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Supporting Information

Bis[(dialkylamino)cyclopropenimine]-Stabilized P^{III}- and P^{V}-Centered Dications

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Experimental procedures:

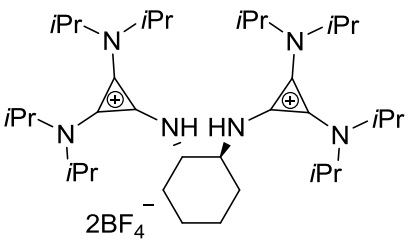
General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropiate drying agents and were transferred under Ar. IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}; all measurements were carried out on solid samples. 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 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 separations were 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. Optical rotations ($[\alpha]_{20}^{D}$) were measured with a Perkin-Elmer model 343 polarimeter.

All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received. 2,3-bis(di*iso*propylamino)-1-chlorocyclopropenium tetrafluoroborate **3**, [1] was prepared according to literature procedures.

Elemental analysis measured at the microanalysis laboratories of H. Kolbe.

[1] R. Weiss, K. G. Wagner, C. Priesner, J. Macheleid, *J. Am. Chem. Soc.* **1985**, *107*, 4491.

Compound **4:**



Triethylamine (0.25 mL, 1.84 mmol) and chlorocyclopropenium salt **3** (660 mg, 1.84 mmol) were added to a solution of (*1R,2R*)-1,2-diaminocyclohexane (100 mg, 0.88 mmol) in dry CH_2Cl_2 (4 mL) and the resulting mixture was stirred at room temperature for 2 days. The mixture was then diluted with CH_2Cl_2 (6 mL) and washed with a saturated aq. $NaBF_4$ solution (3 x 12 mL). Once dried over Na_2SO_4, the organic phase was concentrated and the residue purified by column chromatography (CH_2Cl_2/MeOH: 98/2) affording the desired compound as a white solid (374 mg, 56 %). $[\alpha]_{20}^{D}$ = +10.0 (c = 1.0, $CHCl_3$)

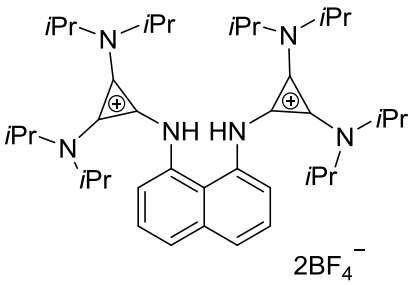
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.30 (overlap of two doublets, *J* = 6.8 Hz, 48H), 1.35-1.37 (m, 2H), 1.64-1.76 (m, 2H), 1.78-1.84 (m, 2H), 2.04 (d, *J* = 13.4 Hz, 2H), 3.64 (m, 2H), 3.86 (sept, *J* = 6.8 Hz, 8H), 6.11-6.17 (m, 2H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.9, 22.3, 24.4, 34.8, 51.0, 59.9, 115.2, 115.4 ppm.

HRMS *calcd.* for $[C_{36}H_{68}N_6BF_4]^+$: 671.552911; *found* 671.552990.

IR (solid) $\tilde{\nu}$ = 764, 991, 1033, 1072, 1116, 1138, 1154, 1211, 1346, 1368, 1452, 1472, 1509, 2938, 2982, 3319 cm^{-1}.

Compound **5:**



Triethylamine (0.85 mL, 11.13 mmol) and chlorocyclopropenium salt **3** (4 g, 11.13 mmol) were added to a stirred solution of 1,8-diaminonaphtalene (0.80 g, 5.06 mmol) in dry THF (18 mL) and the resulting mixture was heated at 60 °C for 1 day. After cooling to room temperature, the solvent was removed under vacuum, the residue suspended in CH_2Cl_2 (40 mL) and washed with a saturated aq. $NaBF_4$ solution (3 x 50 mL). The organic phase was dried over Na_2SO_4 and concentrated. Finally, the desired compound was obtained by recrystallizing from CH_2Cl_2/Et_2O as a light brown solid (2.34 g, 57 %).

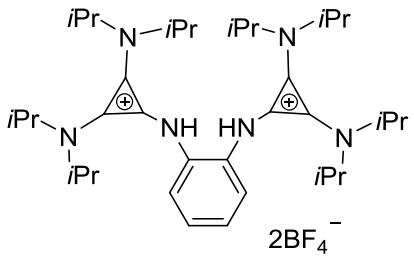
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.21 (d, *J* = 6.8 Hz, 48H), 3.69 (sept, *J* = 6.8 Hz, 8H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 8.44 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.0, 51.7, 112.7, 119.0, 123.4, 124.6, 126.7, 128.6, 135.8, 136.9 ppm.

HRMS *calcd.* for $[C_{40}H_{64}N_6BF_4]^+$: 715.521500; *found* 715.521611.

IR (solid) $\tilde{\nu}$ = 518, 729, 763, 830, 1031, 1049, 1078, 1136, 1192, 1212, 1280, 1344, 1452, 1497, 1536, 2937, 2981, 3310, 3360 cm^{-1}.

Compound **6:**



Triethylamine (0.56 mL, 4.07 mmol) and chlorocyclopropenium salt **3** (1.46 g, 4.07 mmol) were added to a stirred solution of *o*-phenylenediamine (200 mg, 1.85 mmol) in dry CH_2Cl_2 (8 mL) and the resulting mixture was stirred at room temperature for 3 days. The mixture was then diluted with CH_2Cl_2 (10 mL), and washed with a saturated aq. $NaBF_4$ solution (3 x 20 mL). The organic phase was dried over Na_2SO_4 and concentrated. Finally, the desired compound was obtained by recrystallizing from CH_2Cl_2/Et_2O as a white solid (953 mg, 68 %).

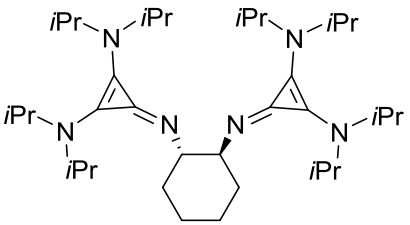
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (d, *J* = 6.8 Hz, 48H), 3.71 (sept, *J* = 6.8 Hz, 8H), 7.21 (br, 4H), 8.05 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 22.1, 50.9, 112.6, 115.6, 125.8, 126.3, 134.5 ppm.

HRMS *calcd.* for $[C_{36}H_{62}N_6BF_4]^+$: 665.505961; *found* 665.505720.

IR (solid) $\tilde{\nu}$ = 521, 780, 1014, 1047, 1066, 1141, 1218, 1288, 1350, 1367, 1452, 1500, 1520, 2934, 2960, 2983, 3321 cm^{-1}.

Compound **7:**



Salt **4** (350 mg, 0.46 mmol) was added to a stirred suspension of KH (148 mg, 3.69 mmol) in dry THF (6 mL) and the resulting suspension was heated at 60 °C for 16 hours. After cooling to room temperature, the solvent was evaporated and the residue extracted with Et_2O. Concentration of the combined ethereal extracts afforded the title compound as a light yellow solid (244 mg, 91 %). $[\alpha]_{20}^{D}$ = +108.1 (c = 1.0 , $CHCl_3$)

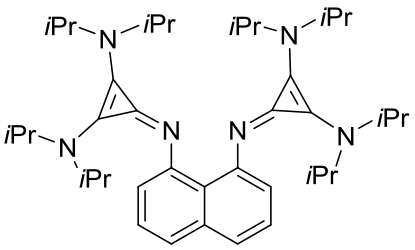
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.17 (d, *J* = 6.8 Hz, 24H), 1.24 (d, *J* = 6.8 Hz, 24H), 1.26-1.33 (m, 4H), 1.60-1.73 (m, 4H), 3.08-3.13 (m, 2H), 3.59 (sept, *J* = 6.8 Hz, 8H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.4, 22.6, 26.3, 36.5, 49.4, 68.3, 113.0, 127.6 ppm.

HRMS *calcd.* for $[C_{36}H_{67}N_6]^+$: 583.542167; *found* 583.542200.

IR (solid) $\tilde{\nu}$ = 490, 1128, 1155, 1205, 1222, 1301, 1367, 1421, 1565, 2842, 2870, 2915, 2966 cm^{-1}.

Compound **8:**



Salt **5** (2 g, 2.49 mmol) was added to a stirred suspension of KH (800 mg, 19.94 mmol) in dry THF (20 mL) and the resulting suspension was heated at 60 °C for 2 days. After cooling to room temperature, the solvent was removed under vacuum and the residue extracted with Et_2O. Concentration of the combined ethereal extracts afforded the title compound as a light brown solid (1.37 g, 88 %).

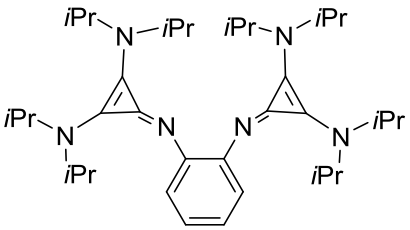
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (d, *J* = 6.8 Hz, 48H), 3.83 (sept, *J* = 6.8 Hz, 8H), 6.48 (dd, *J* = 6.1, 2.4 Hz, 2H), 7.21 – 7.25 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 22.4, 51.1, 113.0, 117.6, 118.5, 120.4, 120.7, 126.0, 136.9, 146.1 ppm.

HRMS *calcd.* for $[C_{40}H_{63}N_6]^+$: 627.510550; *found* 627.510867.

IR (solid) $\tilde{\nu}$ = 505, 559, 758, 826, 914, 1024, 1120, 1133, 1161, 1218, 1308, 1363, 1432, 1483, 1529, 1888, 2870, 2930, 2963, 3042 cm^{-1}.

Compound **9:**



Salt **6** (1 g, 1.33 mmol) was added to a stirred suspension of KH (426 mg, 10.63 mmol) in dry THF (10 mL) and the resulting mixture was heated at 60 °C for 2 days. After cooling to room temperature, the solvent was evaporated and the residue extracted with Et_2O. Concentration of the combined ethereal extracts afforded the title compound as a light red solid (696 mg, 91 %).

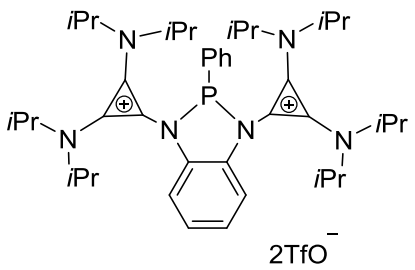
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.18 (d, *J* = 6.8 Hz, 48H), 3.60 (sept, *J* = 6.8 Hz, 8H), 6.61 (dd, *J* = 5.7, 3.5 Hz, 2H), 6.70 (dd, *J* = 5.7, 3.5 Hz, 2H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.4, 49.5, 113.7, 119.6, 122.8, 124.2, 149.0 ppm.

HRMS *calcd.* for $[C_{36}H_{61}N_6]^+$: 577.495217; *found* 577.494840.

IR (solid) $\tilde{\nu}$ = 497, 741, 1022, 1037, 1130, 1158, 1193, 1214, 1271, 1301, 1320, 1365, 1441, 1469, 1489, 1621, 2872, 2931, 2967 cm^{-1}.

Compound **10:**



$PhPCl_2$ (85 µL, 0.62 mmol) and TMSOTf (226 µL, 1.25 mmol) were added to a solution of compound **9** (300 mg, 0.52 mmol) in dry CH_2Cl_2 (3 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then removed under vacuum and the remaining residue washed with Et_2O (3 x 5 mL). Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a white solid (333 mg, 65 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.23 (d, *J* = 6.7 Hz, 24H), 1.28 (d, *J* = 6.7 Hz, 24H), 3.82 (br, 8H), 7.20 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.28 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.36-7.42 (m, 2H), 7.49-7.58 (m, 3H) ppm.

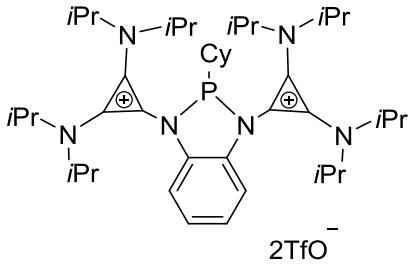
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 98.5 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.8, 21.8, 22.1, 52.7, 107.1 (d, J_{PC} = 22.4 Hz), 117.2, 121.4 (q, J_{FC} = 321.3 Hz), 125.6, 127.3, 129.7 (d, J_{PC} = 8.9 Hz), 131.2 (d, J_{PC} = 27.8 Hz), 134.1, 137.1 (d, J_{PC} = 3.0 Hz), 138.7 (d, J_{PC} = 31.3 Hz) ppm.

HRMS *calcd.* for $[C_{43}H_{65}N_6O_3F_3PS]^+$: 883.452310; *found* 883.451790.

IR (solid) $\tilde{\nu}$ = 434, 515, 635, 1028, 1141, 1260, 1354, 1444, 1536, 2977 cm^{-1}.

Compound **11:**



$CyPCl_2$ (96 µL, 0.62 mmol) and TMSOTf (226 µL, 1.25 mmol) were added to a solution of compound **9** (300 mg, 0.52 mmol) in dry CH_2Cl_2 (3 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then removed under vacuum and the residue thus obtained washed with Et_2O (3 x 5 mL). Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a light brown solid (412 mg, 80 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.99-1.22 (m, 5H), 1.36 (d, *J* = 6.8 Hz, 24H), 1.37 (d, *J* = 6.8 Hz, 24H), 1.63-1.82 (m, 6H), 3.89 (sept, *J* = 6.8 Hz, 8H), 7.22-7.29 (m, 4H) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 126.3 ppm.

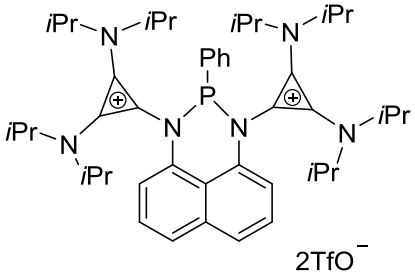
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.1, 22.1, 22.1, 22.5, 26.0, 26.7 (d, J_{PC} = 10.7 Hz), 27.1 (d, J_{PC} = 13.0 Hz), 45.5 (d, J_{PC} = 25.1 Hz), 51.5, 53.2, 109.5 (d, J_{PC} = 18.7 Hz), 118.2, 121.4 (q, J_{FC} = 321.9 Hz), 125.0, 126.0, 138.2 ppm.

HRMS *calcd.* for $[C_{43}H_{71}N_6O_3F_3PS]^+$: 839.499260; *found* 839.498740.

Elemental Analisis *calcd* (%). C 53.43; H 7.24; N 8.50; P 3.13; *found* C 53.70; H 7.27; N 8.38; P 3.30.

IR (solid) $\tilde{\nu}$ = 515, 634, 749, 1028, 1136, 1210, 1255, 1348, 1359, 1451, 1472, 1536, 1562, 1916, 2933, 2981 cm^{-1}.

Compound **12:**



$PhPCl_2$ (130 µL, 0.96 mmol) and TMSOTf (346 µL, 1.91 mmol) were added to a solution of compound **8** (500 mg, 0.80 mmol) in dry CH_2Cl_2 (5 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then evaporated and the residue washed with Et_2O (3 x 7 mL). Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a white solid (516 mg, 63 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.35 (br, 48H), 3.88 (br, 8H), 7.11-7.18 (m, 3H), 7.23-7.31 (m, 4H), 7.52 (t, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H) ppm.

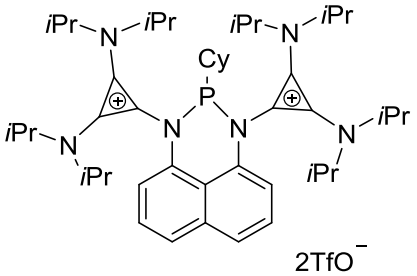
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ = 72.1 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.2, 53.0, 110.9 (d, J_{PC} = 28.9 Hz), 119.3, 120.9, 121.4 (q, J_{FC} = 321.2 Hz), 125.0 (d, J_{PC} = 28.9 Hz), 126.9, 127.0, 129.3 (d, J_{PC} = 4.2 Hz), 130.3 (d, J_{PC} = 17.1 Hz), 130.6, 134.2, 134.7 (d, J_{PC} = 7.3 Hz), 135.1 ppm.

HRMS *calcd.* for $[C_{47}H_{67}N_6O_3F_3PS]^+$: 883.467370; *found* 883.467960.

IR (solid) $\tilde{\nu}$ = 427, 515, 572, 635, 747, 766, 828, 987, 1029, 1141, 1220, 1262, 1355, 1374, 1445, 1537, 2939, 2976 cm^{-1}.

Compound **13:**



$CyPCl_2$ (147 µL, 0.96 mmol) and TMSOTf (346 µL, 1.91 mmol) were added to a solution of compound **8** (500 mg, 0.80 mmol) in dry CH_2Cl_2 (5 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then removed under vacuum and the residue washed with Et_2O (3 x 7 mL). Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a light brown solid (673 mg, 81 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.71-0.85 (m, 2H), 1.01-1.19 (m, 2H), 1.31 (br, 48H), 1.51-1.74 (m, 7H), 3.85 (br, 8H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 79.2 ppm.

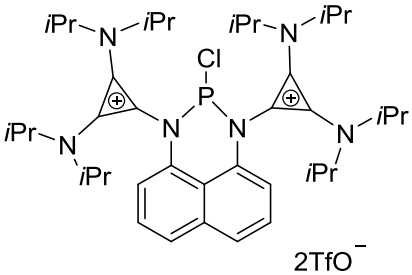
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.3, 22.4, 22.4, 25.8, 26.3 (d, J_{PC} = 12.5 Hz), 27.5, (d, J_{PC} = 18.1 Hz), 37.8 (d, J_{PC} = 11.8 Hz), 53.5, 54.2, 111.6 (d, J_{PC} = 25.3 Hz), 119.6, 121.2, 121.4 (q, J_{FC} = 321.7 Hz), 124.6 (d, J_{PC} = 4.2 Hz), 127.3, 127.5, 133.4, 135.1 ppm.

HRMS *calcd.* for $[C_{47}H_{73}N_6O_3F_3PS]^+$: 889.514910; *found* 889.514330.

Elemental Analisis *calcd* (%). C 55.48; H 7.08; N 8.09; P 2.98; *found* C 55.21; H 7.22; N 7.96; P 2.73.

IR (solid) $\tilde{\nu}$ = 516, 575, 635, 729, 769, 830, 989, 1031, 1143, 1221, 1269, 1348, 1439, 1464, 1528, 1544, 2938, 2978 cm^{-1}.

Compound **14:**



PCl_3 (84 µL, 0.96 mmol) and TMSOTf (346 µL, 1.91 mmol) were added to a solution of compound **8** (500 mg, 0.80 mmol) in dry CH_2Cl_2 (5 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then removed under vacuum and the residue washed with Et_2O (3 x 7

mL). Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a light brown solid (683 mg, 86 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.98 (br, 12H), 1.42 (br, 30H), 1.60 (br, 6H), 3.44 (br, 2H), 3.92 (br, 4H), 4.19 (br, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H) ppm.

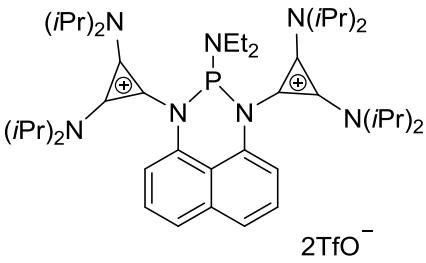
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 84.6 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.0 (bs), 21.7, 22.0, 22.4, 22.8, 49.6, 53.0, 53.4, 55.8, 106.1 (d, J_{PC} = 35.5 Hz), 117.6, 118.1, 121.2 (q, J_{FC} = 321.2), 126.7, 127.6, 128.0, 131.3, 135.4 ppm.

HRMS *calcd.* for $[C_{41}H_{62}N_6O_3ClF_3PS]^+$: 841.398050; *found* 841.397688.

IR(solid) $\tilde{\nu}$ = 451, 635, 762, 822, 972, 1030, 1145, 1255, 1358, 1376, 1448, 1556, 1918, 2940, 2979 cm^{-1}.

Compound **15:**



$N(Et_2)PCl_2$ (139 µL, 0.96 mmol) and TMSOTf (346 µL, 1.91 mmol) were added to a solution of compound **8** (500 mg, 0.80 mmol) in dry CH_2Cl_2 (5 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then evaporated and the residue washed with Et_2O (3 x 7 mL). Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a light brown solid (482 mg, 59 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.78 (t, *J* = 7.0 Hz, 6H), 1.32 (br, 48H), 2.88 (q, *J* = 7.0 Hz, 2H), 2.91 (q, J = 7.0 Hz, 2H), 3.85 (br, 8H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H) ppm.

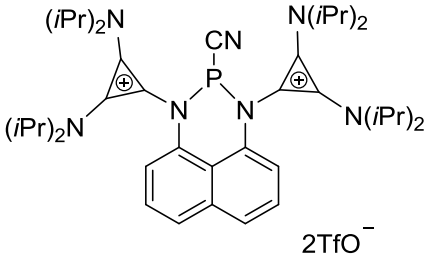
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 69.7 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 14.2 (d, J_{PC} = 3.8 Hz), 22.1, 42.6 (d, J_{PC} = 20.4 Hz), 53.0, 110.0, (d, J_{PC} = 32.3 Hz), 117.7, 118.7, 121.3 (q, J_{FC} = 321.3 Hz), 125.6, 126.1 (d, J_{PC} = 6.1 Hz), 128.1, 134.9, 135.3 ppm.

HRMS *calcd.* for $[C_{45}H_{72}N_7O_3F_3PS]^+$: 878.510159; *found* 878.510500.

IR (solid) $\tilde{\nu}$ = 515, 572, 636, 766, 1029, 1141, 1263, 1351, 1442, 1536, 2937, 2978 cm^{-1}.

Compound **16:**



TMSCN (19 µL, 0.15 mmol) was added to a stirred solution of compound **14** (126 mg, 0.13 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then evaporated and the residue washed with Et_2O (2 x 3 mL) affording the title compound as a light brown solid (102 mg, 82 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.92 (d, *J* = 6.3 Hz, 6H), 0.97 (d, *J* = 6.3 Hz, 6H), 1.42 (d, *J* = 6.3 Hz, 30H), 1.61 (d, *J* = 6.3 Hz, 6H), 3.36 (sept, *J* = 6.3 Hz, 2H), 3.87 (sept, *J* = 6.3 Hz, 4H), 4.23 (sept, *J* = 6.3 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H) ppm.

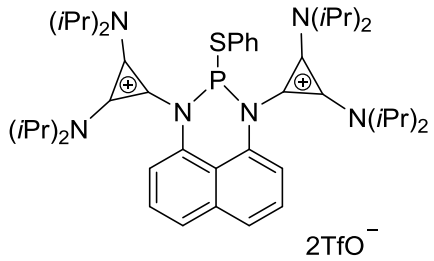
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 16.6 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.6, 20.8, 21.6, 21.8, 22.0, 22.2, 22.5, 23.6, 48.4, 52.3, 54.0, 56.4, 106.6 (d, J_{PC} = 36.9 Hz), 118.2 (d, J_{PC} = 103.5 Hz), 118.4, 119.4, 121.2 (q, J_{FC} = 321.3 Hz), 127.3, 127.5 (d, J_{PC} = 15.1 Hz), 127.6, 133.5, 135.7 ppm.

HRMS *calcd.* for $[C_{42}H_{62}N_7O_3F_3PS]^+$: 832.431908; *found* 832.431720.

IR (solid) $\tilde{\nu}$ = 516, 566, 635, 760, 823, 1029, 1145, 1254, 1355, 1375, 1450, 1465, 1559, 1918, 2882, 2937, 2978 cm^{-1}.

Compound **17:**



TMSSPh (32 µL, 0.17 mmol) was added to a stirred solution of compound **14** (150 mg, 0.15 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then evaporated and the residue washed with Et_2O (2 x 3 mL) affording the title compound as a light brown solid (84 mg, 52 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.27 (br, 48H), 3.75 (br, 8H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.36-7.43 (m, 5H), 7.69 (t, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 2H) ppm.

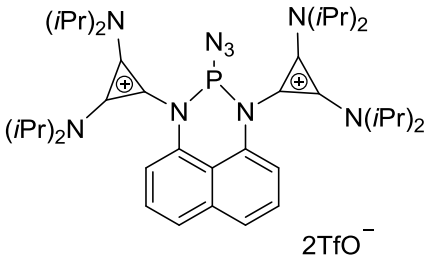
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 91.0 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.1, 53.4 (bs), 108.9 (d, J_{PC} = 29.3 Hz), 119.2, 120.2, 121.3 (q, J_{FC} = 321.3 Hz), 125.5 (bs), 127.0 (d, J_{PC} = 12.1 Hz), 127.2, 127.5, 130.5, 133.4, 135.3, 136.2, 136.2 ppm.

HRMS *calcd.* for $[C_{47}H_{67}N_6O_3F_3PS_2]^+$: 915.440032; *found* 915.439430.

IR (solid) $\tilde{\nu}$ = 517, 636, 752, 824, 1029, 1143, 1261, 1353, 1376, 1441, 1543, 2976 cm^{-1}.

Compound **18:**



$TMSN_3$ (24 µL, 0.18 mmol) was added to a stirred solution of compound **14** (150 mg, 0.15 mmol) in dry CH_2Cl_2 (1 mL) and the resulting mixture was stirred at room temperature for 3 days. The solvent was then evaporated and the residue washed with Et_2O (2 x 3 mL) affording the title compound as a light brown solid (111 mg, 74 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.97 (br, 12H), 1.43 (br, 36H), 3.40 (br, 2H), 3.90 (br, 4H), 4.19 (br, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.63 (t, *J* = 7.9 Hz. 2H), 7.81 (d, *J* = 7.9 Hz, 2H) ppm.

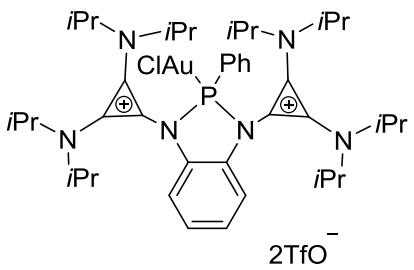
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 74.0 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.0 (bs), 22.4, 56.1, 107.2 (d, J_{PC} = 34.2 Hz), 117.6, 118.2, 121.3 (q, J_{FC} = 320.5 Hz), 126.6 – 128.5 (br), 126.7, 127.6, 131.8, 135.4 ppm.

HRMS *calcd.* for $[C_{41}H_{62}N_9O_3F_3PS]^+$: 848.438056; *found* 848.437900.

IR (solid) $\tilde{\nu}$ = 516, 635, 765, 825, 1030, 1135, 1256, 1345, 1376, 1451, 1550, 1921, 2120, 2361, 2981 cm^{-1}

Compound **19:**



$[AuCl(SMe_2)]$ (29 mg, 0.10 mmol) was added to a solution of compound **10** (95 mg, 0.10 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 (113 mg, 96 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.43 (br, 6H), 0.99 (br, 6H), 1.06 (br, 6H), 1.25-1.61 (m, 30H), 3.47 (br, 2H), 3.82 (br, 2H), 4.07 (br, 2H), 4.19 (br, 2H), 7.27 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.52 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.60 (td, *J* = 7.8, 3.3 Hz, 2H), 7.81 (t, *J* = 7.8 Hz, 1H), 8.01 (dd, *J* = 16.1, 7.8 Hz, 2H) ppm.

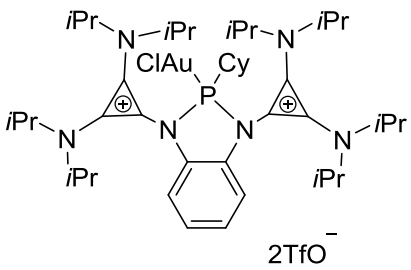
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 100.1 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.2, 21.4, 21.6, 22.3, 22.8, 25.4, 49.1, 49.4, 57.6, 58.2, 97.9 (d, J_{PC} = 14.8 Hz), 115.5, 121.3 (q, J_{FC} = 321.2 Hz), 125.9, 130.9 (d, J_{PC} = 14.2 Hz), 132.6 (d, J_{PC} = 2.9 Hz), 133.4 (d, J_{PC} = 21.6 Hz), 135.6 (d, J_{PC} = 59.4 Hz), 135.6, 137.7 ppm.

HRMS *calcd.* for $[C_{43}H_{65}N_6O_3AuClF_3PS]^+$: 1065.387715; *found* 1065.388470.

IR (solid) $\tilde{\nu}$ = 516, 594, 636, 756, 922, 1029, 1106, 1143, 1200, 1222, 1259, 1351, 1376, 1454, 1577, 1901, 2980 cm^{-1}.

Compound **20:**



[AuCl(SMe$_2$)] (30 mg, 0.10 mmol) was added to a solution of compound **11** (100 mg, 0.10 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 (120 mg, 97 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.08-1.35 (m, 5H), 1.46 (d, *J* = 6.7 Hz, 48H), 1.69-1.78 (m, 1H), 1.82-1.91 (m, 2H), 1.99-2.10 (m, 2H), 2.30-2.41 (m, 1H), 4.04 (br, 8H), 7.29 (dd, *J* = 5.8, 3.2 Hz, 2H), 7.41 (dd, *J* = 5.8, 3.2 Hz, 2H) ppm.

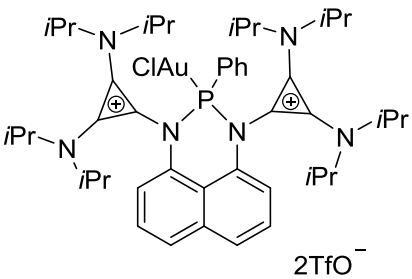
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 127.1 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.2, 22.4, 22.5, 25.6, 26.2 (d, J_{PC} = 16.1 Hz), 26.7, 49.2 (d, J_{PC} = 30.1 Hz), 54.3, 101.9 d (J_{PC} = 9.1 Hz), 116.6, 121.3 d (J_{FC} = 321.3 Hz), 126.8, 134.8, 134.8 ppm.

HRMS *calcd.* for $[C_{43}H_{71}N_6O_3AuClF_3PS]^+$: 1071.434666; *found* 1071.435150.

IR (solid) $\tilde{\nu}$ = 516, 594, 635, 758, 919, 1029, 1144, 1194, 1221, 1261, 1346, 1375, 1449, 1571, 1892, 2937, 2980 cm^{-1}.

Compound **21:**



[AuCl(SMe$_2$)] (57 mg, 0.19 mmol) was added to a solution of compound **12** (200 mg, 0.19 mmol) in dry CH_2Cl_2 (2 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 (231 mg, 94 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.90 (d, *J* = 6.8 Hz, 6H), 1.01 (d, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H), 1.32 (d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.48 (d, *J* = 6.8 Hz, 18H), 3.54 (sept, *J* = 6.8 Hz, 2H), 3.69 (sept, *J* = 6.8 Hz, 2H), 4.08 (sept, *J* = 6.8 Hz, 2H), 4.28 (sept, *J* = 6.8 Hz, 2H), 7.43 (td, *J* = 7.9, 3.7 Hz, 2H), 7.55 (dd, *J* = 15.9, 7.9 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 77.1 ppm.

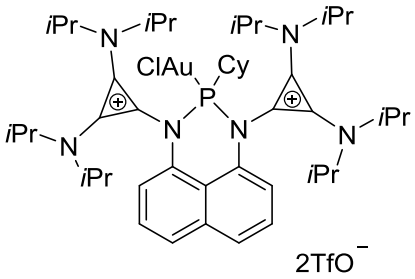
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.3, 21.0, 21.6, 21.7, 22.7, 22.8, 23.1, 25.0, 49.5, 53.8, 55.3, 57.4, 102.9 (d, J_{PC} = 16.0 Hz), 116.1, 119.2, 121.4 (q, J_{FC} = 321.0 Hz), 127.1, 129.1, 130.7 (d, J_{PC} = 14.3 Hz), 131.3 (d, J_{PC} = 3.9 Hz), 131.5 (d, J_{PC} = 1.5 Hz), 132.3, 132.6 (d, J_{PC} = 20.3 Hz), 132.9, 134.5 (d, J_{PC} = 1.9 Hz), 135.6, 136.1 (d, J_{PC} = 2.4 Hz) ppm.

