

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

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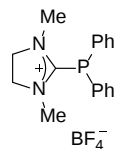
Experimental Procedures

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; ^1H 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 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$: 97/3) to give the title compound as a transparent oil that solidified on standing (1.11 g, 66%).

^1H 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.

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

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_{17}\text{H}_{20}\text{N}_2\text{P}]^+$: 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.

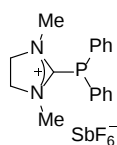
³ J. Petušková, H. Bruns, M. Alcarazo, *Angew. Chem. Int. Ed.* 2011, **50**, 3799–3802.

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:



NaSbF₆ (3.10 g, 11.83 mmol) was added to a solution of compound **1(Cl)** (1.00 g, 5.91 mmol) in CH₃CN (15 mL) and the resulting mixture stirred at room temperature overnight. Evaporation of the solvent under vacuum and extraction with CH₂Cl₂ afforded 2-chloro-1,3-dimethyl-4,5-dihydro-1H-imidazol-3-ium hexafluoroantimonate as a white solid (1.96 g, 90%). TMSPPH₂ (1.36 mL, 5.31 mmol) was added to a solution of the previously prepared salt (1.96 g, 5.31 mmol) in dry CH₂Cl₂ (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 (CH₂Cl₂/MeOH: 97/3) to give the title compound as a white solid (2.61 g, 95%).

¹H NMR (300 MHz, CD₂Cl₂) δ = 2.75 (s, 6H), 3.88 (d, J = 1.2 Hz, 4H), 7.55 - 7.35 (m, 10H) ppm.

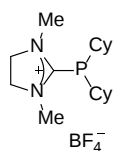
³¹P{¹H} NMR (121 MHz, CD₂Cl₂) δ = -14.32 ppm.

¹³C{¹H} NMR (101 MHz, CD₂Cl₂) 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 [C₁₇H₂₀N₂P]⁺: 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:



Cy₂PH (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 Et₂O (3 x 8 mL) and diluted with CH₃CN (5 mL). NaBF₄ (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 CH₂Cl₂. Evaporation of the solvent and purification of the crude product by column chromatography (CH₂Cl₂/acetone: 90/10) gave the title compound as a white solid (819 mg, 59%).

¹H NMR (400 MHz, CD₂Cl₂) 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.

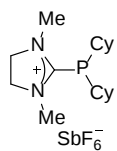
³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ = -10.4 ppm.

¹³C{¹H} NMR (101 MHz, CD₂Cl₂) 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 [C₁₇H₃₂N₂P]⁺: 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:



NaSbF₆ (699 mg, 2.70 mmol) was added to a solution of compound **4** (516 mg, 1.35 mmol) in CH₃CN (5 mL) and the resulting mixture stirred at room temperature for 12 hours. The solvent was then evaporated and the crude extracted with CH₂Cl₂. Evaporation of the solvent under vacuum afforded the desired product as a white solid (524 mg, 73%).

¹H NMR (300 MHz, CDCl₃) 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.

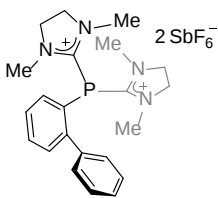
³¹P{¹H} NMR (121 MHz, CDCl₃) δ = -9.5 ppm.

¹³C{¹H} NMR (101 MHz, CD₂Cl₂) 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 [C₁₇H₃₂N₂P]⁺: 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 Et₃N (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°C overnight. After cooling to room temperature, the solvent was evaporated under vacuum. The resulting white solid was dissolved in CH₂Cl₂, washed with saturated aq. solution of NaSbF₆ (2 x 5 mL) and dried with Na₂SO₄. After

filtration, the solvent was evaporated under vacuum to give the crude product, which could be recrystallized from CH₃CN/Et₂O yielding the title compound as white solid (61 mg, 24%).

¹H NMR (400 MHz, CD₃CN) 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.

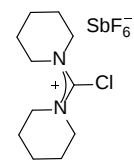
³¹P{¹H} NMR (121 MHz, CD₃CN) δ = -43.1 ppm.

¹³C{¹H} NMR (101 MHz, CD₃CN) 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 [C₂₂H₂₉N₄F₆PSb]⁺: 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:



NaSbF₆ (2.40 g, 9.26 mmol) was added under argon to a solution of known **7(Cl)** (1.16 g, 4.63 mmol) in CH₃CN (10 mL). The resulting mixture was stirred at room temperature overnight. The solvent was then removed and extracted with CH₂Cl₂. Evaporation of the solvent afforded **7** as a white solid (1.70 g, 84%).

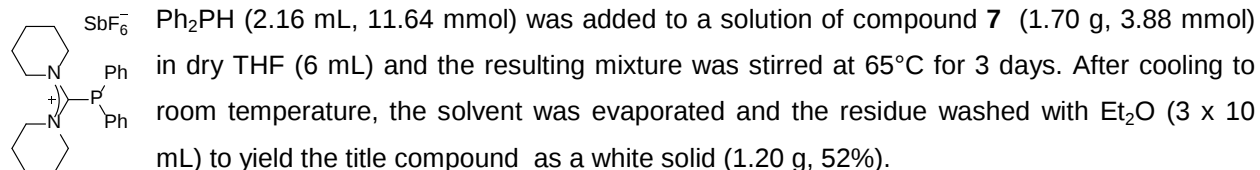
¹H NMR (300 MHz, CD₂Cl₂) δ = 1.89 - 1.73 (m, 12H), 3.74 (t, J = 5.1 Hz, 8H) ppm.

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

HRMS *calcd.* for $[\text{C}_{11}\text{H}_{20}\text{N}_2\text{Cl}]^+$: 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:



^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.

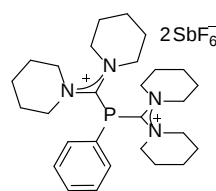
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) δ = -4.1 ppm.

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_{23}\text{H}_{30}\text{N}_2\text{P}]^+$: 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 dissolved 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.

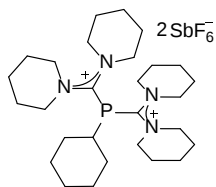
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_3CN) δ = -15.3 ppm.

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_{28}\text{H}_{45}\text{N}_4\text{SbF}_6\text{P}]^+$: 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 dissolved with CH₃CN (5 mL). NaSbF₆ (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 CH₂Cl₂. Removal of the solvents under vacuum afforded a solid that was further washed with Et₂O. The title compound was obtained as a white solid (297 mg, 73%).

¹H NMR (400 MHz, CD₃CN) δ = 1.84 - 1.26 (m, 30H), 1.92 - 1.84 (m, 4H), 3.32 - 3.13 (m, 1H), 3.68 (m, 16H) ppm.

³¹P{¹H} NMR (121 MHz, CD₃CN) δ = -3.7 ppm.

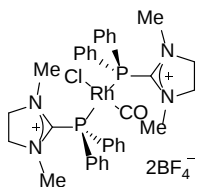
¹³C{¹H} NMR (101 MHz, CD₃CN) δ = 23.3, 25.7 (d, J_{PC} = 2.1 Hz), 26.5, 27.1 (d, J_{PC} = 15.9 Hz), 32.8 (d, J_{PC} = 17.8 Hz), 38.9 (d, J_{PC} = 23.2 Hz), 55.9 (d, J_{PC} = 5.1 Hz), 174.5 (d, J_{PC} = 34.7 Hz) ppm.

HRMS *calcd.* for [C₂₈H₅₁N₄SbF₆P]⁺: 709.278630; *found* 709.278753.

Anal. *Calcd.* for C₂₈H₅₁F₁₂N₄PSb₂: 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 CH₂Cl₂ (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%).

¹H NMR (300 MHz, CD₂Cl₂) δ = 2.89 (s, 12H), 4.14 (s, 8H), 7.62 - 7.76 (m, 12H), 8.00 - 8.11 (m, 8H) ppm.

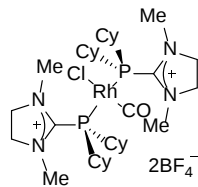
³¹P{¹H} NMR (121 MHz, CD₂Cl₂) δ = 35.8 (d, J_{RhP} = 132.0 Hz) ppm.

¹³C{¹H} NMR (101 MHz, CD₂Cl₂) 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 [C₃₅H₄₀BClF₄N₄OP₂Rh]⁺: 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 CH₂Cl₂ (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%).

¹H NMR (400 MHz, CD₂Cl₂) 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.

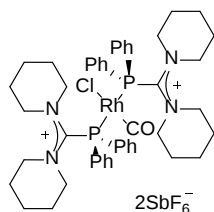
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ = 50.1 (d, J_{RhP} = 127.8 Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) 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 $[\text{C}_{35}\text{H}_{64}\text{N}_4\text{OBClF}_4\text{P}_2\text{Rh}]^+$: 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:



$[\text{RhCl}(\text{CO})_2]_2$ (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%).

^1H 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.

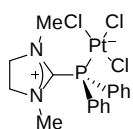
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ = 45.4 (d, J_{RhP} = 127.9 Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_{47}\text{H}_{60}\text{ClN}_4\text{OF}_6\text{P}_2\text{RhSb}]^+$: 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 $\text{DMSO}/\text{CH}_2\text{Cl}_2$ affording the desired product as a yellow solid (122 mg, 77%).

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$) δ = 2.62 (s, 6H), 3.95 (s, 4H), 7.56 - 7.76 (m, 6H), 8.26 - 8.43 (m, 4H) ppm.

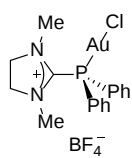
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $(\text{CD}_3)_2\text{SO}$) δ = 4.4 (J_{PtP} = 3941.6 Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) 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 $[\text{C}_{19}\text{H}_{26}\text{Cl}_2\text{N}_2\text{OPPtS}]^+$: 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(SMe₂)] (81 mg, 0.27 mmol) was added to a solution of compound **2** (100 mg, 0.27 mmol) in dry CH₂Cl₂ (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%).

¹H NMR (400 MHz, CD₂Cl₂) 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.

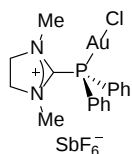
³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ = 23.3 ppm.

¹³C{¹H} NMR (101 MHz, CD₂Cl₂) 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 [C₁₇H₂₀N₂AuCIP]⁺: 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(SMe₂)] (57 mg, 0.19 mmol) was added to a solution of compound **3** (100 mg, 0.19 mmol) in dry CH₂Cl₂ (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%).

¹H NMR (300 MHz, CD₃CN) 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.

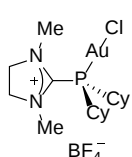
³¹P{¹H} NMR (121 MHz, CD₂Cl₂) δ = 24.3 ppm.

¹³C{¹H} NMR (75 MHz, CD₃CN) 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 [C₁₇H₂₀AuClN₂P]⁺: 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(SMe₂)] (62 mg, 0.21 mmol) was added to a solution of compound **4** (80 mg, 0.21 mmol) in dry CH₂Cl₂ (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 %).

¹H NMR (400 MHz, CD₃CN) 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.

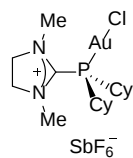
³¹P{¹H} NMR (162 MHz, CD₃CN) δ = 42.4 ppm.

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_{17}\text{H}_{32}\text{N}_2\text{AuClP}]^+$: 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**:



$[\text{AuCl}(\text{SMe}_2)]$ (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.

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

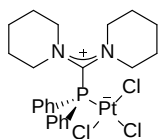
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) δ = 25.8 (d, J_{PC} = 2.0 Hz), 26.5 (d, J_{PC} = 16.9 Hz), 26.7 (d, J_{PC} = 13.6 Hz), 30.9, 33.5 (d, J_{PC} = 6.6 Hz), 36.7 (d, J_{PC} = 27.1 Hz), 38.7 (d, J_{PC} = 3.7 Hz), 53.8 (d, J_{PC} = 2.0 Hz), 160.7 (d, J_{PC} = 23.6 Hz) ppm.

HRMS *calcd.* for $[\text{C}_{17}\text{H}_{32}\text{AuClN}_2\text{P}]^+$: 527.165167; *found*: 527.165410.

Anal. Calcd. for $\text{C}_{17}\text{H}_{32}\text{AuClF}_6\text{N}_2\text{PSb}$: 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 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ affording the desired product as a pale pink solid (145 mg, 90%).

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$) 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.

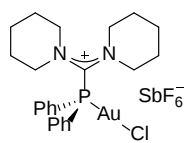
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $(\text{CD}_3)_2\text{SO}$) δ = 16.4 (J_{PtP} = 3914.6 Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) 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 $[\text{C}_{25}\text{H}_{36}\text{Cl}_2\text{N}_2\text{OPPtS}]^+$: 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(SMe₂)] (505 mg, 1.71 mmol) was added to a solution of compound **8** (1.03 g, 1.71 mmol) in dry CH₂Cl₂ (10 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated and the residue recrystallized from CH₃CN/Et₂O affording the desired product as a white solid (898 mg, 63%).

¹H NMR (400 MHz, CD₂Cl₂) 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.

³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ = 34.8 ppm.

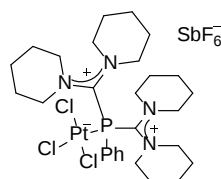
¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ = 22.6, 26.1, 56.2 (d, *J*_{PC} = 3.8 Hz), 123.5 (d, *J*_{PC} = 62.0 Hz), 131.2 (d, *J*_{PC} = 12.8 Hz), 134.9 (d, *J*_{PC} = 2.7 Hz), 135.9 (d, *J*_{PC} = 15.5 Hz), 169.5 (d, *J*_{PC} = 52.0 Hz) ppm.

HRMS *calcd.* for [C₂₃H₃₀AuClN₂P]⁺: 597.149518; *found* 597.149810.

Anal. Calcd. for C₂₃H₃₀AuClF₆N₂PSb: 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**:



K₂PtCl₄ (44 mg, 0.11 mmol) was added to a solution of bis(piperidin-1-ylmethanylylidene)phenylphosphine (100 mg, 0.11 mmol) in dry CH₃CN (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 CH₂Cl₂. Extraction with CH₃CN and evaporation of the solvent under vacuum gave the crude product, which was recrystallized from CH₃CN/Et₂O to afford the title compound as a yellow solid (24 mg, 21%).

¹H NMR (400 MHz, CD₃CN) 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.

³¹P{¹H} NMR (121 MHz, CD₃CN) δ = 26.0 (d, *J*_{PtP} = 3818.7 Hz) ppm.

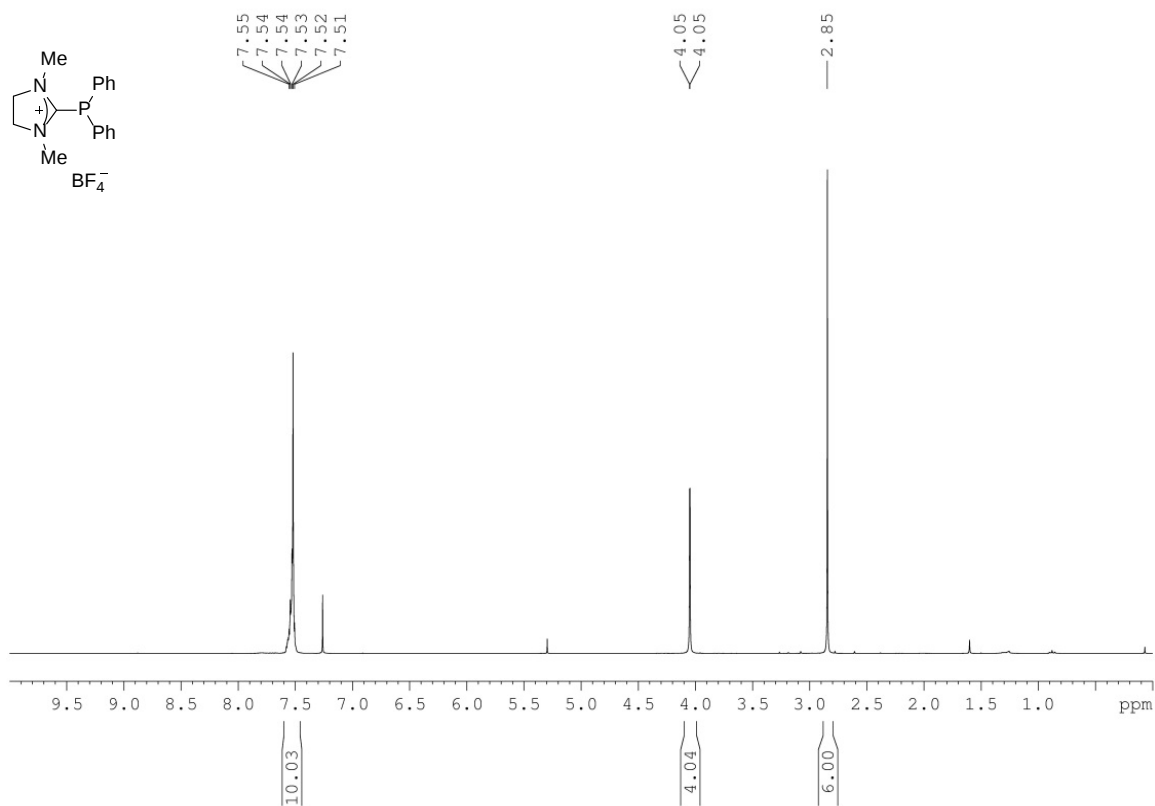
¹³C{¹H} NMR (101 MHz, CD₃CN) δ = 22.6, 26.0 (br), 55.9 (br), 122.5 (d, *J*_{PC} = 60.2 Hz), 131.9 (d), 136.0 (d, *J*_{PC} = 2.8 Hz), 138.7 (dm, *J*_{PC} = 122.1 Hz), 171.0 (br) ppm.

HRMS *calcd.* for [C₂₈H₄₅N₄Cl₃PPT]⁺: 768.209320; *found* 768.209006.

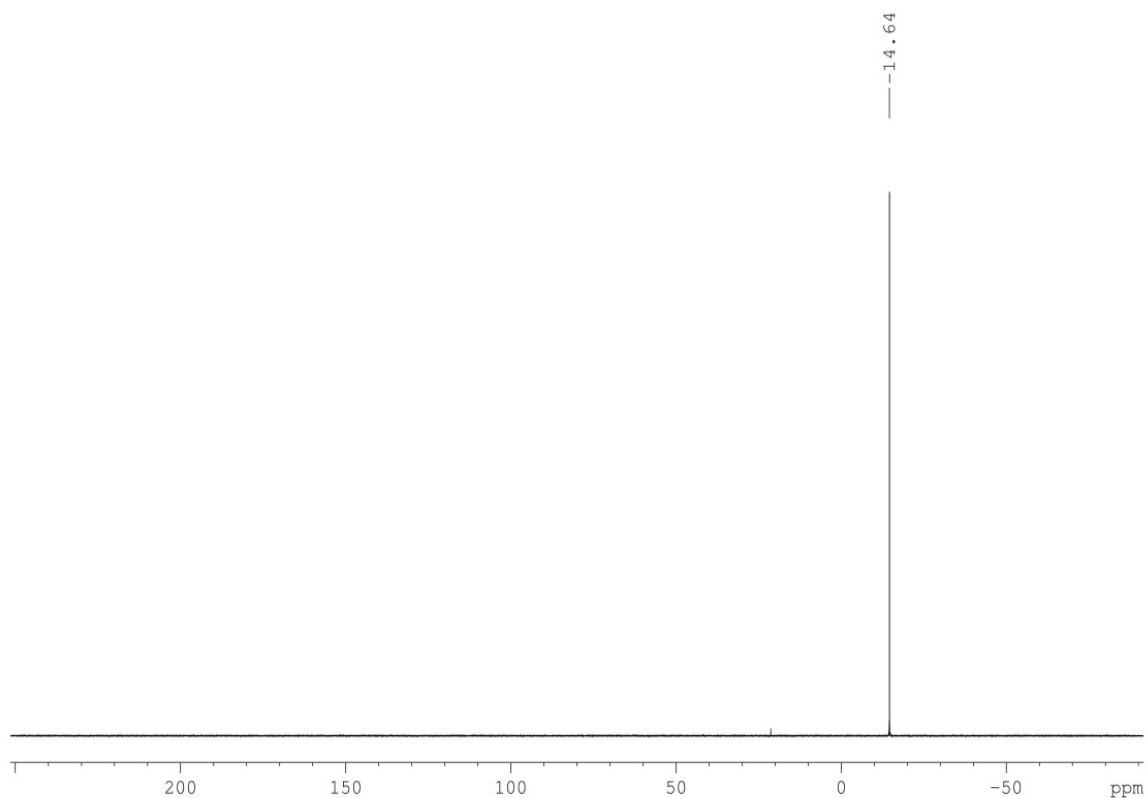
IR(solid) $\tilde{\nu}$ = 425, 467, 495, 505, 583, 654, 751, 778, 858, 925, 952, 1010, 952, 1089, 1130, 1159, 1255, 1358, 1440, 1548, 2862, 2946 cm⁻¹.

NMR Spectra

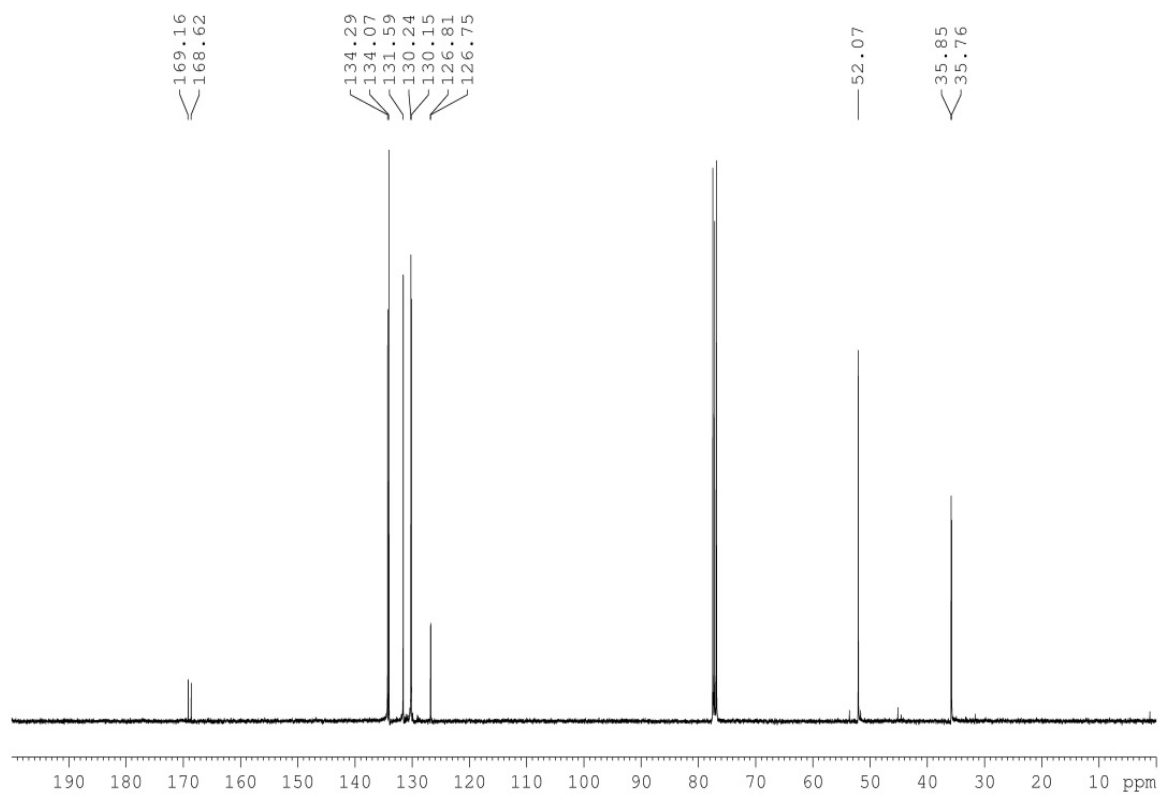
^1H NMR (300 MHz, CDCl_3) **2**



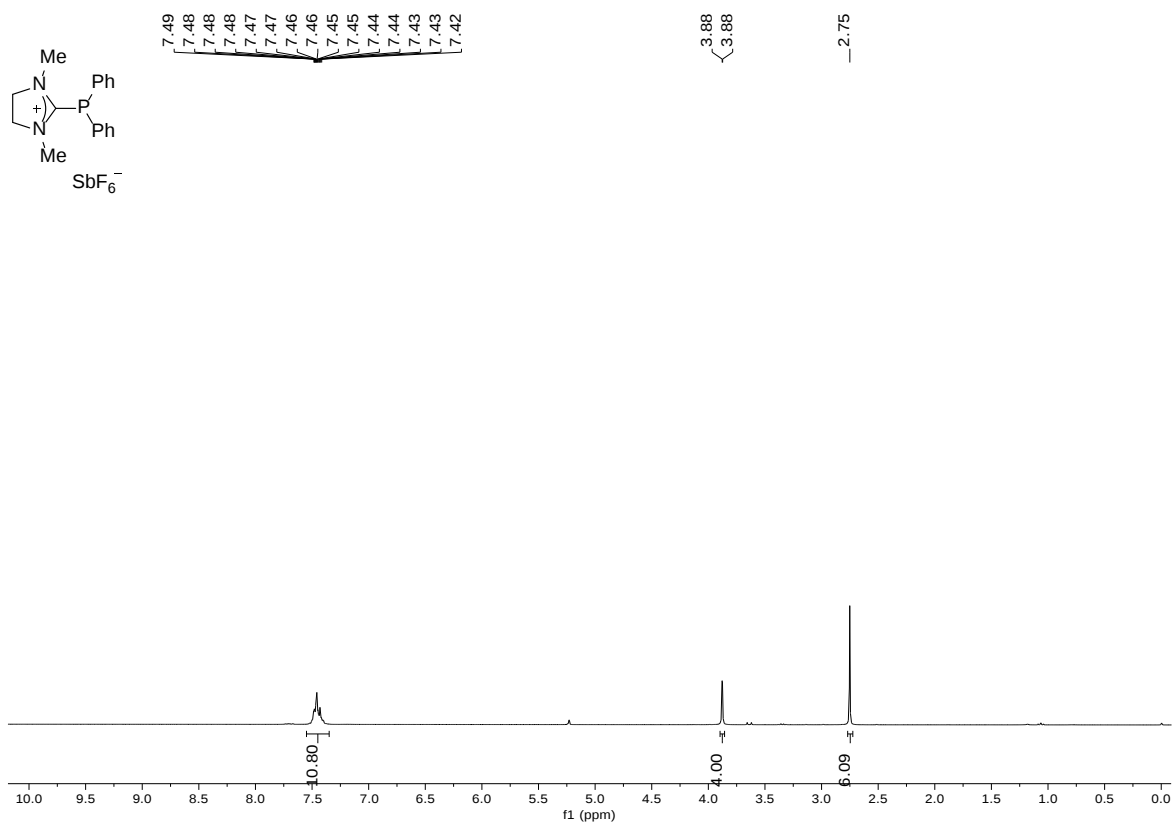
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) **2**



