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Supporting Information

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Synthesis, Structure, and Applications of Pyridiniophosphines**

*Hendrik Tinnermann, Christian Wille, and Manuel Alcarazo**

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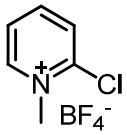
General procedures: All reactions were carried out in flame-dried glassware under Argon. All the solvents were purified by distillation over the drying agents indicated and were transferred under Argon. CH_2Cl_2 (CaH_2), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; ^{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. All commercially available compounds (Acros, Fluka, Lancaster, Alfa Aesar, Aldrich) were used as received unless stated otherwise. Compounds **7**[1], **35**[2] and **37**[3] were prepared accordingly to the procedure described in the literature.

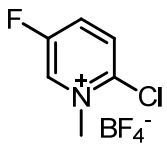
[1] K. H. Müller, M. W. Drewes, P. Dahmen, D. Feucht, DE 100 24 938 A 1
[2] S. J. Pastine, S. W. Youn, D. Sames, *Org. Lett.* **2003**, *5*, 1055.
[3] A. Fürstner, P. W. Davies, T. Gress, *J. Am. Chem. Soc.* **2005**, *127*, 8244.

General procedure for the Alkylation of 2-Chloropyridines. A solution of the corresponding 2-chloropyridine (1 equiv.) in DCM (0.05 M) was added to solid Me_3OBF_4 or Et_3OBF_4 (1 equiv.) and the suspension stirred overnight. Then, the solvent was filtered off and the remaining white solid washed twice with dichloromethane and dried in vacuum.



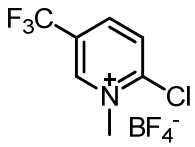
Compound 6: Prepared from 2-chloropyridine (2.0 g, 17.6 mmol) and Me_3OBF_4 (2.6 g, 17.6 mmol) following the general procedure. After washing with DCM (2 x 20 ml), **6** was obtained as a white solid (3.47 g, 91%).

^{1}H NMR (300 MHz, CD_3CN) δ = 8.75 (d, *J* = 6.2 Hz, 1H), 8.47 (td, *J* = 8.2, 1.5 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.94 (t, ^3J = 6.8 Hz, 1H), 4.30 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 148.98, 148.96, 148.38, 131.00, 127.40, 48.62; IR (neat) ṽ = 712, 735, 778, 805, 1024, 1123, 1177, 1274, 1286, 1314, 1446, 1499, 1574, 1623, 3059, 3094, 3115, 3138 cm^{-1} HRMS *calcd.* for $C_{12}H_{14}BCl_2F_4N_2$: 343.056684; *found*: 343.056646.



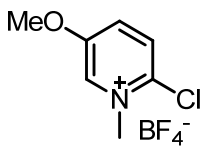
Compound 8: Prepared from 2-chloro-5-fluoropyridine (1.0 g, 7.6 mmol) and Me_3OBF_4 (1.12 g, 7.6 mmol) following the general procedure. After washing with DCM (2 x 20 ml), **8** was obtained as a white solid (1.75 g, 99%).

^{1}H NMR (300 MHz, CD_3CN) δ = 8.88 (t, *J* = 3.1 Hz, 1H), 8.36 (ddd, *J* = 9.4, 6.7, 2.9 Hz, 1H), 8.16 (dd, *J* = 9.3, 4.9 Hz, 1H), 4.31 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 159.92 (d, $J_{C\text{-}F}$ = 255.1 Hz), 145.62, 138.70 (d, $J_{C\text{-}F}$ = 40.0 Hz), 136.23 (d, $J_{C\text{-}F}$ = 19.8 Hz), 132.21 (d, $J_{C\text{-}F}$ = 7.9 Hz), 49.46; ^{19}F NMR (282 MHz, CD_3CN) δ = -120.22, -151.77, -151.82; IR (neat) ṽ = 655, 698, 743, 767, 854, 901, 1022, 1126, 1165, 1282, 1392, 1439, 1509, 1593, 1641, 3084, 3104 cm^{-1}; HRMS *calcd.* for $C_{12}H_{12}N_2BCl_2F_6$: 379.036928; *found*: 379.037035.



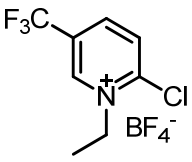
Compound 9: Prepared from 2-chloro-5-(trifluoromethyl)pyridine (400 mg, 2.2 mmol) and Me_3OBF_4 (325 mg, 2.2 mmol) following the general procedure. After washing with DCM (2 x 2 ml), **9** was obtained as a white solid (620 mg, 99%).

^{1}H NMR (300 MHz, CD_3CN) δ = 9.23 (s, 1H), 8.75 (dd, *J* = 8.7, 2.0 Hz, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 4.39 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 153.30, 147.41 (m), 144.96 (q, $J_{C\text{-}F}$ = 3.0 Hz), 132.13, 129.37 (q, $J_{C\text{-}F}$ = 37.0 Hz), 122.32 (q, $J_{C\text{-}F}$ = 272.7 Hz), 49.45; ^{19}F NMR (282 MHz, CD_3CN) δ = -63.45, -151.99, -152.04; IR (neat) ṽ = 663, 690, 722, 804, 861, 888, 916, 944, 998, 1025, 1125, 1192, 1268, 1331, 1435, 1479, 1590, 1639, 2296, 2342, 2383, 3055 cm^{-1}; HRMS *calcd.* for $C_7H_6NClF_3$: 196.013540; *found*: 196.013563.



Compound 11: Prepared from 2-chloro-5-methoxypyridine (965 mg, 6.72 mmol) and Me_3OBF_4 (994 mg, 6.72 mmol) in DCM (20 ml) following the general procedure. After washing with DCM (2 x 20 ml), **11** was obtained as a white solid (1.47 g, 89%).

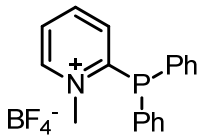
^{1}H NMR (300 MHz, CD_3CN) δ = 8.47 (d, *J* = 2.7 Hz, 1H), 8.10 – 7.93 (m, 2H), 4.27 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 158.33, 140.00, 136.02, 134.07, 130.94, 58.76, 48.98; ^{19}F NMR (282 MHz, CD_3CN) δ = -151.67, -151.72; IR (neat) ṽ = 697, 739, 847, 875, 936, 1013, 1037, 1099, 1159, 1177, 1197, 1271, 1308, 1391, 1425, 1445, 1469, 1513, 1590, 1622, 3101, 3156 cm^{-1}; HRMS *calcd.* for $C_{14}H_{18}N_2BCl_2F_4O_2$: 403.077864; *found*: 403.078070.



Compound 10: Prepared from 2-chloro-5-(trifluoromethyl)pyridine (1 g, 5.5 mmol) and Et_3OBF_4 (1.05 g, 5.5 mmol) in DCM (20 ml) following the general procedure and purified by filtration and washing with DCM (2 x 10 ml) to afford **10** as a white solid (1.6 g, 5.4 mmol, 99%).

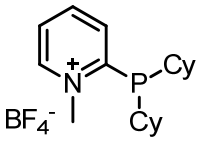
^{1}H NMR (300 MHz, CD_3CN) δ = 9.24 (d, *J* = 0.7 Hz, 1H), 8.74 (dd, *J* = 8.7, 2.1 Hz, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 4.82 (q, *J* = 7.3 Hz, 2H), 1.62 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR (75 MHz, CD_3CN) = 152.27, 146.25, 144.89 (q, J_{C-F} = 3.0 Hz), 132.79, 129.92 (q, J_{C-F} = 36.9 Hz), 122.21 (q, J_{C-F} = 273.7 Hz); ^{19}F NMR (282 MHz, CD_3CN) δ = -63.46, -151.88, -151.94; IR (neat) ṽ =727, 740, 767, 809, 858, 939, 1023, 1056, 1095, 1110, 1146, 1183, 1193, 1233, 1299, 1328, 1395, 1413, 1453, 1473, 1509, 1586, 1639, 3089 cm^{-1}; HRMS *calcd.* for $C_8H_8NClF_3$: 210.029185; *found*: 210.028857.

General procedure for the Preparation of Pyridiniophosphines. To a solution of the corresponding 1-alkyl/aryl-2-chloropyridinium tetrafluoroborate (1 equiv.) in THF (2 ml) was added the desired secondary phosphine (2.5-3.0 equiv.) and the resulting suspension heated for 1 to 7 days. After cooling to rt, the solvents were evaporated and the crude reaction mixture washed with *n*-Pentan (2 x 2 ml), solved in DCM and washed with sat. $NaBF_4$ aqueous solution. The organic phase was dried over $NaSO_4$ and the solvent evaporated. If necessary, the resulting solid could be further purified by an additional wash with THF (1-2 ml).



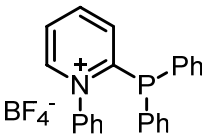
Compound 12: Prepared by heating a THF suspension of **6** (400 mg, 1.8 mmol) and diphenylphosphine (1.1 ml, 5.6 mmol) at 65°C for 3 days. White solid (477 mg, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.04 (d, *J* = 5.7 Hz, 1H), 8.25 (td, *J* = 7.9, 0.9 Hz, 1H), 8.03 – 7.95 (m, 1H), 7.57 – 7.43 (m, 6H), 7.39 – 7.27 (m, 5H), 4.30 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.02 (d, J_{C-P} = 33.4 Hz), 149.54, 144.04, 134.70 (d, J_{C-P} = 21.7 Hz), 132.63, 131.60, 130.20 (d, J_{C-P} = 8.4 Hz), 129.03 (d, *J* = 6.7 Hz), 127.96, 47.64 (d, J_{C-P} = 21.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = -8.61; IR (neat) ṽ = 696, 724, 748, 798, 954, 1000, 1038, 1051, 1161, 1181, 1265, 1310, 1436, 1492, 1571, 1610, 3055, 3103, 3134 cm^{-1}; HRMS *calcd.* for $C_{18}H_{17}NP$: 278.109315; *found*: 278.109239.



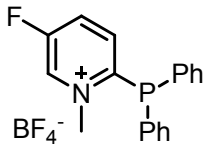
Compound 13: Prepared by heating a THF suspension of **6** (500 mg, 2.3 mmol) and dicyclohexylphosphine (0.75 ml, 5.8 mmol) at 65°C for 3 days. White solid (699 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.11 (d, *J* = 5.2 Hz, 1H), 8.48 (t, *J* = 7.8 Hz, 1H), 8.05 (dd, *J* = 14.3, 7.5 Hz, 2H), 4.59 (s, 3H), 2.11 (t, *J* = 11.8 Hz, 2H), 1.91 (d, *J* = 12.0 Hz, 2H), 1.81 (d, *J* = 12.8 Hz, 2H), 1.69 (t, *J* = 11.9 Hz, 4H), 1.51 (d, *J* = 12.5 Hz, 2H), 1.41 – 1.01 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.33 (d, J_{C-P} = 42.5 Hz), 149.73, 143.58, 133.44 (d, J_{C-P} = 3.2 Hz), 128.24, 48.82 (d, J_{C-P} = 26.1 Hz), 34.36 (d, J_{C-P} = 15.1 Hz), 29.95 (d, J_{C-P} = 15.9 Hz), 29.44 (d, J_{C-P} =8.6 Hz), 26.78 (d, J_{C-P} = 12.5 Hz), 26.65 (d, J_{C-P} = 8.8 Hz), 25.91; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.52; IR (neat) ṽ = 728, 779, 851, 915, 1053, 1179, 1262, 1448, 1497, 1571, 1610, 2851, 2925 cm^{-1}; HRMS *calcd.* for $C_{18}H_{29}NP$: 290.203217; *found*: 290.203415.



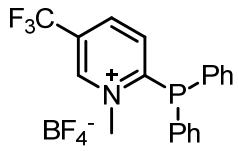
Compound 14: Prepared by heating a THF suspension of **7** (650 mg, 2.3 mmol) and diphenylphosphine (1.2 ml, 6.9 mmol) at 130°C for 12 h in a μwave oven. White solid (715 mg, 71%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 5.1 Hz, 1H), 8.46 (td, *J* = 8.0 Hz, 1.3, 1H), 8.06 (t, *J* = 6.9 Hz, 1H), 7.66 – 7.50 (m, 4H), 7.50 – 7.37 (m, 6H), 7.32 – 7.21 (m, 6H); ^{13}C NMR (75 MHz, CD_3CN) δ = 149.53, 146.74, 135.83 (d, J_{C-P} = 22.5 Hz), 134.40, 132.53, 132.11, 131.40 (d, J_{C-P} = 8.2 Hz), 130.58 (d, J_{C-P} = 7.6 Hz), 128.25, 127.40 (d, J_{C-P} = 3.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -151.82, -151.87; ^{31}P NMR (121 MHz, CDCN) δ = -7.74; IR (neat) ṽ = 692, 699, 734, 748,757, 786, 841, 863, 901, 931, 979, 997, 1011, 1035, 1047, 1079, 1163, 1178, 1254, 1288, 1315, 1438, 1455, 1475, 1492, 1563, 1589, 1607, 3070, 3117 cm^{-1}; HRMS *calcd.* for $C_{23}H_{19}NP$: 340.124626; *found*: 360.124961.



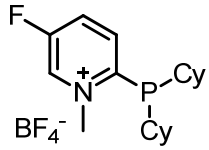
Compound 15: Prepared by heating a THF suspension of **8** (500 mg, 2.14 mmol) and diphenylphosphine (0.92 ml, 5.35 mmol) at 65°C for 3 days. White solid (351 mg, 43%).

^{1}H NMR (300 MHz, CD_3CN) δ = 8.94 – 8.82 (m, 1H), 8.18 – 8.07 (m, 1H), 7.58 (m, 6H), 7.42 (m, 5H), 4.23 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCN) δ = 160.91 (d, J_{C-F} = 255.7 Hz), 139.81 (d, J_{C-P} = 38.2 Hz), 135.66 (d, J_{C-P} = 0.9 Hz), 135.62 (d, J_{C-P} = 21.9 Hz), 132.84 (d, J_{C-P} = 17.4 Hz), 132.43 (d, J_{C-P} = 0.6 Hz), 130.92 (d, J_{C-P} = 8.3 Hz), 130.28 (d, J_{C-P} = 6.7 Hz), 49.12 (d, J_{C-P} = 21.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = -9.34; IR (neat) ν̃ = 699, 715, 738, 753, 760, 858, 895, 931, 958, 998, 1024, 1143, 1165, 1181, 1273, 1314, 1384, 1436, 1479, 1500, 1583, 1623 cm^{-1}; HRMS *calcd.* for $C_{18}H_{16}NFP$: 296.099965; *found*: 296.099889.



Compound 16: Prepared by heating a THF suspension of **9** (500 mg, 1.8 mmol) and diphenylphosphine (0.62 ml, 4.4 mmol) at 65°C for 1 day. White solid (451 mg, 60%).

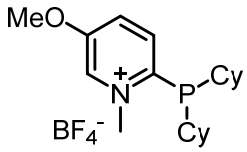
^{1}H NMR (300 MHz, CD_3CN) δ = 9.18 (s, 1H), 8.51 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.72 – 7.50 (m, 7H), 7.50 – 7.38 (m, 4H), 4.25 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 167.44 (d, J_{C-P} = 35.6 Hz), 147.74, 141.70 (q, J_{C-F} = 3.0 Hz), 135.92 (d, J_{C-P} = 22.0 Hz), 134.82 (d, J_{C-P} = 1.2 Hz), 132.72, 131.05 (d, J_{C-P} = 8.6 Hz), 129.85 (q, J_{C-F} = 36.1), 129.43 (d, J_{C-P} = 6.0 Hz), 122.51 (q, J_{C-F} = 272.6 Hz), 49.24 (d, J_{C-P} = 20.7); ^{19}F NMR (282 MHz, CD_3CN) δ = -63.67, -151.79, -151.84; ^{31}P NMR (121 MHz, CD_3CN) δ = -6.00; IR (neat) ν̃ = 693, 702, 727, 743, 752, 862, 892, 913, 996, 1048, 1090, 1115, 1148, 1174, 1267, 1342, 1435, 1504, 1579, 1639, 3103 cm^{-1}; HRMS *calcd.* for $C_{19}H_{16}NF_3P$: 346.09727; *found*: 346.097027.



Compound 17: Prepared by heating a THF suspension of **8** (500 mg, 2.14 mmol) and dicyclohexylphosphine (1.08 ml, 5.35 mmol) at 65°C during 12 hours. White solid (648 mg, 77%).

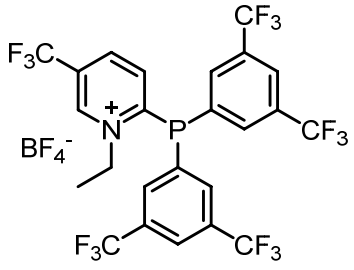
^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.06 (d, *J* = 2.3 Hz, 1H), 8.34 – 8.21 (m, 1H), 8.21 – 8.08 (m, 1H), 4.64 (s, 3H), 2.12 (t, *J* = 11.5 Hz, 2H), 1.98 – 1.61 (m, 8H), 1.52 (d, *J* = 11.7 Hz, 2H), 1.44 – 1.02 (m, 10H); ^{13}C NMR (75 MHz, CD_3CN) δ = 160.88 (d, J_{C-F} = 255.9 Hz), 158.18 (dd, J_{C-P} = 43.7, J_{C-F} = 4.2 Hz), 140.06 (d, J_{C-P} = 36.1 Hz), 136.29 (dd, J_{C-P} = 7.4 Hz, J_{C-F} = 3.4 Hz), 131.93 (d, J_{C-P} = 17.2 Hz), 50.13 (d, J_{C-P} = 26.4 Hz), 34.72 (d, J_{C-P} = 14.3 Hz), 30.48 (d, J_{C-P} = 16.2 Hz), 30.01 (d, J_{C-P} = 8.7 Hz), 27.42 (d, J_{C-P} = 10.9 Hz), 27.28 (d, J_{C-P} = 10.9 Hz), 26.61; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -118.61, -151.62, -151.67; ^{31}P NMR (121 MHz, CD_3CN) δ = -4.49; IR (neat) ν̃ = 704, 738, 765, 817, 851, 889, 920, 958, 1004, 1025, 1040,

1057, 1112, 1170, 1182, 1202, 1269, 1279, 1433, 1450, 1504, 1582, 1626, 2852, 2925, 3077 cm^{-1}; HRMS *calcd.* for $C_{18}H_{17}NP$: 308.193442; *found*: 308.193793.



Compound 18: Prepared by heating a THF suspension off **11** (500 mg, 2.05 mmol) and dicyclohexylphosphin (1.25 ml, 6.16 mmol) at 65°C during 12 hours. White solid (744 mg, 89%).

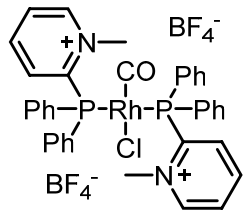
^1H NMR (300 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 2.1 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.94 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.43 (s, 3H), 4.01 (s, 3H), 2.21 – 2.08 (m, 2H), 1.85 – 0.96 (m, 20H); ^{13}C NMR (75 MHz, CD_3CN) δ = 159.15, 138.13, 135.35, 135.31, 58.35, 49.85 (d, J_{C-P} = 27.5 Hz), 34.82 (d, J_{C-P} = 13.5 Hz), 30.76 (d, J_{C-P} = 16.9 Hz), 29.97 (d, J_{C-P} = 8.1 Hz), 27.48 (d, *J* = 13.2 Hz), 27.34 (d, J_{C-P} = 8.8 Hz), 26.73 (d, J_{C-P} = 1.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -151.83, -151.88 ; ^{31}P NMR (121 MHz, CDCN) δ = -7.27; IR (neat) ṽ = 704, 741, 816, 842, 884, 916, 1000, 1015, 1035, 1046, 1163, 1187, 1196, 1286, 1317, 1434, 1447, 1507, 1574, 1615, 2845, 2920 cm^{-1}; HRMS *calcd.* for $C_{19}H_{31}NOP$: 320.213778; *found*: 320.213335.



Compound 19: To a suspension of KH (8.75 mg, 0.22 mmol) in THF (2 ml) was added bis(3,5-bis(trifluoromethyl)phenyl) phosphine (100 mg, 0.22 mmol) at -78 °C and the resulting deep red suspension stirred for 1 hour. Then, the suspension was transferred at the same temperature to a precooled suspension (-78 °C) of **10** (64.9 mg, 0.22 mmol) in THF (2 ml) and the mixture allowed to warm up to rt and stirred for 3 days. After evaporation of the solvent and washing with DCM (2x 2ml), compound **19** was obtained as an off white solid (48 mg, 30%).

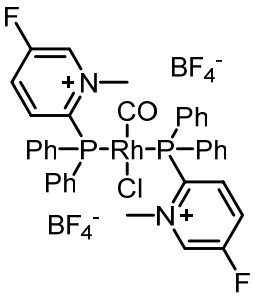
^1H NMR (300 MHz, $CDCl_3$) δ = 9.32 (s, 1H), 8.62 (d, *J* = 7.7 Hz, 1H), 8.25 (s, 2H), 8.02 (d, *J* = 7.2 Hz, 4H), 7.92 (d, *J* = 7.9 Hz, 1H), 4.88 (m, 2H), 1.56 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 161.99 (d, J_{C-P} = 33.4 Hz), 147.95 – 146.40 (m), 143.99 – 142.39 (m), 137.44, 136.89 – 136.01 (m), 133.59 (qd, J_{C-F} =33.9 Hz, J_{C-P} = 7.7 Hz), 133.19 (d, J_{C-P} = 13.5 Hz), 132.18 (d, J_{C-P} = 36.9 Hz), 124.10 (q, J_{C-F} = 272.4 Hz), 121.46 (q, J_{C-F} = 273.0 Hz), 58.60 (d, J_{C-P} = 23.4 Hz), 16.29 (d, J_{C-P} = 3.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -63.52, -63,68, -151.80, -151.85; ^{31}P NMR (121 MHz, CDCN) δ = -10.52; IR (neat) ṽ = 682, 700, 741, 767, 846, 862, 900, 913, 1051, 1095, 1120, 1279, 1331, 1356, 1405, 1459, 1502, 1588, 1634, 2001, 3090 cm^{-1}; HRMS *calcd.* for $C_{24}H_{14}F_{15}NP$: 632.062949; *found*: 632.061889.

General procedure for the preparation of pyridiniophosphine rhodium complexes: $[Rh(CO)_2Cl]_2$ (0.25 equiv.) was added to a solution of the corresponding pyridiniophosphine ligand (1 equiv.) in DCM (2 ml). The resulting suspension was stirred for 1 hour at rt and after evaporation of the solvent, the solid was washed with *n*-pentan (2 x 2 ml) and dried in vacuum. These compounds can be crystalized from acetonitrile/ether mixtures.



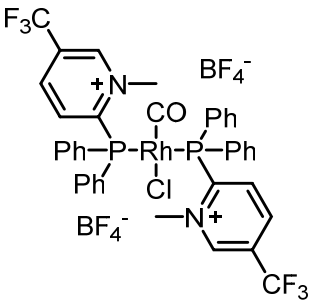
Compound 20: Prepared from **12** (100 mg, 0.274 mmol) and $[Rh(CO)Cl_2]_2$ (26.6 mg, 0.063 mmol) following the general procedure. Yellow solid (121 mg, 99%).

^{1}H NMR (300 MHz, CDCN) δ = 8.84 (d, *J* = 5.9 Hz, 2H), 8.38 (t, *J* = 7.7 Hz, 2H), 8.11 – 8.02 (m, 2H), 7.84 (s, 8H), 7.79 – 7.72 (m, 4H), 7.72 – 7.58 (m, 10H), 4.50 (s, 6H); ^{13}C NMR (75 MHz, CDCN) δ = 186.07 (dt, $J_{C\text{-}Rh}$ = 31.9 Hz, $J_{C\text{-}P}$ = 15.6 Hz), 153.59 (t, $J_{C\text{-}P}$ = 18.1 Hz), 151.14, 145.60, 136.20, 134.99, 134.20, 131.14, 130.07, 126.58 (t, $J_{C\text{-}P}$ = 24.3 Hz), 50.82; ^{31}P NMR (121 MHz, CDCN) δ = 37.82 (d, $J_{P\text{-}Rh}$ = 130.7 Hz); IR (neat) ṽ = 692, 707, 752, 773, 799, 900, 931, 998, 1056, 1165, 1182, 1274, 1314, 1411, 1438, 1481, 1499, 1576, 1610, 1996, 3093, 3138 cm^{-1}; HRMS *calcd.* for $C_{37}H_{34}BClF_4N_2OP_2Rh$: 809.092884; *found*: 809.093025.



Compound 21: Prepared from **15** (75 mg, 0.2 mmol) and $[Rh(CO)_2Cl]_2$ (19.3 mg, 0.05 mmol) following the general procedure. Yellow solid (121 mg, 69%).

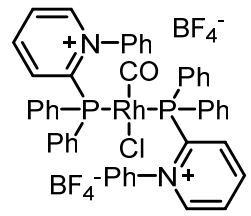
^{1}H NMR (300 MHz, CDCN) δ = 8.98 (s, 2H), 8.27 – 8.16 (m, 2H), 7.84 (s, 8H), 7.76 (t, *J* = 7.4 Hz, 4H), 7.68 (t, *J* = 7.6 Hz, 10H), 4.54 (s, 6H); ^{13}C NMR (75 MHz, CDCN) δ = 161.59 (d, $J_{C\text{-}F}$ = 259.3 Hz), 150.65, 141.69 (d, $J_{C\text{-}F}$ = 38.2 Hz), 136.72 (d, $J_{C\text{-}P}$ = 8.5 Hz), 136.17, 134.35, 132.75 (d, $J_{C\text{-}F}$ = 17.3 Hz), 131.22, 126.48, 51.51 (d, $J_{C\text{-}P}$ = 1.6 Hz); ^{31}P NMR (121 MHz, CDCN) δ = 39.02 (d, $J_{Rh\text{-}P}$ = 130.7 Hz); IR (neat) ṽ = 694, 738, 754, 850, 962, 998, 1054, 1169, 1282, 1437, 1482, 1505, 1590, 1624, 1994, 3087 cm^{-1}; HRMS *calcd.* for $C_{37}H_{32}BClF_6N_2OP_2Rh$: 845.074040; *found*: 845.073864.



Compound 22: Prepared from **16** (100 mg, 0.231 mmol) and $[Rh(CO)_2Cl]_2$ (22.5 mg, 0.058 mmol) following the general procedure. Yellow solid (68 mg, 57%).

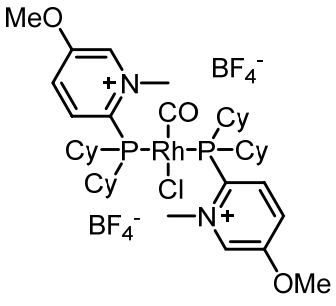
^{1}H NMR (300 MHz, CDCN) δ = 9.28 (s, 2H), 8.65 (d, *J* = 8.2 Hz, 2H), 7.95 – 7.63 (m, 22H), 4.56 (s, 6H); ^{13}C NMR (75 MHz, CDCN)

δ = 167.45 (d, $J_{C\text{-}P}$ = 36.8 Hz), 147.80, 141.73, 136.46 (d, $J_{C\text{-}P}$ = 22.1 Hz), 134.84, 132.76, 131.08 (d, $J_{C\text{-}P}$ = 8.5 Hz), 129.81 (d, $J_{C\text{-}P}$ = 36.7 Hz), 129.44 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.54 (q, $J_{C\text{-}F}$ = 272.8 Hz), 47.26 (d, $J_{C\text{-}P}$ = 20.6 Hz); ^{31}P NMR (121 MHz, CDCN) δ = 40.44 (d, $J_{Rh\text{-}P}$ = 131.0 Hz); IR (neat) ν̃ = 691, 705, 752, 858, 890, 932, 998, 1052, 1090, 1118, 1159, 1177, 1243, 1275, 1334, 1392, 1438, 1482, 1509, 1586, 1634, 1741, 2004, 3092 cm^{-1}; HRMS *calcd.* for $C_{39}H_{32}BClF_{10}N_2OP_2Rh$: 945.067689; *found*: 945.067581.



Compound 23: Prepared from **14** (100 mg, 0.253 mmol) and $[Rh(CO)_2Cl]_2$ (24.6mg, 0.063 mmol) following the general procedure. Yellow solid (94 mg, 78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ =8.62 (d, *J* = 5.6 Hz, 2H), 8.49 (t, *J* = 7.9 Hz, 2H), 8.17 – 8.07 (m, 4H), 7.78 (dd, *J* = 12.7, 6.3 Hz, 8H), 7.54 (ddd, *J* =22.9, 14.9, 7.8 Hz, 16H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 8.0 Hz, 4H); ^{13}C NMR (101 MHz, CDCN) δ = 154.96, 151.72, 146.24, 142.28, 136.52 (t, $J_{C\text{-}P}$ = 7.2 Hz), 136.12 – 135.26 (m), 133.73, 132.75, 130.74 (t, $J_{C\text{-}P}$ = 5.5 Hz), 130.48, 129.97, 128.15, 127.91, 127.71; ^{31}P NMR (121 MHz, $CDCl_3$) δ = 42.09 (d, $J_{Rh\text{-}P}$ = 134.4 Hz); IR (neat) ν̃ = 692, 749, 925, 998, 1034, 1048, 1182, 1254, 1286, 1318, 1437, 1457, 1479, 1587, 1603, 1981, 2350, 3060 cm^{-1}; HRMS *calcd.* for $C_{47}H_{38}BClF_4N_2OP_2Rh$: 933.124354; *found*: 933.123835.

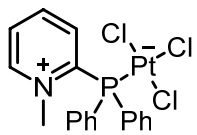


Compound 24: Prepared from **18** (75 mg, 0.184 mmol) and $[Rh(CO)_2Cl]_2$ (17.9 mg, 0.046 mmol) following the general procedure. Yellow solid (67 mg, 74%).

^{1}H NMR (300 MHz, DMSO) δ = 9.11 (s, 2H), 8.38 (d, *J* = 9.1 Hz, 2H), 8.20 (dd, *J* = 9.0, 2.3 Hz, 2H), 4.90 (s, 6H), 4.08 (s, 6H), 2.17 (s, 4H), 2.02 – 0.94 (m, 40H); ^{13}C NMR (101 MHz, DMSO) δ = 185.13 (dt, $J_{C\text{-}Rh}$ = 33.4 Hz, $J_{C\text{-}P}$ = 16.4 Hz), 158.14, 140.35, 138.33 (t, $J_{C\text{-}P}$ = 12.9 Hz), 134.89, 127.44, 57.59, 51.11 (t, $J_{C\text{-}P}$ = 4.2 Hz), 36.04, 33.28, 29.39, 28.39, 27.61, 26.59, 25.77, 25.49; ^{31}P NMR (121 MHz, DMSO) δ = 40.26 (d, $J_{Rh\text{-}P}$ = 123.0 Hz) ; IR (neat) ν̃ = 706, 739, 765, 815, 854, 888, 918, 940, 1018, 1050, 1098, 1172, 1180, 1207, 1269, 1317, 1415, 1450, 1475, 1515, 1614, 1974, 2850, 2928 cm^{-1}; HRMS *calcd.* for $C_{39}H_{62}BClF_4N_2O_3P_2Rh$: 893.301860; *found*: 893.302947.

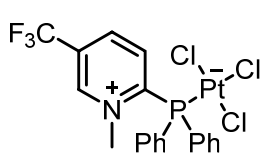
General procedure for the preparation of the phosphine platinum complexes. Finely grounded K_2PtCl_4 (1 equiv) was added to a solution of the pyridiniophosphine salt (1 equiv.)

in MeCN (2 ml) and the resulting suspension stirred overnight at rt. After evaporation of the solvent, the solid was washed with *n*-Pentan (2 x 2 ml), crystallized from DMSO/DCM and dried in vacuum to yield the desired platinum complexes.



Compound 28: Prepared from **12** (100 mg, 0.274 mmol) and K_2PtCl_4 (114 mg, 0.274 mmol) following the general procedure. White solid (127 mg, 80%).

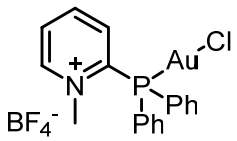
^{1}H NMR (300 MHz, DMSO) δ = 9.18 (d, *J* = 5.7 Hz, 1H), 8.53 (t, *J* = 7.9 Hz, 1H), 8.20 (t, *J* = 6.9 Hz, 1H), 8.02 (dd, *J* = 12.3 Hz, *J* = 7.2 Hz, 4H), 7.79 – 7.57 (m, 6H), 7.39 (t, *J* = 7.0 Hz, 1H), 4.35 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 150.13, 144.54 (d, $J_{C\text{-}P}$ = 5.7 Hz), 135.32 (d, $J_{C\text{-}P}$ = 11.6 Hz), 132.81 (d, $J_{C\text{-}P}$ = 7.5 Hz), 132.63 (d, $J_{C\text{-}P}$ = 2.5 Hz), 129.28 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.78, 124.56, 123.71, 48.32 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (121 MHz, DMSO) δ = 8.49 ($J_{C\text{-}Pt}$ = 1954 Hz); IR (neat) ṽ = 673, 822, 1003, 1023, 1051, 1659, 2126, 2253, 2342, 2383 cm^{-1}; HRMS for DMSO adduct *calcd.* for $C_{20}H_{23}Cl_2NOPPtS$: 621.024487; *found*: 621.024734.



Compound 29: Prepared from **16** (100 mg, 0.231 mmol) and K_2PtCl_4 (96 mg, 0.231 mmol) following the general procedure. White solid (59 mg, 40%).

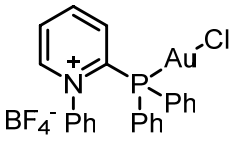
^{1}H NMR (300 MHz, DMSO) δ = 9.85 (s, 1H), 8.98 (d, *J* = 8.2 Hz, 1H), 8.05 (dd, *J* = 12.4 Hz, *J* = 7.4 Hz, 4H), 7.81 – 7.60 (m, 6H), 7.55 (dd, *J* = 7.5 Hz, *J* = 7.1 Hz, 1H), 4.42 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 155.07 (d, $J_{C\text{-}P}$ = 46.9 Hz), 148.54, 141.59, 135.47 (d, $J_{C\text{-}P}$ = 11.7 Hz), 133.48 (d, $J_{C\text{-}P}$ = 7.7 Hz), 132.99, 129.46 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.77 (d, $J_{C\text{-}P}$ = 36.1 Hz), 123.54 (d, $J_{C\text{-}P}$ = 64.0 Hz), 121.24 (q, $J_{C\text{-}P}$ = 273.6 Hz), 49.19 (d, $J_{C\text{-}P}$ = 6.8 Hz); ^{31}P NMR (121 MHz, DMSO) δ = 10.63 ($J_{C\text{-}Pt}$ = 1953 Hz); IR (neat) ṽ = 692, 704, 725, 755, 872, 890, 1036, 1114, 1148, 1179, 1192, 1270, 1332, 1388, 1438, 1481, 1508, 1631, 3001, 3044 cm^{-1}; HRMS for DMSO adduct *calcd.* for $C_{21}H_{22}Cl_2F_3NOPPtS$: 689.013152; *found*: 689.014029.

General procedure for the preparation of the phosphine gold complexes. $AuCl{\cdot}SMe_2$ (1 equiv.) was added to a solution of the desired pyridiniophosphine salt (1 equiv.) in DCM (2 ml) and the resulting suspension stirred for 1 hour at rt. After evaporation of the solvent, the resulting solid washed with *n*-Pentan (2 x 2 ml) and dried in vacuum to yield the desired gold complexes.



