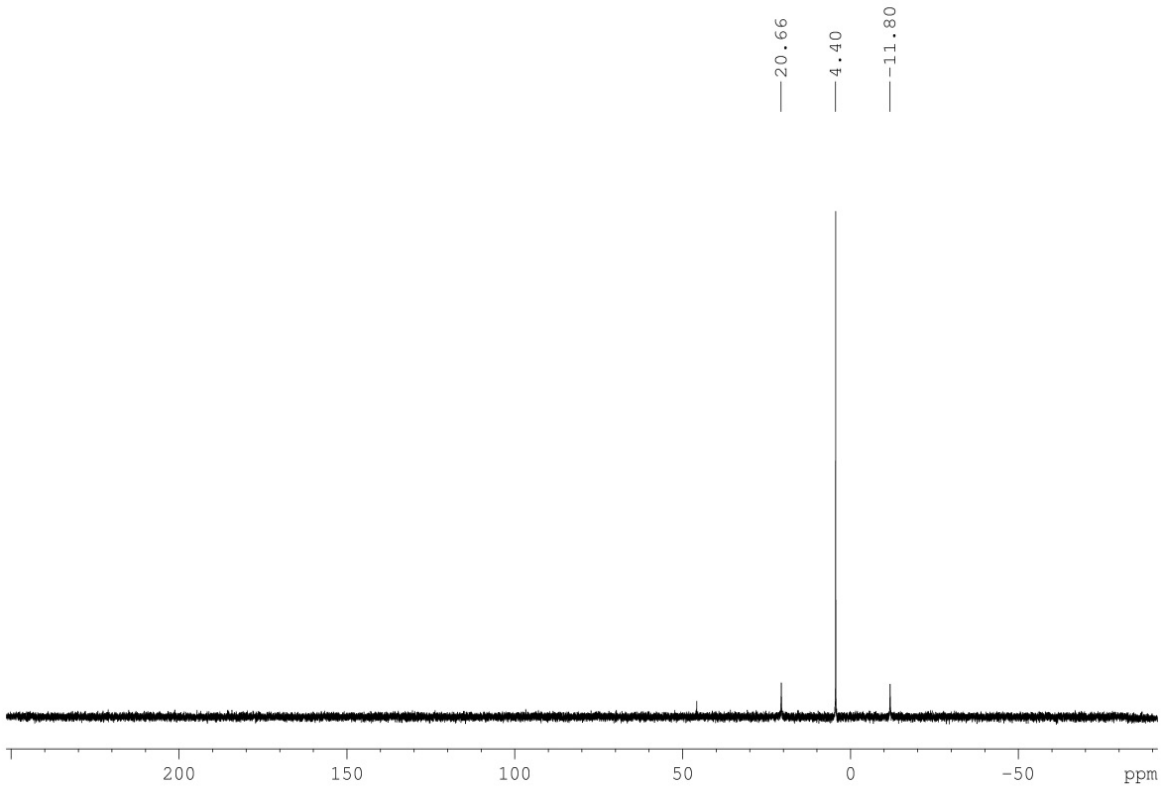
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **13**



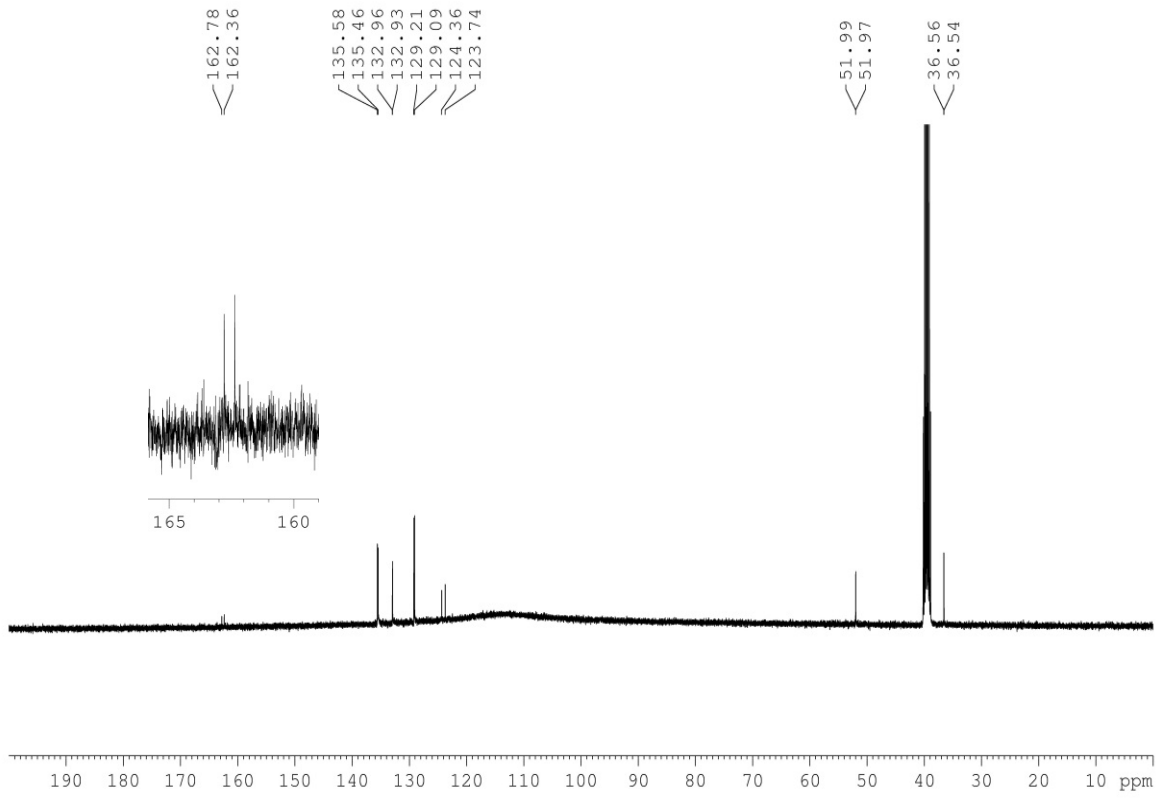
^{1}H NMR (300 MHz, $(CD_3)_2SO$) **16**



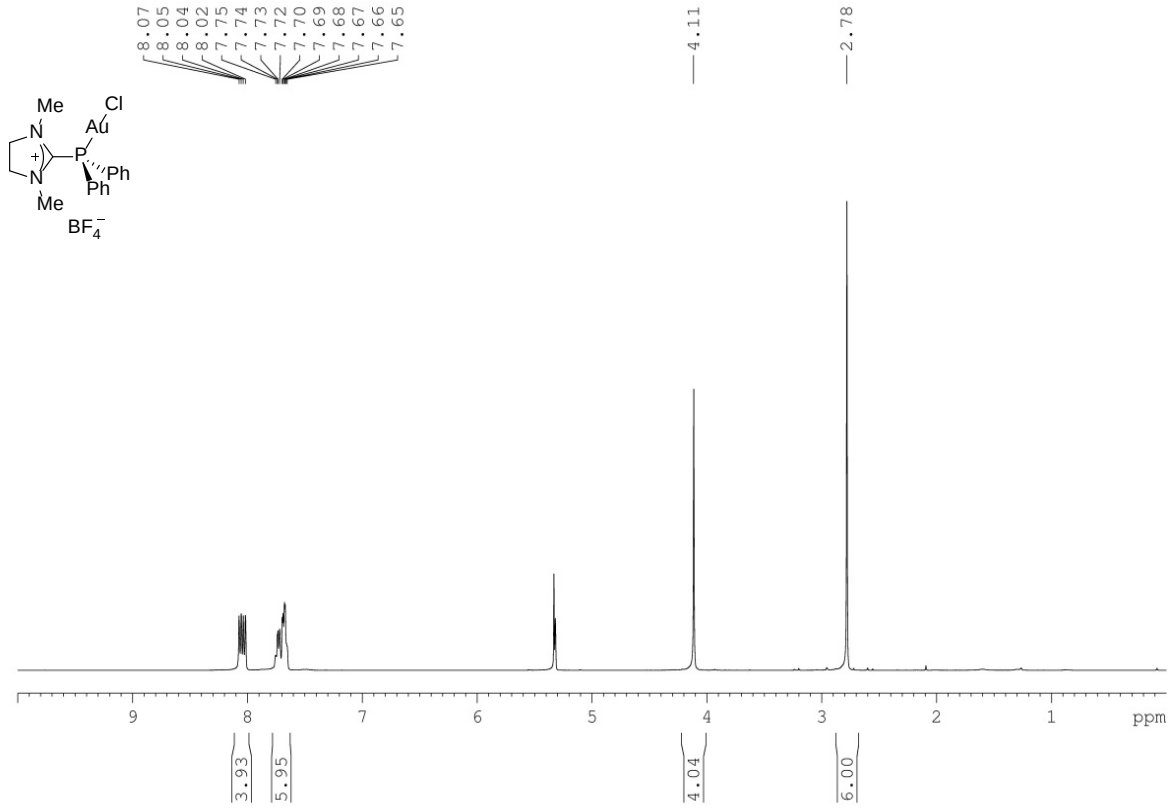
$^{31}P\{^{1}H\}$ NMR (121 MHz, $(CD_3)_2SO$) **16**



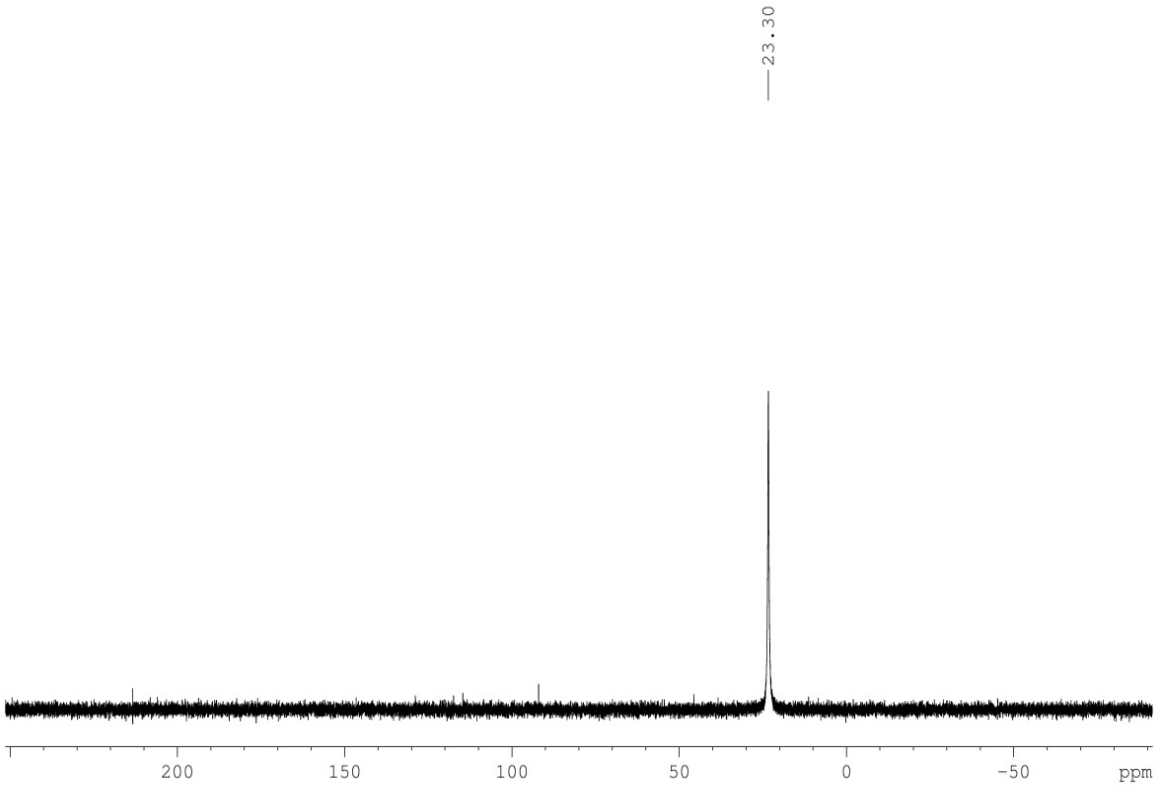
$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) **16**