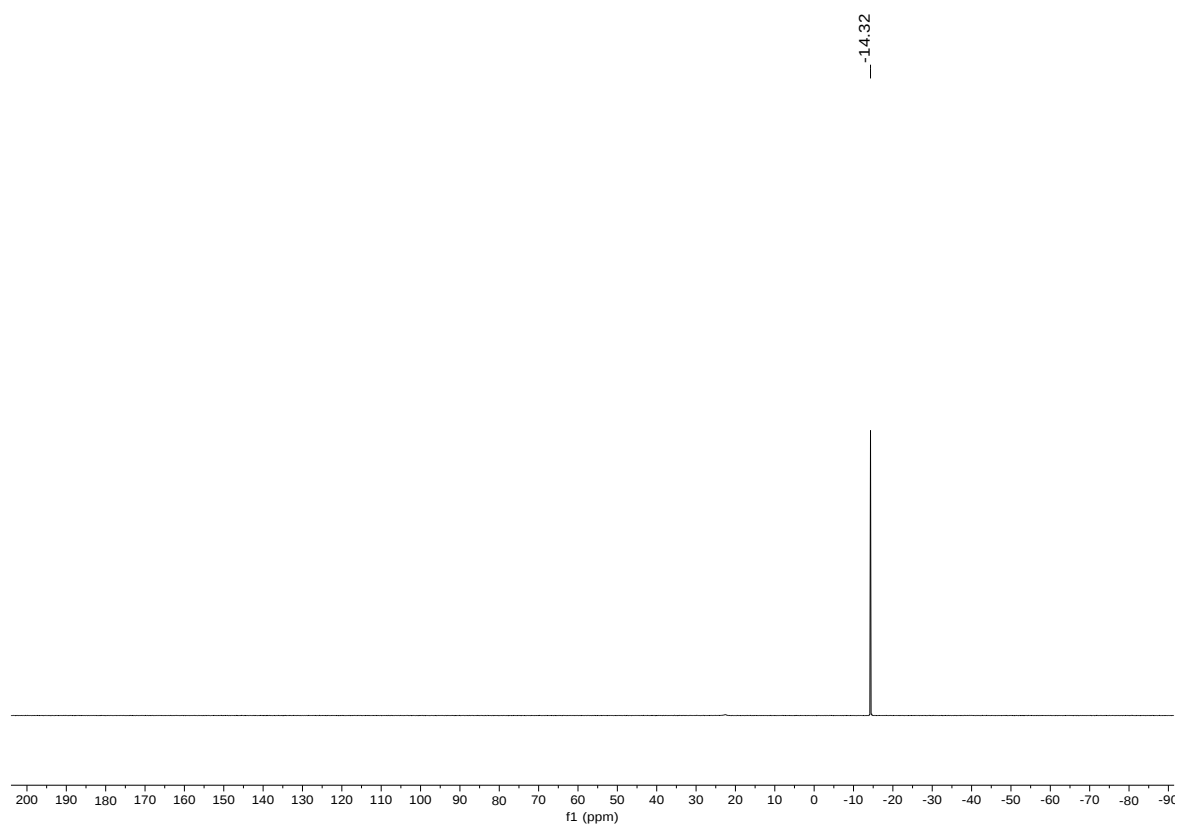
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) **2**



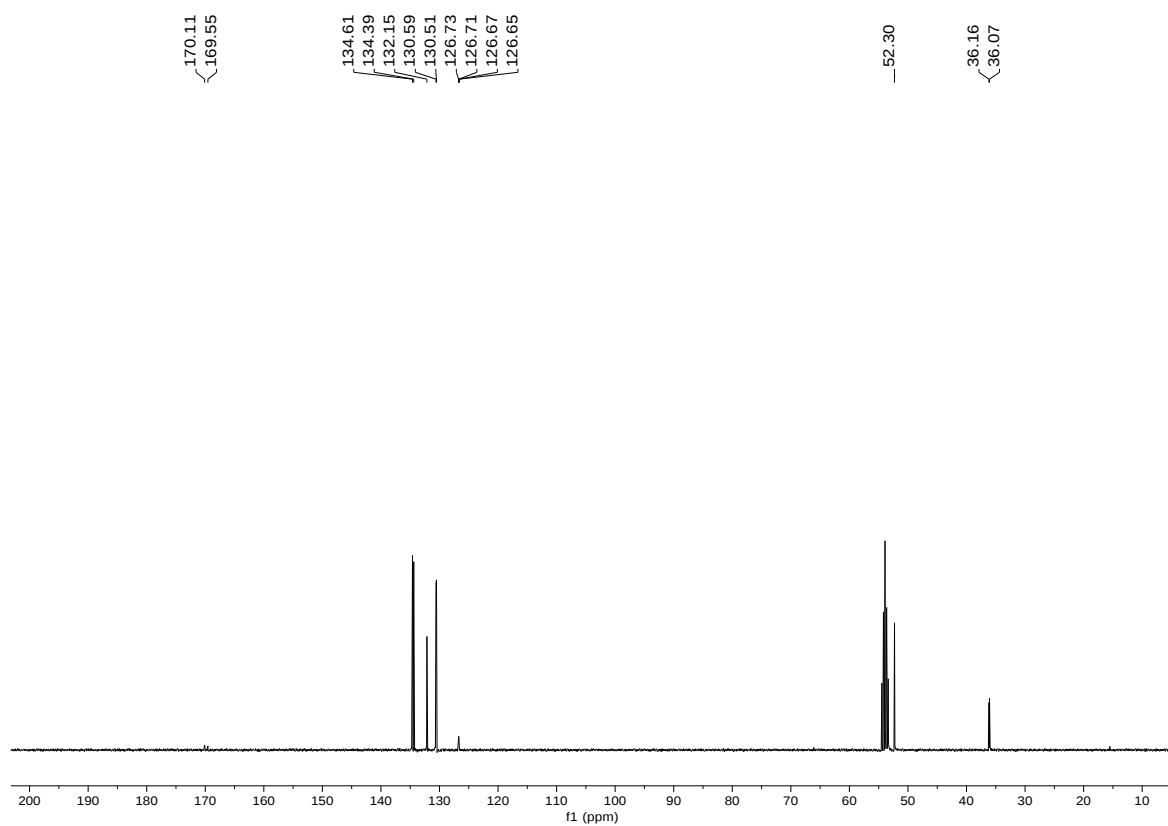
^1H NMR (300 MHz, CD_2Cl_2) **3**



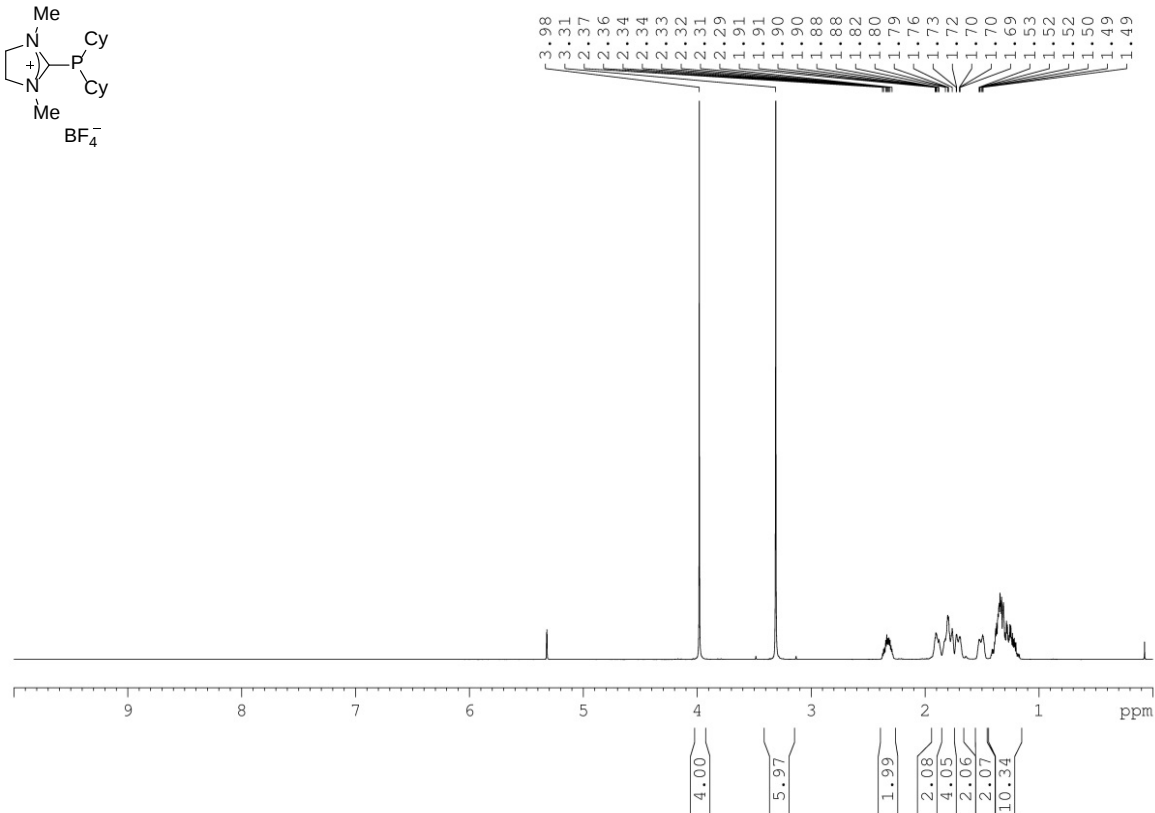
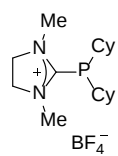
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) **3**



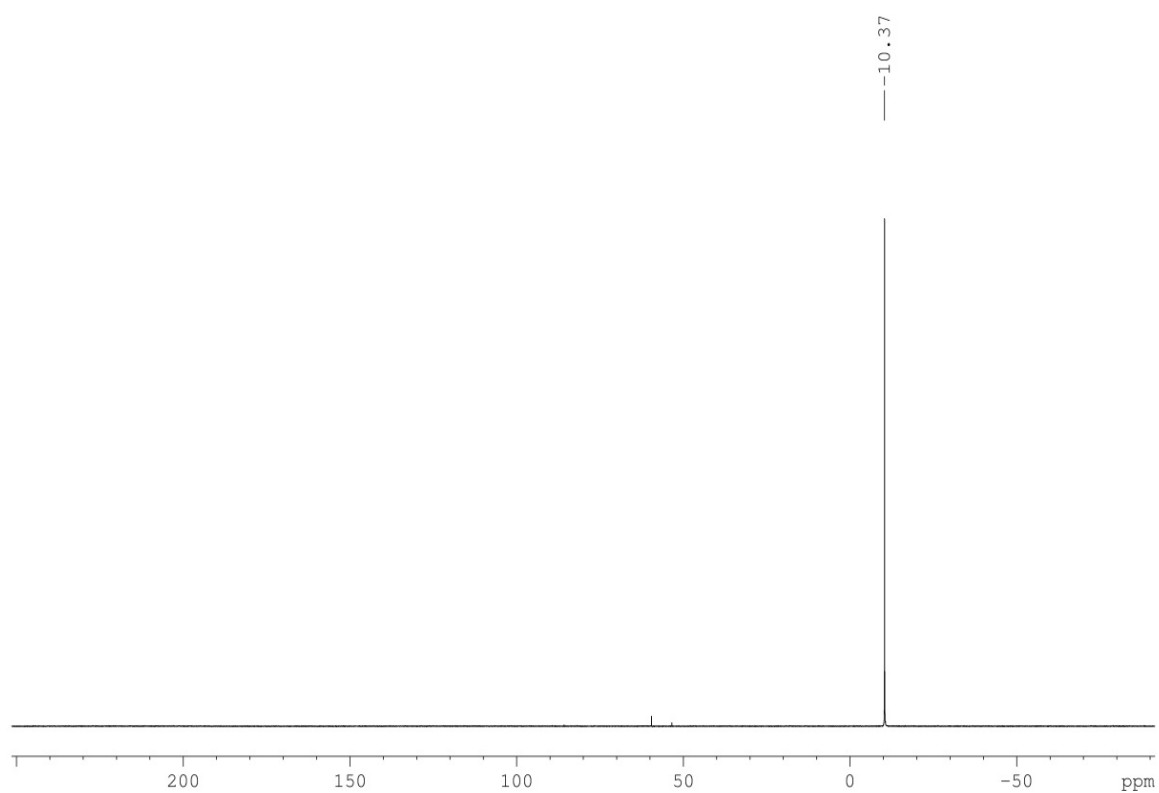
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **3**



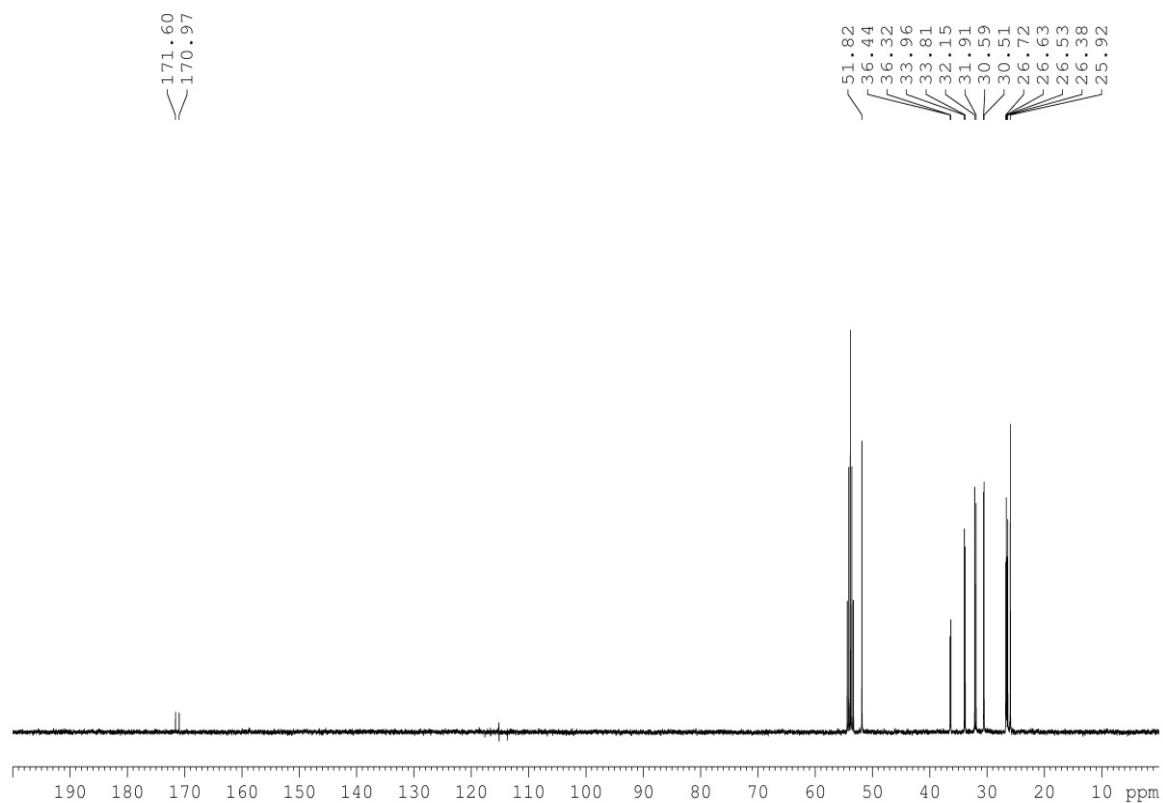
^1H NMR (400 MHz, CD_2Cl_2) **4**



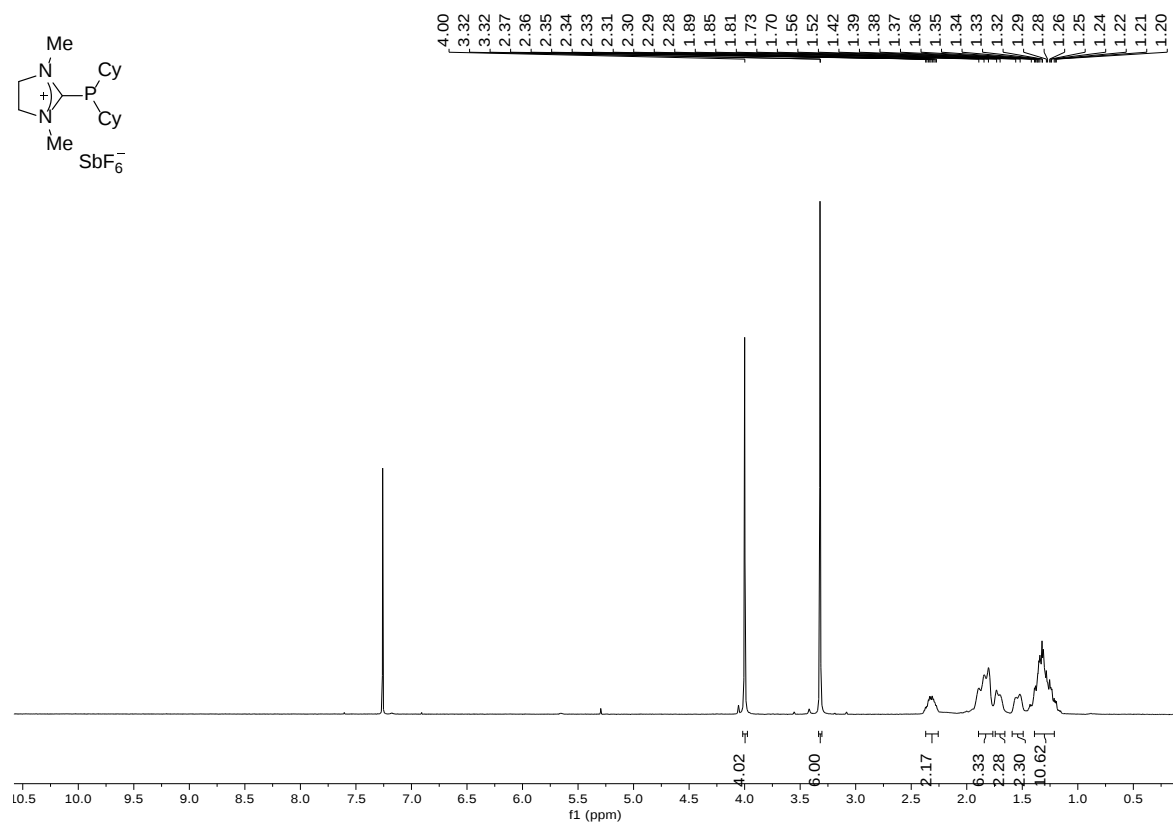
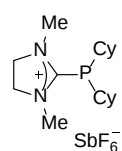
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) **4**



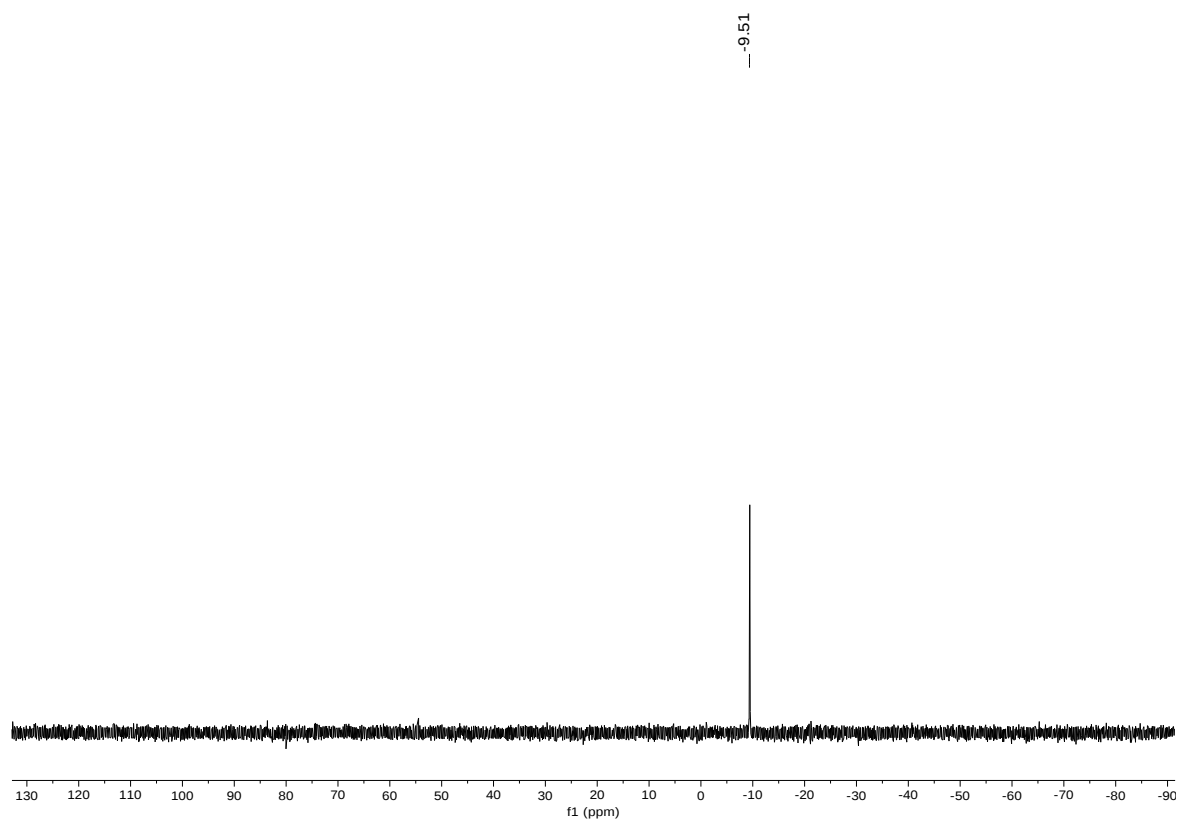
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **4**



