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Supporting Information

P(V)-bis(amidophenolate) ligand cooperation: Stoichiometric C=O-bond cleavage in aldehydes and ketones

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Contents

General Information

Working methods:

Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere in flame-dried glassware on a Schlenk line or under nitrogen atmosphere in an MBraun UNIlab plus glovebox. Dry solvents were obtained using an MBraun MB-SPS-7 solvent purification system (THF, diethyl ether, toluene, pentane, dichloromethane, acetonitrile), deoxygenated in a nitrogen stream and stored over 3 Å molecular sieves under a nitrogen atmosphere. Flash chromatography was performed on Macherey Nagel 60 (40-63 µm) silica gel. Air-insensitive reactions were controlled by thin layer chromatography (TLC) analysis, performed using polygram SIL G/UV254 from Macherey Nagel and visualized by UV irradiation (λ = 254 nm), phosphomolybdic acid or iodine stains.

Starting materials:

Unless otherwise specified, all reagents were used as received from commercial suppliers (ABCR, AcrosOrganics, Alfa Aesar, Chempur GmbH, J and K Scientific, Sigma Aldrich, Thermo Fisher Scientific, Tokyo Chemical Industry). PCl_3 was freshly distilled under a nitrogen atmosphere prior to use. 4-Dimethylaminopyridine (DMAP) and $GaCl_3$ were purified under nitrogen atmosphere by sublimation at 10^{-3} mbar and stored in a nitrogen-filled glovebox. Chlorophosphorane **1**,[1] sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $Na^+[(CF_3)_2C_6H_3]_4B^-$ (NaBArF),[2] and 1-adamantyl carbaldehyde[3] were synthesized according to the published procedures. Liquid aldehydes and ketones were deoxygenated and dried over 3 Å molecular sieves prior to use.

NMR spectroscopy:

The NMR spectra were recorded on a Bruker Avance III 300 MHz, Bruker Avance III HD 300 MHz, Bruker Avance III 400, Bruker Avance III HD 400 MHz or Bruker Avance Neo 400 MHz at 298 K. ^1H and ^{13}C chemical shifts are given in ppm relative to TMS, using the solvent signals as references and converting the chemical shifts to the TMS scale.^{11}B, ^{19}F and ^{31}P chemical shifts are given in ppm relative to $BF_3{\cdot}OEt_2$, $CFCl_3$ and H_3PO_4, respectively (external standard). The chemical shifts are given in parts per million (ppm), and the coupling constants (*J*) in Hertz (Hz). Solvents for NMR spectroscopy were deoxygenated in a nitrogen stream and stored over 3 Å molecular sieves in a glove box.

Mass spectrometry:

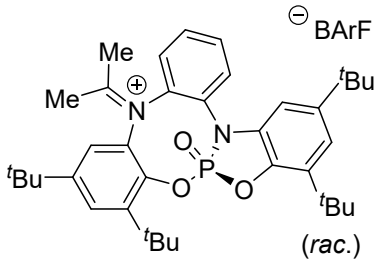
Mass spectrometry analyses were performed using the following equipment: Bruker Daltronik microTOF (ESI), Bruker Daltronik maXis (ESI), Joel AccuTOF (LIFDI).

Infrared spectroscopy:

Neat samples were measured on a JASCO FT/IR-4100 or JASCO FT/IR-4600 at room temperature. The vibrational frequencies are reported in wavenumbers (cm^{-1}).

Syntheses

Synthesis of Compound **2**



A Schlenk flask equipped with a magnetic stirring bar was charged with chlorophosphorane **1** (50.0 mg, 86.3 µmol, 1.00 equiv.) and NaBArF (76.5 mg, 86.3 µmol, 1.00 equiv.). DCM (2 mL) and acetone (10 µL, 0.13 mmol, 1.5 equiv.) was added and the suspension was stirred at ambient temperature for 16 h. The suspension was filtered and the residue was extracted with additional DCM (1 mL). The filtrate was dried and washed with pentane (3 × 1 mL). *Note: After adding pentane, the iminium borate tends to form an oil. For effective washing, the salt was solidified by a combination of freezing in liquid nitrogen and sonicating the salt/pentane mixture using an ultrasonic bath.* Drying of the residue *in vacuo* gave the title compound as a colorless solid (96.2 mg, 65.7 µmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.68 (m, 9H), 7.62 (tt, *J* = 8.5, 1.5 Hz, 1H), 7.58 (t, *J* = 2.0 Hz, 1H), 7.53 (s, 4H), 7.32 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.13 (t, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.84 (s, 1H), 2.67 (s, 3H), 2.54 (s, 3H), 1.44 (s, 9H), 1.19 (s, 9H), 1.19 (s, 9H), 1.16 (s, 9H).

^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 208.7, 161.9 (q, *J* = 49.8 Hz), 151.7, 148.6, 143.1 (d, *J* = 6.3 Hz), 142.2 (d, *J* = 9.5 Hz), 139.7, 136.5 (d, *J* = 9.1 Hz), 134.9, 133.6, 132.4 (d, *J* = 4.0 Hz), 131.7, 129.6, 129.4 (d, *J* = 2.1 Hz), 129.4, 129.1 (qq, *J* = 31.5, 2.9 Hz), 127.4, 125.7, 124.7 (q, *J* = 272.6 Hz), 122.3 (d, *J* = 6.5 Hz), 120.4, 119.4, 118.2 – 117.2 (m), 108.8 (d, *J* = 9.2 Hz), 36.1, 35.3, 35.2, 35.1, 31.4, 30.8, 30.2, 30.0, 28.4, 26.9.