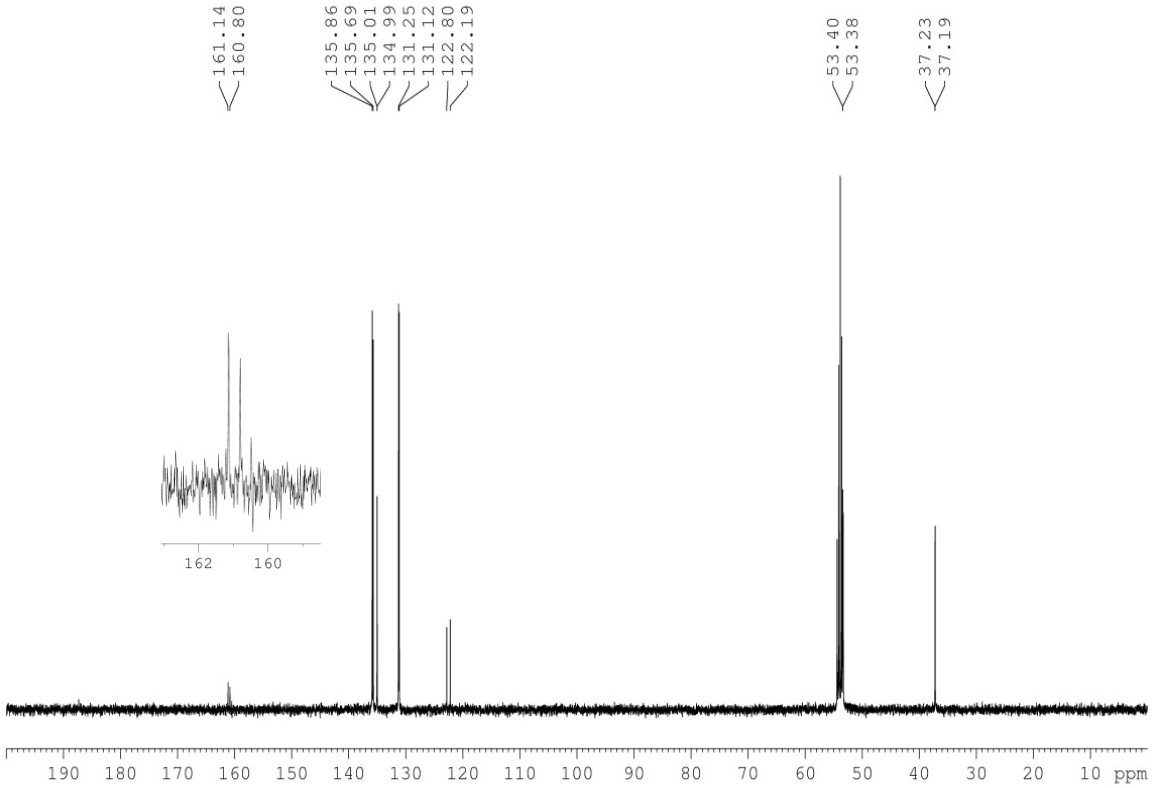
^{1}H NMR (400 MHz, CD_2Cl_2) **17**



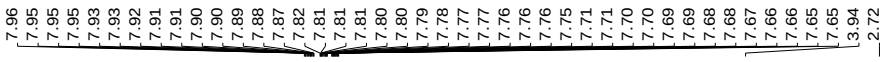
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) **17**

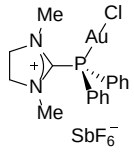


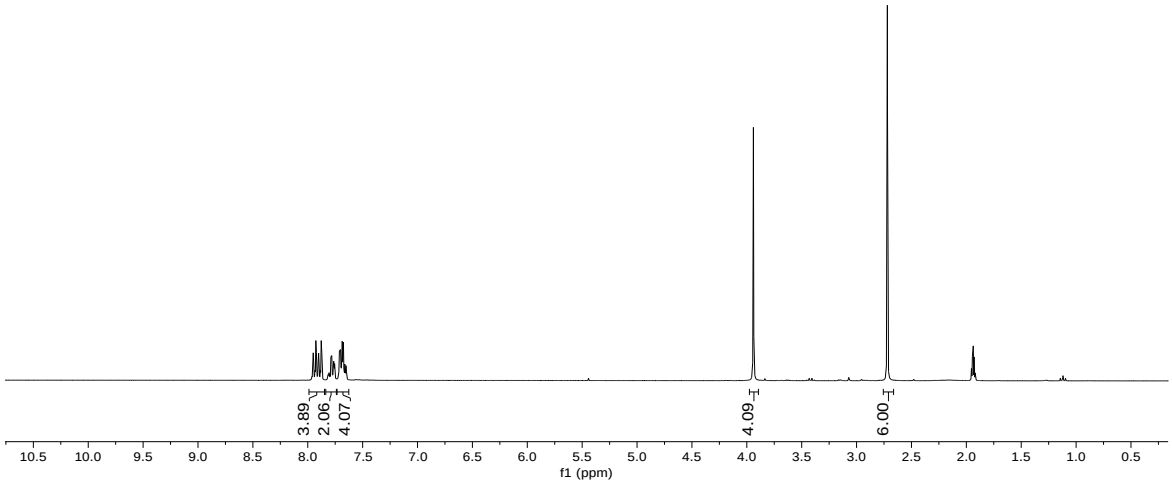
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **17**