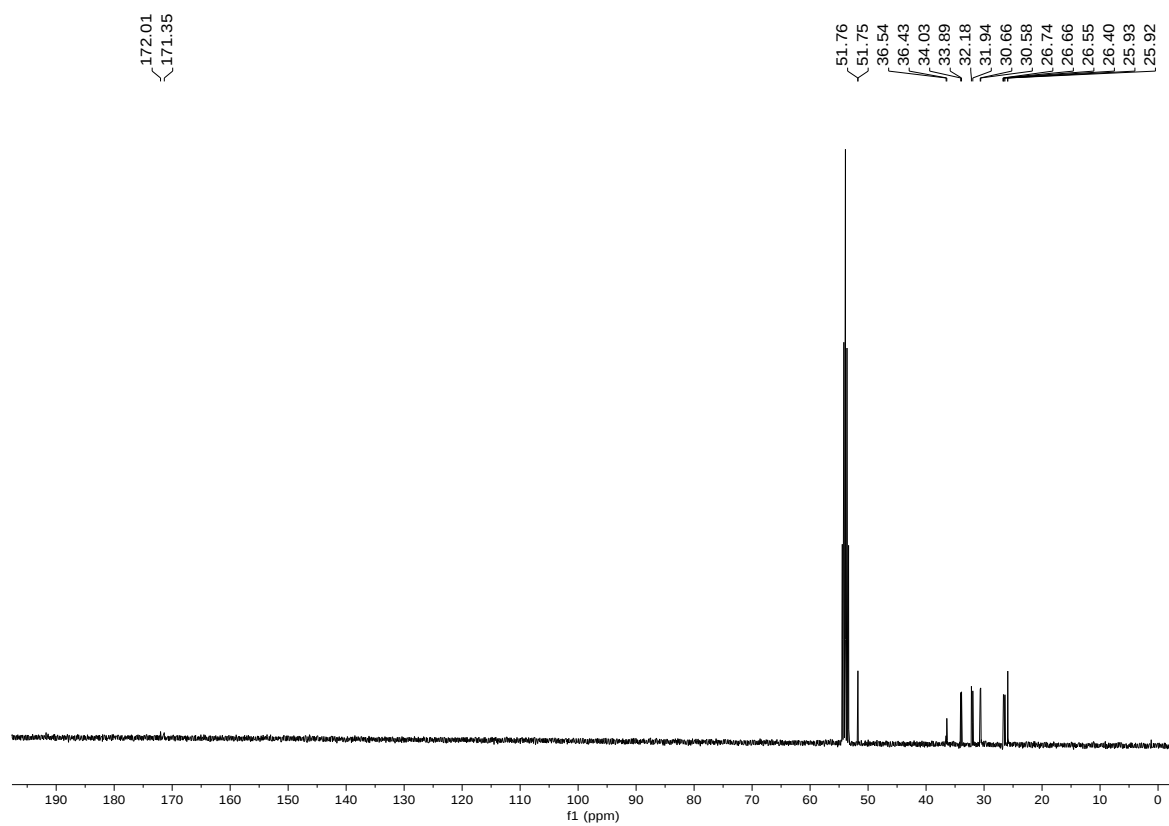
^1H NMR (300 MHz, CDCl_3) **5**



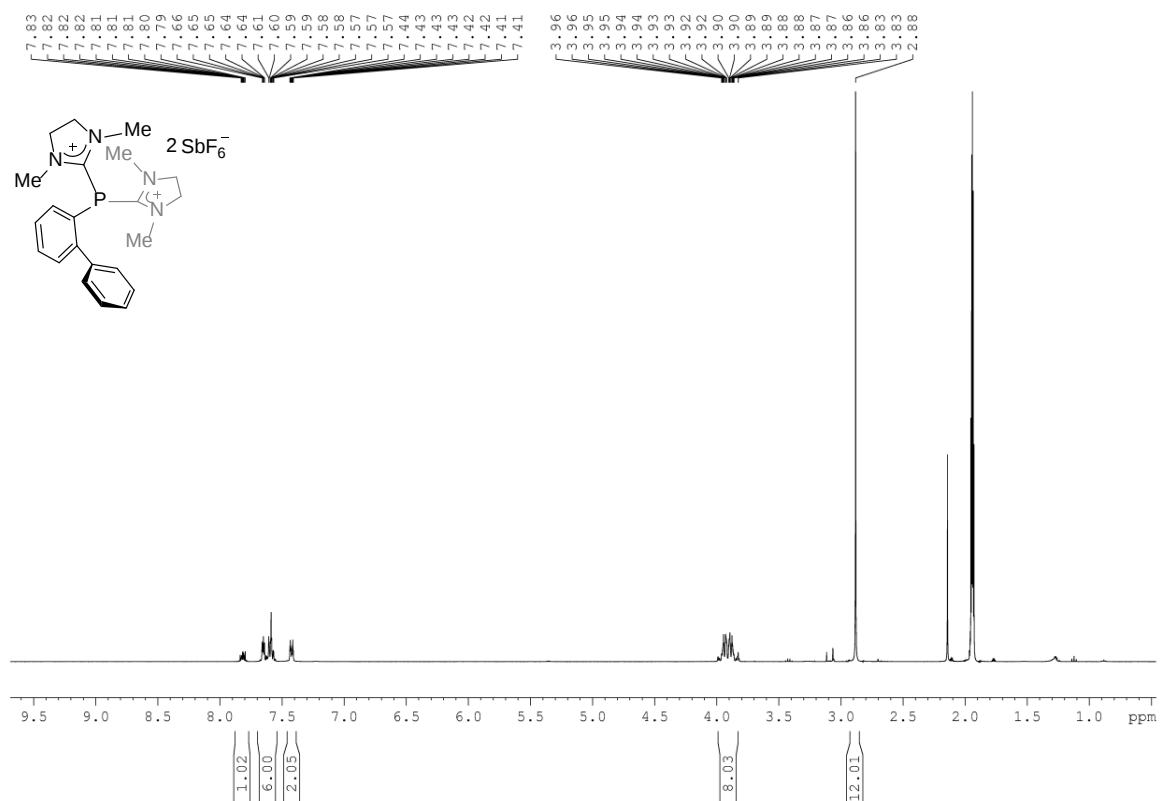
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3) **5**



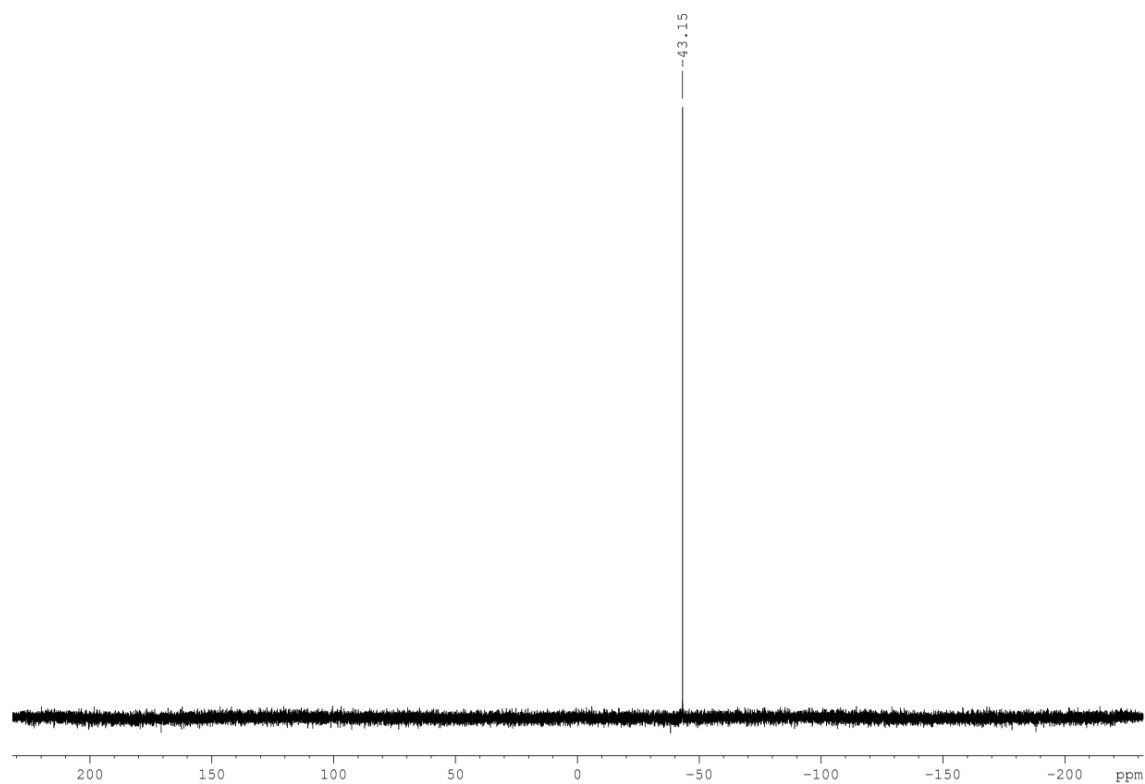
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **5**



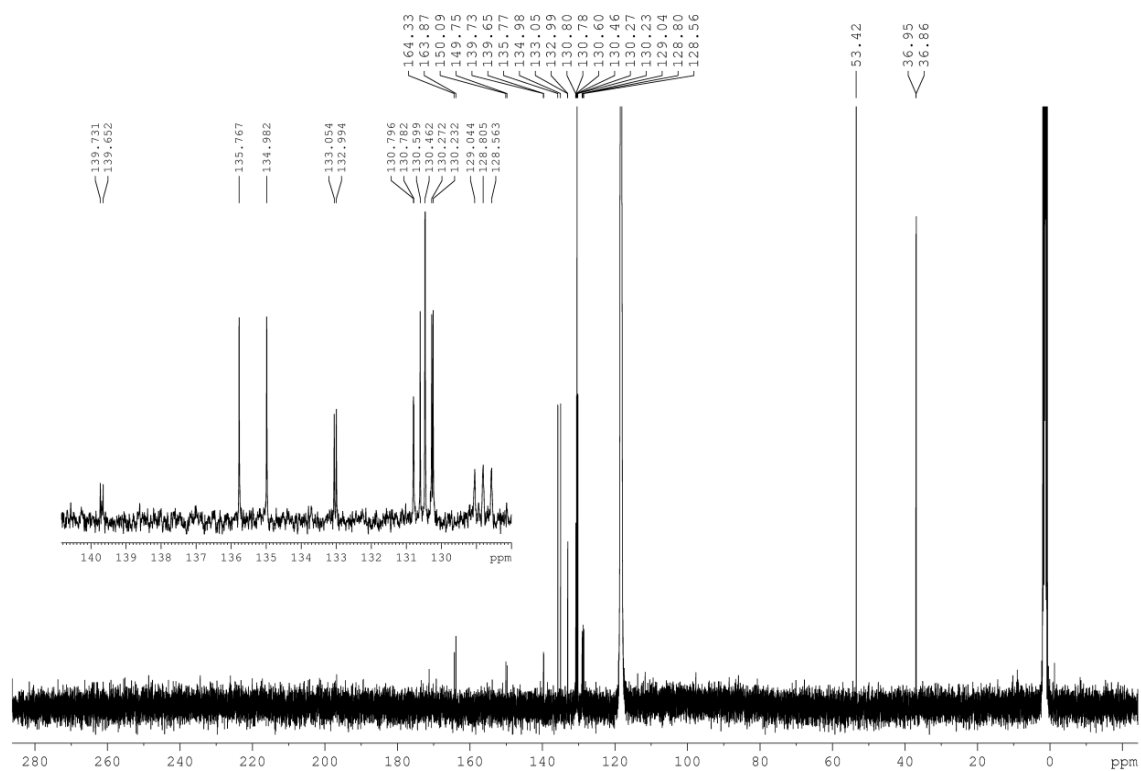
^1H NMR (400 MHz, CD_3CN) **6**



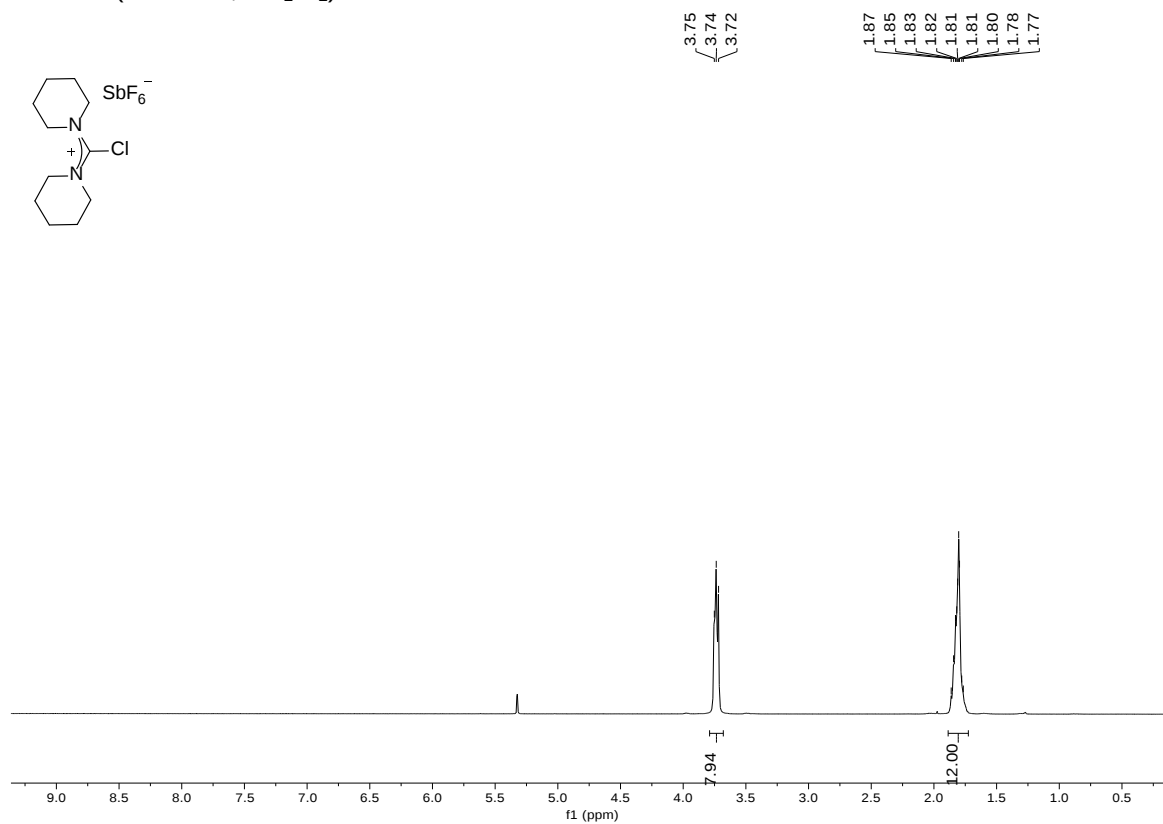
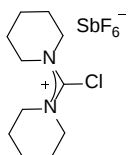
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_3CN) **6**



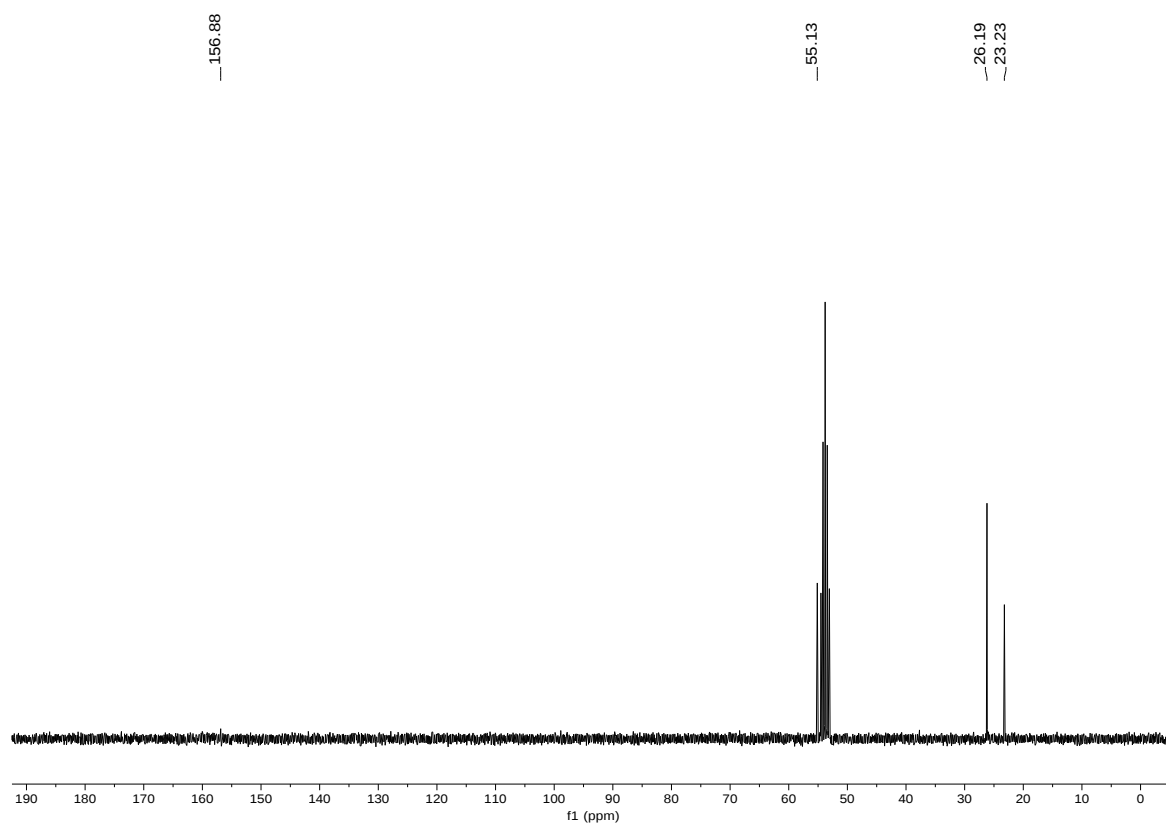
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) **6**



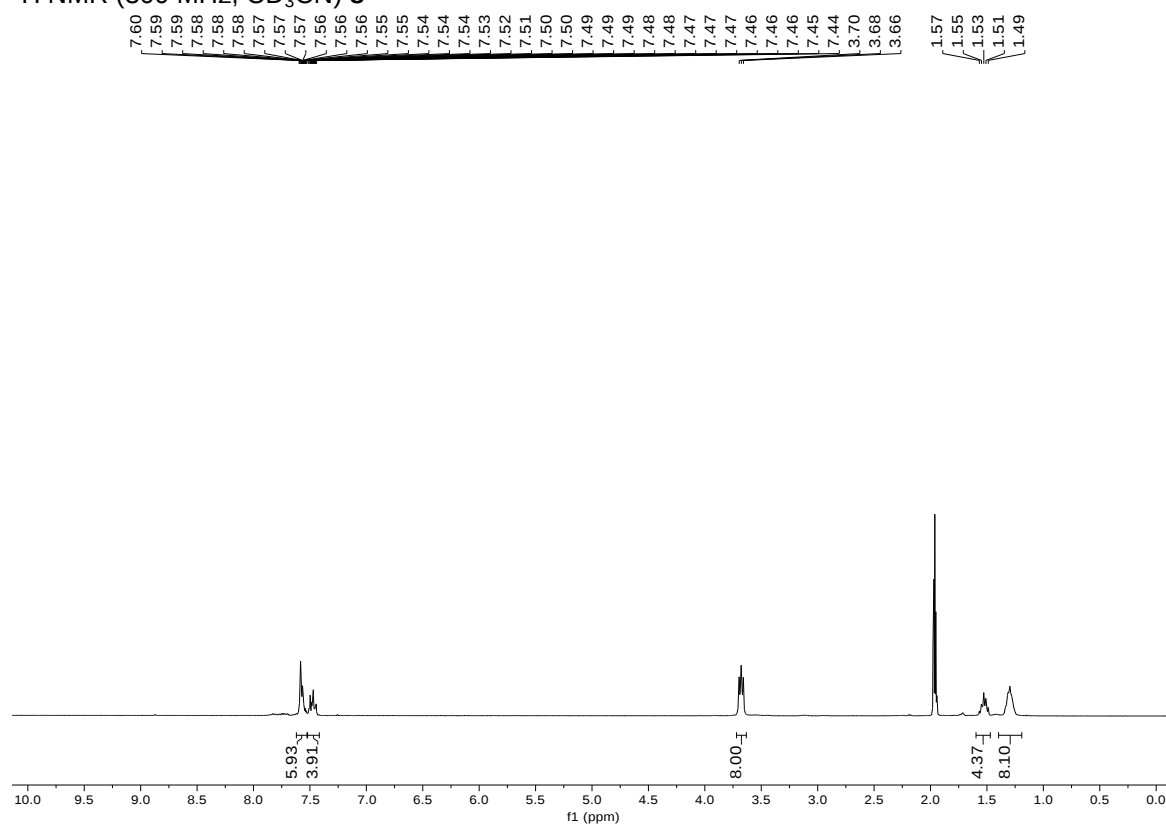
^1H NMR (300 MHz, CD_2Cl_2) **7**



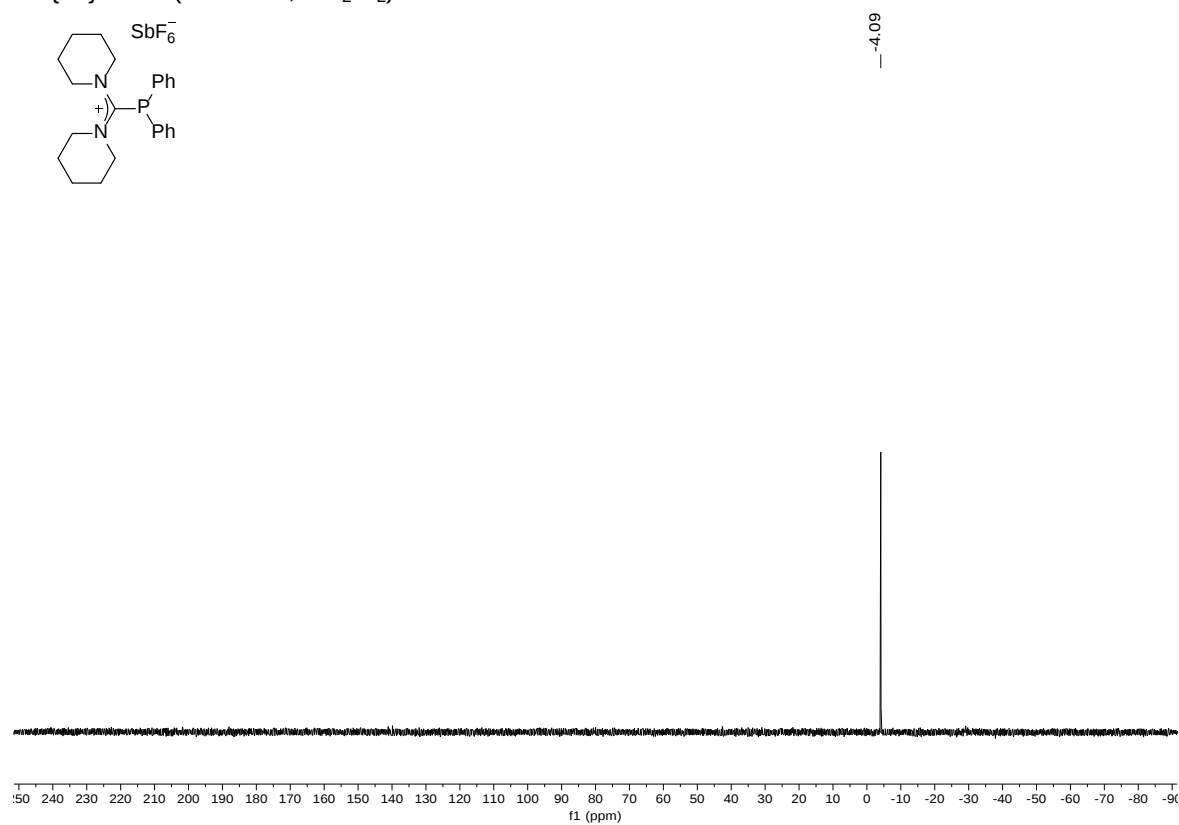
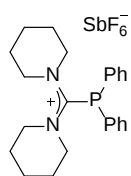
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2) **7**



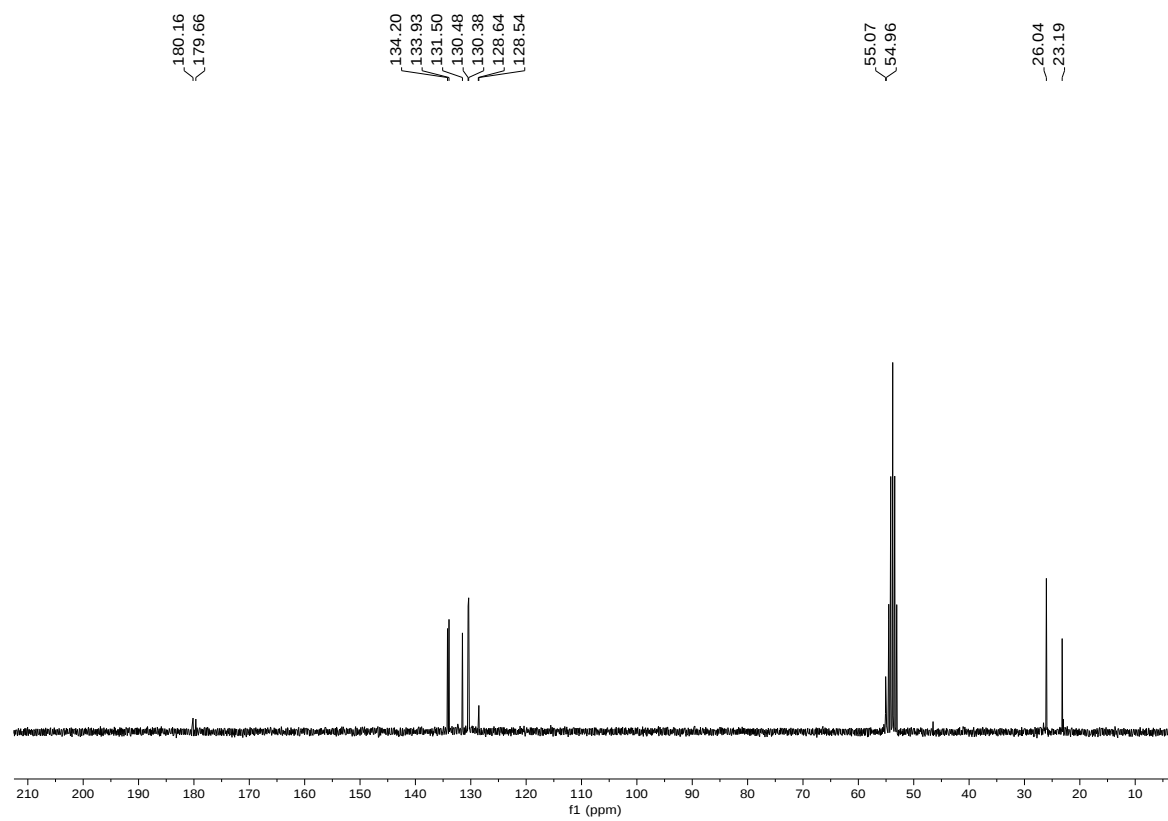
^1H NMR (300 MHz, CD_3CN) **8**



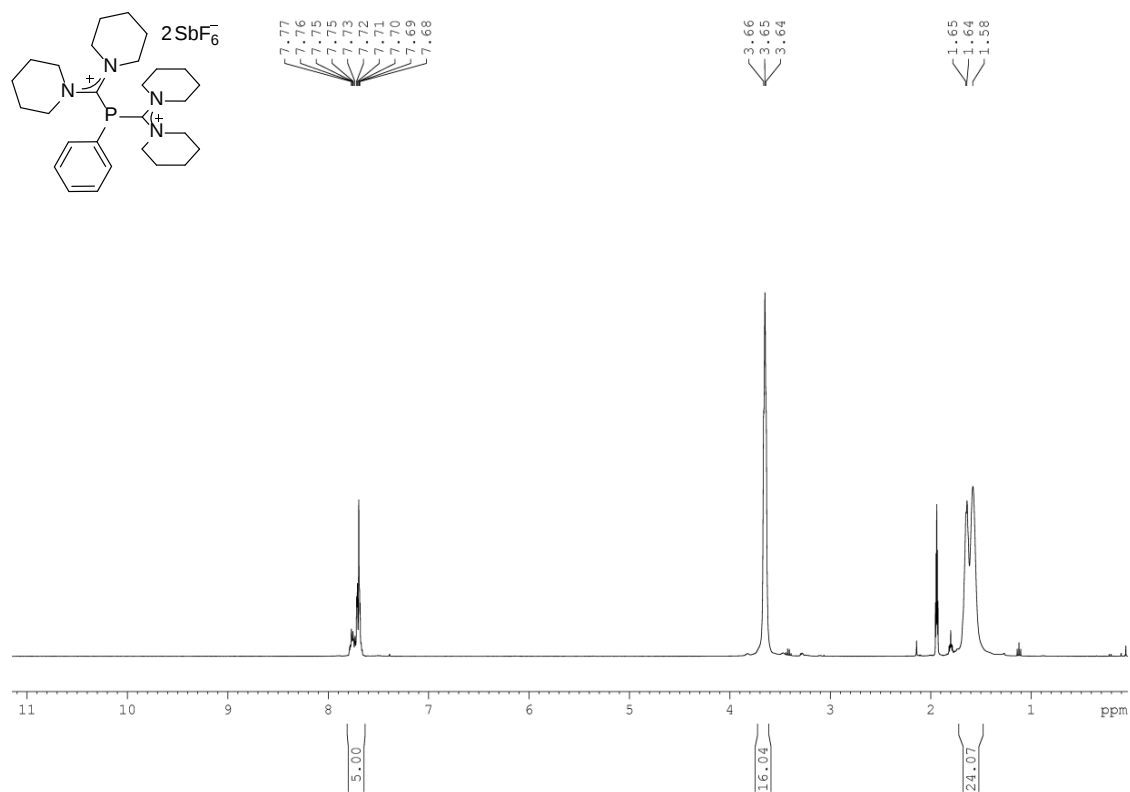
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) **8**