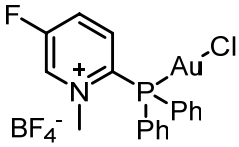
Compound 30: Prepared from **12** (100 mg, 0.274 mmol) and AuCl·SMe_2 (80.7 mg, 0.274 mmol) following the general procedure. White solid (159 mg, 99%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.06 (d, *J* = 0.5 Hz, 1H), 8.44 (t, *J* = 7.7 Hz, 1H), 8.20 (t, *J* = 6.4 Hz, 1H), 7.86 – 7.53 (m, 10H), 7.38 (*t*, *J* = 7.5 Hz, 1H), 4.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.71, 147.12 (d, $J_{C\text{-}P}$ = 52.2 Hz), 145.39 (d, *J* = 5.6 Hz), 134.83 (d, $J_{C\text{-}P}$ = 15.6 Hz), 134.05 (d, $J_{C\text{-}P}$ = 2.0 Hz), 133.77 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.48 (d, $J_{C\text{-}P}$ = 12.8 Hz), 122.55, 121.90, 48.64 (d, $J_{C\text{-}P}$ = 11.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = 30.88; IR (neat) ν̃ = 692, 729, 913, 998, 1055, 1097, 1162, 1185, 1278, 1438, 1482, 1500, 1609, 3061, 3138 cm^{-1}; HRMS *calcd.* for $C_{18}H_{17}NAuClP$: 510.044722; *found*: 510.044585.



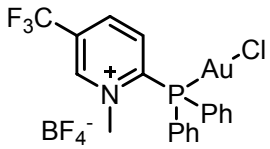
Compound 31: Prepared from **14** (50 mg, 0.12 mmol) and AuCl·SMe_2 (34.5 mg, 0.12 mmol) following the general procedure. White solid (53 mg, 68%).

^{1}H NMR (400 MHz, CD_3CN) δ = 8.94 (s, 1H), 8.63 (t, *J* = 8.0 Hz, 1H), 8.29 (t, *J* = 6.7 Hz, 1H), 7.83 – 7.59 (m, 12H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (101MHz, CD_3CN) δ = 152.22, 148.28 (d, $J_{C\text{-}P}$ = 5.2 Hz), 141.55 (d, $J_{C\text{-}P}$ = 4.5 Hz), 136.26 (d, $J_{C\text{-}P}$ = 15.9 Hz), 136.10 (d, $J_{C\text{-}P}$ = 8.2 Hz), 134.89 (d, $J_{C\text{-}P}$ = 2.5 Hz), 133.32, 131.31 (d, $J_{C\text{-}P}$ = 3.2 Hz), 131.17, 131.01, 127.87, 125.84, 125.22; ^{31}P NMR (162 MHz, CD_3CN) δ = 31.36; IR (neat) ν̃ = 668, 689, 712, 735, 753, 765, 786, 853, 926, 980, 997, 1030, 1044, 1099, 1144, 1162, 1189, 1256, 1283, 1433, 1442, 1458, 1483, 1587, 1603, 3060 cm^{-1}; HRMS *calcd.* for $C_{23}H_{19}NAuClP$: 572.060365; *found*: 572.060083.



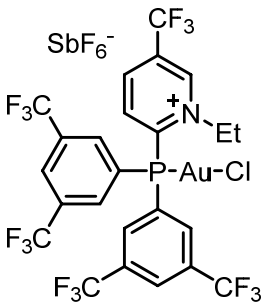
Compound 32: Prepared from **15** (100 mg, 0.26 mmol) and AuCl·SMe_2 (76.6 mg, 0.26 mmol) following the general procedure. White solid (166 mg, 97%).

^{1}H NMR (400 MHz, CD_3CN) δ = 9.02 (dd, *J* = 6.0 Hz, 2.7, 1H), 8.27 (ddd, *J* = 9.1, 6.6, 2.6 Hz, 1H), 7.88 – 7.63 (m, 10H), 7.58 – 7.48 (m, 1H), 4.40 (s, 3H); ^{13}C NMR (101MHz, CD_3CN) δ = 162.24 (d, $J_{C\text{-}F}$ = 260.5 Hz), 142.99 (d, $J_{C\text{-}P}$ = 37.3 Hz), 137.51 (dd, $J_{C\text{-}F}$ =10.0 Hz, $J_{C\text{-}P}$ = 8.4 Hz), 136.23 (d, $J_{C\text{-}P}$ = 15.9 Hz), 135.36 (d, $J_{C\text{-}P}$ = 2.6 Hz), 133.81 (d, $J_{C\text{-}P}$ = 6.2 Hz), 133.58 (d, $J_{C\text{-}P}$ = 6.3 Hz), 131.65 (d, $J_{C\text{-}P}$ = 12.8 Hz), 123.98 (d, $J_{C\text{-}P}$ = 62.6 Hz), 50.70 (d, $J_{C\text{-}P}$ = 11.9 Hz); ^{31}P NMR (162 MHz, CD_3CN) δ = 28.68; IR (neat) ν̃ = 690, 717, 737, 751, 852, 964, 996, 1034, 1048, 1170, 1279, 1437, 1478, 1505, 1594, 1615, 3055, 3079 cm^{-1}; HRMS *calcd.* for $C_{18}H_{16}NAuClFP$: 528.035295; *found*: 528.035127.



Compound 33: Prepared from **16** (100 mg, 0.23 mmol) and AuCl·SMe_2 (68 mg, 0.23 mmol) following the general procedure. White solid (151 mg, 99%).

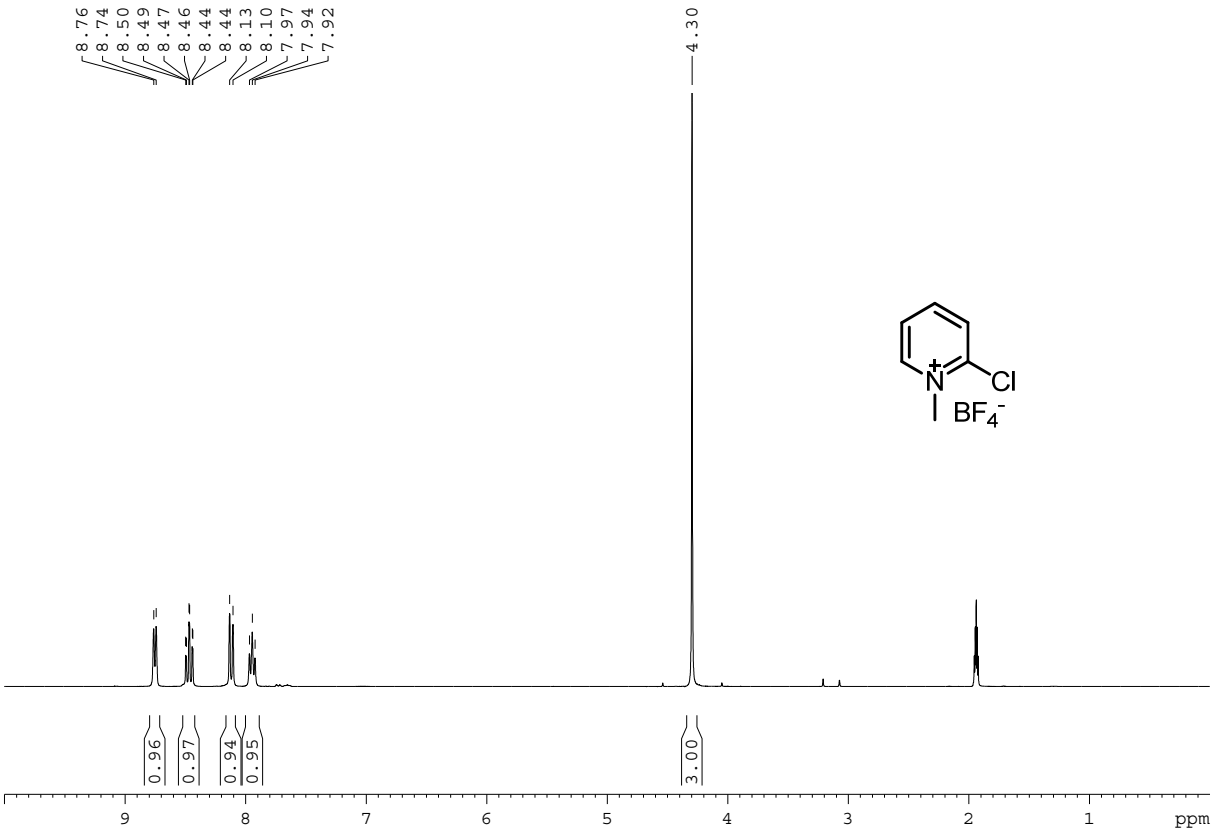
^{1}H NMR (300 MHz, CD_3CN) δ = 9.38 (s, 1H), 8.80 – 8.71 (m, 1H), 7.90 – 7.67 (m, 11H), 4.47 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ = 153.75 (d, $J_{C\text{-}P}$ = 46.8 Hz), 150.38 (d, $J_{C\text{-}P}$ = 2.5 Hz), 143.92 (td, $J_{C\text{-}P}$ = 6.1, $J_{C\text{-}F}$ = 3.0 Hz), 136.42 (d, $J_{C\text{-}P}$ = 15.7 Hz), 136.41, 135.62 (d, $J_{C\text{-}P}$ = 2.7 Hz), 133.42 – 131.99 (dq, $J_{C\text{-}P}$ =37.1 Hz, $J_{C\text{-}F}$ = 1.6 Hz), 131.74 (d, $J_{C\text{-}P}$ = 13.0 Hz), 123.16 (d, $J_{C\text{-}P}$ = 64.7 Hz), 122.07 (q, $J_{C\text{-}F}$ = 273.3 Hz), 50.82 (d, $J_{C\text{-}P}$ = 11.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ= -63.71, -151.49, -151.54; ^{31}P NMR (121 MHz, CD_3CN) δ = 31.54; IR (neat) ṽ = 691, 705, 715, 752, 873, 892, 996, 1053, 1118, 1162, 1200, 1280, 1334, 1393, 1440, 1481, 1510, 1590, 1634, 3092 cm^{-1}; HRMS *calcd.* for $C_{20}H_{18}F_3NP$: 578.032104; *found*: 578.032257.



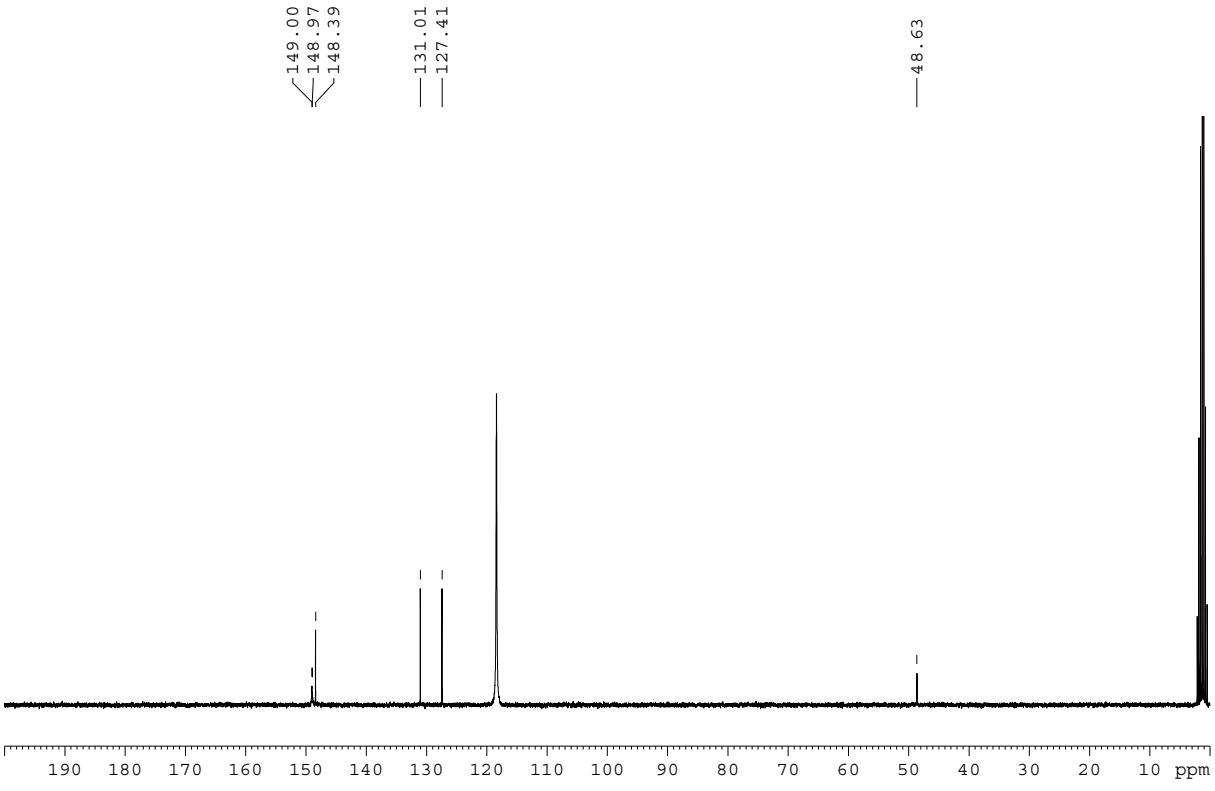
Compound 34: Prepared from **19**(SbF_6) (160 mg, 0.18 mmol) and AuCl·SMe_2 (54.3 mg, 0.18 mmol) following the general procedure to yield **34** as a white solid (104 mg, 51%).

^{1}H NMR (400 MHz, CD_3CN) δ = 9.42 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 2H), 8.29 (d, *J* = 13.8 Hz, 4H), 7.89 (t, *J* = 7.8 Hz, 1H), 4.80 (qd, *J* = 7.1, 1.0 Hz, 2H), 1.64 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CD_3CN) δ = 149.19, 144.37 (dd, $J_{C\text{-}P}$ = 6.0 Hz, $J_{C\text{-}F}$ = 3.1 Hz), 138.51 (d, $J_{C\text{-}P}$ = 9.8), 137.13 (d, $J_{C\text{-}P}$ = 3.1), 136.96 (d, $J_{C\text{-}P}$ = 3.0), 134.11 (qd, $J_{C\text{-}F}$ = 34.5 Hz, $J_{C\text{-}P}$ = 13.3 Hz), 134.00 (d, $J_{C\text{-}P}$ = 37.6 Hz), 130.09 (d, $J_{C\text{-}P}$ = 2.9 Hz), 126.33 (d, $J_{C\text{-}P}$ = 64.9), 123.64 (q, $J_{C\text{-}F}$ = 272.5), 121.94 (q, $J_{C\text{-}F}$ = 268.7 Hz), 58.97 (d, $J_{C\text{-}P}$ = 12.4), 16.47; ^{19}F NMR (282 MHz, CDCN) δ = -63.49, -63.59, -124.01 (sext, $J_{F\text{-}121Sb}$ = 1940 Hz) , -124.01 (oct, $J_{F\text{-}123Sb}$ = 1060 Hz); ^{31}P NMR (121 MHz, CD_3CN) δ = 32.21; IR (neat) ṽ = 681, 699, 718, 731, 742, 764, 847, 866, 899, 927, 997, 1032, 1058, 1097, 1123, 1186, 1280, 1337, 1358, 1405, 1447, 1505, 1630, 3093 cm^{-1}; HRMS *calcd.* for $C_{24}H_{14}NAuClF_{15}P$: 863.997295; *found*: 863.997181.

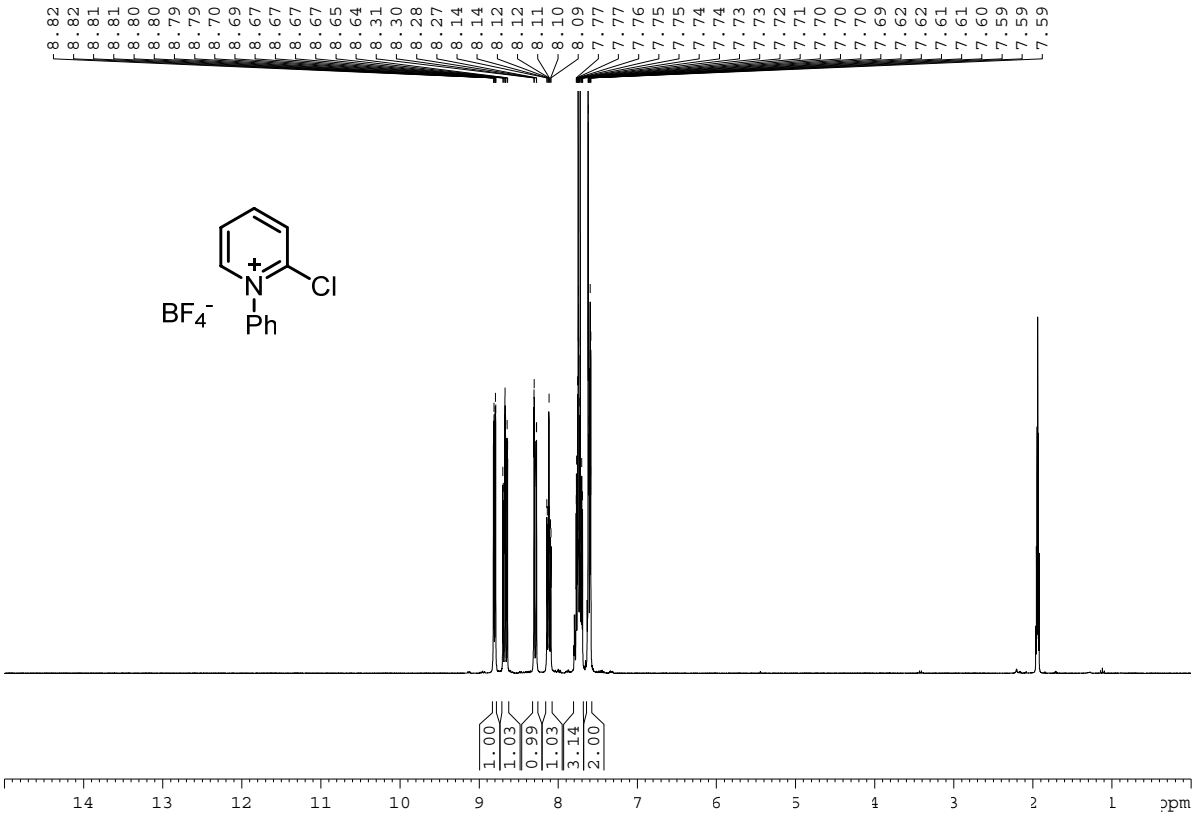
Compound 6: ^{1}H-NMR (300 MHz, CD_3CN)



Compound 6: ^{13}C NMR (75 MHz, CD_3CN)

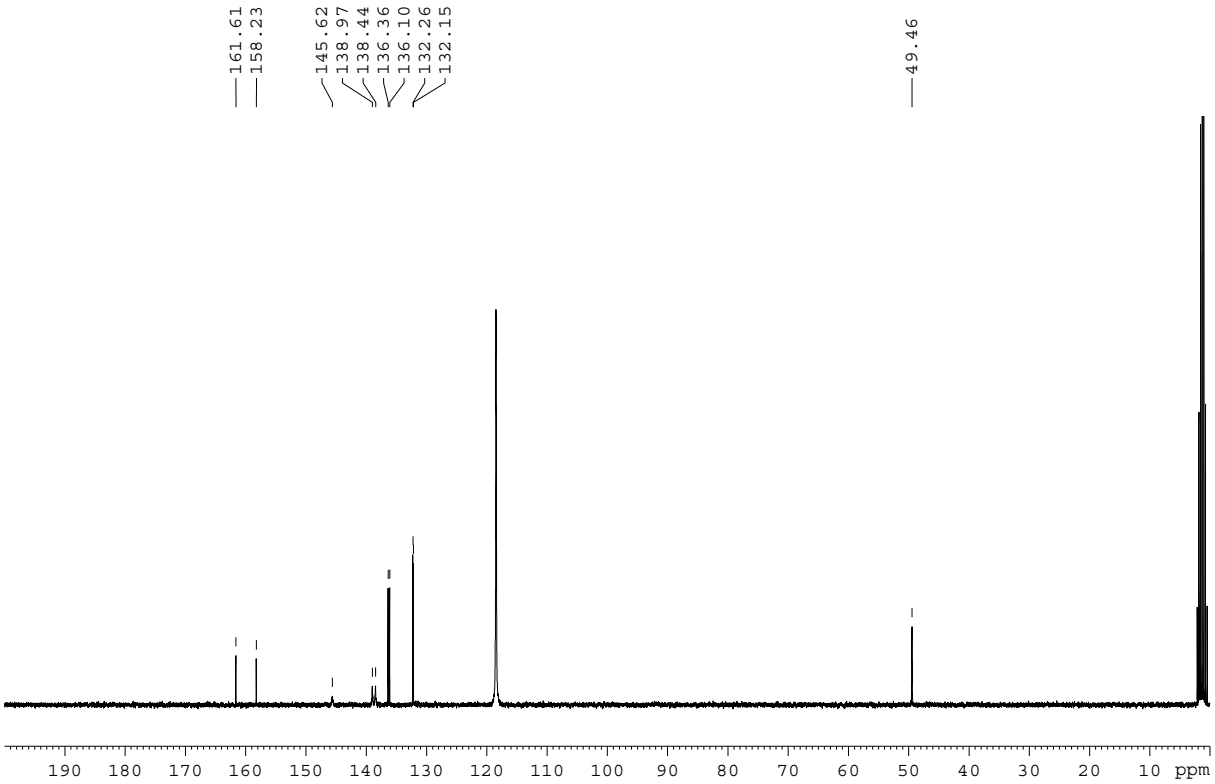


Compound 7 : ^{1}H NMR (300 MHz, $CDCl_3$)

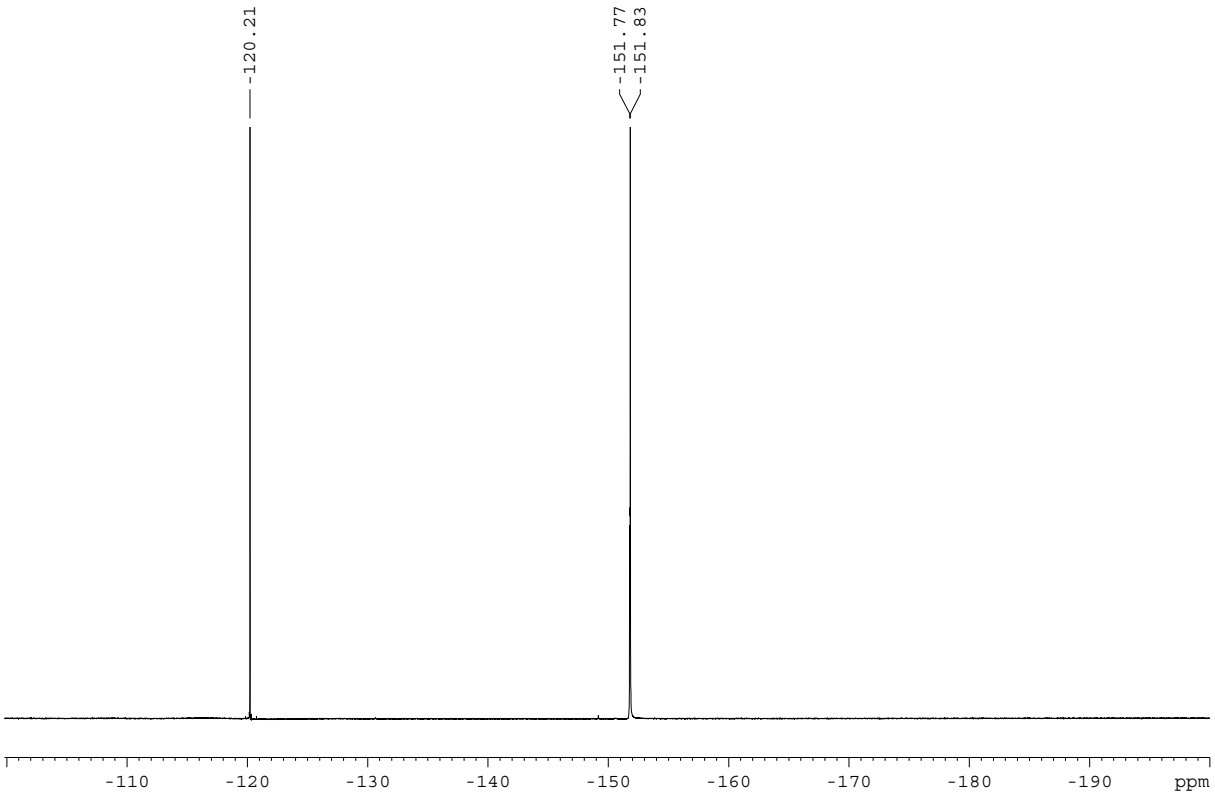


Compound 8: ^{1}H-NMR (300 MHz, CD_3CN)

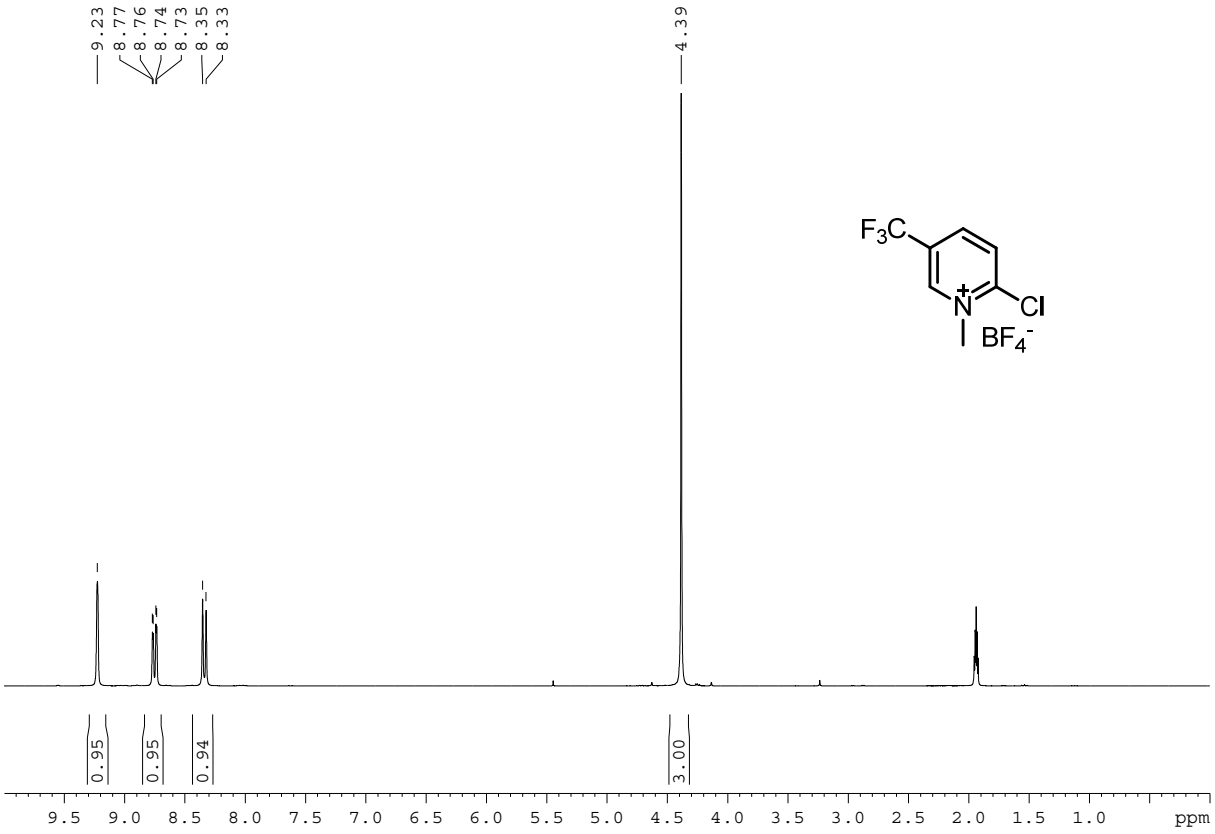
Compound 8: ^{13}C NMR (75 MHz, CD_3CN)



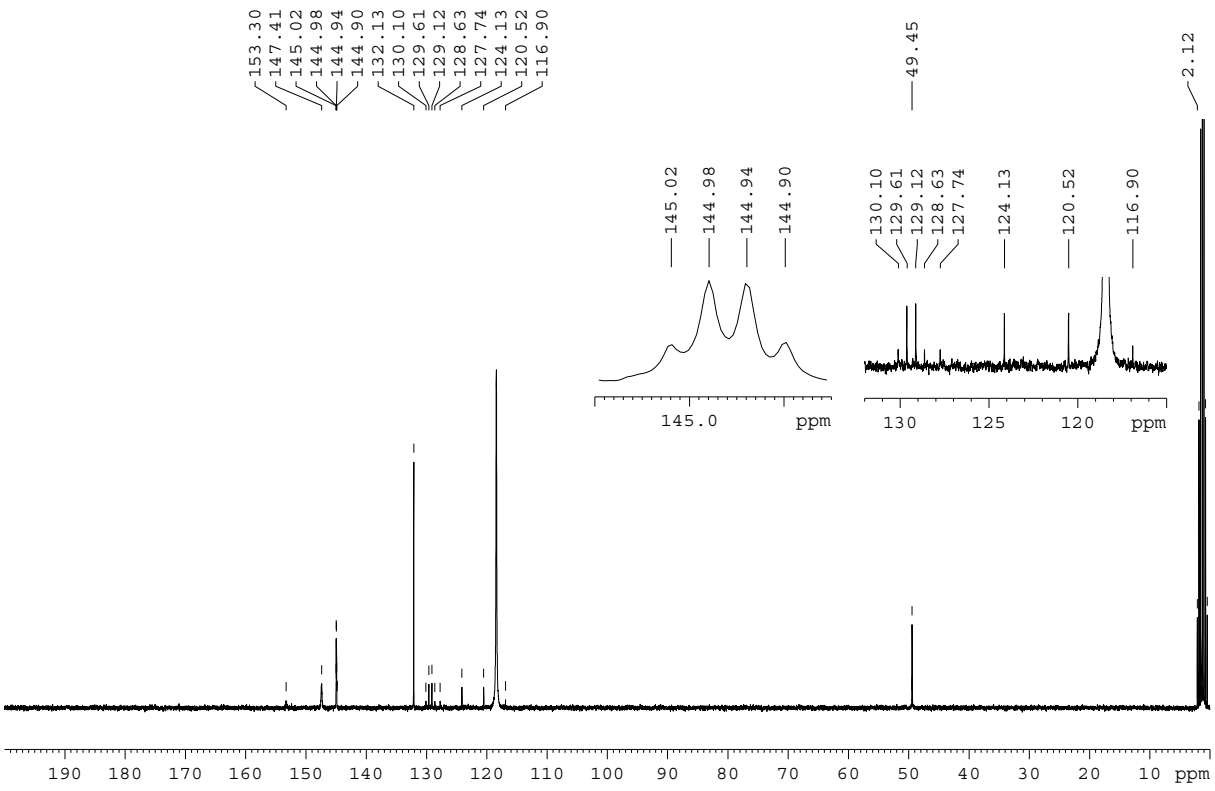
Compound 8: **^{19}F NMR** (282 MHz, CD_3CN)



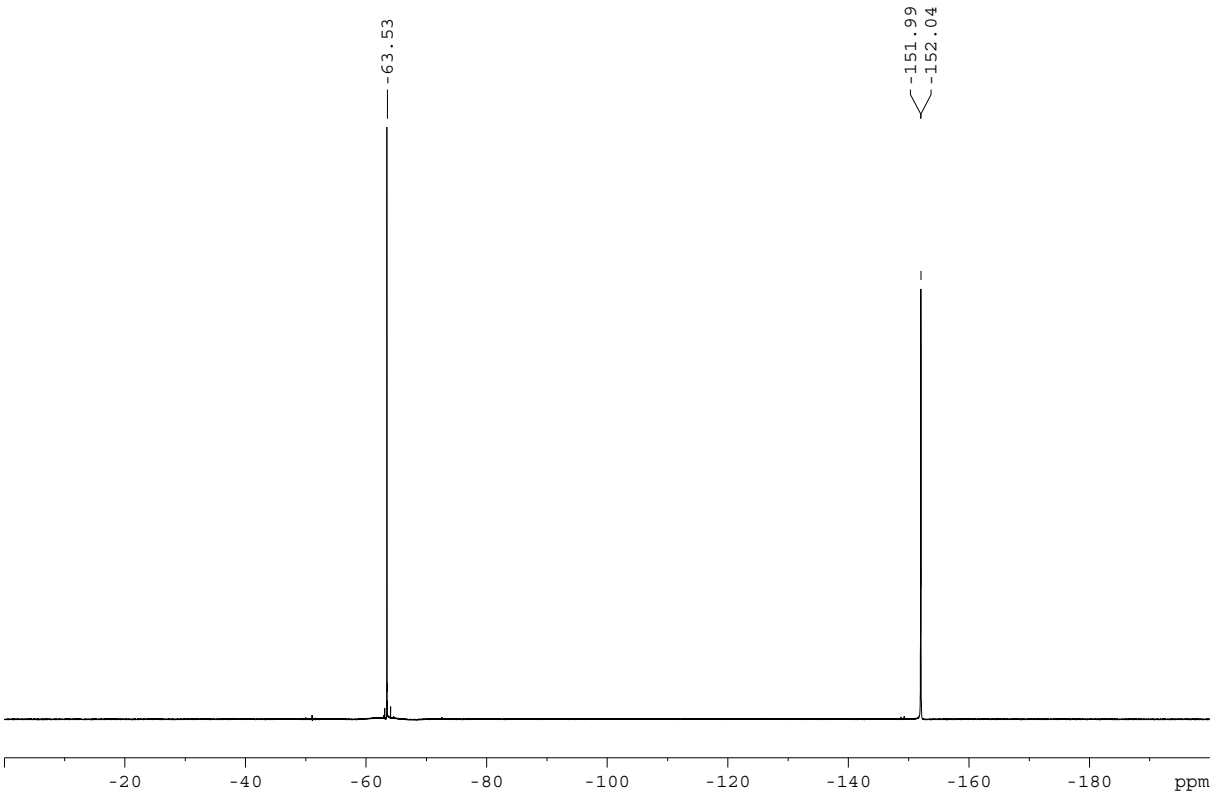
Compound 9: ^{1}H-NMR (300 MHz, CD_3CN)



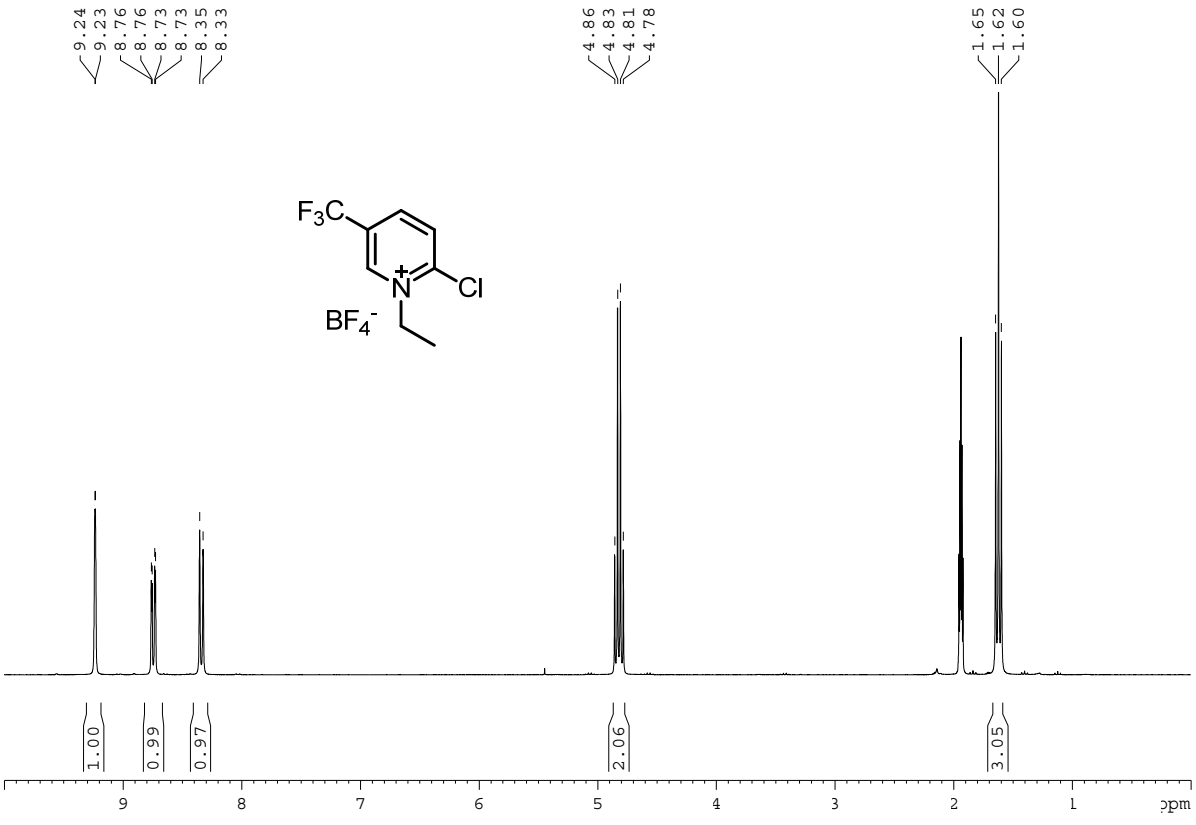
Compound 9: ^{13}C NMR (75 MHz, CD_3CN)