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ –62.3.

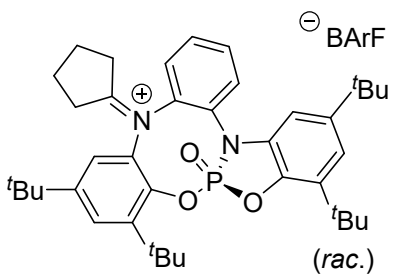
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 6.1.

IR (ATR, neat) [cm^{-1}]: 2969, 2941, 2913, 2876, 1610, 1484, 1413, 1355, 1276, 1120, 887, 839, 712, 670, 451.

HR-MS-ESI(+) calcd. for $C_{37}H_{50}N_2O_3P^+$ $[M–BArF]^+$ 601.3554; found 601.3553.

m.p. 98 °C.

Synthesis of Compound **3**



A Schlenk flask equipped with a magnetic stirring bar was charged with chlorophosphorane **1** (50.0 mg, 86.3 µmol, 1.00 equiv.) and NaBArF (76.5 mg, 86.3 µmol, 1.00 equiv.). A solution of cyclopentanone (8.0 mg, 95 µmol, 1.1 equiv.) in DCM (2 mL) was added and the suspension was stirred at ambient temperature for 16 h. The suspension was filtered and the residue was extracted with additional DCM (1 mL). The filtrate was dried and washed with pentane (4 × 2 mL). *Note: After adding pentane, the iminium borate tends to form an oil. For effective washing, the salt was solidified by a combination of freezing in liquid nitrogen and sonicating the salt/pentane mixture using an ultrasonic bath.* Drying of the residue *in vacuo* gave the title compound as a colorless solid (80.1 mg, 53.7 µmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.69 (m, 9H), 7.65 – 7.55 (m, 2H), 7.53 (s, 4H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 7.03 (s, 1H), 6.88 (s, 1H), 3.11 – 2.82 (m, 3H), 2.65 (dd, *J* = 21.2, 7.8 Hz, 1H), 2.29 – 2.10 (m, 3H), 2.06 – 1.88 (m, 1H), 1.44 (s, 9H), 1.20 (s, 18H), 1.16 (s, 9H).

^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 222.8, 161.9 (q, *J* = 49.8 Hz), 151.7, 148.6, 143.1 (d, *J* = 6.5 Hz), 141.7 (d, *J* = 9.4 Hz), 139.8, 136.4 (d, *J* = 9.1 Hz), 134.9, 133.4, 132.8, 132.0 (d, *J* = 4.1 Hz), 130.2 (d, *J* = 4.7 Hz), 129.6, 129.6 – 128.5 (m), 129.5, 129.2, 127.5, 125.1, 124.7 (q, *J* = 272.7 Hz), 122.1 (d, *J* = 6.5 Hz), 120.6, 120.4, 119.0, 117.8 – 117.4 (m), 108.9 (d, *J* = 9.1 Hz), 40.6, 38.8, 36.1, 35.3, 35.2, 35.1, 31.4, 30.8, 30.2, 29.9, 25.7, 24.9.

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ –62.3.

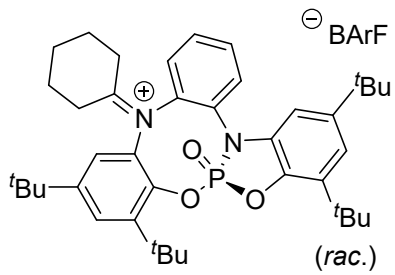
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 6.5.

IR (ATR, neat) [cm^{-1}]: 2967, 2912, 2878, 1613, 1595, 1494, 1414, 1355, 1317, 1275, 1118, 996, 920, 888, 839, 767, 713, 682, 671, 450.

HR-MS-ESI(+) calcd. for $C_{39}H_{52}N_2O_3P^+$ $[M–BArF]^+$ 627.3710; found 627.3704.

m.p. 148 °C.

Synthesis of Compound **4**



A Schlenk flask equipped with a magnetic stirring bar was charged with chlorophosphorane **1** (50.0 mg, 86.3 µmol, 1.00 equiv.) and NaBArF (76.5 mg, 86.3 µmol, 1.00 equiv.). A solution of cyclohexanone (9.3 mg, 95 µmol, 1.1 equiv.) in DCM (2 mL) was added and the suspension was stirred at ambient temperature for 16 h. The suspension was filtered and the residue was extracted with additional DCM (1 mL). The filtrate was dried and washed with pentane (4 × 2 mL). *Note: After adding pentane, the iminium borate tends to form an oil. For effective washing, the salt was solidified by a combination of freezing in liquid nitrogen and sonicating the salt/pentane mixture using an ultrasonic bath.* Drying of the residue *in vacuo* gave the title compound as a colorless solid (95.2 mg, 63.3 µmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.69 (m, 9H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.53 (s, 4H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.13 (s, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.84 (s, 1H), 3.10 – 2.94 (m, 1H), 2.85 – 2.73 (m, 2H), 2.60 – 2.50 (m, 1H), 2.32 – 2.19 (m, 1H), 2.19 – 2.08 (m, 1H), 2.07 – 1.75 (m, 3H), 1.75 –1.62 (m, 1H), 1.44 (s, 9H), 1.19 (s, 9H), 1.18 (s, 9H), 1.16 (s, 9H).