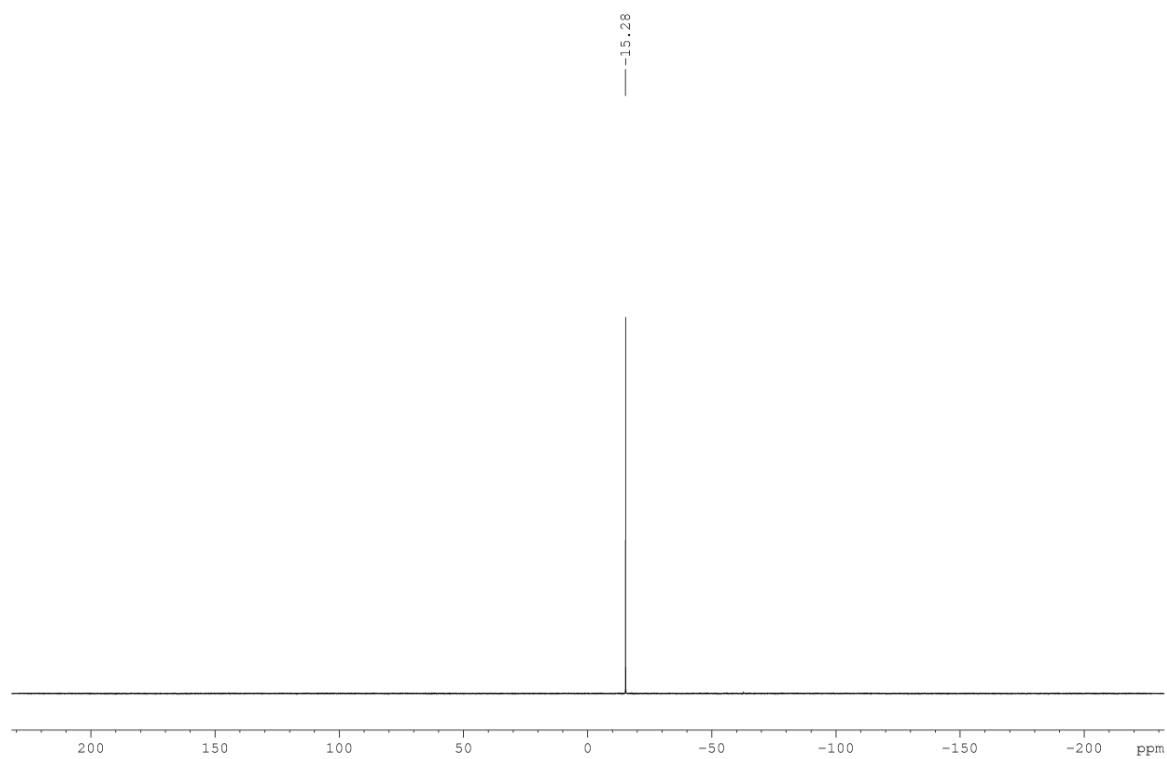
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2) **8**



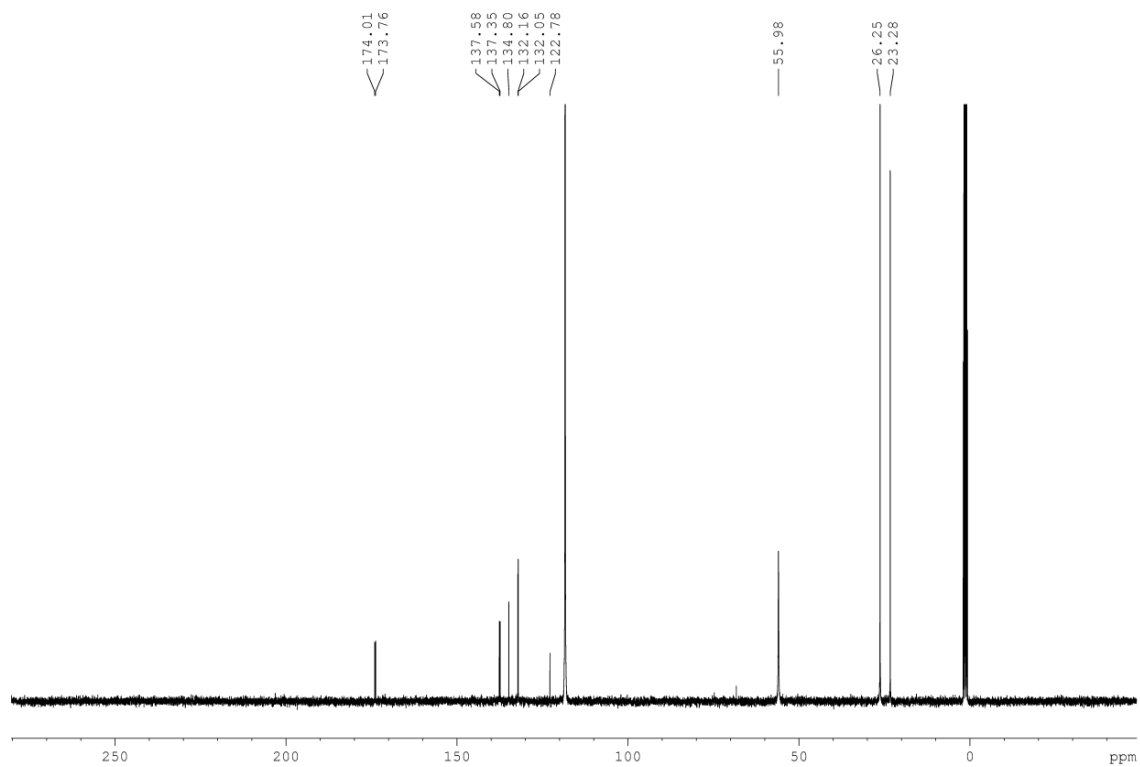
^1H NMR (400 MHz, CD_3CN) **9**



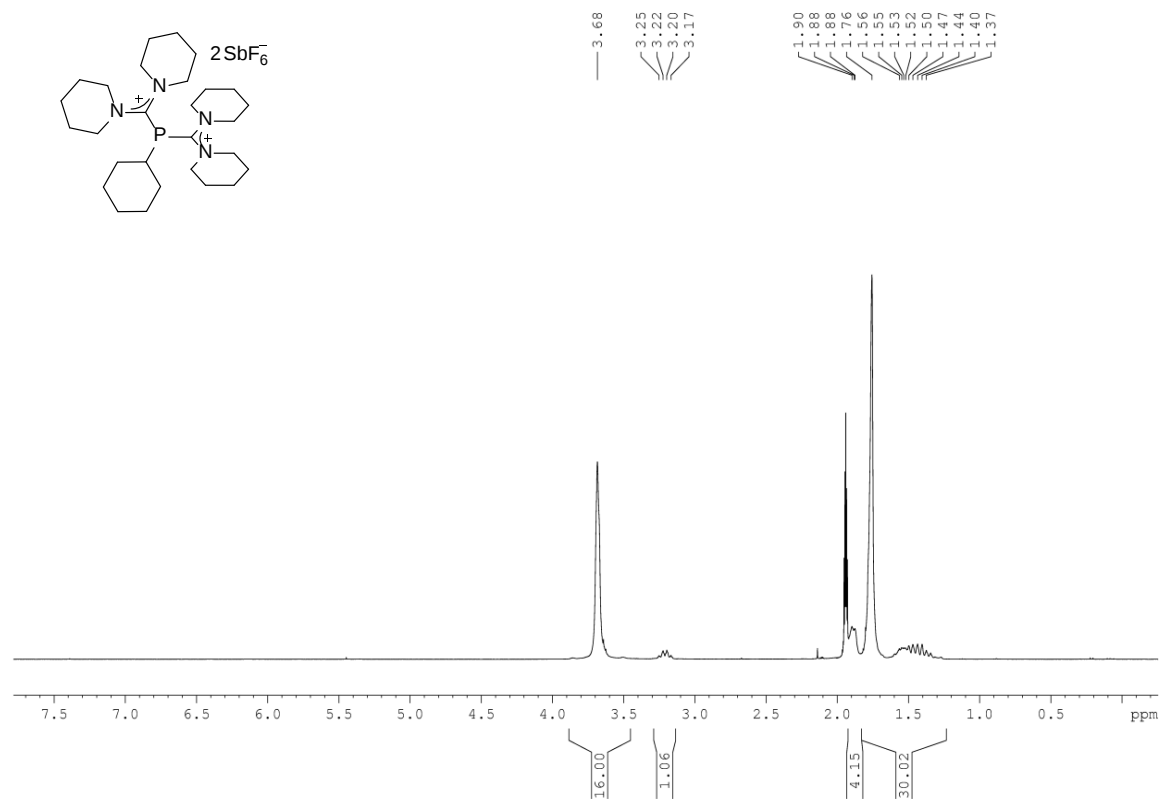
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_3CN) **9**



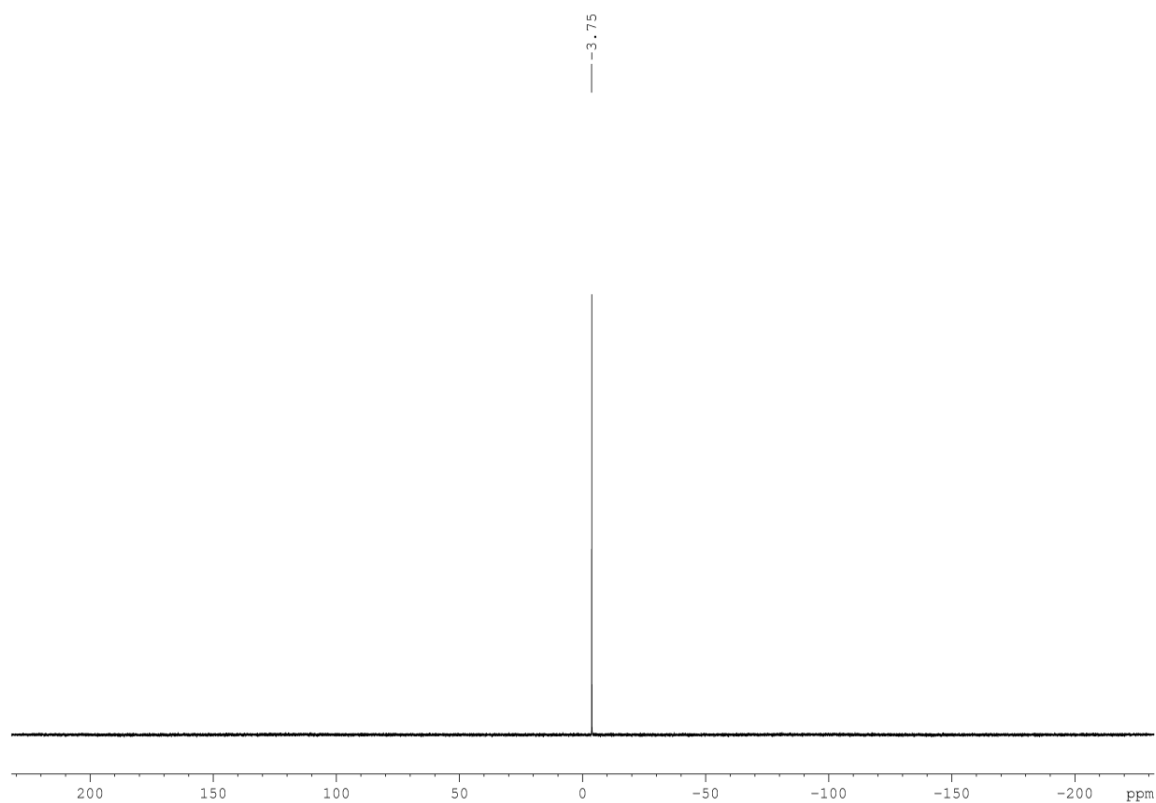
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN) **9**



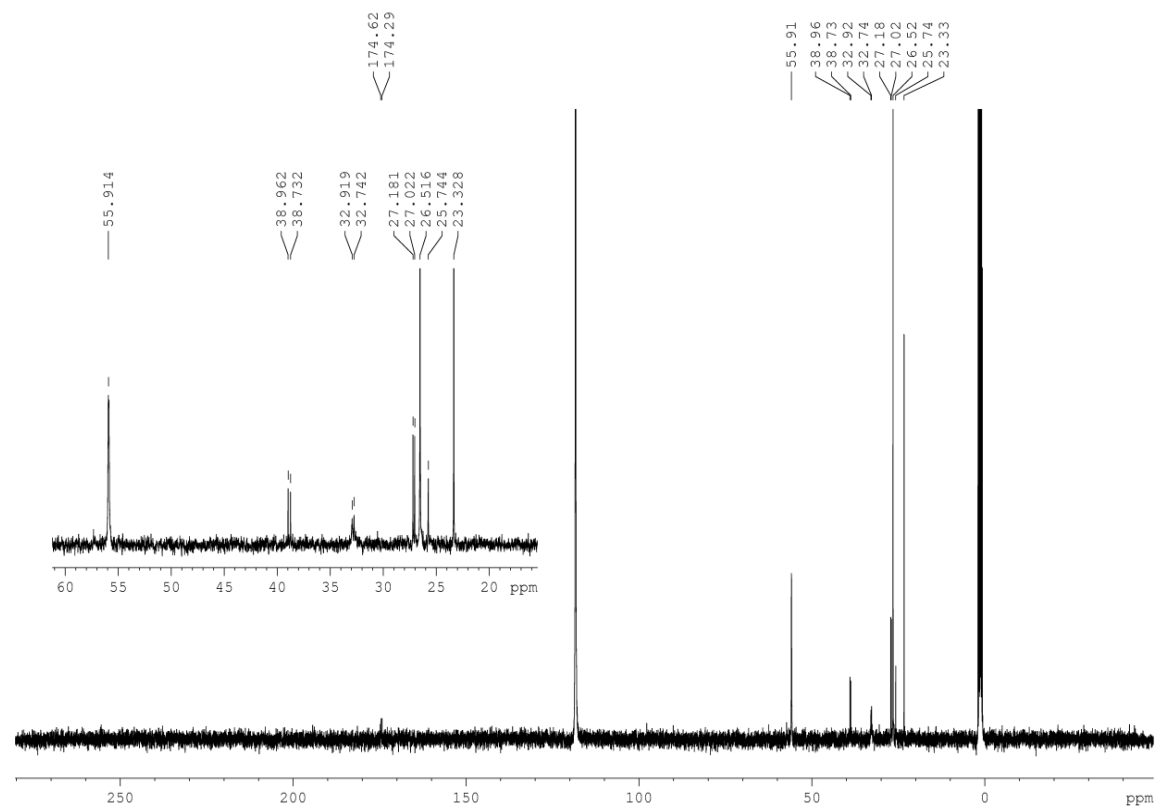
^1H NMR (400 MHz, CD_3CN) 10



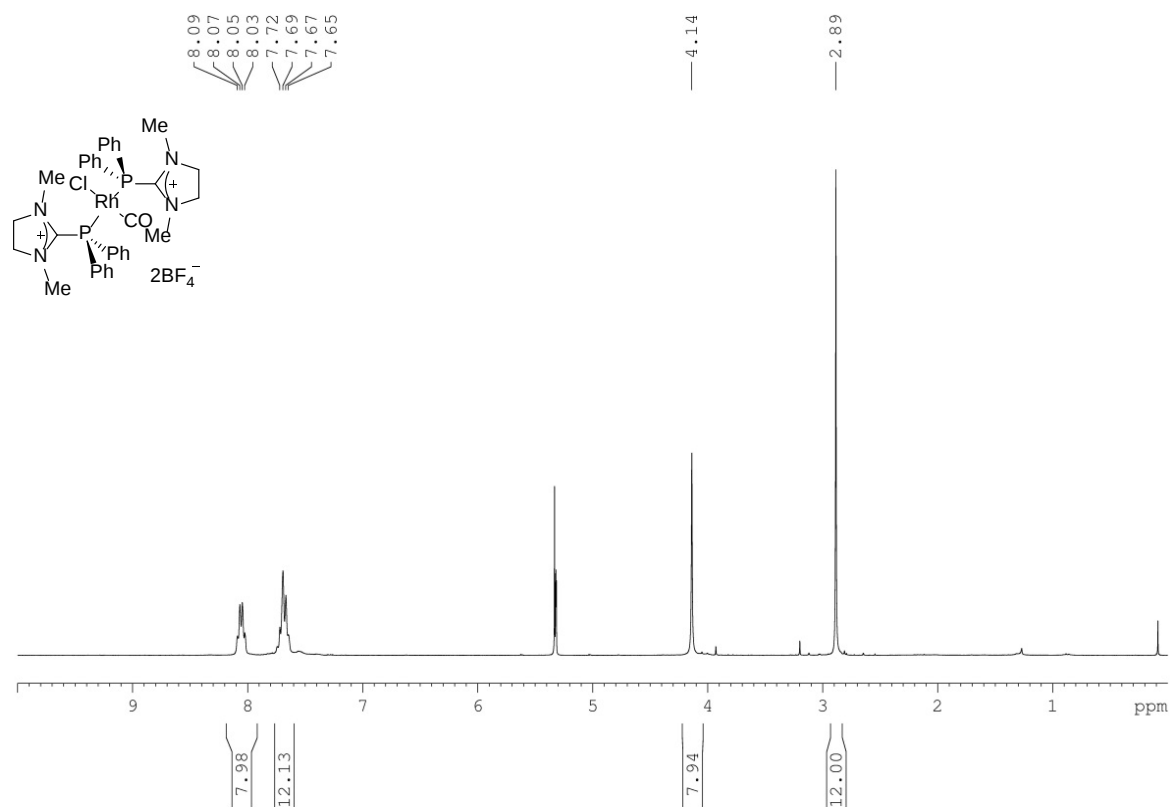
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_3CN) **10**



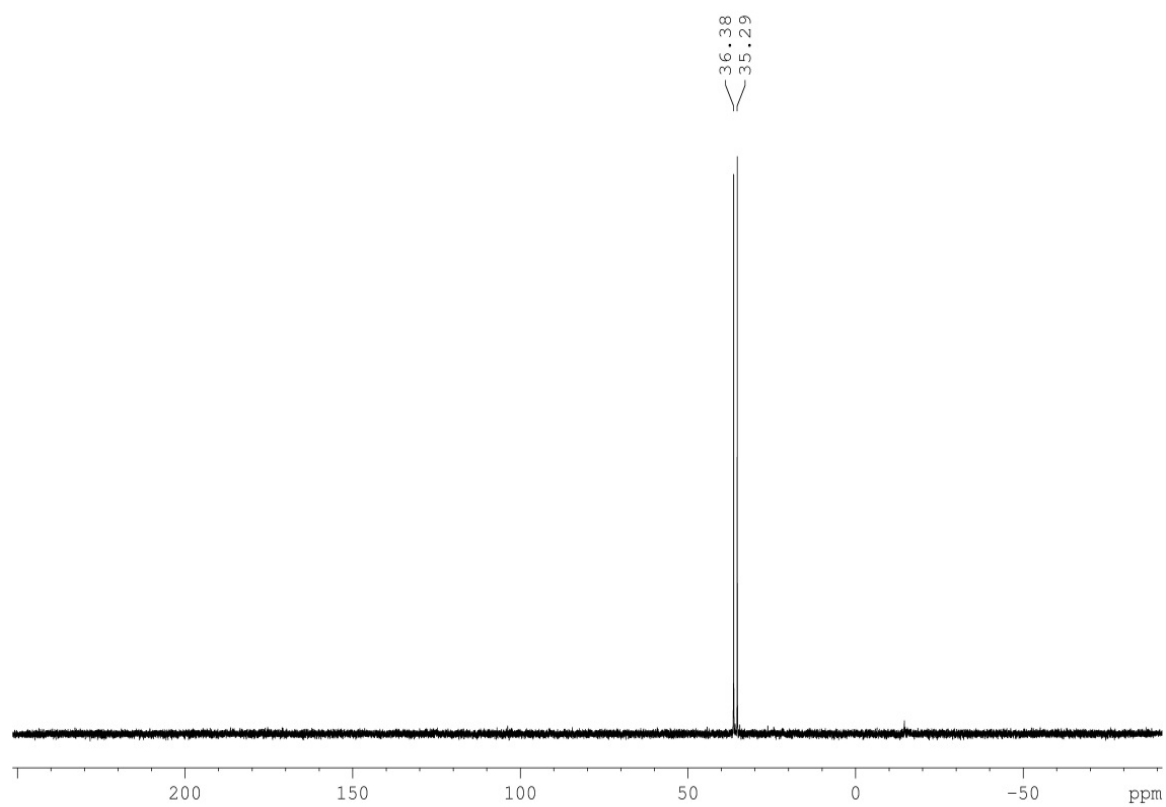
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) **10**



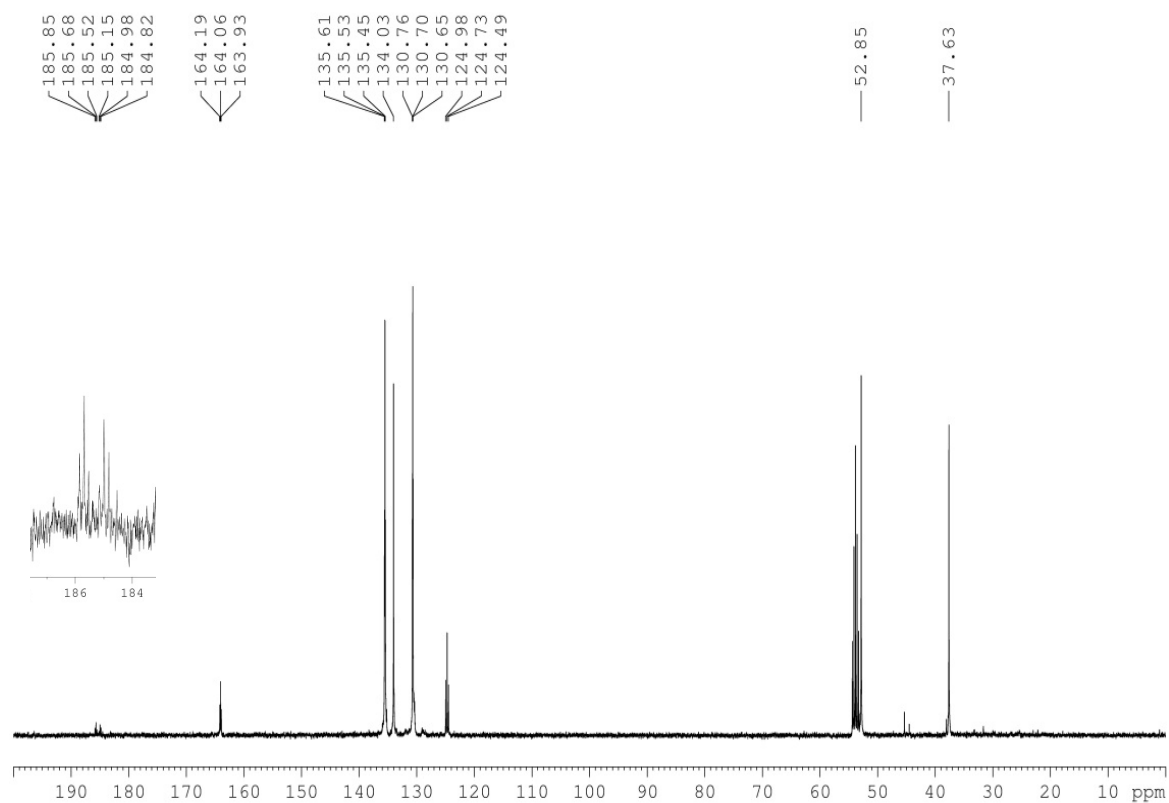
^1H NMR (300 MHz, CD_2Cl_2) **11**



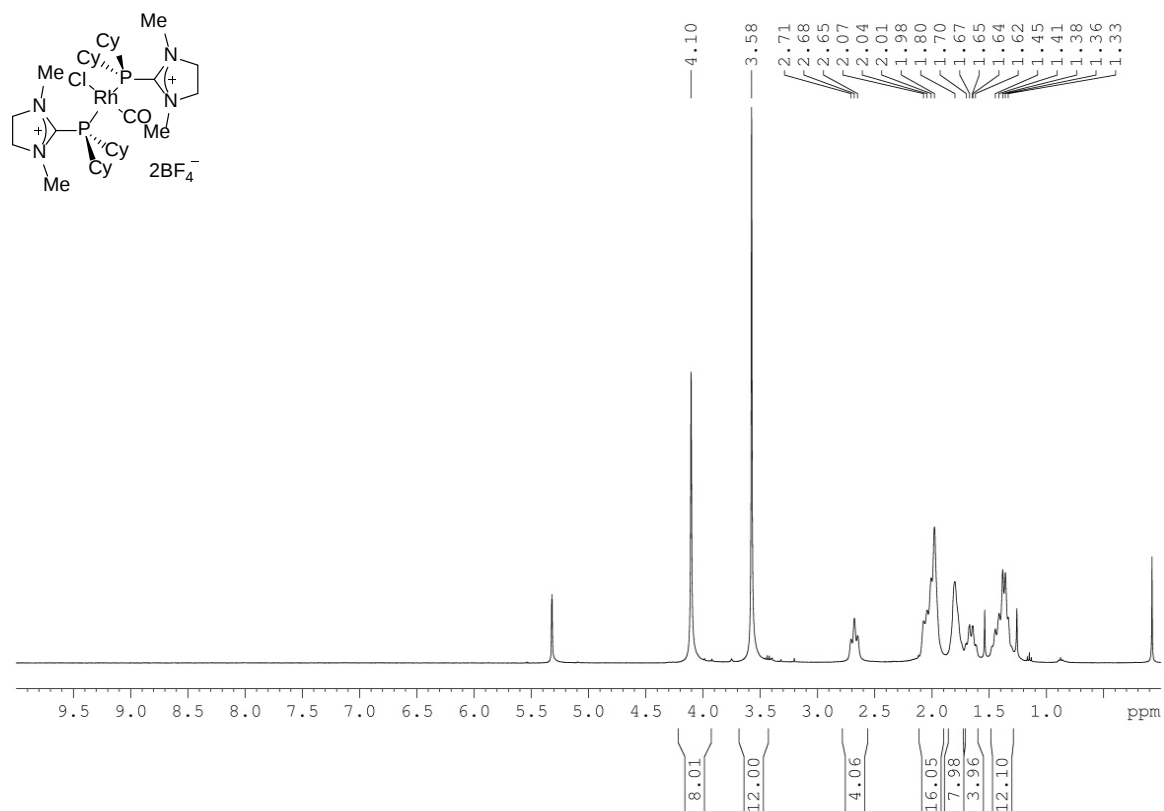
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) **11**