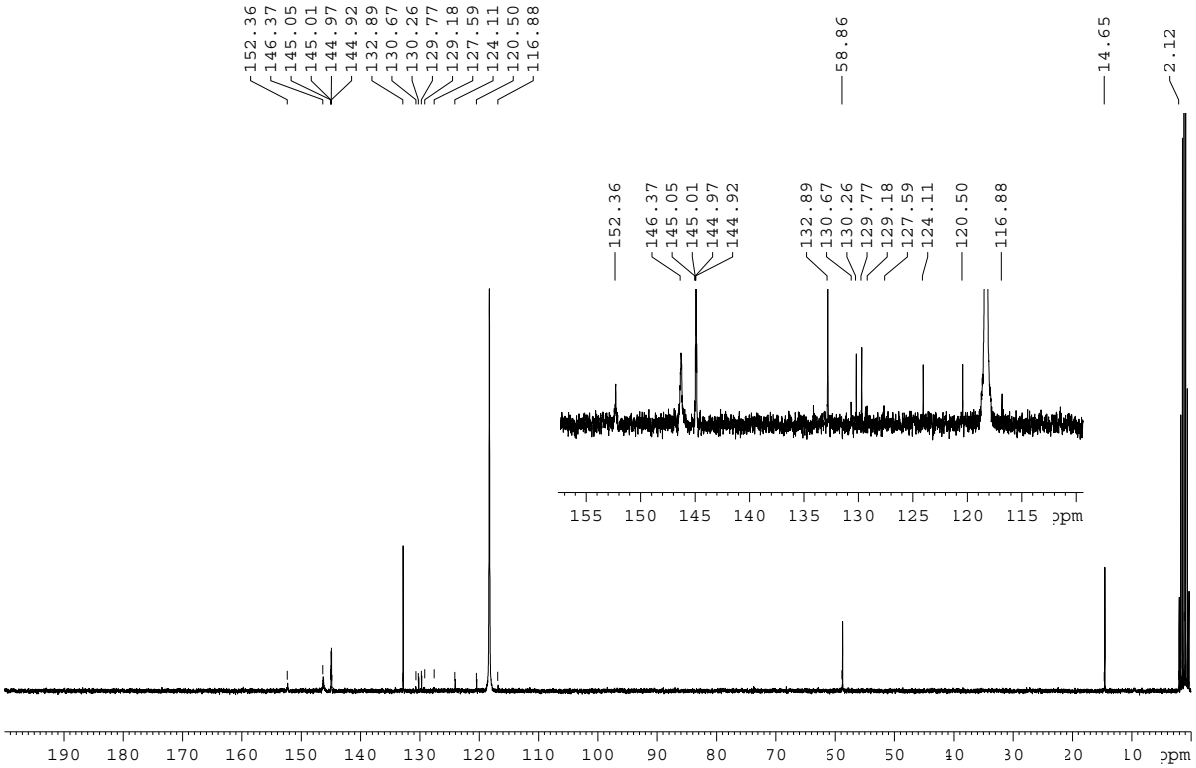
Compound 9: ^{19}F NMR (282 MHz, CD_3CN)



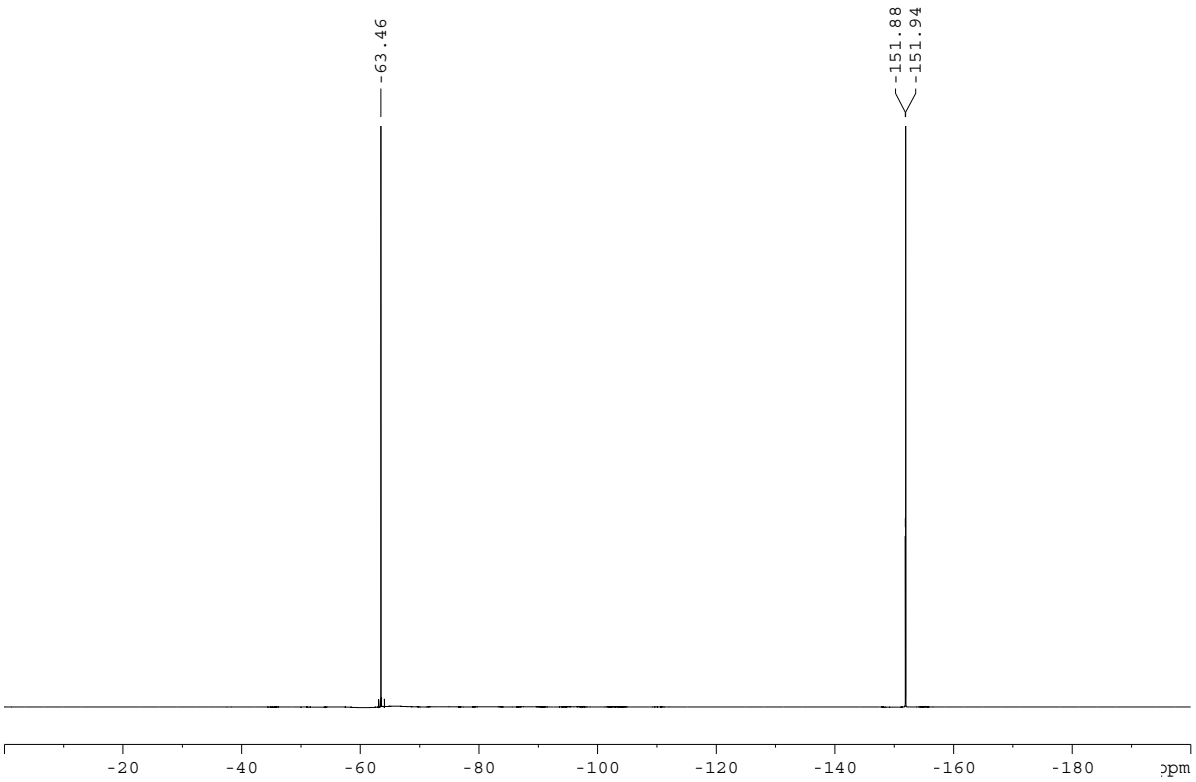
Compound 10: ^{1}H NMR (300 MHz, CDCN)



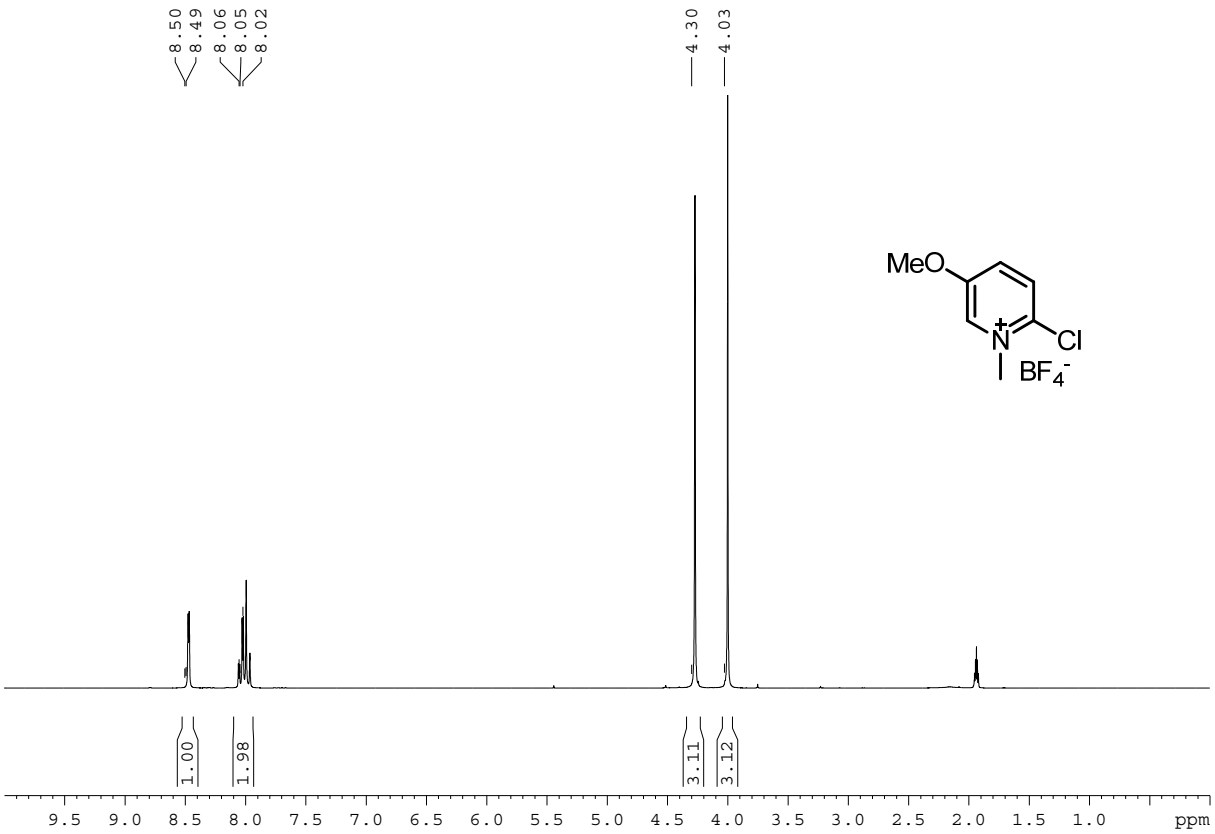
Compound 10: ^{13}C NMR (75 MHz, CDCN)



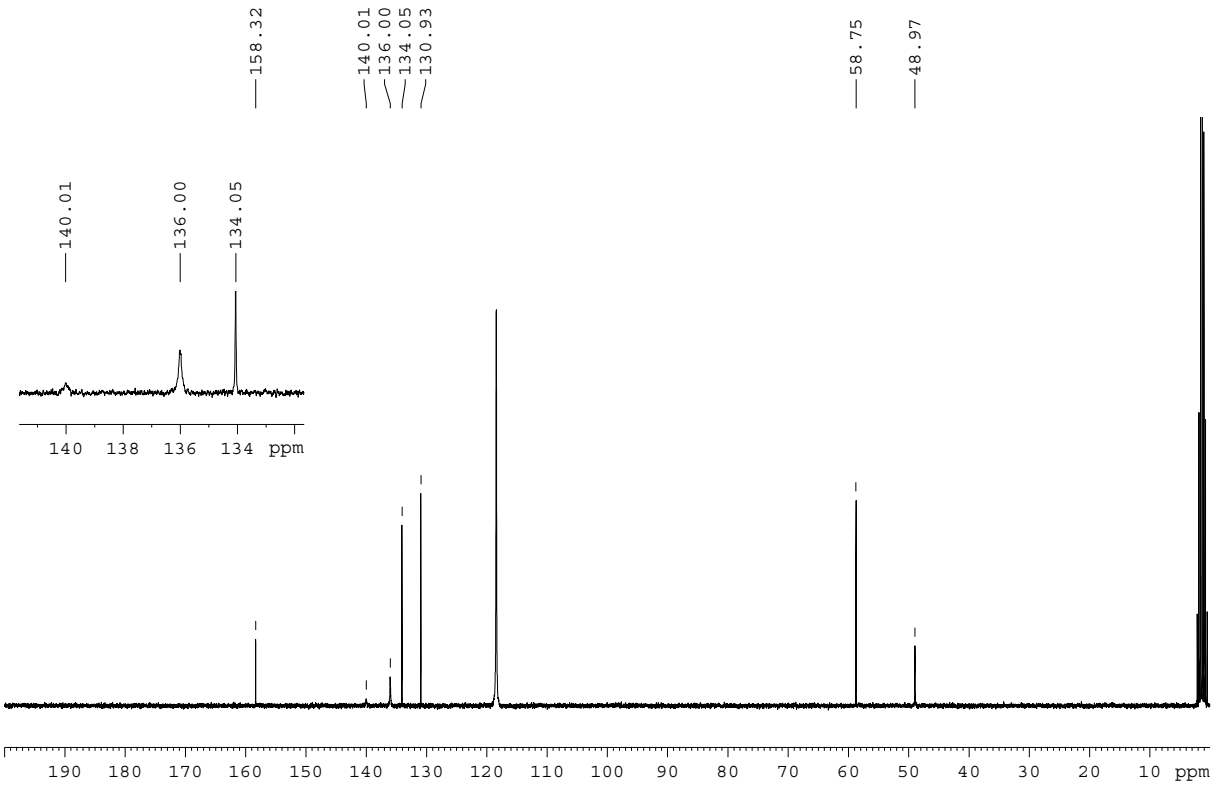
Compound 10: ^{19}F NMR (282 MHz, CDCN)



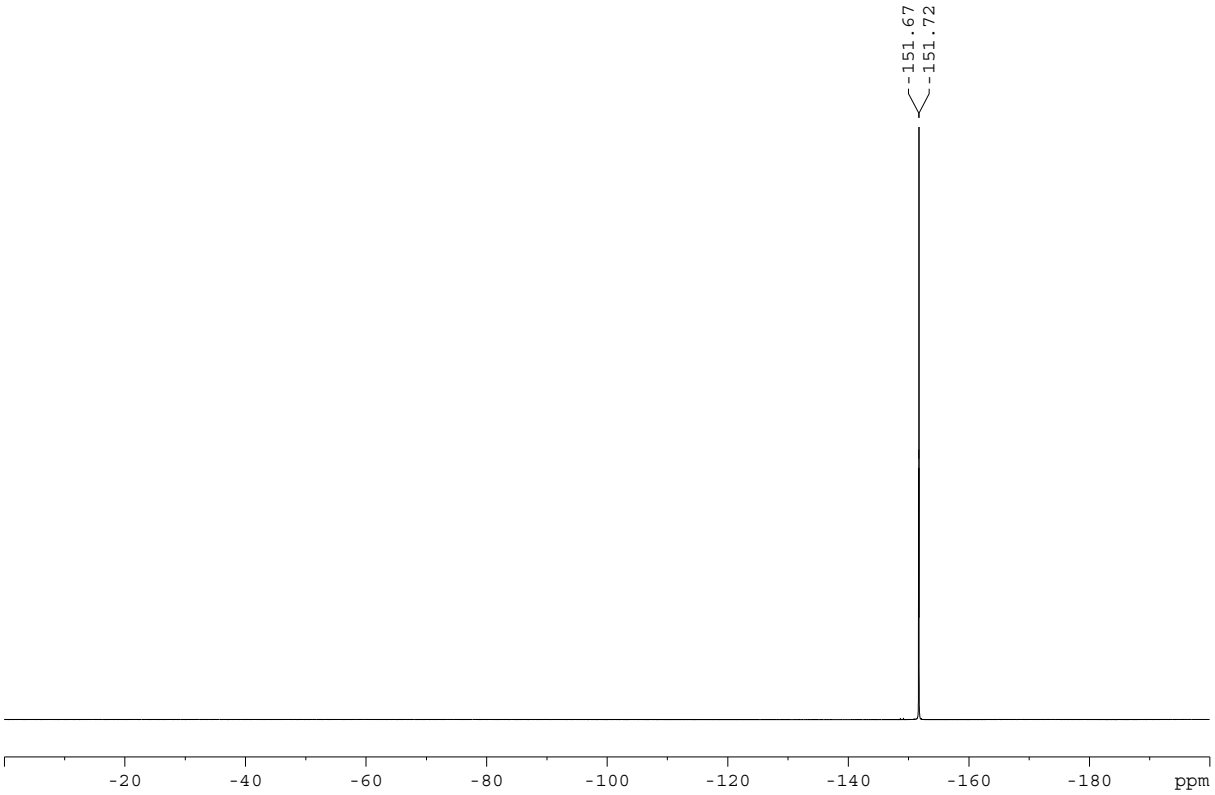
Compound 11: ^{1}H-NMR (300 MHz, CD_3CN)



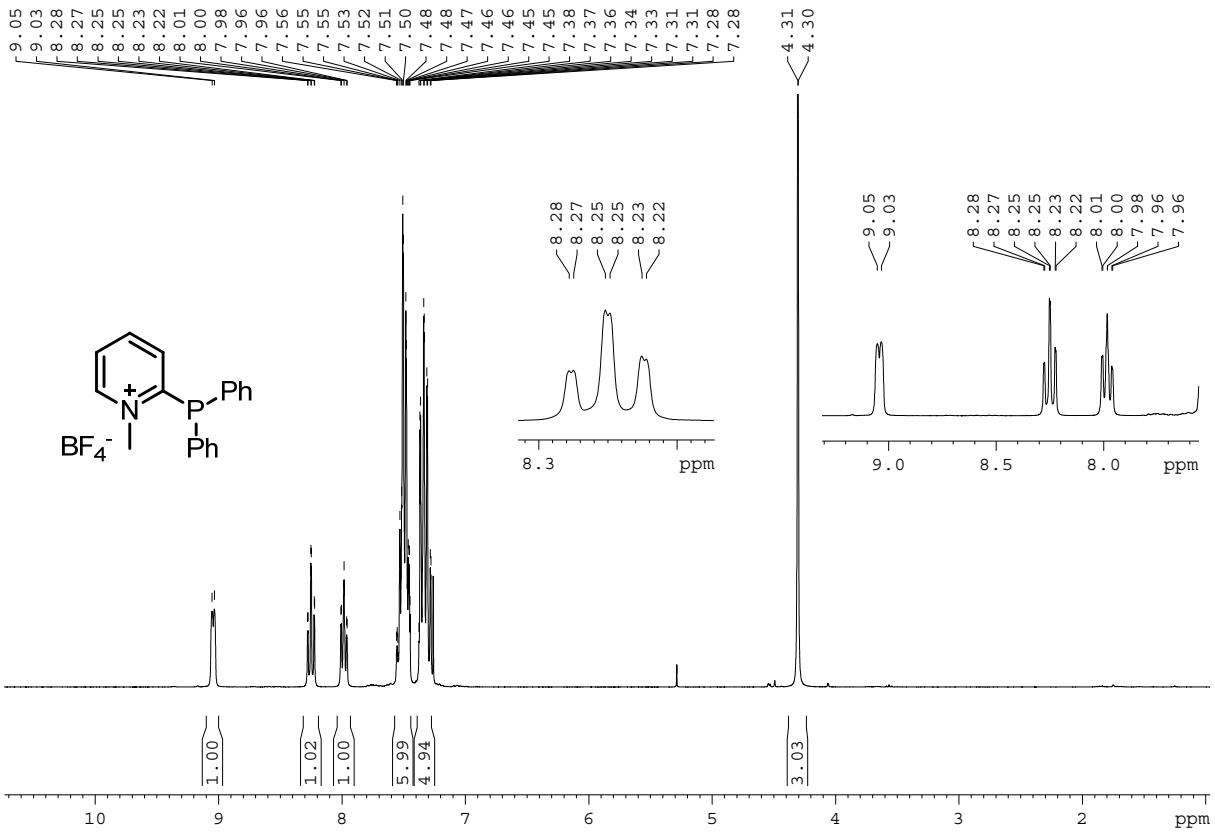
Compound 11: ^{13}C NMR (75 MHz, CD_3CN)



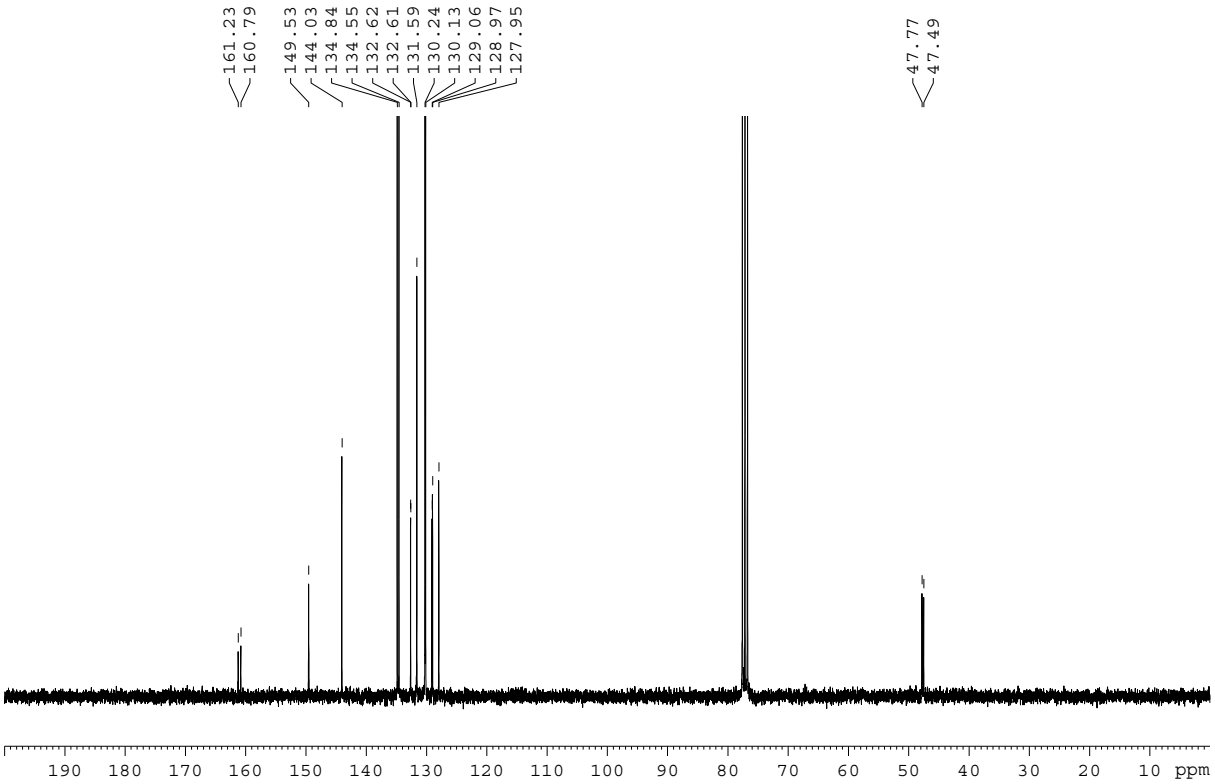
Compound 11: ^{19}F NMR (282 MHz, CD_3CN)



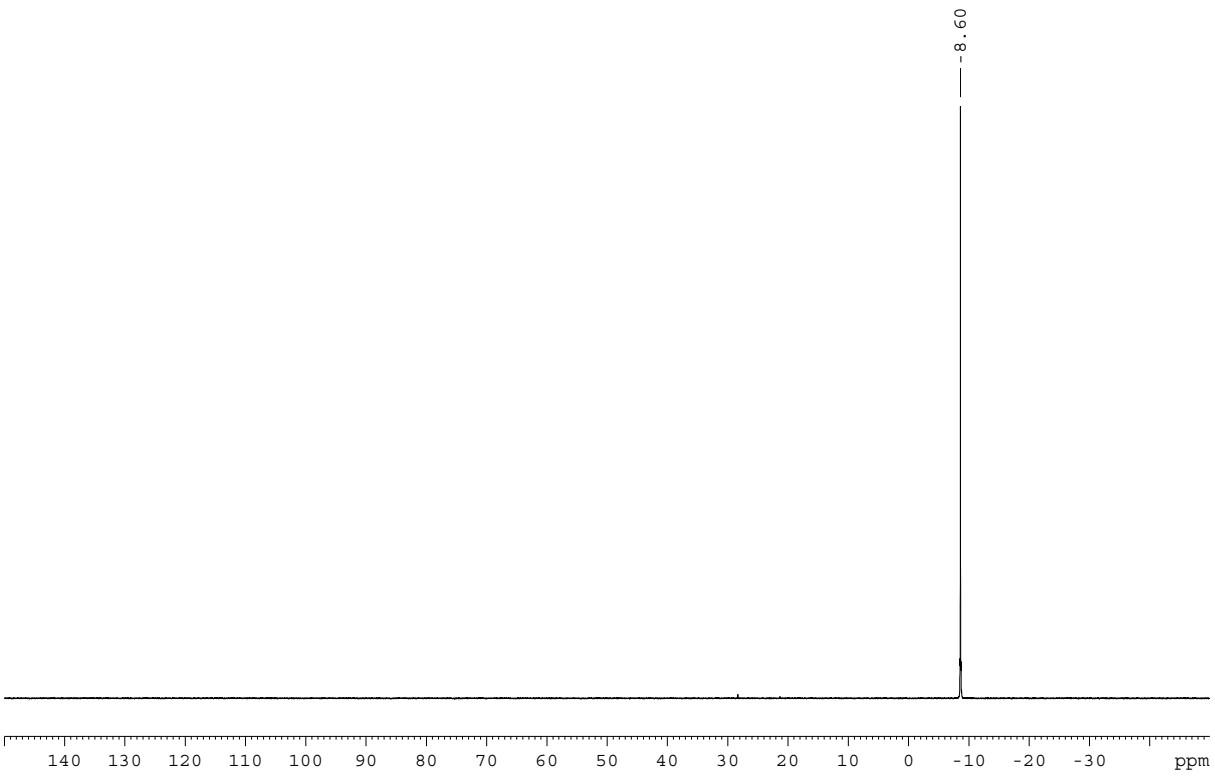
Compound 12: ^{1}H NMR (300 MHz, CD_3CN)



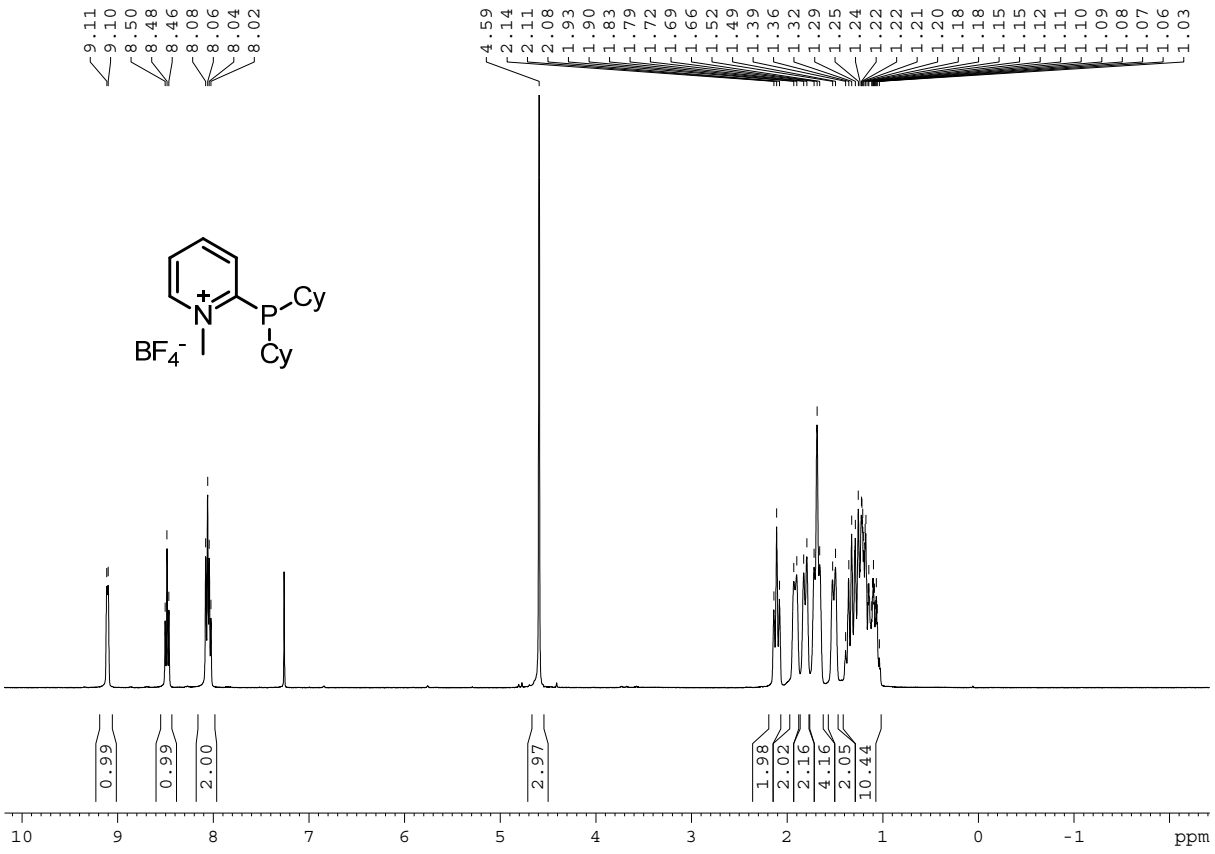
Compound 12: ^{13}C NMR (75 MHz, $CDCl_3$)



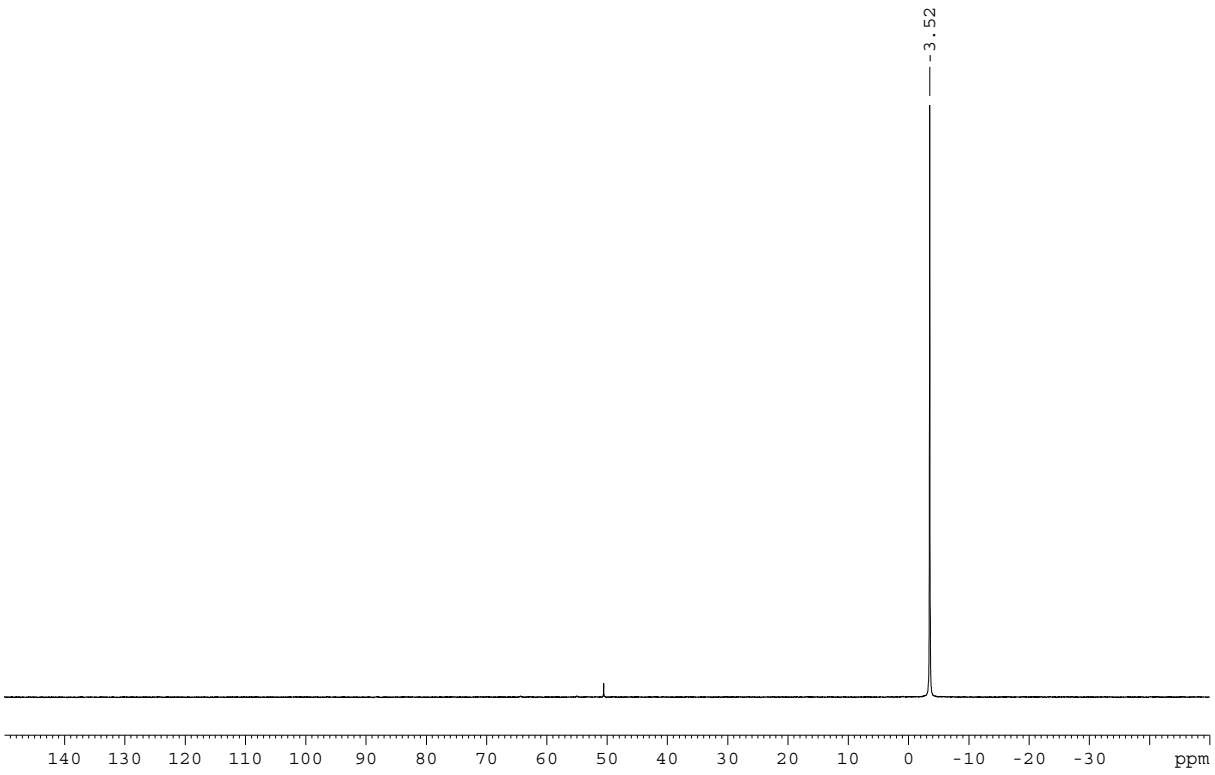
Compound 12: ^{31}P (121 MHz, $CDCl_3$):



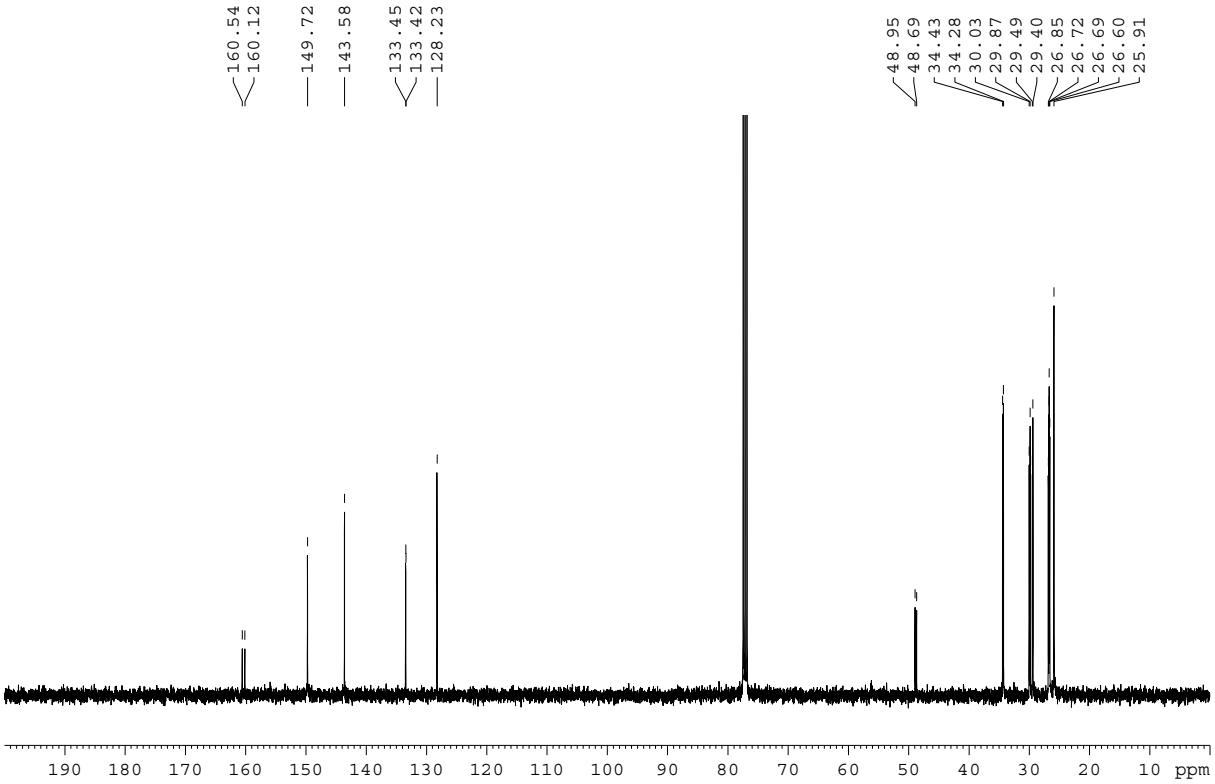
Compound 13: ^{1}H NMR (400 MHz, $CDCl_3$)