^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 214.4, 161.9 (q, *J* = 49.8 Hz), 151.5, 148.6, 143.0 (d, *J* = 6.4 Hz), 142.0 (d, *J* = 9.3 Hz), 139.8, 136.4 (d, *J* = 9.1 Hz), 134.9, 133.4, 132.5 (d, *J* = 4.1 Hz), 131.3, 129.7, 129.60 – 128.50 (m), 129.3, 129.2, 127.2, 125.9, 124.7 (q, *J* = 272.5 Hz), 122.3 (d, *J* = 6.5 Hz), 120.4, 119.8, 117.8 – 117.4 (m), 108.8 (d, *J* = 9.1 Hz), 37.0, 36.2, 36.1, 35.3, 35.2, 35.1, 31.3, 30.8, 30.2, 30.0, 27.2, 26.7, 23.3.

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ –62.3.

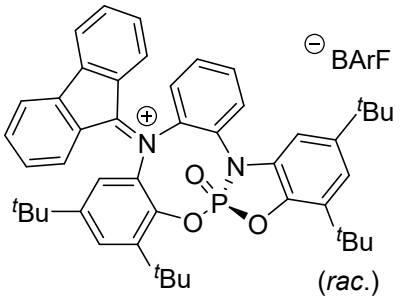
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 6.7.

IR (ATR, neat) [cm^{-1}]: 2963, 2914, 2876, 1609, 1573, 1493, 1412, 1354, 1276, 1117, 996, 922, 889, 839, 767, 713, 682, 671, 552, 450.

HR-MS-ESI(+) calcd. for $C_{40}H_{54}N_2O_3P^+$ [M–BArF]$^+$ 641.3867; found 641.3856.

m.p. 155 °C.

Synthesis of Compound **5**



A Schlenk flask equipped with a magnetic stirring bar was charged with chlorophosphorane **1** (50.0 mg, 86.3 µmol, 1.00 equiv.), NaBArF (76.5 mg, 86.3 µmol, 1.00 equiv.) and fluorenone (15.6 mg, 86.3 µmol, 1.00 equiv.). DCM (2 mL) was added and the suspension was stirred at ambient temperature for 16 h. The deep red suspension was filtered and the residue was extracted with additional DCM (1 mL). The filtrate was dried and washed with pentane (3 × 2 mL). Drying of the residue *in vacuo* gave the title compound as a red solid (126.3 mg, 79.6 µmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.68 (m, 10H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 4H), 7.46 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.12 (s, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.84 (s, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.34 (d, *J* = 8.1 Hz, 1H), 1.40 (s, 9H), 1.23 (s, 9H), 1.22 (s, 9H), 1.20 (s, 9H).

^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.0, 161.9 (q, *J* = 49.8 Hz), 152.4, 148.3, 146.7, 146.0, 143.9 (d, *J* = 6.3 Hz), 143.2 (d, *J* = 9.8 Hz), 141.2, 140.8, 139.7, 136.3 (d, *J* = 9.0 Hz), 134.9, 134.1, 133.4, 132.9 (d, *J* = 3.3 Hz), 132.4, 131.1, 131.0, 130.9, 130.9, 130.4 (d, *J* = 6.1 Hz), 129.9 (d, *J* = 17.2 Hz), 129.2, 129.7 – 128.4 (m), 128.2, 127.4, 124.7 (q, *J* = 272.5 Hz), 122.7, 122.6, 122.5, 120.3, 120.2, 117.8 – 117.4 (m), 108.6 (d, *J* = 9.3 Hz), 36.3, 35.4, 35.2, 35.1, 31.3, 30.9, 30.2, 30.0.

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ –62.4.

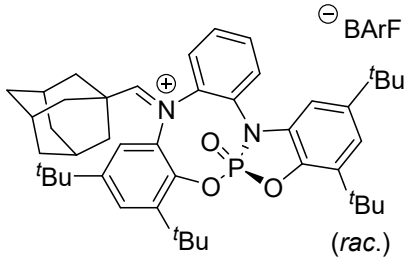
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 6.2.

IR (ATR, neat) [cm^{-1}]: 2968, 2910, 2875, 1355, 1321, 1275, 1119, 1000, 884, 839, 724, 713, 682, 668, 631.

HR-MS-ESI(+) calcd. for $C_{47}H_{52}N_2O_3P^+$ [M–BArF]$^+$ 723.3710; found 723.3700.

m.p. 235 °C (decomp.).

Synthesis of Compound **6**



A Schlenk flask equipped with a magnetic stirring bar was charged with chlorophosphorane **1** (500.0 mg, 863.3 µmol, 1.00 equiv.), NaBArF (765.1 mg, 863.3 µmol, 1.00 equiv.) and 1-adamantyl carbaldehyde (141.8 mg, 863.3 µmol, 1.00 equiv.). DCM (10 mL) was added and the suspension was stirred at ambient temperature for 16 h. The yellow suspension was filtered, and the residue was extracted with additional DCM (2 × 2 mL). The filtrate was dried and washed with pentane (3 × 5 mL). The residue was recrystallized from hot toluene (8 mL). The crystals were collected by filtration at 0 °C and washed with pentane (2 × 2 mL). Lyophilization of the residue from C_6H_6/DCM gave the title compound as a yellow solid (1.051 g, 668.9 µmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.72 (br s, 9H), 7.65 – 7.56 (m, 2H), 7.52 (s, 4H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.7 Hz, 2H), 7.12 (s, 1H), 7.04 (s, 1H), 6.87 (s, 1H), 2.05 (s, 3H), 1.81 – 1.70 (m, 9H), 1.57 (d, *J* = 12.9 Hz, 3H), 1.44 (s, 9H), 1.18 (s, 27H).