HRMS *calcd.* for $[C_{47}H_{67}N_6O_3AuClF_3PS]^+$: 1115.403366; *found* 1115.402800.

Elemental Analisis *calcd* (%). C 45.55; H 5.34; N 6.64; P 2.45; *found* C 45.02; H 5.24; N 6.35; P 2.62.

IR (solid) $\tilde{\nu}$ = 515, 596, 636, 709, 754, 822, 1029, 1141, 1222, 1258, 1348, 1376, 1449, 1570, 1895, 2937, 2980 cm^{-1}.

Compound **22:**



[AuCl(SMe_2)] (57 mg, 0.19 mmol) was added to a solution of compound **13** (200 mg, 0.19 mmol) in dry CH_2Cl_2 (2 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solvent was then evaporated affording the desired product as a light brown solid (245 mg, 91 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.86 (d, *J* = 6.2 Hz, 6H), 1.06 (d, *J* = 6.2 Hz, 6H), 1.10-1.34 (m, 5H), 1.37-1.45 (m, 12H), 1.56 (d, *J* = 6.2 Hz, 12H), 1.61 (d, *J* = 6.2 Hz, 12H), 1.75-1.89 (m, 5H), 2.19-2.34 (m, 1H), 3.28 (sept, *J* = 6.2 Hz, 2H), 4.13 (sept, *J* = 6.2 Hz, 2H), 4.34 (bs, 4H), 7.77 (t, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 2H) ppm.

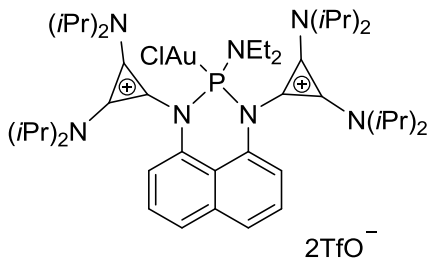
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 97.5 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.4, 21.6, 22.2, 22.5, 23.4, 23.9, 25.1, 25.9 (d, J_{PC} = 17.2 Hz), 27.0 (d, J_{PC} = 3.6 Hz), 40.8 (d, J_{PC} = 46.2 Hz), 53.1, 54.0, 54.2, 56.0, 106.5 (d, J_{PC} = 10.8Hz), 117.7 (d, J_{PC} = 2.8Hz), 121.4 (q, J_{FC} = 321.3 Hz), 122.1 (d, J_{PC} = 1.7 Hz), 128.2, 128.8, 130.5, 131.8, 135.3 ppm.

HRMS *calcd.* for [$C_{47}H_{73}N_6O_3AuF_3PS_1$]: 1121.450865; *found* 1121.449140.

IR (solid) $\tilde{\nu}$ = 516, 635, 759, 826, 992, 1029, 1143, 1222, 1258, 1350, 1376, 1441, 1536, 1571, 1894, 2936, 2979 cm^{-1}.

Compound **23:**



[AuCl(SMe_2)] (25 mg, 0.09 mmol) was added to a solution of compound **15** (89 mg, 0.09 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 and the residue washed with Et_2O. The desired product was isolated as a light brown solid (94 mg, 86 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.85 (d, *J* = 6.8 Hz, 6H), 0.91 (t, *J* = 7.0 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.46 (d, *J* = 6.8 Hz, 6H), 1.51-1.59 (m, 24H), 3.22 (overlap of two quartets, *J* = 7.0 Hz, 4H), 3.56 (sept, *J* = 6.8 Hz, 2H), 4.12 (bs, 4H), 4.24 (sept, *J* = 6.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.8 Hz, 2H) ppm.

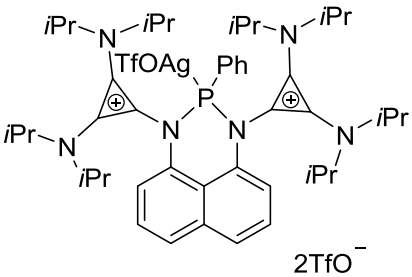
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 79.1 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 13.7 (d, J_{PC} = 3.0 Hz), 20.8, 21.3, 22.1, 22.5, 23.4, 24.4, 42.4 (d, J_{PC} = 9.4 Hz), 51.4, 56.2, 104.6 (d, J_{PC} = 17.1 Hz), 118.9, 121.3 (q, J_{FC} = 322.5 Hz), 126.7, 129.1, 130.5 (d, J_{PC} = 5.2 Hz), 132.6, 132.8, 135.3 ppm.

HRMS *calcd.* for [$C_{45}H_{72}N_7O_3AuClF_3PS$]$^+$: 1110.445564; *found* 1110.446680.

IR (solid) $\tilde{\nu}$ = 516, 636, 799, 821, 1029, 1147, 1260, 1353, 1377, 1447, 1565, 1890, 2973 cm^{-1}.

Compound **24:**



AgOTf (25 mg, 0.09 mmol) was added to a solution of compound **12** (100 mg, 0.09 mmol) in dry CH_2Cl_2 (2 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then evaporated affording the desired product as a white solid (121 mg, 97 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.63-1.07 (m, 18H), 1.42 (br, 30H), 3.22 (br, 2H), 3.70 (br, 2H), 4.03 (br, 2H), 4.25 (br, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 7.38 (td, *J* = 8.1, 2.7 Hz, 2H), 7.52-7.63 (m, 3H), 7.71 (t, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H) ppm.

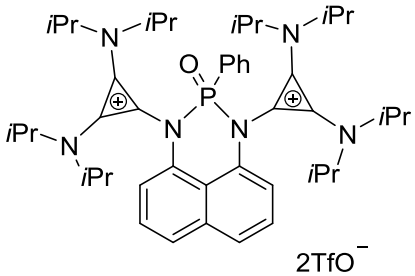
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 69.1 (d, *J* = 715.8 Hz) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 19.9, 21.2, 21.5, 22.4, 23.1, 23.7, 48.5, 52.3, 55.2, 57.8, 101.8 (d, J_{PC} = 21.6 Hz), 116.3, 116.5, 120.9 (q, J_{FC} = 319.7 Hz), 126.4, 128.4, 130.5 (d, J_{PC} = 13.2 Hz), 132.6, 132.6, 132.9, 133.9 (d, J_{PC} = 20.9 Hz), 135.3, 136.0 ppm.

HRMS *calcd.* for $[C_{48}H_{67}N_6O_6AgF_6PS]^+$: 1139.324956; *found* 1139.325840.

IR (solid) $\tilde{\nu}$ =515, 594, 635, 795, 1020, 1071, 1095, 1150, 1222, 1259, 1347, 1377, 1450, 1569, 1896, 2963 cm^{-1}.

Compound **25:**



m-CPBA (43 mg, 0.19 mmol) was added to a solution of compound **12** (200 mg, 0.19 mmol) in dry CH_2Cl_2 (2 mL) and the resulting mixture was stirred at room temperature for 4 hours. The solvent was then evaporated and the residue washed with Et_2O (3 x 4 mL) affording the desired product (186 mg, 92 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.77 (br, 6H), 0.90 (br, 12H), 1.27-1.52 (m, 30H), 3.32 (br, 2H), 3.70 (br, 2H), 4.00 (br, 2H), 4.25 (br, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.39-7.46 (m, 2H), 7.54 (dd, *J* = 14.1, 7.7 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H) ppm.

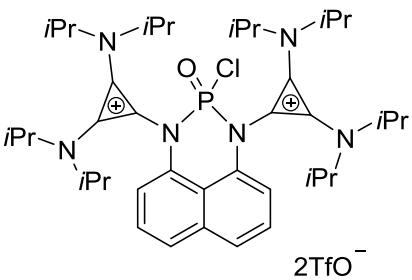
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = -0.1 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.5, 21.3, 21.7, 22.4, 49.2, 53.0, 54.7, 57.4, 100.2 (d, J_{PC} = 4.7 Hz), 115.2, 116.7 (d, J_{PC} = 4.3 Hz), 121.4 (q, J_{FC} = 321.2 Hz), 126.2, 129.0, 129.2, 130.2 (d, J_{PC} = 15.2 Hz), 130.8, 131.3 (d, J_{PC} = 10.6 Hz), 133.0, 133.5 (d, J_{PC} = 1.9 Hz), 134.4, 135.2 (d, J_{PC} = 2.9 Hz), 135.8 ppm.

HRMS *calcd.* for $[C_{47}H_{67}N_6O_4F_3PS]^+$: 899.462875; *found* 899.462410.

IR (solid) $\tilde{\nu}$ = 516, 573, 636, 713, 754, 823, 994, 1029, 1065, 1139, 1222, 1258, 1348, 1377, 1449, 1567, 1901, 2941, 2980 cm^{-1}.

Compound **26:**



$POCl_3$ (36 µL, 0.38 mmol) and TMSOTf (139 µL, 0.77 mmol) were added to a solution of compound **8** (200 mg, 0.32 mmol) in dry CH_2Cl_2 (2 mL) and the resulting mixture was stirred at room temperature for 16 hours. The solvent was then evaporated and the residue washed with Et_2O (3 x 3 mL).

Recrystallization from CH_2Cl_2/Et_2O gave the title compound as a light brown solid (259 mg, 81 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.92 (d, *J* = 6.7 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.37 (d, *J* = 6.7 Hz, 6H), 1.42 (d, *J* = 6.7 Hz, 6H), 1.45-1.82 (m, 18H), 1.54 (d, *J* = 6.7 Hz, 6H), 3.72 (sept, *J* = 6.7 Hz, 2H), 3.93 (sept, *J* = 6.7 Hz, 2H), 4.11 (sept, *J* = 6.7 Hz, 2H), 4.31 (sept, *J* = 6.7 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 2H) ppm.

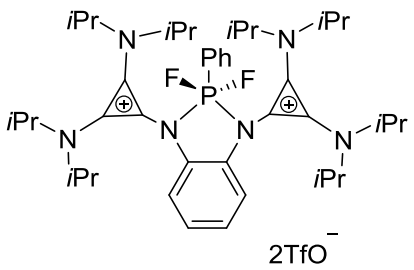
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = -8.9 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.1, 21.1, 21.4, 21.9, 21.99, 22.2, 22.4, 22.9, 48.7, 52.9, 55.6, 58.0, 97.2 (d, J_{PC} = 3.7 Hz), 115.7 (d, J_{PC} = 3.9 Hz), 117.2 (d, J_{PC} = 5.8 Hz), 121.4 (q, J_{FC} = 321.1 Hz), 126.8, 129.0, 132.0, 133.1 (d, J_{PC} = 4.6 Hz), 134.7, 135.9 ppm.

HRMS *calcd.* for $[C_{41}H_{62}N_6O_4ClF_3PS]^+$: 857.392603; *found* 857.392260.

IR (solid) $\tilde{\nu}$ = 516, 599, 636, 765, 829, 1009, 1030, 1077, 1146, 1224, 1260, 1348, 1377, 1449, 1575, 1907, 2941, 2984 cm^{-1}.

Compound **27:**



XeF_2 (30 mg, 0.18 mmol) was added to a stirred solution of compound **10** (160, 0.16 mmol) in dry CH_2Cl_2 (1 mL) in a glovebox and the resulting mixture was stirred at room temperature for 20 minutes. Et_2O (0.5 mL) was then slowly added to the CH_2Cl_2 solution, causing precipitation of the crude product. After filtration, the solid was recrystallized from CH_2Cl_2/Et_2O, affording the title compound as a white microcrystalline solid (74 mg, 45 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.20 (br, 48H), 3.87 (br, 8H), 7.16-7.24 (m, 4H), 7.50-7.59 (m, 2H), 7.65-7.74 (m, 3H) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = -49.8 (t, J_{PF} = 940.4 Hz) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.6, 53.8, 54.0, 54.3, 103.4, 113.3 (d, J_{PC} = 7.1 Hz), 121.5 (q, J_{FC} = 321.2 Hz), 124.7, 128.7 (d, J_{PC} = 14.9 Hz), 130.0 (d, J_{PC} = 19.8 Hz), 131.3 (d, J_{PC} = 12.9 Hz), 132.3 (dt, J_{PC} = 236.1 Hz, J_{FC} = 25.5 Hz), 133.1, 135.1 (d, J_{PC} = 3.9 Hz) ppm.

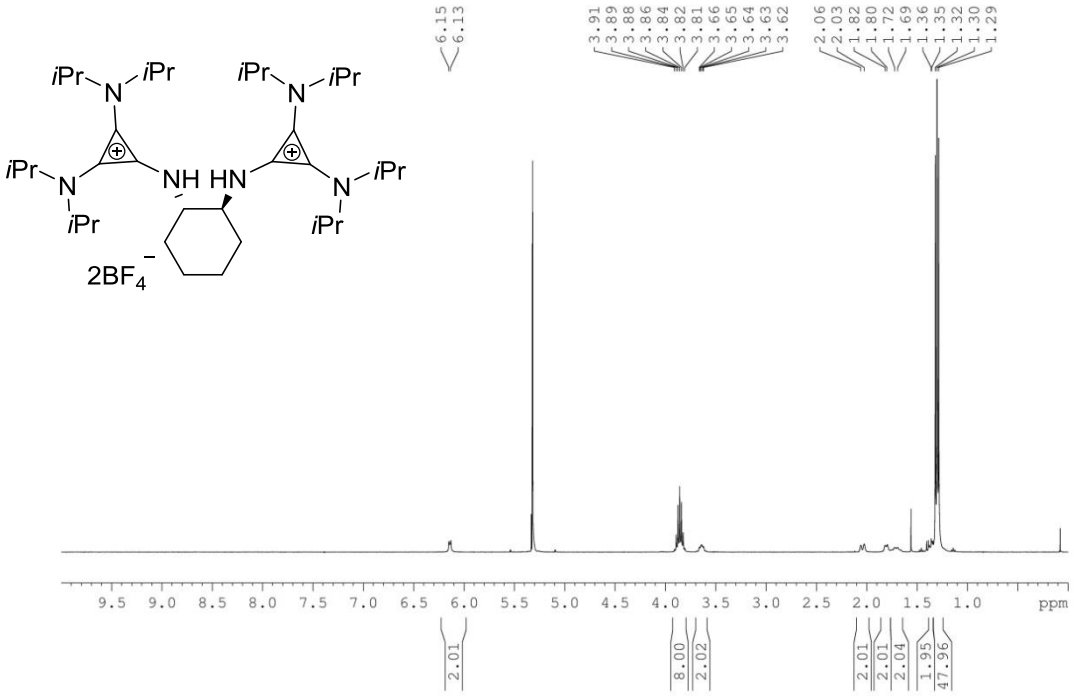
^{19}F NMR (282 MHz, CD_2Cl_2) δ = -78.8, -34.3 (d, J_{PF} = 940.4 Hz) ppm.

HRMS *calcd.* for $[C_{43}H_{65}N_6O_3F_5PS]^+$: 871.449117; *found* 871.449530.

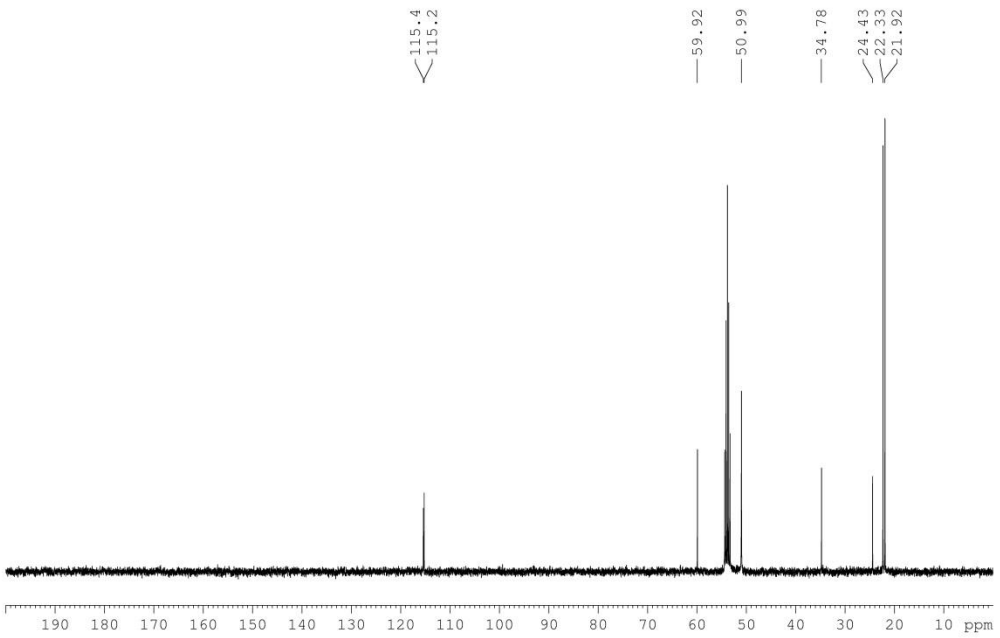
IR (solid) $\tilde{\nu}$ = 516, 530, 563, 600, 636, 729, 752, 815, 886, 941, 1029, 1135, 1222, 1262, 1347, 1455, 1497, 1568, 1905, 2940, 2980 cm^{-1}.