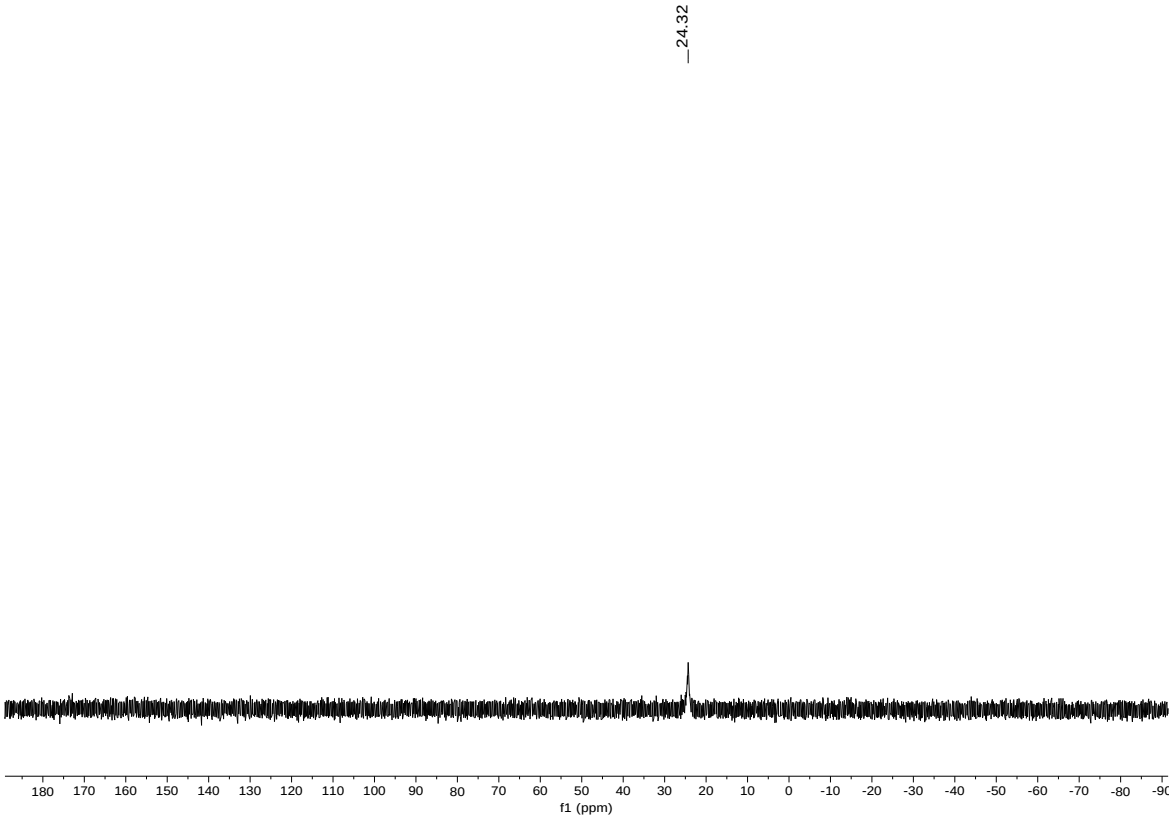
^{1}H NMR (300 MHz, CD_3CN) **18**



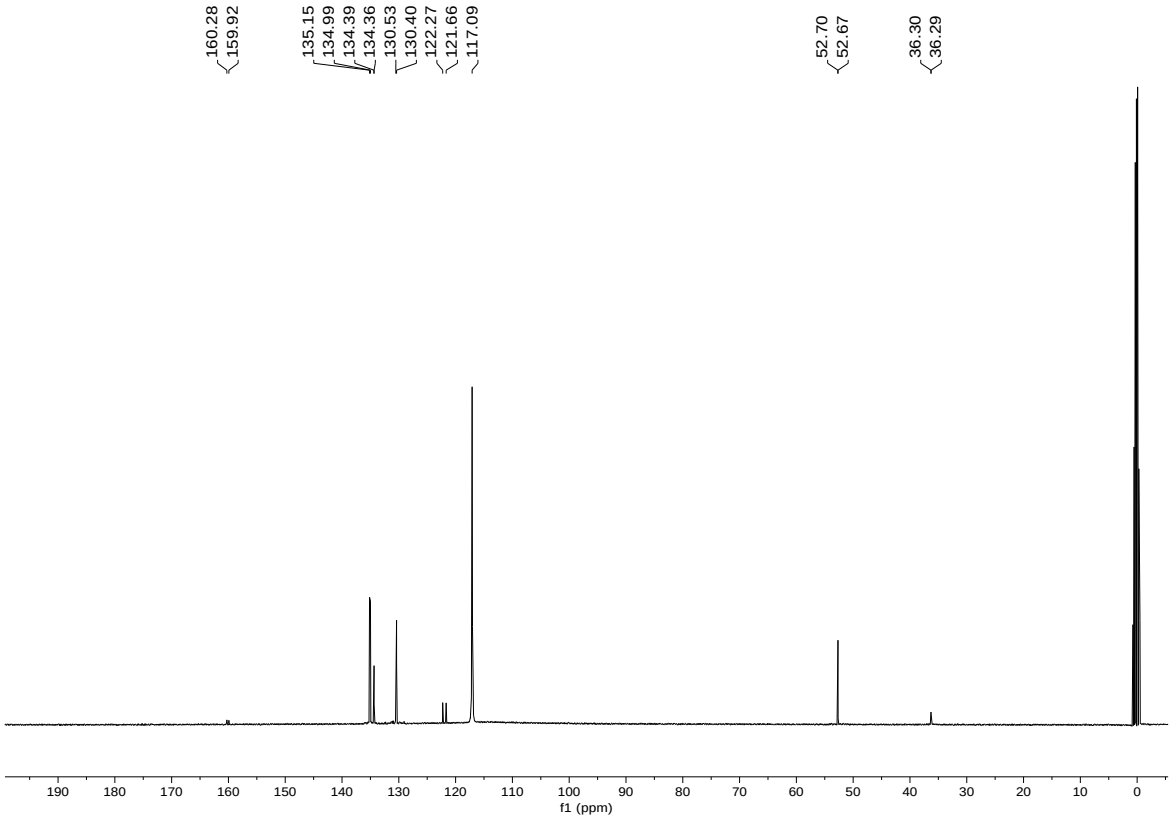




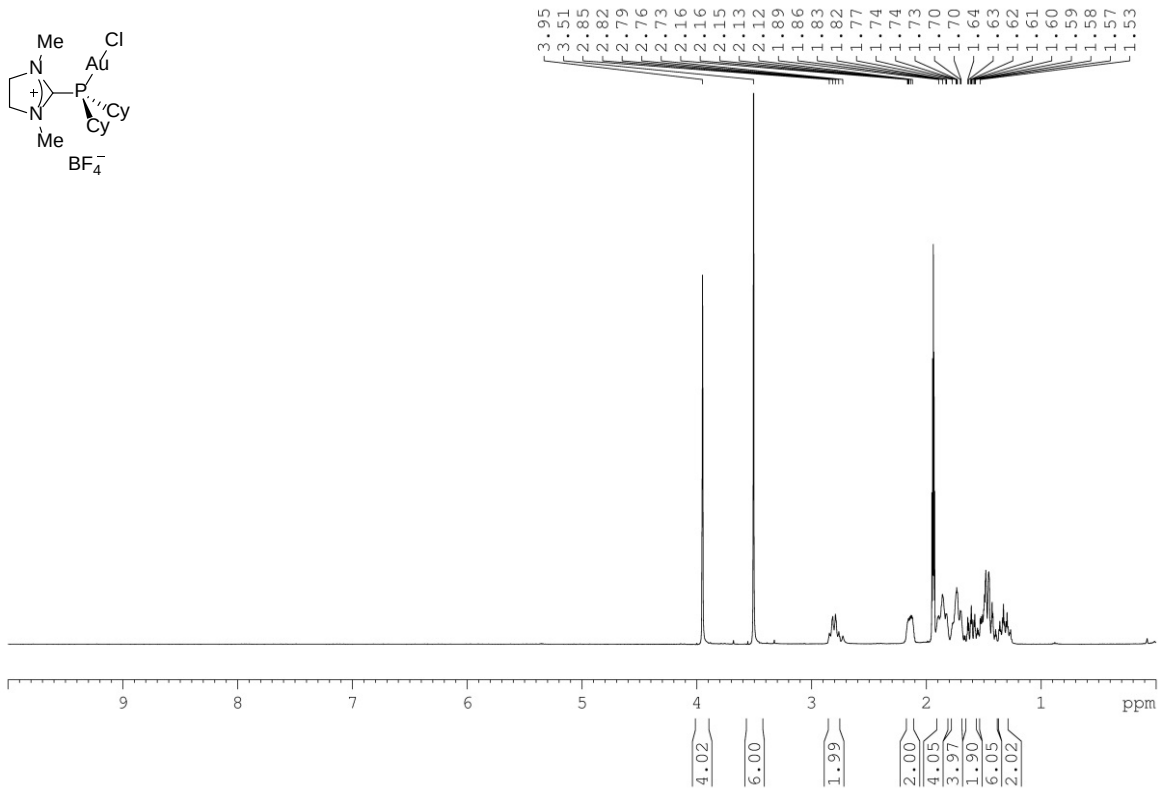
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) **18**



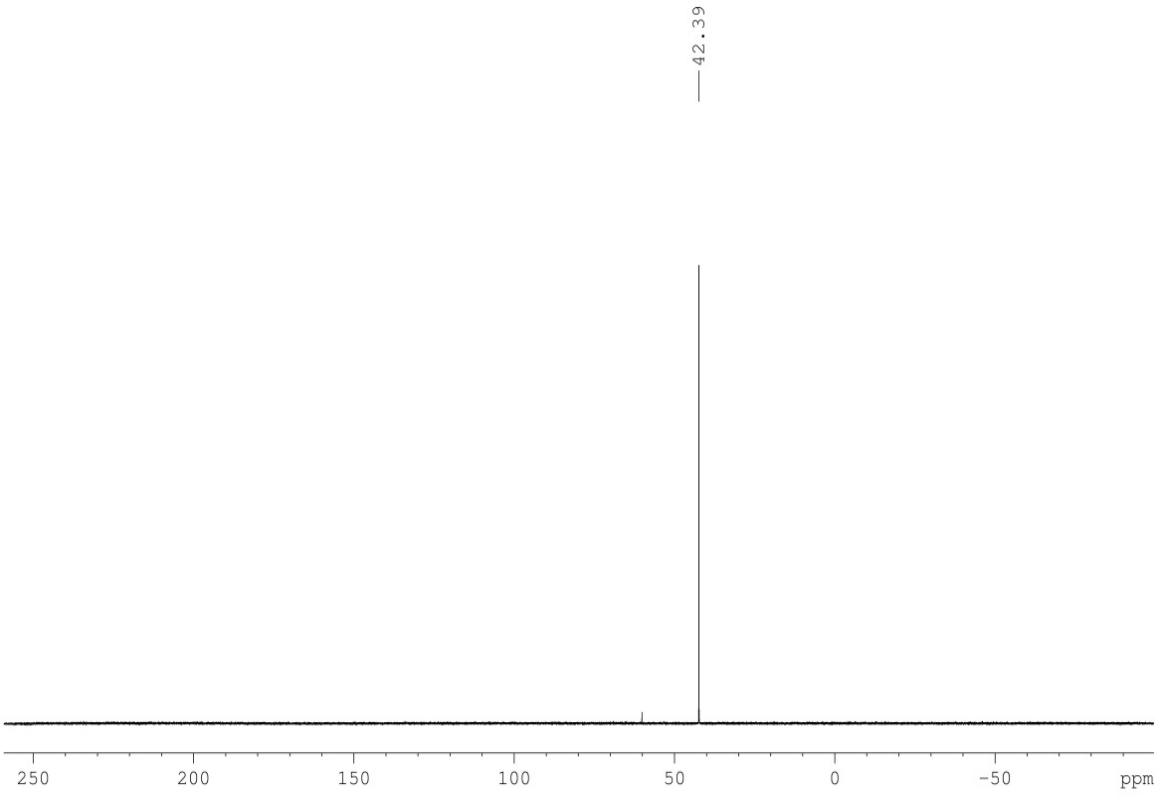
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN) **18**



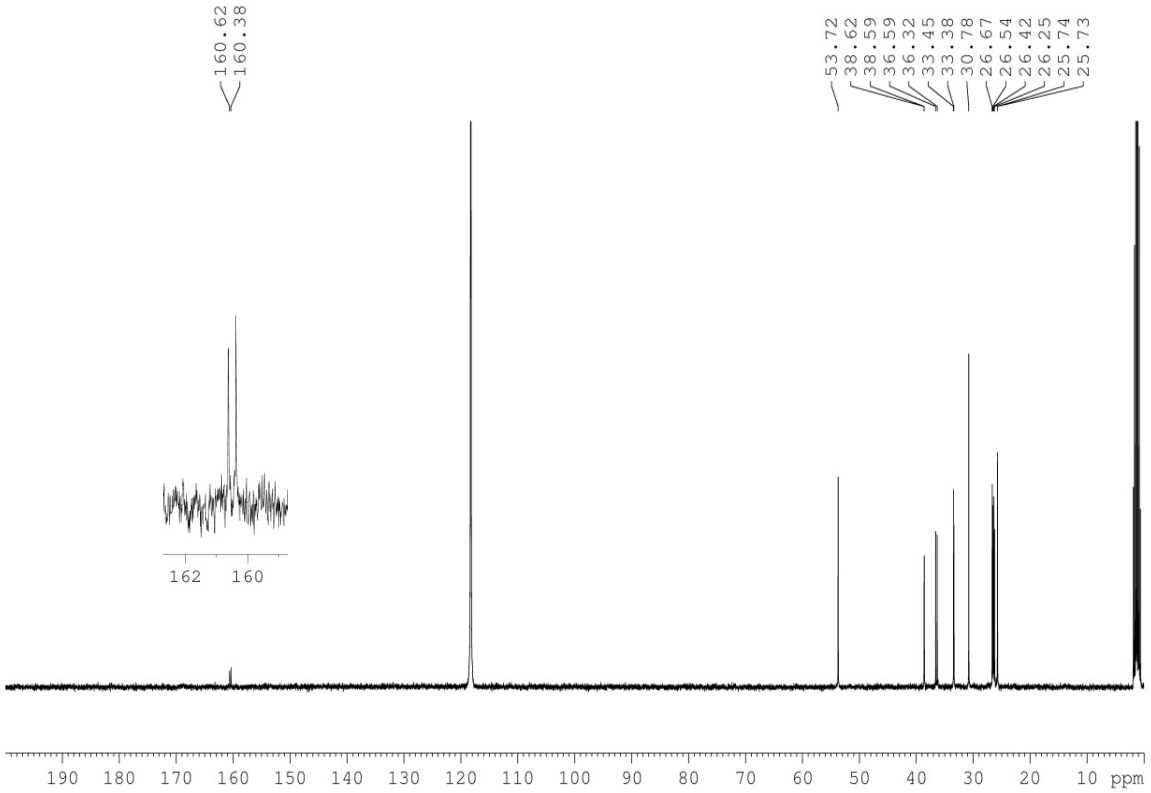
^{1}H NMR (400 MHz, CD_3CN) **19**



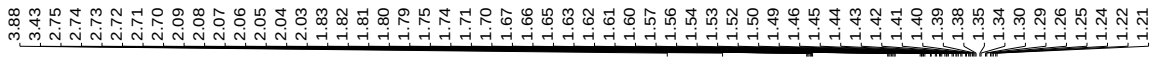
^{31}P{^{1}H} NMR (162 MHz, CD_3CN) **19**

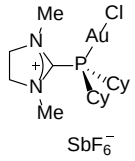


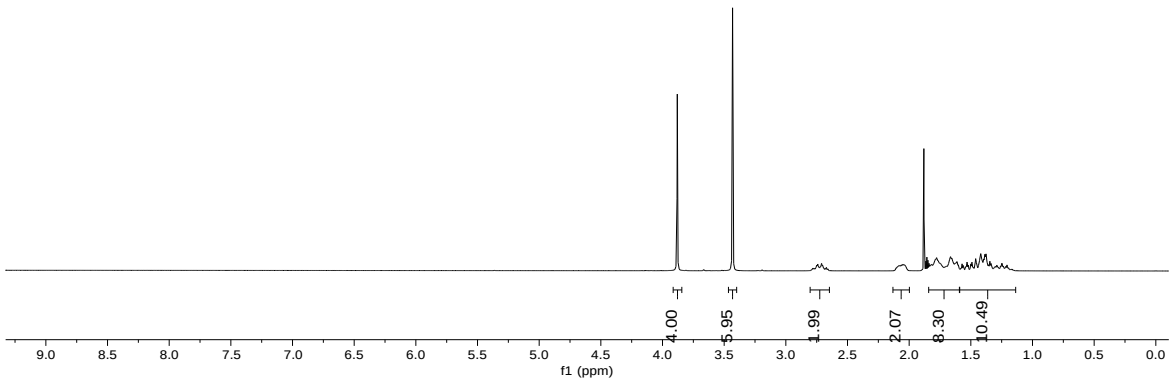
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) **19**