^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 200.0, 161.9 (d, *J* = 49.9 Hz), 150.7, 148.7, 142.7 (d, *J* = 8.8 Hz), 142.4 (d, *J* = 6.7 Hz), 139.9, 137.2 (d, *J* = 1.4 Hz), 136.4 (d, *J* = 9.2 Hz), 134.9, 134.1, 131.0 (d, *J* = 4.5 Hz), 129.6, 129.4, 129.0 (qq, *J* = 31.3, 2.9 Hz), 127.9, 127.6 (d, *J* = 4.6 Hz), 126.4, 124.7 (q, *J* = 272.6 Hz), 121.9 (d, *J* = 6.5 Hz), 121.0, 120.4, 118.0 – 117.2 (m), 108.5 (d, *J* = 9.2 Hz), 45.9, 37.4, 35.9, 31.3, 30.8, 30.0, 30.0, 26.6.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ –62.3.

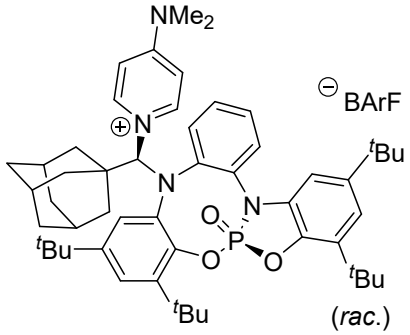
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 6.1.

IR (ATR, neat) [cm^{-1}]: 2972, 2912, 2875, 2862, 1606, 1579, 1494, 1354, 1274, 1114, 994, 885, 839, 729, 713, 682, 667, 630.

HR-MS-ESI(+) calcd. for $C_{45}H_{60}N_2O_3P^+$ $[M–BArF]^+$ 707.4336; found 707.4301.

m.p. 158 °C (decomp.).

Synthesis of Compound **7**



A Schlenk flask equipped with a magnetic stirring bar was charged with iminium borate **6** (50.0 mg, 31.8 µmol, 1.00 equiv.) and DCM (1.5 mL) was added. A solution of 4-DMAP (3.9 mg, 32 µmol, 1.0 equiv.) in DCM (0.5 mL) was slowly added at –78 °C. The solution immediately decolorized, and the cooling bath was removed. The reaction mixture was stirred for an additional 30 min at ambient temperature before the solvent was removed under reduced pressure and the residue washed with pentane (3 × 1 mL). Crystallization from $CHCl_3$/pentane provided the title compound as a colorless solid (18.2 mg, 10.8 µmol, 34%, *d.r.* 91:9).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.90 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.91 (d, *J* = 6.7 Hz, 1H), 7.73 (s, 8H), 7.57 (s, 4H), 7.39 – 7.28 (m, 2H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.14 – 7.07 (m, 1H), 7.06 – 7.00 (m, 2H), 6.96 (s, 1H), 6.65 (s, 1H), 6.63 (s, 1H), 6.52 (d, *J* = 0.9 Hz, 1H), 5.47 (s, 1H),

3.14 (s, 3H), 3.12 (s, 3H), 1.87 – 1.81 (m, 3H), 1.57 (d, *J* = 12.6 Hz, 3H), 1.45 (s, 9H), 1.43 – 1.31 (m, 9H), 1.21 (s, 9H), 1.20 (s, 9H), 1.10 (s, 9H).

^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 162.3 (q, *J* = 49.9 Hz), 157.0 149.2, 147.5 (d, *J* = 9.2 Hz), 147.0, 143.4, 143.0, 141.7 (d, *J* = 6.6 Hz), 141.1, 139.9, 135.4, 135.1 (d, *J* = 8.4 Hz), 134.5 (d, *J* = 5.6 Hz), 133.3 (d, *J* = 4.4 Hz), 131.9 (d, *J* = 19.0 Hz), 129.4 (qd, *J* = 31.0, 3.1 Hz), 125.9 (d, *J* = 7.6 Hz), 125.7, 125.2 (q, *J* = 272.4 Hz), 124.5, 123.1 (d, *J* = 7.5 Hz), 121.5, 118.7, 118.1 (p, *J* = 4.2 Hz), 107.8, 107.8, 106.4, 92.4, 41.6, 40.8, 40.6, 39.6, 36.4, 36.0, 35.3, 35.3, 35.2, 31.5, 31.3, 31.1, 30.5, 28.9.

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): δ –62.3.

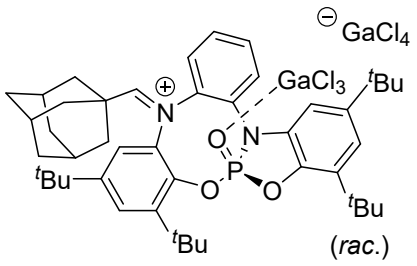
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 10.3.

IR (ATR, neat) [cm^{-1}]: 2960, 2934, 2909, 2874, 2857, 1650, 1574, 1354, 1119, 995, 885, 839, 713, 681.

HR-MS-ESI(+) calcd. for $C_{52}H_{70}N_4O_3P^+$ [M–BArF]$^+$ 829.5180; found 829.5177.

m.p. 99 °C (decomp.).