NMR spectra

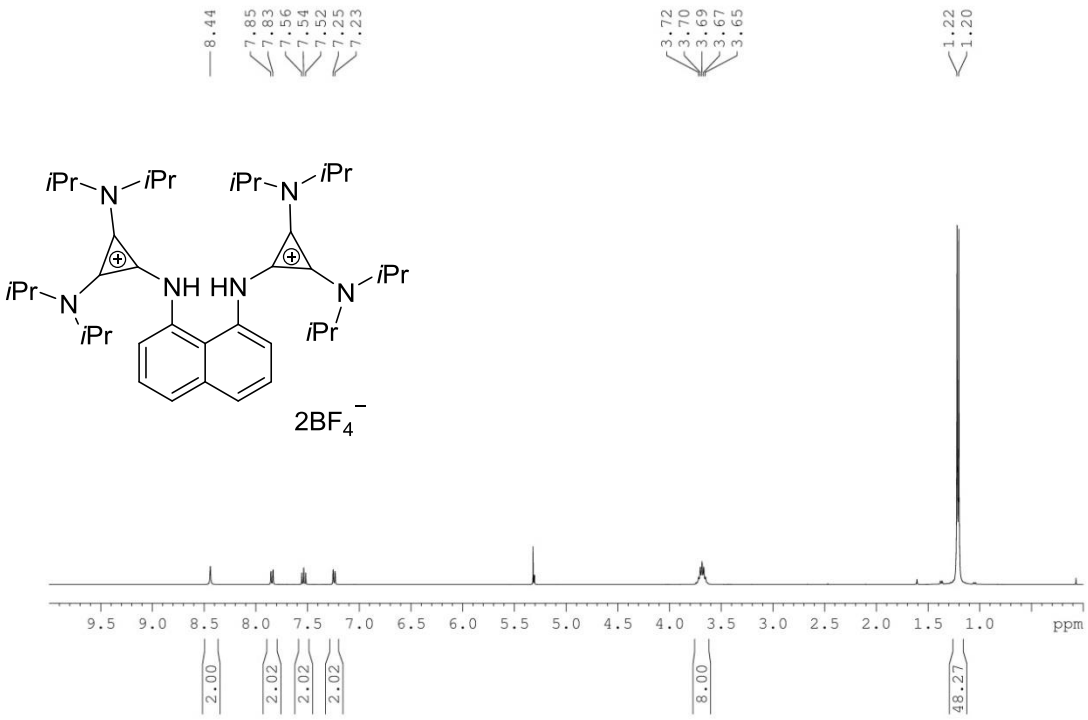
^{1}H NMR (400 MHz, CD_2Cl_2) **4**



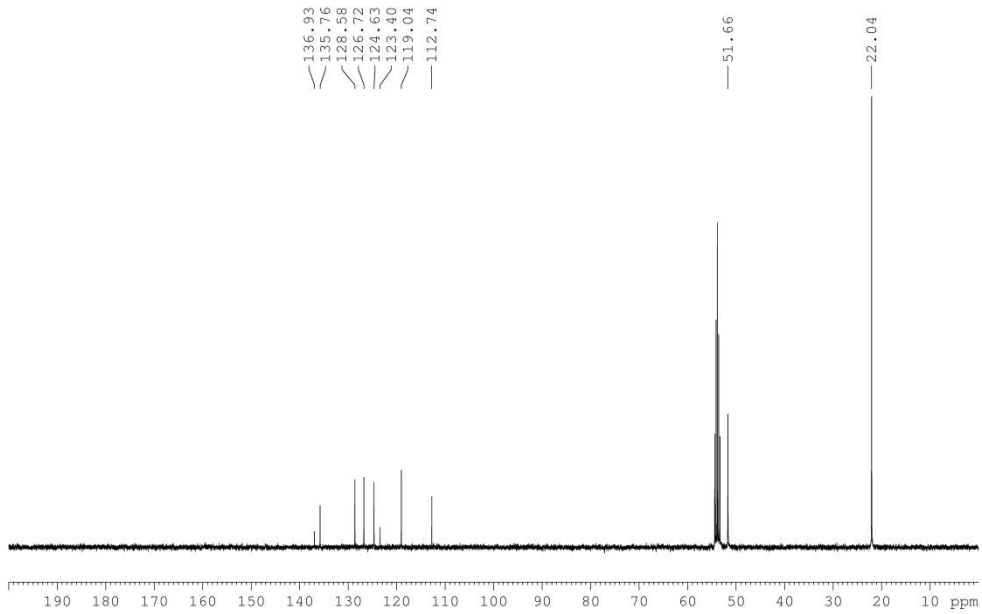
^{13}C NMR (101 MHz, CD_2Cl_2) **4**



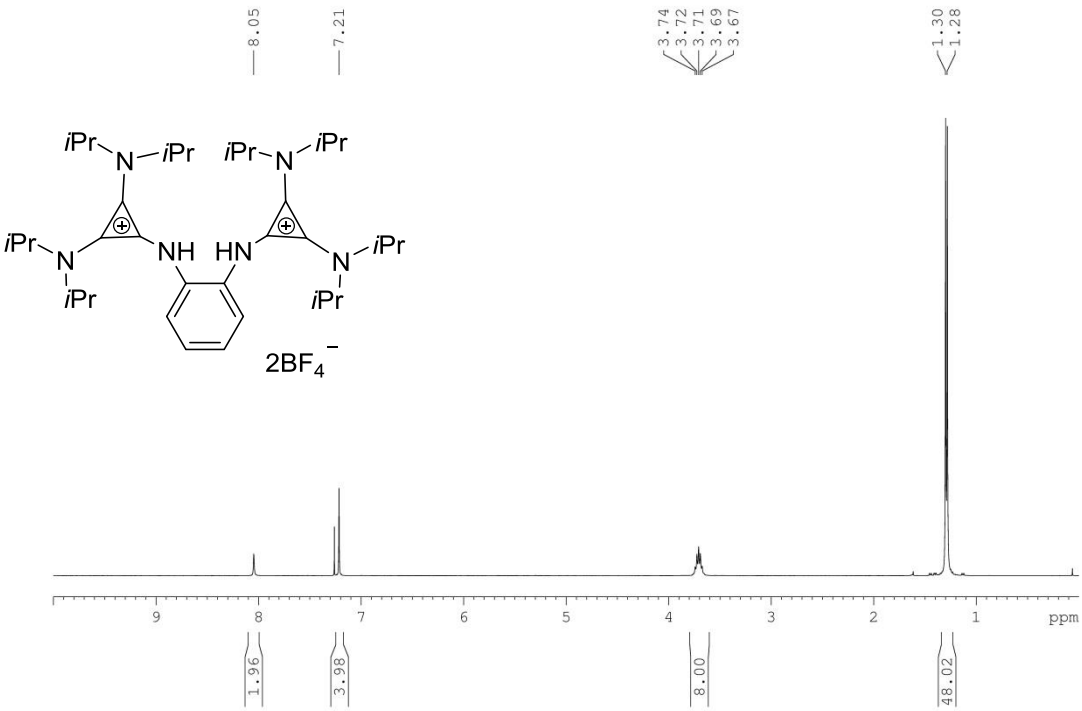
^{1}H NMR (400 MHz, CD_2Cl_2) **5**



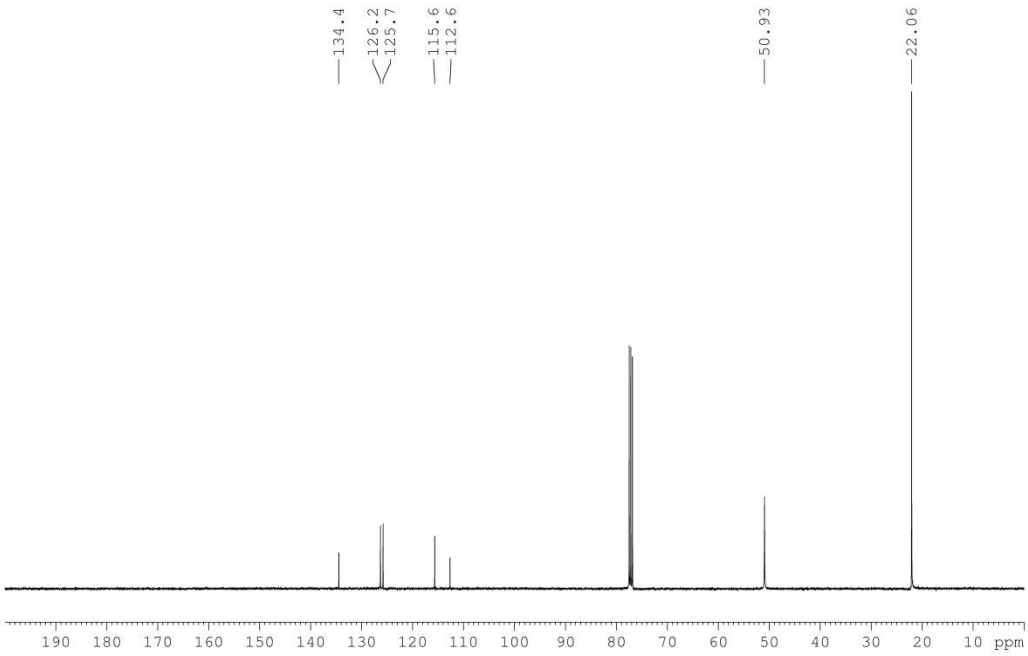
^{13}C NMR (101 MHz, CD_2Cl_2) **5**



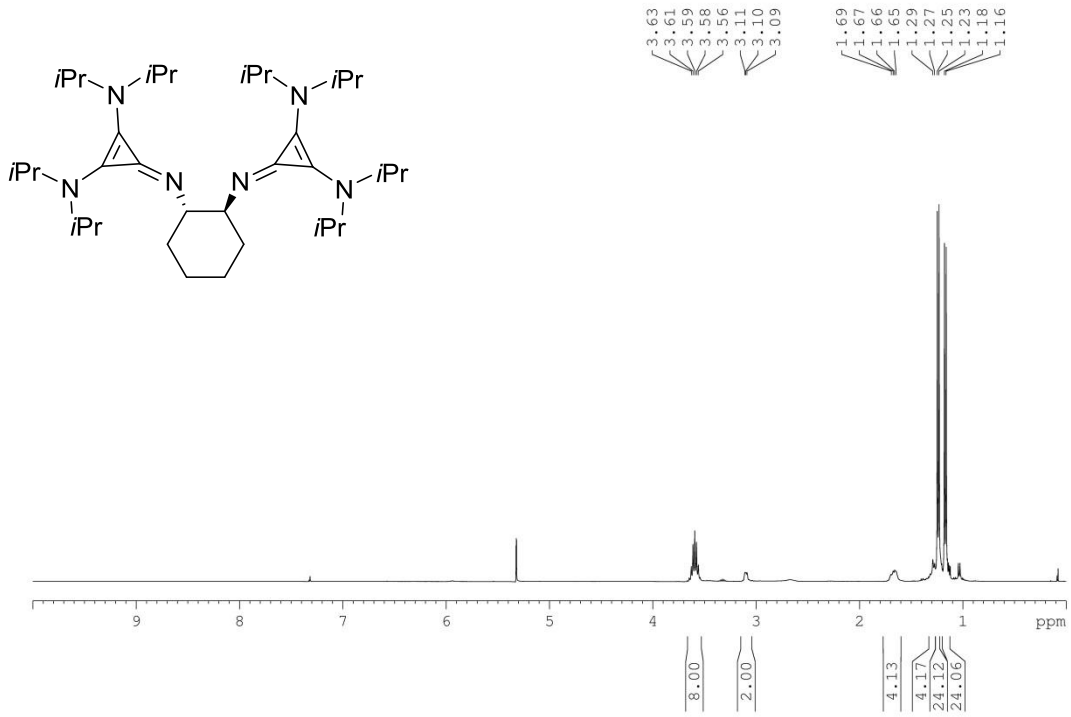
^{1}H NMR (400 MHz, CD_2Cl_2) **6**



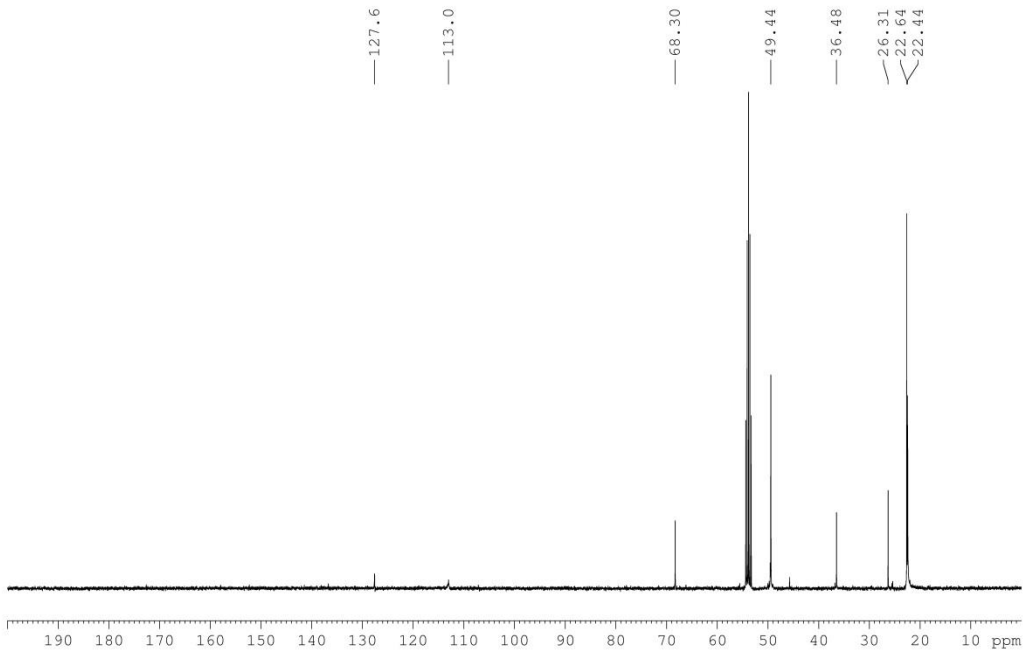
^{13}C NMR (101 MHz, CD_2Cl_2) **6**



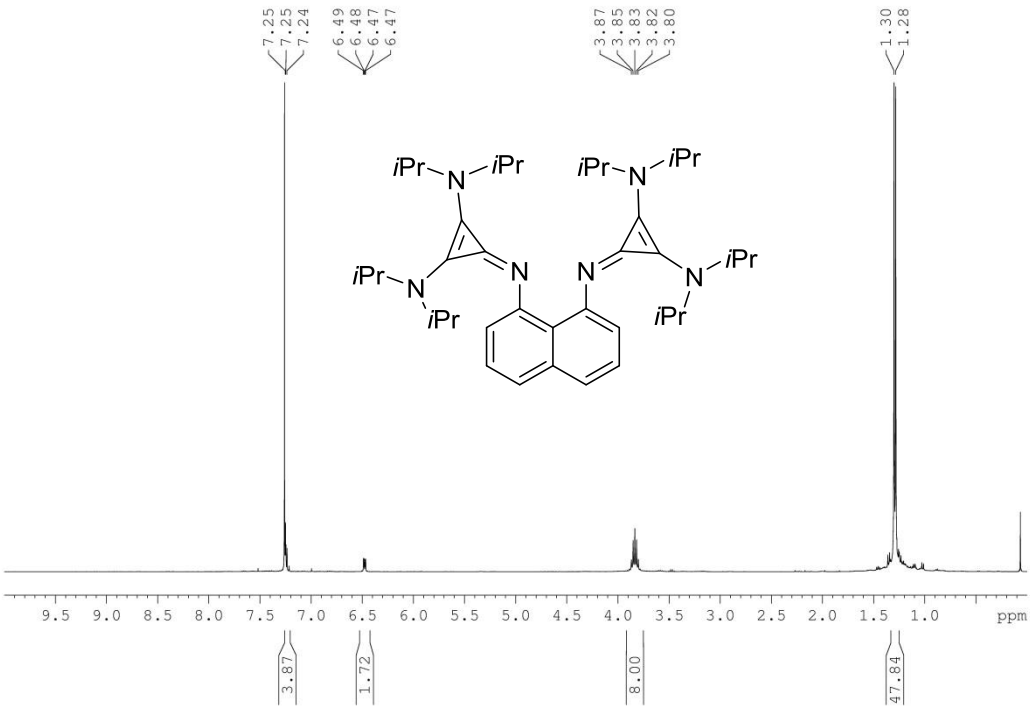
^{1}H NMR (400 MHz, CD_2Cl_2) **7**



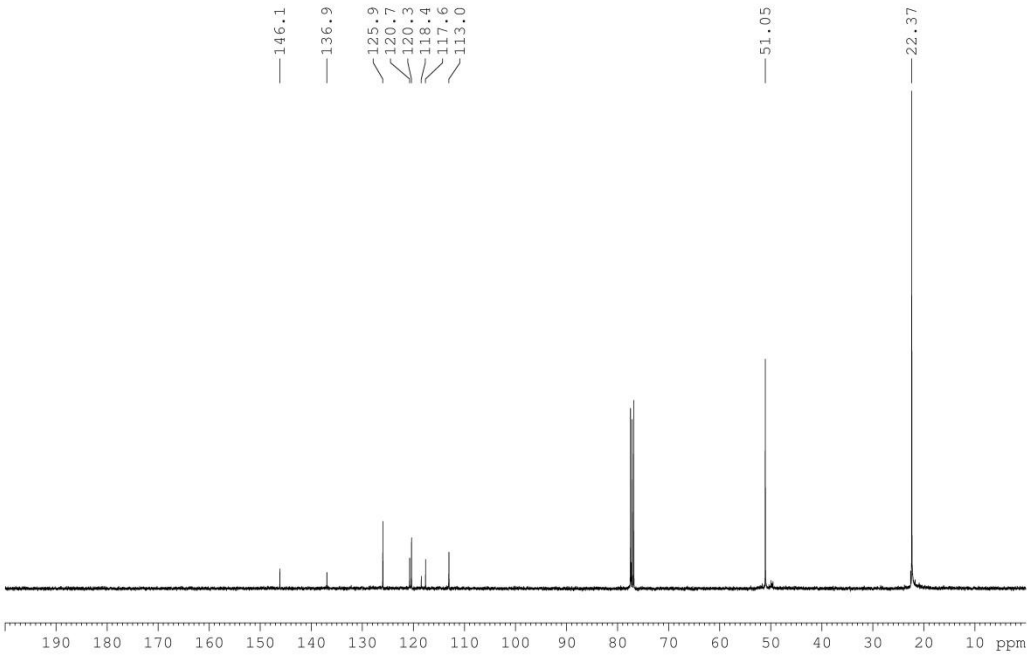
^{13}C NMR (101 MHz, CD_2Cl_2) **7**



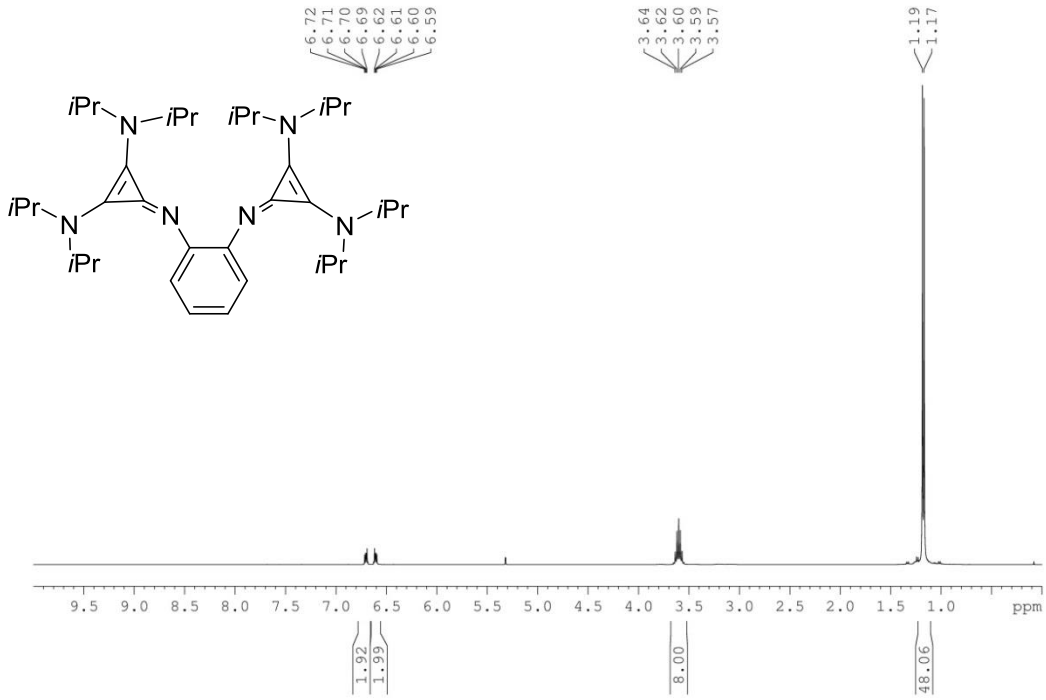
^{1}H NMR (400 MHz, $CDCl_3$) **8**



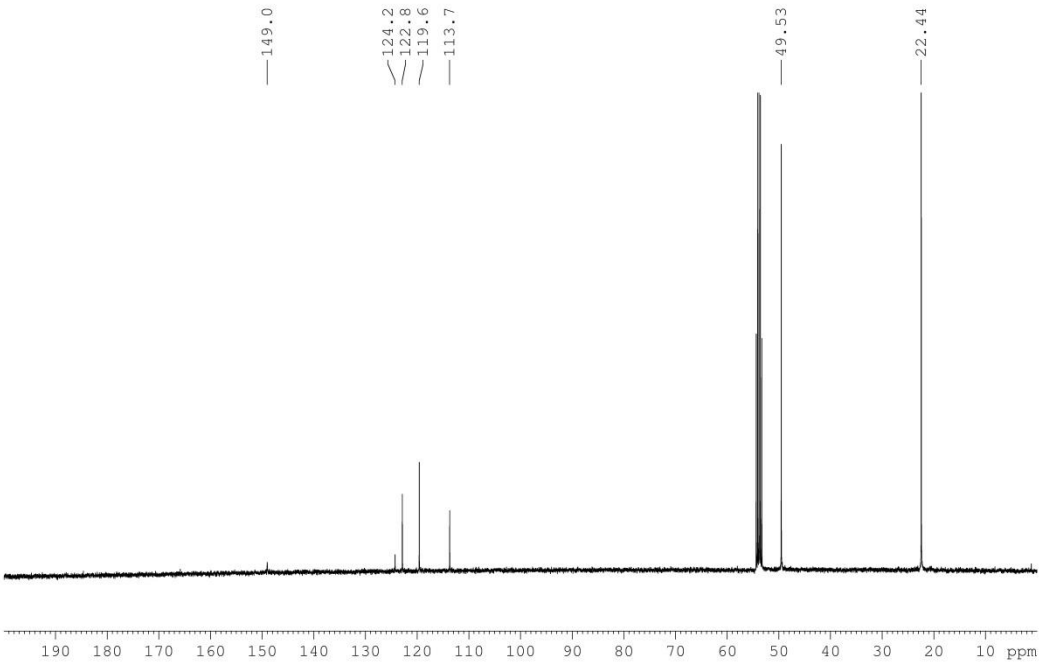
^{13}C NMR (101 MHz, $CDCl_3$) **8**



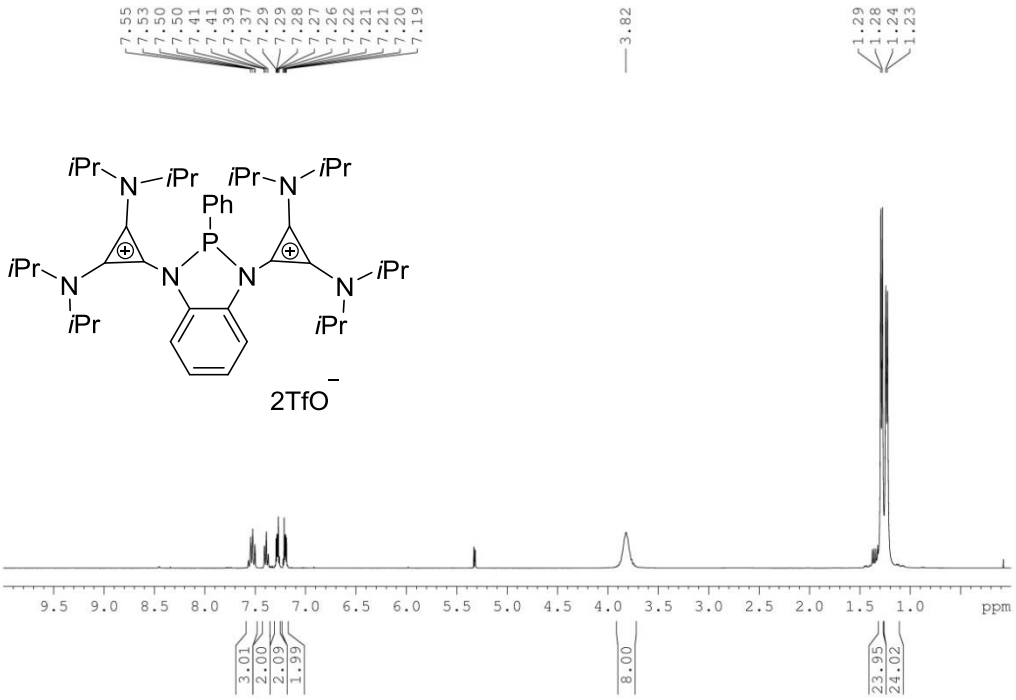
^{1}H NMR (400 MHz, CD_2Cl_2) **9**



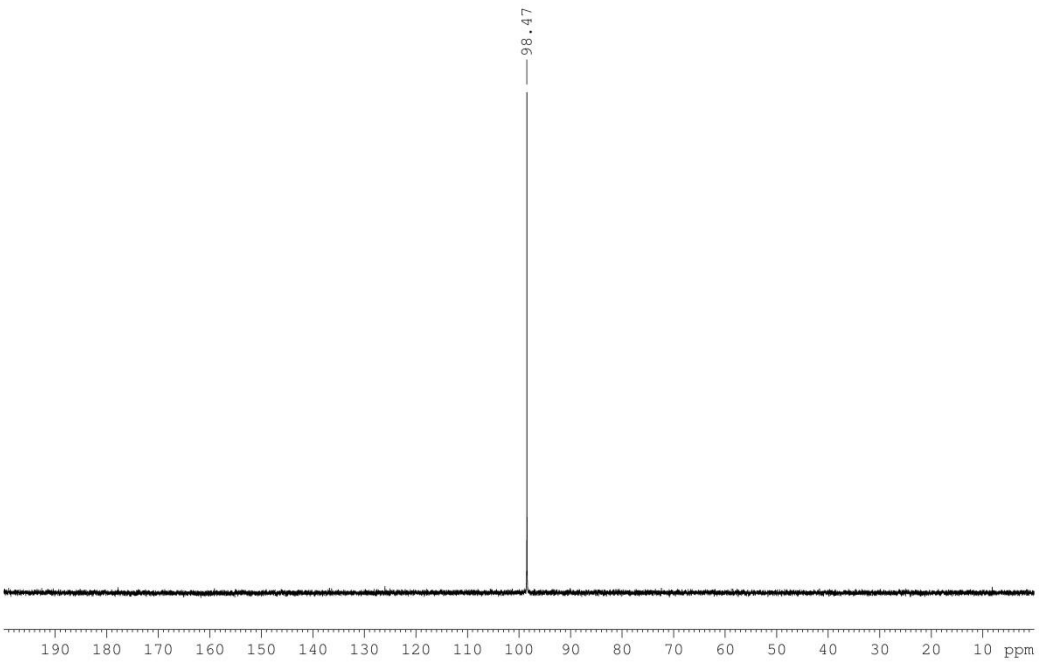
^{13}C NMR (101 MHz, CD_2Cl_2) **9**



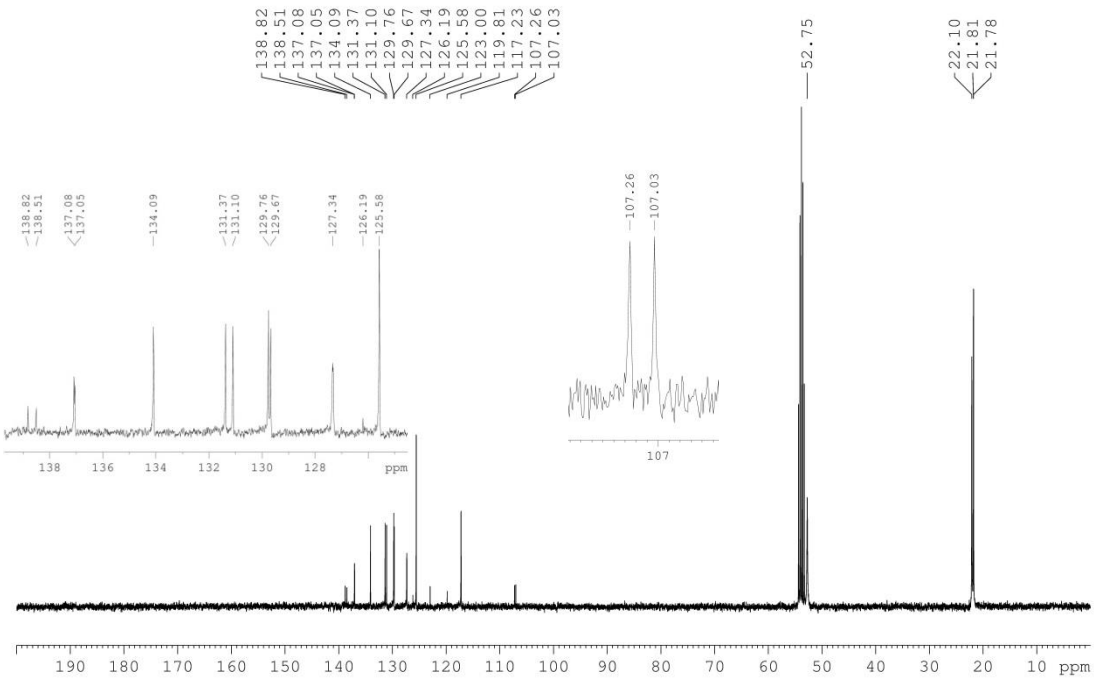
^{1}H NMR (400 MHz, CD_2Cl_2) **10**



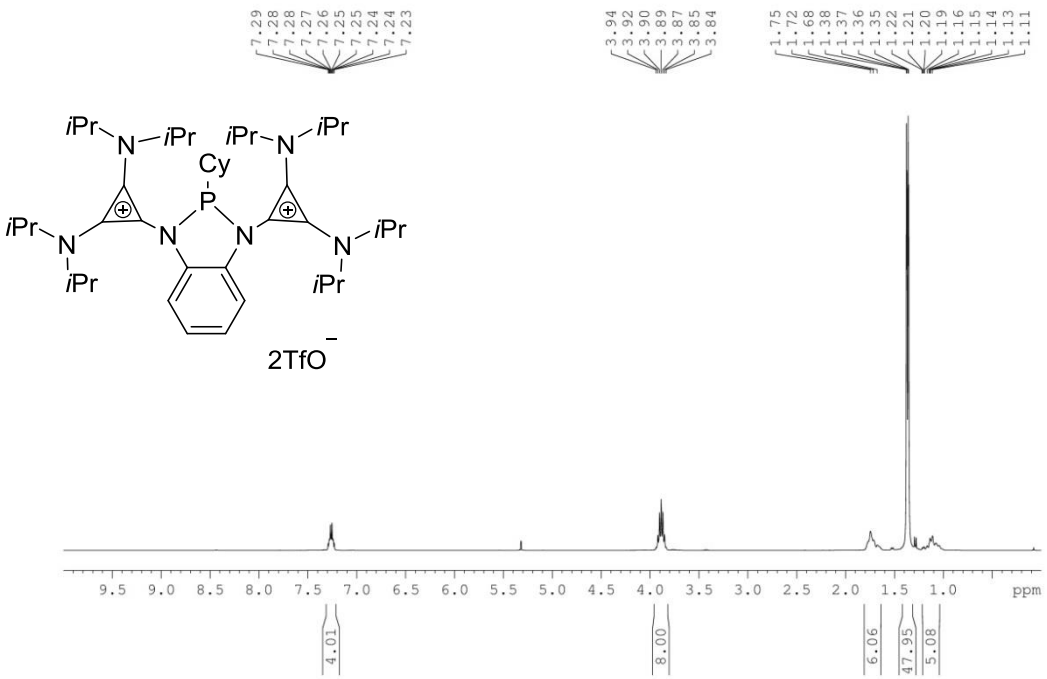
^{31}P NMR (162 MHz, CD_2Cl_2) **10**



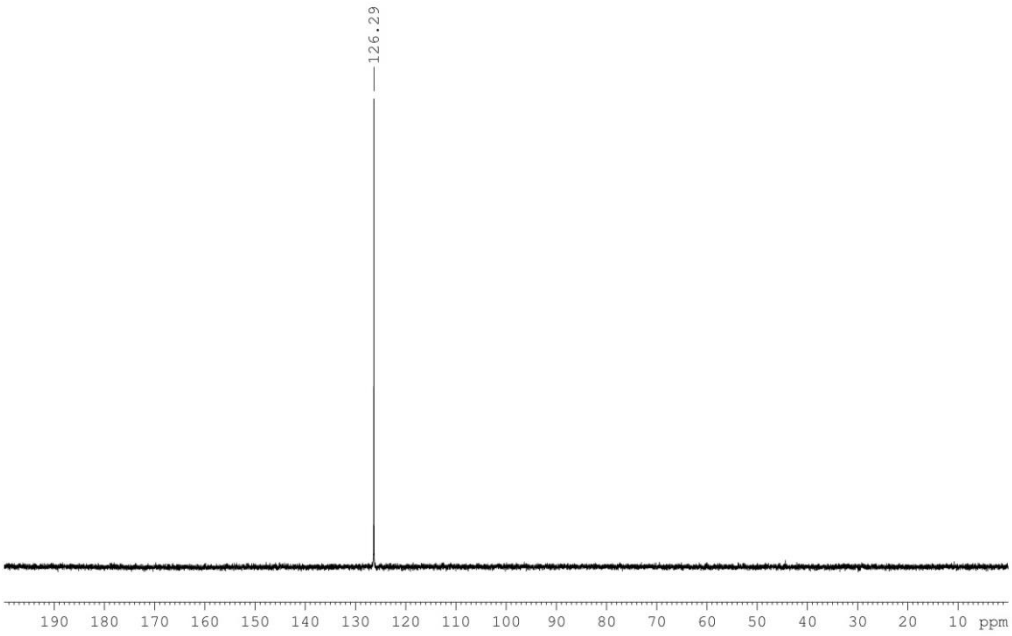
^{13}C NMR (101 MHz, CD_2Cl_2) **10**



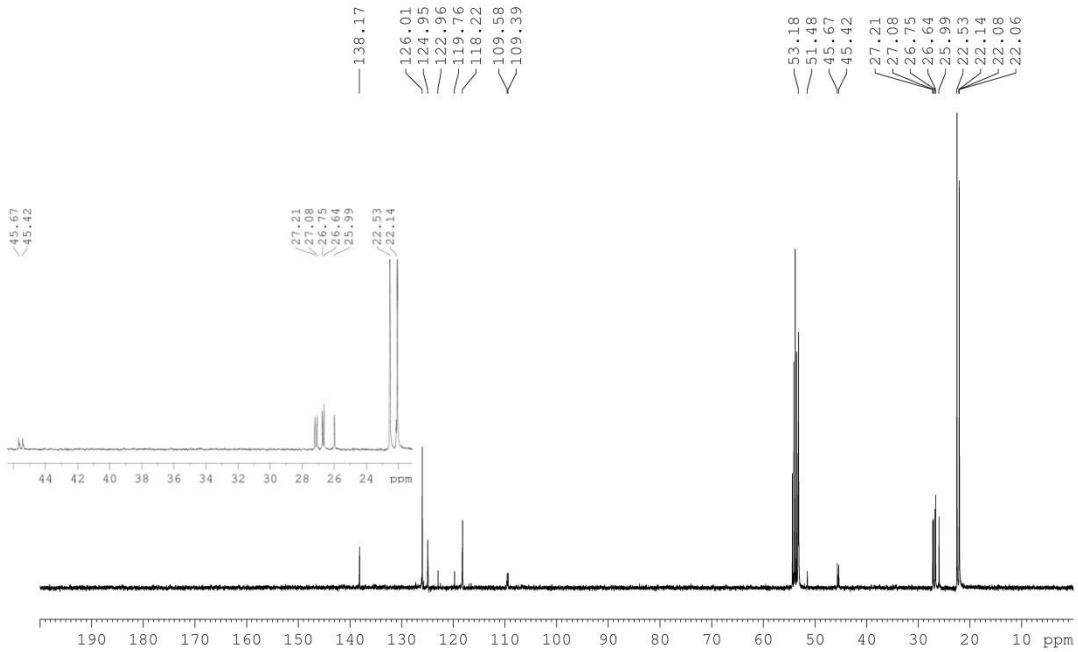
^{1}H NMR (400 MHz, CD_2Cl_2) **11**



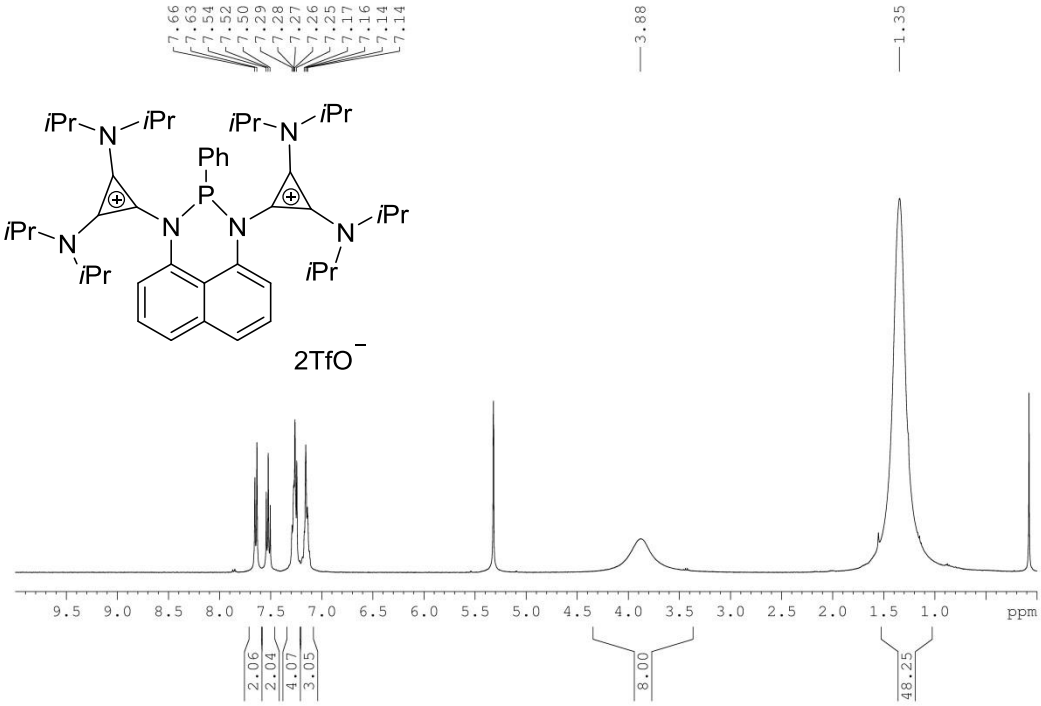
^{31}P NMR (162 MHz, CD_2Cl_2) **11**



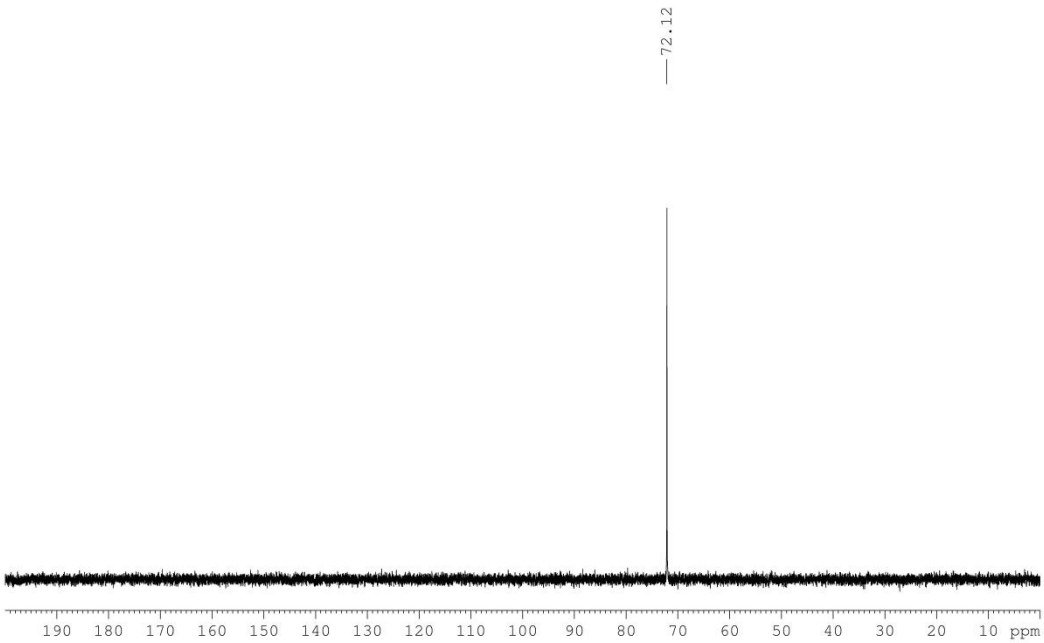
^{13}C NMR (101 MHz, CD_2Cl_2) **11**



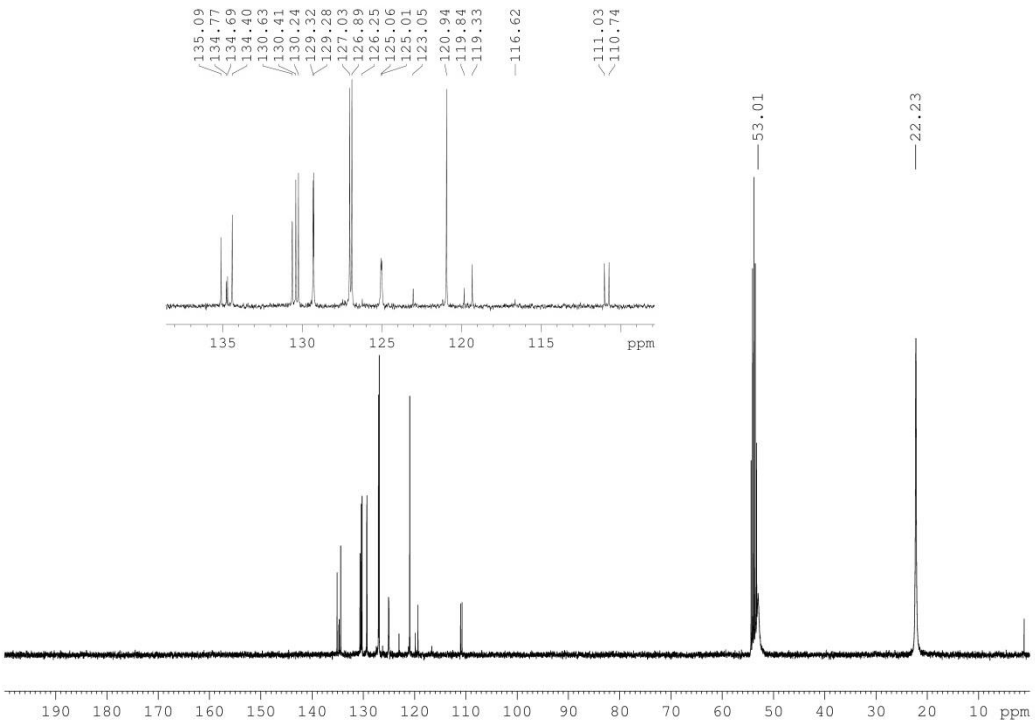
^{1}H NMR (400 MHz, CD_2Cl_2) **12**



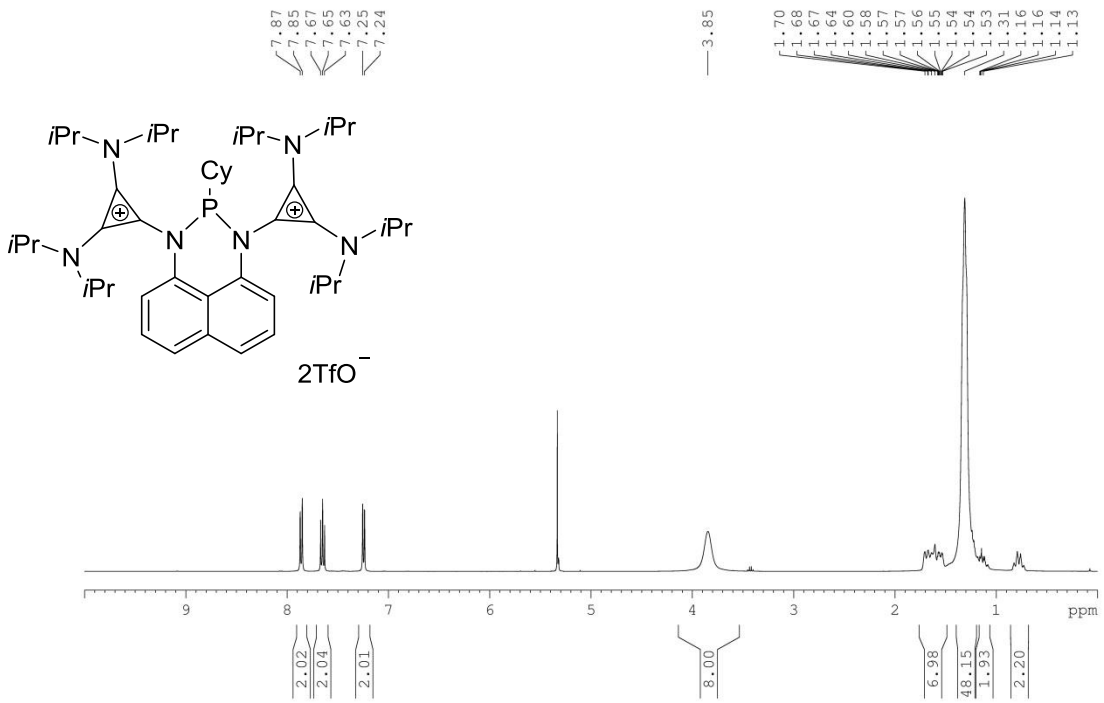
^{31}P NMR (162 MHz, CD_2Cl_2) **12**



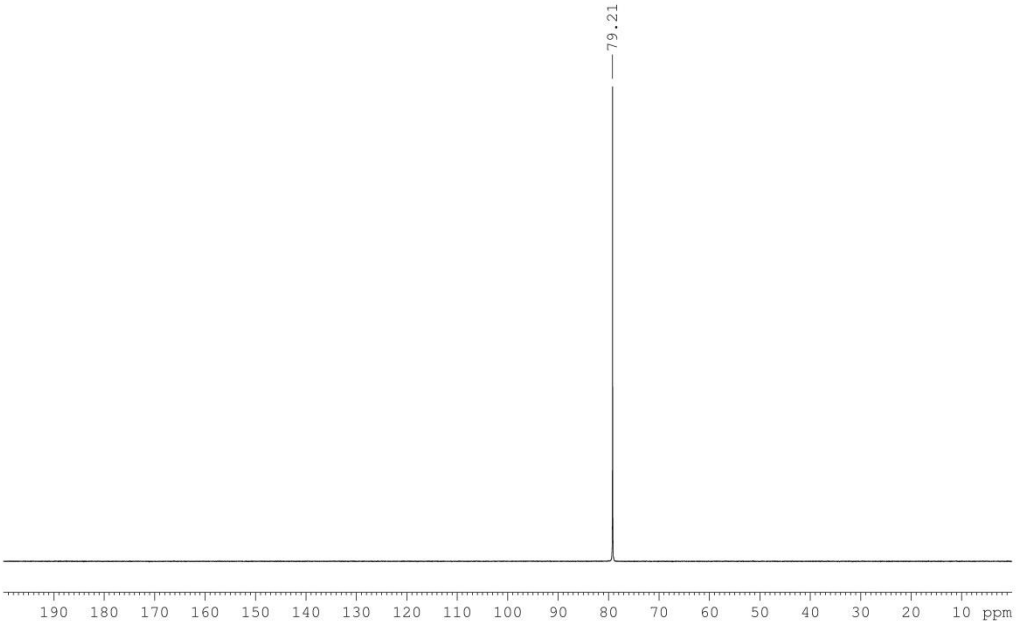
^{13}C NMR (101 MHz, CD_2Cl_2) **12**



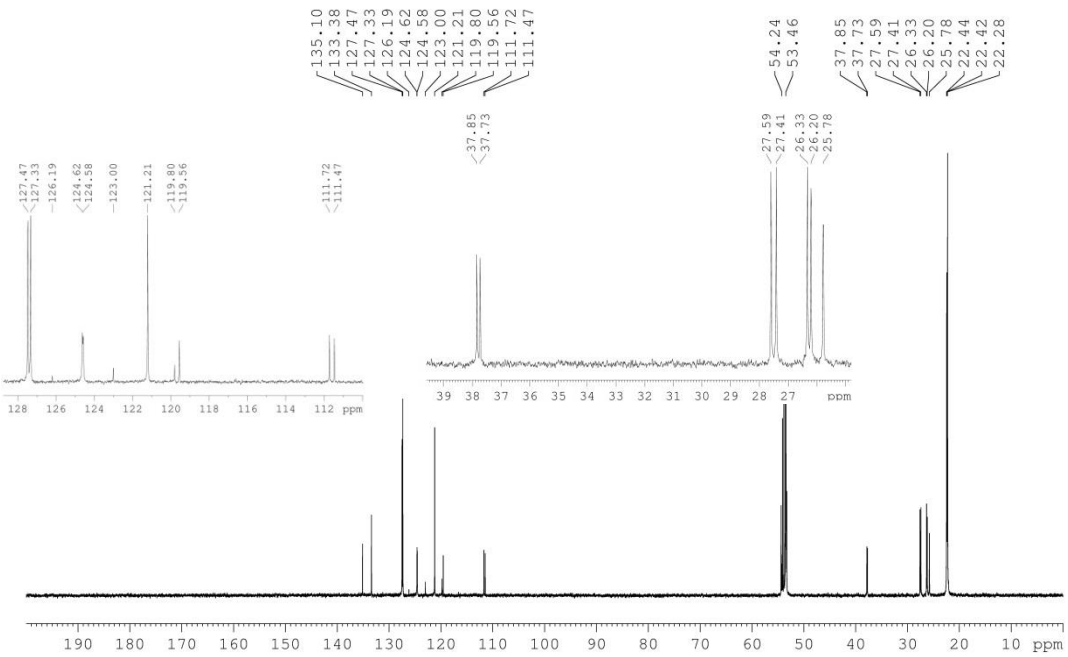
^{1}H NMR (400 MHz, CD_2Cl_2) **13**



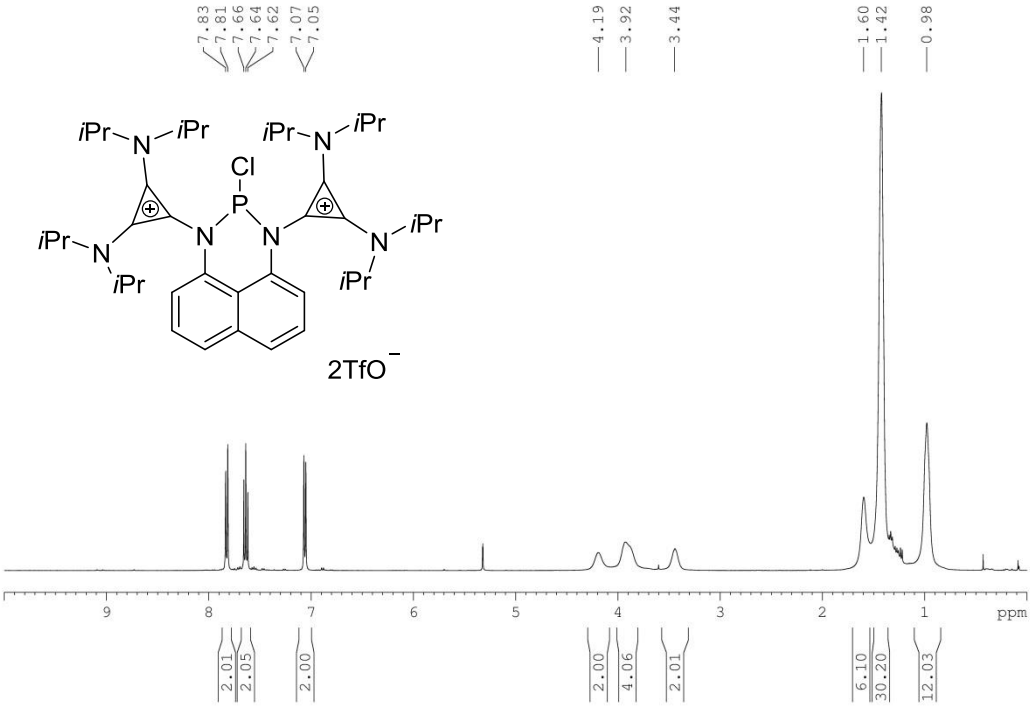