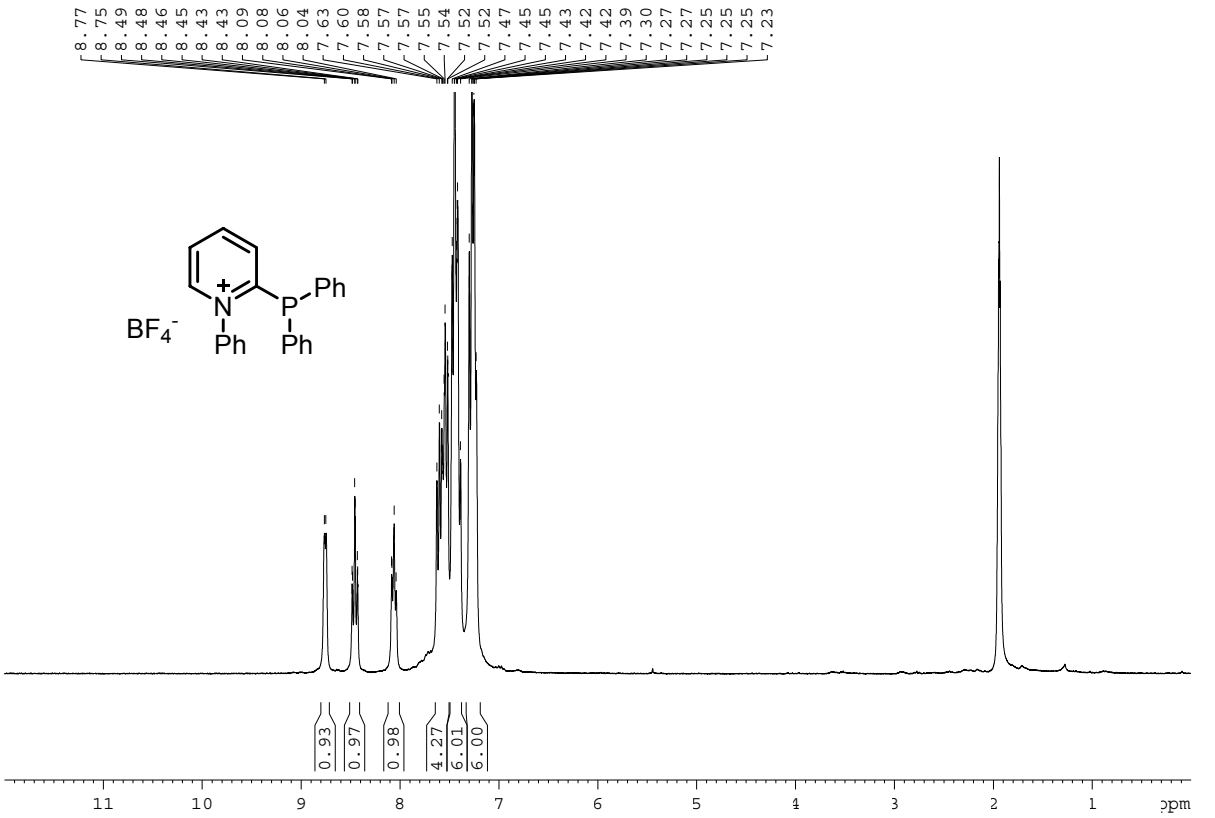
Compound 13: ^{31}P NMR (162 MHz, $CDCl_3$)



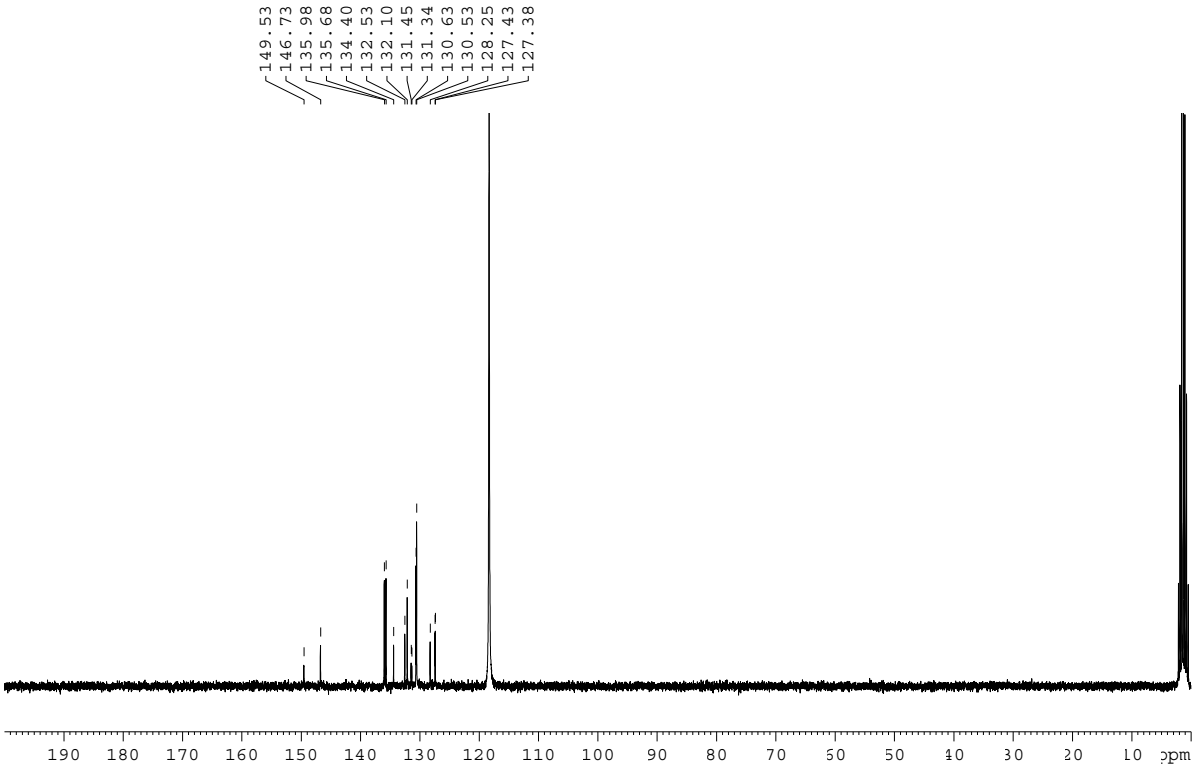
Compound 13: ^{13}C NMR (101 MHz, $CDCl_3$)



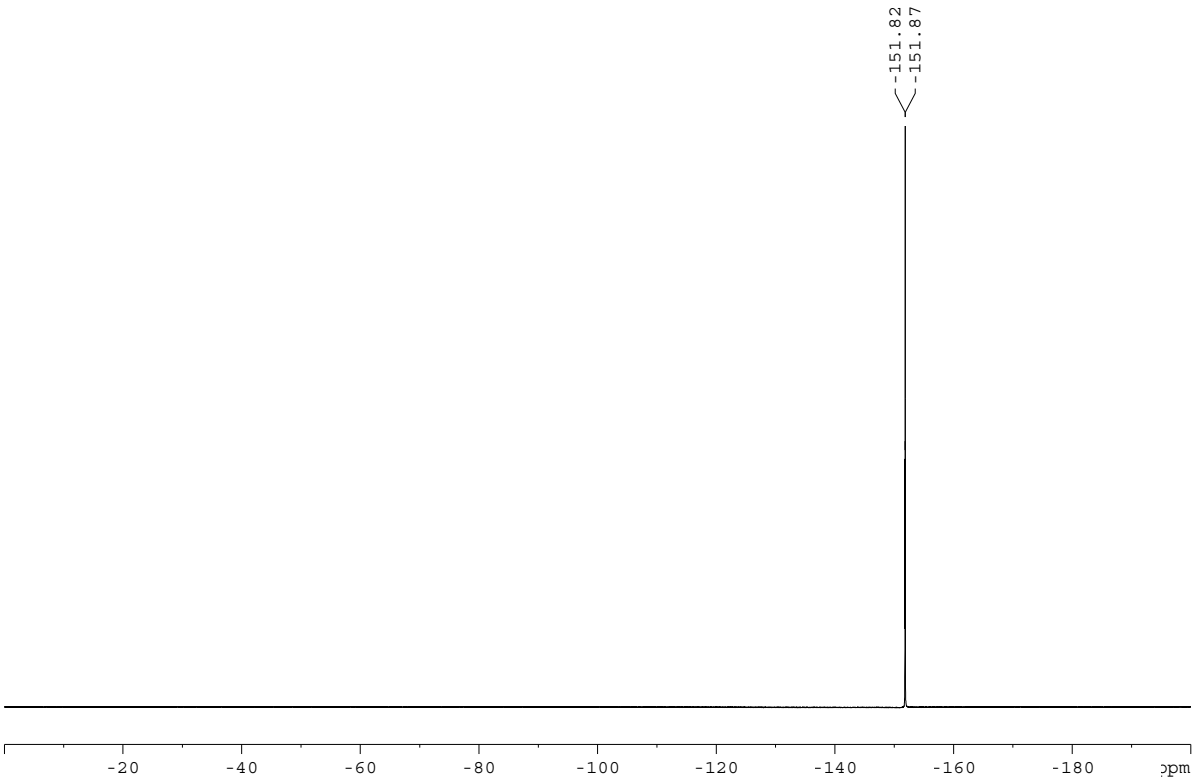
Compound 14: ^{1}H NMR (300 MHz, CDCN)



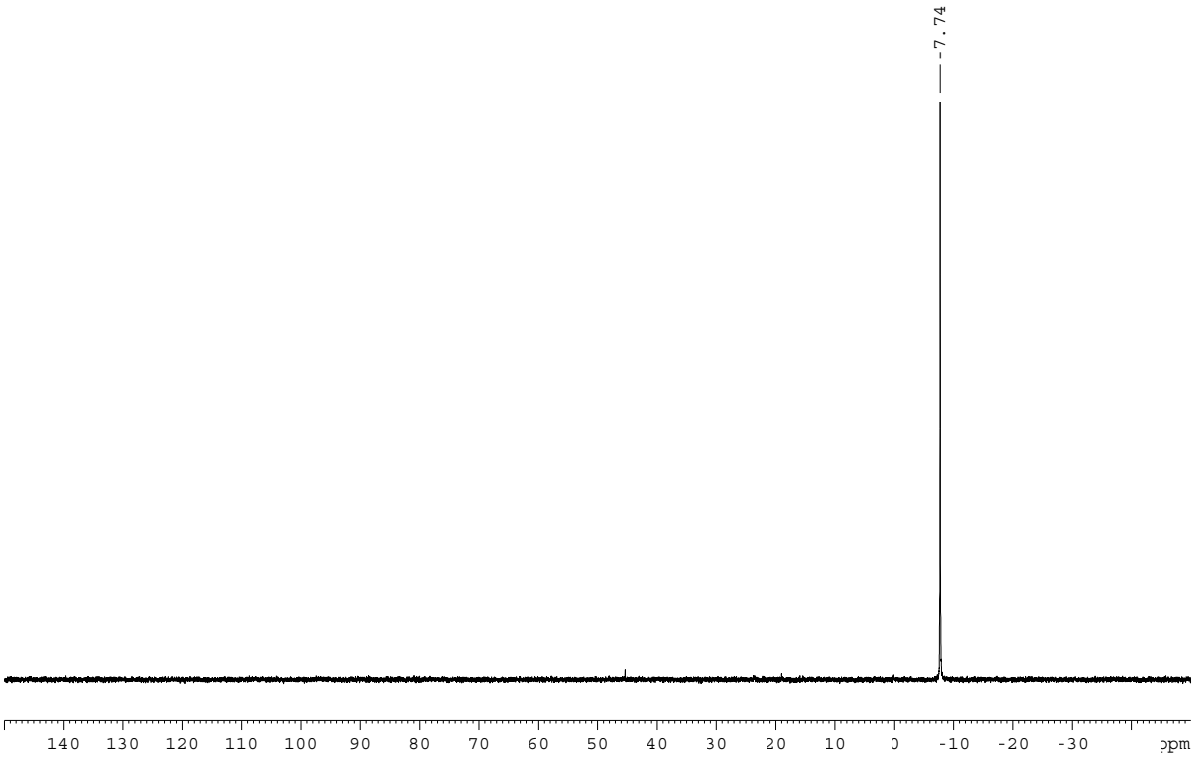
Compound 14: ^{13}C NMR (75 MHz, CDCN)



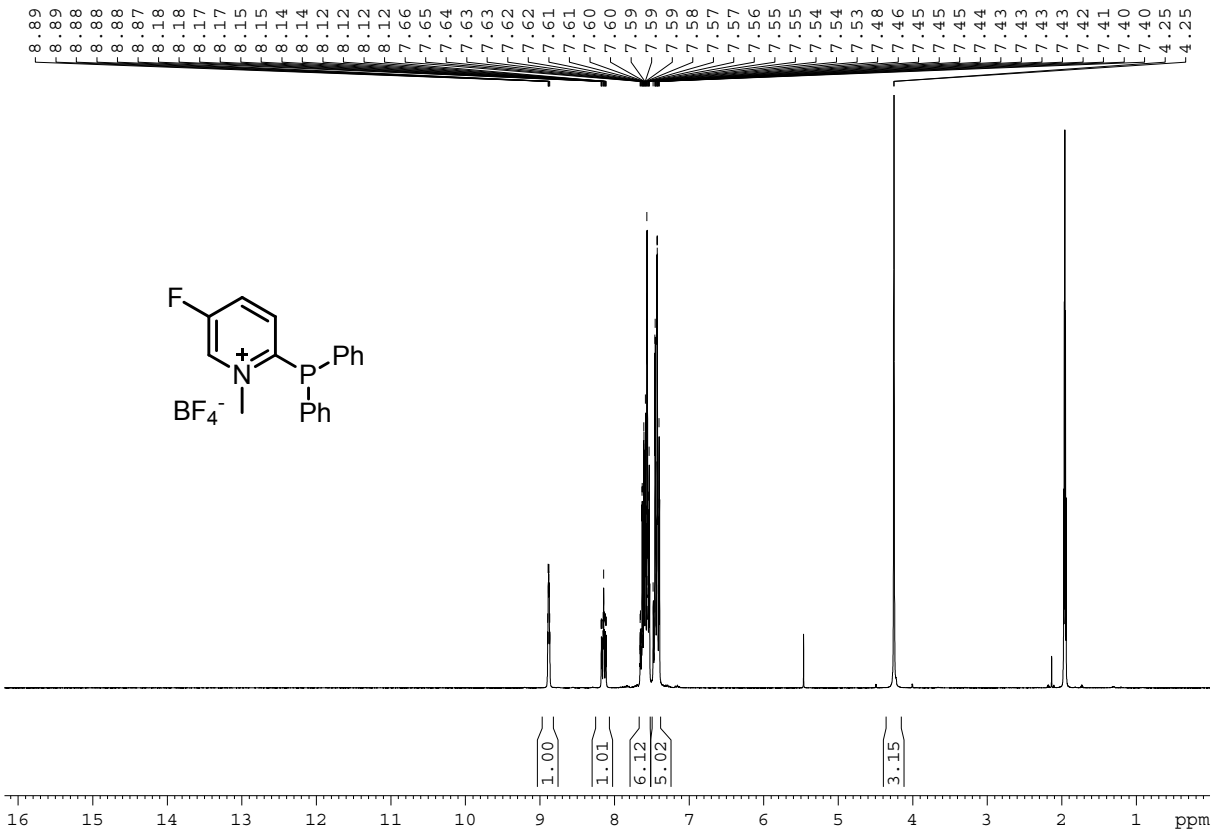
Compound 14: ^{19}F NMR (282 MHz, CDCN)



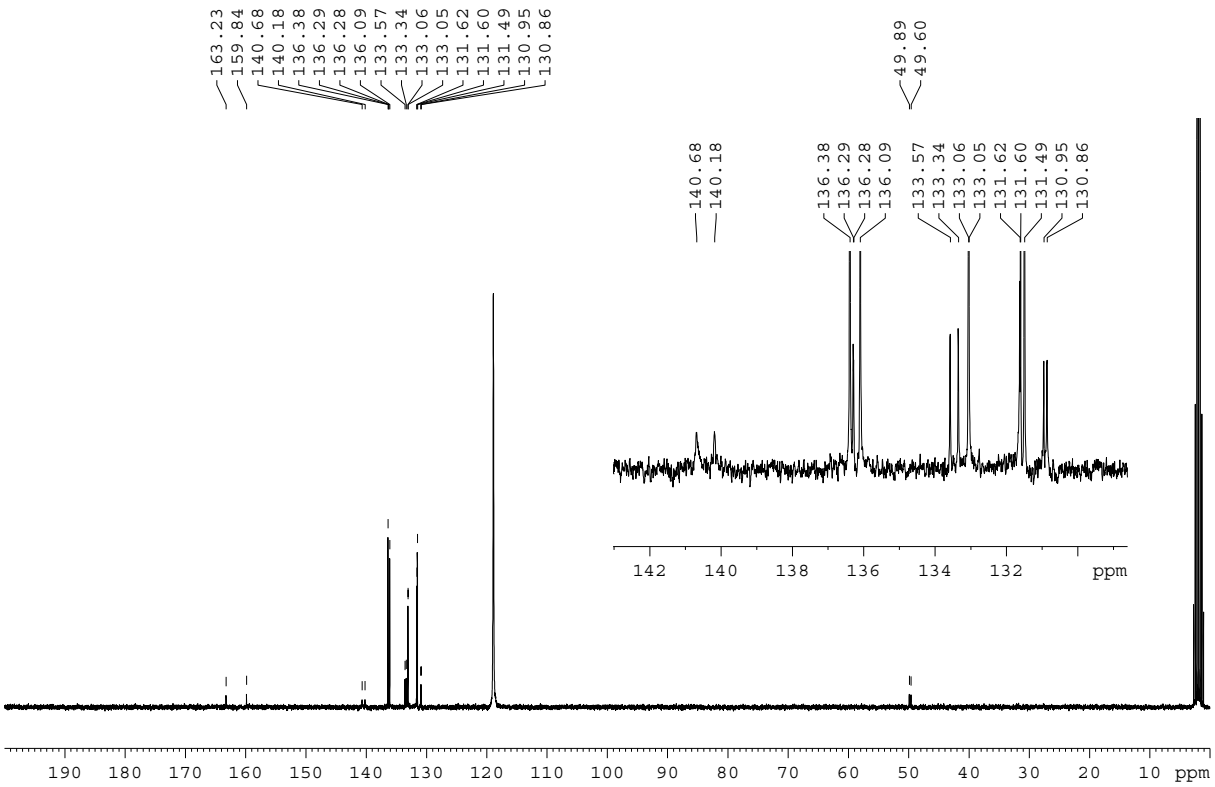
Compound 14: ^{31}P NMR (121 MHz, CDCN)



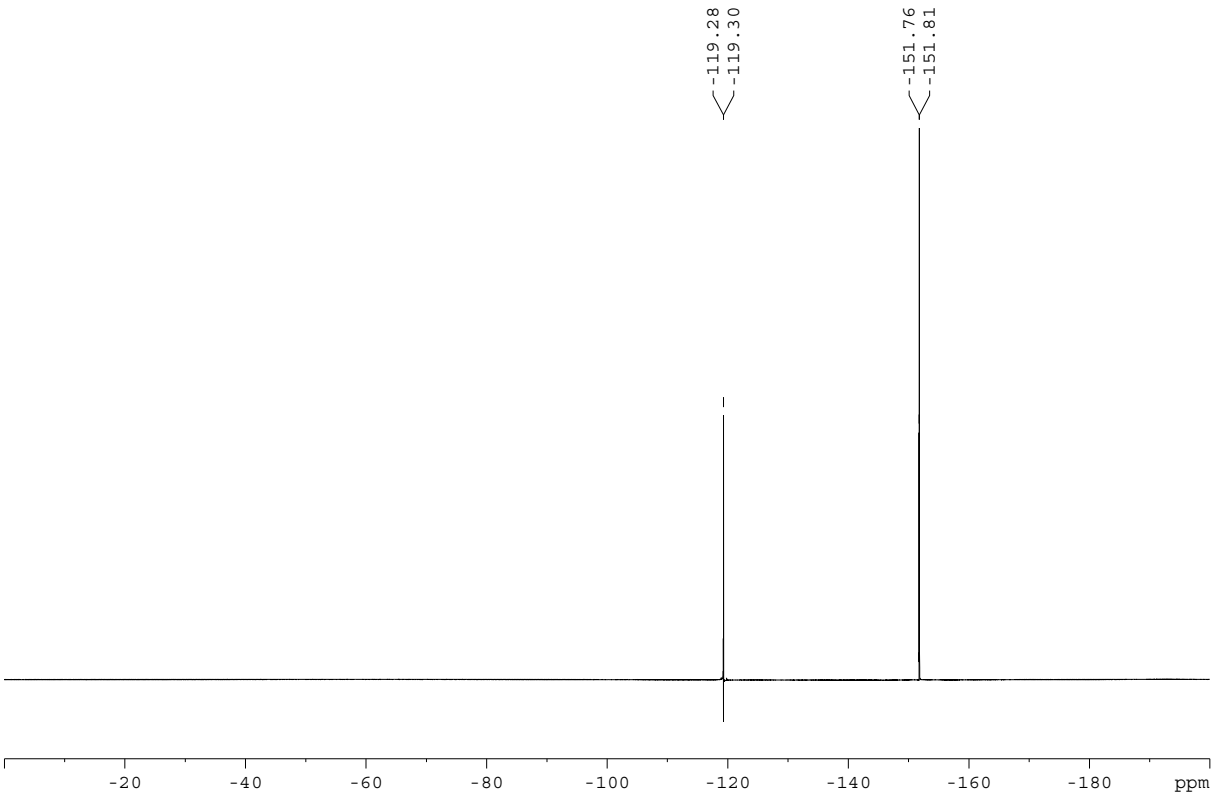
Compound 15: ^{1}H NMR (300 MHz, CD_3CN)



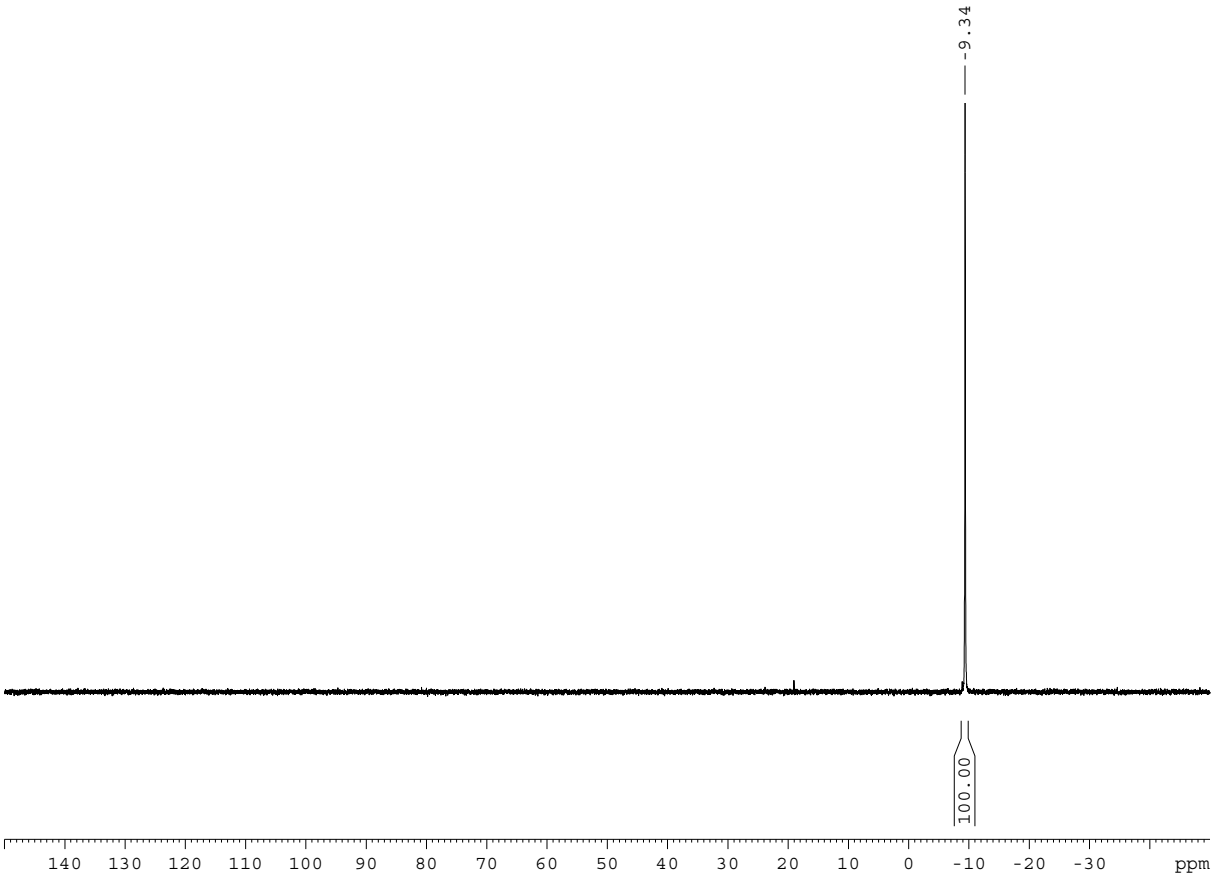
Compound 15: ^{13}C NMR (282 MHz, CDCN)



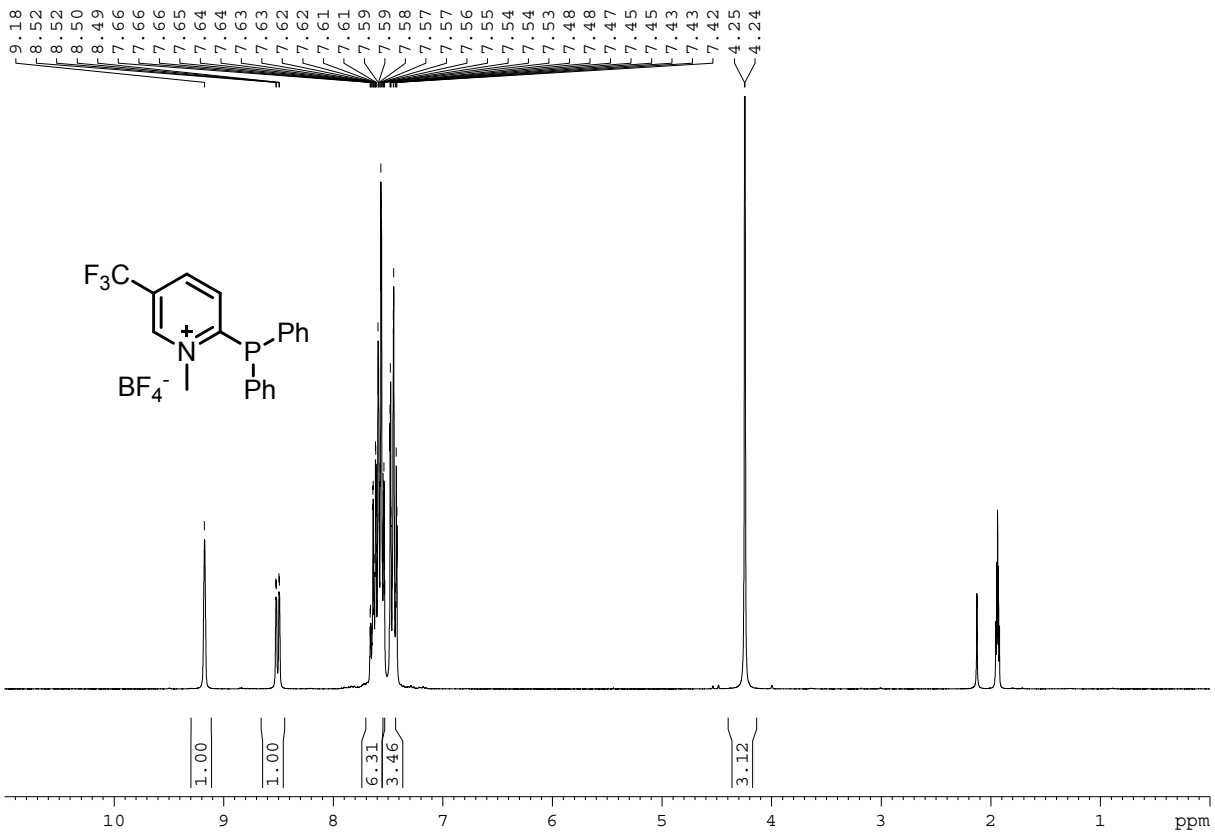
Compound 15: ^{19}F NMR (282 MHz, CDCN)



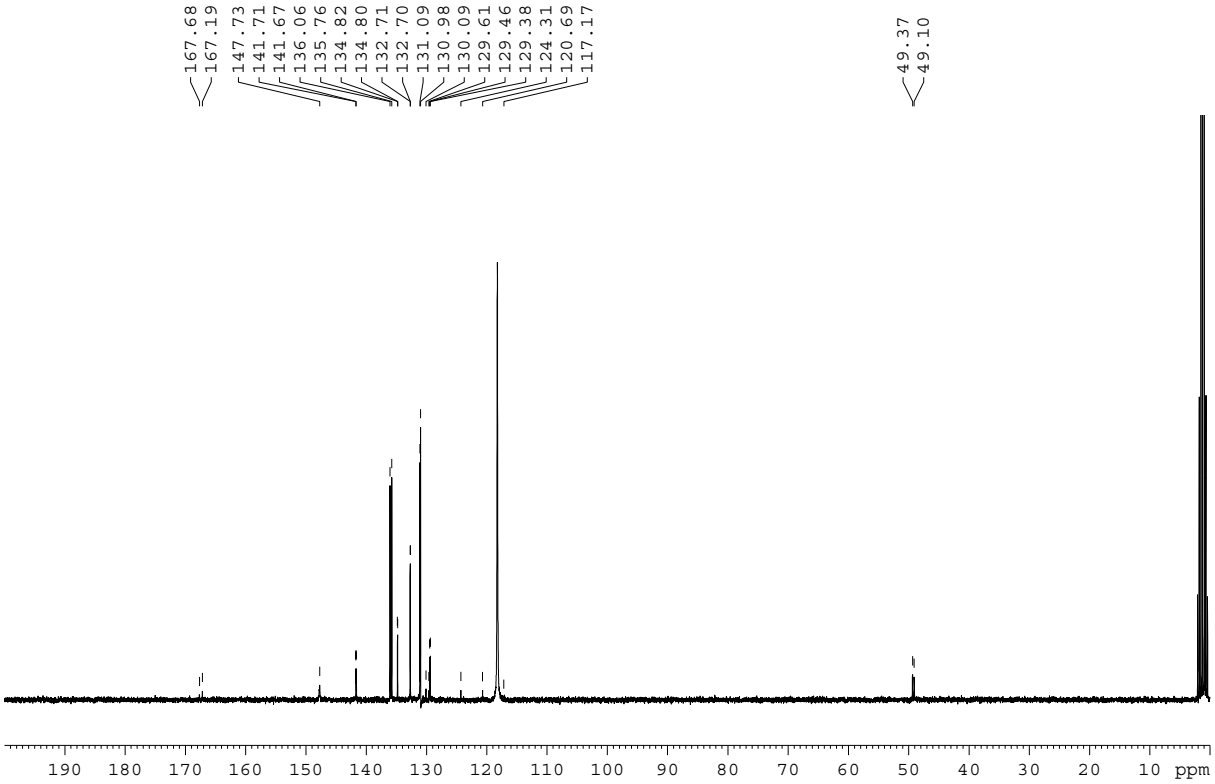
Compound 15: ^{31}P NMR (75 MHz, CDCN)



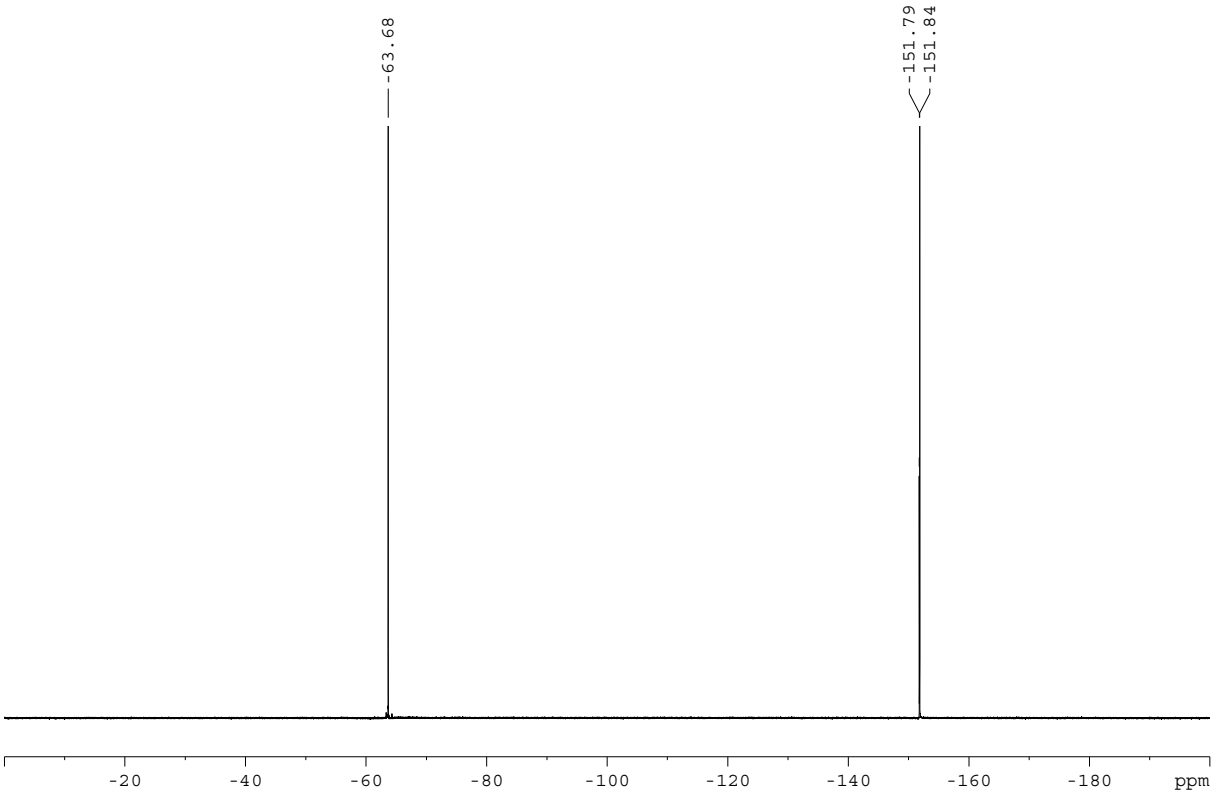
Compound 16: ^{1}H NMR (300 MHz, CDCN)