Synthesis of Compound **8**



In a Schlenk flask equipped with a magnetic stirring bar, iminium borate **6** (50.0 mg, 31.8 µmol, 1.00 equiv.) was dissolved in toluene (1 mL) and $GaCl_3$ (16.8 mg, 95.5 µmol, 3.00 equiv.) in toluene (1 mL) was added *via* syringe. The deep orange reaction mixture was stirred for 1 h at ambient temperature and filtered afterwards. The residue was extracted with toluene (0.5 mL) and the filtrate layered with pentane. Storing this solution at –20 °C yielded crystalline material which was collected by filtration. The collected crystals were redissolved in $CHCl_3$ and crystallized by pentane vapor diffusion. Drying of the thus obtained crystals yielded the title compound as an orange solid (15.9 mg, 14.5 µmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.71 – 7.60 (m, 2H), 7.20 (s, 1H), 6.94 (s, 1H), 2.09 (s, 3H), 1.90 – 1.71 (m, 9H), 1.64 (d, *J* = 12.8 Hz, 3H), 1.43 (s, 9H), 1.32 (s, 9H), 1.31 (s, 9H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 200.3, 153.2, 150.1, 141.7 (d, *J* = 14.0 Hz), 141.7, 139.6 (d, *J* = 3.2 Hz), 137.0 (d, *J* = 1.4 Hz), 136.9 (d, *J* = 9.7 Hz), 134.6, 131.4, 129.5, 129.1, 128.9, 128.5 (d, *J* = 4.6 Hz), 127.3 (d, *J* = 3.1 Hz), 123.9, 122.9 (d, *J* = 6.8 Hz), 121.3, 109.4 (d, *J* = 10.1 Hz), 46.5, 37.3, 36.0, 35.8, 35.6, 35.2 (*superposition of two signals*), 31.4, 31.2, 30.6, 30.1, 26.6.

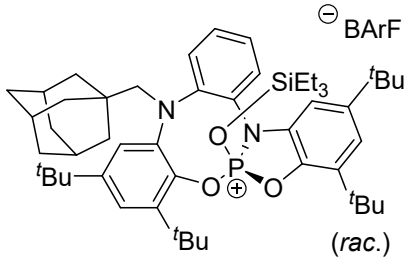
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 12.7.

IR (ATR, neat) [cm^{-1}]: 2960, 2932, 2929, 2870, 2858, 1589, 1493, 1411, 1296, 1279, 1130, 995, 922, 738, 629.

HR-MS-ESI(+) calcd. for $C_{45}H_{60}N_2O_3P^+$ [M–Ga_2Cl_7]$^+$ 707.4336; found 707.4345.

m.p. 123 °C (decomp.).

Synthesis of Compound **9**



A Schlenk flask equipped with a magnetic stirring bar was charged with iminium borate **6** (250.0 mg, 159.1 µmol, 1.00 equiv.) and DCM (10 mL) was added. Triethyl silane (92.5 mg, 796 µmol, 5.00 equiv.) was added and the suspension was stirred at ambient temperature for 16 h. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 2 mL). Lyophilization from C_6H_6 gave the title compound as a colorless solid (207.5 mg, 123.0 µmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.5 Hz, 1H), 7.72 (s, 8H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.52 (s, 4H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.31 – 7.27 (m, 2H), 7.24 (s, 1H), 7.21 (s, 1H), 3.66 (dd, *J* = 13.4, 7.4 Hz, 1H), 3.25 (d, *J* = 13.4 Hz, 1H), 1.87 (s, 3H), 1.65 (d, *J* = 12.4 Hz, 4H), 1.49 (s, 9H), 1.47 – 1.34 (m, 6H), 1.30 (s, 9H), 1.24 (s, 18H), 1.18 (d, *J* = 12.2 Hz, 3H), 0.86 (s, 15H).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ –6.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.9 (q, *J* = 49.9 Hz), 150.0, 147.2, 142.2 (d, *J* = 4.2 Hz), 138.7 (d, *J* = 2.9 Hz), 138.3 (d, *J* = 11.5 Hz), 135.2 (d, *J* = 8.6 Hz), 135.0, 134.0 (d, *J* = 5.4 Hz), 132.2 (d, *J* = 12.1 Hz), 131.8 (d, *J* = 9.9 Hz), 130.6, 129.0 (qq, *J* = 31.6, 2.8 Hz), 126.4 (d, *J* = 21.4 Hz), 125.6, 125.6, 124.7 (q, *J* = 272.5 Hz), 122.1, 120.4, 118.2 (d, *J* = 3.3 Hz), 117.6 (hept, *J* = 4.3, 3.8 Hz), 114.5 (d, *J* = 11.4 Hz), 108.9 (d, *J* = 13.3 Hz), 71.2, 41.8, 36.2, 36.0, 35.3, 35.3, 35.1, 34.9, 31.5, 31.1, 30.1, 29.6, 28.2, 5.8, 5.2 (d, *J* = 2.0 Hz).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ –62.4.

^{29}Si{^{1}H}-INEPT NMR (80 MHz, $CDCl_3$): δ 41.03 (d, *J* = 18.5 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ –7.9.

IR (ATR, neat) [cm^{-1}]: 2964, 2938, 2910, 2881, 2855, 1610, 1495, 1485, 1420, 1353, 1274, 1119, 999, 839, 743, 712, 681, 669.