^{31}P NMR (162 MHz, CD_2Cl_2) **13**



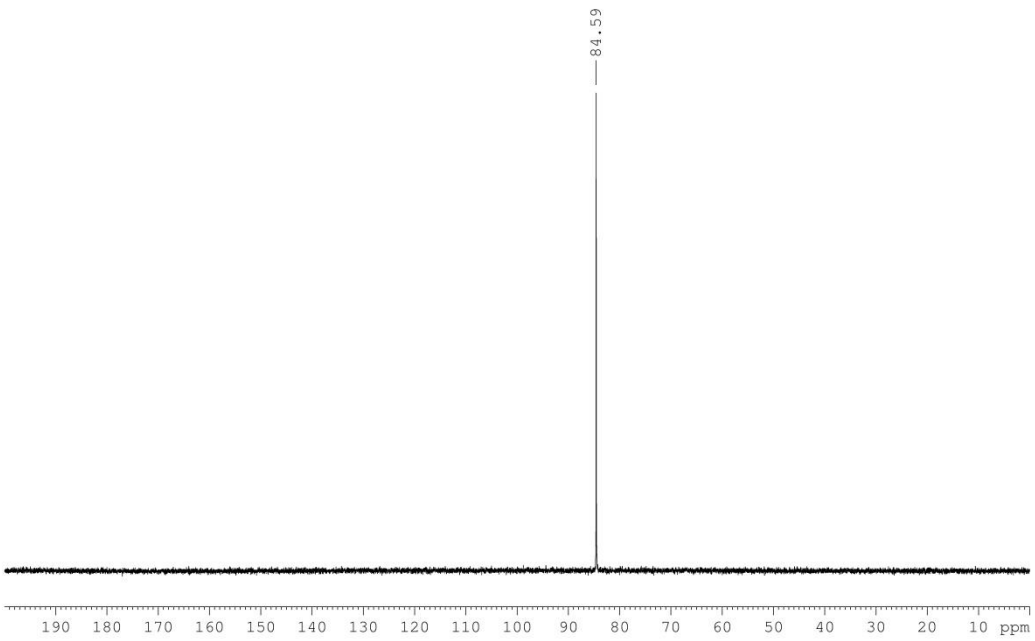
^{13}C NMR (101 MHz, CD_2Cl_2) **13**



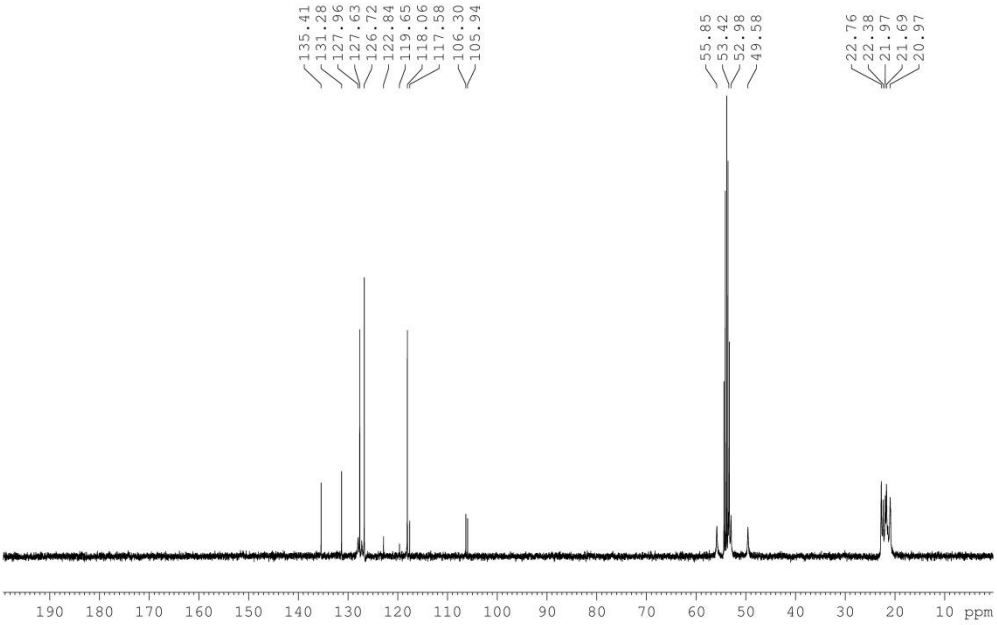
^{1}H NMR (400 MHz, CD_2Cl_2) **14**



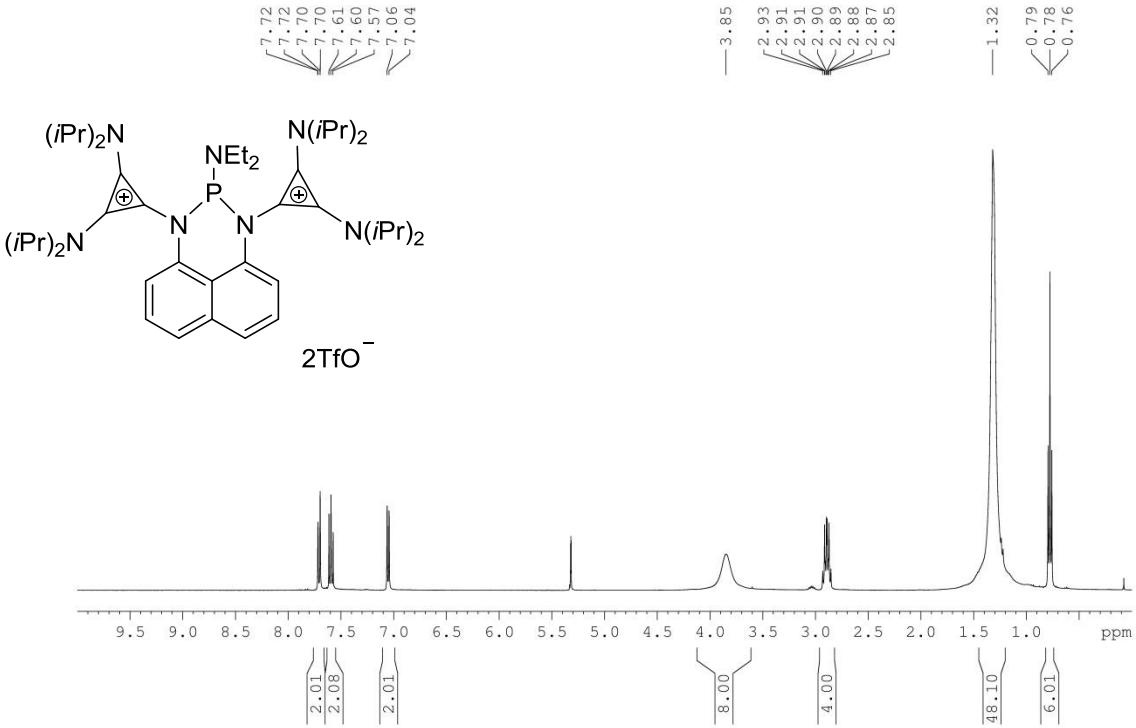
^{31}P NMR (162 MHz, CD_2Cl_2) **14**



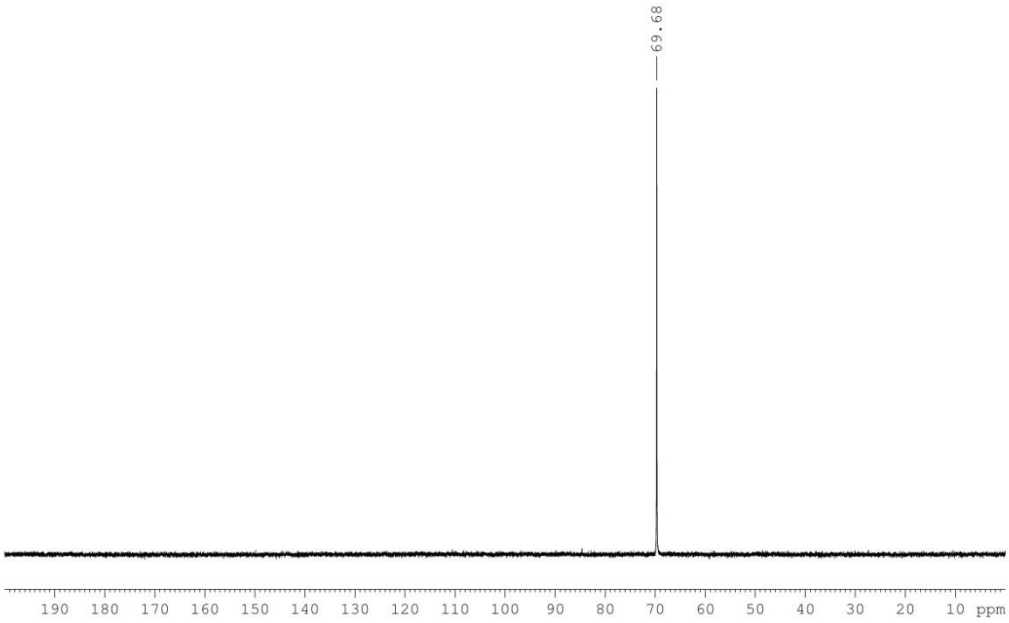
^{13}C NMR (101 MHz, CD_2Cl_2) **14**



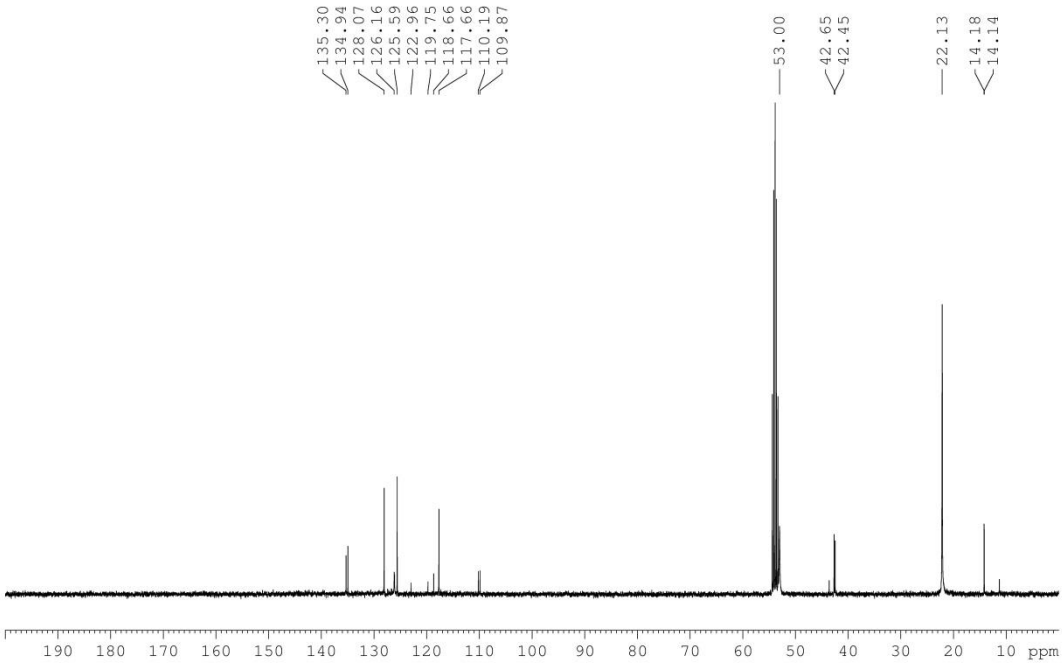
^{1}H NMR (400 MHz, CD_2Cl_2) **15**



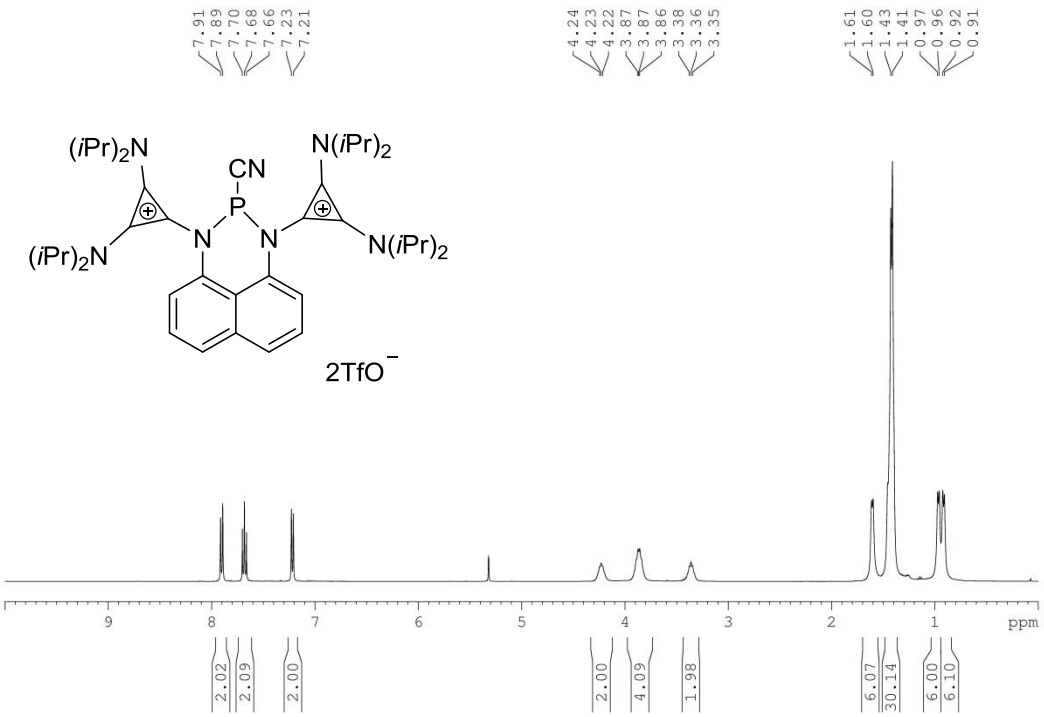
^{31}P NMR (162 MHz, CD_2Cl_2) **15**



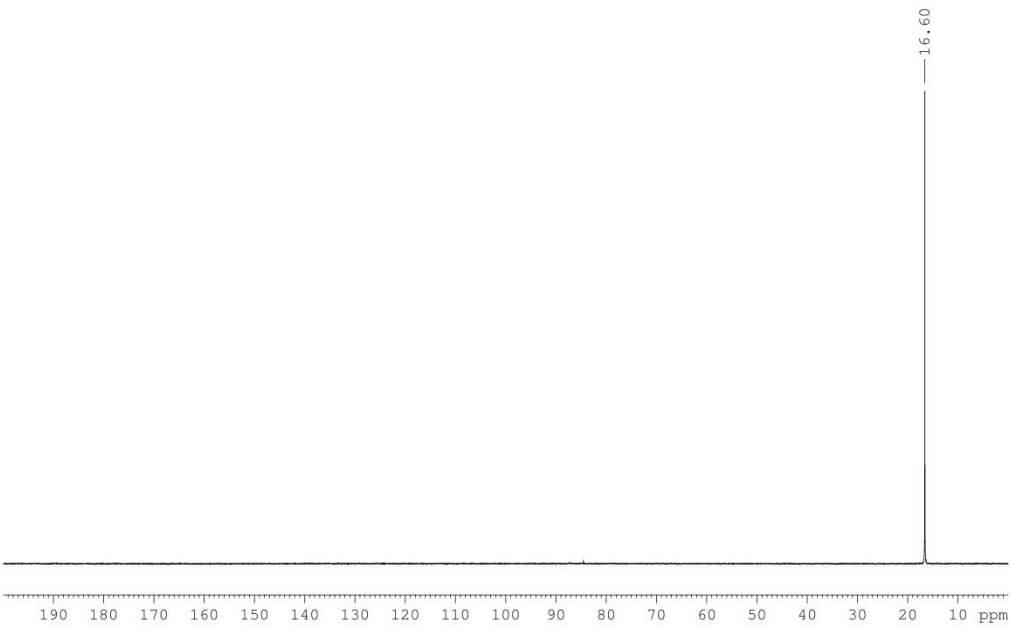
^{13}C NMR (101 MHz, CD_2Cl_2) **15**



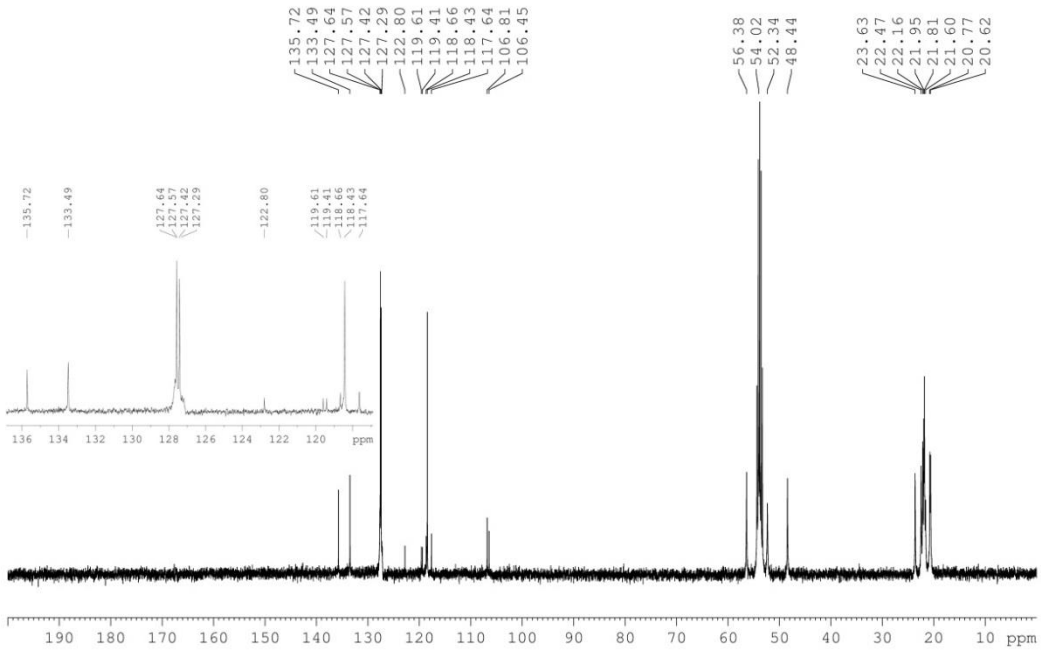
^{1}H NMR (400 MHz, CD_2Cl_2) **16**



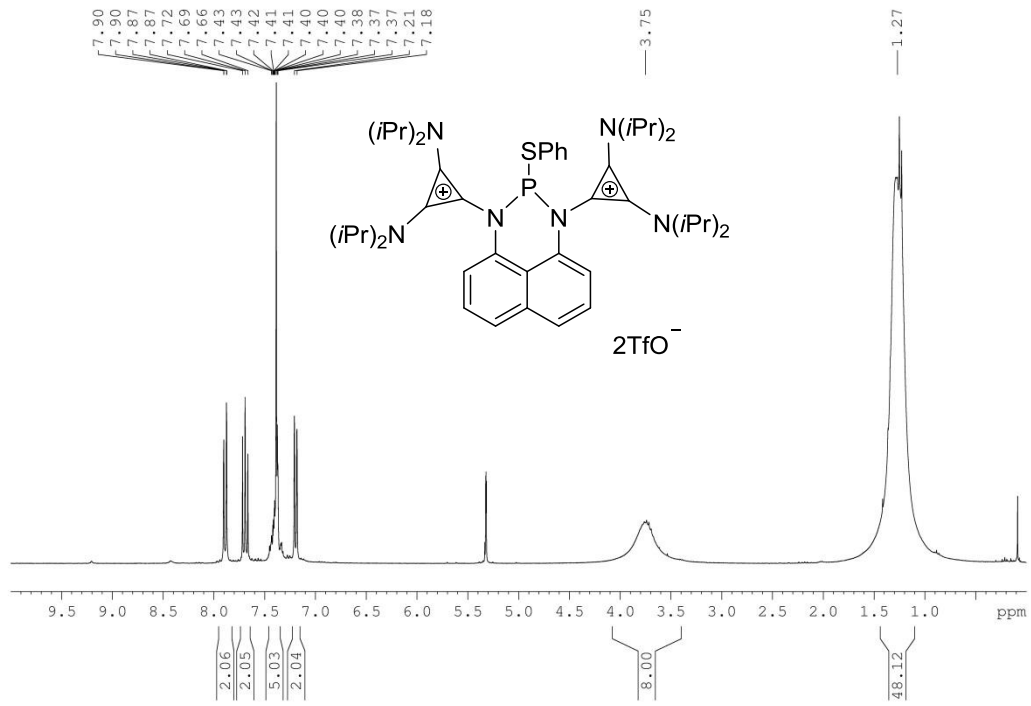
^{31}P NMR (162 MHz, CD_2Cl_2) **16**



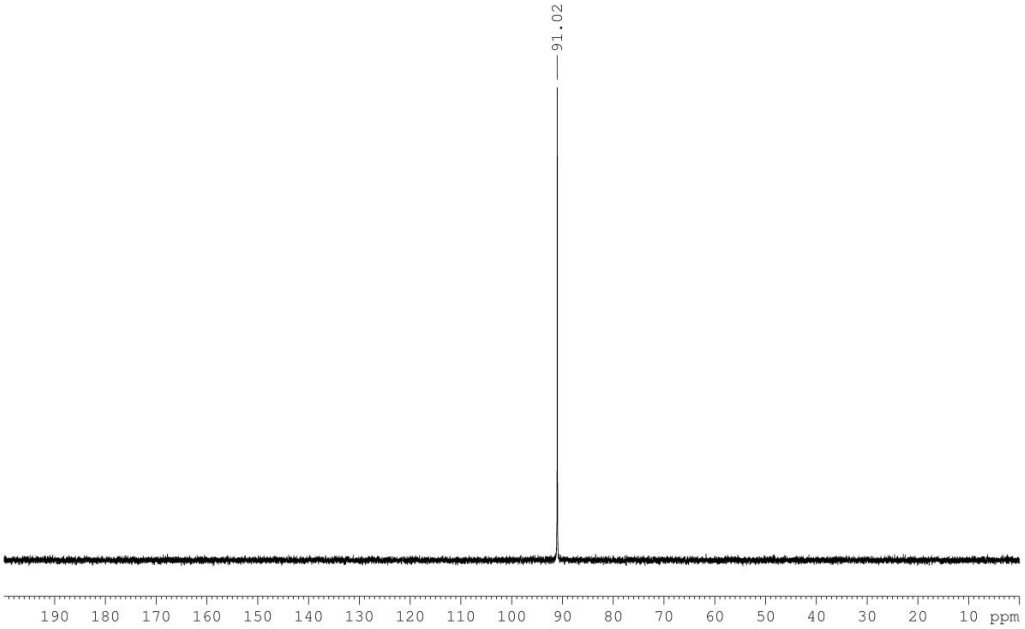
^{13}C NMR (101 MHz, CD_2Cl_2) **16**



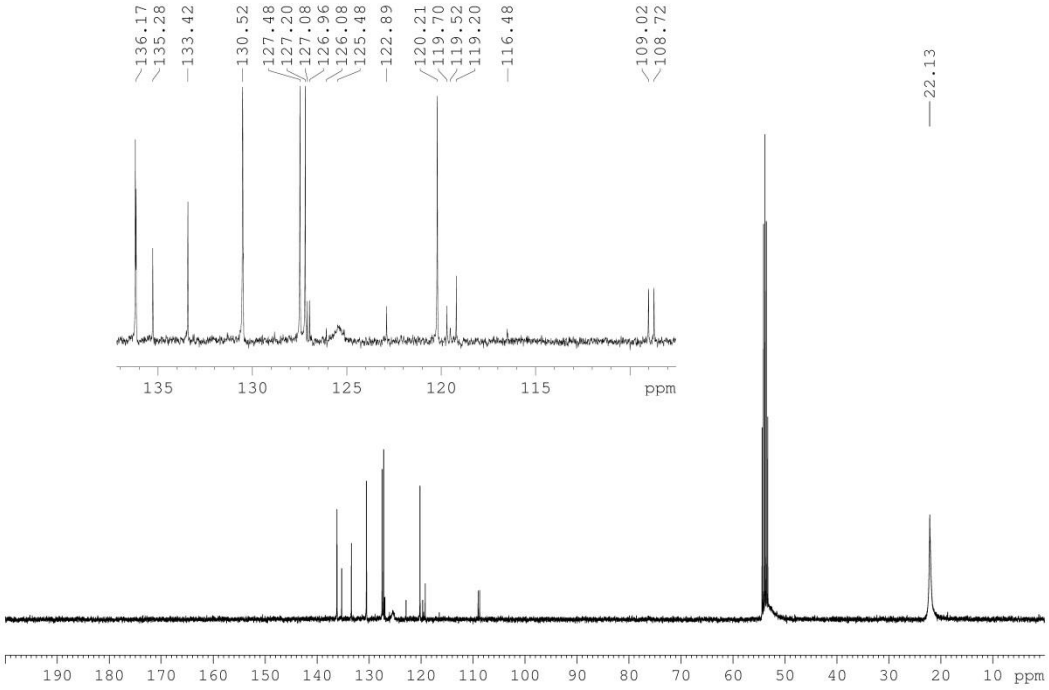
^{1}H NMR (400 MHz, CD_2Cl_2) **17**



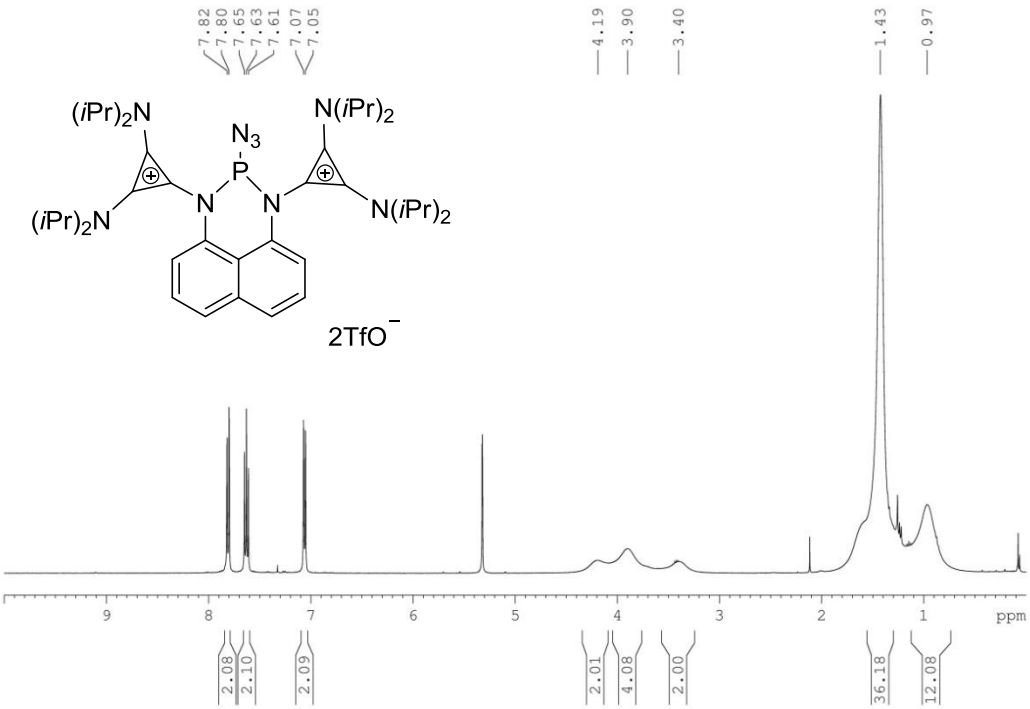
^{31}P NMR (162 MHz, CD_2Cl_2) **17**



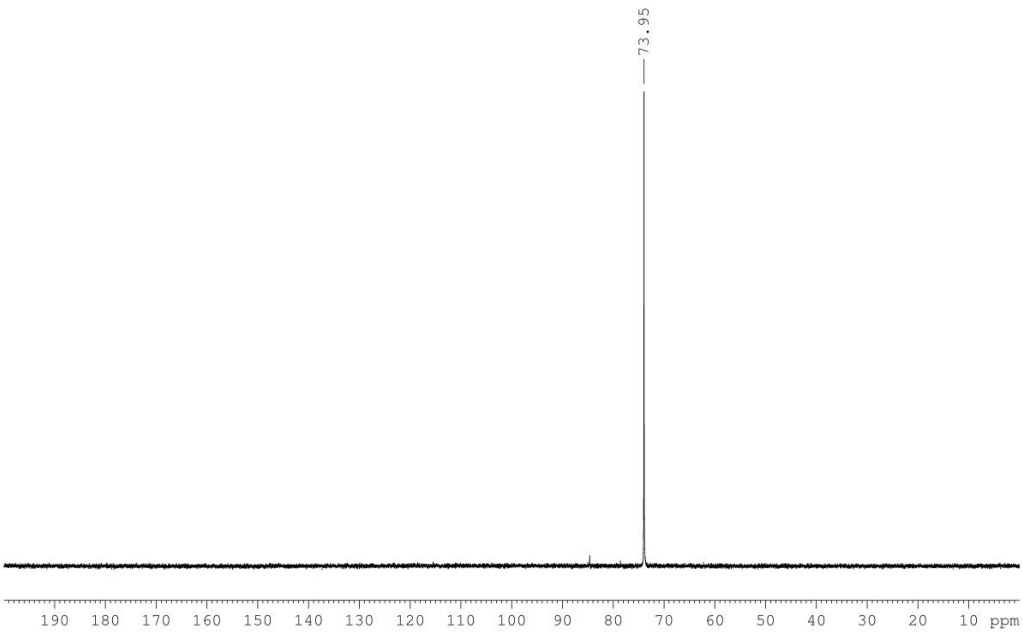
^{13}C NMR (101 MHz, CD_2Cl_2) **17**



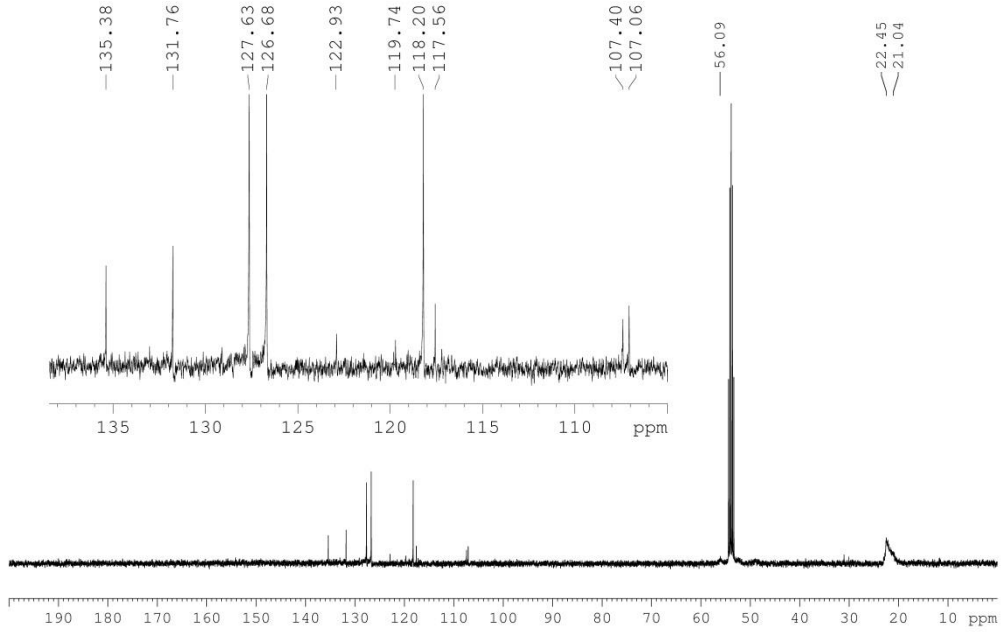
^{1}H NMR (400 MHz, CD_2Cl_2) **18**



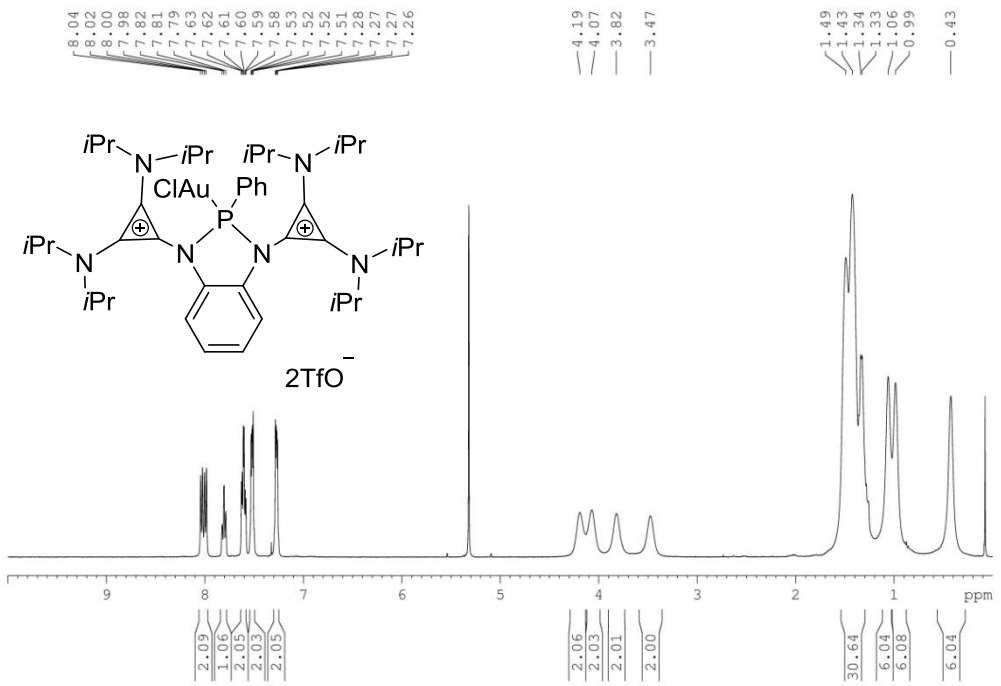
^{31}P NMR (162 MHz, CD_2Cl_2) **18**



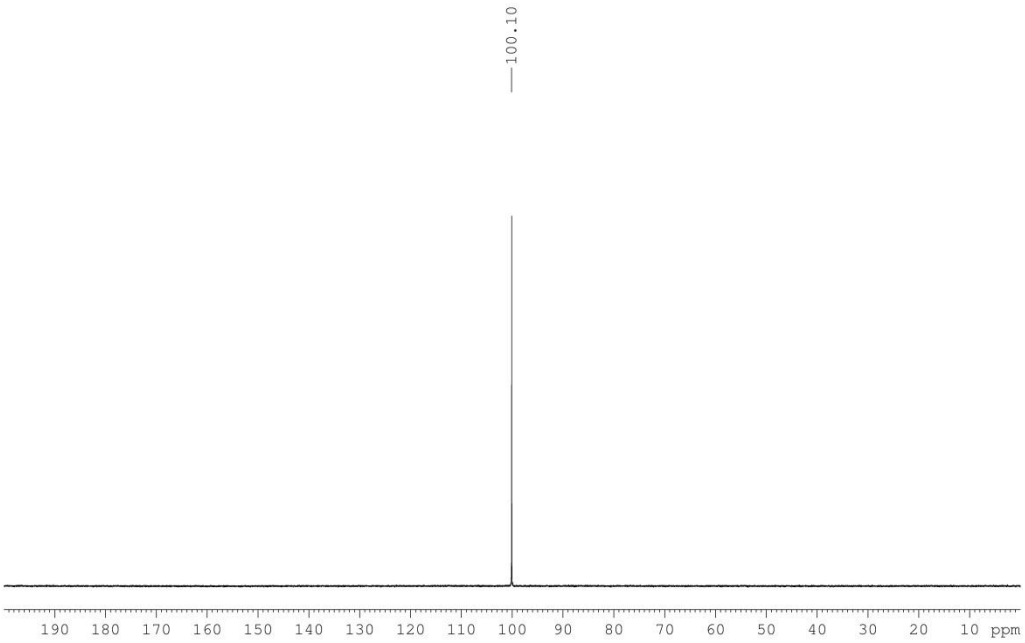
^{13}C NMR (101 MHz, CD_2Cl_2) **18**



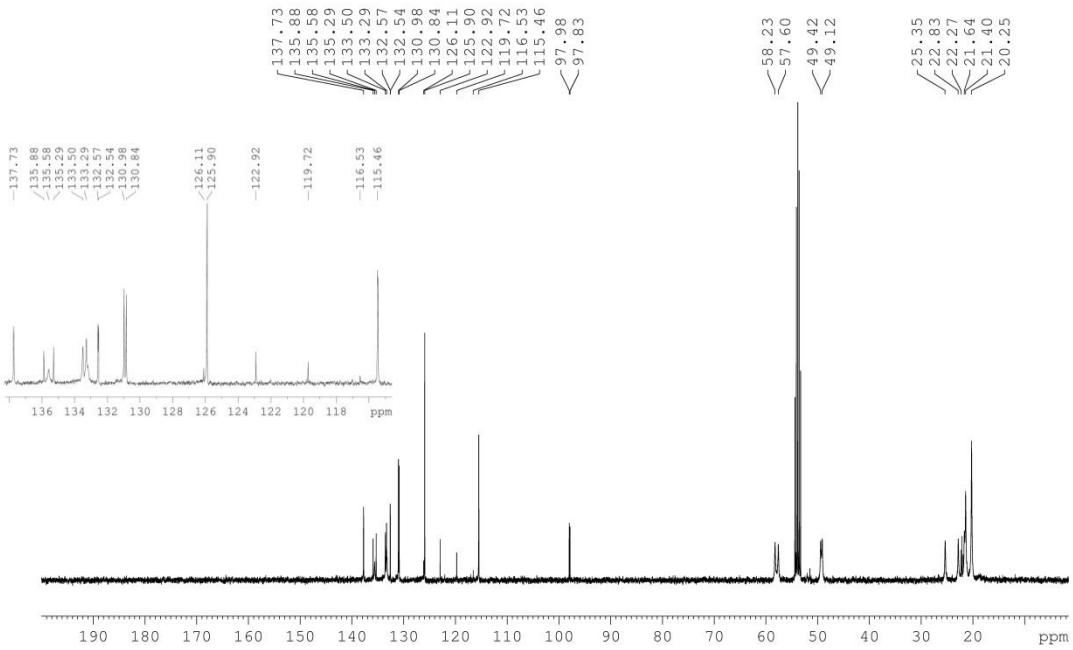
^{1}H NMR (400 MHz, CD_2Cl_2) **19**



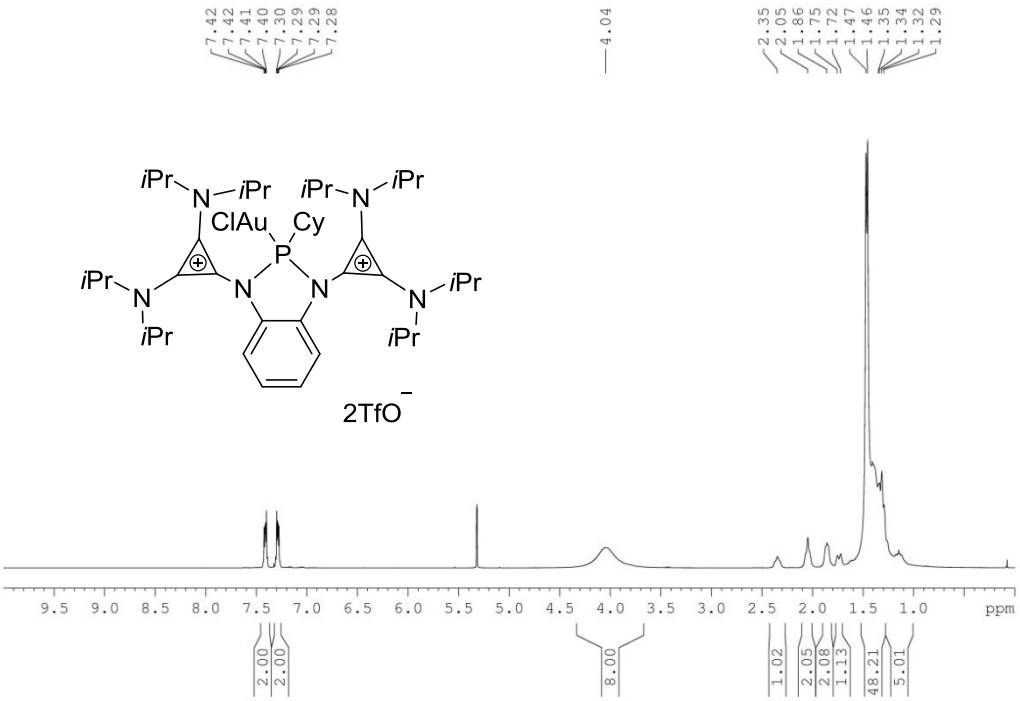
^{31}P NMR (162 MHz, CD_2Cl_2) **19**



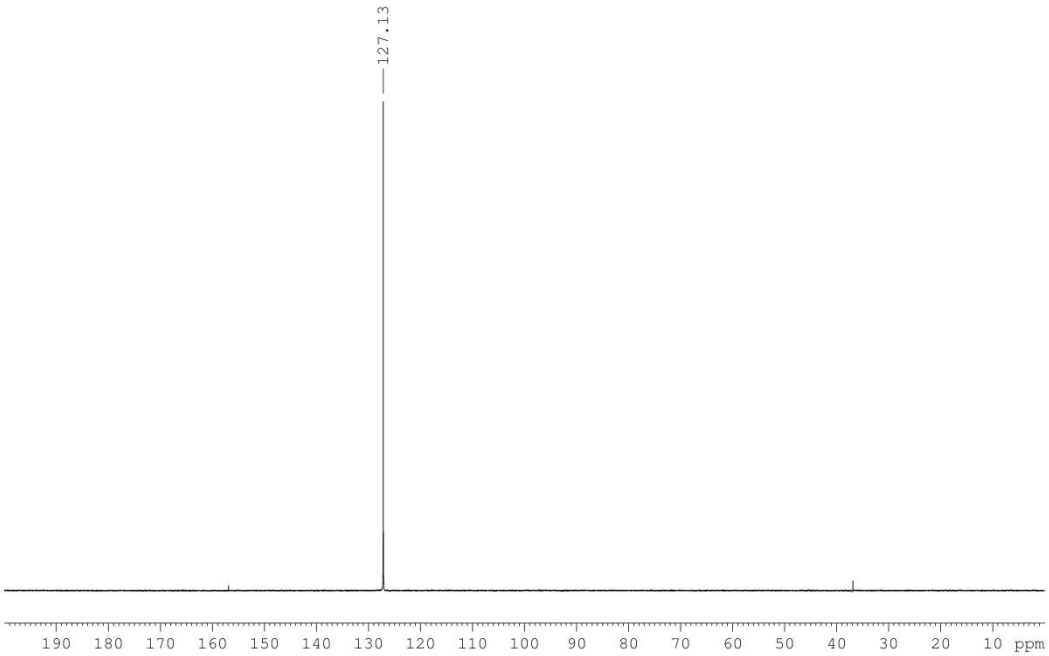
^{13}C NMR (101 MHz, CD_2Cl_2) **19**



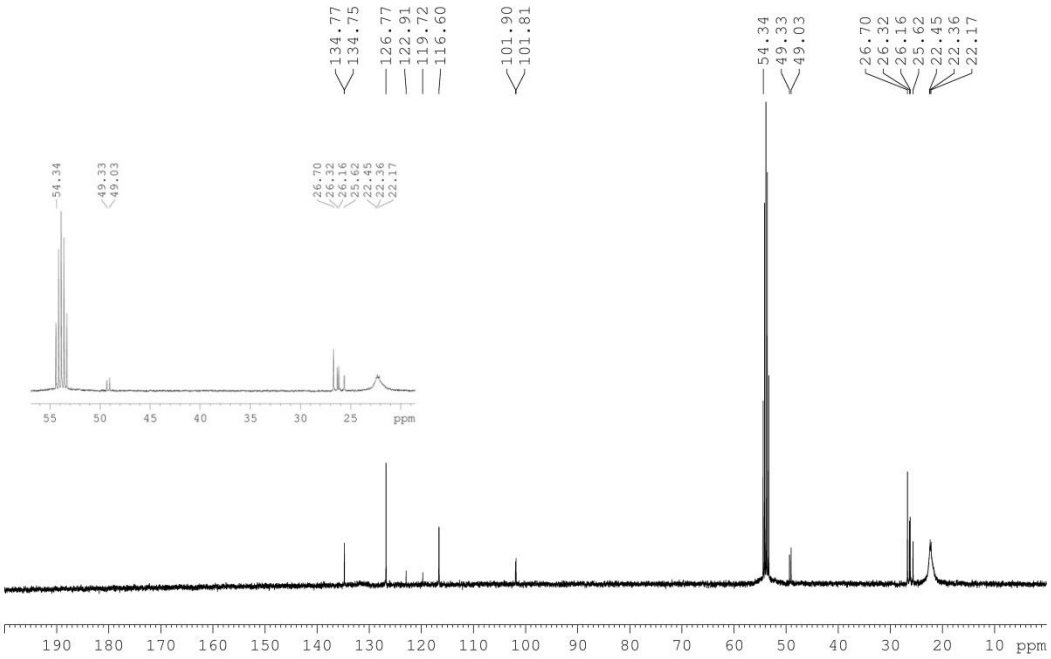
^{1}H NMR (400 MHz, CD_2Cl_2) **20**



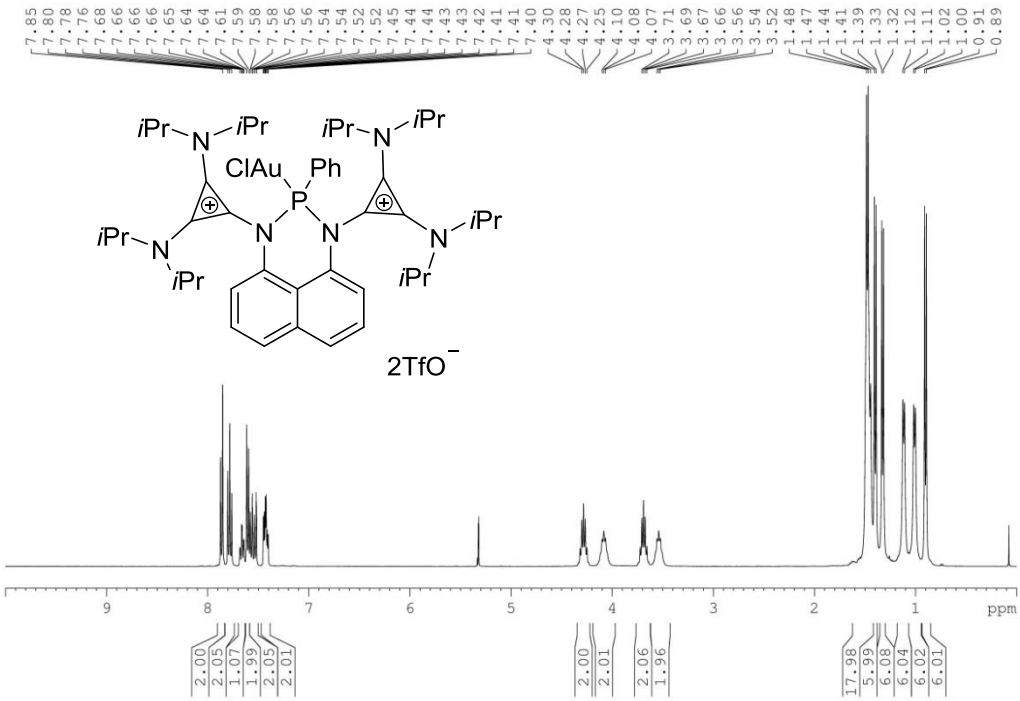
^{31}P NMR (162 MHz, CD_2Cl_2) **20**



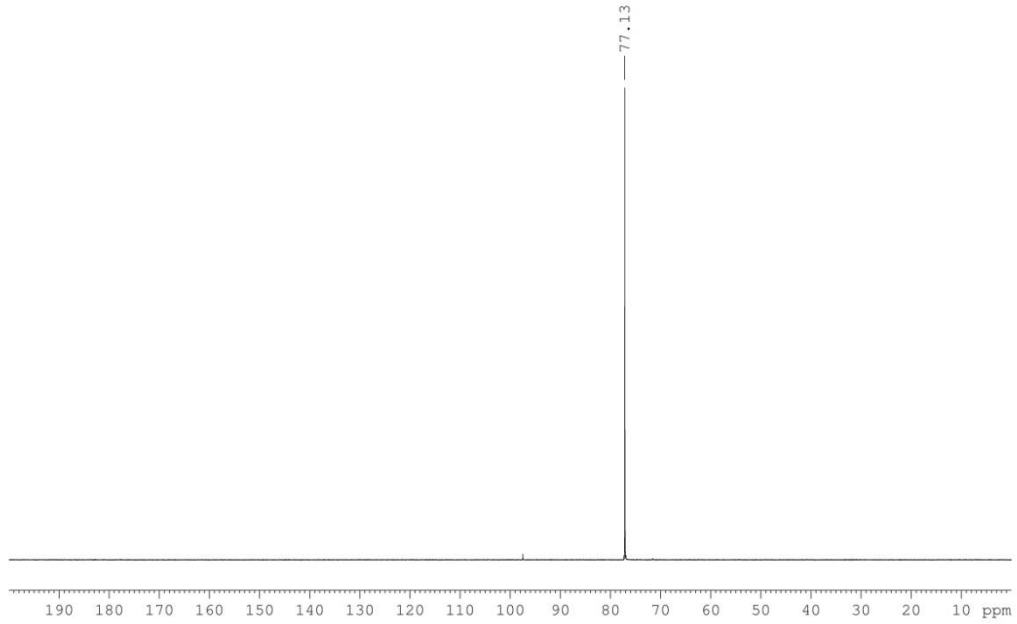