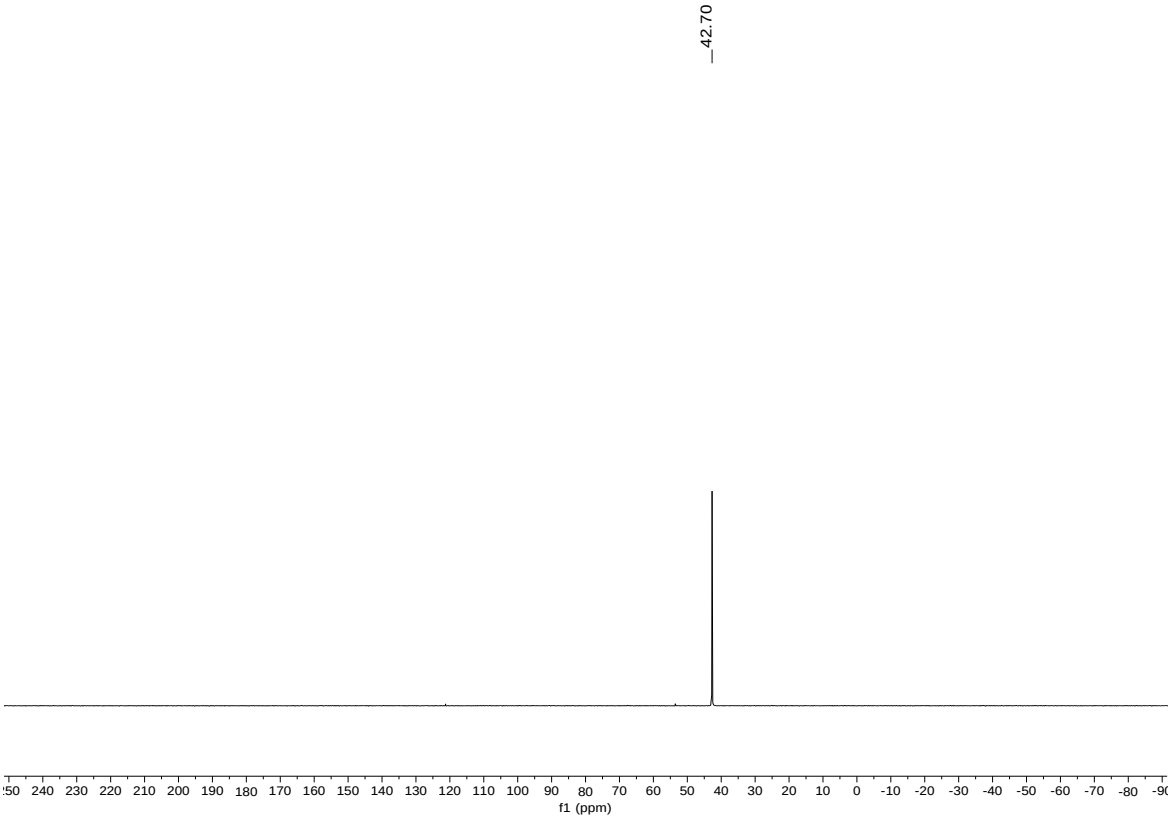
^{1}H NMR (300 MHz, CD_3CN) **20**



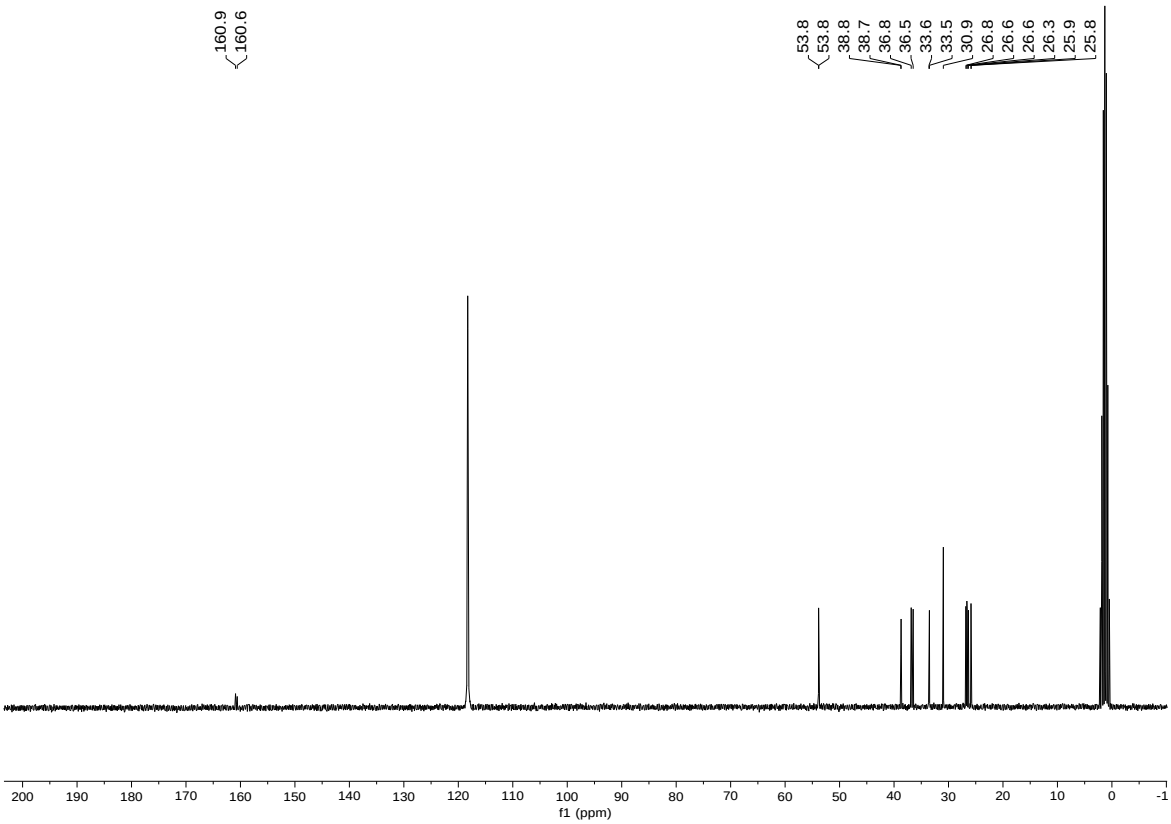




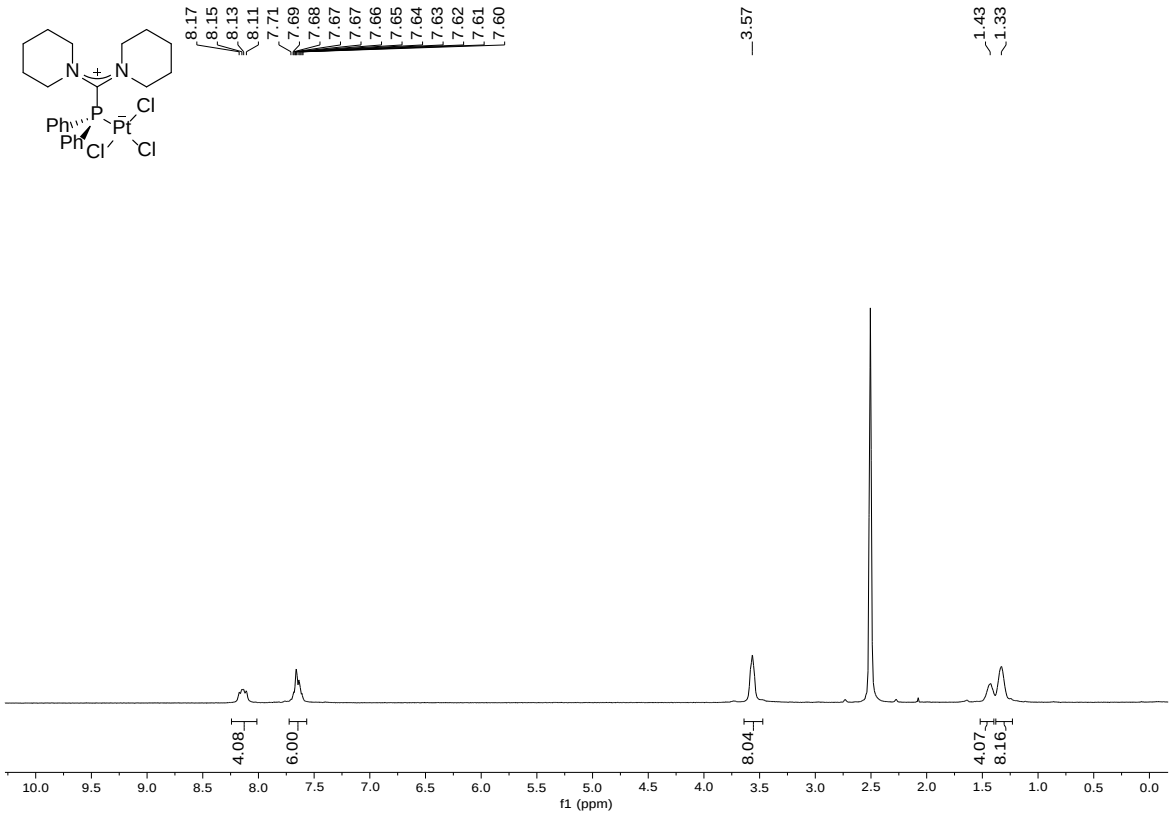
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_3CN) **20**



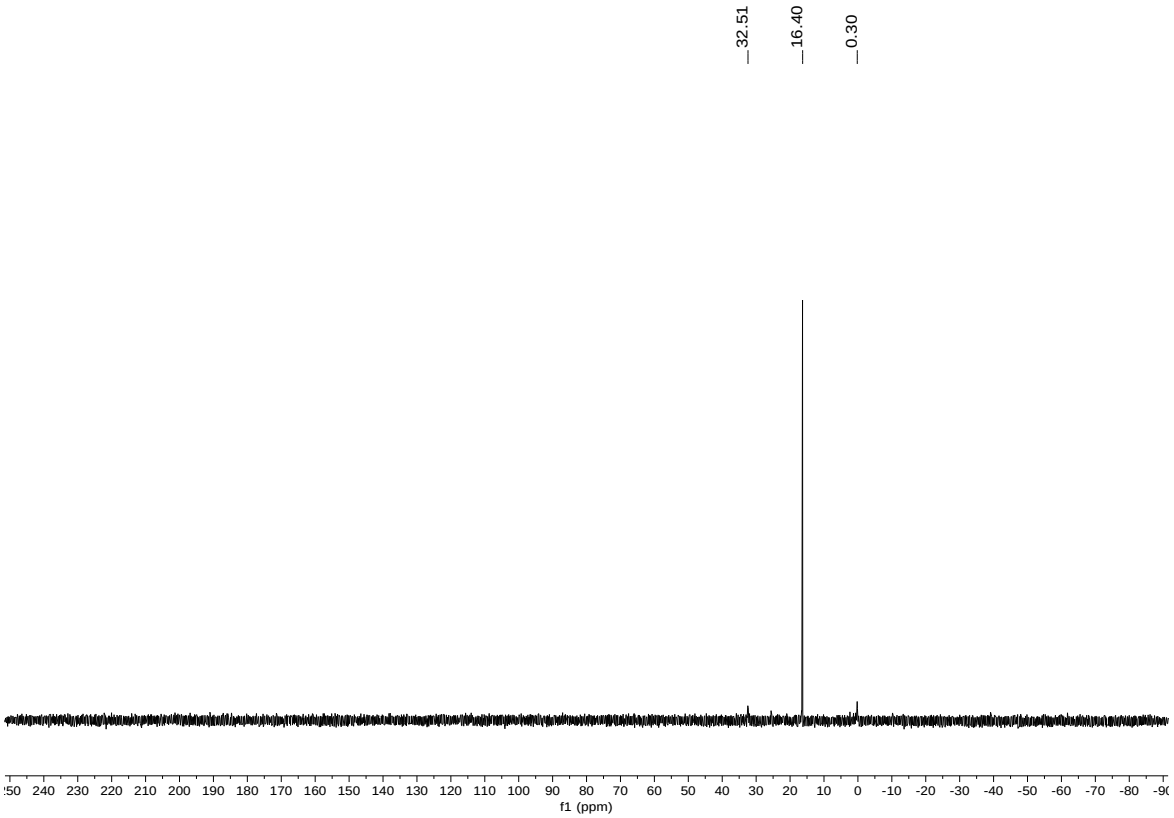
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN) **20**