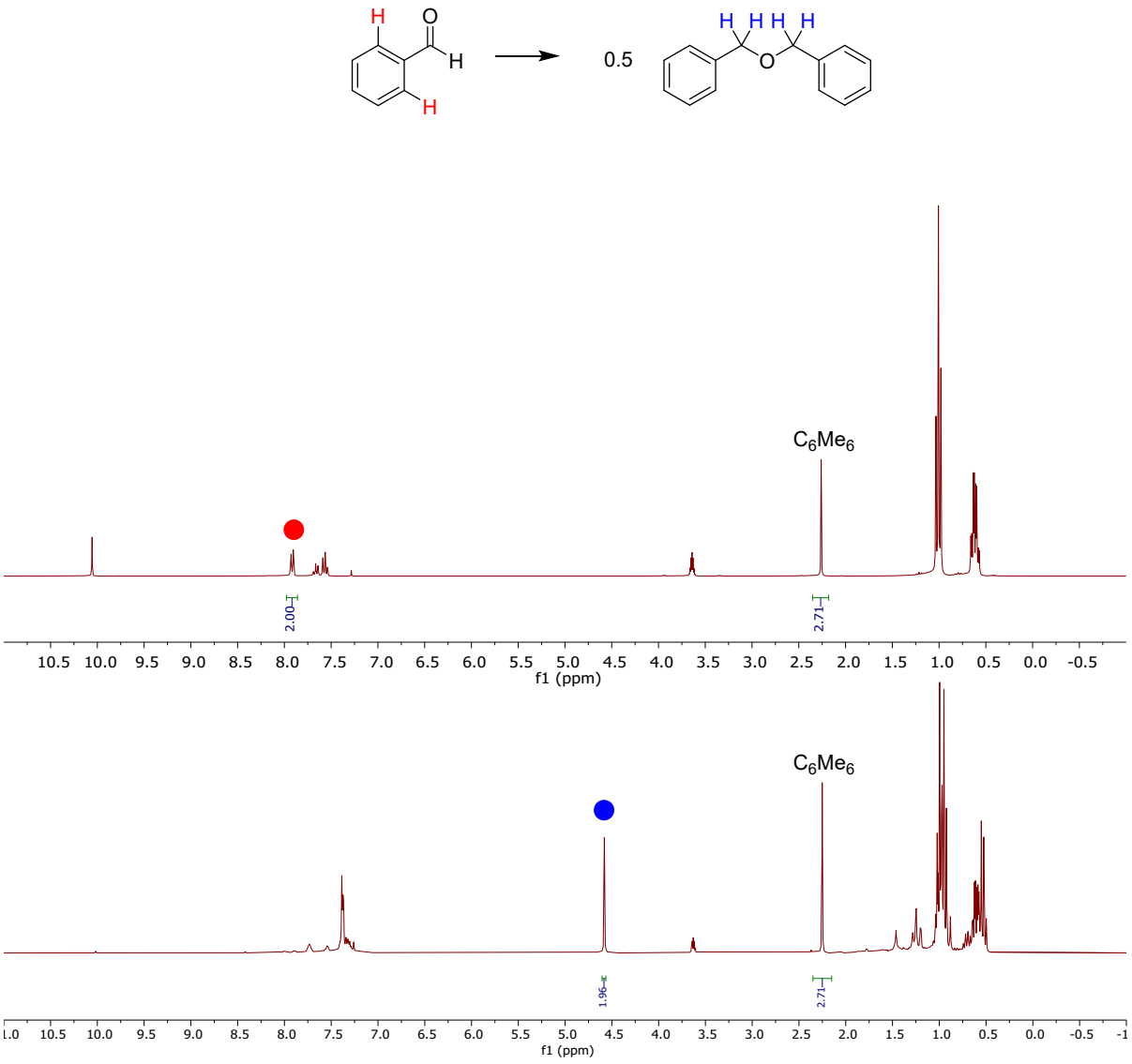
HR-MS-ESI(+) calcd. for $C_{51}H_{76}N_2O_3PSi^+$ $[M–BArF]^+$ 823.5357; found 823.5326.

m.p. 64 °C (decomp.).

Reductive Etherification of Aldehydes and Ketones

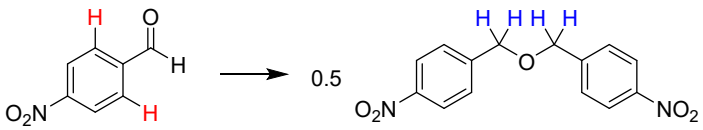
Representative Procedure: Reductive Etherification of Benzaldehyde