^{13}C NMR (101 MHz, CD_2Cl_2) **20**



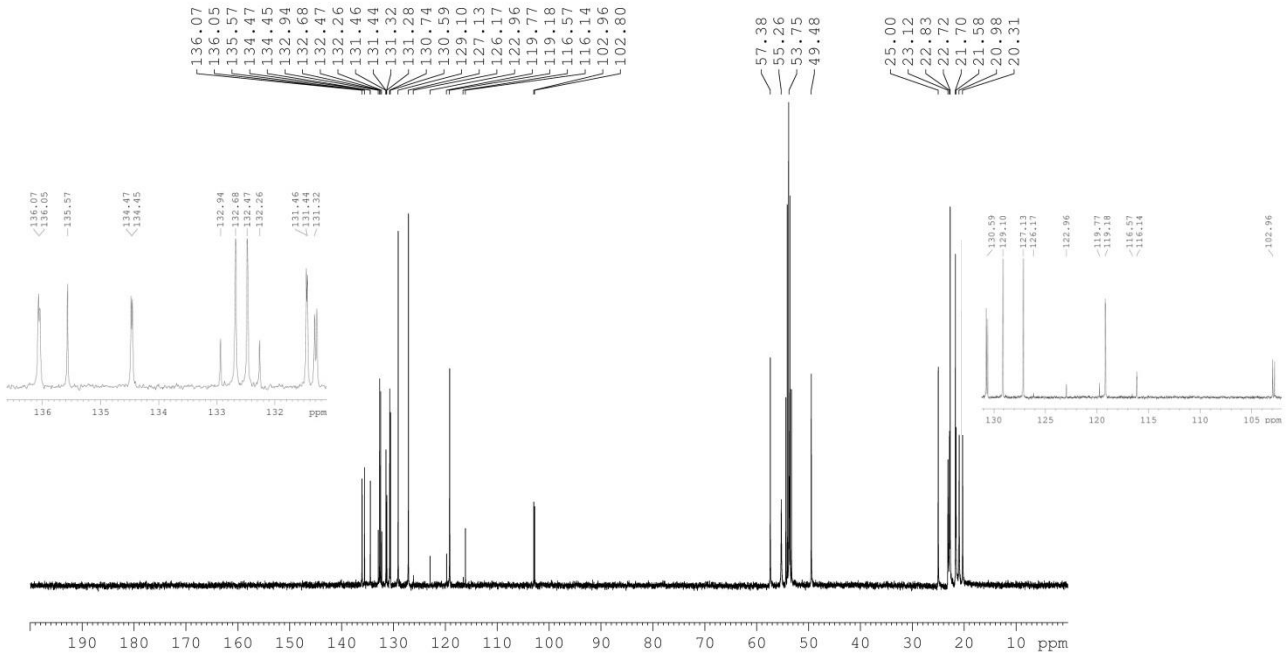
^{1}H NMR (400 MHz, CD_2Cl_2) **21**



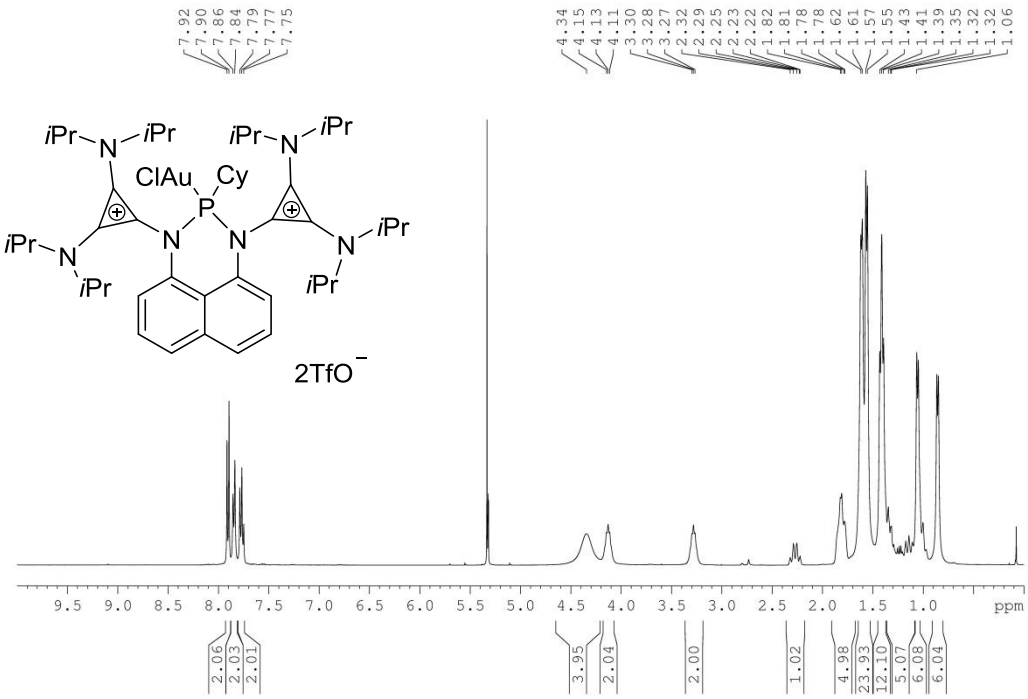
^{31}P NMR (162 MHz, CD_2Cl_2) **21**



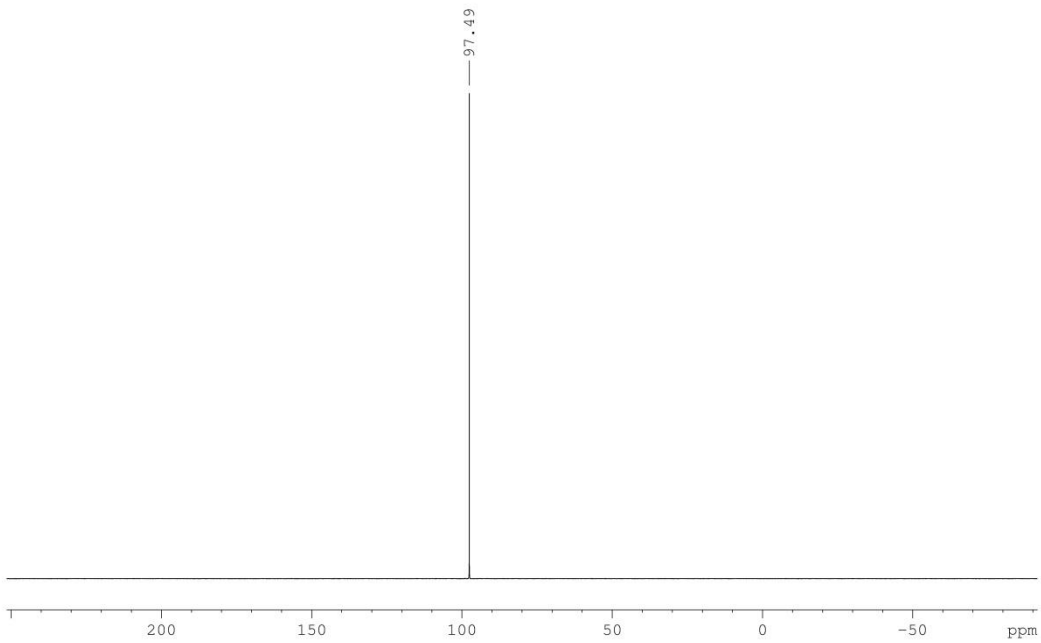
^{13}C NMR (101 MHz, CD_2Cl_2) **21**



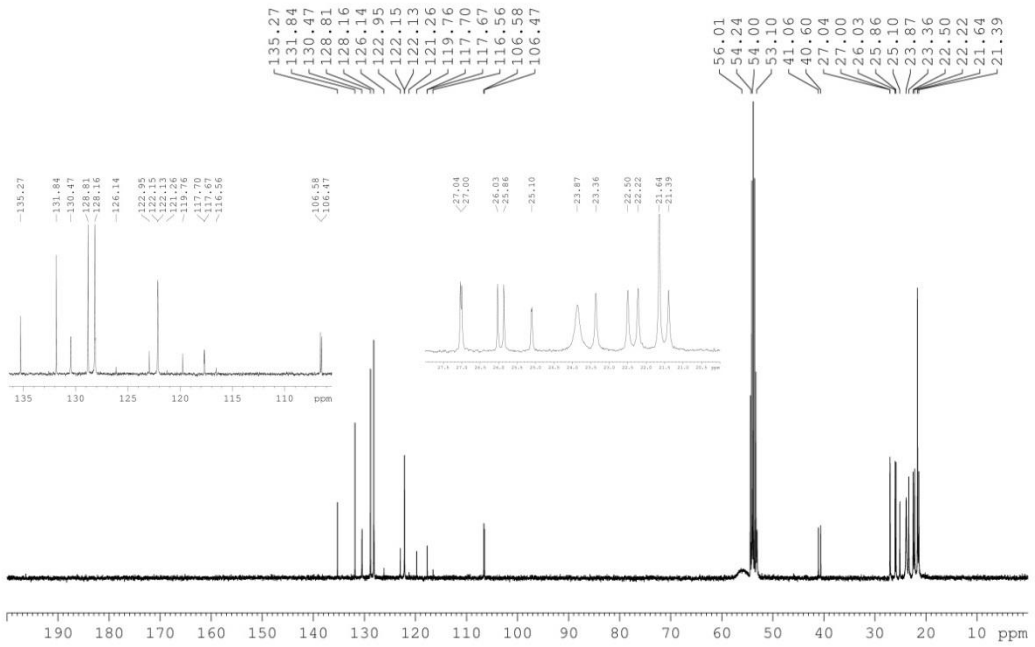
^{1}H NMR (400 MHz, CD_2Cl_2) **22**



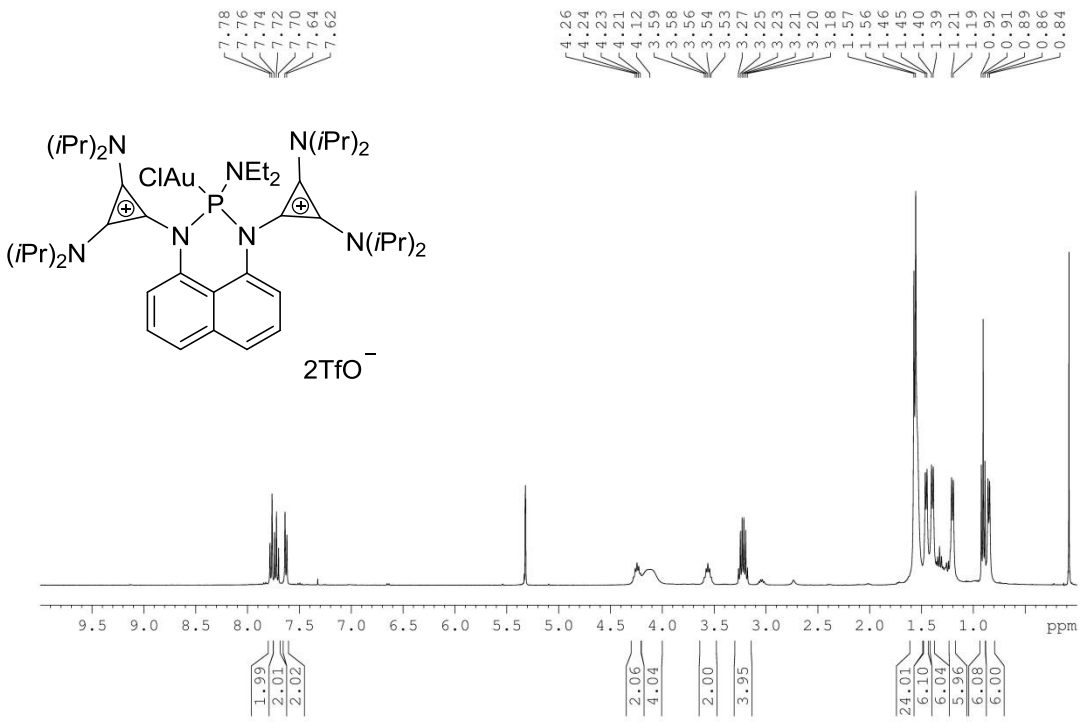
^{31}P NMR (162 MHz, CD_2Cl_2) **22**



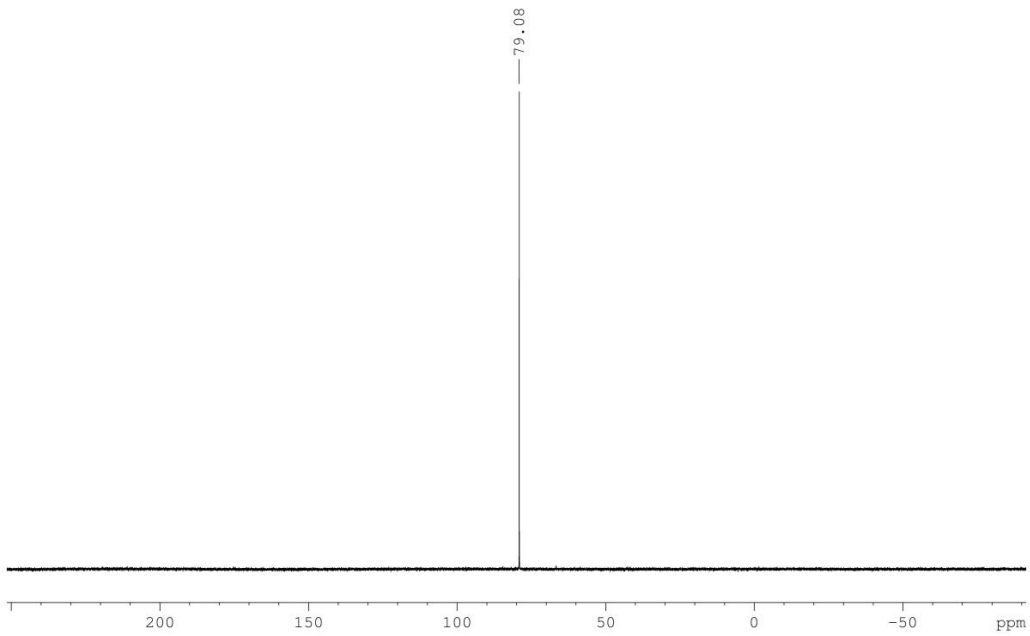
^{13}C NMR (101 MHz, CD_2Cl_2) **22**



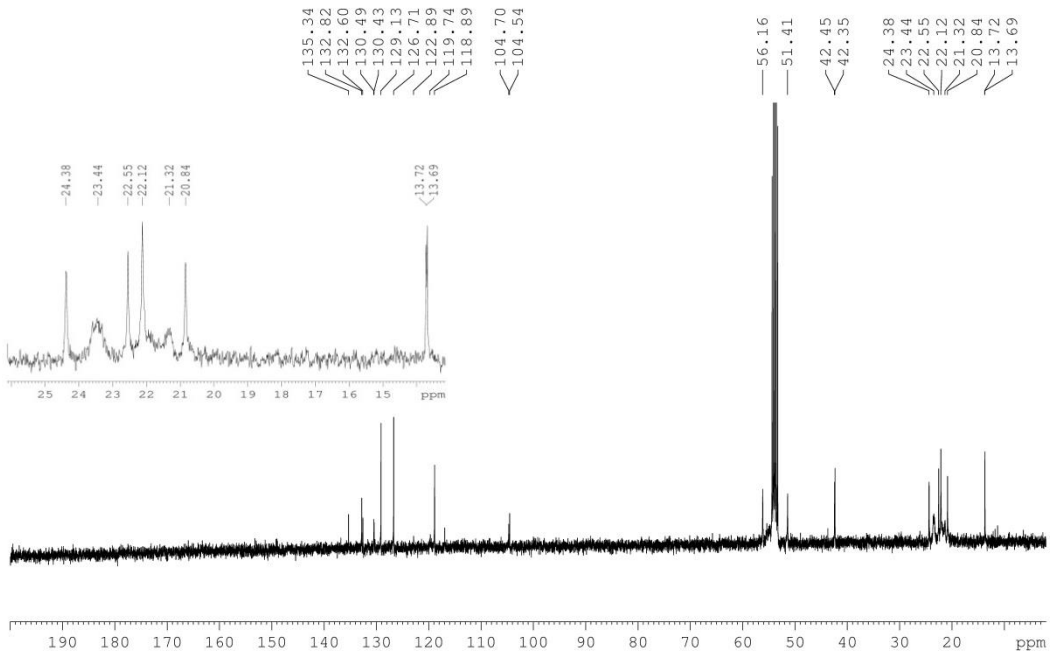
^{1}H NMR (400 MHz, CD_2Cl_2) **23**



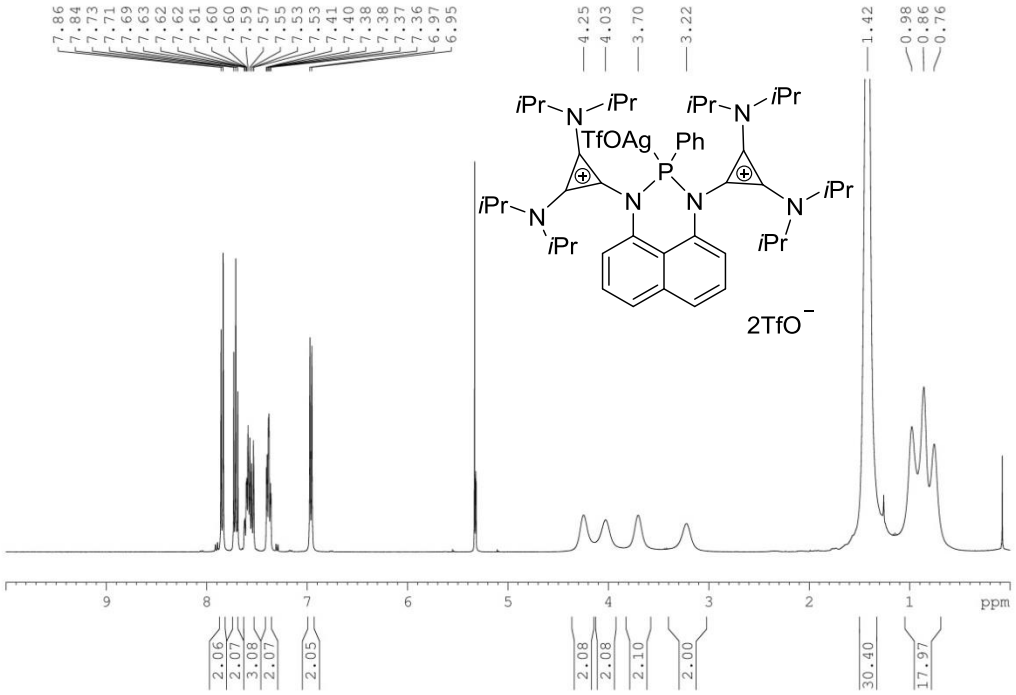
^{31}P NMR (162 MHz, CD_2Cl_2) **23**



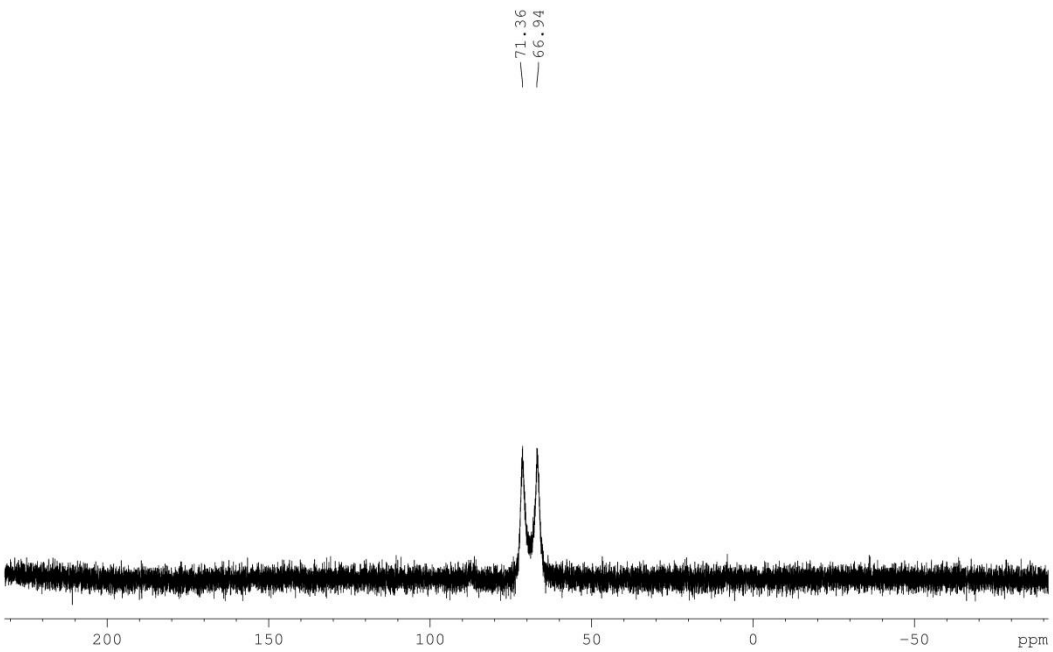
^{13}C NMR (101 MHz, CD_2Cl_2) **23**



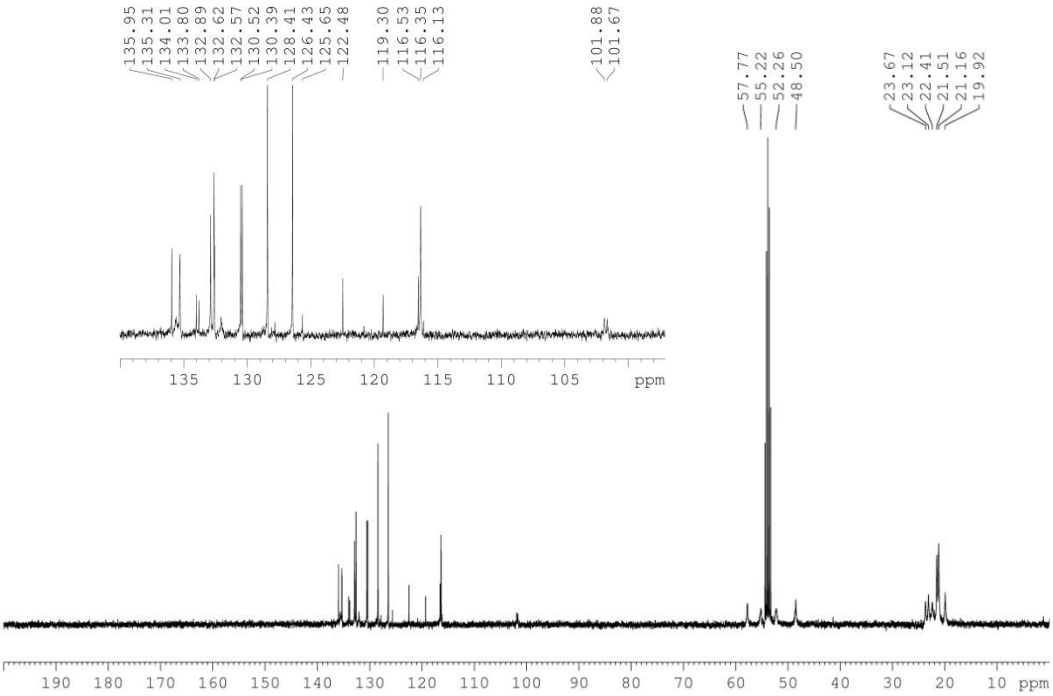
^{1}H NMR (400 MHz, CD_2Cl_2) **24**



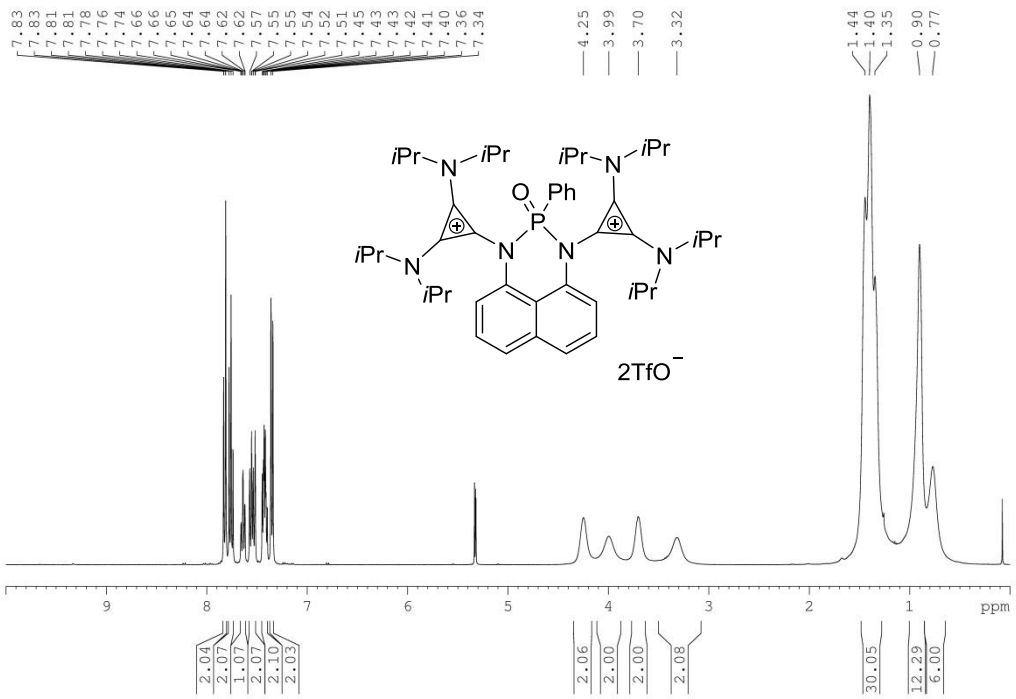
^{31}P NMR (162 MHz, CD_2Cl_2) **24**



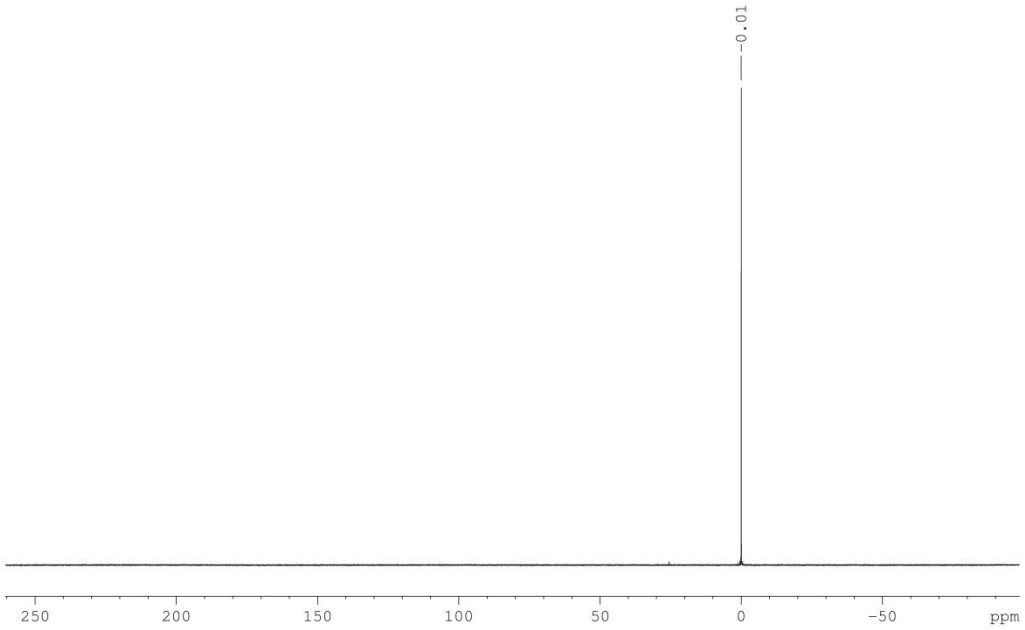
^{13}C NMR (101 MHz, CD_2Cl_2) **24**



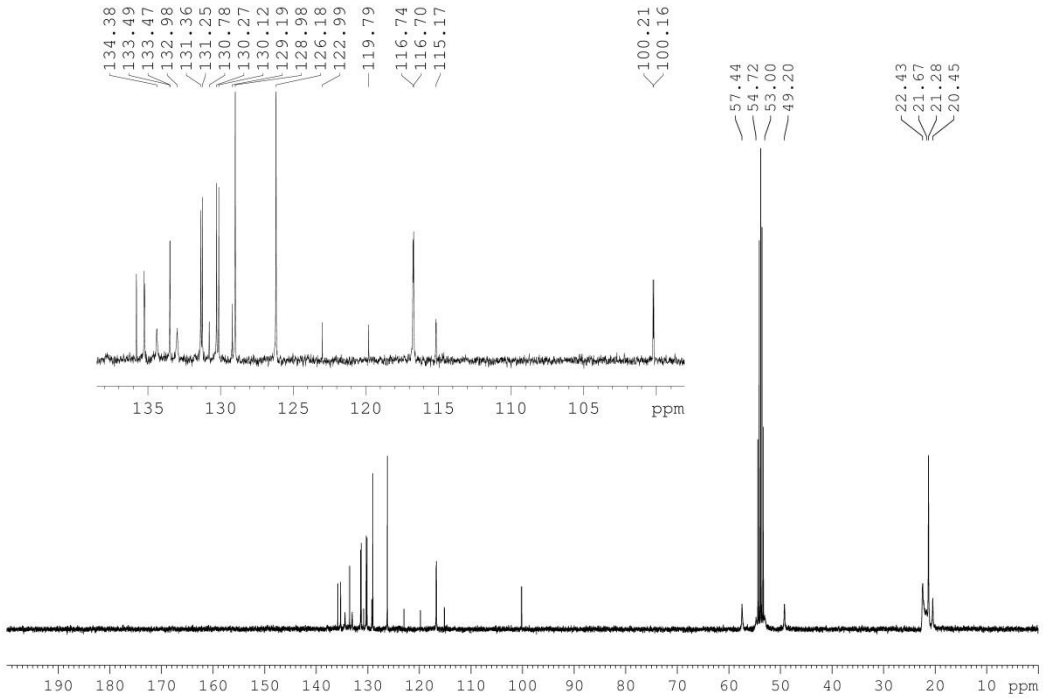
^{1}H NMR (400 MHz, CD_2Cl_2) **25**



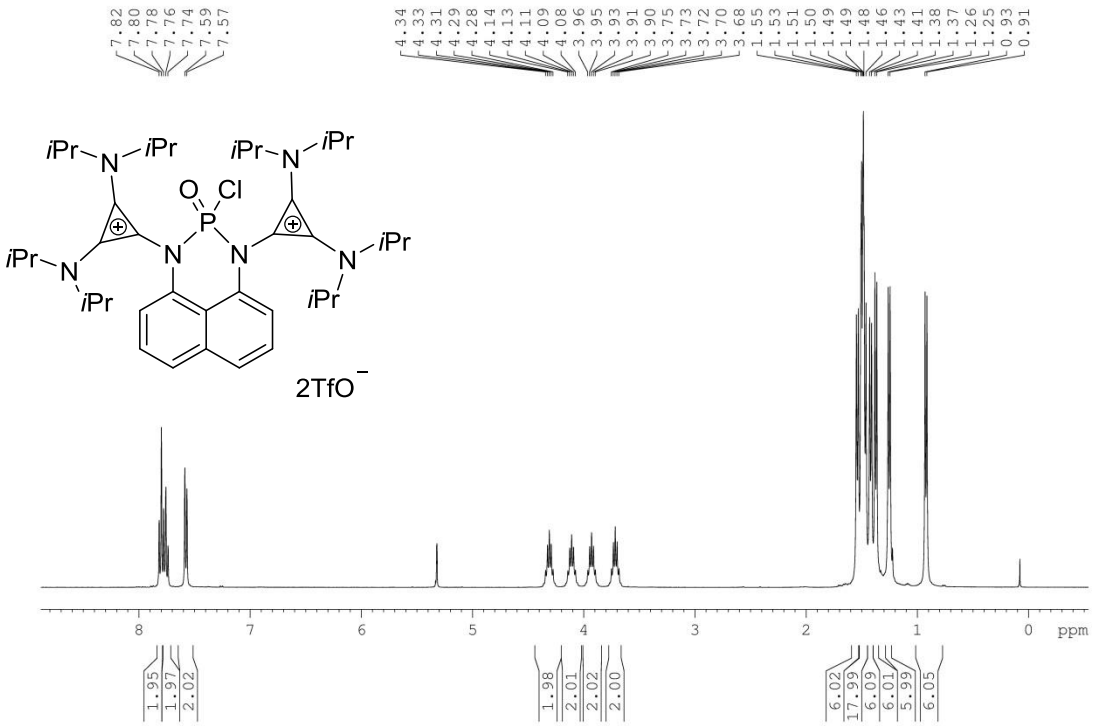
^{31}P NMR (162 MHz, CD_2Cl_2) **25**



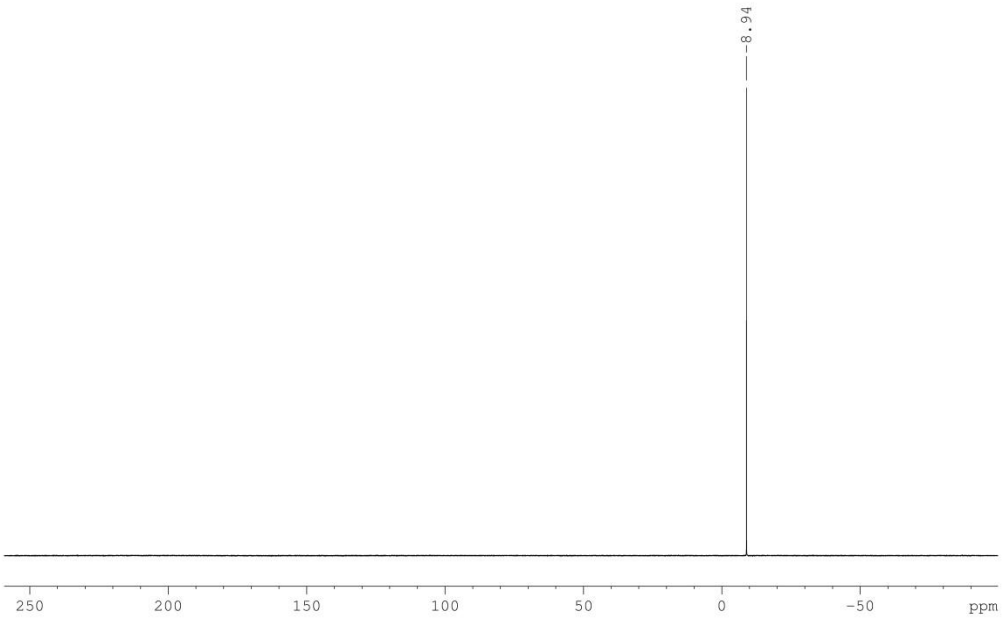
^{13}C NMR (101 MHz, CD_2Cl_2) **25**



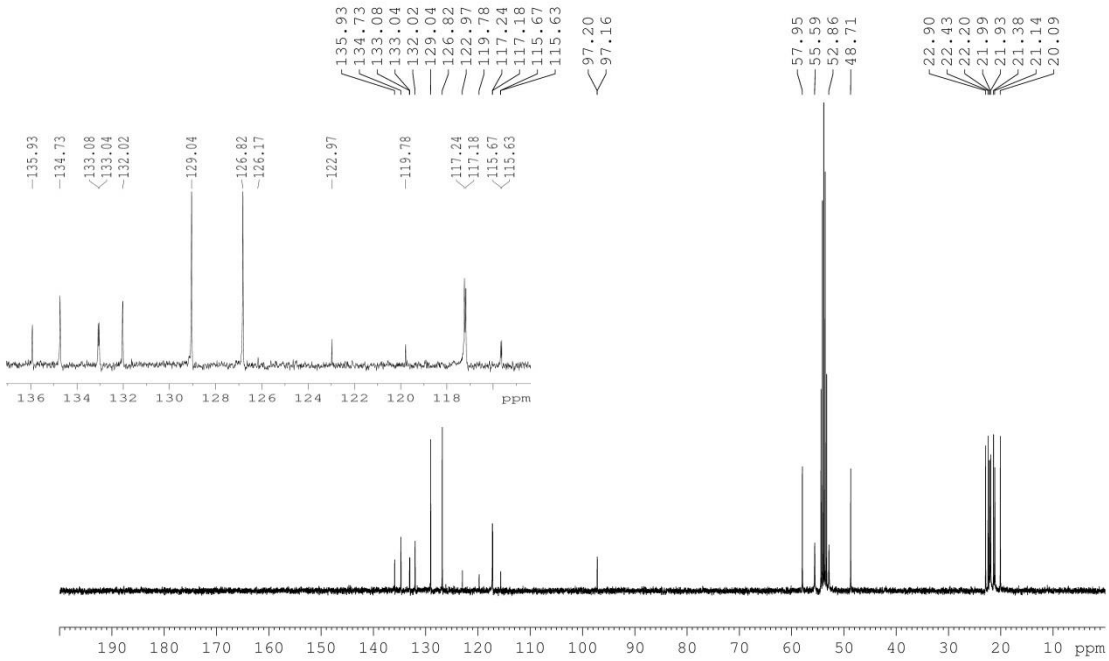
^{1}H NMR (400 MHz, CD_2Cl_2) **26**



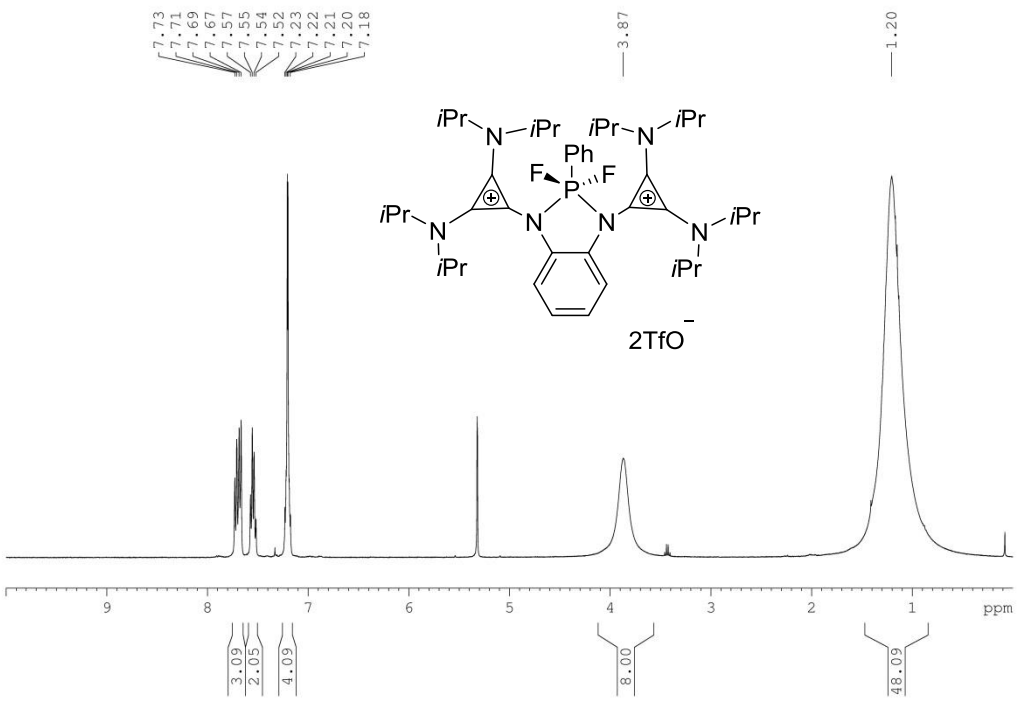
^{31}P NMR (162 MHz, CD_2Cl_2) **26**



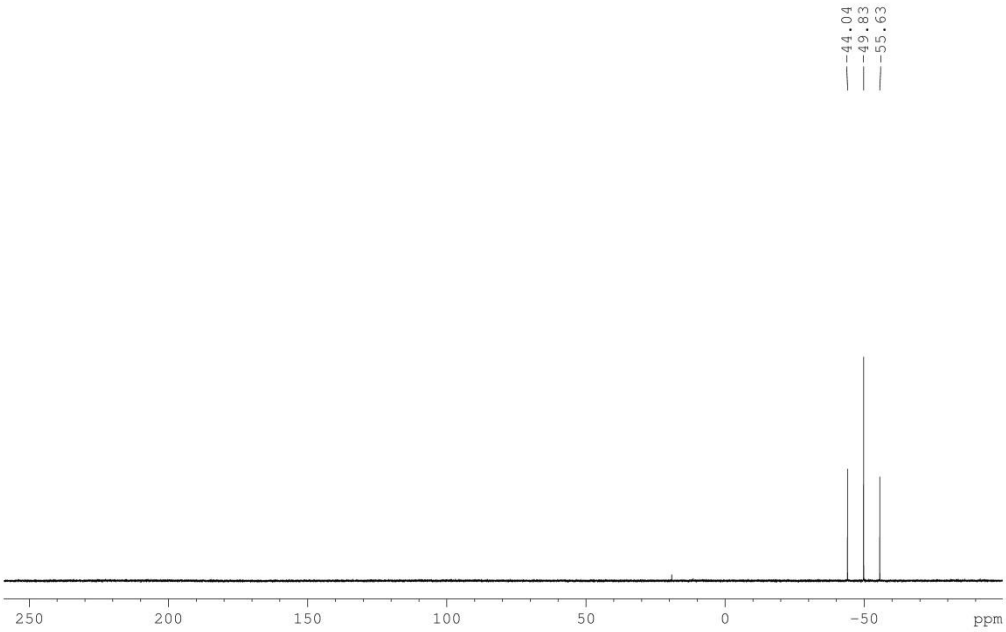
^{13}C NMR (101 MHz, CD_2Cl_2) **26**



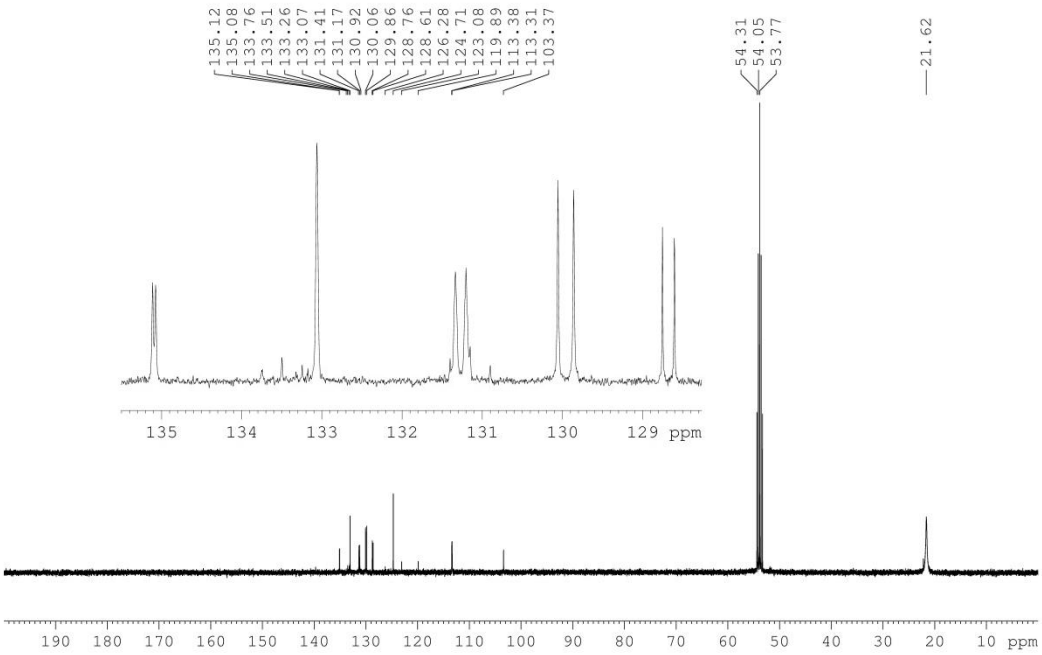
^{1}H NMR (400 MHz, CD_2Cl_2) **27**



^{31}P NMR (162 MHz, CD_2Cl_2) **27**



^{13}C NMR (101 MHz, CD_2Cl_2) **27**

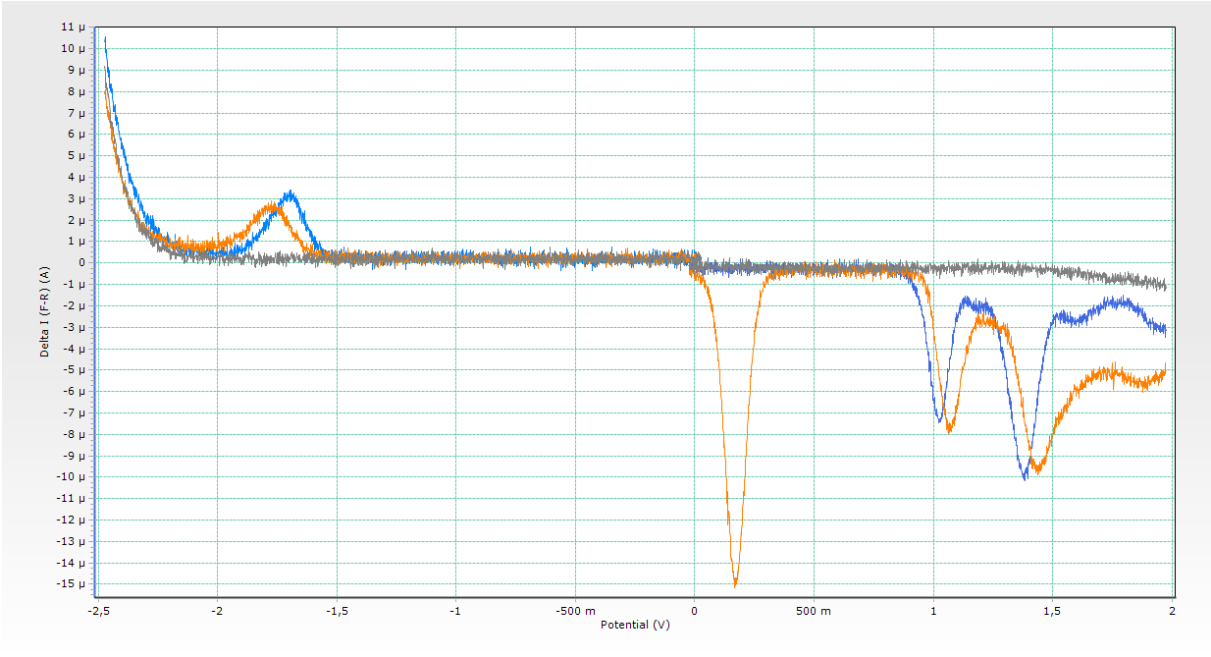


Cyclic Voltammetry experiments:

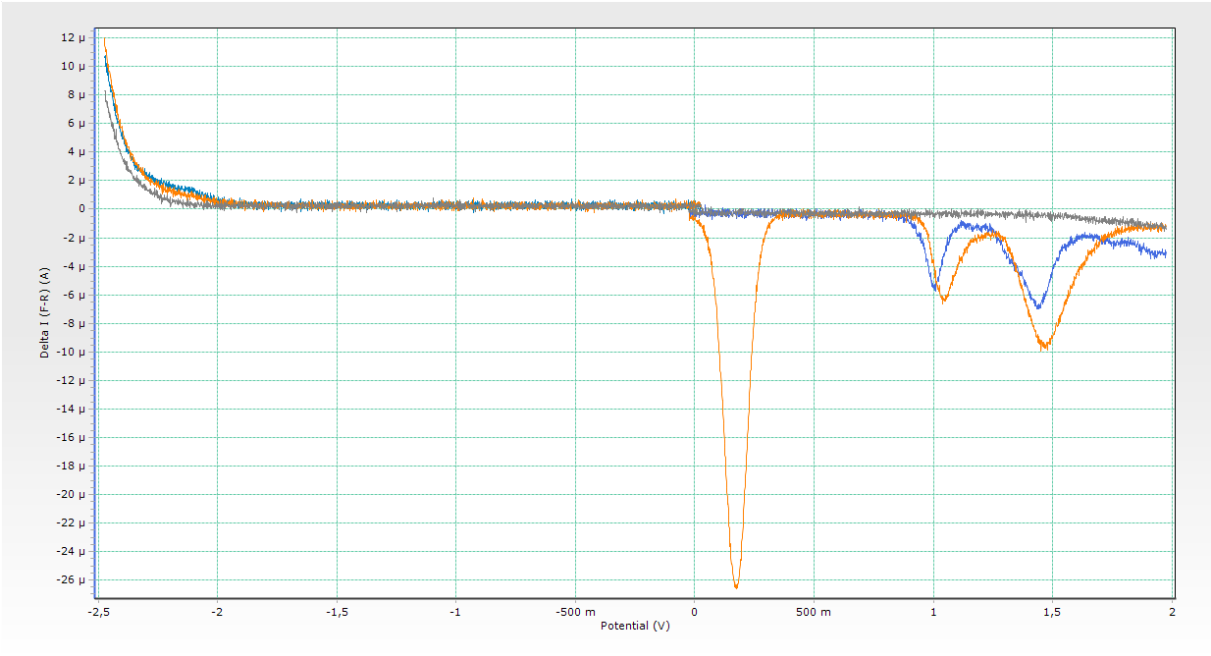