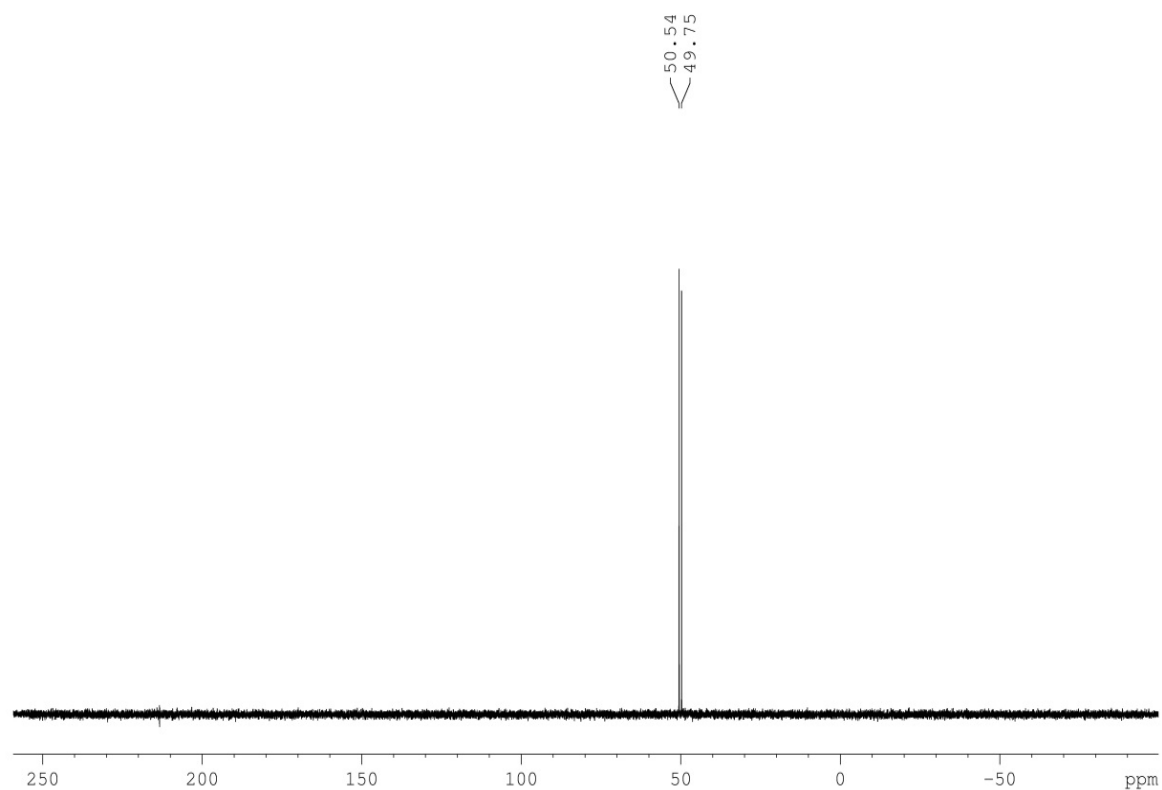
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **11**



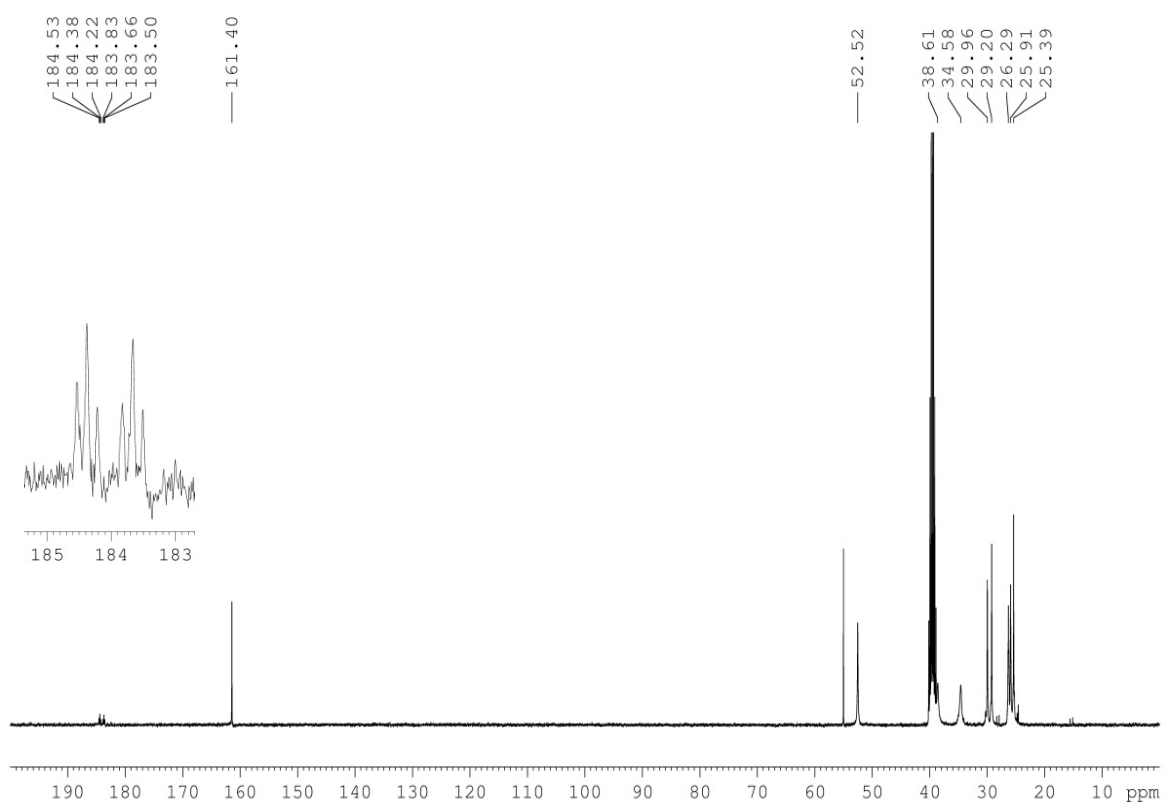
^1H NMR (400 MHz, CD_2Cl_2) **12**



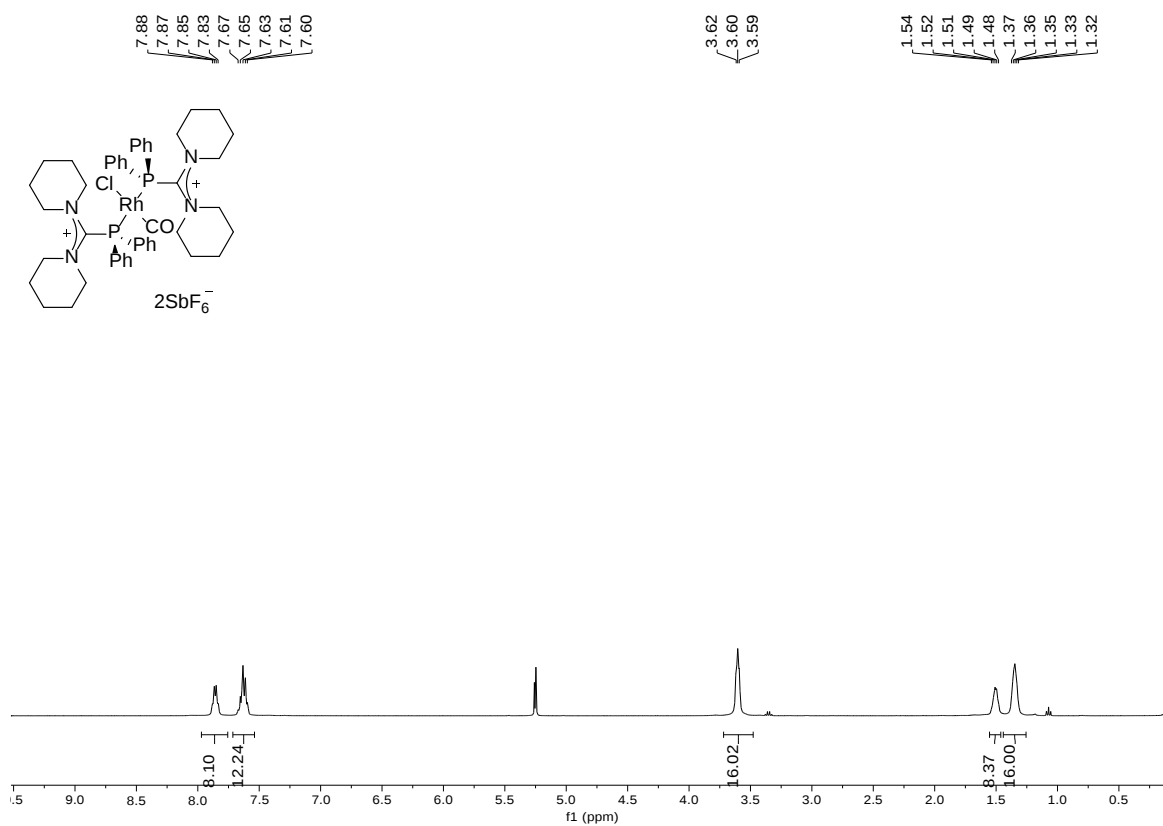
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) **12**



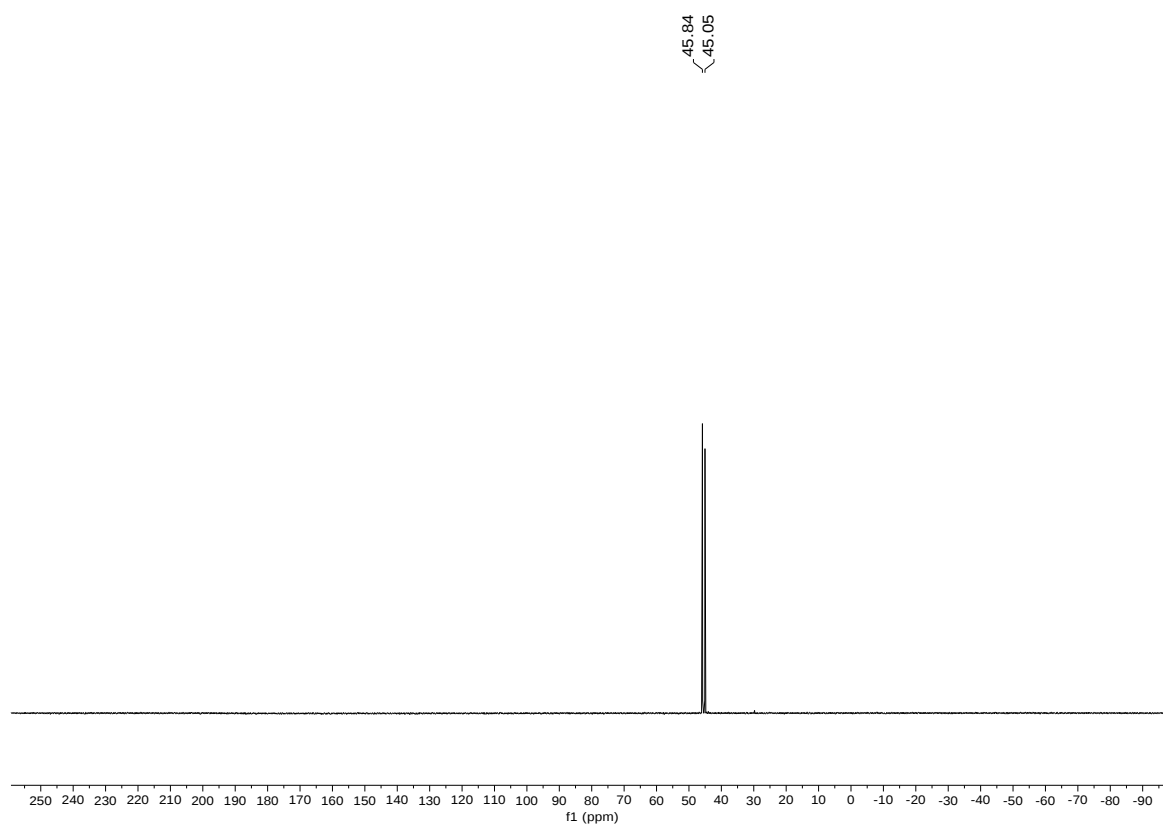
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) **12**



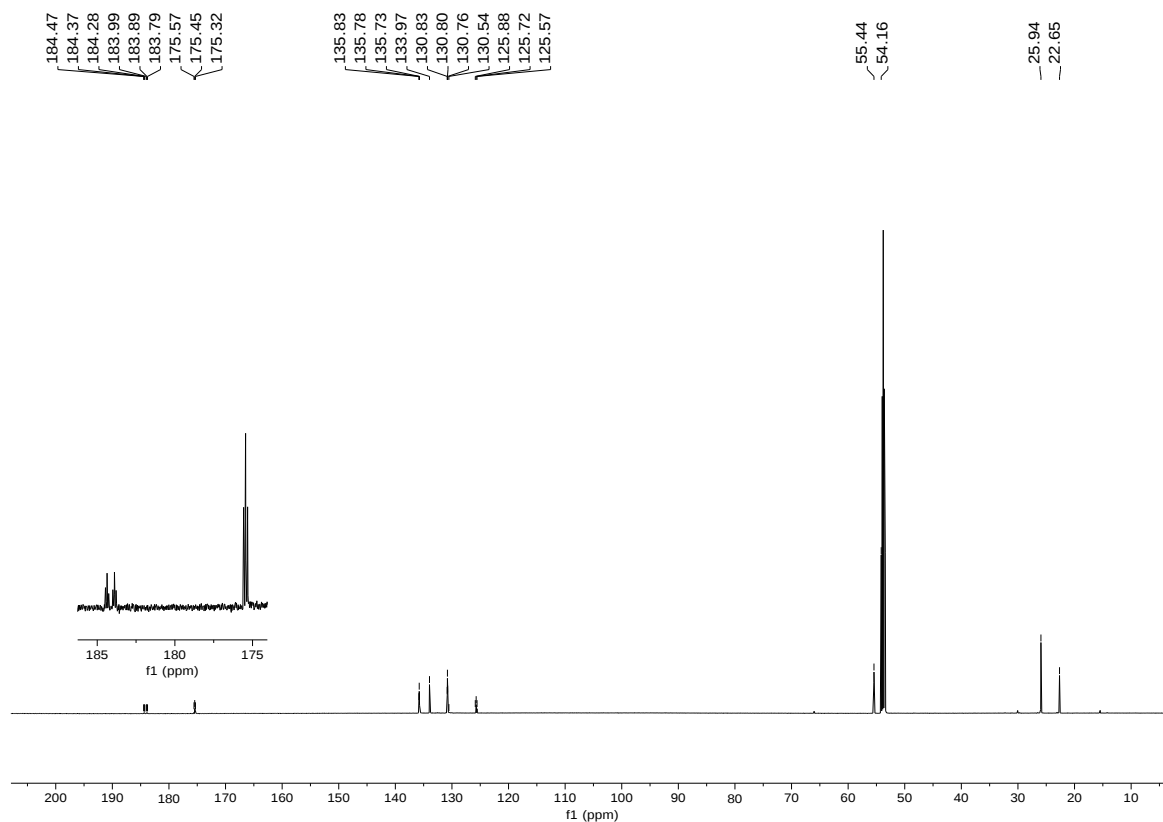
^1H NMR (400 MHz, CD_2Cl_2) **13**



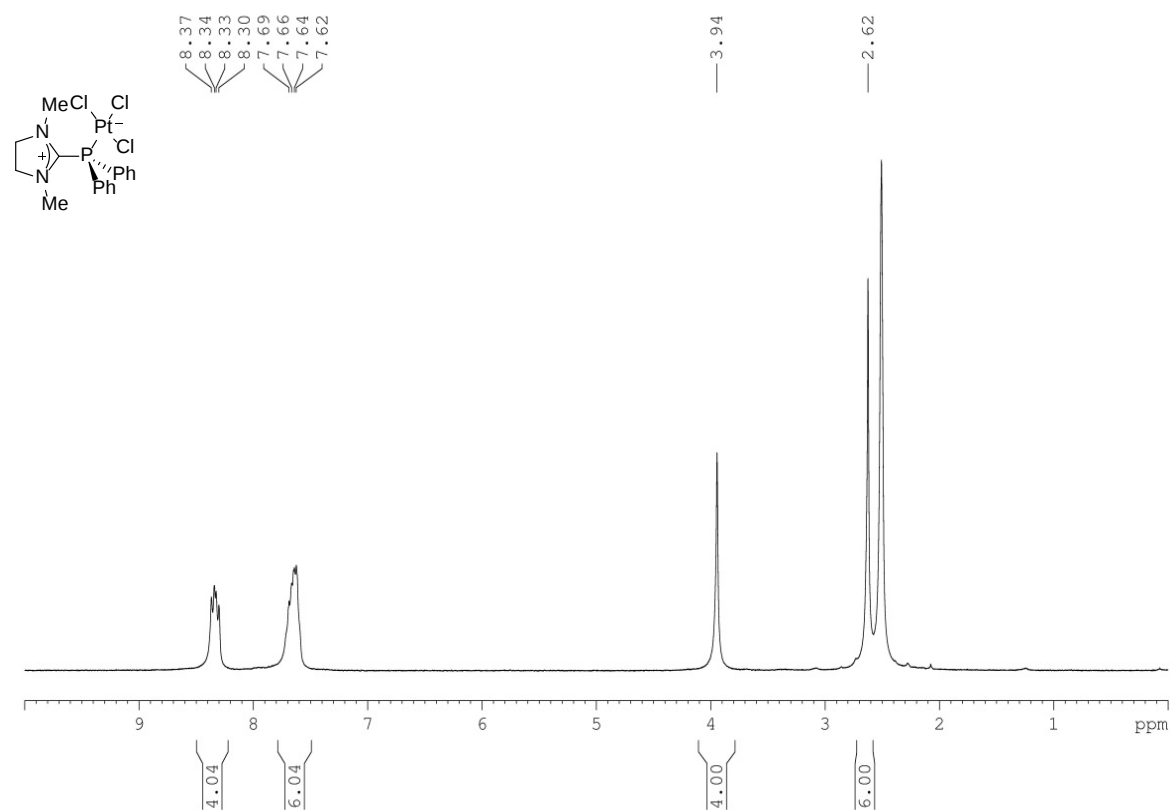
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) **13**



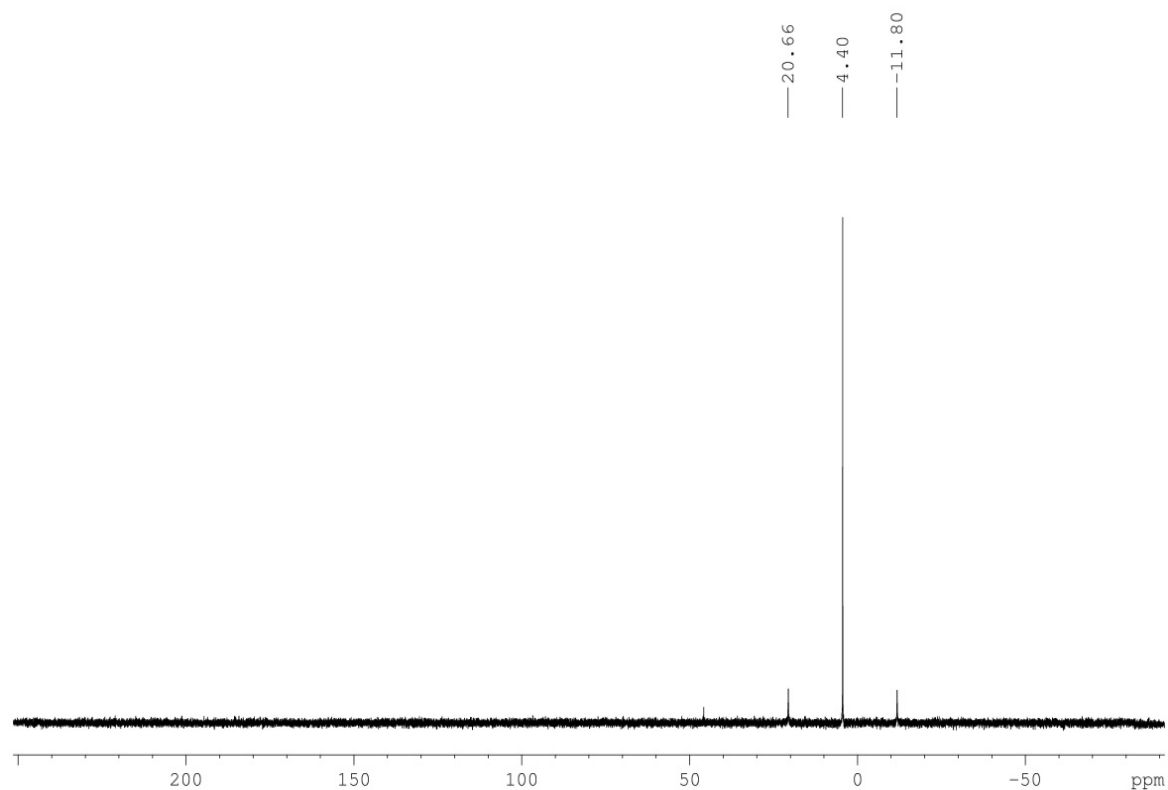
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **13**



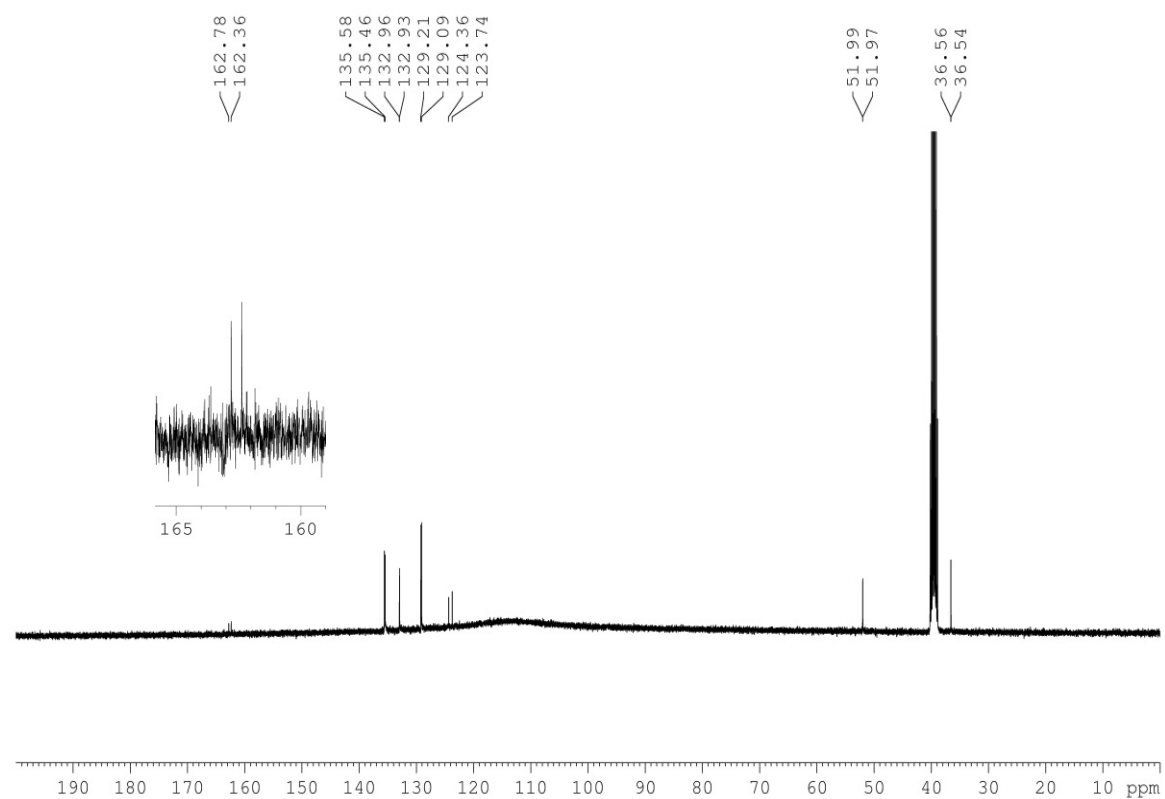
^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$) **16**