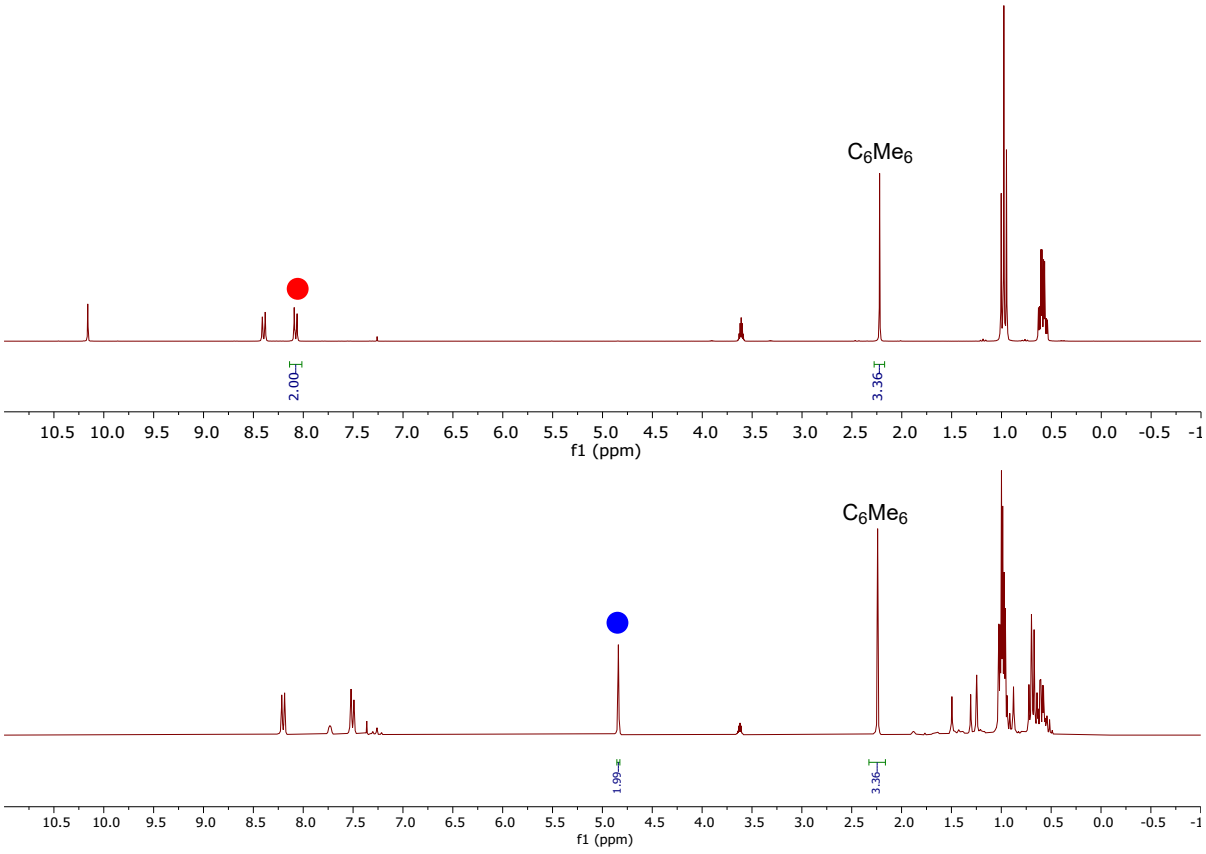
Inside a nitrogen-filled glovebox, a Young-NMR tube was charged with a solution of benzaldehyde (10.6 mg, 100 µmol, 1.00 equiv.), triethyl silane (23.2 mg, 200 µmol, 2.00 equiv.) and hexamethylbenzene (internal standard) in $CDCl_3$ (0.5 mL). An ^1H NMR spectrum was recorded and **6** (15.7 mg, 10.0 µmol, 10.0 mol-%) was added inside the glovebox. After 2.5 h of reaction time, ^1H NMR analysis evidenced the formation of dibenzyl ether in a spectroscopic yield of 98%. The compound was identified by comparison to its literature reported ^1H NMR spectrum.[4]



Reductive Etherification of 4-Nitrobenzaldehyde

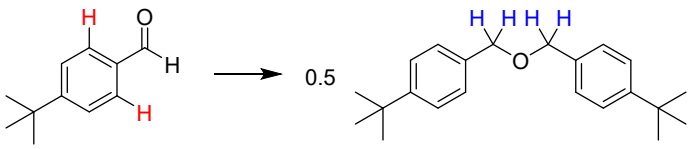
Performed according to the representative procedure using 4-nitrobenzaldehyde (15.1 mg, 100 µmol). Reaction time: 24 h. Yield: 99%. The compound was identified by comparison to its literature reported ^{1}H NMR spectrum.[5]