Oxidation peak potentials reported in V and calibrated versus ferrocene/ferricinium, Bu_4NPF_6 (0.1 M) in CH_2Cl_2. Square waves shown.

Grey line	Baseline
Blue line	Desired compound
Orange line	Desired compound + Ferrocene

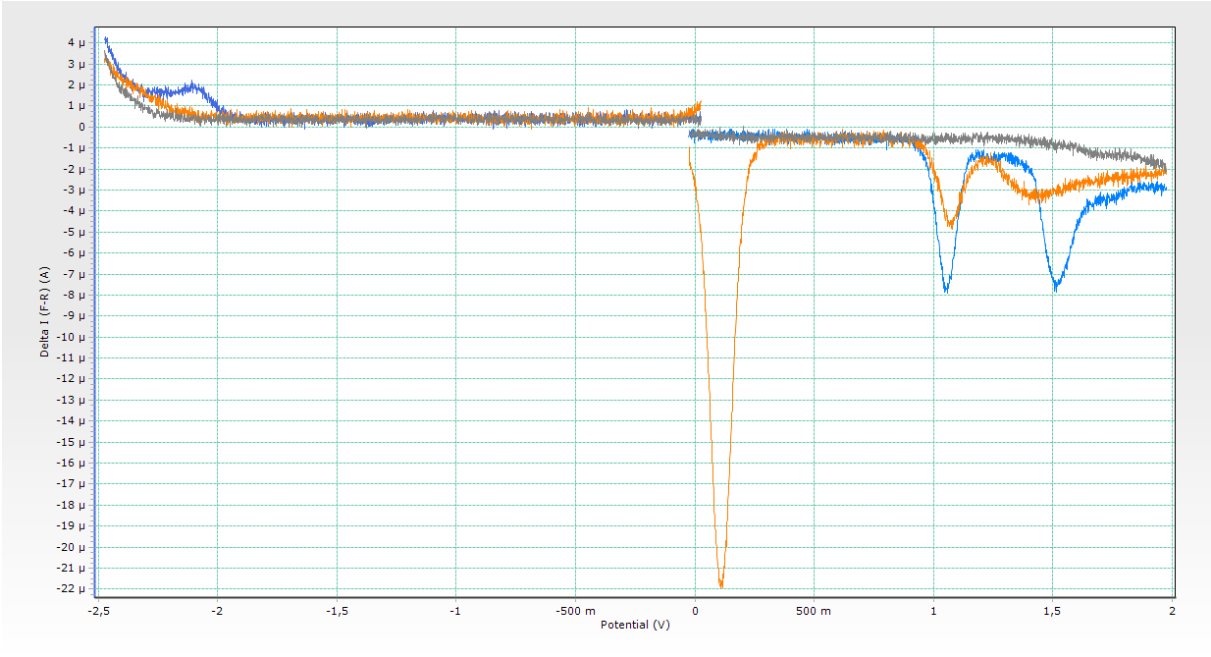
Compound 10



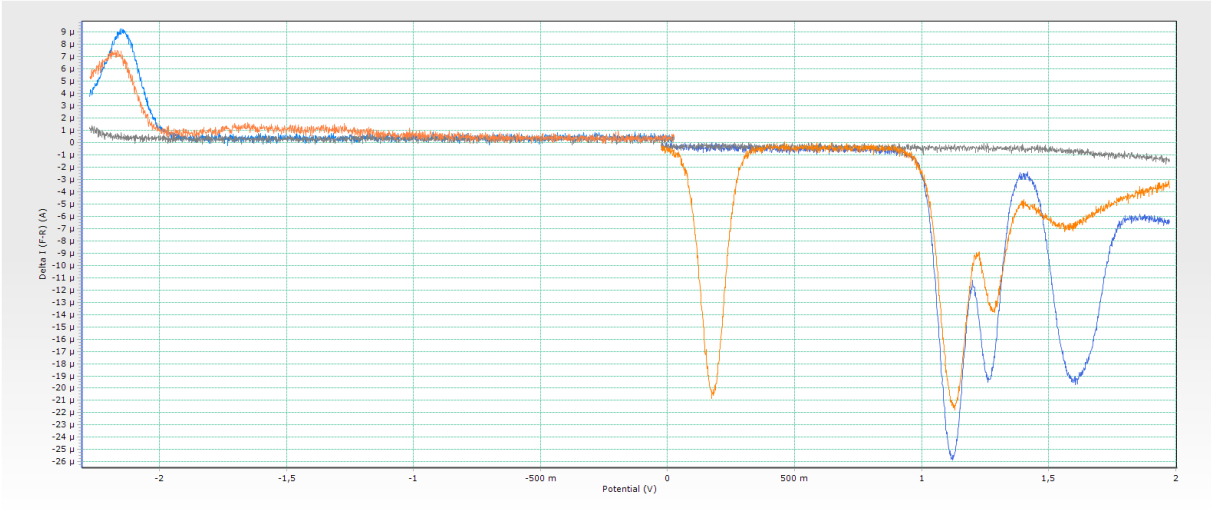
Compound 11



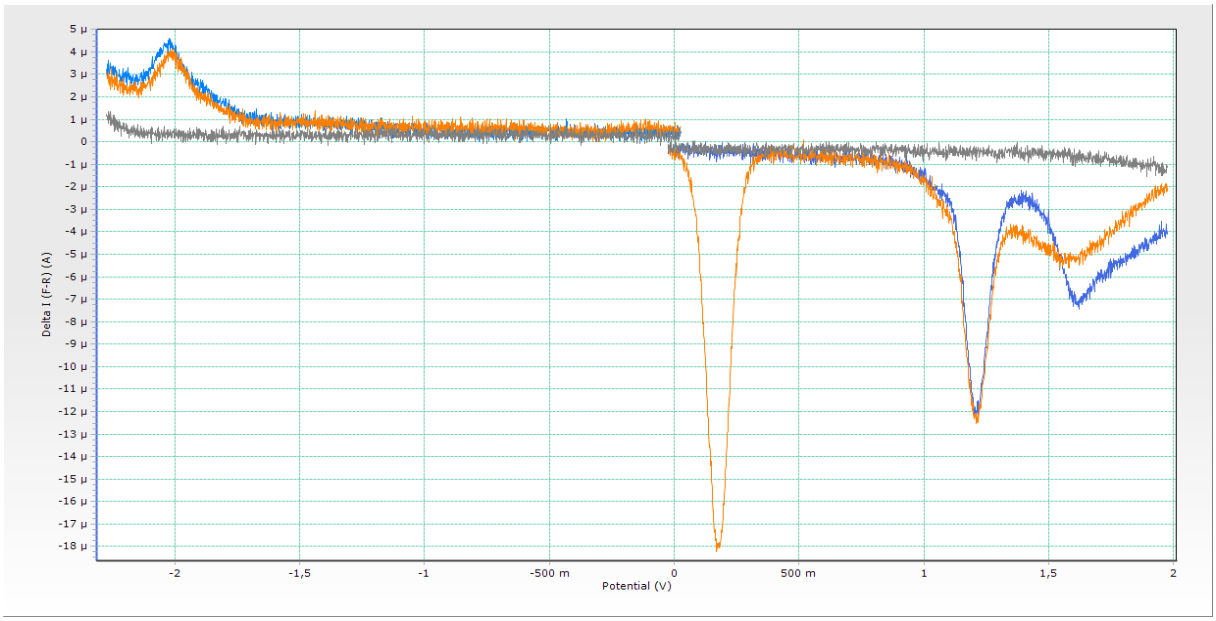
Compound 12:



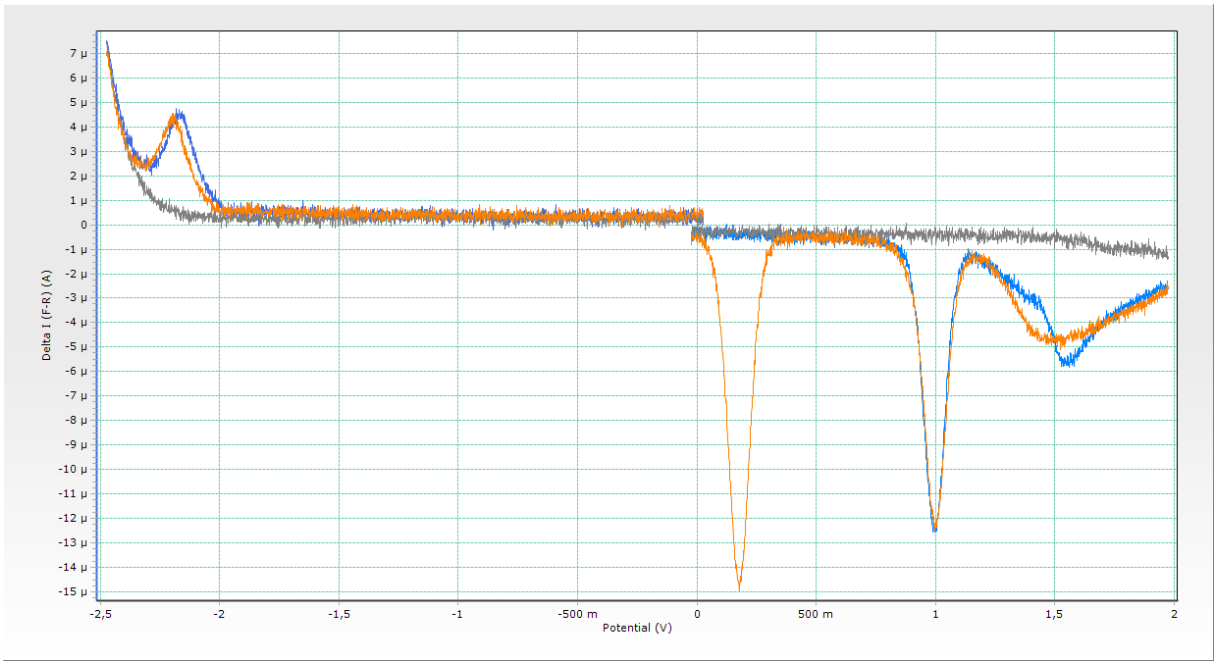
Compound 13:



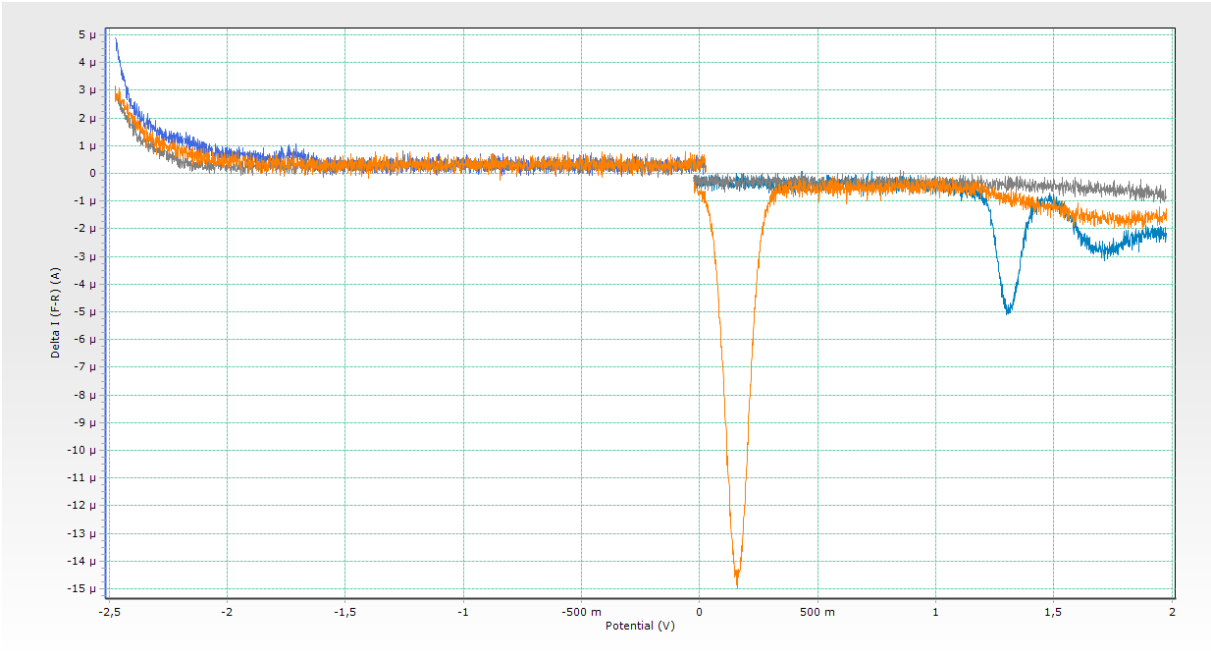
Compound 14:



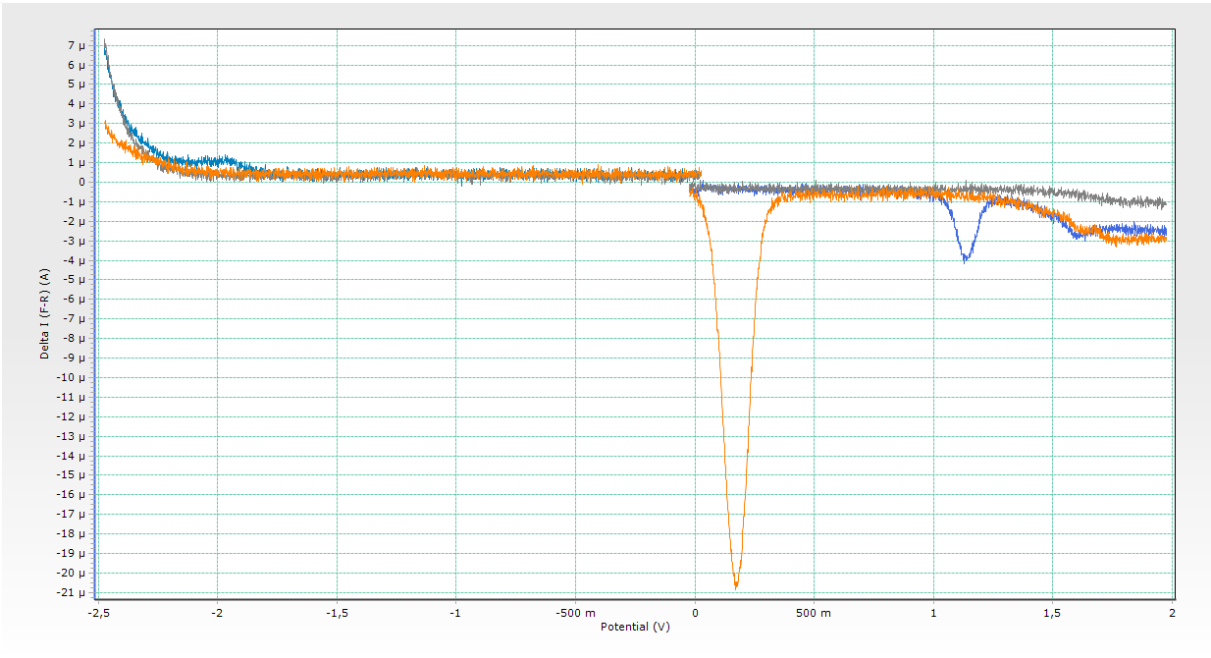
Compound 15:



Compound 16:



Compound 17:



X-Ray structures

For all crystal structures hydrogen atoms were placed in idealized positions. Hydrogen atoms were riding on their respective heavy atoms with displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the corresponding heavy atom for C(H) and C(H,H) groups; a factor of 1.5 was applied for terminal methyl groups.

Compound **4** (6982) CCDC 1048789
No disordered solvent or ligand molecules

Compound **6** (9038) CCDC 1048797
No disordered solvent or ligand molecules

Compound **8** (8682) CCDC 1048792
No disordered solvent or ligand molecules

Compound **10** (9039) CCDC 1048798
One of the two CF_3SO_3 anions is disordered. This disorder was treated by splitting the CF_3 group over two equally populated positions. The dichloromethane solvent molecule exhibits disorder to and both chlorine atoms were split over three positions at a ratio of 1:2:1. All distances involving disordered atoms were refined without restraints.

Compound **11** (9047) CCDC 1048799
No disordered solvent or ligand molecules

Compound **12** (8667) CCDC 1048790
The CF_3 group of one of the CF_3SO_3 anions (C48, F4, F5, F6) is disordered over three equally populated positions, the SO_3 group of the same anion is disordered over two equally populated positions. Fluorine atom F2 of the other CF_3SO_3 anion was split over two equally populated positions. All distances involving disordered atoms were refined without restraints.