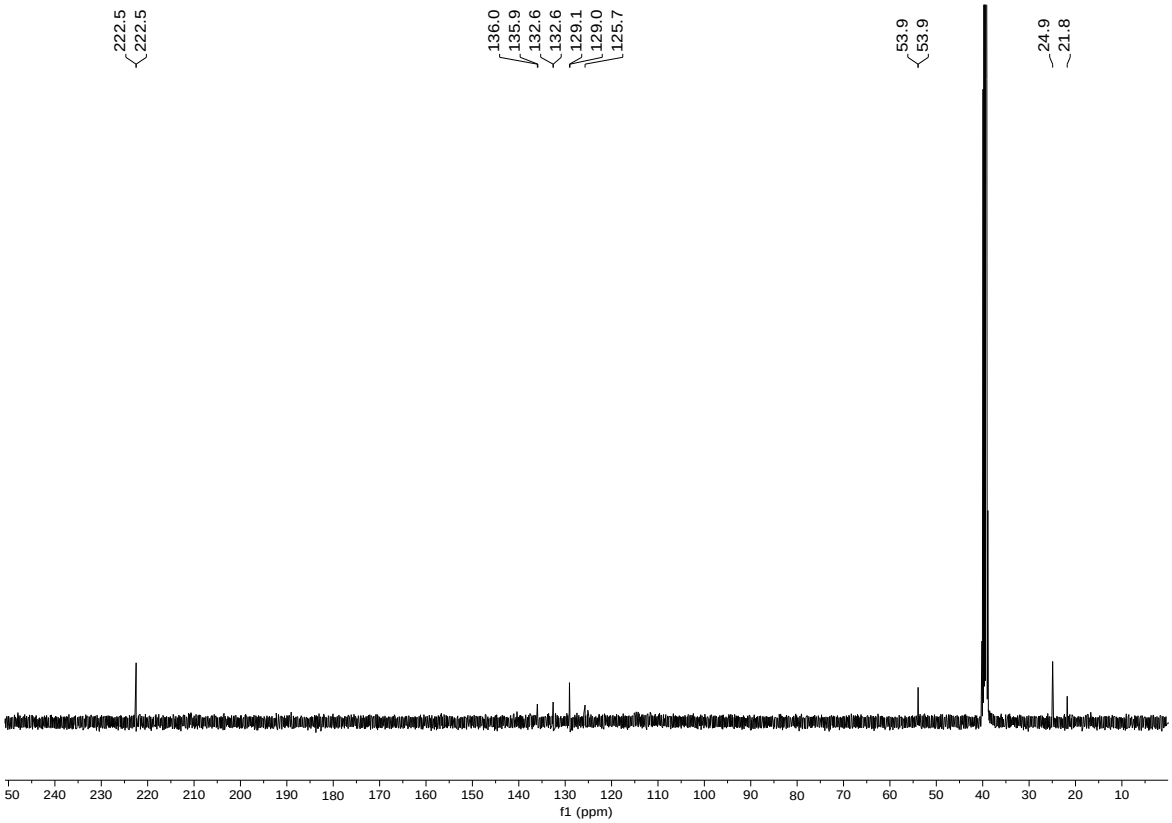
^{1}H NMR (300 MHz, $(CD_3)_2SO$) **21**



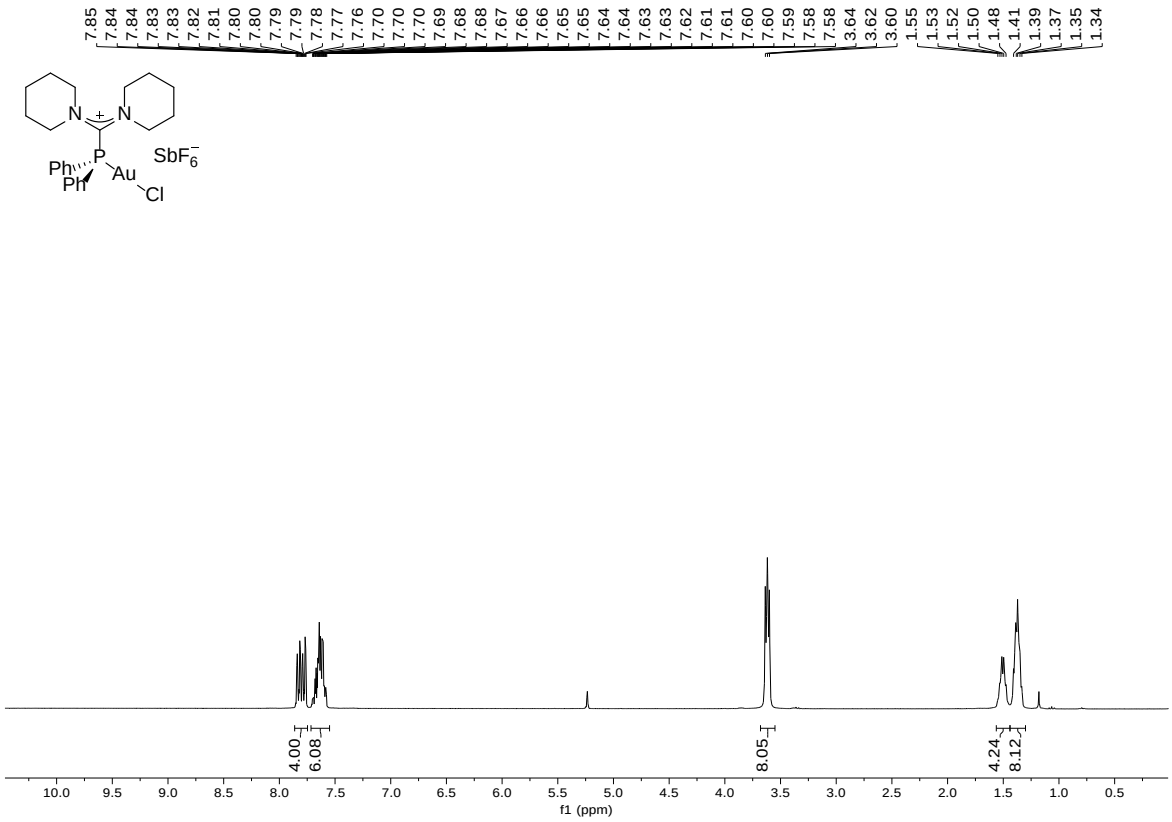
^{31}P{^{1}H} NMR (121 MHz, $(CD_3)_2SO$) **21**



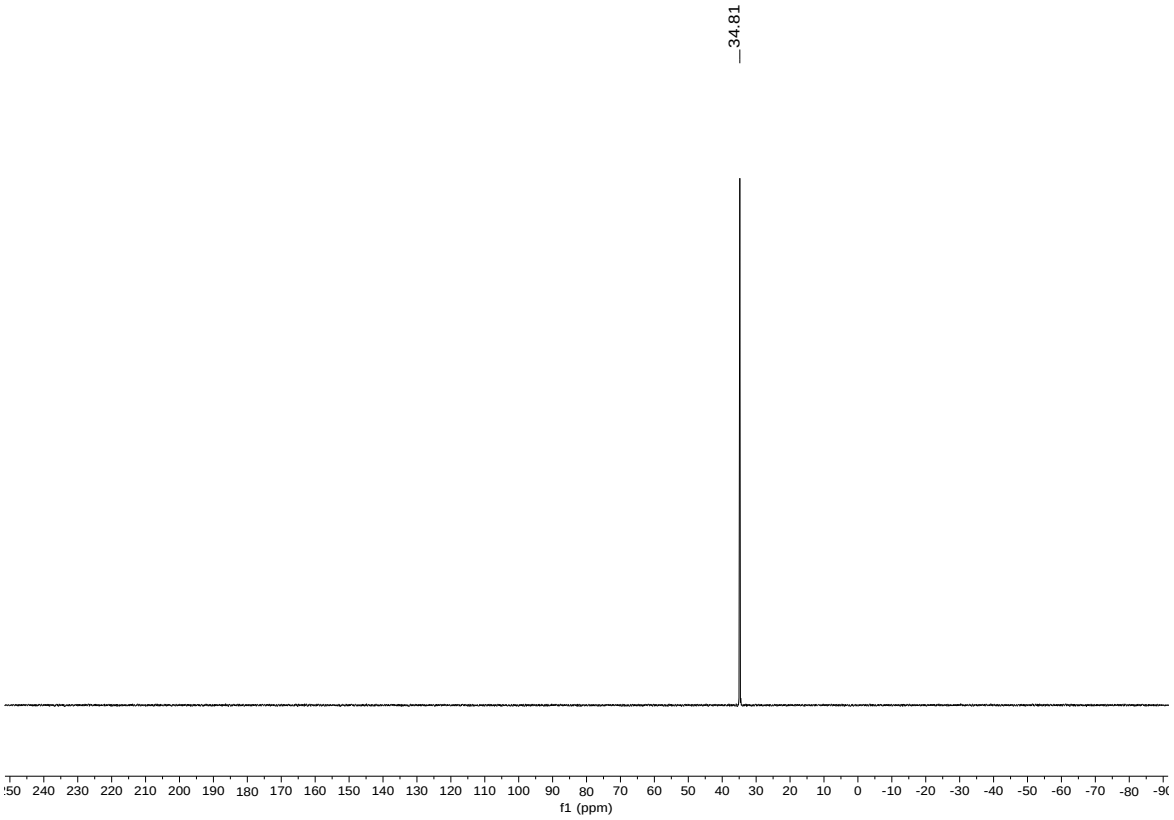
$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) **21**