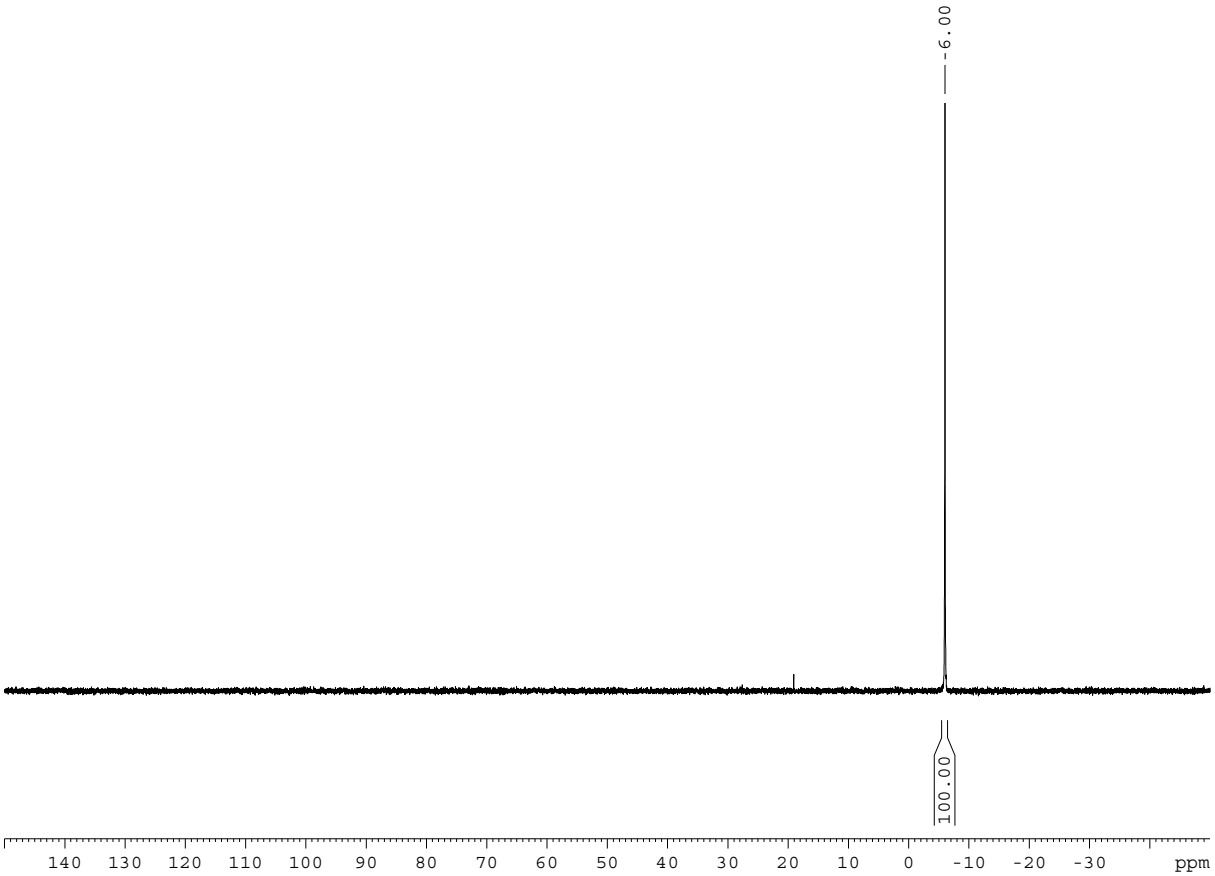
Compound 16: ^{13}C NMR (101 MHz, $CDCl_3$)



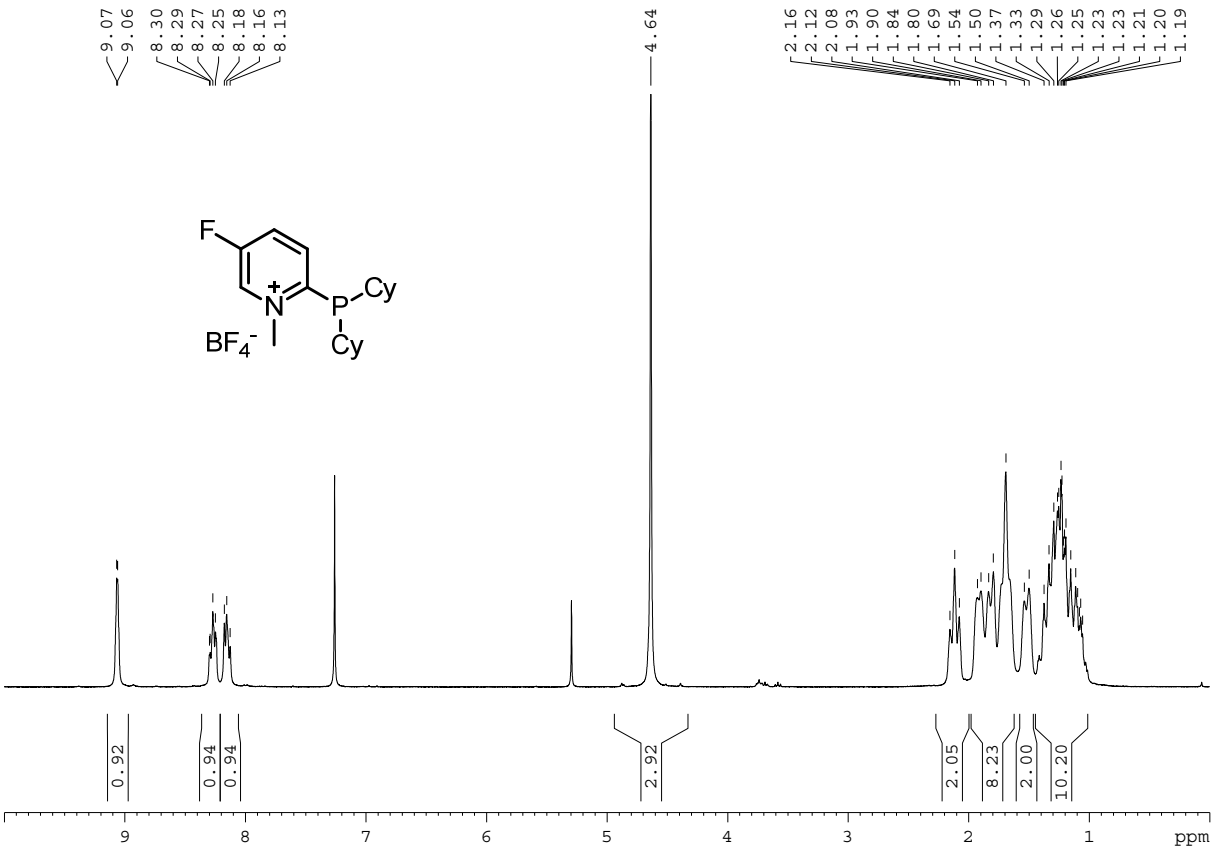
Compound 16: ^{19}F NMR (282 MHz, CD_3CN)



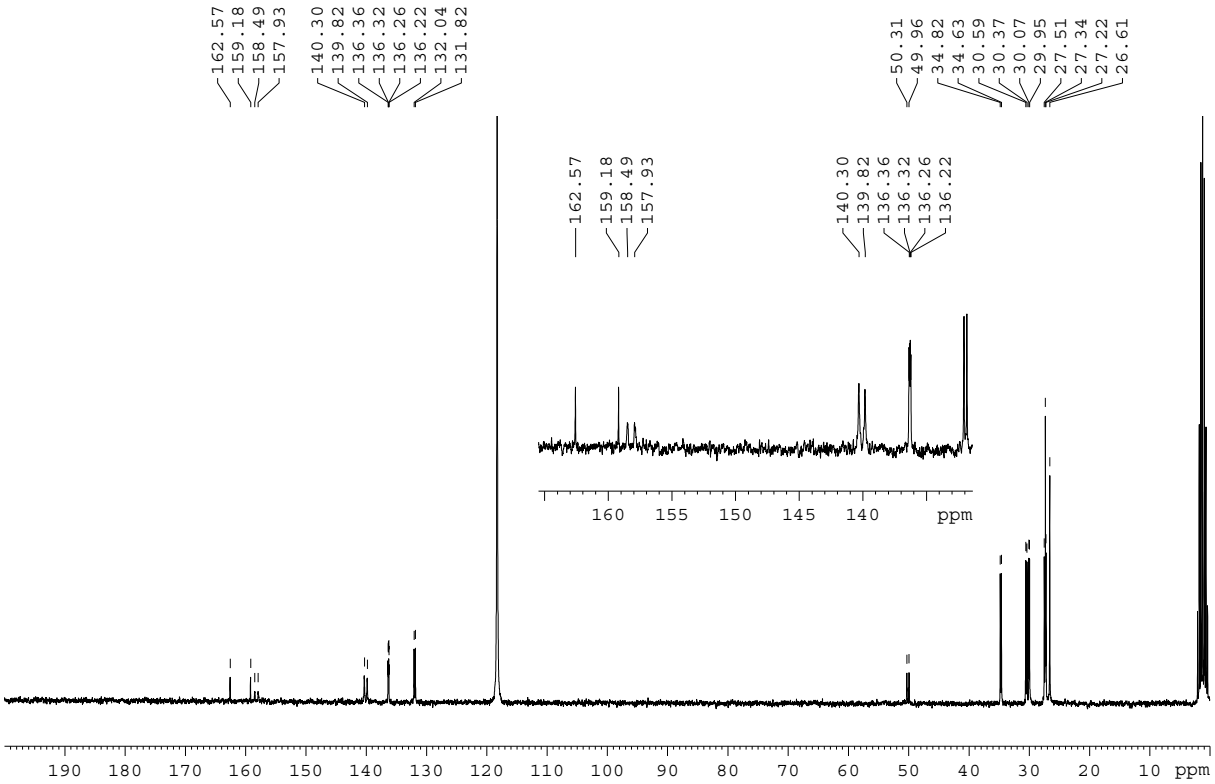
Compound 16: ^{31}P NMR (121 MHz, CD_3CN)



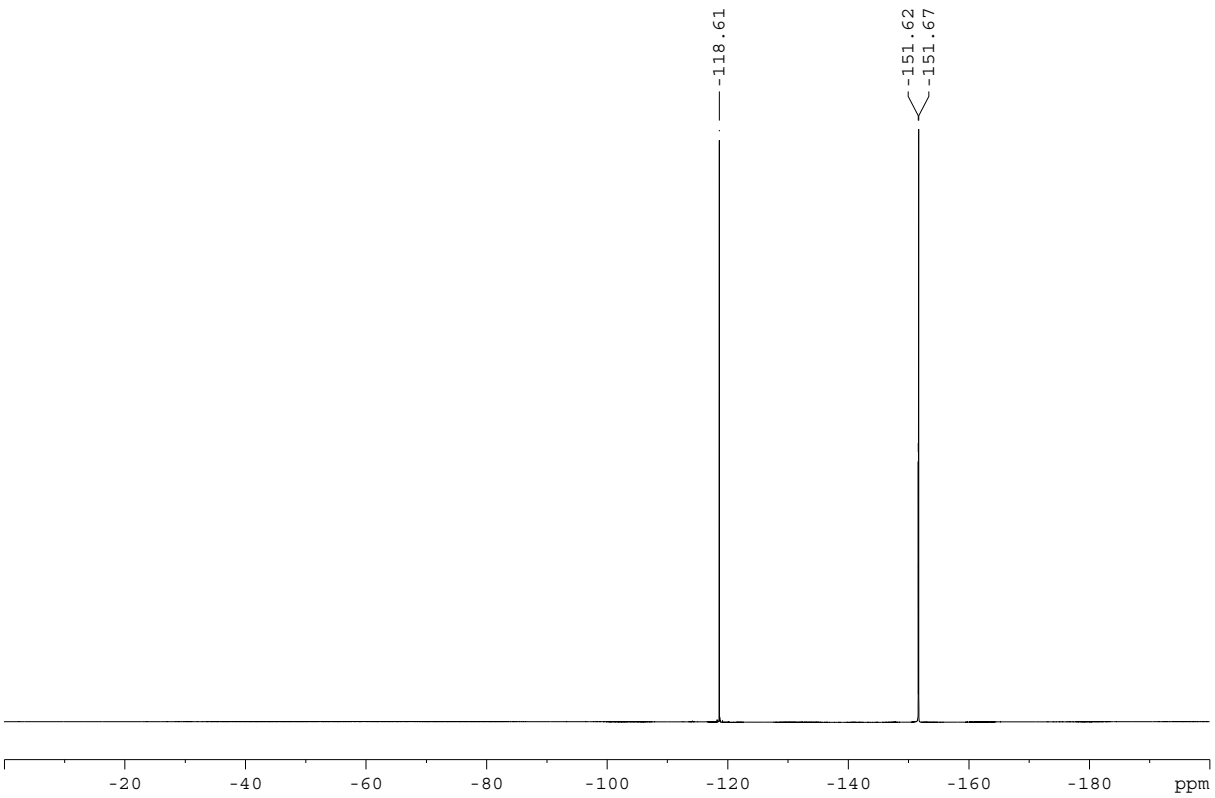
Compound 17: ^{1}H NMR (300 MHz, $CDCl_3$)



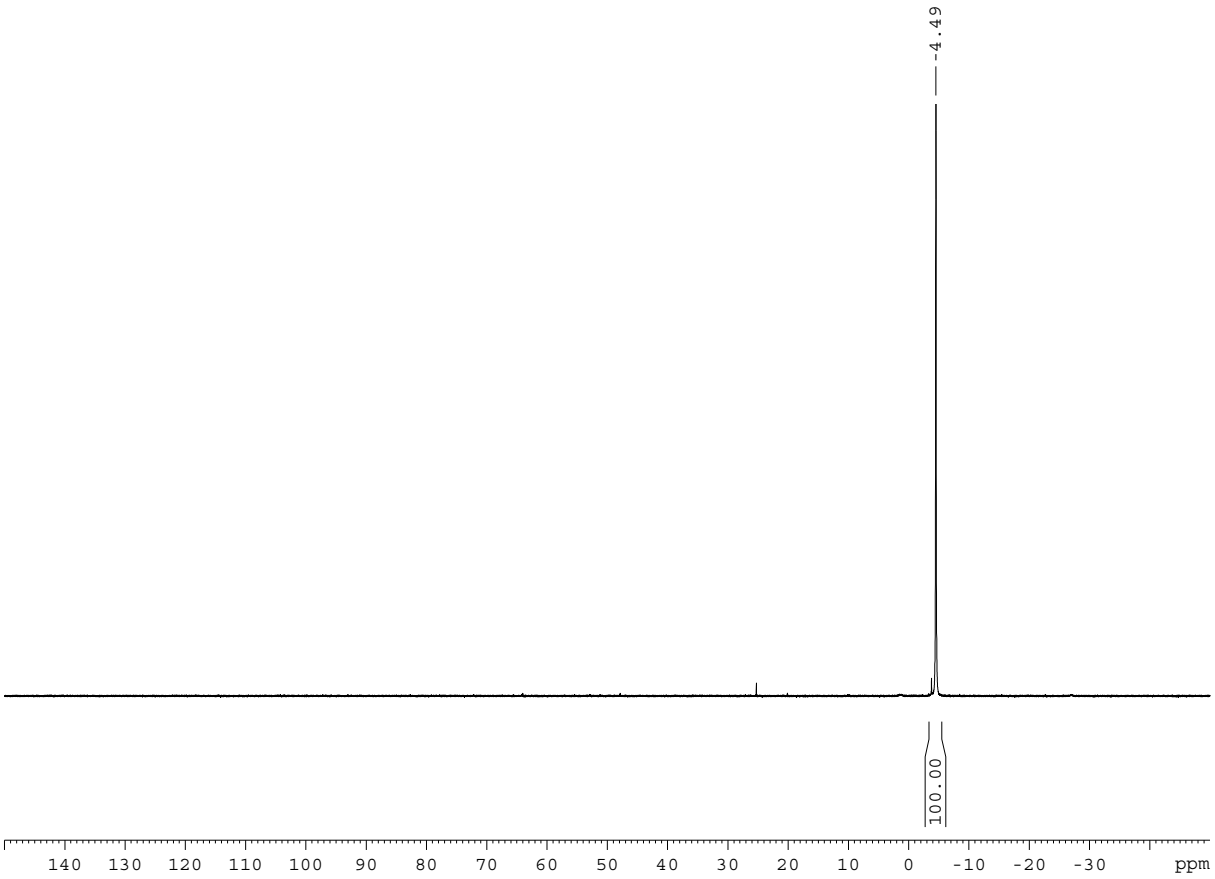
Compound 17: ^{13}C NMR (282 MHz, CDCN)



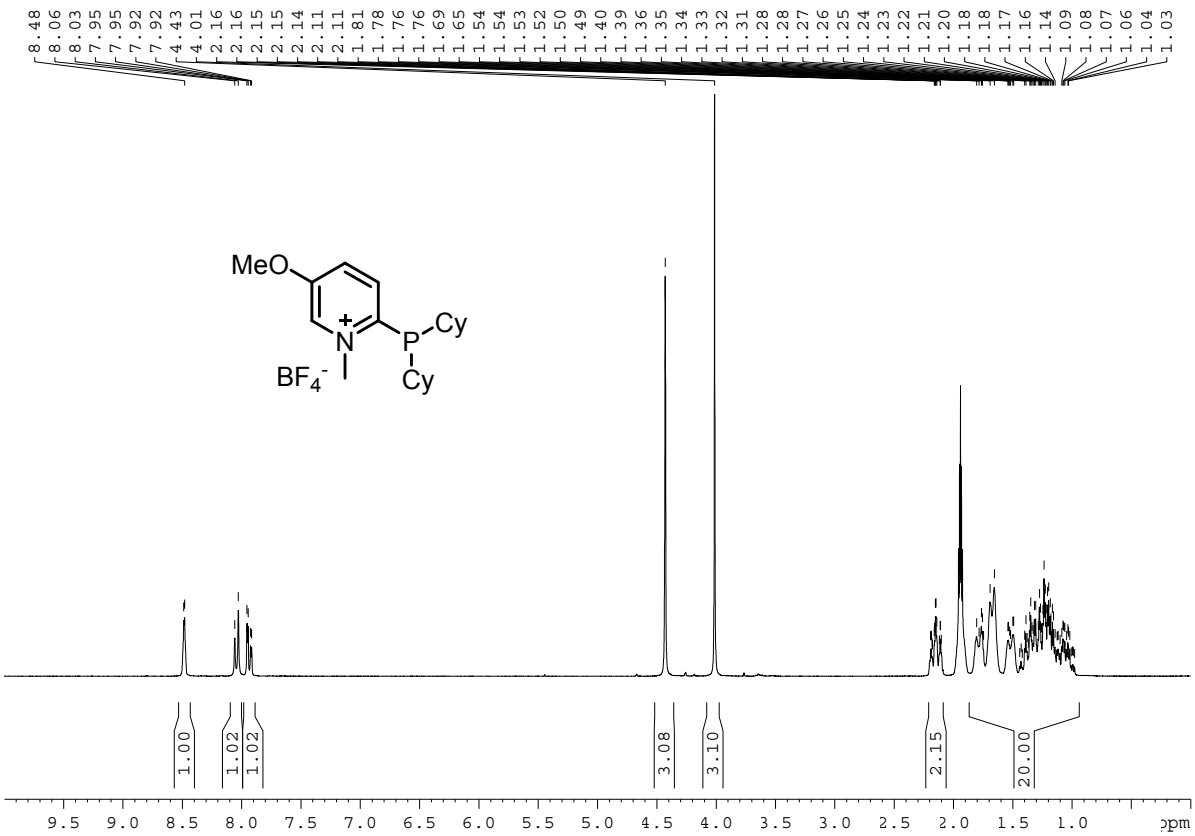
Compound 17: ^{19}F NMR (282 MHz, CDCN)



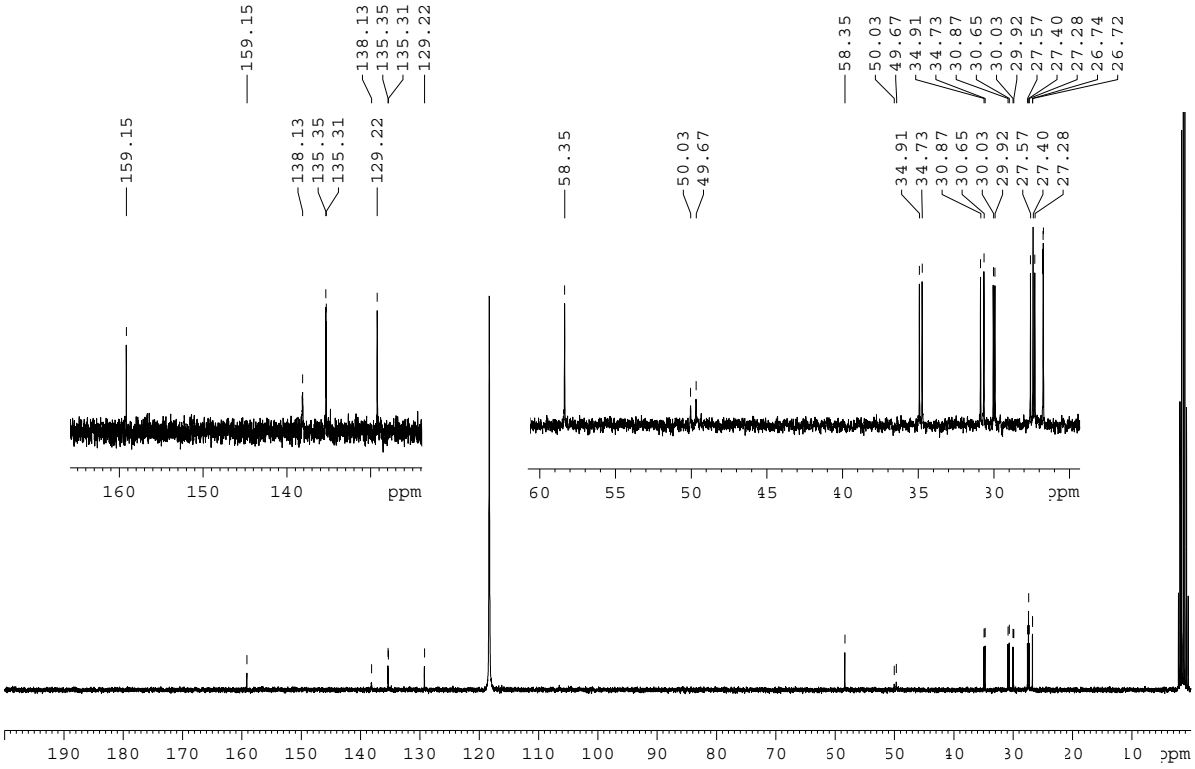
Compound 17: ^{31}P NMR (121 MHz, CDCN)



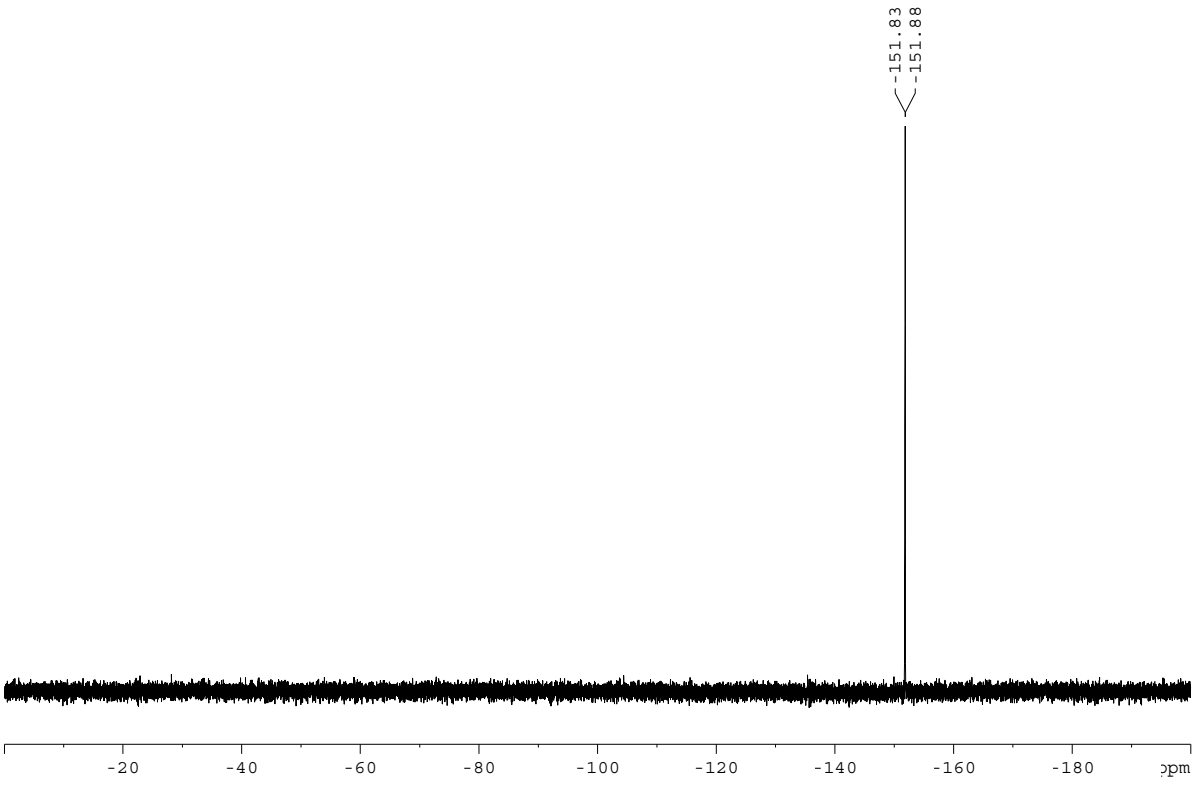
Compound 18: ^{1}H NMR (300 MHz, CDCN)



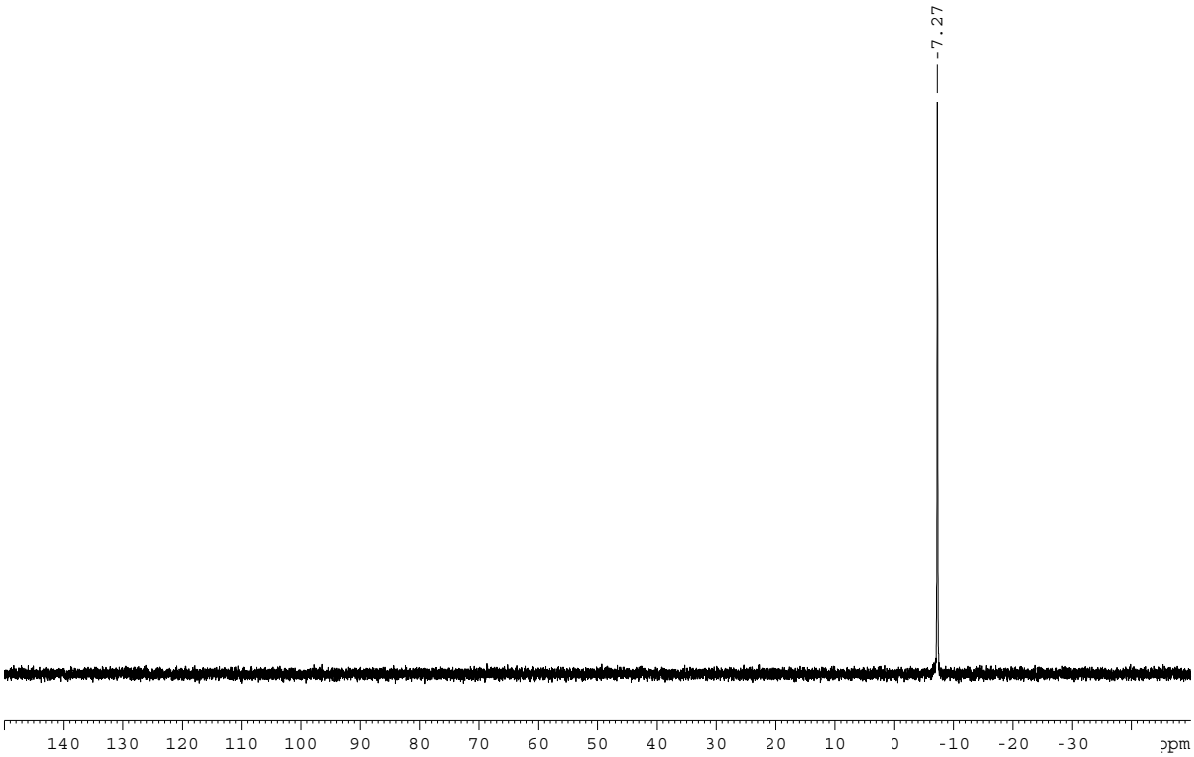
Compound 18: ^{13}C NMR (75 MHz, CDCN)



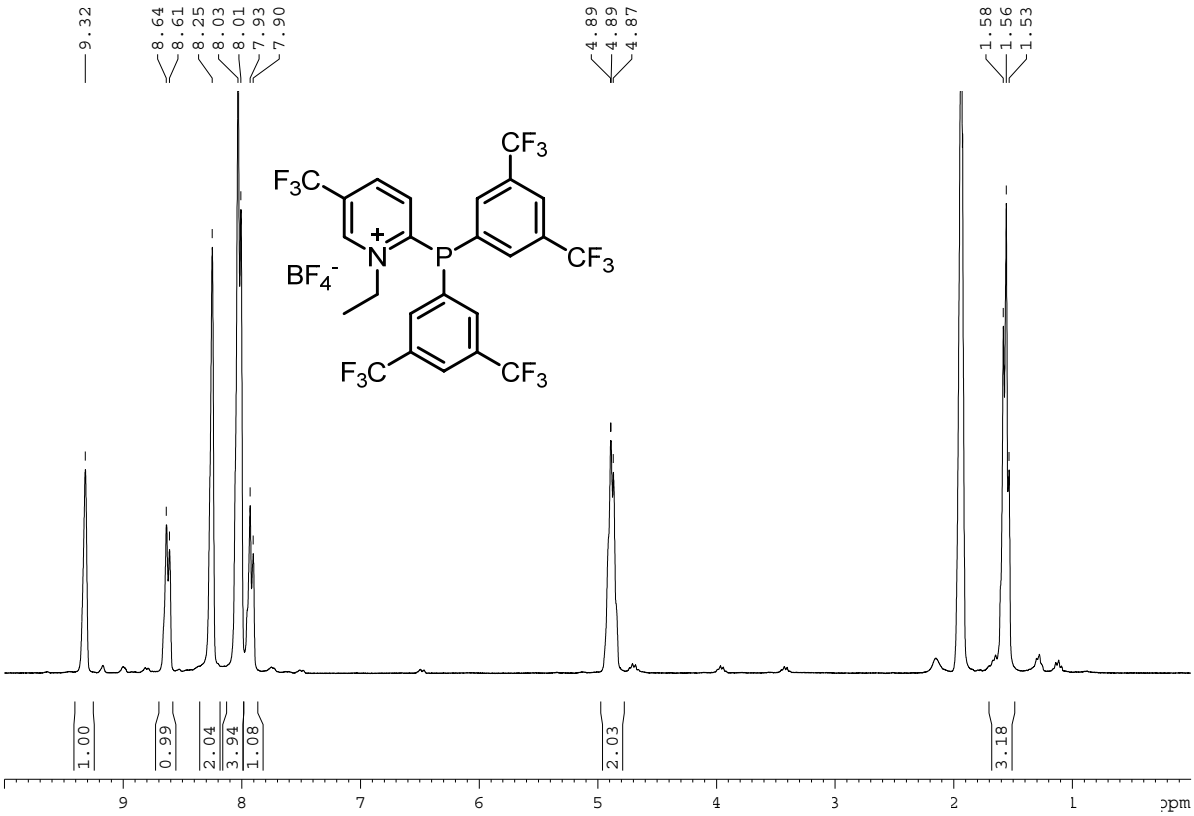
Compound 18: ^{19}F NMR (282 MHz, CDCN)



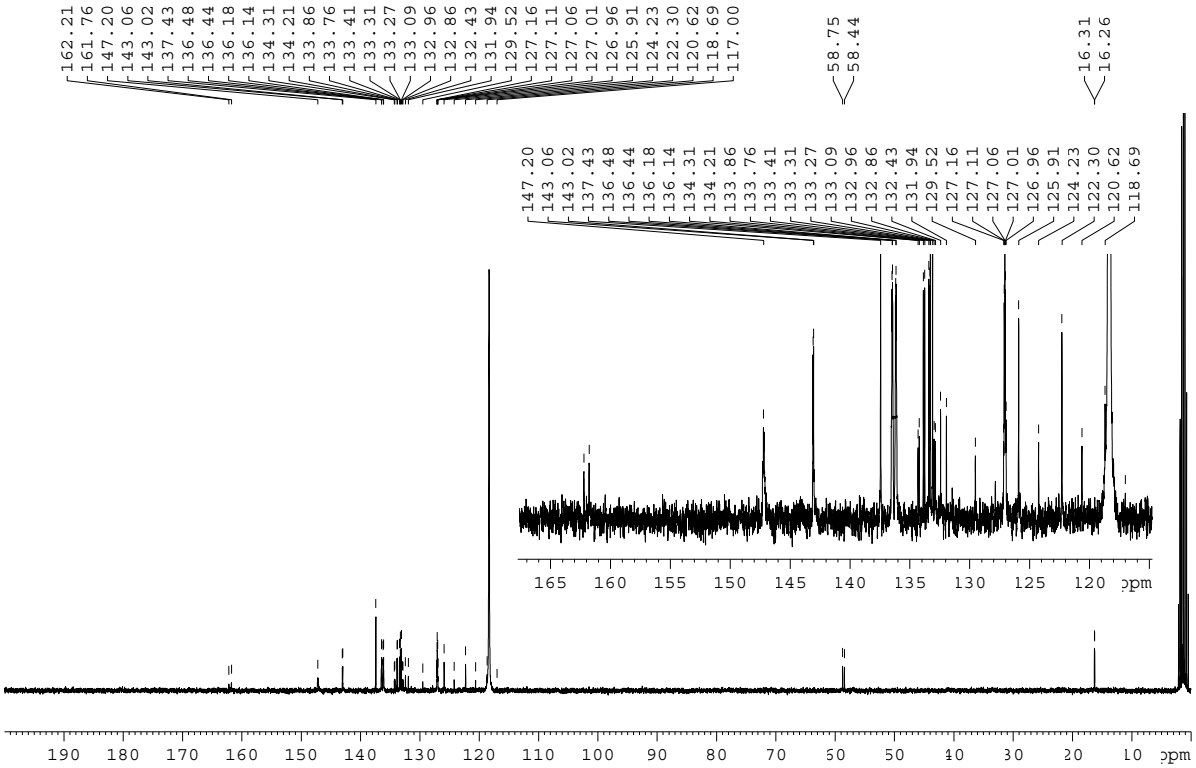
Compound 18: ^{31}P NMR (121 MHz, CDCN)



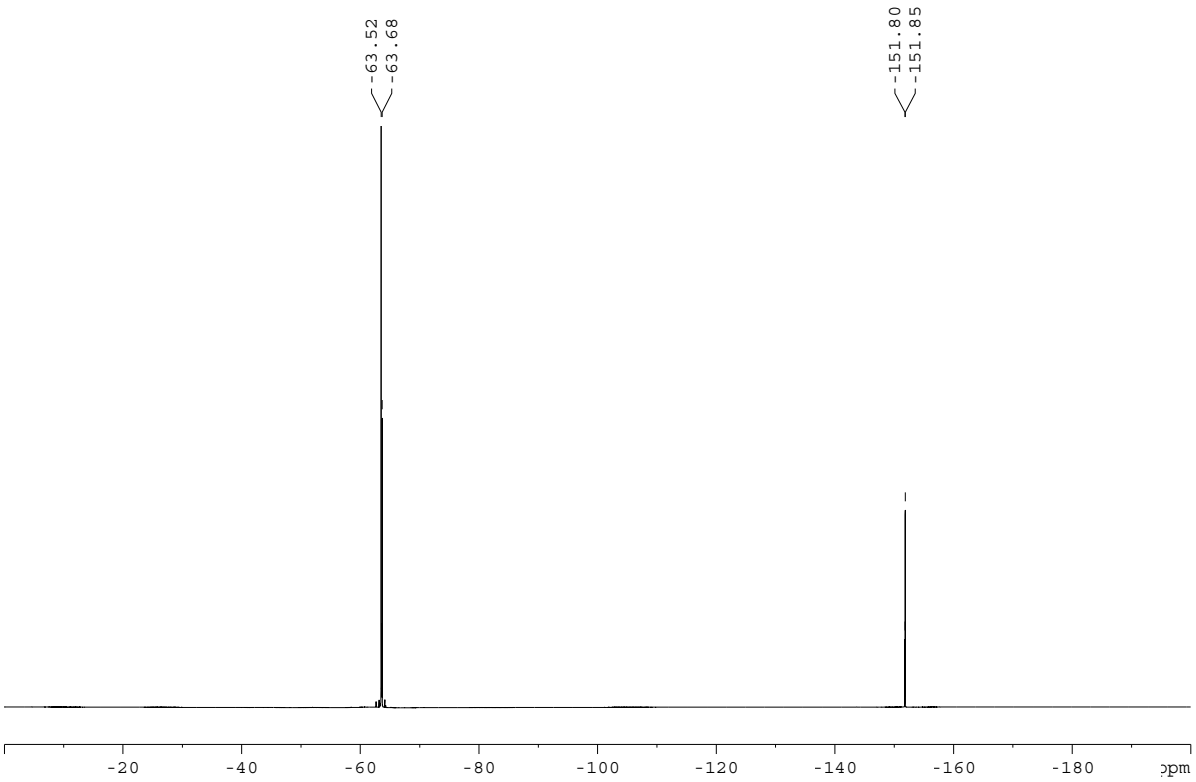
Compound 19: ^{1}H NMR (300 MHz, CDCN)