Compound **13** (8930) CCDC 1048795
One of the two CF_3SO_3 anions is disordered. The CF_3 group of this anion was split over two positions and the sum of the population parameters was constrained to unity. Distances between fluorine atoms within each CF_3 group were restrained to C_3 symmetry, as were all C-F distances. Anisotropic displacement parameters of these fluorine atoms were restrained to resemble an approximately isotropic shape (Shelx ISOR instruction).

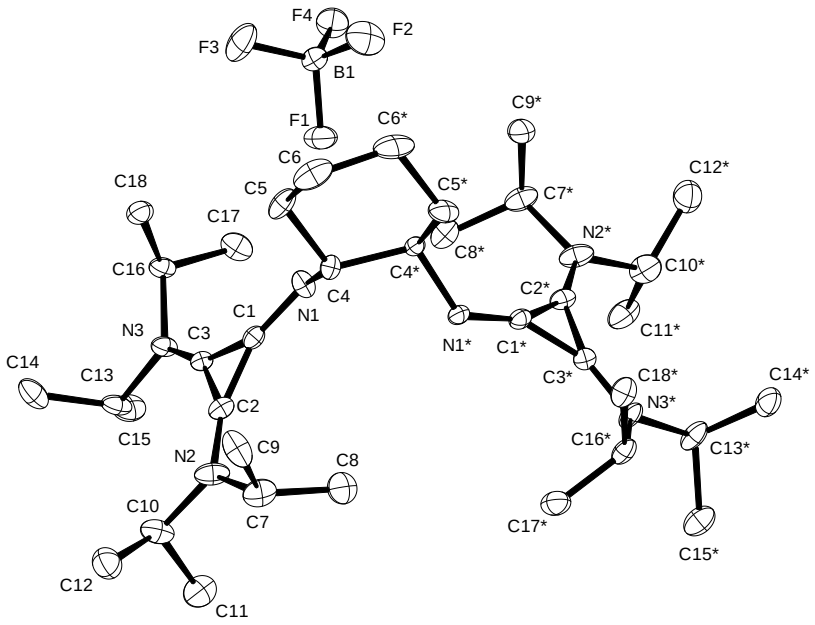
Compound **14** (8682) CCDC 1048791
One of the two CF_3SO_3 anions is disordered. This disorder was treated by splitting S2 and O6 over two positions populated at a ratio of 4:1. The CF_3 group of this anion was split over two equally populated positions. All distances involving disordered atoms were refined without restraints.

Compound **21** (8853) CCDC 1048793
Three of the bis-isopropylamine substituents (N3, C14-C19; C23-C25) displayed large anisotropic displacement parameters and split over two equally populated positions. These atoms were refined with isotropic displacement parameters only and all chemically equivalent C-C and C-N distances in these groups were restrained to be equal within a standard uncertainty of 0.02 Å.

Compound **22** (8946) CCDC 1048796
One of the two CF_3SO_3 anions is disordered. The CF_3 group of this anion was split over two equally populated positions. Distances between fluorine atoms within each CF_3 group were restrained to C_3 symmetry, as were all C-F distances. Anisotropic displacement parameters of these fluorine atoms were restrained to resemble an approximately isotropic shape (Shelx ISOR instruction).