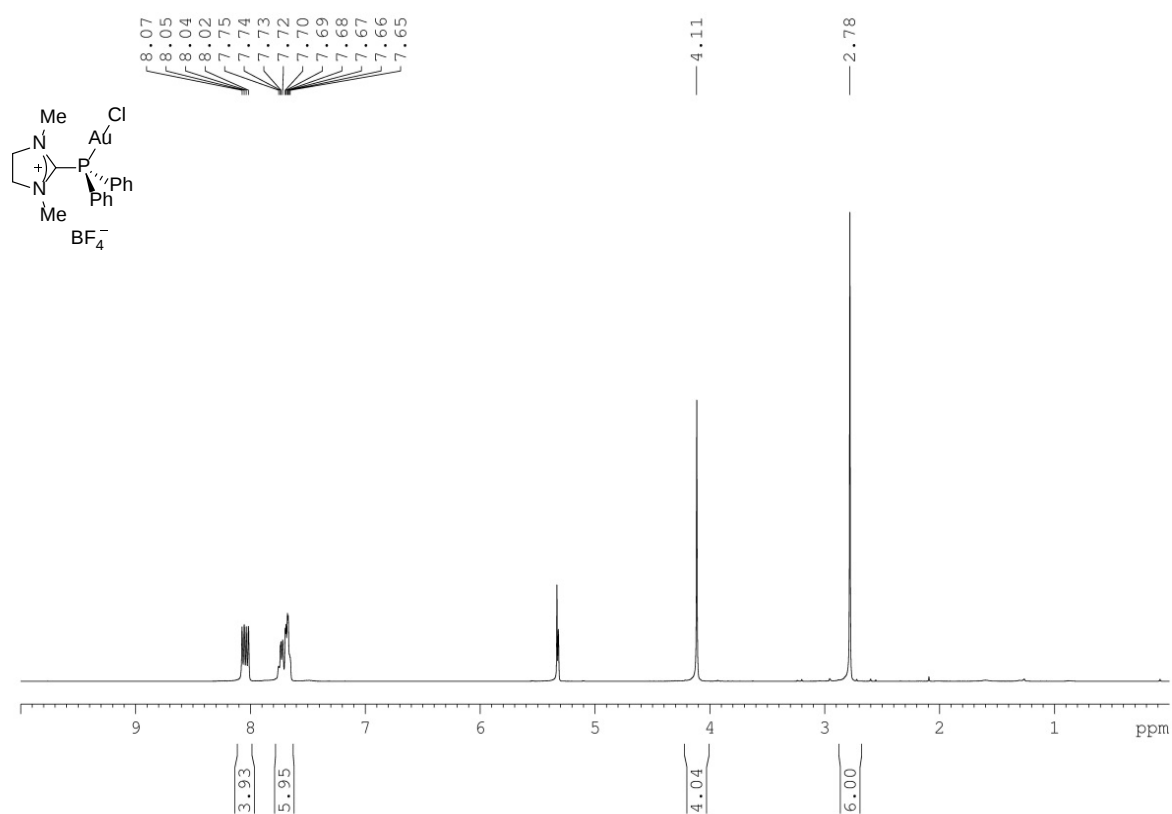
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $(\text{CD}_3)_2\text{SO}$) **16**



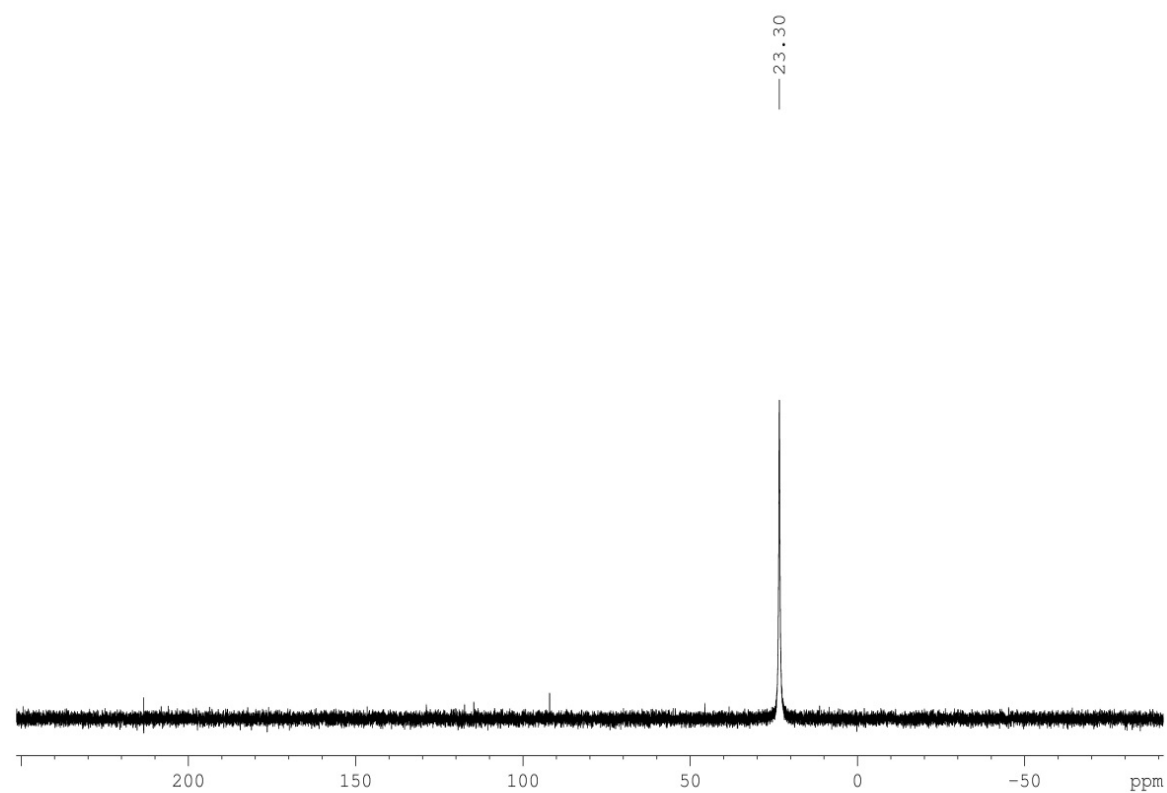
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) **16**



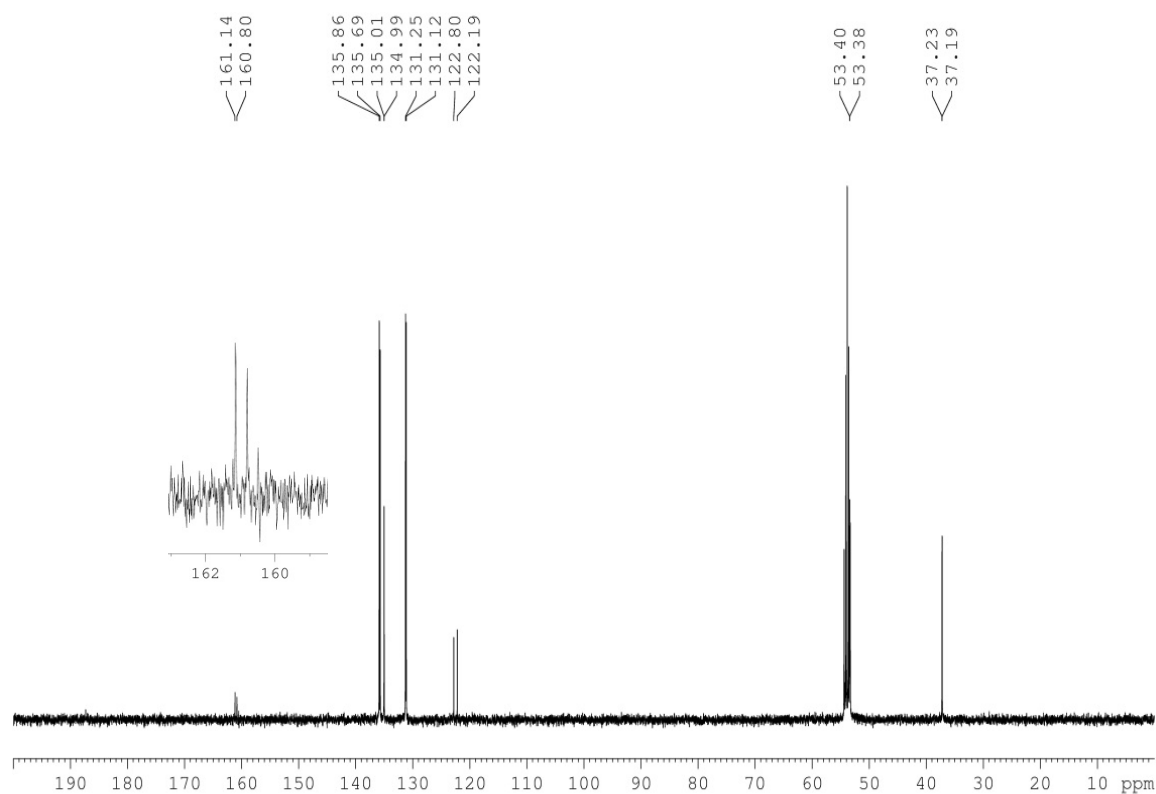
^1H NMR (400 MHz, CD_2Cl_2) **17**



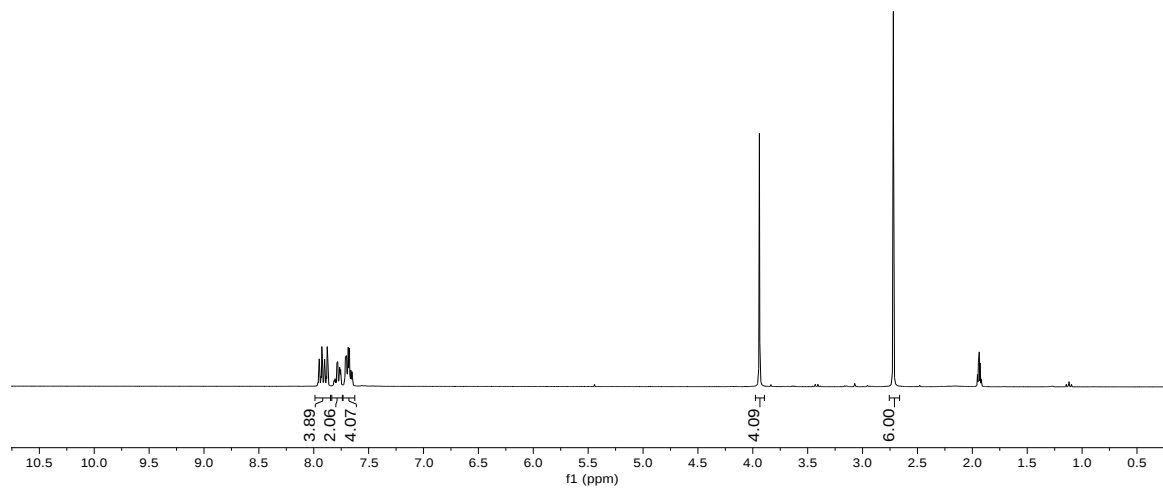
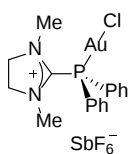
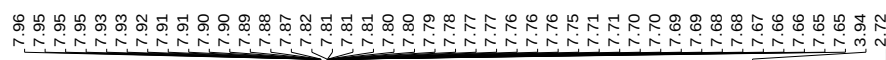
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) **17**



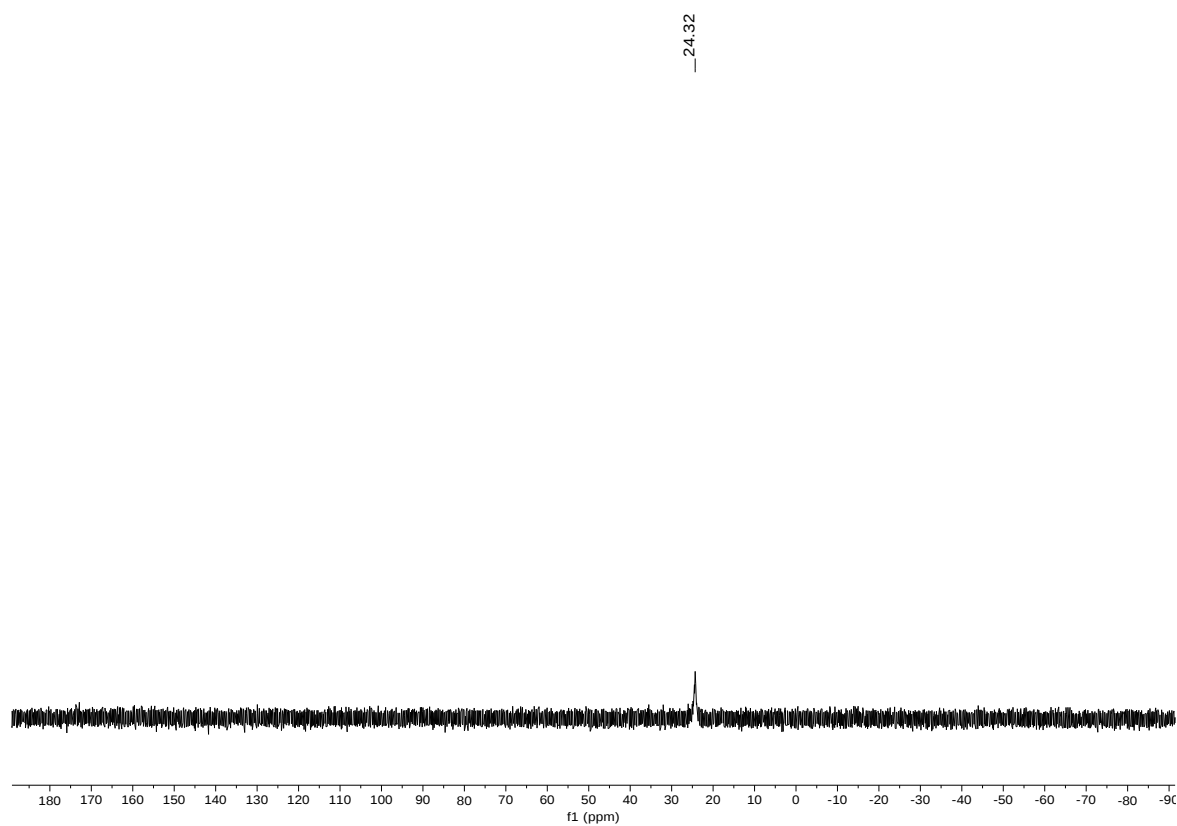
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **17**



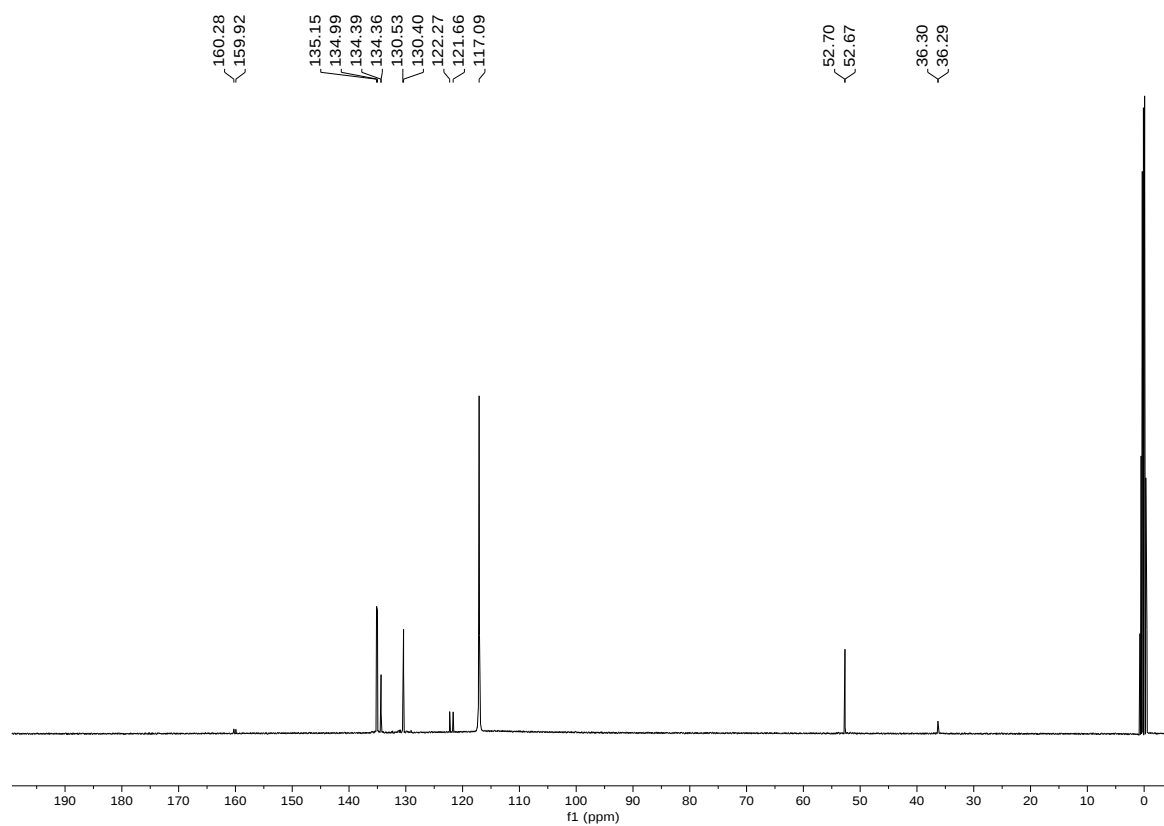
^1H NMR (300 MHz, CD_3CN) **18**



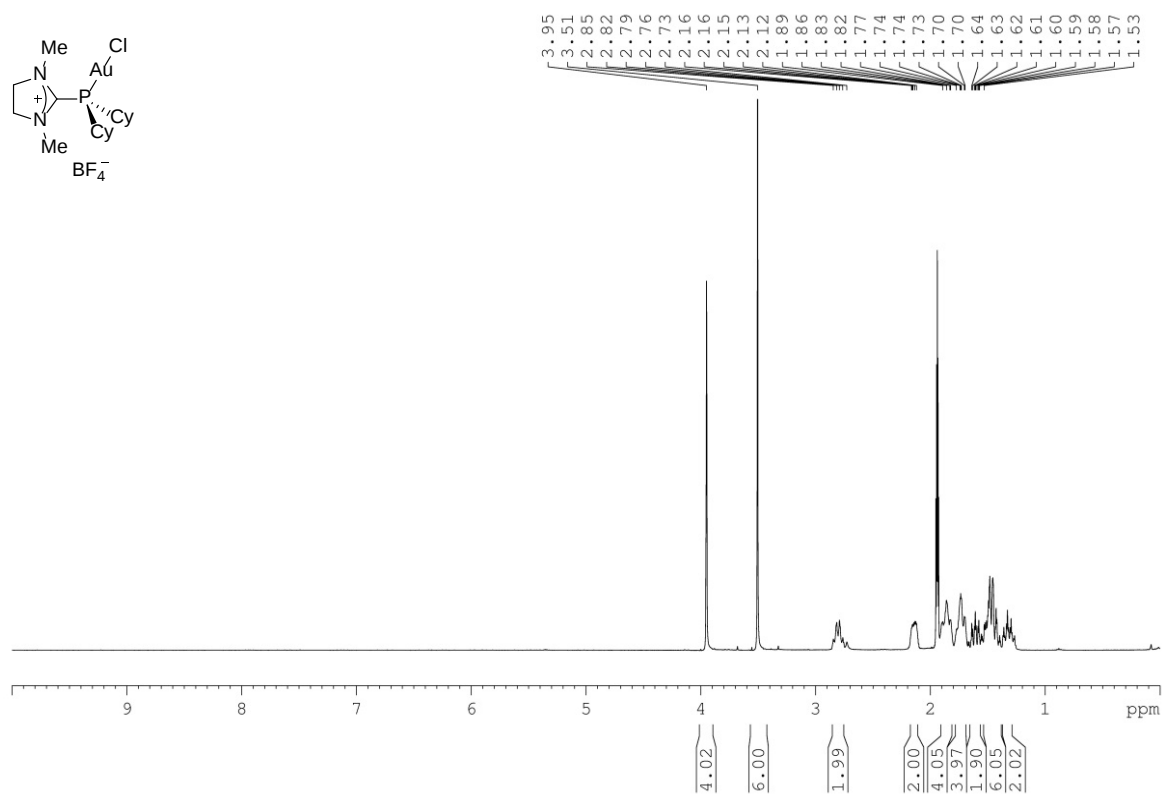
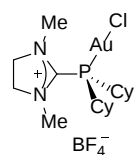
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) **18**



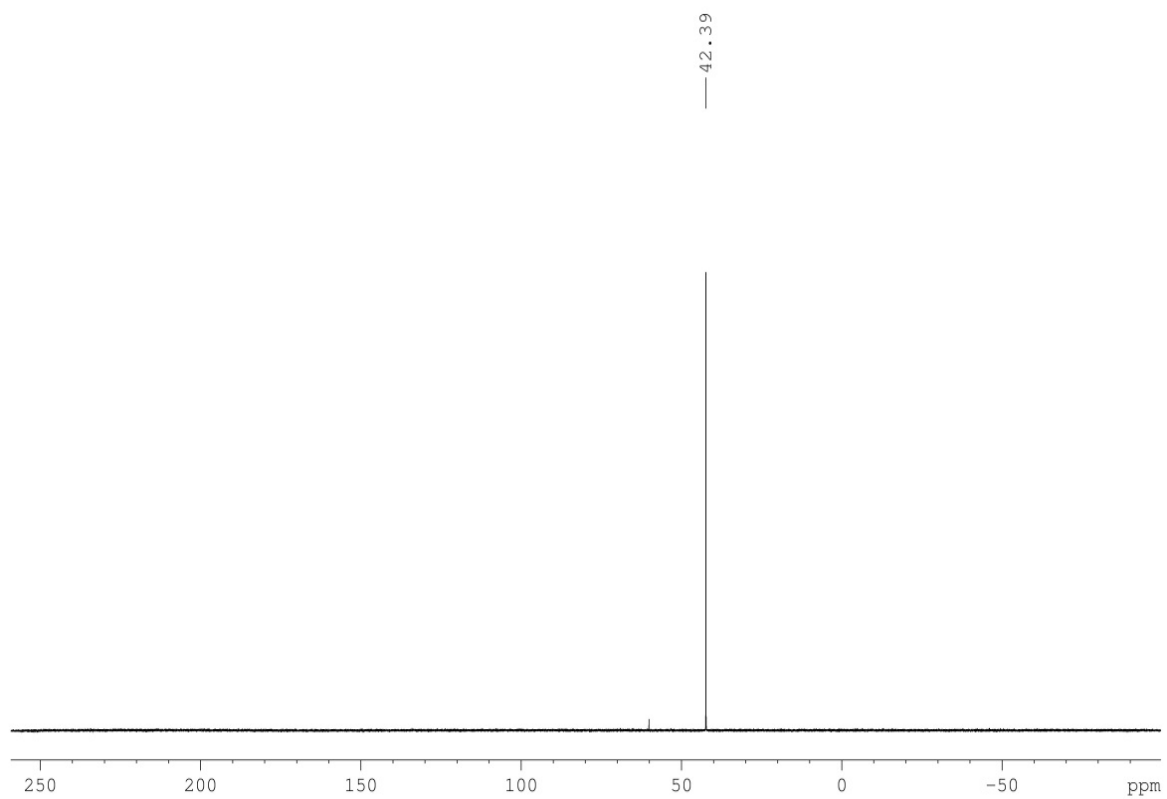
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) **18**



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



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



160.62
160.38

162 160

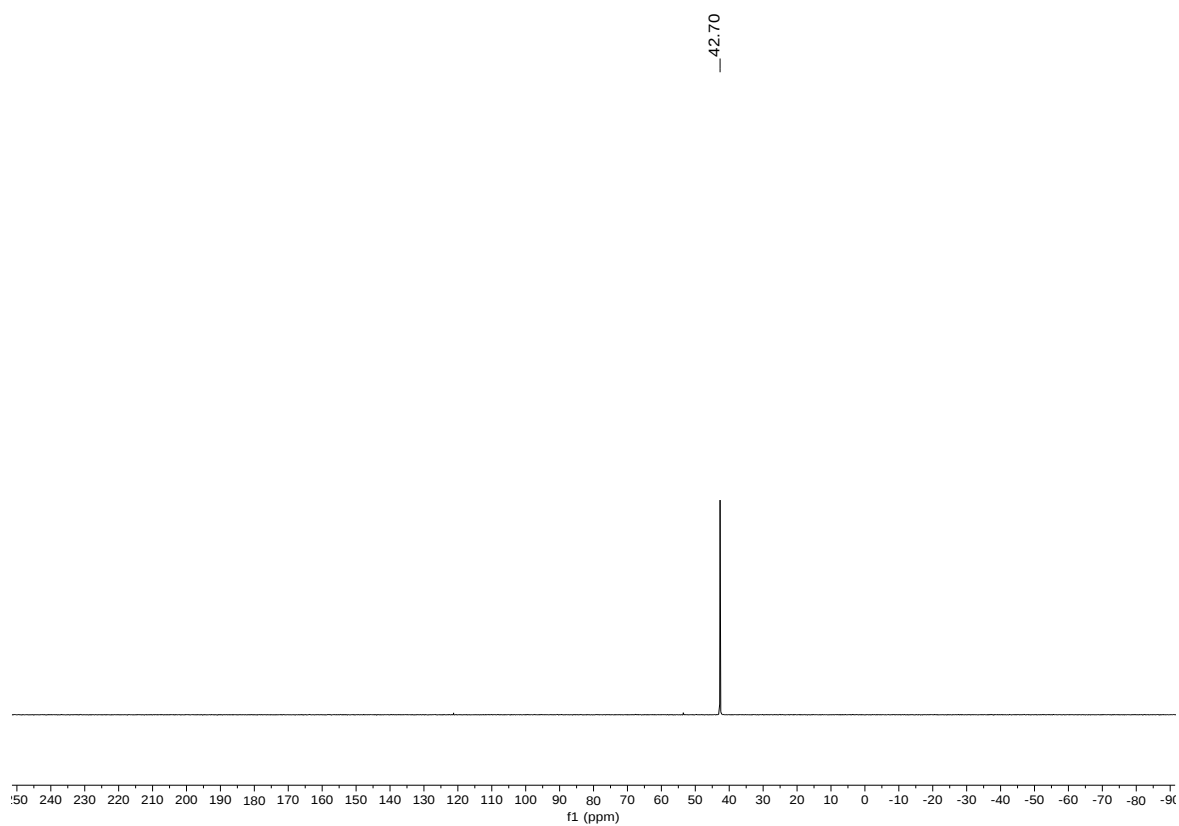
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