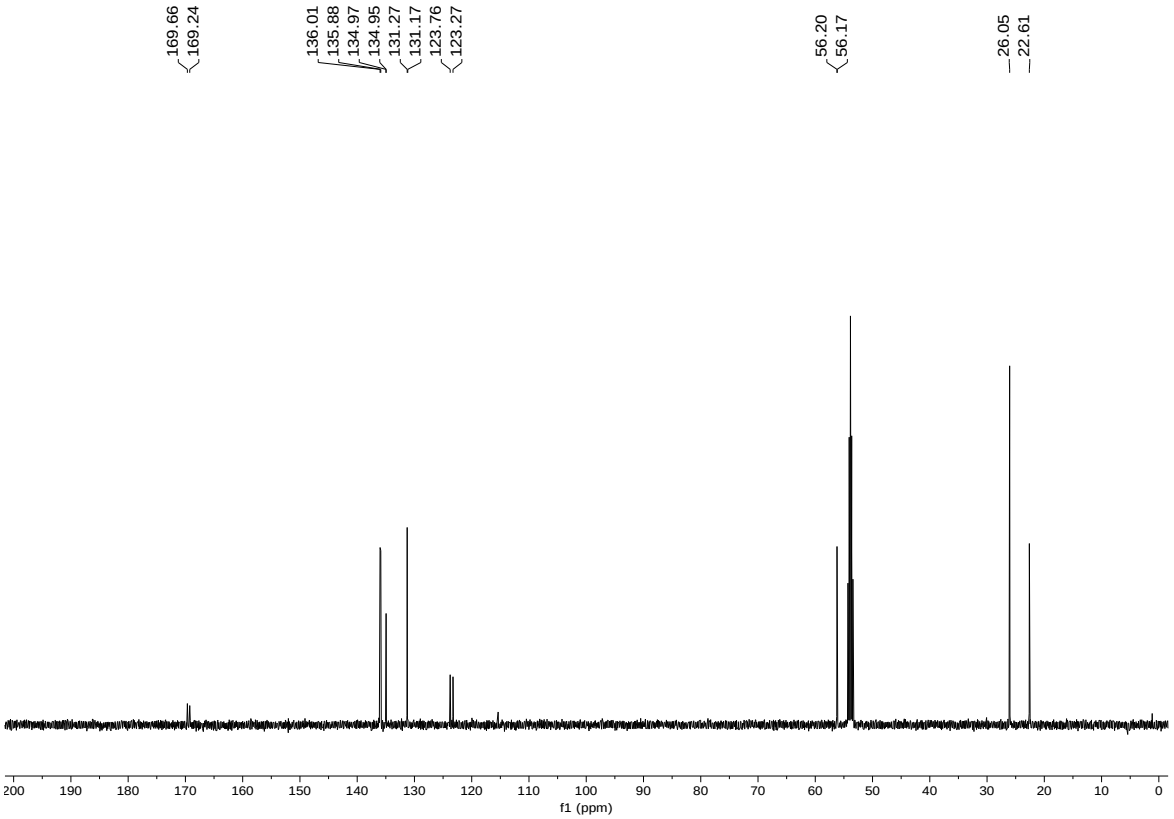
^{1}H NMR (400 MHz, CD_2Cl_2) **22**



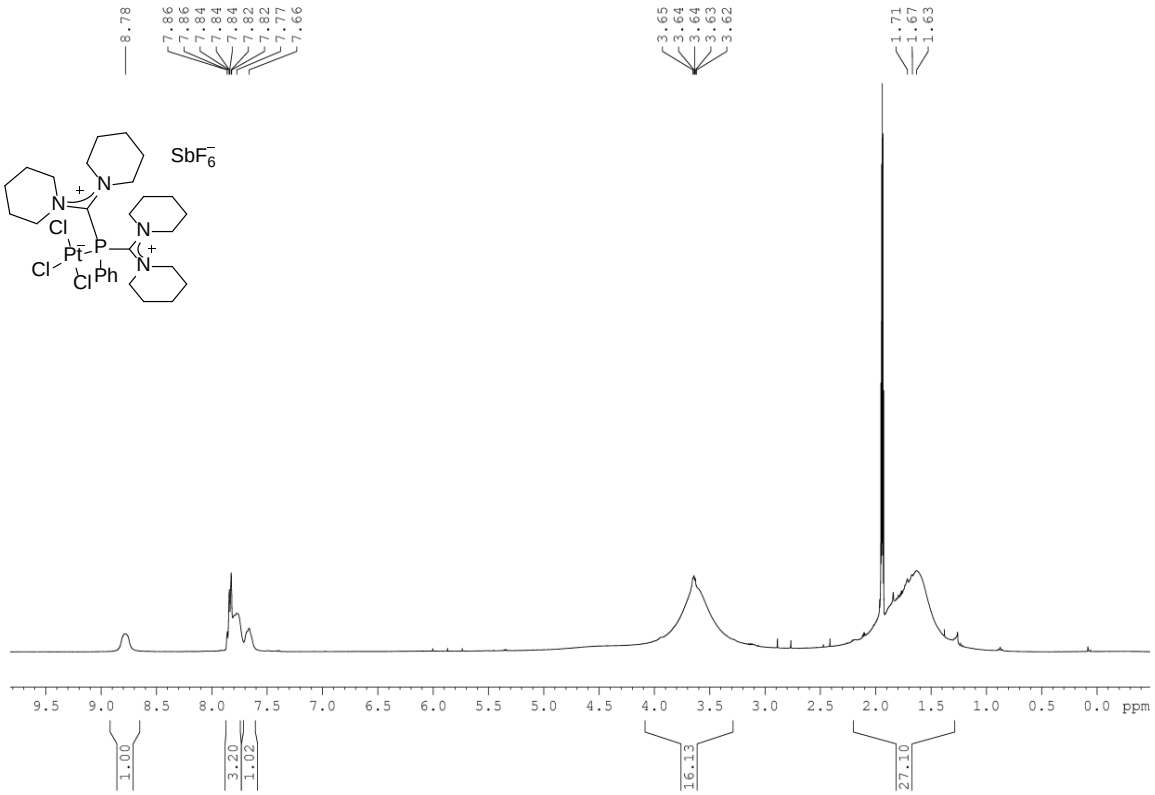
$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) **22**



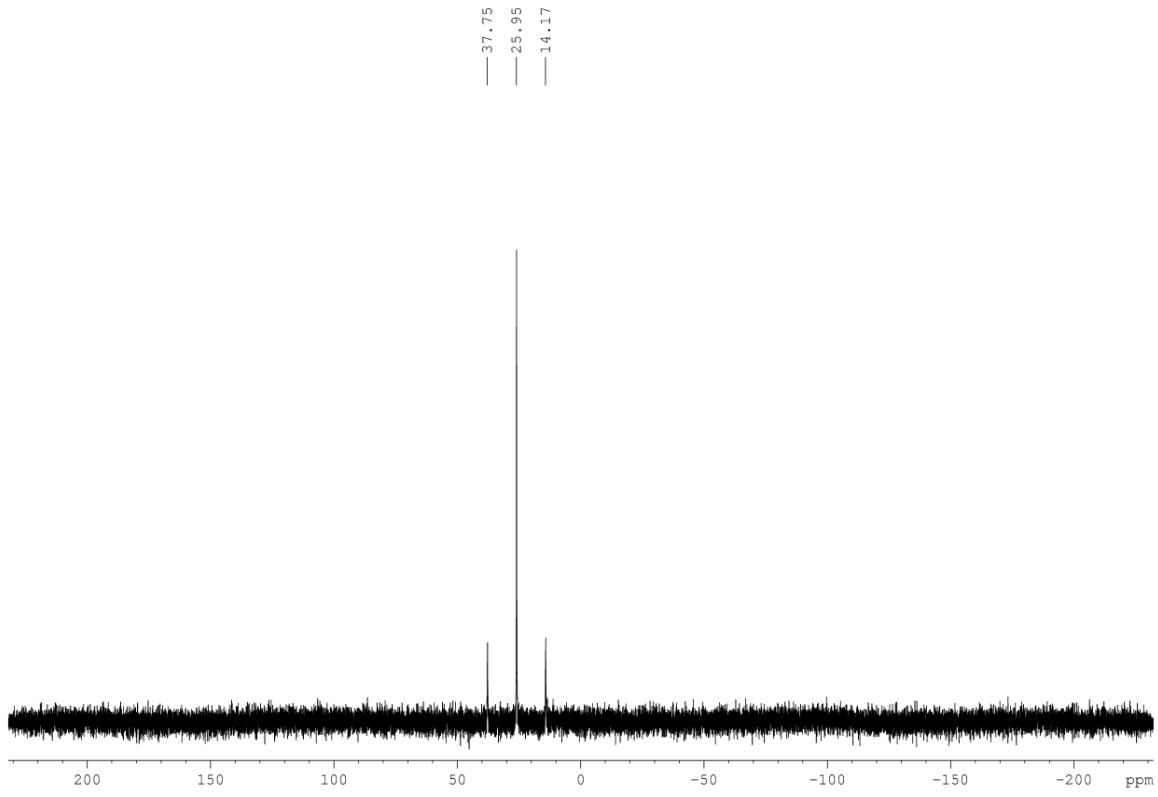
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) **22**