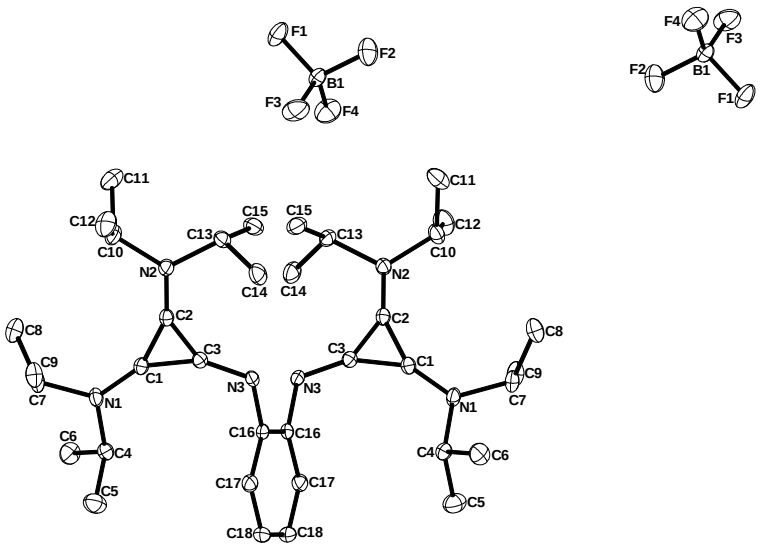
Compound **25** (8868) CCDC 1048794
Two of the dichloromethane solvent molecule exhibit disorder and chlorine atoms Cl3 and Cl5 were split over two positions. Additionally C25 belonging to one of isopropyl substituents required splitting too. The sum of the population parameters was constrained to unity and anisotropic displacement parameters of these atoms were restrained to resemble an approximately isotropic shape (Shelx ISOR instruction).

Compound **4**



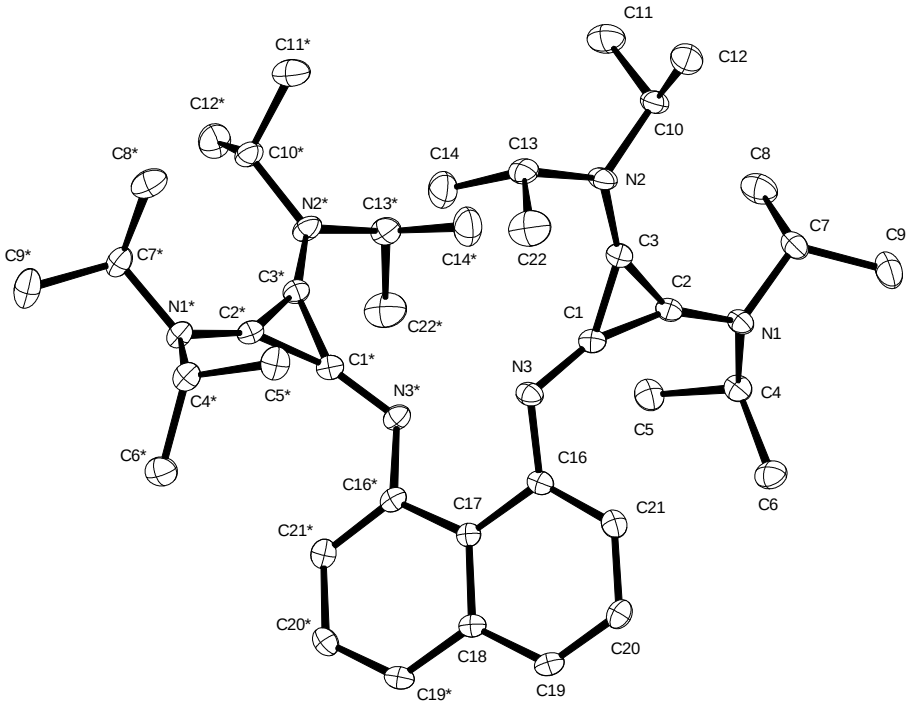
Empirical formula	$C_{36}H_{68}N_6^{2+} \cdot 2\ (BF_4^-)$	
Color	colourless	
Formula weight	758.58 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c, (no. 15)	
Unit cell dimensions	a = 25.0246(8) Å	α= 90°.
	b = 7.9571(8) Å	β= 114.333(8)°.
	c = 22.571(2) Å	γ = 90°.
Volume	4095.1(6) Å^3	
Z	4	
Density (calculated)	1.230 Mg · m^{-3}	
Absorption coefficient	0.098 mm^{-1}	
F(000)	1632 e	
Crystal size	0.23 x 0.18 x 0.08 mm^3	
θ range for data collection	2.71 to 27.50°.	
Index ranges	$-32 \le h \le 32$, $-10 \le k \le 10$, $-29 \le l \le 27$	
Reflections collected	26745	
Independent reflections	4697 [R_{int} = 0.0438]	
Reflections with I>2σ(I)	3689	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4697 / 0 / 243	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2σ(I)]	R_1 = 0.0669	wR^2 = 0.1591
R indices (all data)	R_1 = 0.0861	wR^2 = 0.1754
Largest diff. peak and hole	1.240 and -0.517 e · Å^{-3}	

Compound **6**



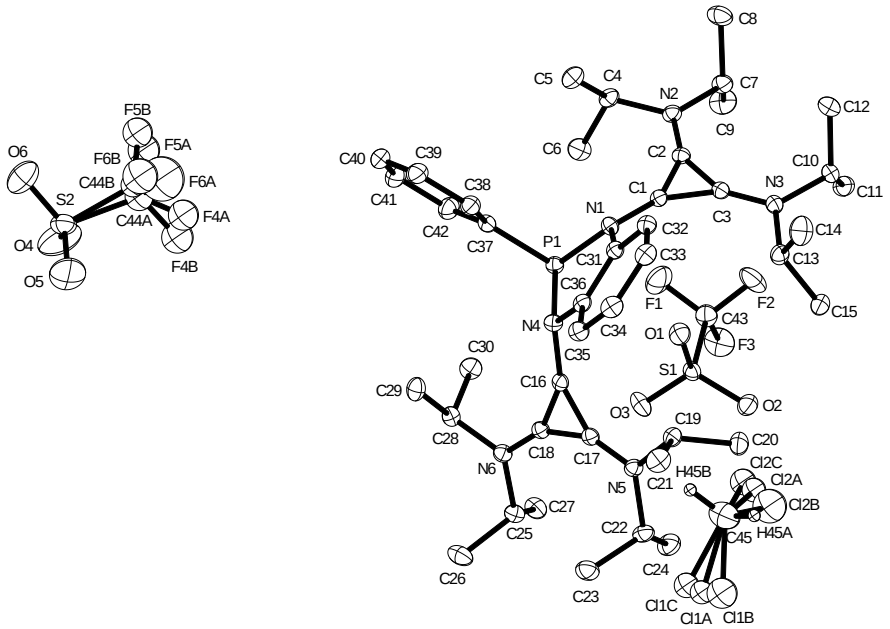
Empirical formula	$C_{36}H_{62}B_2F_8N_6$	
Color	colourless	
Formula weight	752.53 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	c 2/c, (no. 15)	
Unit cell dimensions	a = 28.091(4) Å	α= 90°.
	b = 11.2966(17) Å	β= 91.416(3)°.
	c = 12.9833(19) Å	γ = 90°.
Volume	4118.8(11) $Å^3$	
Z	4	
Density (calculated)	1.214 $Mg \cdot m^{-3}$	
Absorption coefficient	0.097 mm^{-1}	
F(000)	1608 e	
Crystal size	0.29 x 0.21 x 0.04 mm^3	
θ range for data collection	1.450 to 30.672°.	
Index ranges	$-40 \le h \le 40$, $-16 \le k \le 16$, $-18 \le l \le 18$	
Reflections collected	56414	
Independent reflections	6362 [R_{int} = 0.0581]	
Reflections with $I>2\sigma(I)$	5002	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99621 and 0.97173	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6362 / 0 / 247	
Goodness-of-fit on F^2	1.131	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0431	wR^2 = 0.1176
R indices (all data)	R_1 = 0.0633	wR^2 = 0.1376
Extinction coefficient	n/a	
Largest diff. peak and hole	0.426 and -0.357 $e \cdot Å^{-3}$	

Compound **8**



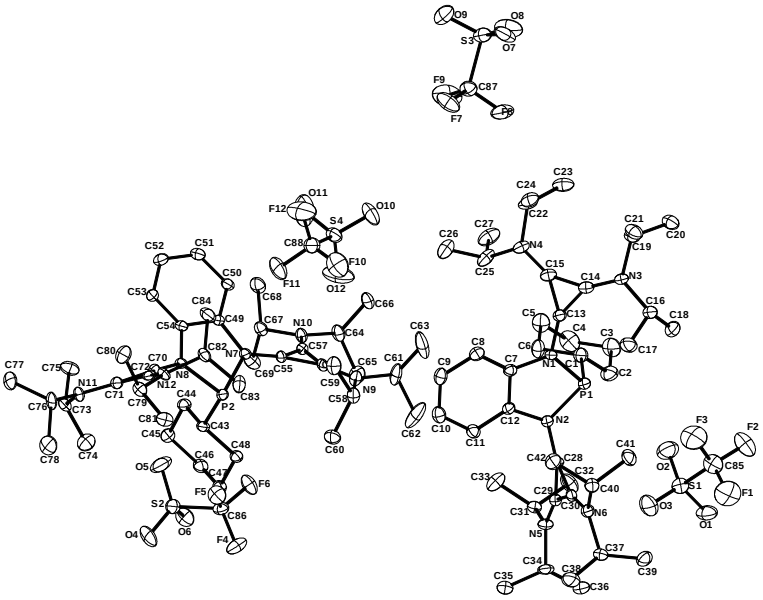
Empirical formula	$C_{40}H_{62}N_6$	
Color	colorless	
Formula weight	626.95 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c, (no. 15)	
Unit cell dimensions	a = 25.030(4) Å	α= 90°.
	b = 13.133(2) Å	β= 124.579(3)°.
	c = 14.480(2) Å	γ = 90°.
Volume	3919.1(11) Å^3	
Z	4	
Density (calculated)	1.063 Mg · m^{-3}	
Absorption coefficient	0.063 mm^{-1}	
F(000)	1376 e	
Crystal size	0.23 x 0.05 x 0.03 mm^3	
θ range for data collection	1.839 to 28.636°.	
Index ranges	$-33 \le h \le 33$, $-17 \le k \le 17$, $-19 \le l \le 19$	
Reflections collected	48213	
Independent reflections	5015 [R_{int} = 0.0835]	
Reflections with I>2σ(I)	3596	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.99	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5015 / 0 / 217	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2σ(I)]	R_1 = 0.0432	wR^2 = 0.1129
R indices (all data)	R_1 = 0.0751	wR^2 = 0.1396
Largest diff. peak and hole	0.3 and -0.4 e · Å^{-3}	

Compound **10**



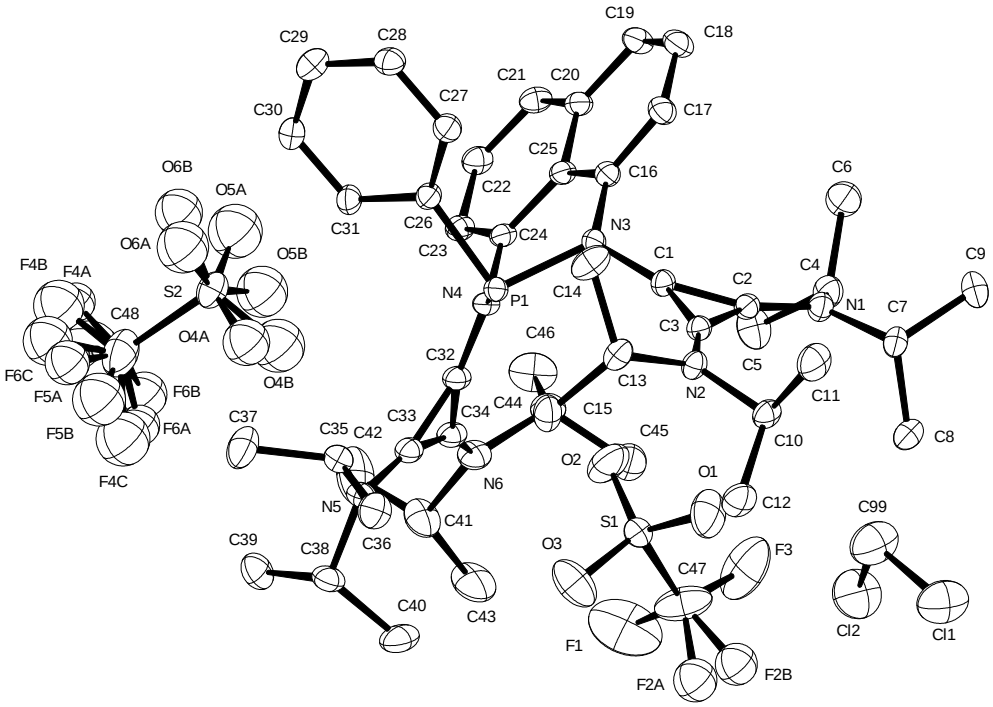
Empirical formula	$C_{45}H_{67}Cl_2F_6N_6O_6PS_2$	
Color	colourless	
Formula weight	1068.03 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1, (no. 2)	
Unit cell dimensions	a = 11.5789(8) Å	α= 112.456(6)°.
	b = 15.7217(13) Å	β= 92.869(5)°.
	c = 16.3126(15) Å	γ = 103.419(7)°.
Volume	2637.5(4) $Å^3$	
Z	2	
Density (calculated)	1.345 $Mg \cdot m^{-3}$	
Absorption coefficient	0.304 mm^{-1}	
F(000)	1124 e	
Crystal size	0.12 x 0.10 x 0.02 mm^3	
θ range for data collection	2.631 to 33.167°.	
Index ranges	$-17 \le h \le 17$, $-24 \le k \le 24$, $-25 \le l \le 24$	
Reflections collected	58156	
Independent reflections	19971 [R_{int} = 0.0591]	
Reflections with $I>2\sigma(I)$	13565	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99609 and 0.97904	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19971 / 0 / 639	
Goodness-of-fit on F^2	1.029	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0680	wR^2 = 0.1586
R indices (all data)	R_1 = 0.1086	wR^2 = 0.1831
Extinction coefficient	0	
Largest diff. peak and hole	1.478 and -1.126 $e \cdot Å^{-3}$	

Compound **11**



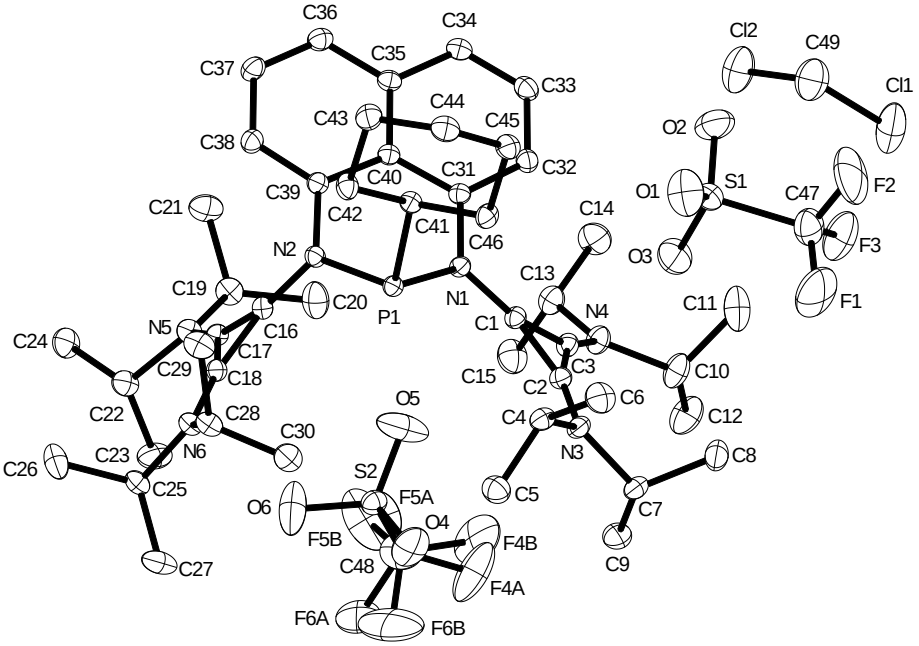
Empirical formula	$C_{44}\ H_{71}\ F_6\ N_6\ O_6\ P\ S_2$	
Color	yellow	
Formula weight	989.15 $g{\cdot}mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	p 2_1 2_1 2_1, (no. 19)	
Unit cell dimensions	a = 16.216(5) Å	α= 90°.
	b = 16.530(5) Å	β= 90°.
	c = 37.757(10) Å	γ = 90°.
Volume	10121(5) $Å^3$	
Z	8	
Density (calculated)	1.298 $Mg{\cdot}m^{-3}$	
Absorption coefficient	0.209 mm^{-1}	
F(000)	4208 e	
Crystal size	0.15 x 0.12 x 0.10 mm^3	
θ range for data collection	2.949 to 28.698°.	
Index ranges	$-21 \le h \le 21$, $-22 \le k \le 22$, $-51 \le l \le 51$	
Reflections collected	223730	
Independent reflections	26115 [R_{int} = 0.1354]	
Reflections with I>2σ(I)	20003	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98300 and 0.97161	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	26115 / 0 / 1203	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2σ(I)]	R_1 = 0.0665	wR^2 = 0.1492
R indices (all data)	R_1 = 0.0943	wR^2 = 0.1648
Absolute structure parameter	0.02(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.819 and -0.521 $e{\cdot}Å^{-3}$	

Compound **12**



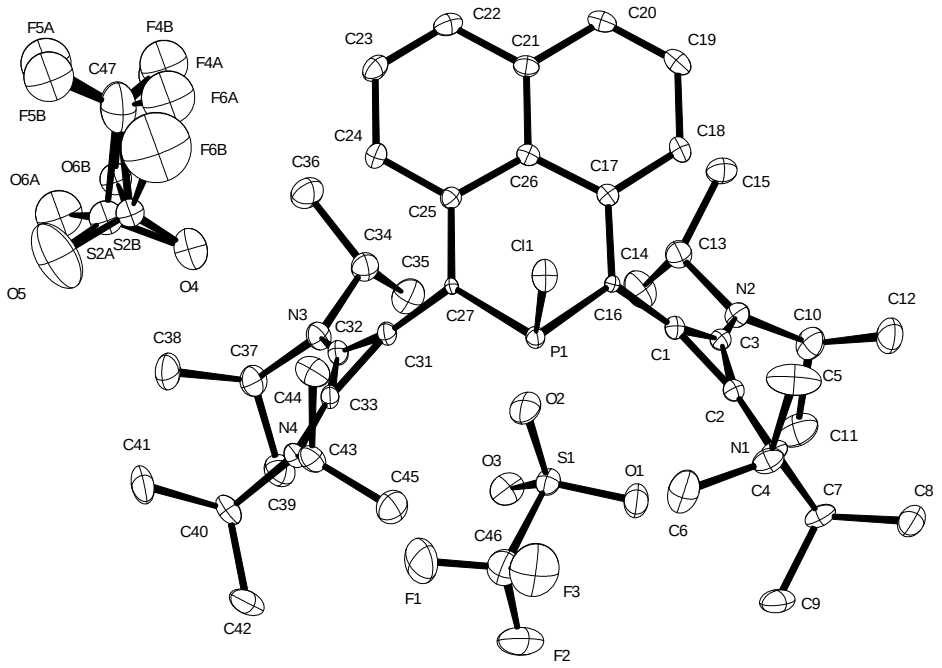
Empirical formula	$C_{49}H_{69}Cl_2F_6N_6O_6PS_2$	
Color	orange yellow	
Formula weight	1118.09 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$Pna2_1$, (no. 33)	
Unit cell dimensions	a = 22.0269(19) Å	α= 90°.
	b = 17.1879(13) Å	β= 90°.
	c = 14.9672(9) Å	γ = 90°.
Volume	5666.5(7) Å^3	
Z	4	
Density (calculated)	1.311 Mg · m^{-3}	
Absorption coefficient	0.286 mm^{-1}	
F(000)	2352 e	
Crystal size	0.22 x 0.12 x 0.05 mm^3	
θ range for data collection	2.885 to 33.126°.	
Index ranges	$-33 \le h \le 33$, $-26 \le k \le 26$, $-23 \le l \le 22$	
Reflections collected	99155	
Independent reflections	21460 [R_{int} = 0.0324]	
Reflections with I>2σ(I)	19101	
Completeness to θ = 25.242°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.99	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21460 / 1 / 670	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2σ(I)]	R_1 = 0.0561	wR^2 = 0.1441
R indices (all data)	R_1 = 0.0655	wR^2 = 0.1519
Absolute structure parameter	0.029(9)	
Largest diff. peak and hole	1.362 and -0.527 e · Å^{-3}	

Compound **13**



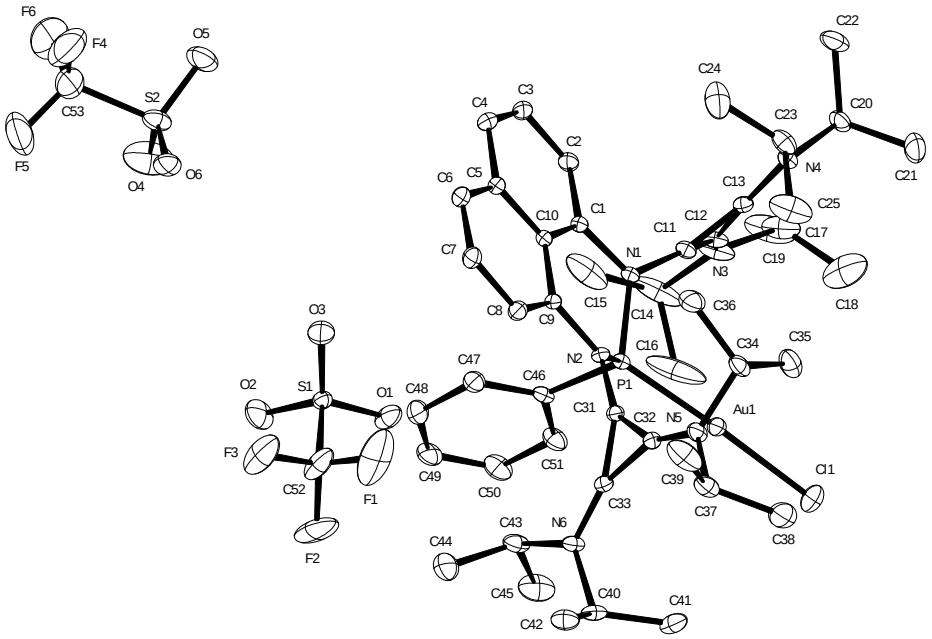
Empirical formula	$C_{49}H_{75}Cl_2F_6N_6O_6PS_2$	
Color	yellow	
Formula weight	1124.14 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P n a 2_1, (no. 33)	
Unit cell dimensions	a = 22.245(4) Å	α= 90°.
	b = 17.313(3) Å	β= 90°.
	c = 14.918(3) Å	γ = 90°.
Volume	5745.1(17) Å^3	
Z	4	
Density (calculated)	1.300 Mg·m^{-3}	
Absorption coefficient	0.283 mm^{-1}	
F(000)	2376 e	
Crystal size	0.16 x 0.09 x 0.09 mm^3	
θ range for data collection	2.871 to 33.173°.	
Index ranges	$-34 \le h \le 34$, $-26 \le k \le 26$, $-22 \le l \le 22$	
Reflections collected	121390	
Independent reflections	21863 [R_{int} = 0.0384]	
Reflections with I>2σ(I)	19679	
Completeness to θ = 25.242°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98498 and 0.97216	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21863 / 67 / 694	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	R_1 = 0.0354	wR^2 = 0.0848
R indices (all data)	R_1 = 0.0435	wR^2 = 0.0899
Absolute structure parameter	0.16(3)	
Extinction coefficient	0	
Largest diff. peak and hole	0.524 and -0.568 e·Å^{-3}	

Compound **14**



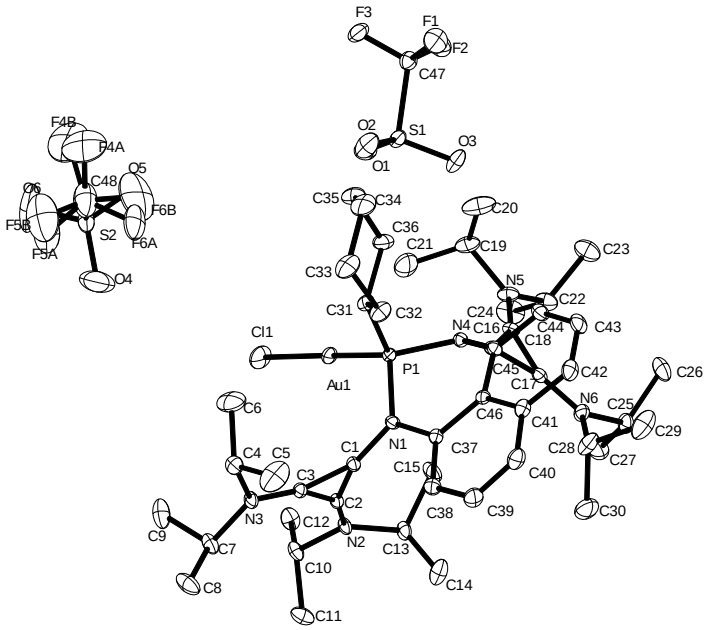
Empirical formula	$C_{44}H_{62}ClF_6N_4O_6PS_2$	
Color	colorless	
Formula weight	987.51 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$, (no. 4)	
Unit cell dimensions	a = 13.201(3) Å	α= 90°.
	b = 14.234(3) Å	β= 91.635(4)°.
	c = 13.385(3) Å	γ = 90°.
Volume	2514.2(9) Å^3	
Z	2	
Density (calculated)	1.304 Mg · m^{-3}	
Absorption coefficient	0.261 mm^{-1}	
F(000)	1040 e	
Crystal size	0.30 x 0.09 x 0.08 mm^3	
θ range for data collection	2.104 to 33.025°.	
Index ranges	$-20 \le h \le 20$, $-21 \le k \le 21$, $-20 \le l \le 20$	
Reflections collected	83744	
Independent reflections	18889 [R_{int} = 0.0370]	
Reflections with I>2σ(I)	17115	
Completeness to θ = 25.242°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98 and 0.91	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18889 / 1 / 588	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2σ(I)]	R_1 = 0.0549	wR^2 = 0.1448
R indices (all data)	R_1 = 0.0620	wR^2 = 0.1513
Absolute structure parameter	0.007(14)	
Largest diff. peak and hole	1.4 and -1.4 e · Å^{-3}	

Compound **21**



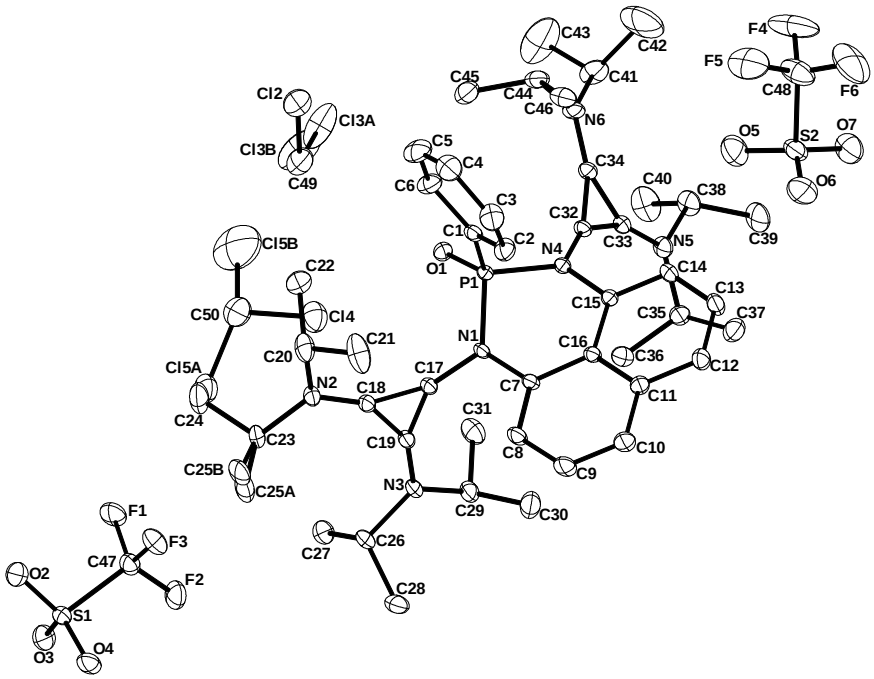
Empirical formula	$C_{48}H_{67}AuClF_6N_6O_6PS_2$	
Color	colorless	
Formula weight	1265.58 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P$\bar{1}$, (no. 2)	
Unit cell dimensions	a = 9.8026(10) Å	α= 74.1395(17)°.
	b = 15.8275(16) Å	β= 88.8135(18)°.
	c = 19.1970(19) Å	γ = 74.8983(18)°.
Volume	2762.0(5) Å^3	
Z	2	
Density (calculated)	1.522 Mg · m^{-3}	
Absorption coefficient	2.887 mm^{-1}	
F(000)	1284 e	
Crystal size	0.18 x 0.08 x 0.05 mm^3	
θ range for data collection	1.104 to 33.142°.	
Index ranges	$-15 \le h \le 15$, $-24 \le k \le 24$, $-29 \le l \le 29$	
Reflections collected	93569	
Independent reflections	21043 [R_{int} = 0.0326]	
Reflections with I>2σ(I)	18959	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.88 and 0.70	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21043 / 0 / 656	
Goodness-of-fit on F^2	1.155	
Final R indices [I>2σ(I)]	R_1 = 0.0231	wR^2 = 0.0613
R indices (all data)	R_1 = 0.0297	wR^2 = 0.0731
Largest diff. peak and hole	0.8 and -1.1 e · Å^{-3}	

Compound **22**



Empirical formula	$C_{48}H_{73}AuClF_6N_6O_6PS_2$	
Color	orange	
Formula weight	1271.63 $g\cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	p 21/n, (no. 14)	
Unit cell dimensions	a = 13.766(2) Å	α= 90°.
	b = 29.691(5) Å	β= 105.121(3)°.
	c = 14.118(2) Å	γ = 90°.
Volume	5570.6(16) $Å^3$	
Z	4	
Density (calculated)	1.516 $Mg\cdot m^{-3}$	
Absorption coefficient	2.863 mm^{-1}	
F(000)	2592 e	
Crystal size	0.20 x 0.12 x 0.09 mm^3	
θ range for data collection	2.989 to 33.182°.	
Index ranges	$-21 \le h \le 21$, $-45 \le k \le 45$, $-21 \le l \le 21$	
Reflections collected	187161	
Independent reflections	21272 [R_{int} = 0.0384]	
Reflections with I>2σ(I)	18511	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.80384 and 0.58211	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21272 / 66 / 683	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2σ(I)]	R_1 = 0.0286	wR^2 = 0.0629
R indices (all data)	R_1 = 0.0367	wR^2 = 0.0658
Extinction coefficient	0	
Largest diff. peak and hole	4.610 and -1.644 $e\cdot Å^{-3}$	

Compound **25**



Empirical formula	$C_{50}H_{71}Cl_4F_6N_6O_7PS_2$	
Color	colourless	
Formula weight	1219.01 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	p -1, (no. 2)	
Unit cell dimensions	a = 8.8243(15) Å	α= 72.431(3)°.
	b = 14.834(3) Å	β= 80.395(3)°.
	c = 23.823(4) Å	γ = 89.145(3)°.
Volume	2929.1(9) Å^3	
Z	2	
Density (calculated)	1.382 Mg·m^{-3}	
Absorption coefficient	0.373 mm^{-1}	
F(000)	1276 e	
Crystal size	0.18 x 0.17 x 0.10 mm^3	
θ range for data collection	1.441 to 31.274°.	
Index ranges	$-12 \le h \le 12$, $-21 \le k \le 21$, $-34 \le l \le 34$	
Reflections collected	72657	
Independent reflections	18676 [R_{int} = 0.0440]	
Reflections with I>2σ(I)	13287	
Completeness to θ = 25.242°	98.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.96878 and 0.92914	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18676 / 24 / 736	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2σ(I)]	R_1 = 0.0555	wR^2 = 0.1524
R indices (all data)	R_1 = 0.0857	wR^2 = 0.1763
Extinction coefficient	n/a	
Largest diff. peak and hole	1.390 and -1.028 e·Å^{-3}	