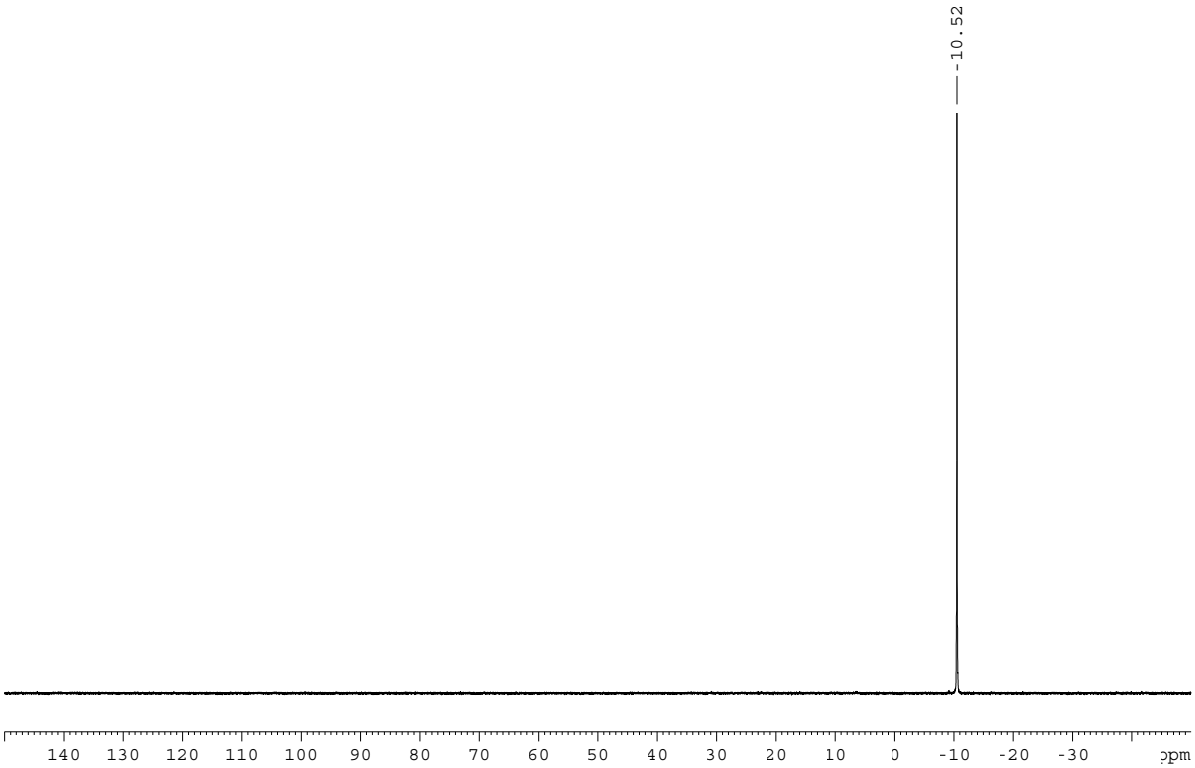
Compound 19: ^{13}C NMR (75 MHz, CDCN)



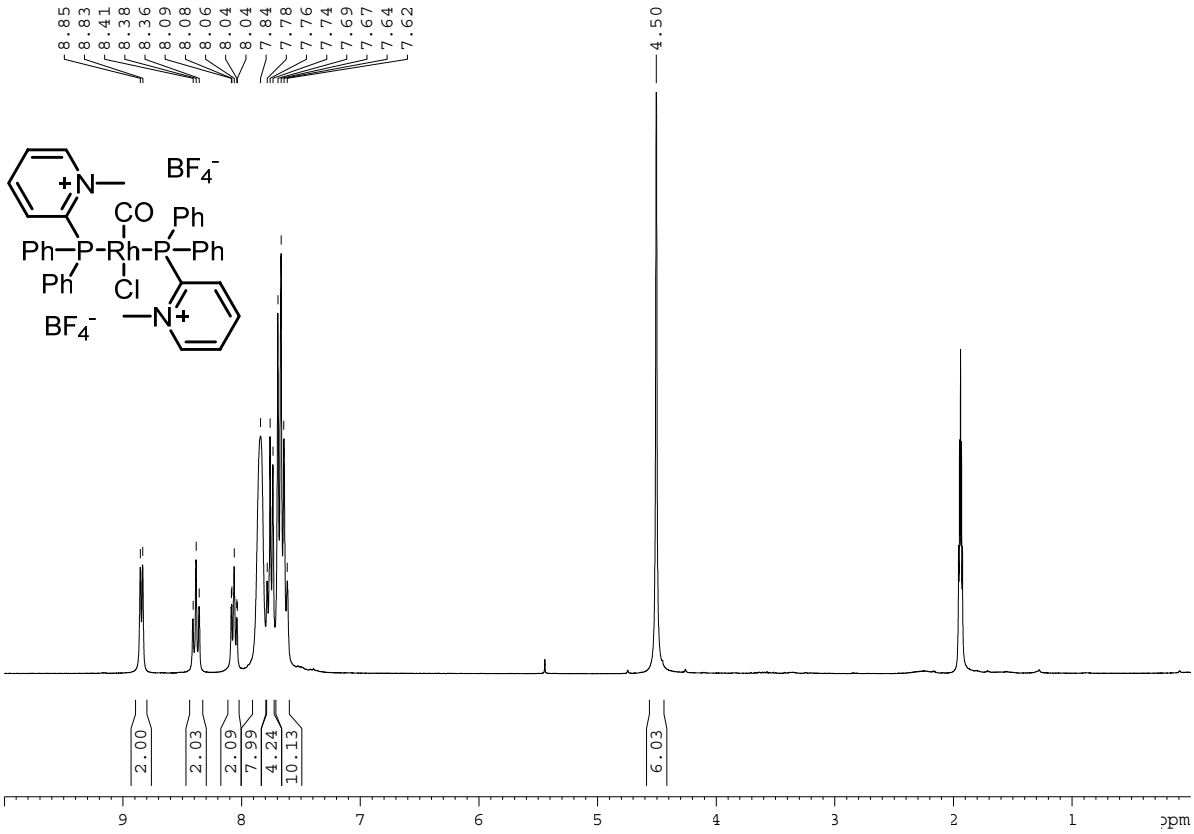
Compound 19: ^{19}F NMR (282 MHz, CDCN)



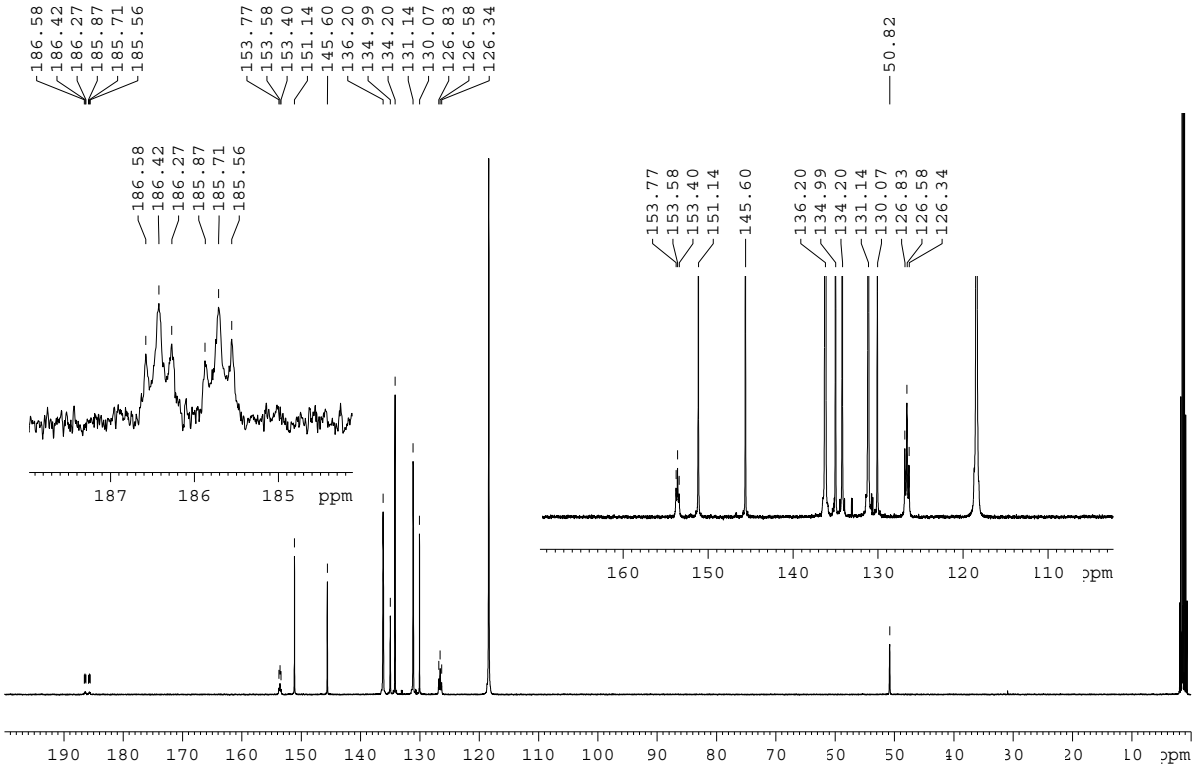
Compound 19: ^{31}P NMR (121 MHz, CDCN)



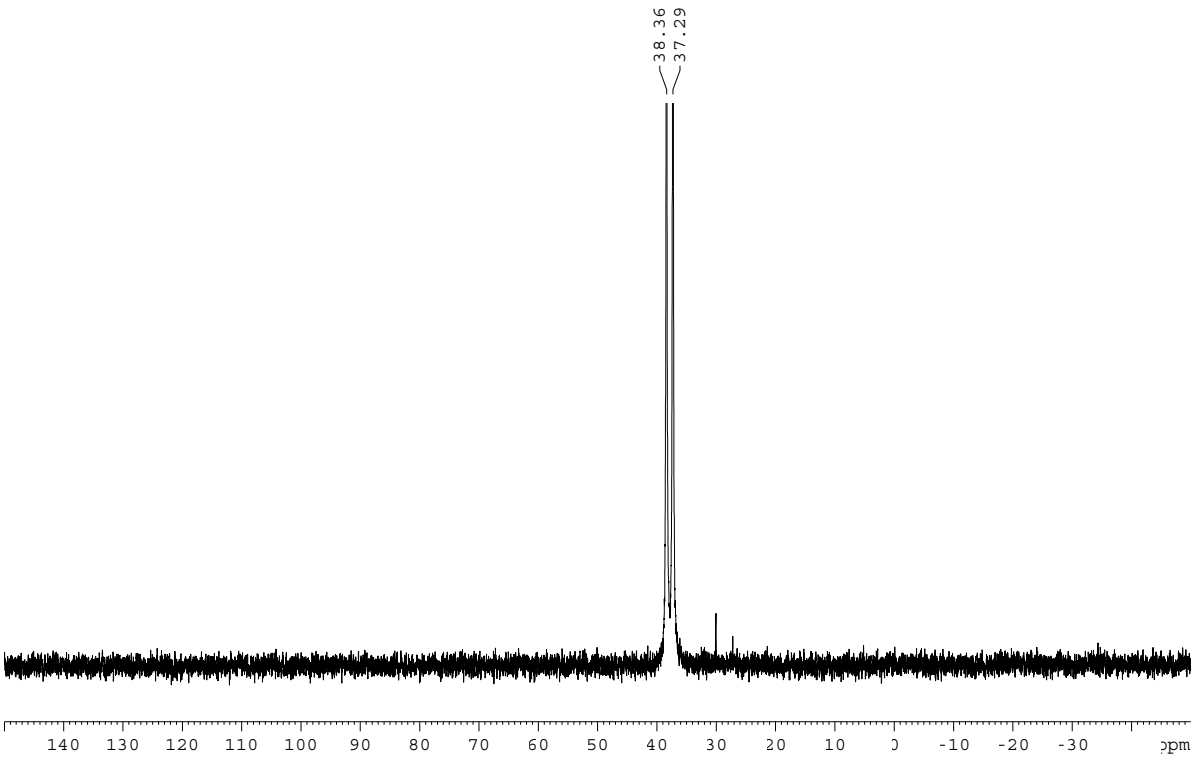
Compound 20: ^{1}H NMR (300 MHz, CDCN)



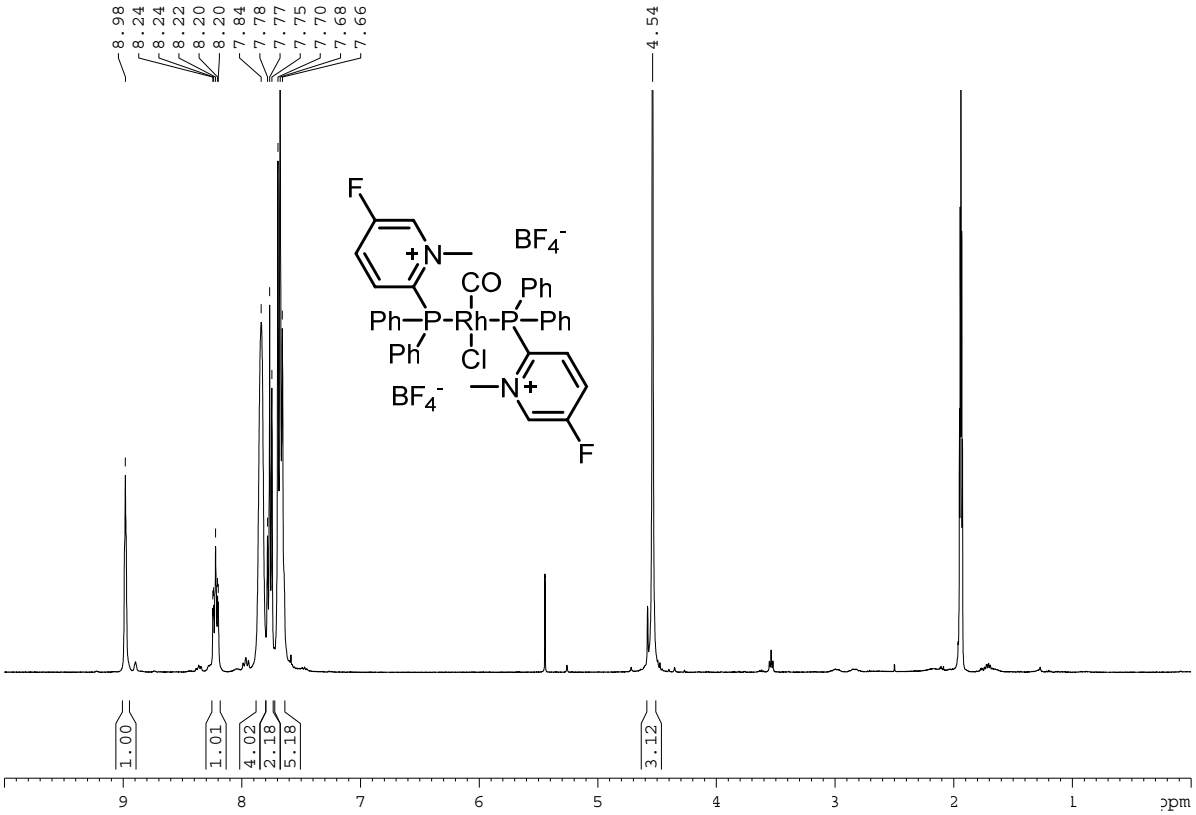
Compound 20: ^{13}C NMR (75 MHz, CDCN)



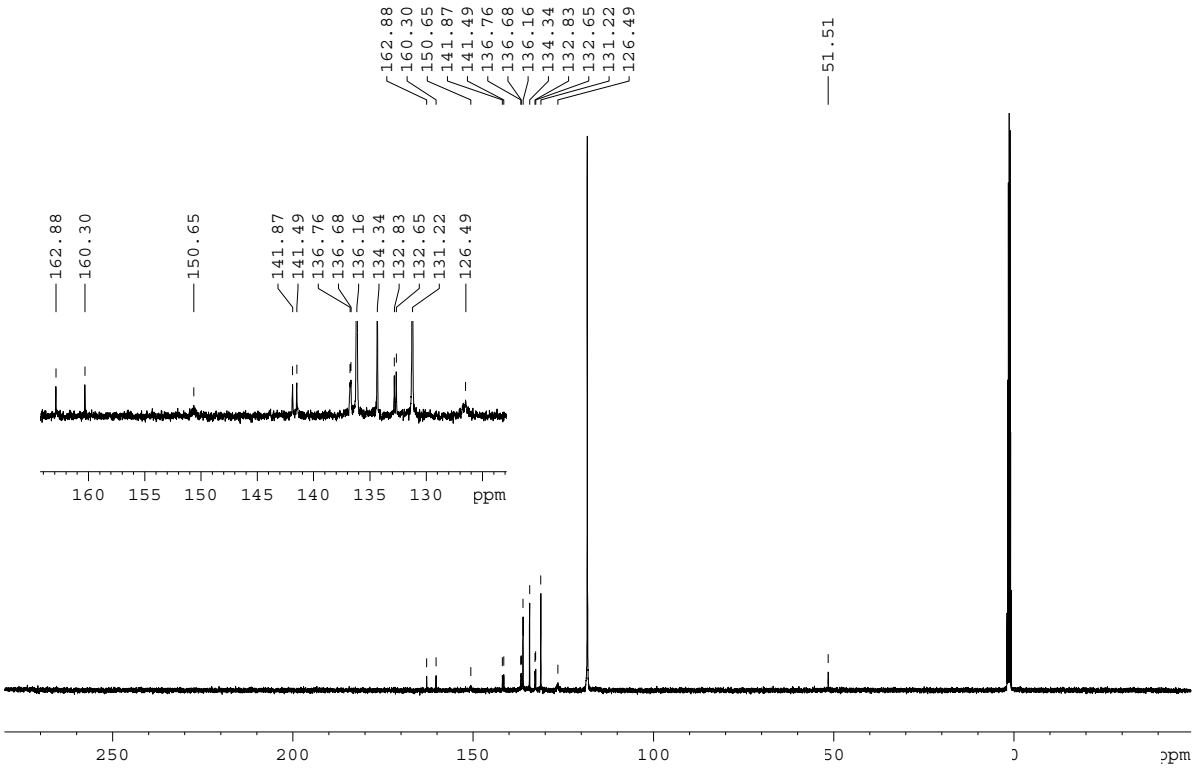
Compound 20: ^{31}P NMR (121 MHz, CDCN)



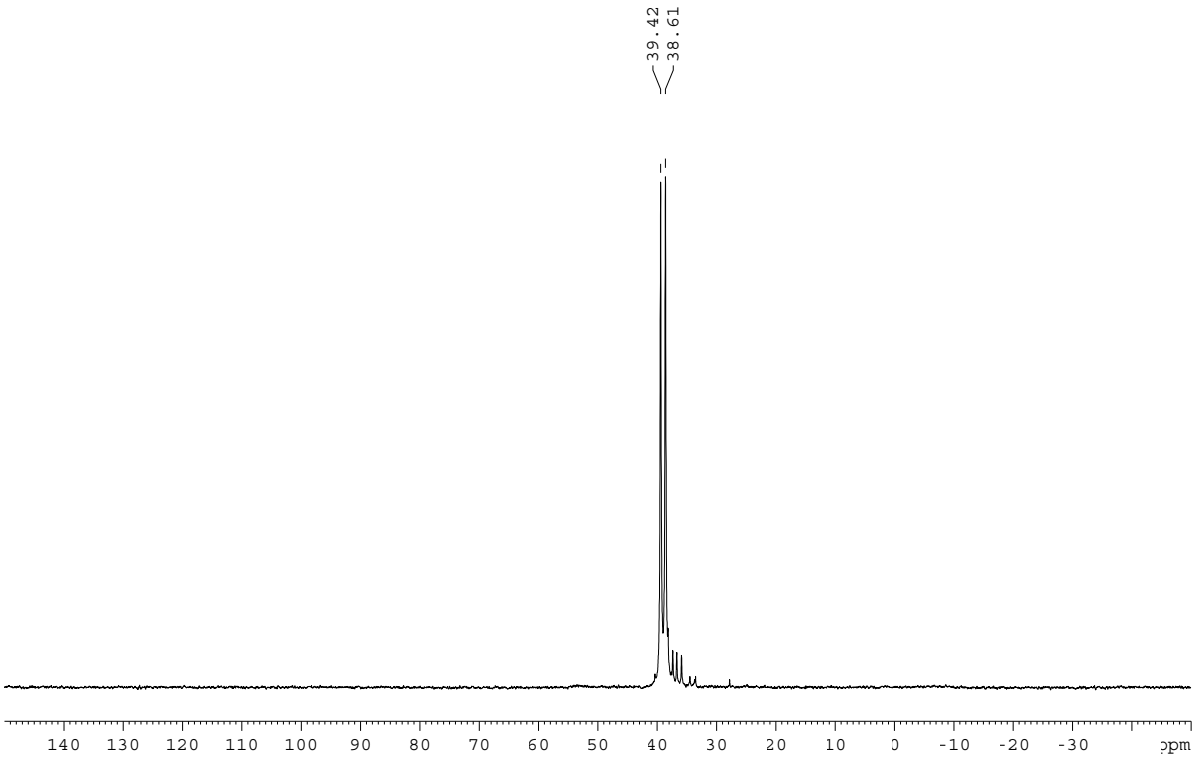
Compound 21: ^{1}H NMR (300 MHz, CDCN)



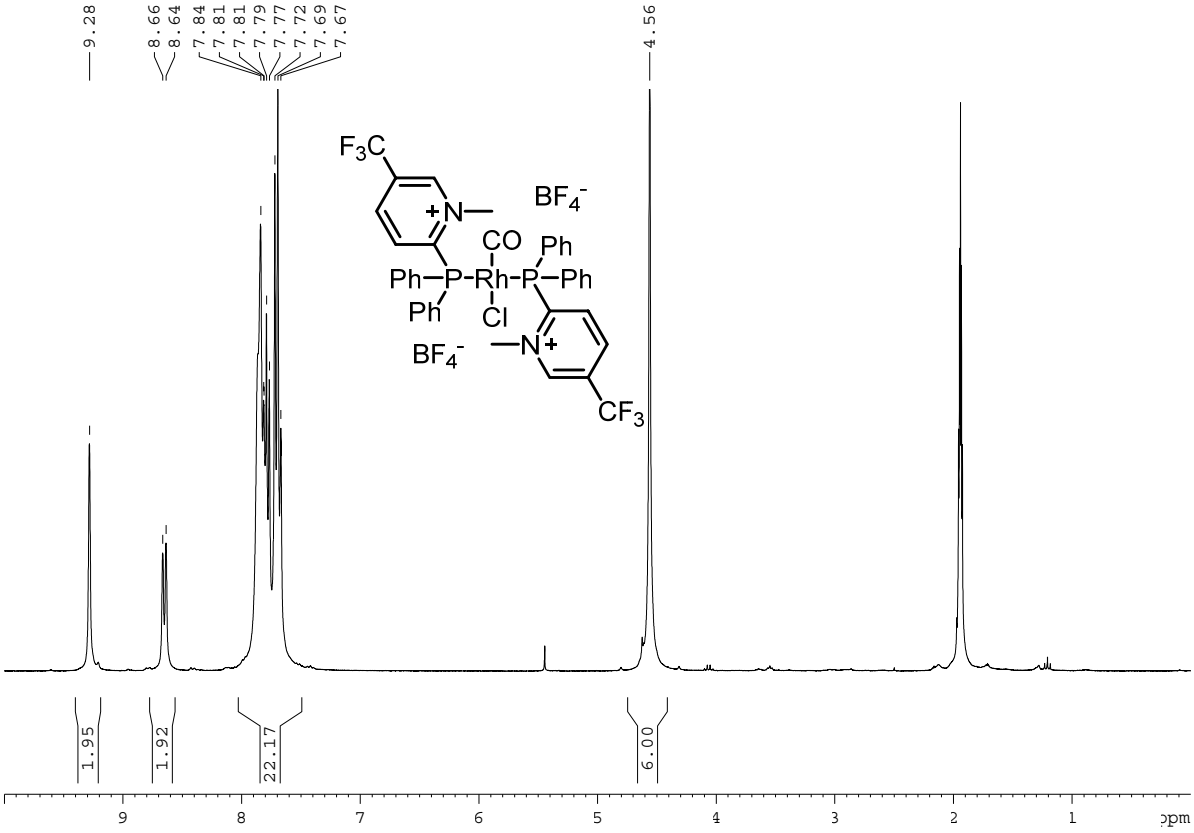
Compound 21: ^{13}C NMR (75 MHz, CDCN)



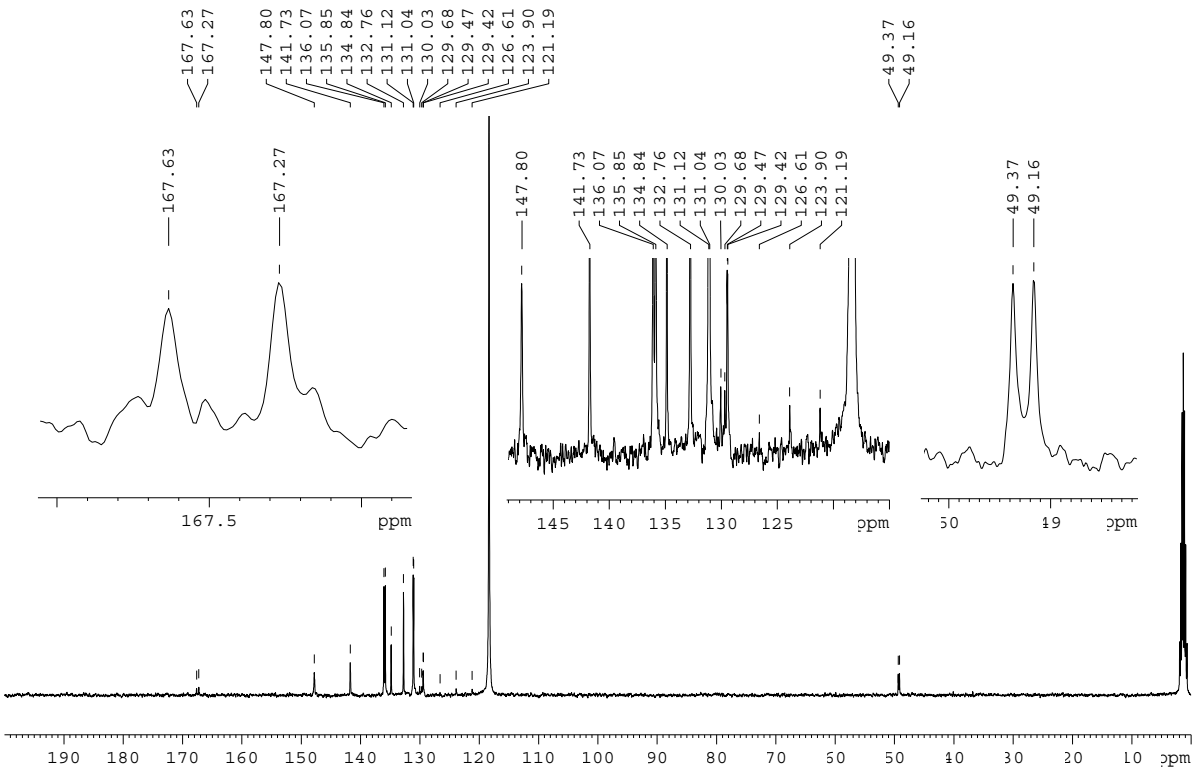
Compound 21: ^{31}P NMR (121 MHz, CDCN)



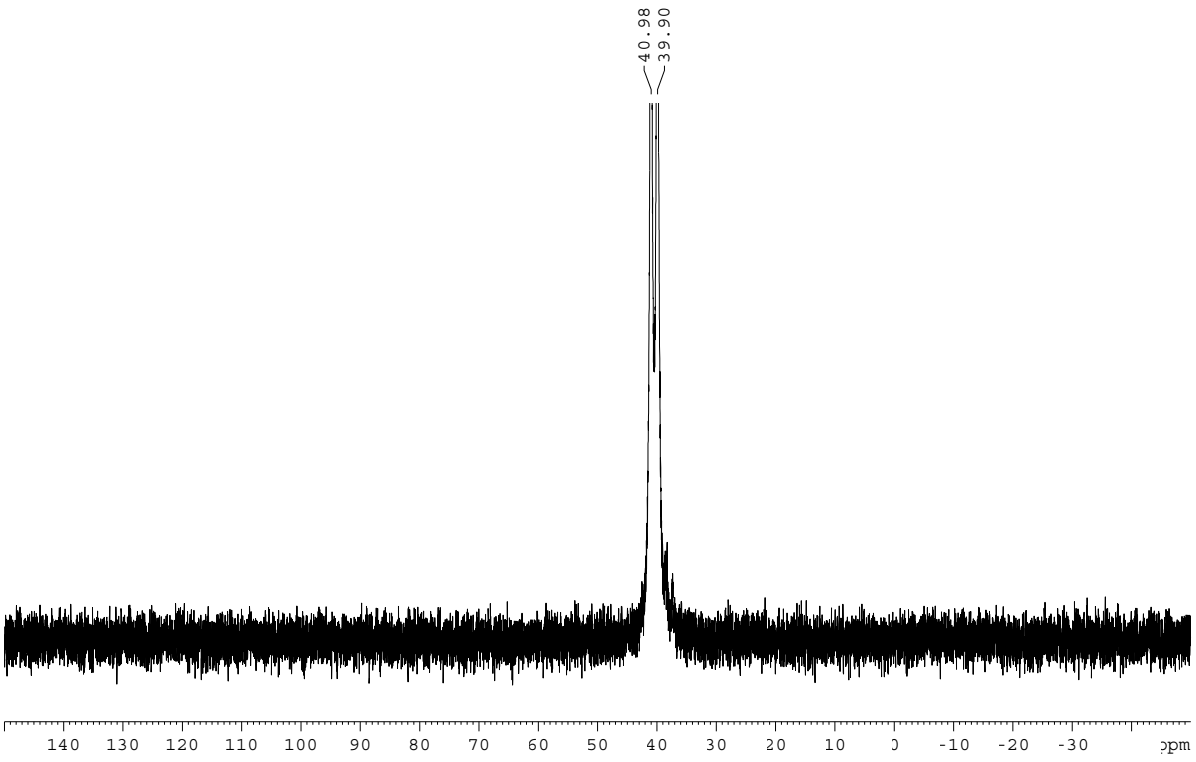
Compound 22: ^{1}H NMR (300 MHz, CDCN)



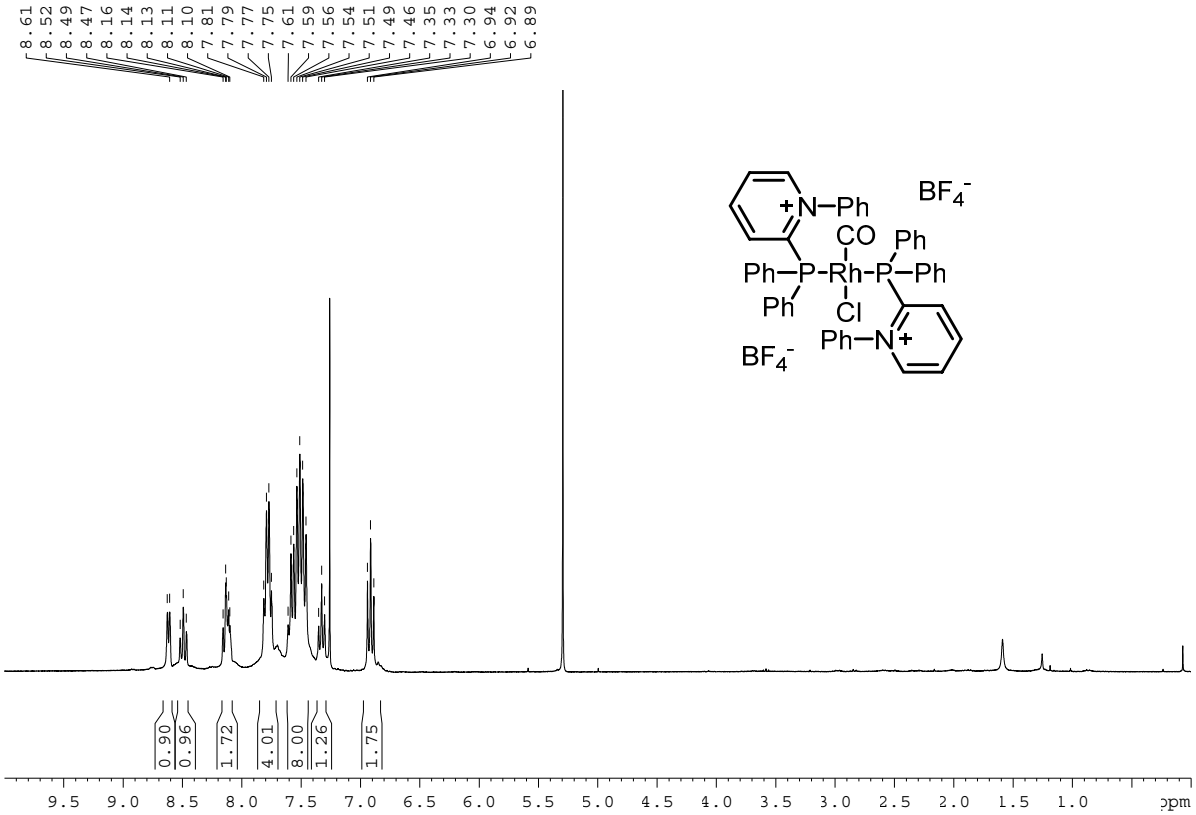
Compound 22: ^{13}C NMR (75 MHz, CDCN)



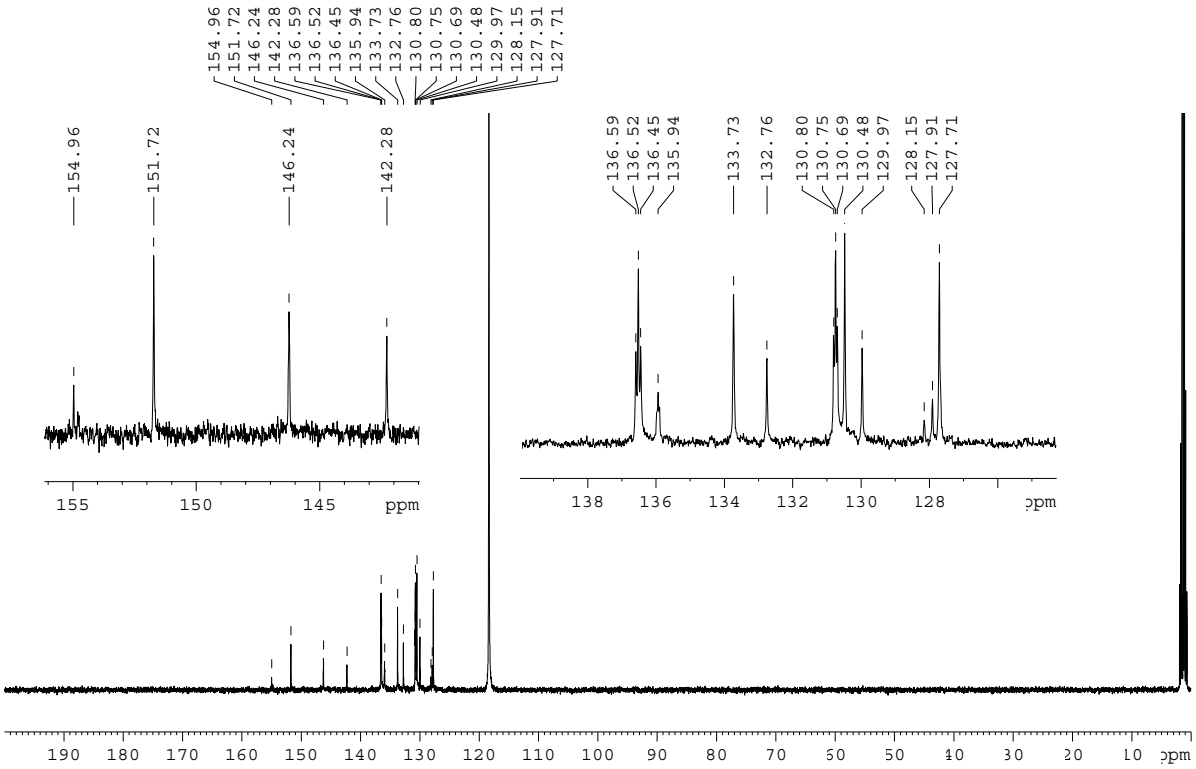
Compound 22: ^{31}P NMR (121 MHz, CDCN)