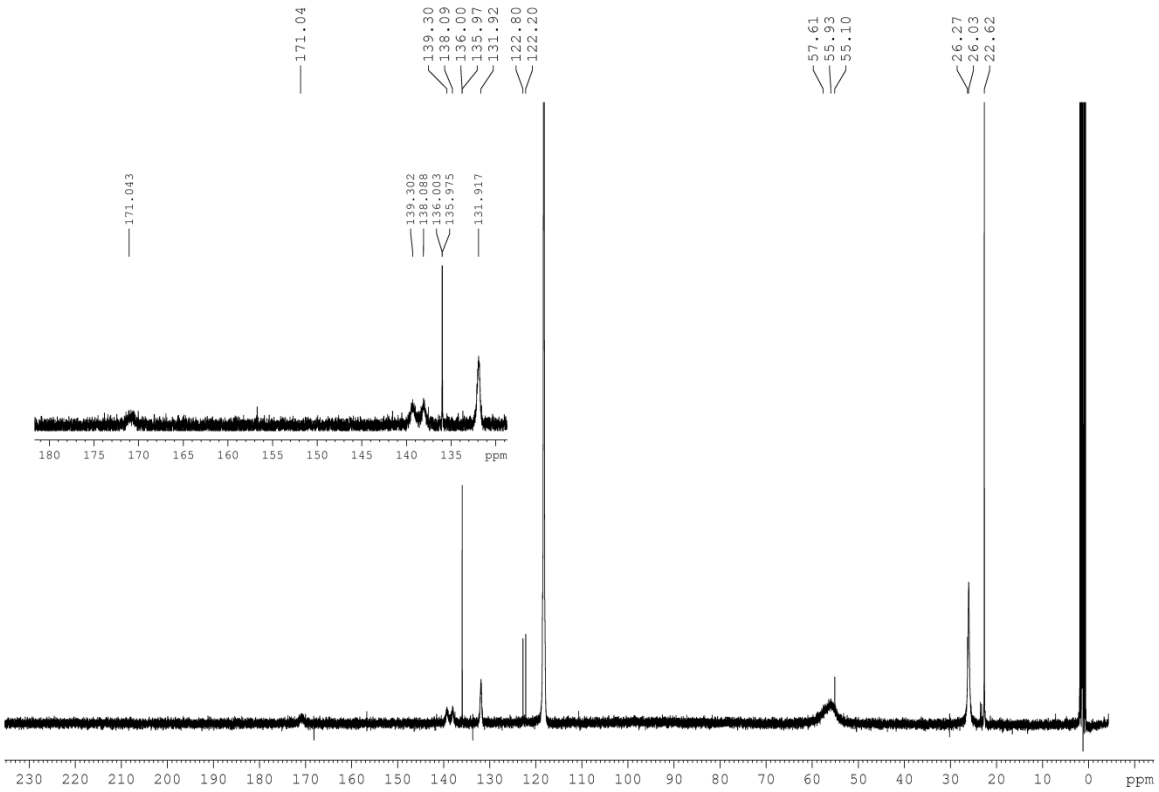
^{1}H NMR (400 MHz, CD_3CN) **23**



^{31}P{^{1}H} NMR (121 MHz, CD_3CN) **23**

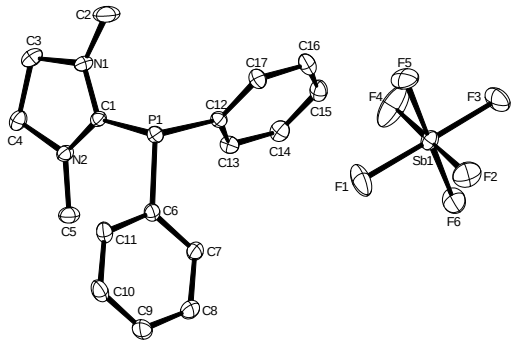


$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) **23**



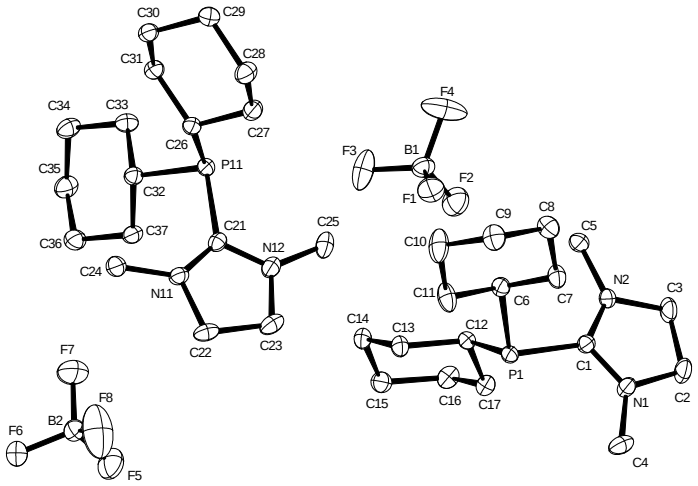
X-Ray Structure Analyses

Compound **3**



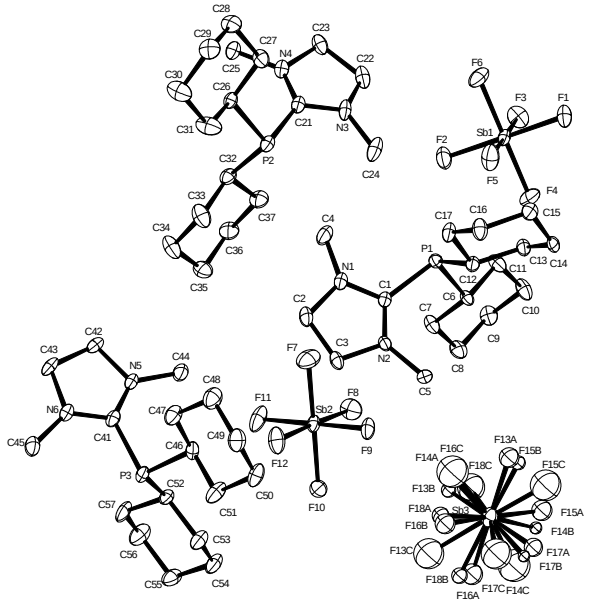
Empirical formula	$C_{17}H_{20}F_6N_2PSb$	
Color	colourless	
Formula weight	519.07 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 7.5835(4) Å	α = 90°.
	b = 11.1050(4) Å	β = 94.658(5)°.
	c = 23.5818(10) Å	γ = 90°.
Volume	1979.38(15) $Å^3$	
Z	4	
Density (calculated)	1.742 $Mg \cdot m^{-3}$	
Absorption coefficient	1.533 mm^{-1}	
F(000)	1024 e	
Crystal size	0.18 x 0.16 x 0.09 mm^3	
θ range for data collection	2.695 to 33.140°.	
Index ranges	-11 ≤ h ≤ 11, -17≤ k ≤ 17, -36 ≤ l ≤ 36	
Reflections collected	50691	
Independent reflections	7487 [R_{int} = 0.0210]	
Reflections with I>2 σ (I)	6963	
Completeness to θ = 25.242°	98.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.86809 and 0.77720	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7487 / 0 / 246	
Goodness-of-fit on F^2	1.173	
Final R indices [I>2 σ (I)]	R_1 = 0.0280	wR^2 = 0.0945
R indices (all data)	R_1 = 0.0307	wR^2 = 0.0976
Extinction coefficient	n/a	
Largest diff. peak and hole	1.900 and -1.182 $e \cdot Å^{-3}$	

Compound **4**



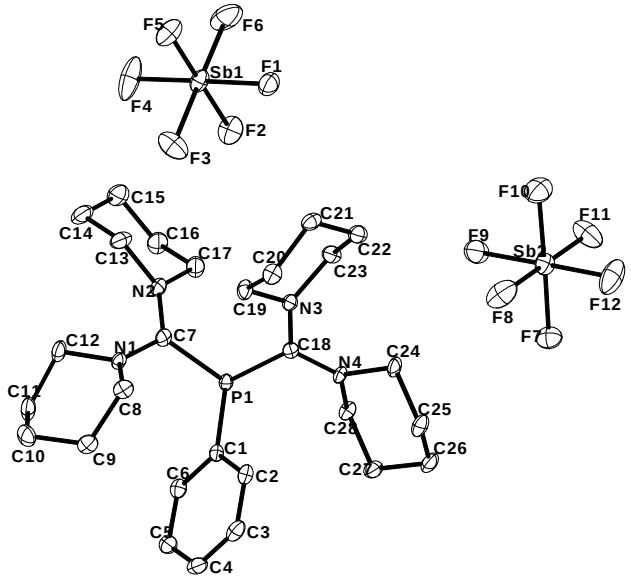
Empirical formula	$C_{17}H_{32}BF_4N_2P$	
Color	colorless	
Formula weight	382.22 g · mol^{-1}	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	MONOCLINIC	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 12.3705(5) Å	α = 90°.
	b = 22.6919(9) Å	β = 113.6237(13)°.
	c = 15.1987(6) Å	γ = 90°.
Volume	3908.9(3) Å^3	
Z	8	
Density (calculated)	1.299 Mg · m^{-3}	
Absorption coefficient	1.598 mm^{-1}	
F(000)	1632 e	
Crystal size	0.33 x 0.13 x 0.10 mm^3	
θ range for data collection	3.724 to 67.698°.	
Index ranges	-14 ≤ h ≤ 14, -27≤ k ≤ 27, -18 ≤ l ≤ 18	
Reflections collected	92285	
Independent reflections	7040 [R_{int} = 0.0467]	
Reflections with I>2 σ (I)	6294	
Completeness to θ = 67.679°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.89 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7040 / 0 / 455	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2 σ (I)]	R_1 = 0.0409	wR^2 = 0.1005
R indices (all data)	R_1 = 0.0464	wR^2 = 0.1046
Largest diff. peak and hole	0.6 and -0.5 e · Å^{-3}	

Compound **5**



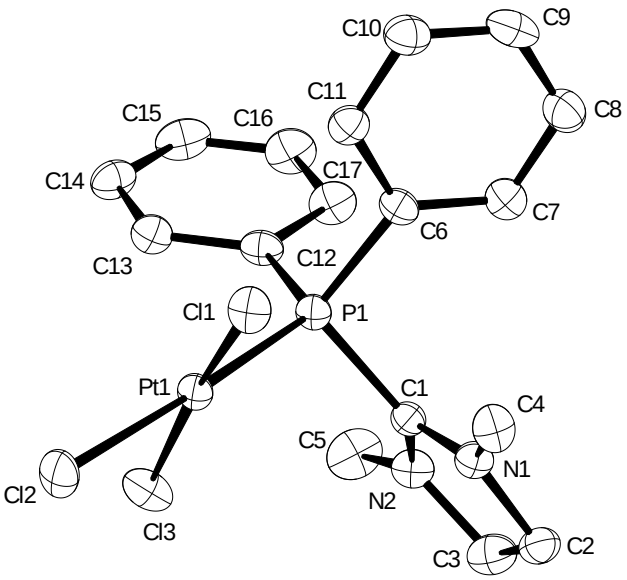
Empirical formula	$C_{17}H_{32}F_6N_2PSb$	
Color	colorless	
Formula weight	531.16 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	a = 15.028(3) Å	α= 75.926(3)°.
	b = 15.072(3) Å	β= 82.983(3)°.
	c = 15.430(3) Å	ɣ = 74.157(3)°.
Volume	3255.4(10) $Å^3$	
Z	6	
Density (calculated)	1.626 $Mg \cdot m^{-3}$	
Absorption coefficient	1.400 mm^{-1}	
F(000)	1608 e	
Crystal size	0.26 x 0.14 x 0.01 mm^3	
θ range for data collection	1.363 to 28.512°.	
Index ranges	-20 ≤ h ≤ 20, -20≤ k ≤ 20, -20 ≤ 1 ≤ 20	
Reflections collected	79160	
Independent reflections	16429 [R_{int} = 0.0710]	
Reflections with I>2σ(I)	11965	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16429 / 171 / 754	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2 σ (I)]	R_1 = 0.0376	wR^2 = 0.0854
R indices (all data)	R_1 = 0.0674	wR^2 = 0.1053
Largest diff. peak and hole	1.1 and -1.7 e $\cdot Å^{-3}$	

Compound **9**



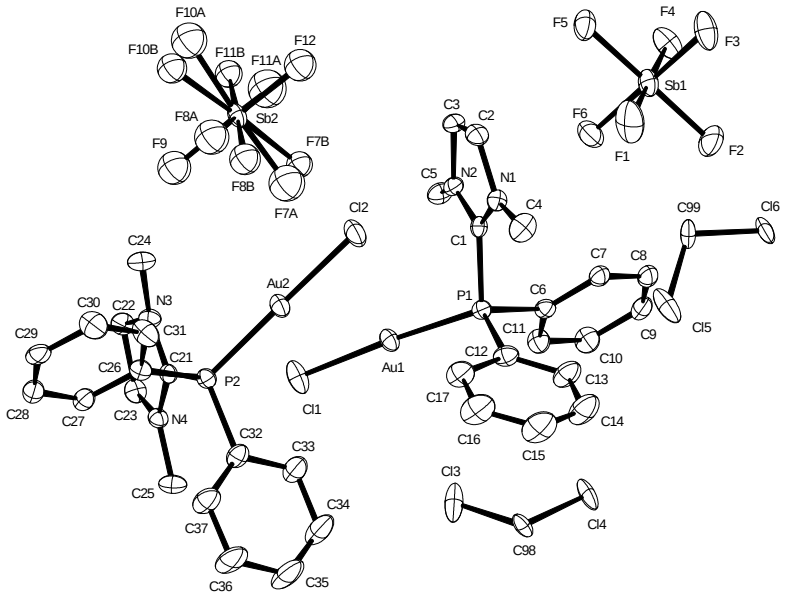
Empirical formula	$C_{28}H_{45}F_{12}N_4PSb_2$	
Color	colourless	
Formula weight	940.15 g·mol^{-1}	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	a = 10.2341(2) Å	α = 82.3872(10)°.
	b = 11.9121(3) Å	β = 82.2212(9)°.
	c = 14.5106(3) Å	γ = 87.2389(10)°.
Volume	1736.43(7) Å^3	
Z	2	
Density (calculated)	1.798 Mg·m^{-3}	
Absorption coefficient	13.602 mm^{-1}	
F(000)	932 e	
Crystal size	0.26 x 0.12 x 0.04 mm^3	
θ range for data collection	3.099 to 67.509°.	
Index ranges	-12 ≤ h ≤ 12, -14≤ k ≤ 14, -16 ≤ l ≤ 17	
Reflections collected	41228	
Independent reflections	6054 [R_{int} = 0.0676]	
Reflections with I>2 σ (I)	5404	
Completeness to θ = 67.679°	96.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.60027 and 0.11584	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6054 / 0 / 424	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2 σ (I)]	R_1 = 0.0320	wR^2 = 0.0778
R indices (all data)	R_1 = 0.0380	wR^2 = 0.0815
Extinction coefficient	n/a	
Largest diff. peak and hole	0.661 and -1.106 e·Å^{-3}	