53.72
38.62
38.59
38.59
36.59
36.32
33.45
33.38
30.78
26.67
26.54
26.42
26.25
25.74
25.73

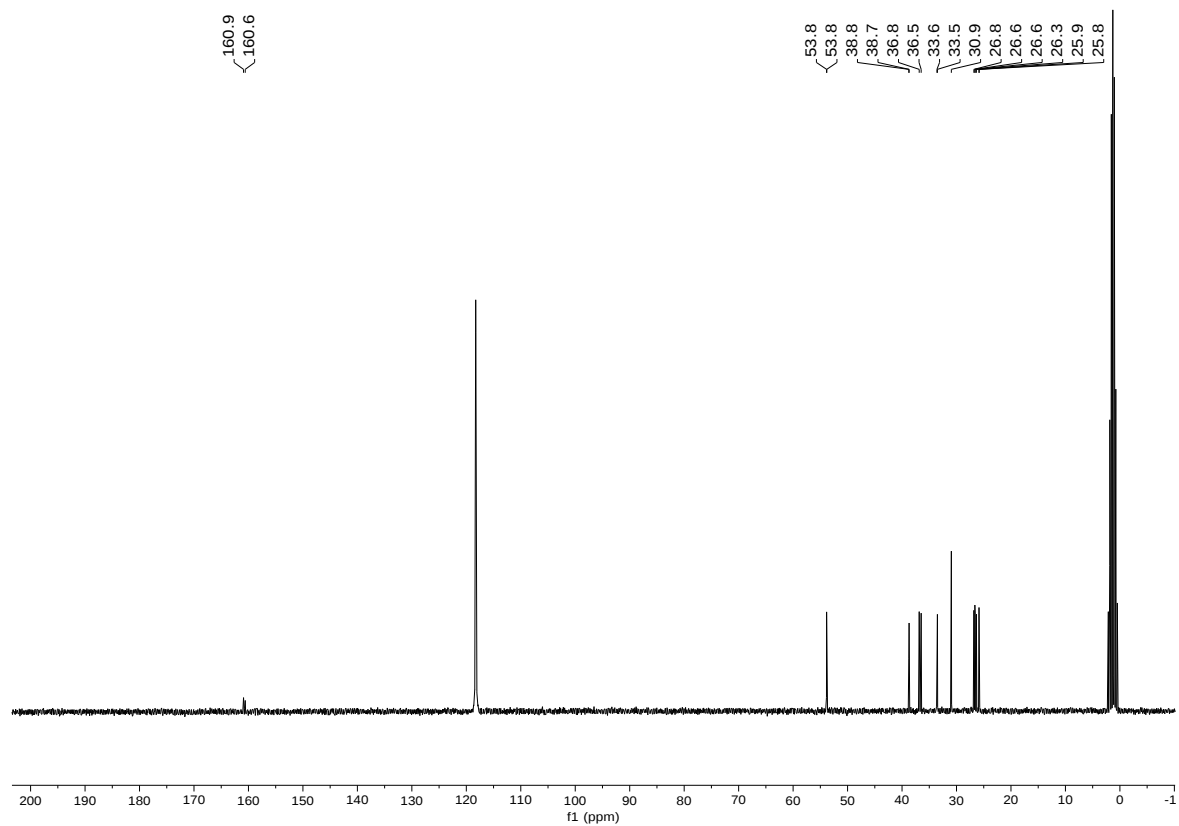
Chemical structure of compound 1: A 2D chemical structure showing a central phosphorus atom (P) bonded to a chlorine atom (Cl), a cyano group (C≡N), and a 2-methyl-2H-imidaz-5-yl group. The counterion is SbF_6^- .

^1H NMR spectrum (CDCl₃) of compound 1. The x-axis represents the chemical shift in ppm, ranging from 0.0 to 9.0. The spectrum shows several peaks, with the following chemical shifts (ppm) listed from top to bottom: 3.88, 3.43, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 1.83, 1.82, 1.81, 1.80, 1.79, 1.75, 1.74, 1.71, 1.70, 1.67, 1.66, 1.65, 1.63, 1.62, 1.61, 1.60, 1.57, 1.56, 1.54, 1.53, 1.52, 1.50, 1.49, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.35, 1.34, 1.30, 1.29, 1.26, 1.25, 1.24, 1.22, and 1.21. Integration values are provided below the baseline: 4.00, 5.95, 1.99, 2.07, 8.30, and 10.49.

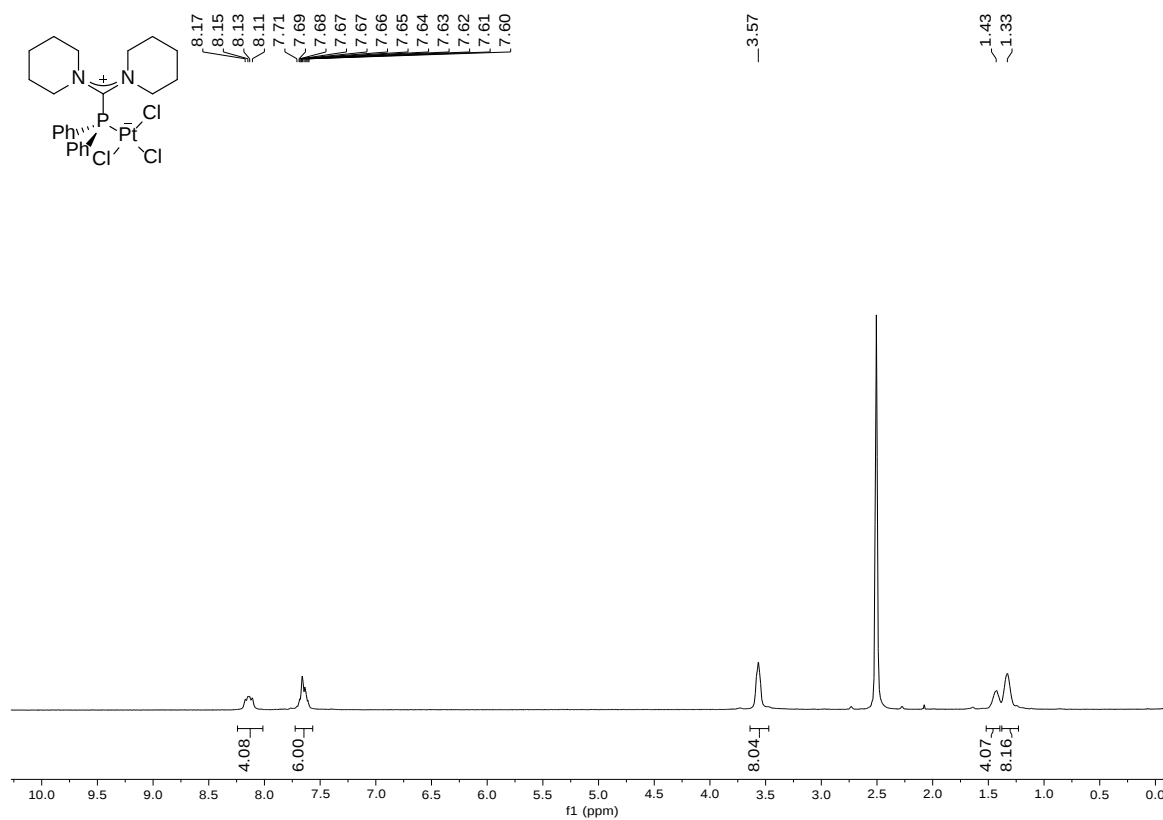
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_3CN) **20**



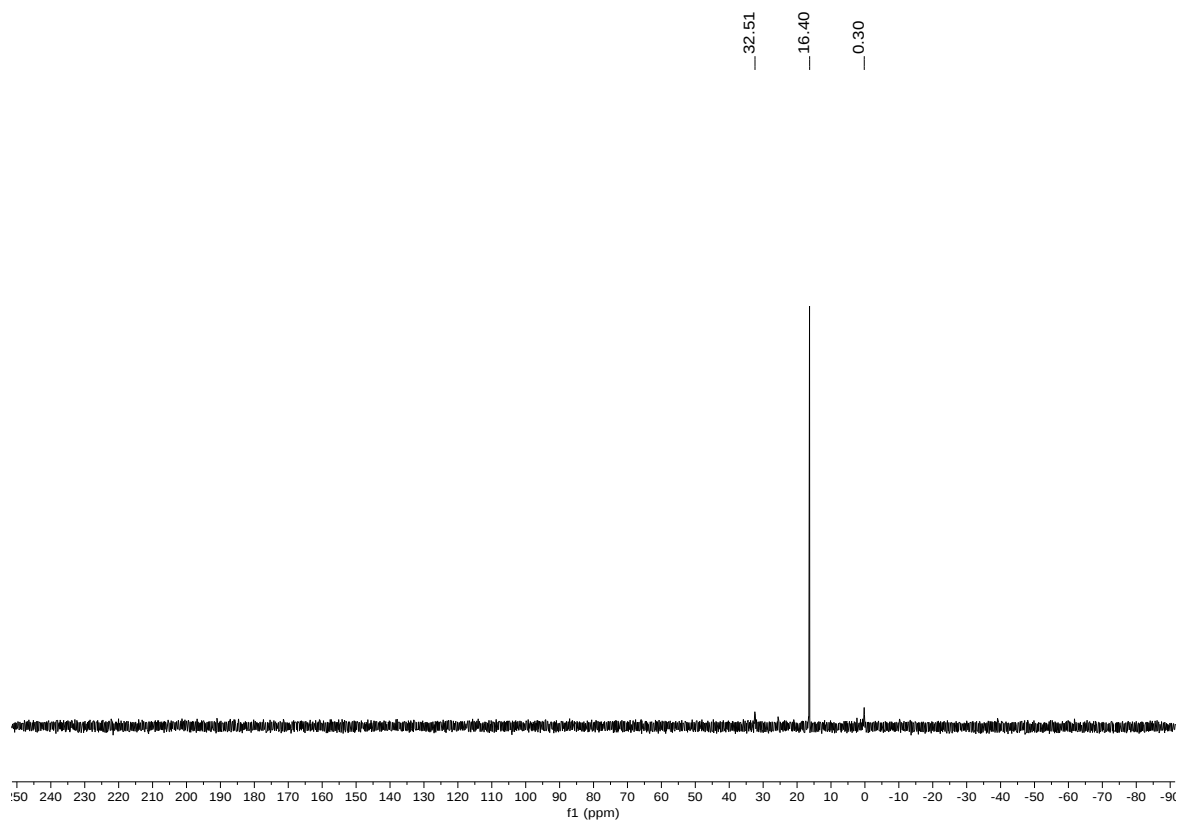
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) **20**



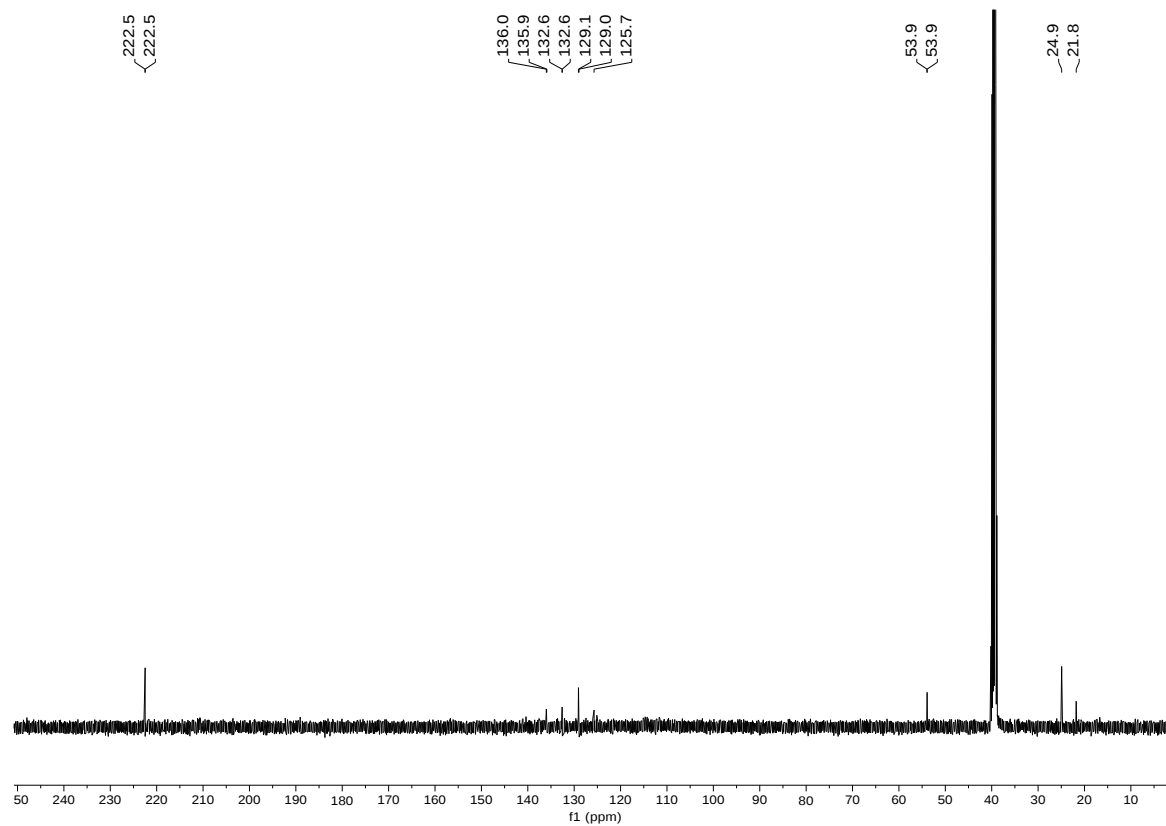
^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$) **21**



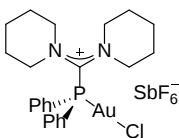
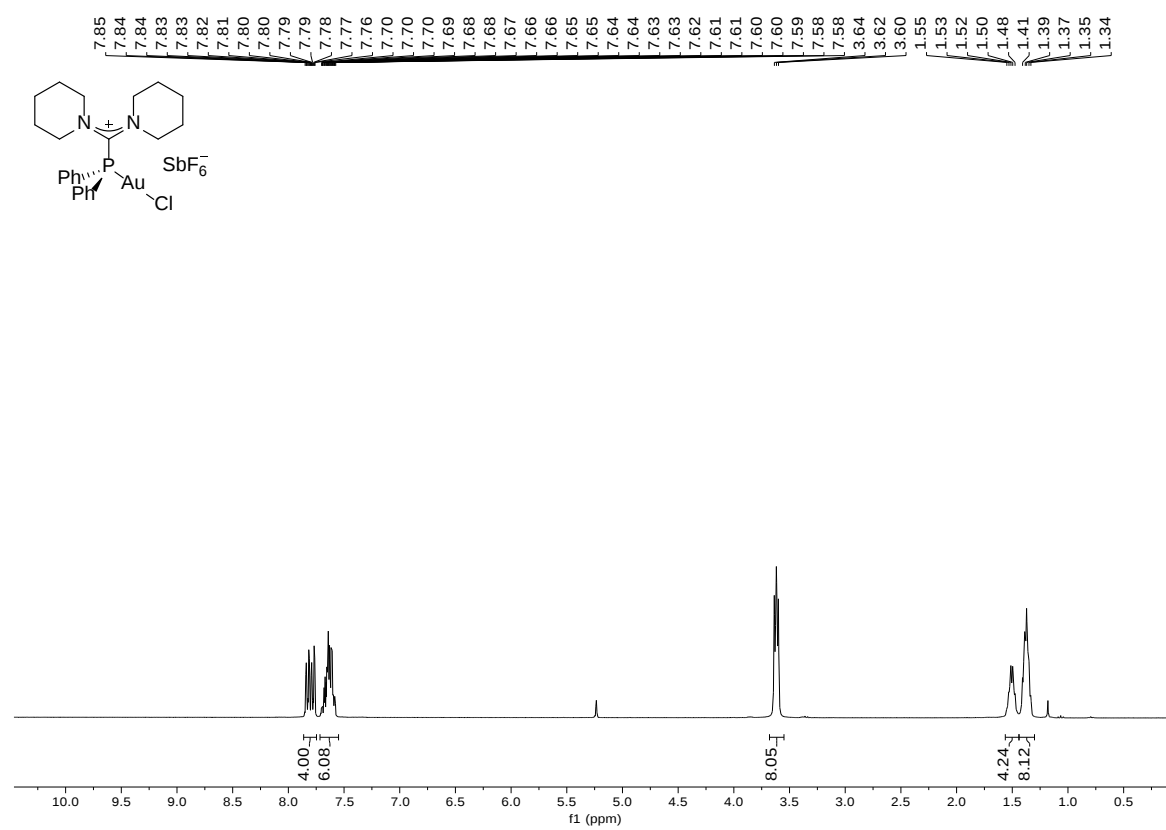
$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $(\text{CD}_3)_2\text{SO}$) **21**



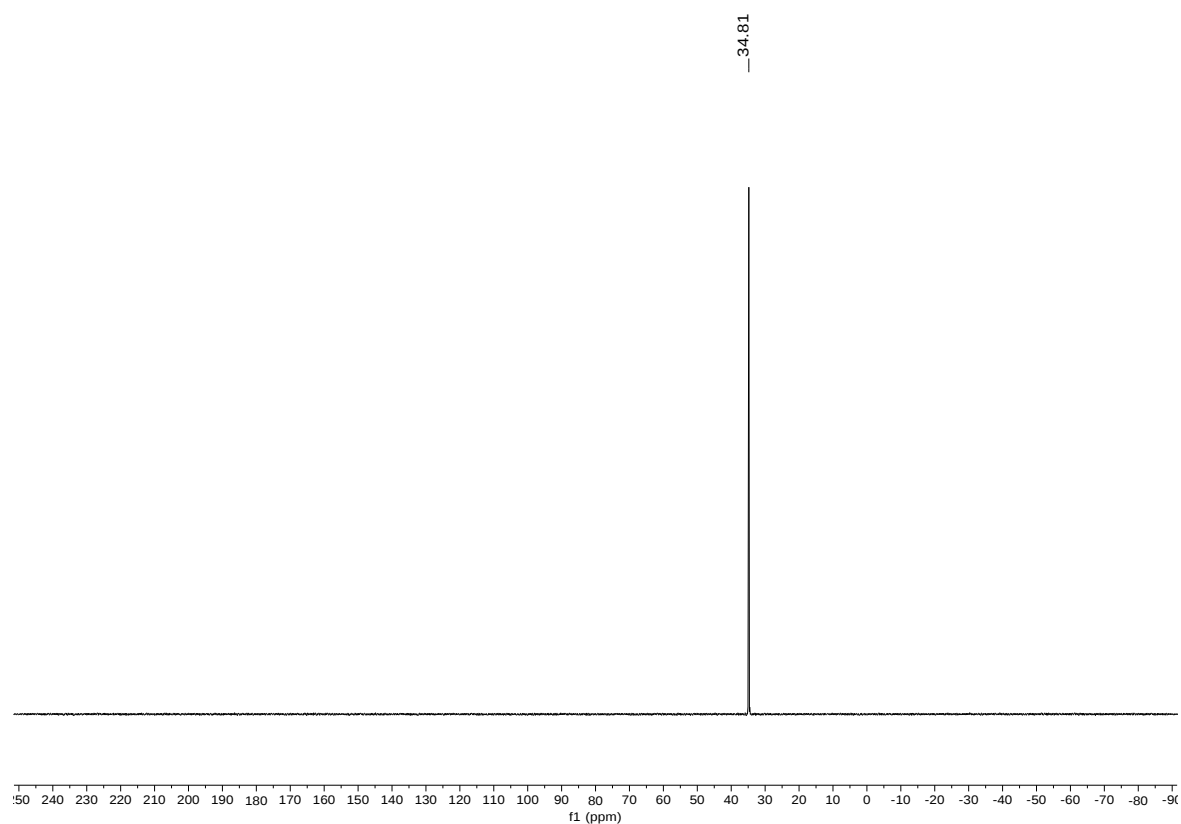
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) **21**



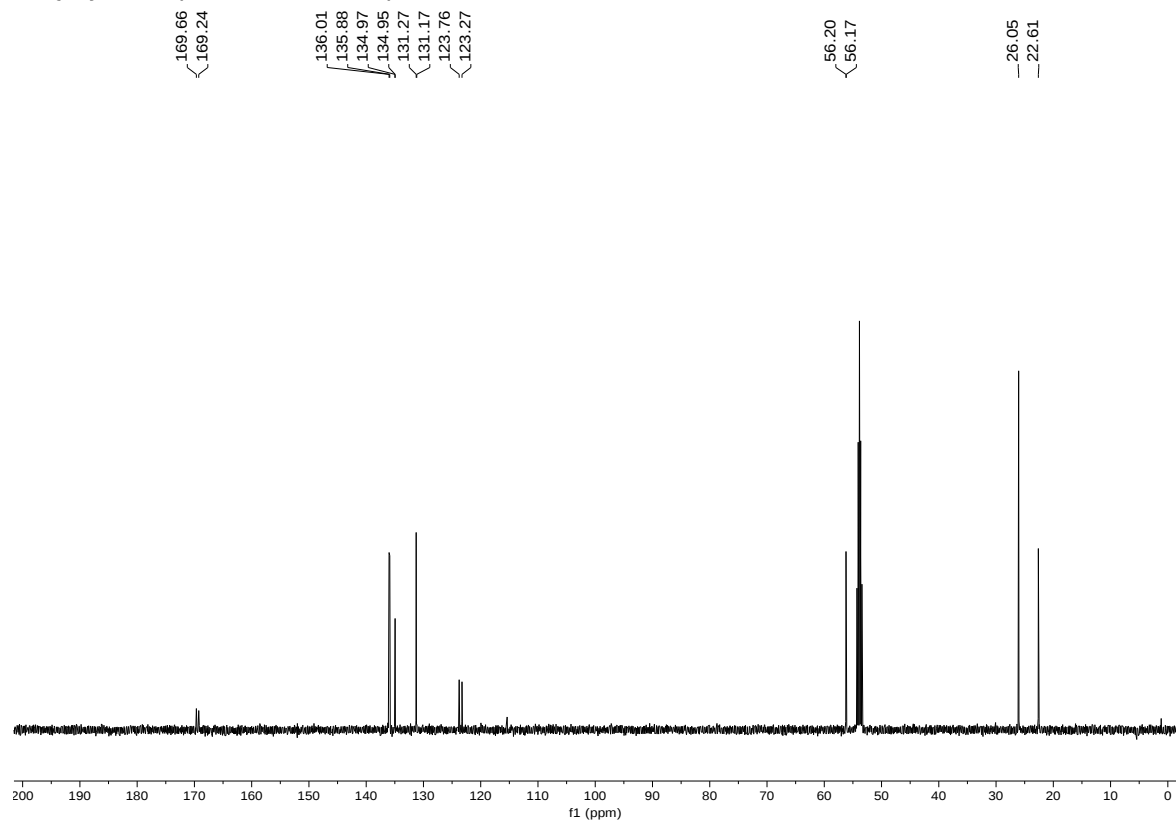
^1H NMR (400 MHz, CD_2Cl_2) **22**



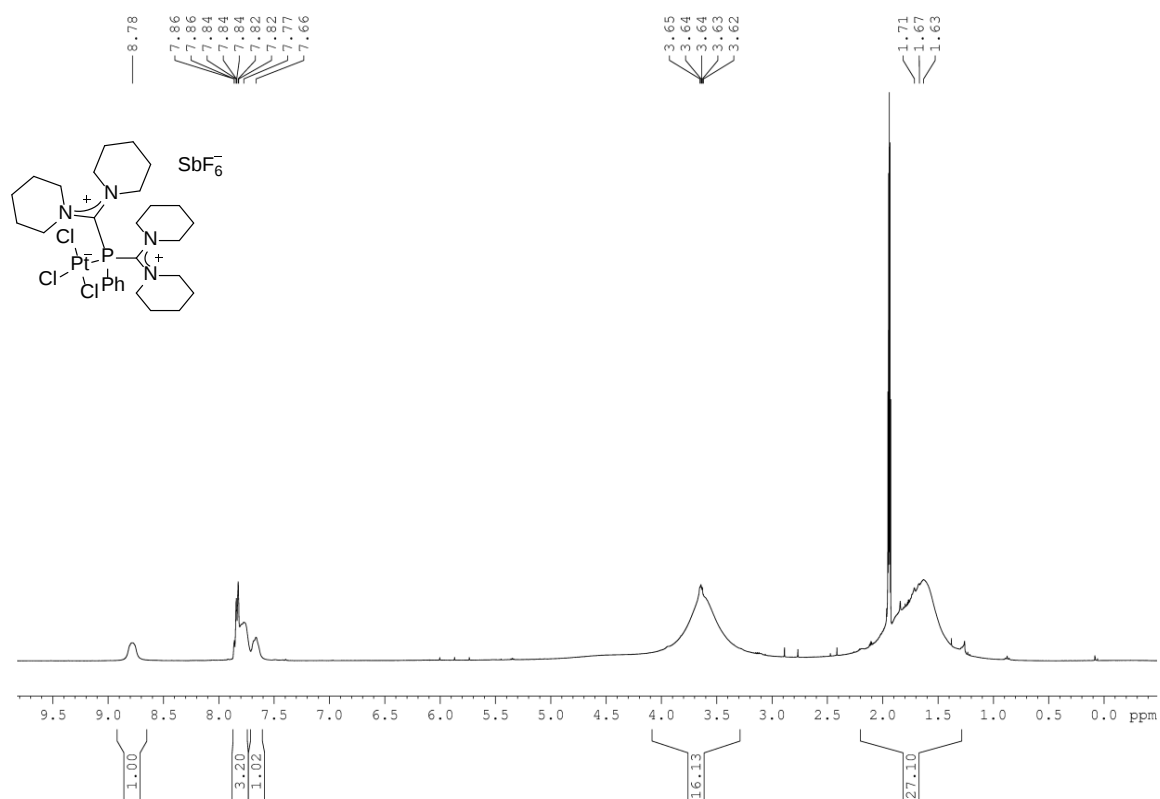
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) **22**