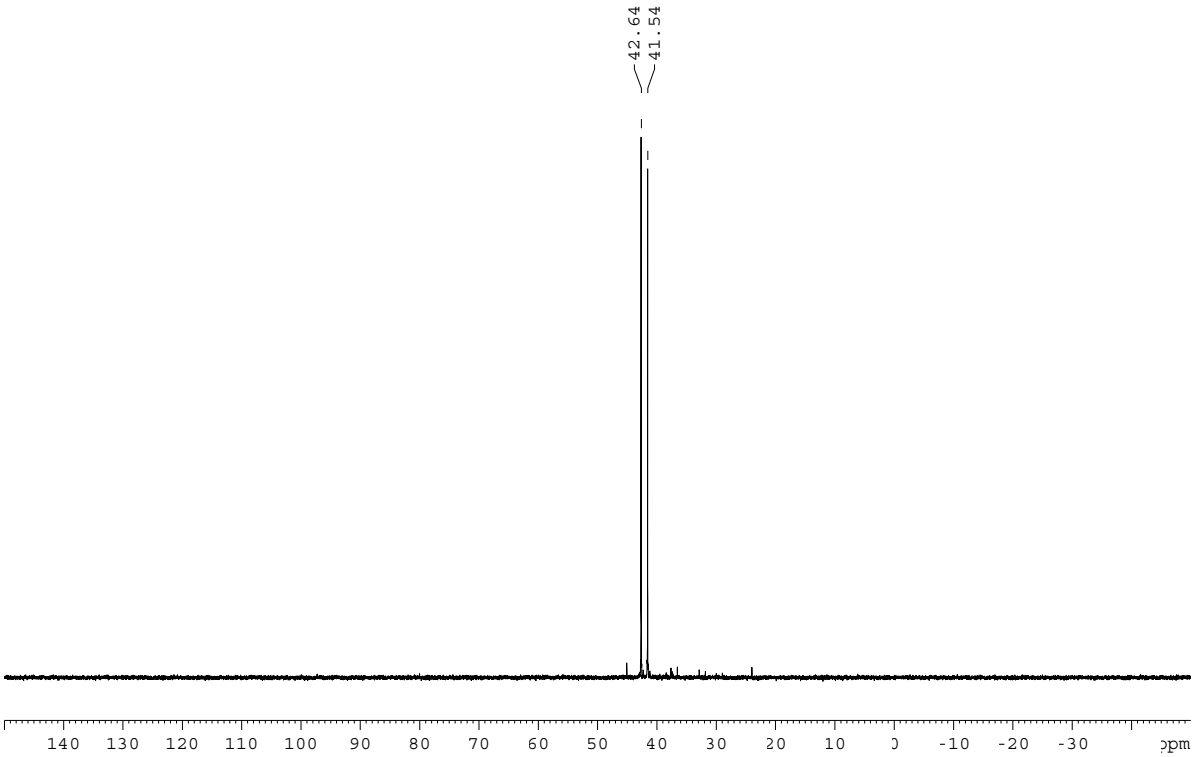
Compound 23: ^{1}H NMR (300 MHz, $CDCl_3$)



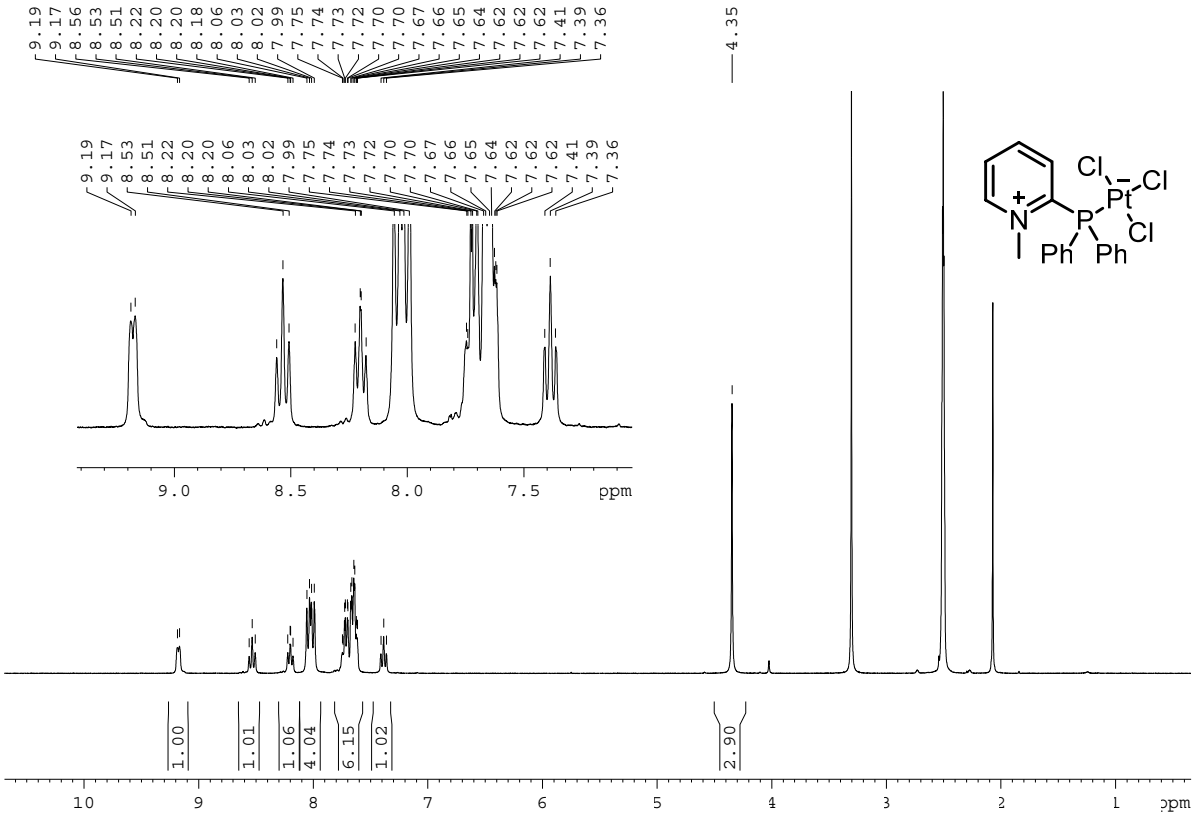
Compound 23: ^{13}C NMR (75 MHz, CD_3CN)



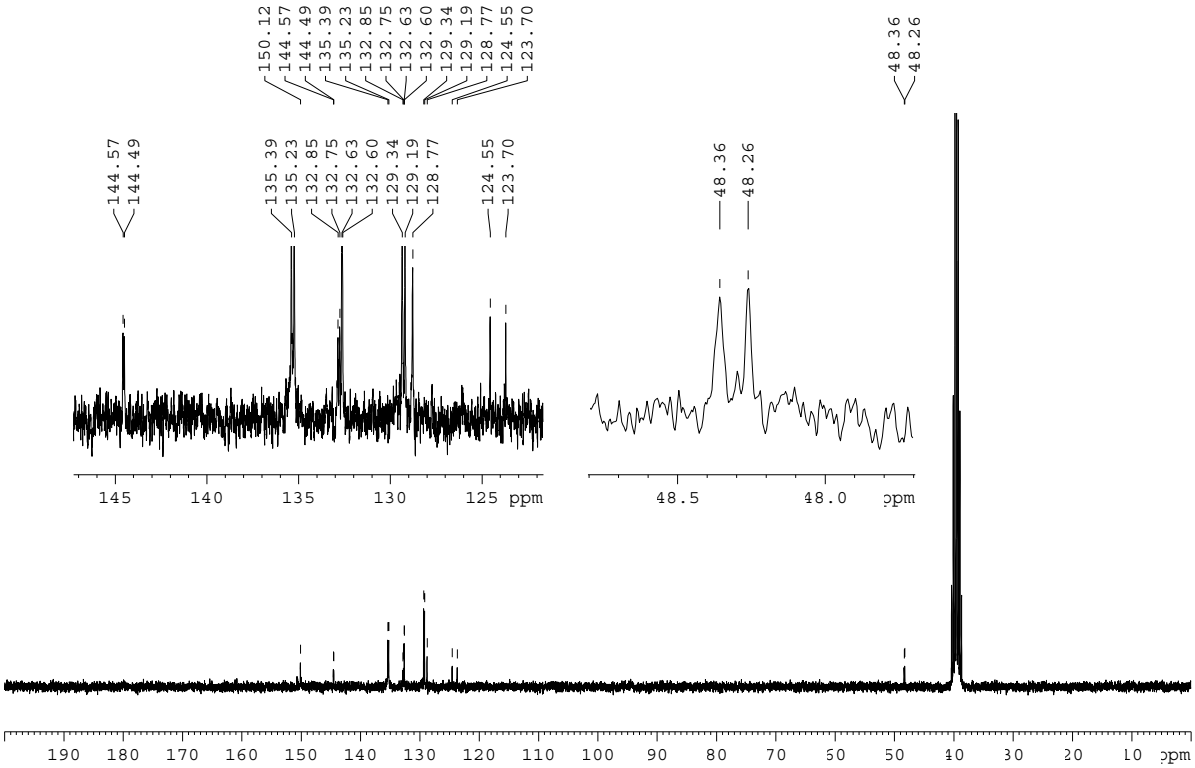
Compound 23: ^{31}P NMR (121 MHz,$CDCl_3$)



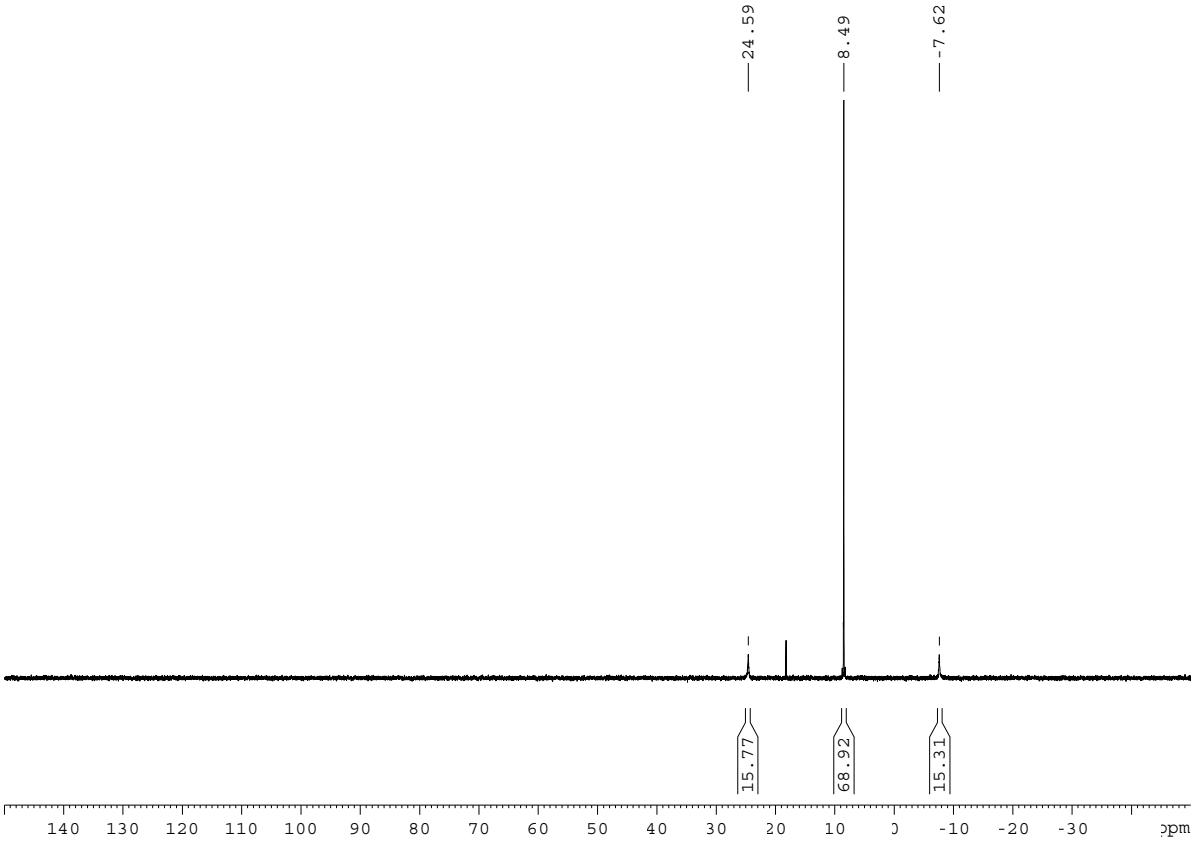
Compound 28: ^{1}H NMR (300 MHz, d_6-DMSO/CD_3CN)



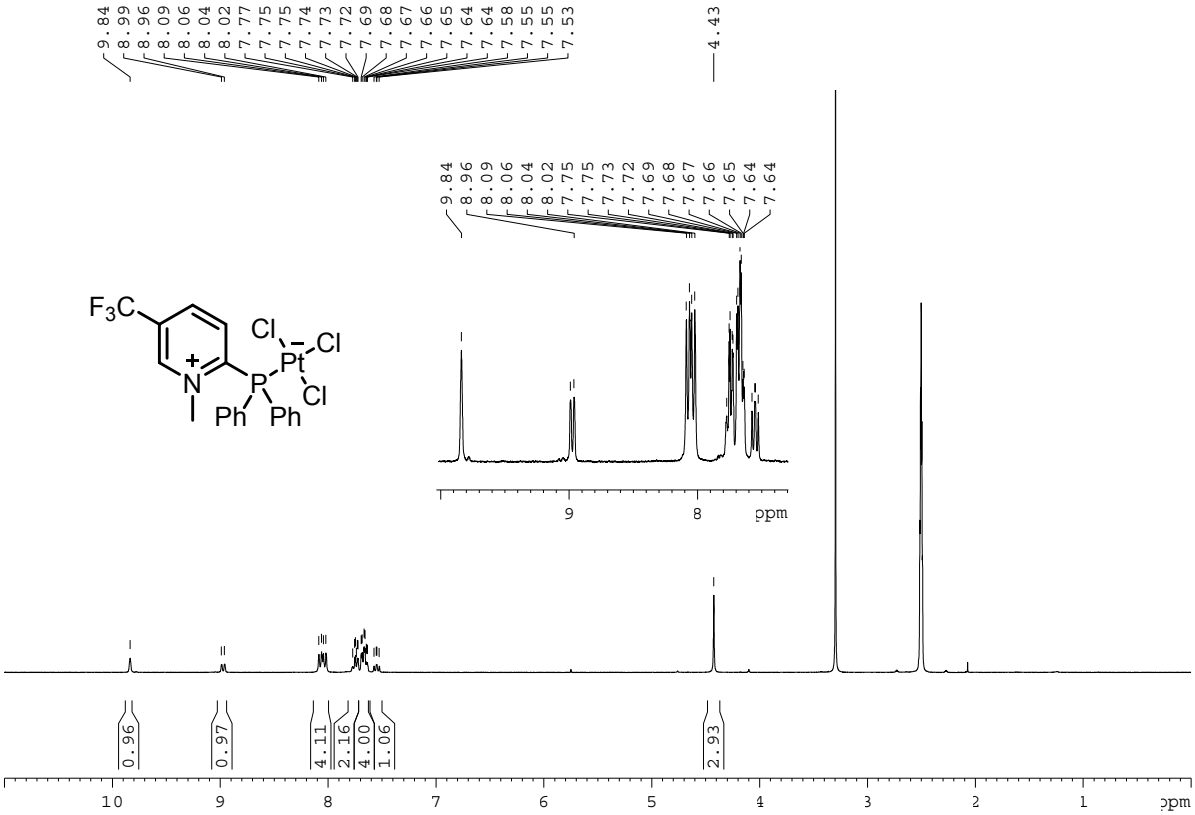
Compound 28: ^{13}C NMR (75 MHz, DMSO)



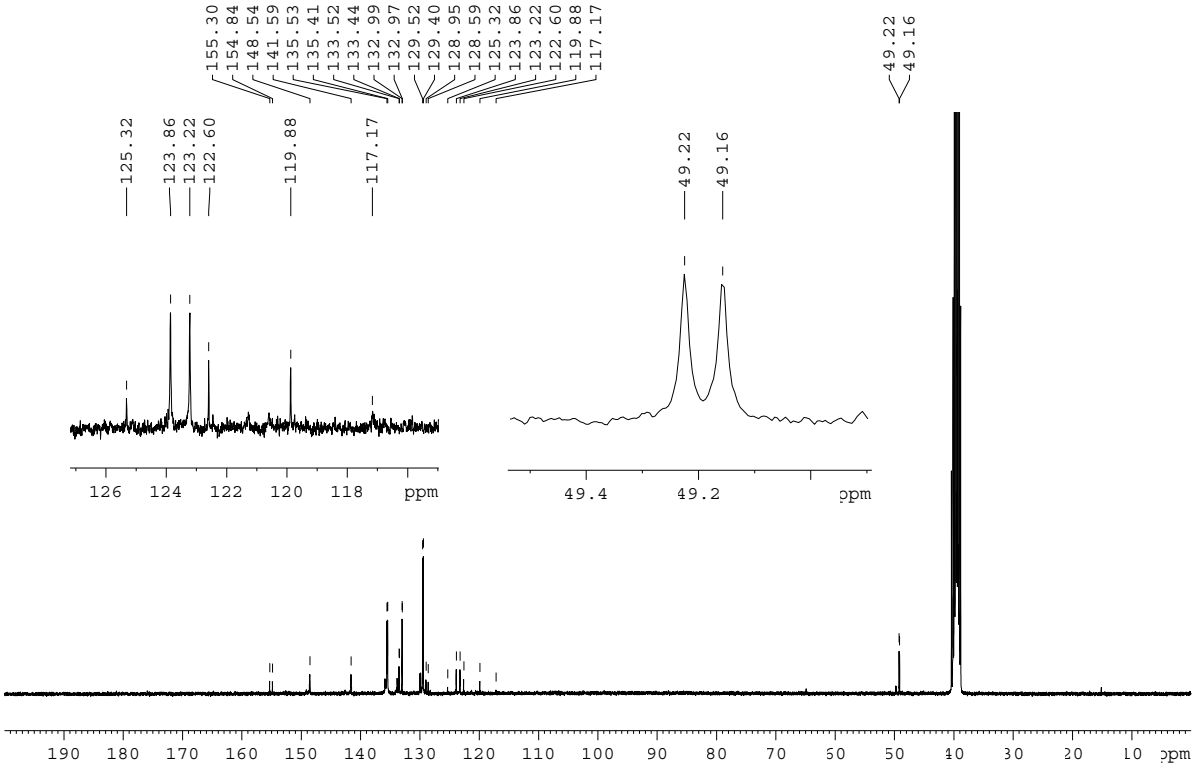
Compound 28: ^{31}P NMR (162 MHz, d_6-DMSO/CD_3CN)



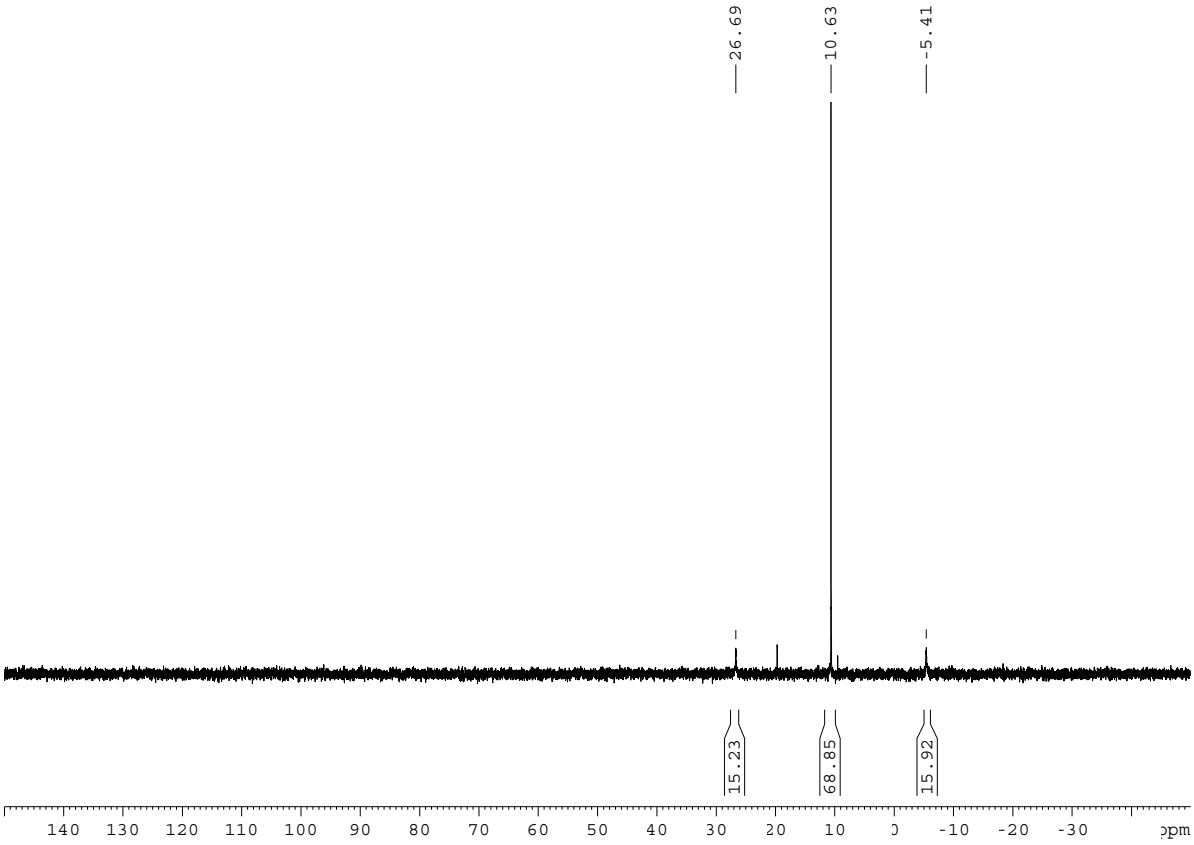
Compound 29: ^{1}H NMR (300 MHz, d_6-DMSO)



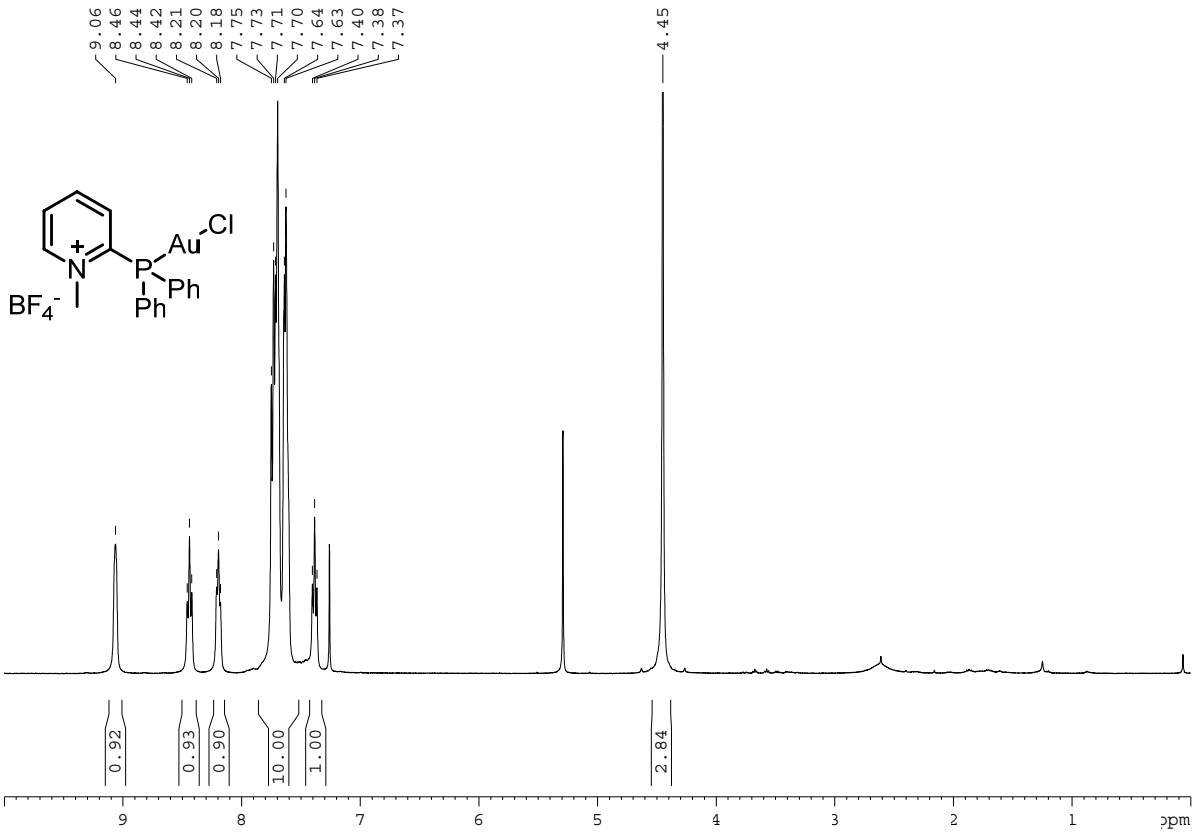
Compound 29: ^{13}C NMR (75 MHz, DMSO)



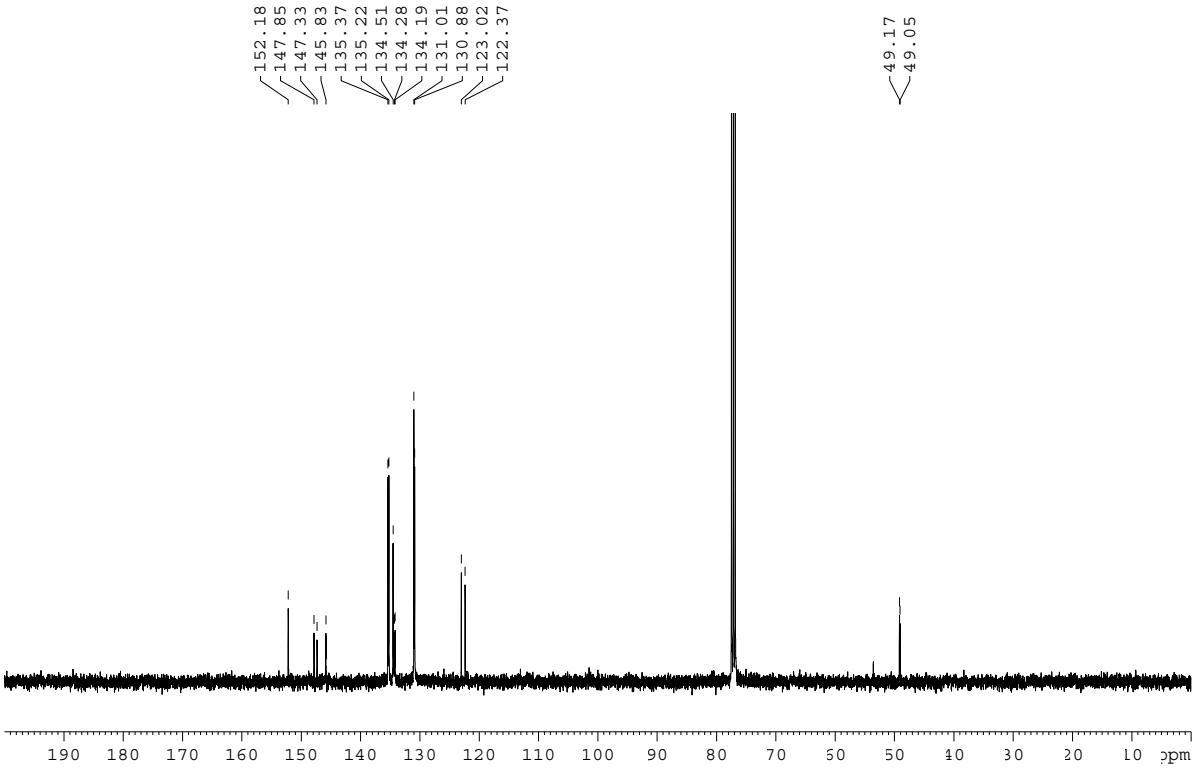
Compound 29: ^{31}P NMR (162 MHz, d_6-DMSO/CD_3CN)



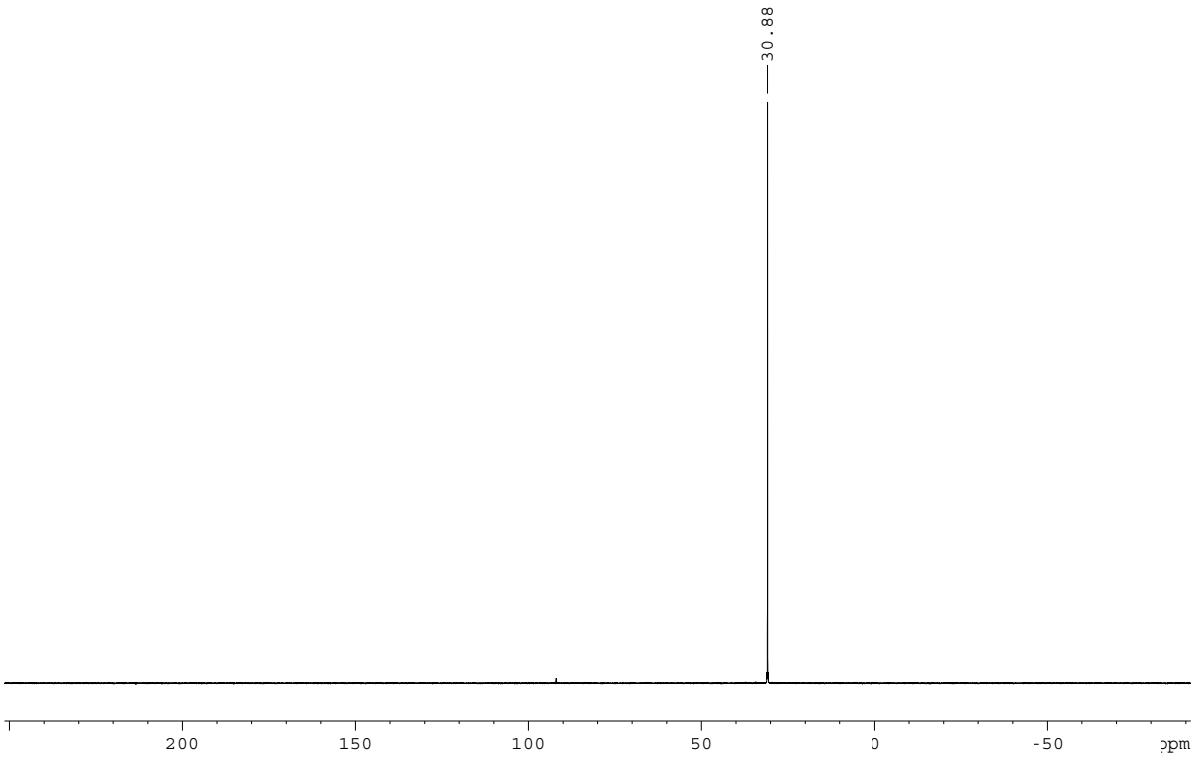
Compound 30: ^{1}H NMR (300 MHz, $CDCl_3$)



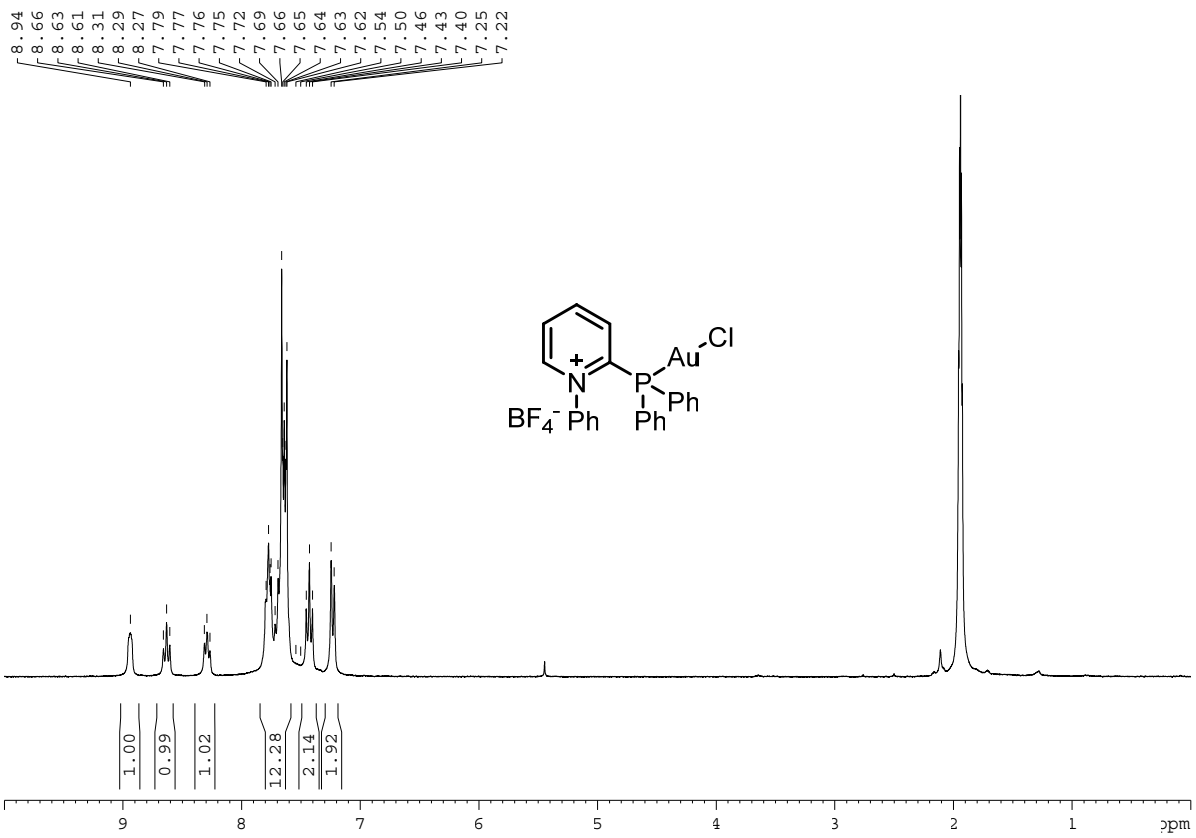
Compound 30: ^{13}C NMR (75 MHz, $CDCl_3$)