Compound **16**



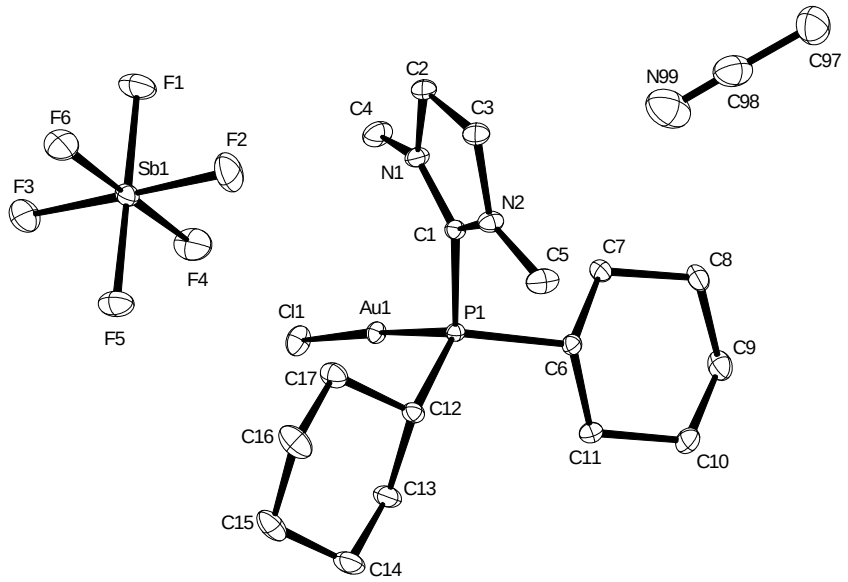
Empirical formula	$C_{17}H_{20}Cl_3N_2PPt$	
Color	yellow	
Formula weight	584.76 g · mol^{-1}	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 10.6985(8) Å	α = 90°.
	b = 17.0969(13) Å	β = 91.790(7)°.
	c = 10.7451(11) Å	ɣ = 90°.
Volume	1964.4(3) Å^3	
Z	4	
Density (calculated)	1.977 Mg · m^{-3}	
Absorption coefficient	7.634 mm^{-1}	
F(000)	1120 e	
Crystal size	0.07 x 0.07 x 0.06 mm^3	
θ range for data collection	2.646 to 33.166°.	
Index ranges	-16 ≤ h ≤ 16, -25≤ k ≤ 26, -15 ≤ l ≤ 16	
Reflections collected	22176	
Independent reflections	7474 [R_{int} = 0.0627]	
Reflections with I>2 σ (I)	5707	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.69 and 0.60	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7474 / 0 / 219	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2 σ (I)]	R_1 = 0.0563	wR^2 = 0.1374
R indices (all data)	R_1 = 0.0775	wR^2 = 0.1527
Largest diff. peak and hole	2.540 and -6.738 e · Å^{-3}	

Compound **18**



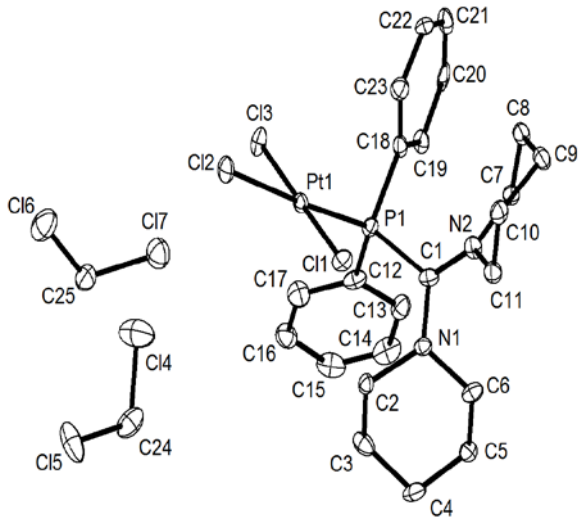
Empirical formula	$C_{35}H_{42}Au_2Cl_4F_{12}N_4P_2Sb_2$	
Color	colorless	
Formula weight	1587.90 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	a = 11.9015(15) Å	α= 88.305(2)°.
	b = 13.6615(18) Å	β= 69.996(2)°.
	c = 16.414(2) Å	ɣ = 88.438(2)°.
Volume	2506.2(6) Å^3	
Z	2	
Density (calculated)	2.104 Mg · m^{-3}	
Absorption coefficient	7.254 mm^{-1}	
F(000)	1492 e	
Crystal size	0.15 x 0.04 x 0.04 mm^3	
θ range for data collection	1.321 to 31.428°.	
Index ranges	-17 ≤ h ≤ 17, -19≤ k ≤ 19, -23 ≤ 1 ≤ 24	
Reflections collected	74031	
Independent reflections	16397 [R_{int} = 0.0334]	
Reflections with I>2σ(I)	13532	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.77 and 0.37	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16397 / 0 / 567	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2σ(I)]	R_1 = 0.0474	wR^2 = 0.1233
R indices (all data)	R_1 = 0.0607	wR^2 = 0.1321
Largest diff. peak and hole	6.4 and -2.3 e · Å^{-3}	

Compound **20**



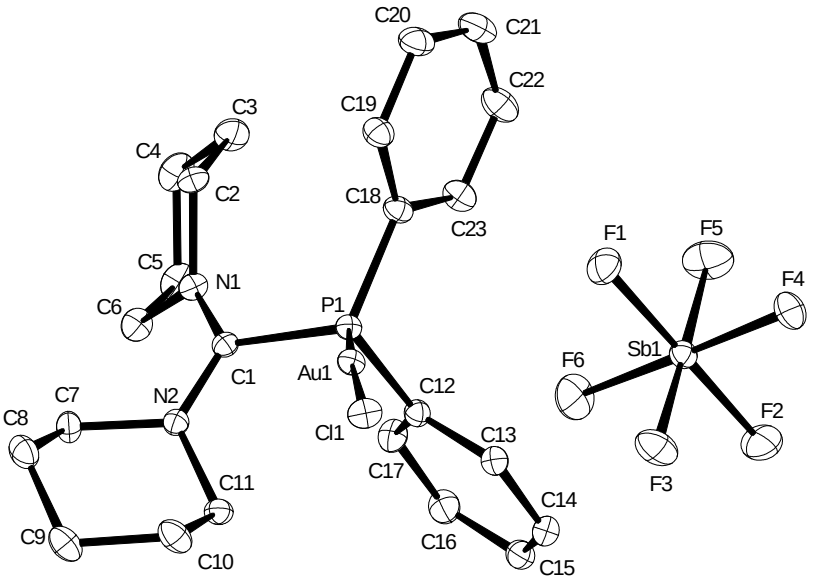
Empirical formula	$C_{19}H_{35}AuClF_6N_3PSb$	
Color	colorless	
Formula weight	804.65 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	a = 8.4612(9) Å	α= 83.9995(16)°.
	b = 8.9156(9) Å	β= 81.0351(17)°.
	c = 19.0961(19) Å	ɣ = 64.5960(15)°.
Volume	1284.2(2) Å^3	
Z	2	
Density (calculated)	2.081 Mg · m^{-3}	
Absorption coefficient	6.982 mm^{-1}	
F(000)	772 e	
Crystal size	0.12 x 0.09 x 0.09 mm^3	
θ range for data collection	2.161 to 33.139°.	
Index ranges	-13 ≤ h ≤ 13, -13≤ k ≤ 13, -29 ≤ 1 ≤ 29	
Reflections collected	42921	
Independent reflections	9751 [R_{int} = 0.0184]	
Reflections with I>2σ(I)	9598	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.63 and 0.50	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9751 / 0 / 292	
Goodness-of-fit on F^2	1.157	
Final R indices [I>2 σ (I)]	R_1 = 0.0160	wR^2 = 0.0392
R indices (all data)	R_1 = 0.0165	wR^2 = 0.0393
Largest diff. peak and hole	2.0 and -1.6 e · Å^{-3}	

Compound **21**



Empirical formula	$C_{25}H_{34}Cl_7N_2PPt$	
Color	yellow	
Formula weight	836.75 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P 2_1 2_1 2_1, (no. 19)	
Unit cell dimensions	a = 8.878(4) Å	α= 90°.
	b = 15.409(6) Å	β= 90°.
	c = 22.384(9) Å	ɣ = 90°.
Volume	3062(2) $Å^3$	
Z	4	
Density (calculated)	1.815 $Mg \cdot m^{-3}$	
Absorption coefficient	5.265 mm^{-1}	
F(000)	1640 e	
Crystal size	0.16 x 0.16 x 0.05 mm^3	
θ range for data collection	2.249 to 37.246°.	
Index ranges	-14 ≤ h ≤ 14, -25≤ k ≤ 25, -37≤ 1 ≤ 37	
Reflections collected	109357	
Independent reflections	15230 [R_{int} = 0.0883]	
Reflections with I>2σ(I)	14276	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.78215 and 0.44340	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15230 / 0 / 326	
Goodness-of-fit on F^2	1.151	
Final R indices [I>2σ(I)]	R_1 = 0.0856	wR^2 = 0.2464
R indices (all data)	R_1 = 0.0892	wR^2 = 0.2478
Absolute structure parameter	0.080(18)	
Extinction coefficient	0	
Largest diff. peak and hole	11.547 and -9.938 $e \cdot Å^{-3}$	

Compound **22**



Empirical formula	$C_{23}H_{30}AuClF_6N_2PSb$	
Color	colorless	
Formula weight	833.62 g · mol^{-1}	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 15.8215(7) Å	α= 90°.
	b = 10.3524(7) Å	β= 115.205(3)°.
	c = 18.0617(5) Å	γ = 90°.
Volume	2676.7(2) Å^3	
Z	4	
Density (calculated)	2.069 Mg · m^{-3}	
Absorption coefficient	6.701 mm^{-1}	
F(000)	1592 e	
Crystal size	0.11 x 0.08 x 0.06 mm^3	
θ range for data collection	3.015 to 33.132°.	
Index ranges	-24 ≤ h ≤ 24, -15 ≤ k ≤ 15, -27 ≤ 1 ≤ 27	
Reflections collected	76143	
Independent reflections	10154 [R_{int} = 0.0246]	
Reflections with I>2σ(I)	9620	
Completeness to θ = 25.242°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.71 and 0.50	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10154 / 0 / 316	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2σ(I)]	R_1 = 0.0138	wR^2 = 0.0321
R indices (all data)	R_1 = 0.0159	wR^2 = 0.0333
Largest diff. peak and hole	0.5 and -1.0 e · Å^{-3}	