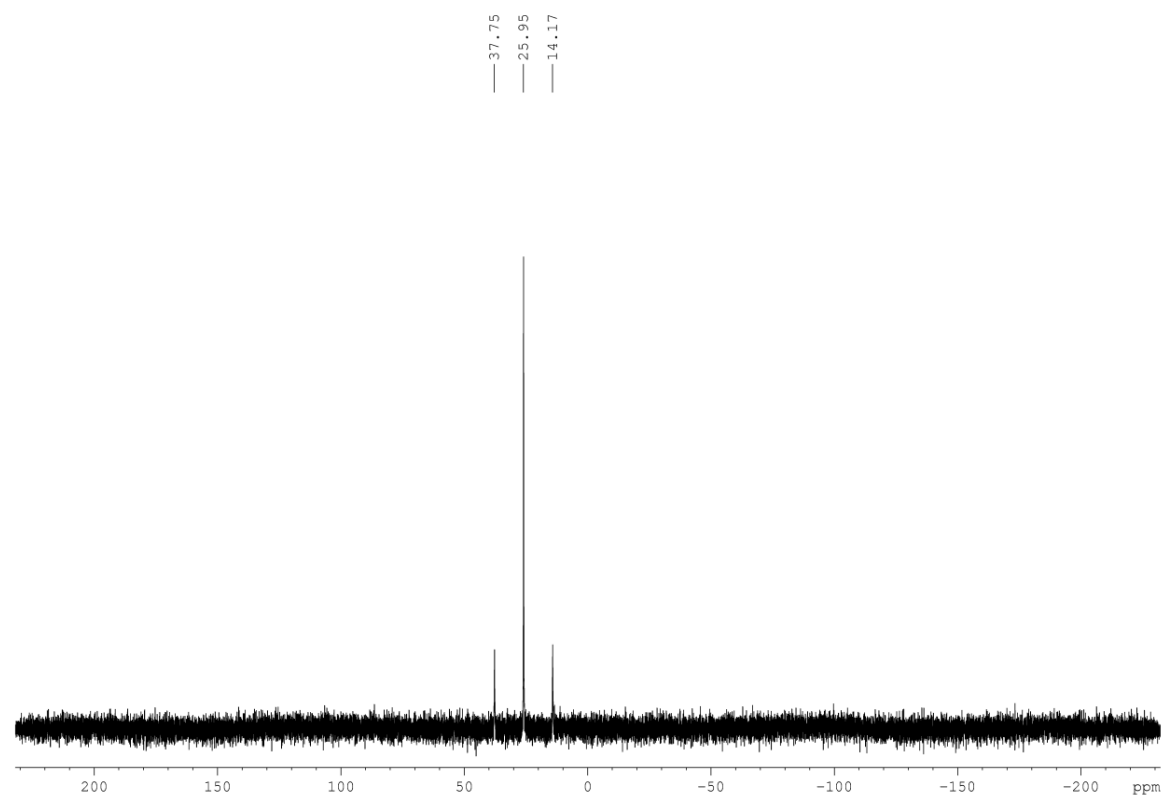
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) **22**



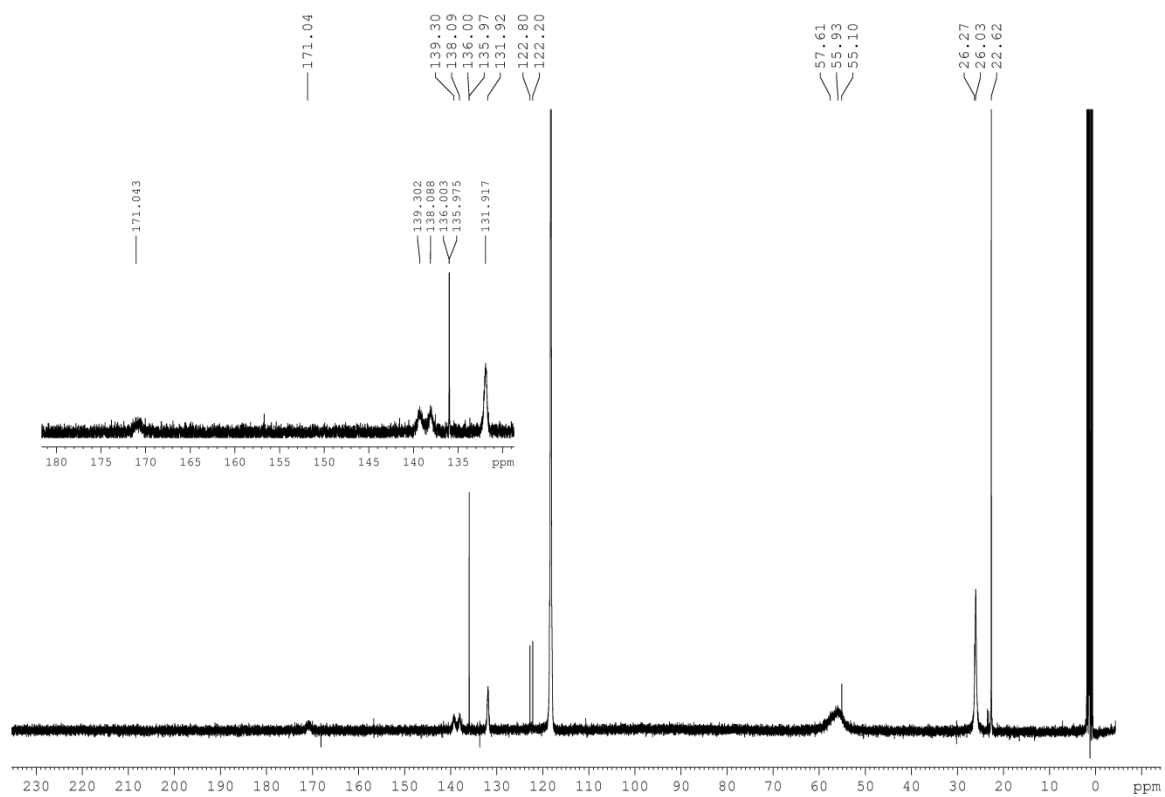
^1H NMR (400 MHz, CD_3CN) **23**



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

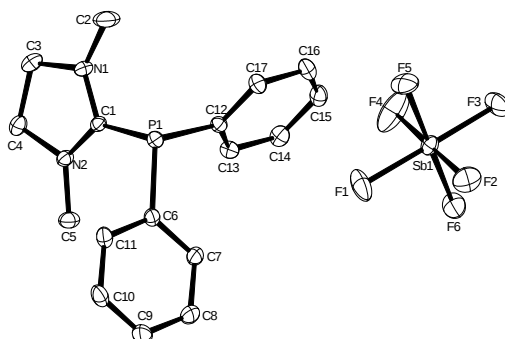


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) **23**



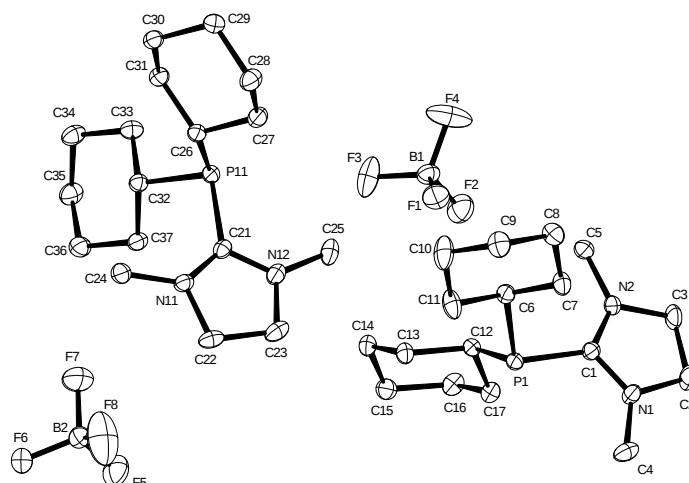
X-Ray Structure Analyses

Compound 3



Empirical formula	$C_{17}H_{20}F_6N_2PSb$	
Color	colourless	
Formula weight	519.07 g·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 b = 11.1050(4) Å c = 23.5818(10) Å	$\alpha = 90^\circ$ $\beta = 94.658(5)^\circ$ $\gamma = 90^\circ$
Volume	1979.38(15) Å ³	
Z	4	
Density (calculated)	1.742 Mg·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 $I > 2\sigma(I)$	6963	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2\sigma(I)$]	$R_1 = 0.0280$	$wR^2 = 0.0945$
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·Å ⁻³	

Compound 4



Empirical formula

Color

Formula weight

Temperature

Wavelength

Crystal system

Space group

Unit cell dimensions

$C_{17}H_{32}BF_4N_2P$

colorless

382.22 g · mol⁻¹

100 K

1.54178 Å

MONOCLINIC

$P2_1/n$, (no. 14)

$a = 12.3705(5)$ Å

$b = 22.6919(9)$ Å

$c = 15.1987(6)$ Å

$\alpha = 90^\circ$.

$\beta = 113.6237(13)^\circ$.

$\gamma = 90^\circ$.

Volume

Z

3908.9(3) Å³

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 mm³

θ range for data collection

3.724 to 67.698°.

Index ranges

$-14 \leq h \leq 14$, $-27 \leq k \leq 27$, $-18 \leq l \leq 18$

Reflections collected

92285

Independent reflections

7040 [$R_{int} = 0.0467$]

Reflections with $I > 2 \sigma(I)$

6294

Completeness to $\theta = 67.679^\circ$

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 [$I > 2 \sigma(I)$]

$R_1 = 0.0409$

$wR^2 = 0.1005$

R indices (all data)

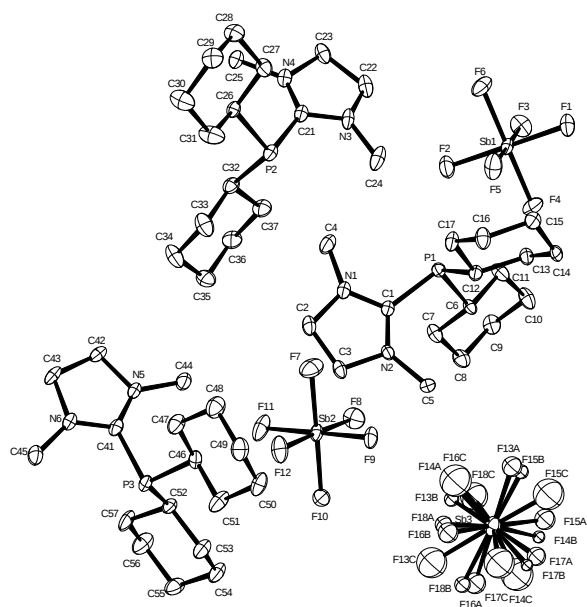
$R_1 = 0.0464$

$wR^2 = 0.1046$

Largest diff. peak and hole

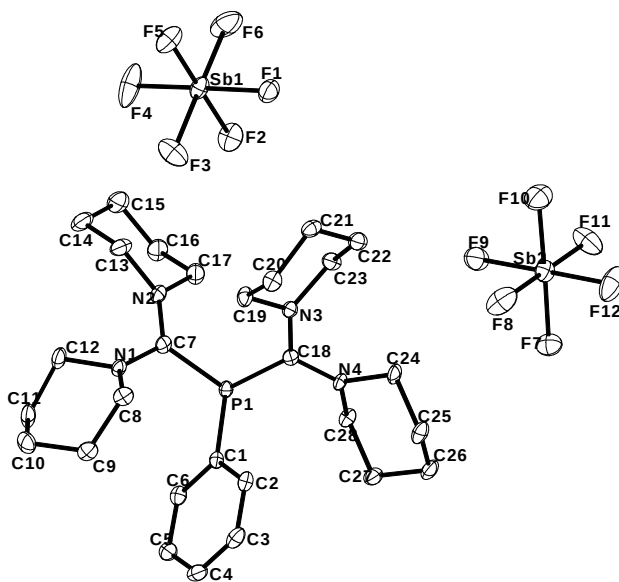
0.6 and -0.5 e · Å⁻³

Compound 5



Empirical formula	$C_{17}H_{32}F_6N_2PSb$	
Color	colorless	
Formula weight	$531.16 \text{ g} \cdot \text{mol}^{-1}$	
Temperature	100 K	
Wavelength	$0.71073 \text{ \AA}$	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	$a = 15.028(3) \text{ \AA}$ $b = 15.072(3) \text{ \AA}$ $c = 15.430(3) \text{ \AA}$	$\alpha = 75.926(3)^\circ$ $\beta = 82.983(3)^\circ$ $\gamma = 74.157(3)^\circ$
Volume	$3255.4(10) \text{ \AA}^3$	
Z	6	
Density (calculated)	$1.626 \text{ Mg} \cdot \text{m}^{-3}$	
Absorption coefficient	1.400 mm^{-1}	
F(000)	1608 e	
Crystal size	$0.26 \times 0.14 \times 0.01 \text{ mm}^3$	
θ range for data collection	1.363 to 28.512°	
Index ranges	$-20 \leq h \leq 20$, $-20 \leq k \leq 20$, $-20 \leq l \leq 20$	
Reflections collected	79160	
Independent reflections	16429 [$R_{\text{int}} = 0.0710$]	
Reflections with $I > 2\sigma(I)$	11965	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2 \sigma(I)$]	$R_1 = 0.0376$	$wR^2 = 0.0854$
R indices (all data)	$R_1 = 0.0674$	$wR^2 = 0.1053$
Largest diff. peak and hole	1.1 and $-1.7 \text{ e} \cdot \text{\AA}^{-3}$	

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

$\alpha = 82.3872(10)^\circ$

$b = 11.9121(3)$ Å

$\beta = 82.2212(9)^\circ$

$c = 14.5106(3)$ Å

$\gamma = 87.2389(10)^\circ$

Volume

1736.43(7) Å³

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 mm³

θ range for data collection

3.099 to 67.509°

Index ranges

$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$

Reflections collected

41228

Independent reflections

6054 [$R_{int} = 0.0676$]

Reflections with $I > 2 \sigma(I)$

5404

Completeness to $\theta = 67.679^\circ$

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 [$I > 2 \sigma(I)$]

$R_1 = 0.0320$

$wR^2 = 0.0778$

R indices (all data)

$R_1 = 0.0380$

$wR^2 = 0.0815$

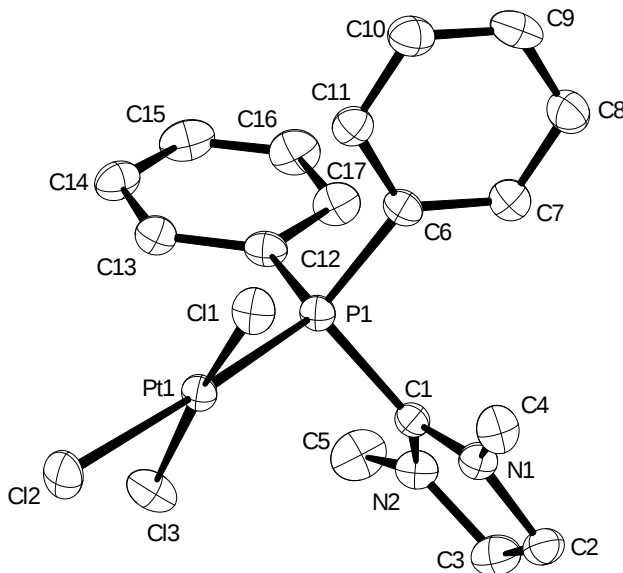
Extinction coefficient

n/a

Largest diff. peak and hole

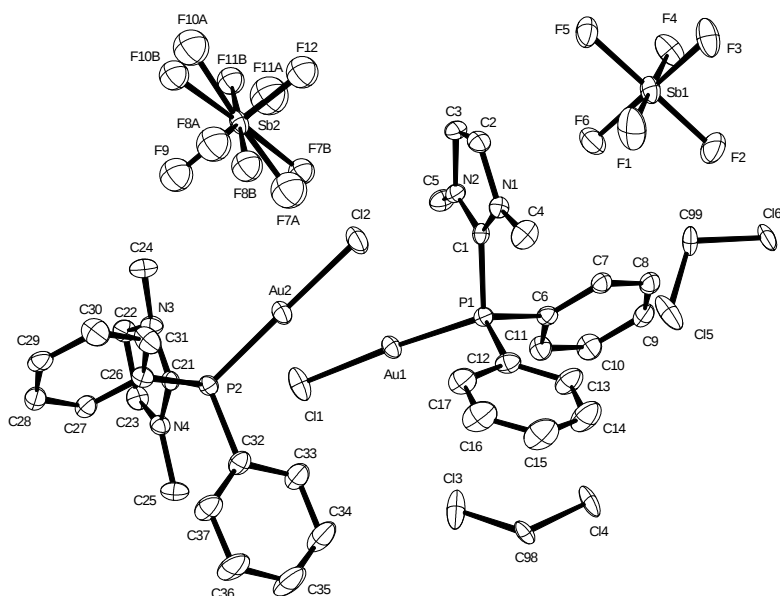
0.661 and -1.106 e·Å⁻³

Compound **16**



Empirical formula	C ₁₇ H ₂₀ Cl ₃ N ₂ Ppt		
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	γ = 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

$\alpha = 88.305(2)^\circ$

$b = 13.6615(18)$ Å

$\beta = 69.996(2)^\circ$

$c = 16.414(2)$ Å

$\gamma = 88.438(2)^\circ$

Volume

2506.2(6) Å³

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 mm³

θ range for data collection

1.321 to 31.428°

Index ranges

$-17 \leq h \leq 17, -19 \leq k \leq 19, -23 \leq l \leq 24$

Reflections collected

74031

Independent reflections

16397 [$R_{int} = 0.0334$]

Reflections with $I > 2\sigma(I)$

13532

Completeness to $\theta = 25.242^\circ$

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 [$I > 2\sigma(I)$]

$R_1 = 0.0474$

$wR^2 = 0.1233$

R indices (all data)

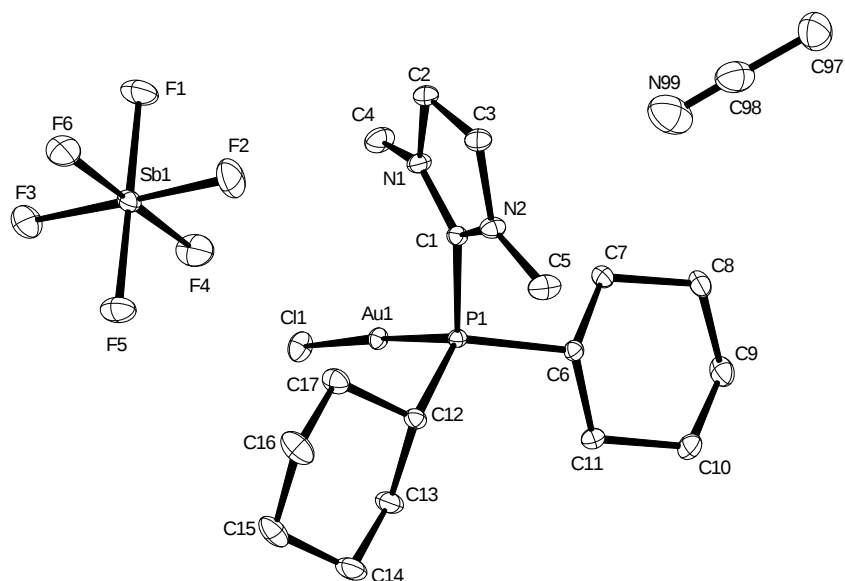
$R_1 = 0.0607$

$wR^2 = 0.1321$

Largest diff. peak and hole

6.4 and -2.3 e · Å⁻³

Compound **20**



Empirical formula

Color

Formula weight

Temperature

Wavelength

Crystal system

Space group

Unit cell dimensions

$C_{19}H_{35}AuClF_6N_3PSb$

colorless

804.65 g · mol⁻¹

100 K

0.71073 Å

TRICLINIC

$P\bar{1}$, (no. 2)

$a = 8.4612(9)$ Å

$b = 8.9156(9)$ Å

$c = 19.0961(19)$ Å

$\alpha = 83.9995(16)^\circ$

$\beta = 81.0351(17)^\circ$

$\gamma = 64.5960(15)^\circ$

Volume

Z

Density (calculated)

Absorption coefficient

$F(000)$

Crystal size

θ range for data collection

Index ranges

Reflections collected

Independent reflections

Reflections with $I > 2\sigma(I)$

Completeness to $\theta = 25.242^\circ$

Absorption correction

Max. and min. transmission

Refinement method

Data / restraints / parameters

Goodness-of-fit on F^2

Final R indices [$I > 2\sigma(I)$]

R indices (all data)

Largest diff. peak and hole

1284.2(2) Å³

2

2.081 Mg · m⁻³

6.982 mm⁻¹

772 e

0.12 x 0.09 x 0.09 mm³

2.161 to 33.139°

$-13 \leq h \leq 13, -13 \leq k \leq 13, -29 \leq l \leq 29$

42921

9751 [$R_{int} = 0.0184$]

9598

99.7 %

Gaussian

0.63 and 0.50

Full-matrix least-squares on F^2

9751 / 0 / 292

1.157

$R_1 = 0.0160$

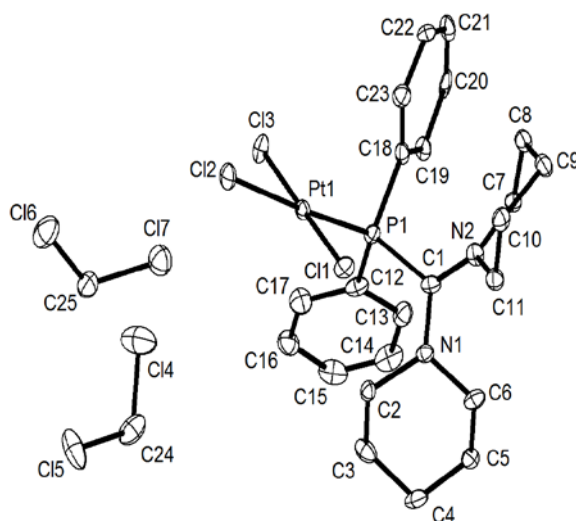
$wR^2 = 0.0392$

$R_1 = 0.0165$

$wR^2 = 0.0393$

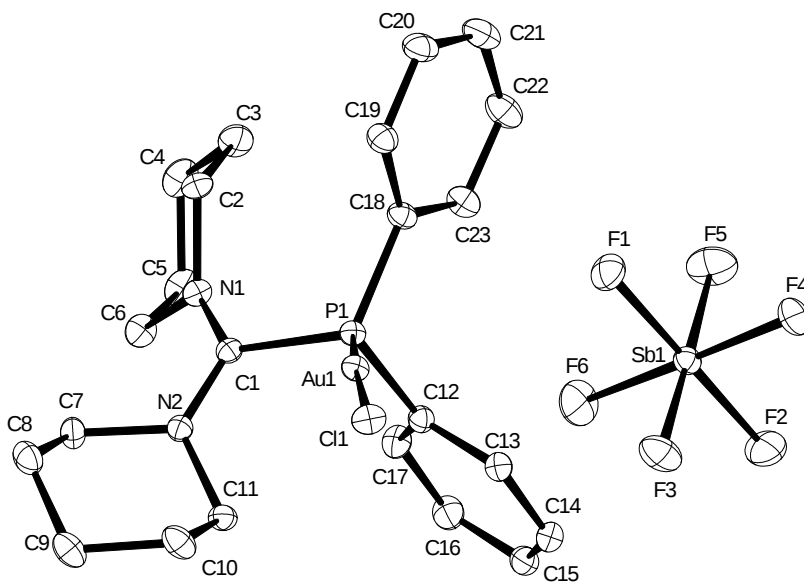
2.0 and -1.6 e · Å⁻³

Compound 21



Empirical formula	C ₂₅ H ₃₄ ClN ₂ Ppt		
Color	yellow		
Formula weight	836.75 g·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	γ = 90°.	
Volume	3062(2) Å ³		
Z	4		
Density (calculated)	1.815 Mg·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 ≤ l ≤ 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·Å ⁻³		

Compound 22



Empirical formula	C ₂₃ H ₃₀ AuClF ₆ N ₂ PSb		
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 ≤ l ≤ 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		