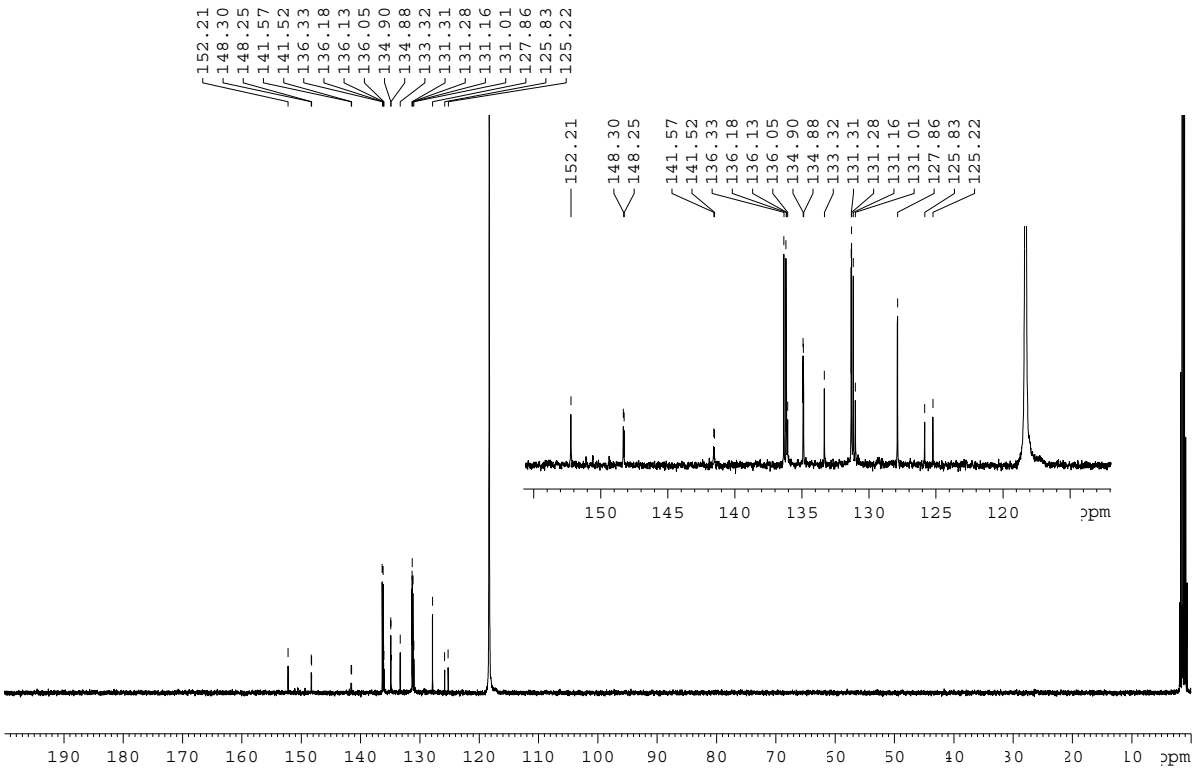
Compound 30: ^{31}P NMR (162 MHz, $CDCl_3$)



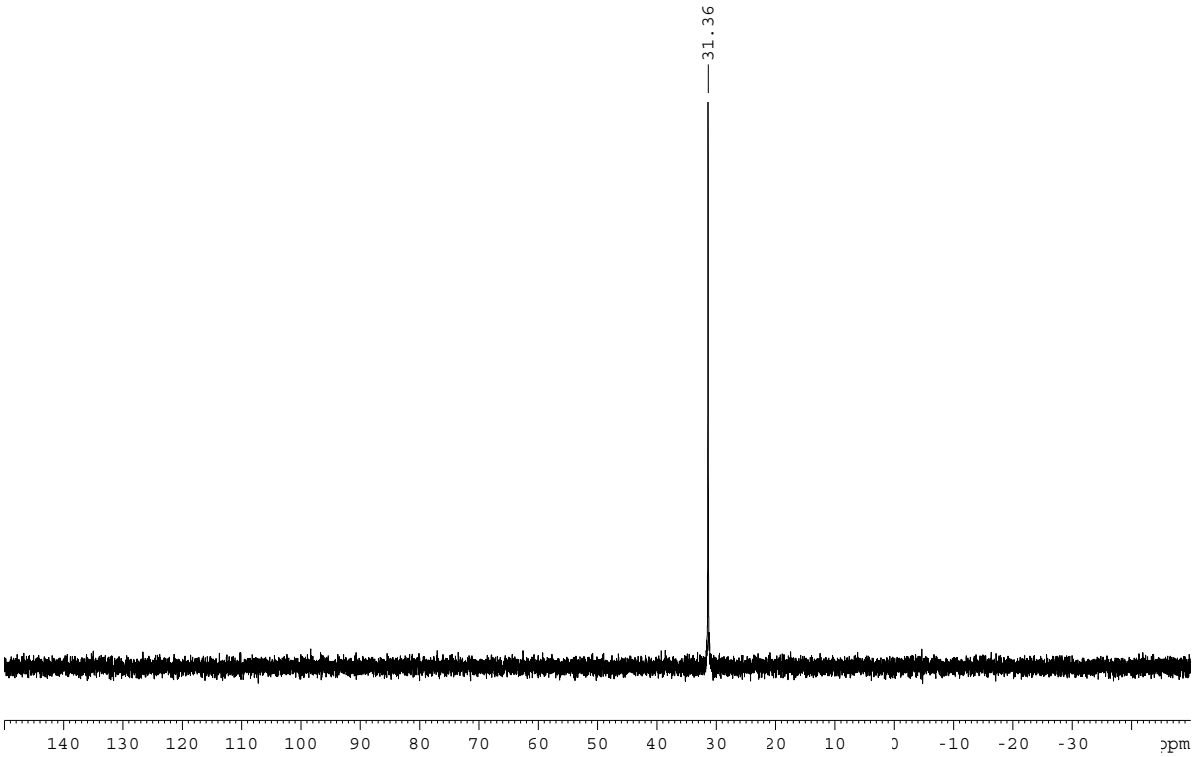
Compound 31: ^{1}H NMR (400 MHz, CD_3CN)



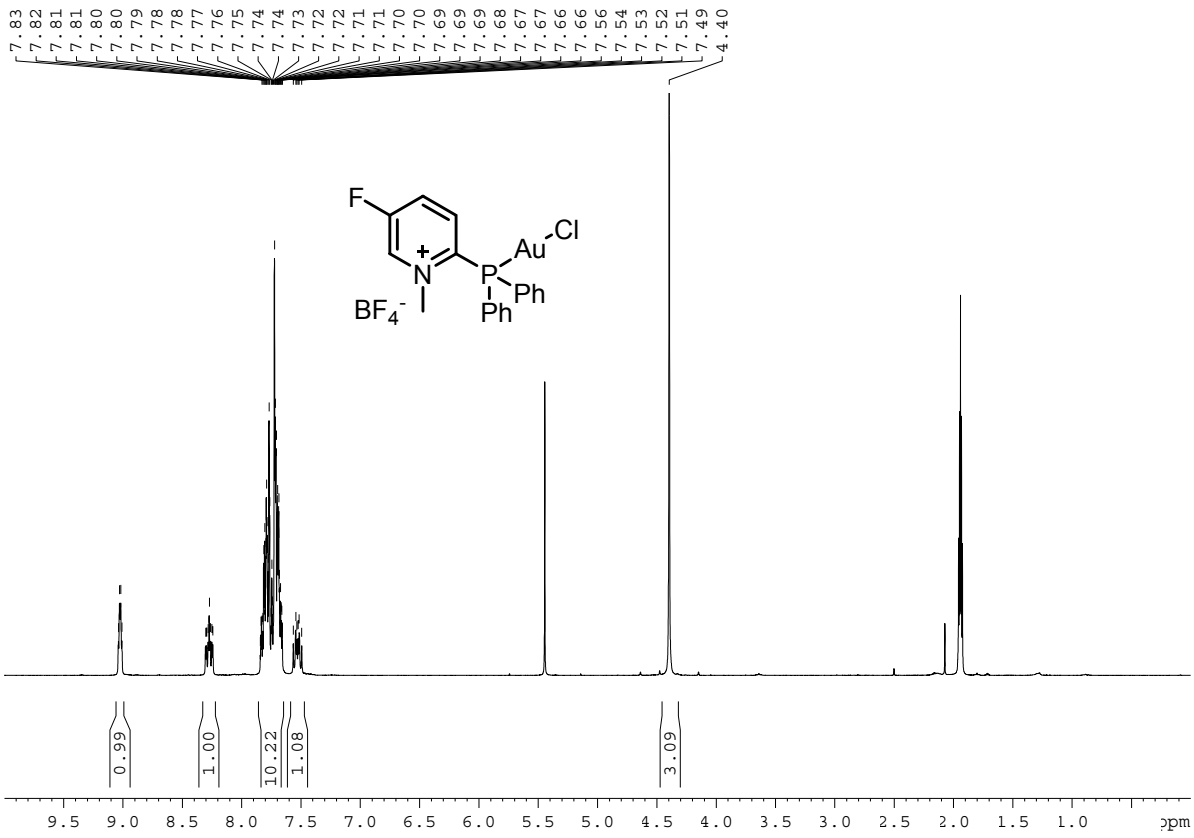
Compound 31: ^{13}C NMR (102 MHz, CD_3CN)



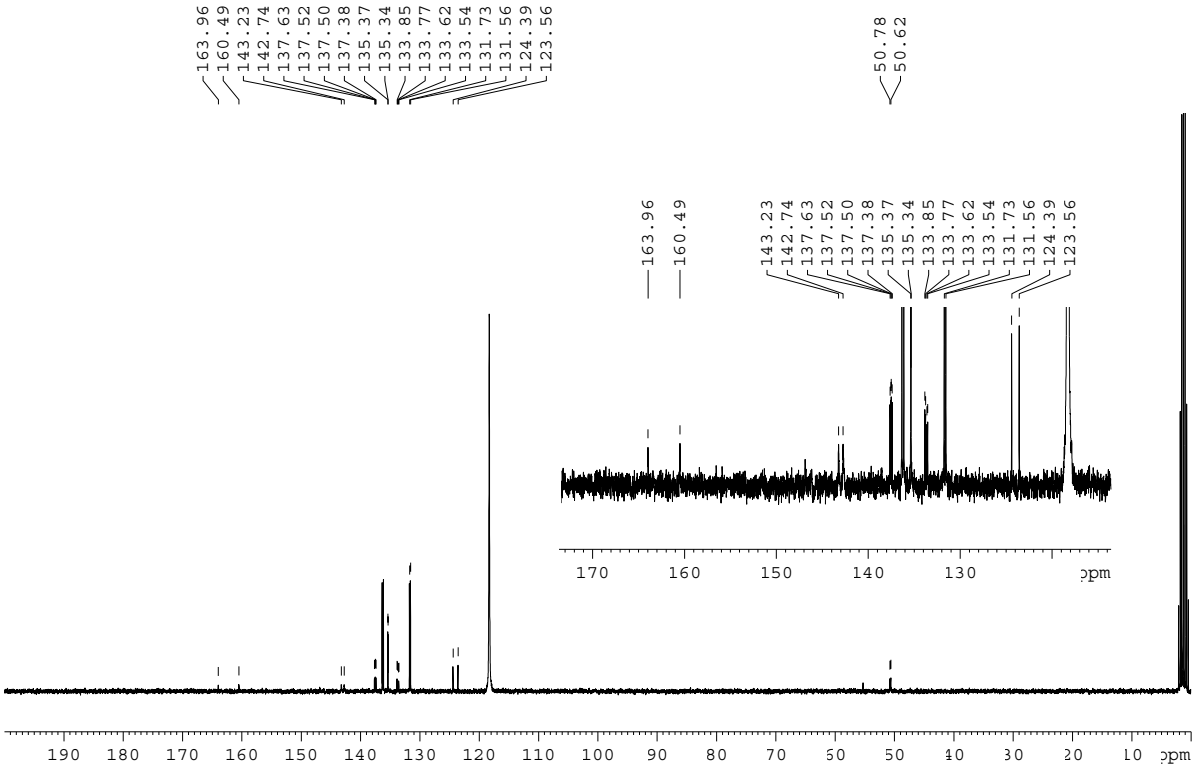
Compound 31: ^{31}P NMR (162 MHz, CD_3CN)



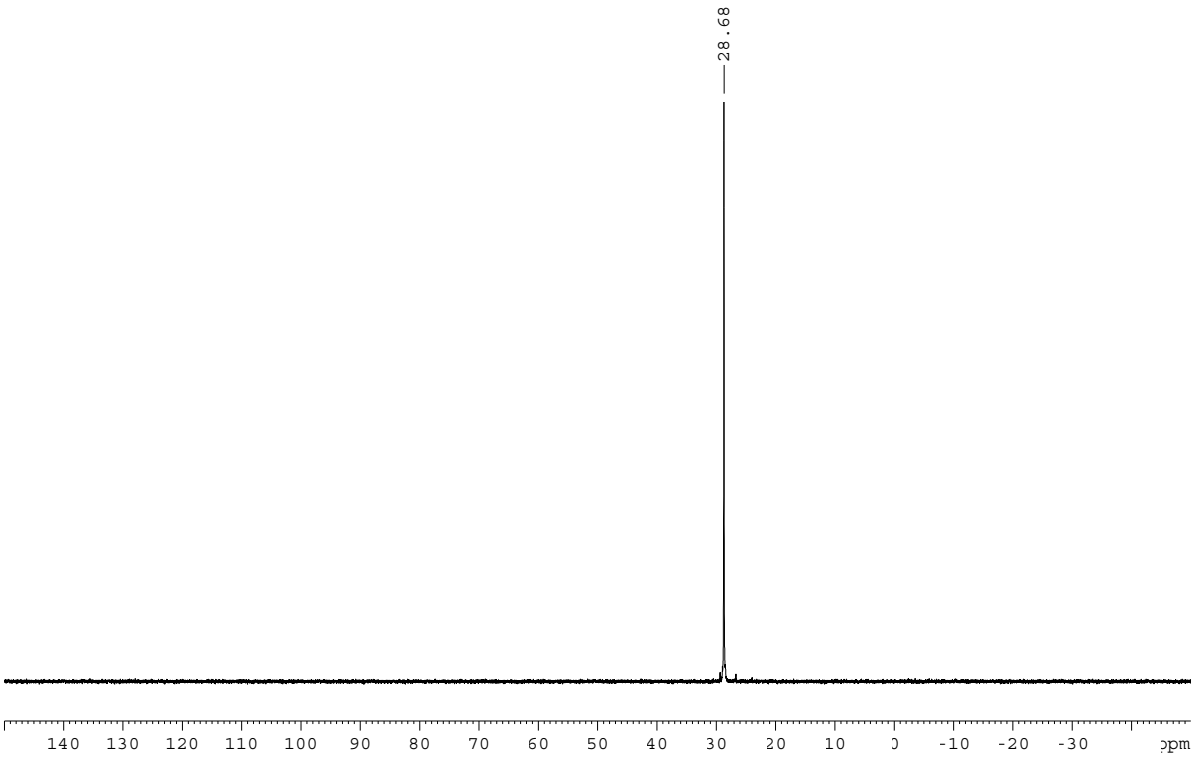
Compound 32: ^{1}H NMR (300 MHz, CD_3CN)



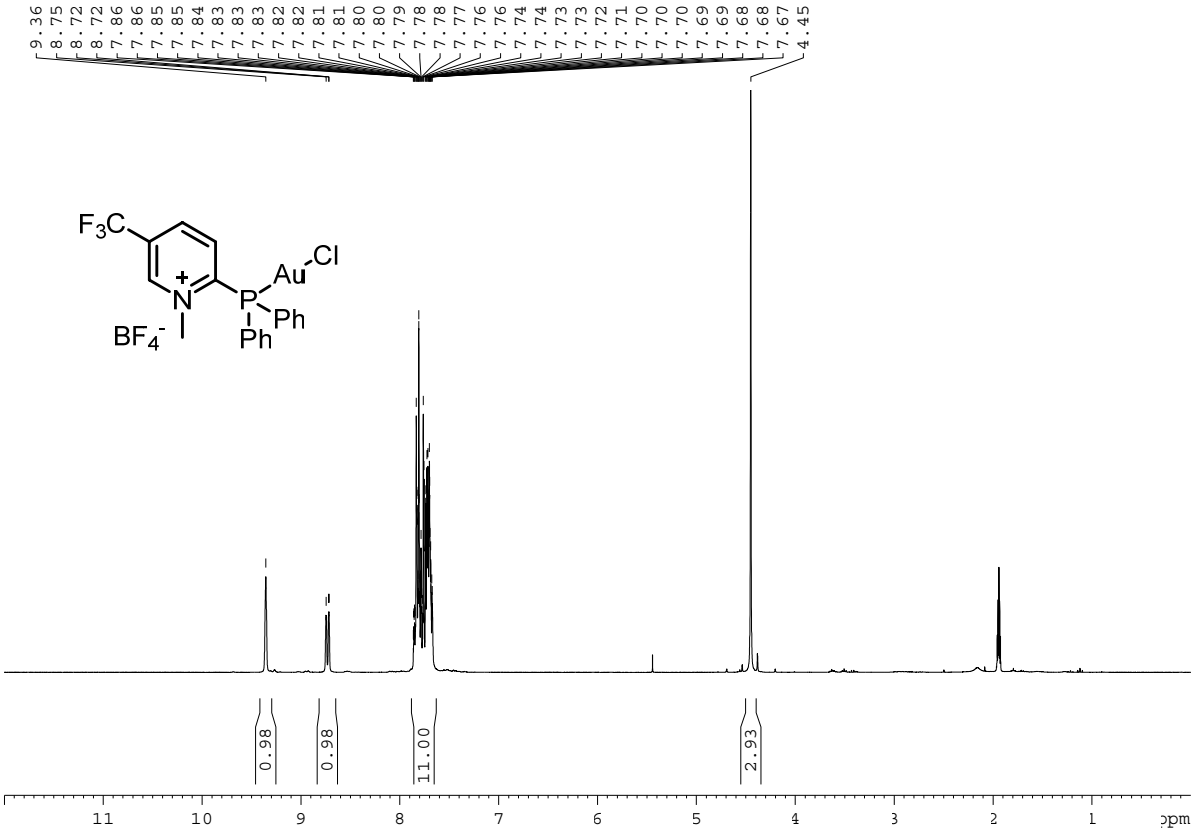
Compound 32: ^{13}C NMR (75 MHz, CD_3CN)



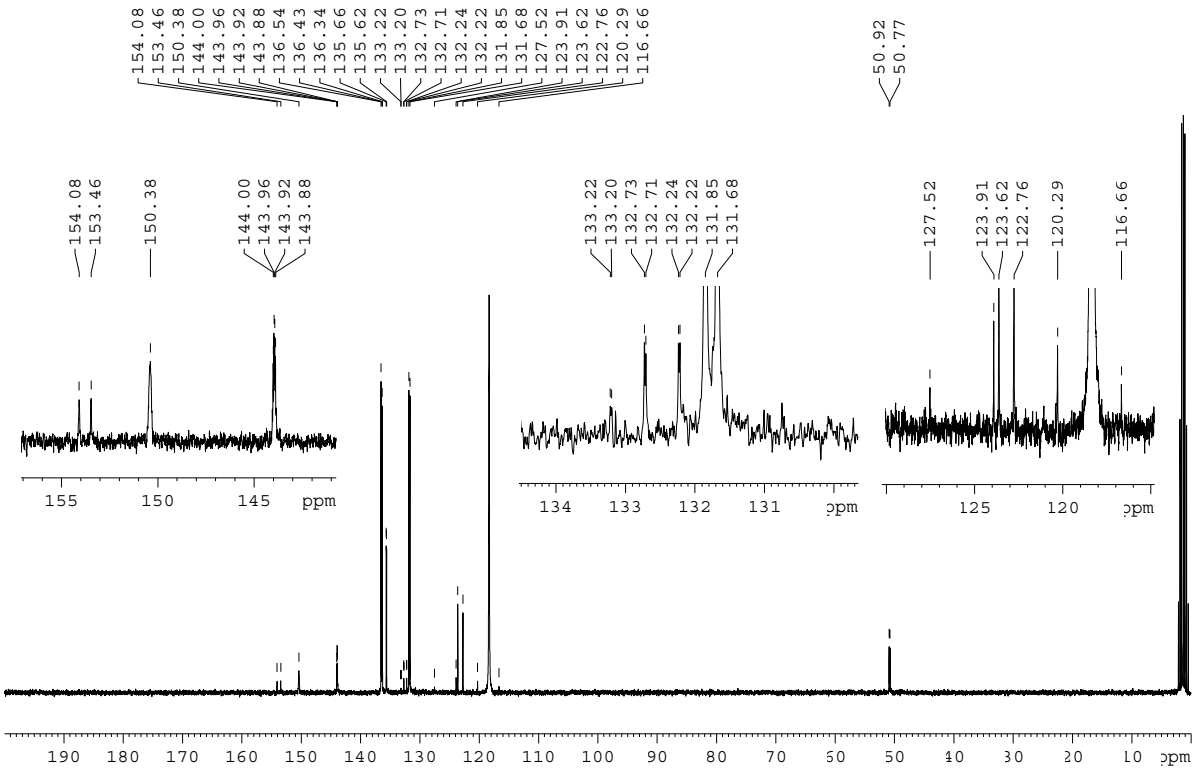
Compound 32: ^{31}P NMR (162 MHz, CD_3CN)



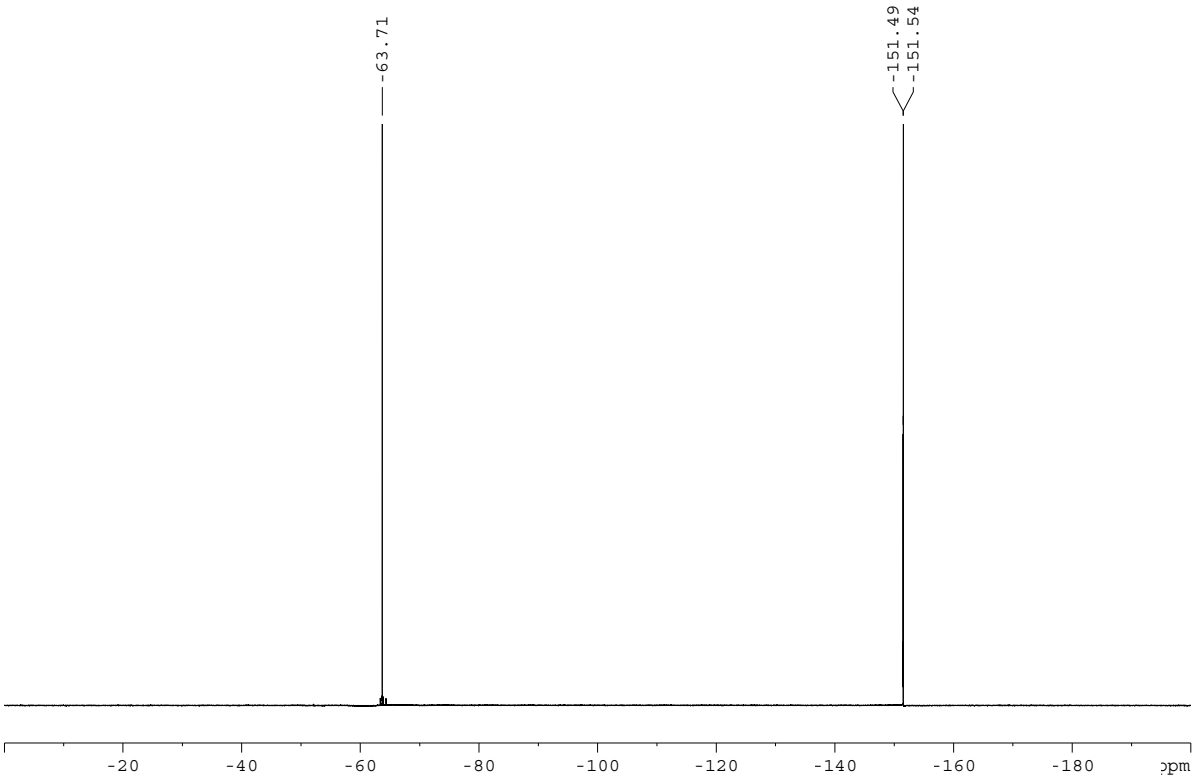
Compound 33: ^{1}H NMR (300 MHz, CD_3CN)



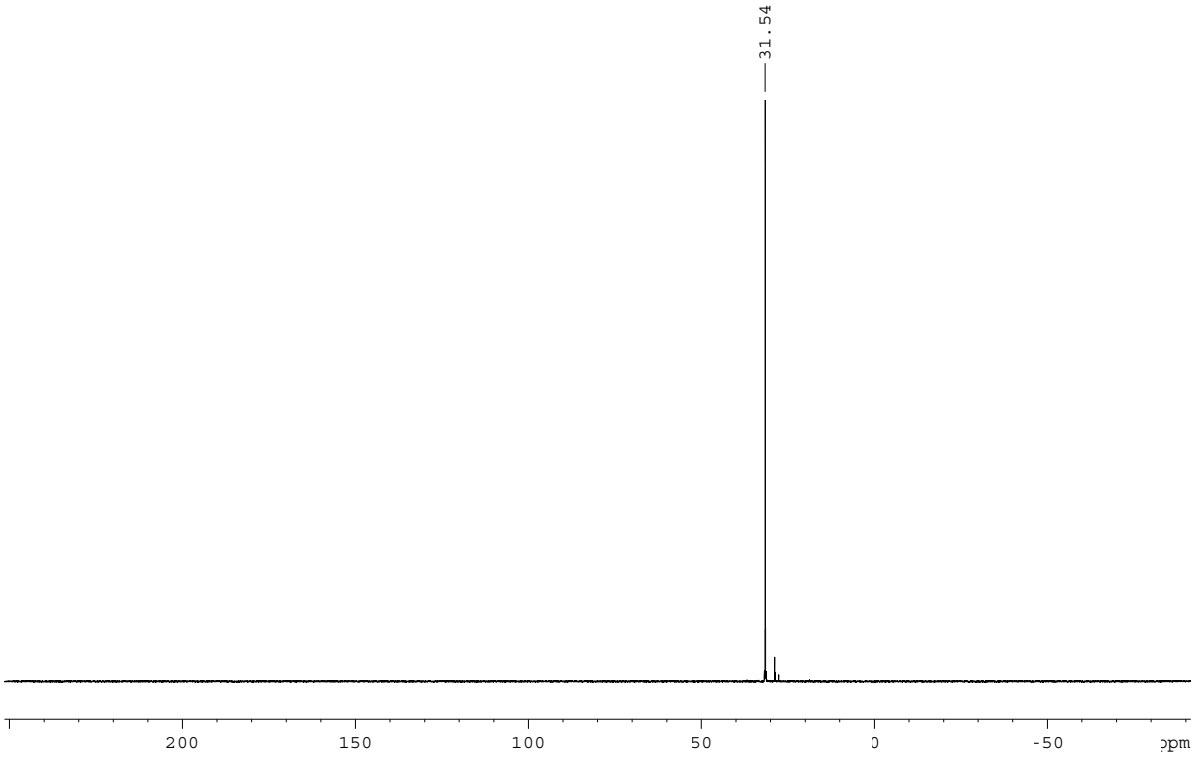
Compound 33: ^{13}C NMR (75 MHz, CD_3CN)



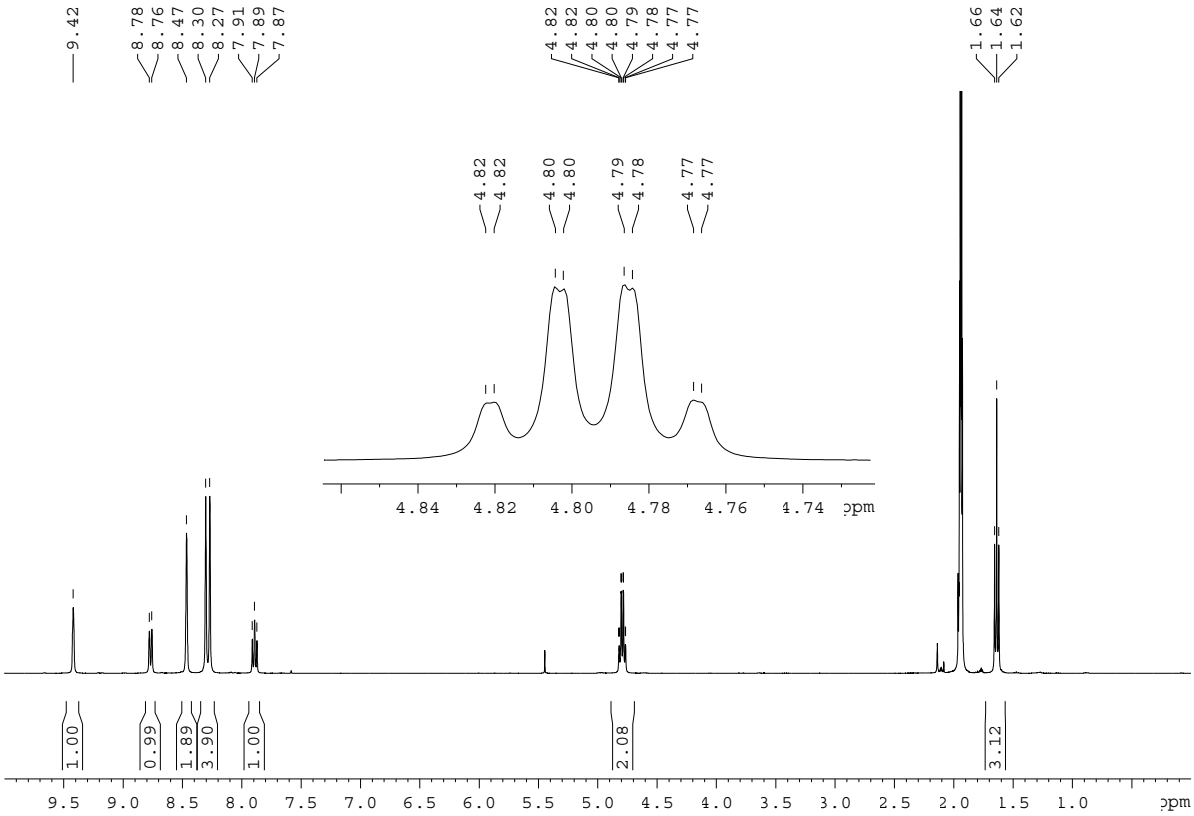
Compound 33: ^{19}F NMR (282 MHz, CD_3CN)



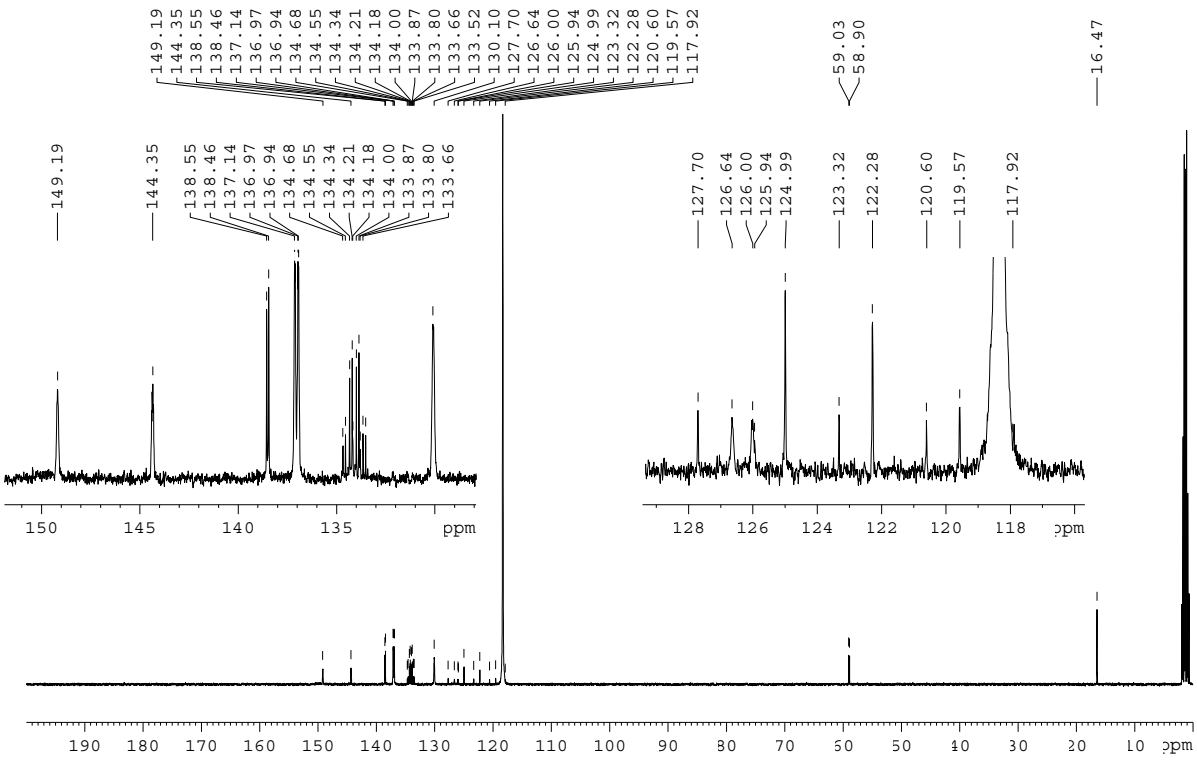
Compound 33: ^{31}P NMR (162 MHz, CD_3CN)



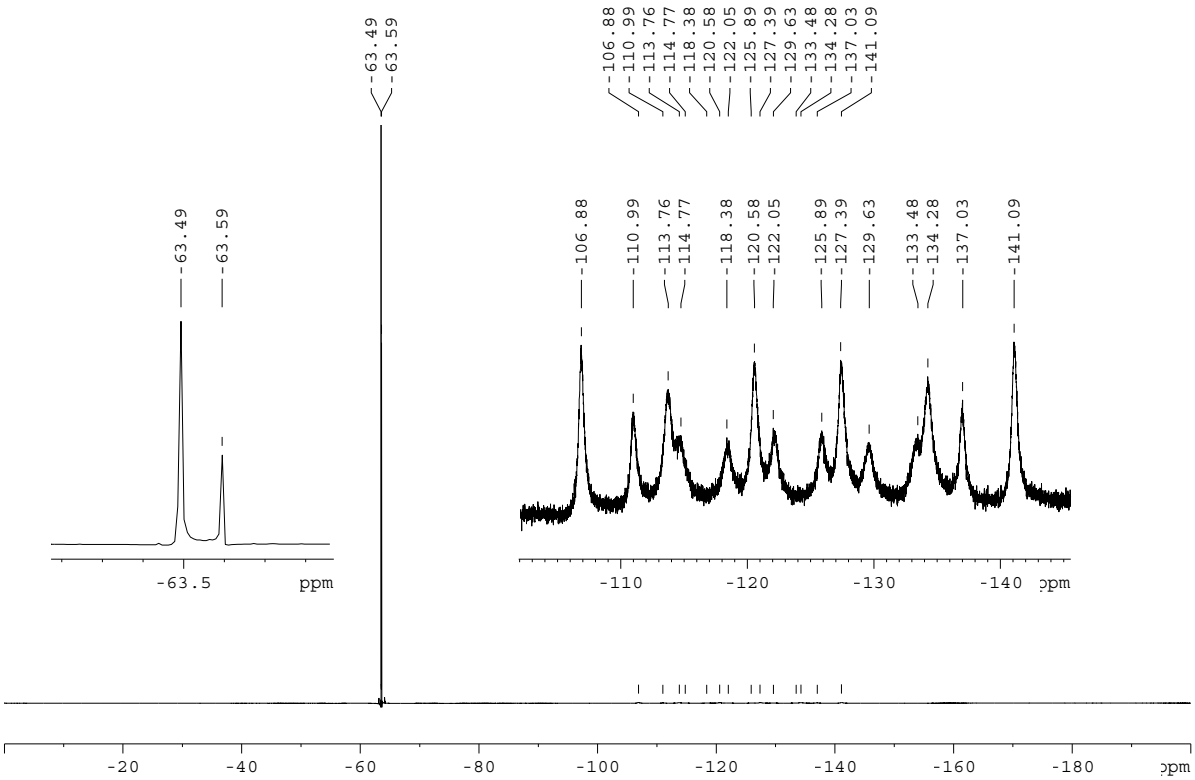
Compound 34: ^{1}H NMR (400 MHz, CD_3CN)



Compound 34: ^{13}C NMR (102 MHz, CD_3CN)



Compound 34: ^{19}F NMR (282 MHz, CD_3CN)



Compound 34: ^{31}P NMR (162 MHz, CD_3CN)