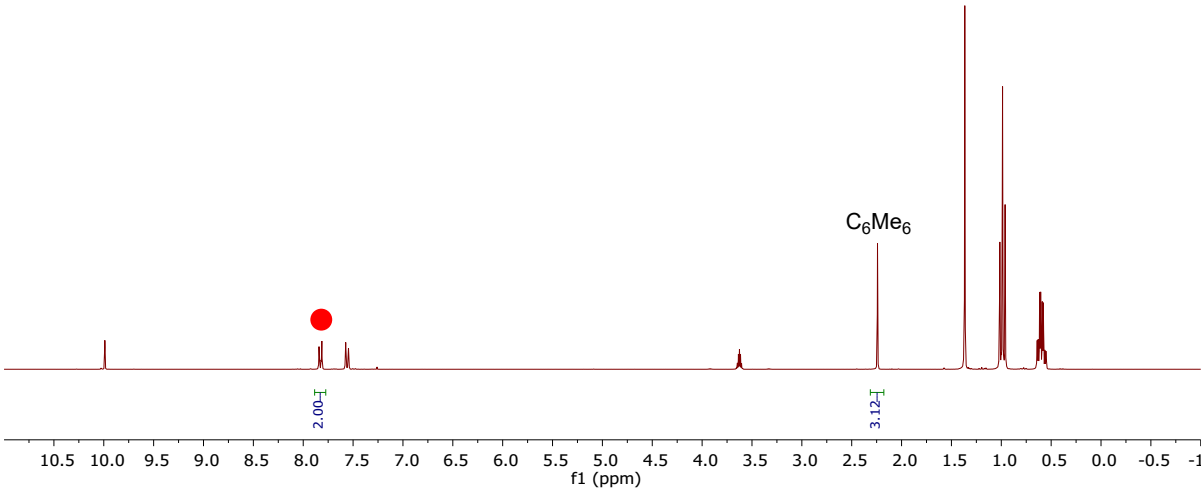


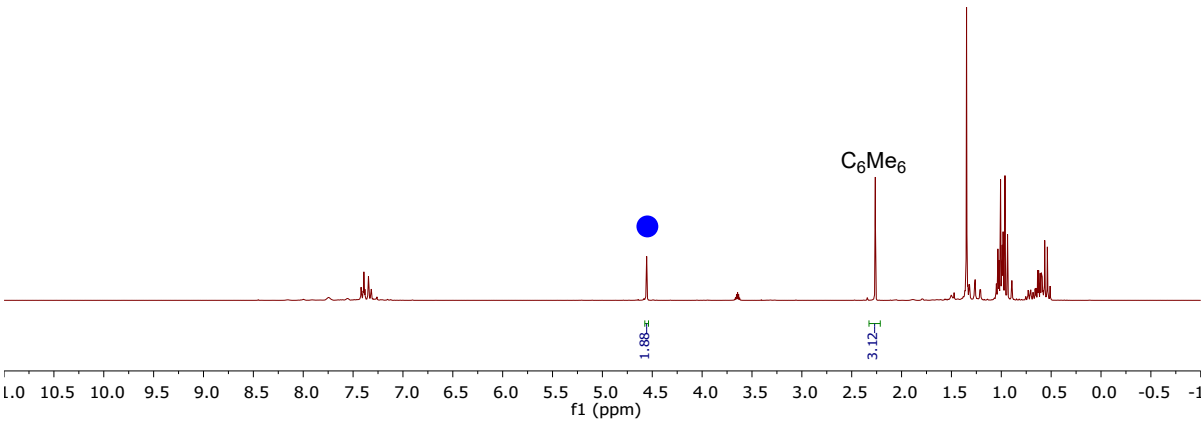


Reductive Etherification of 4-*tert*-Butylbenzaldehyde

Performed according to the representative procedure using 4-*tert*-butylbenzaldehyde (16.2 mg, 100 µmol). Reaction time: 2.5 h. Yield: 94%. The compound was identified by comparison to its literature reported ^{1}H NMR spectrum.[6]

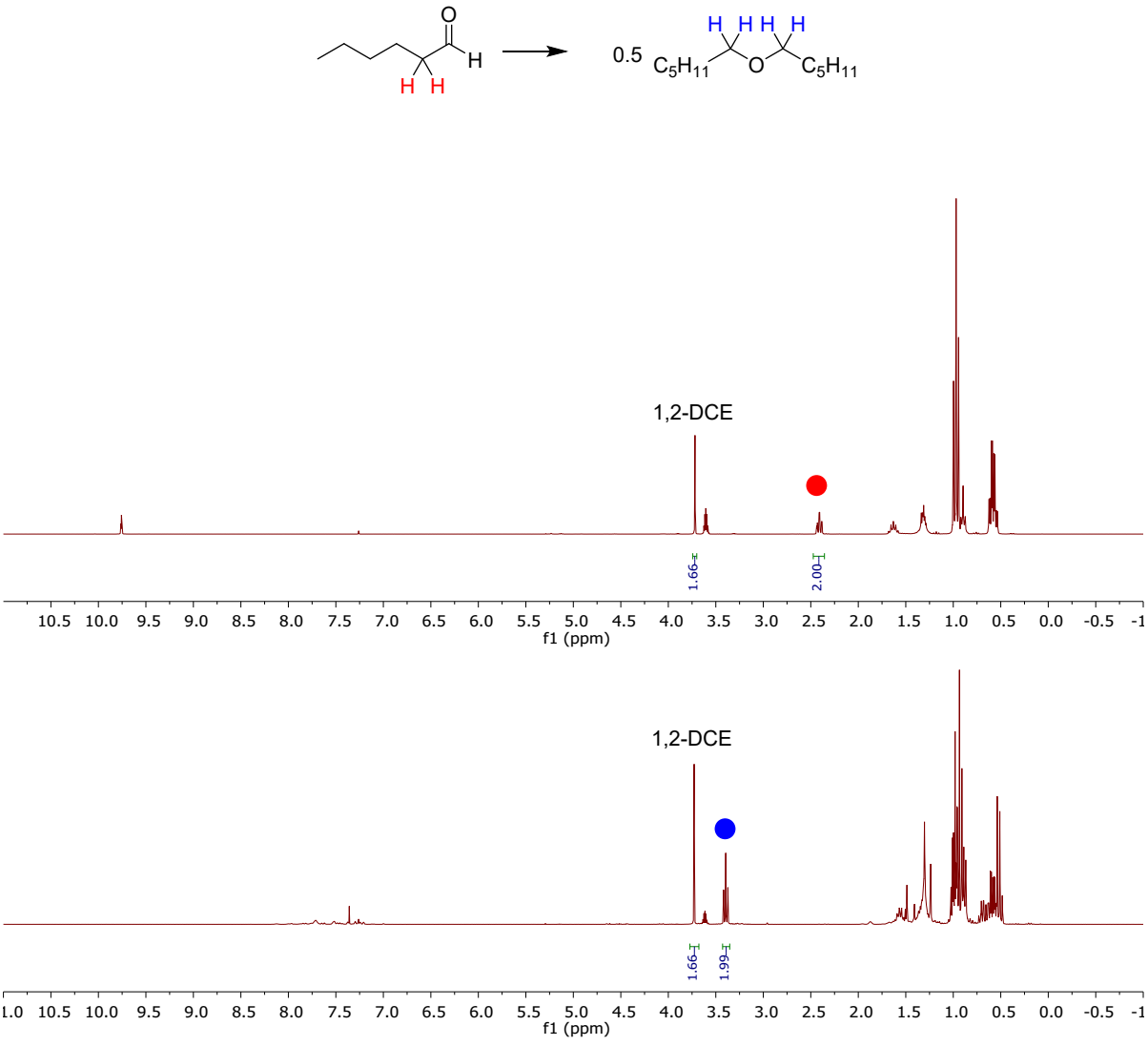






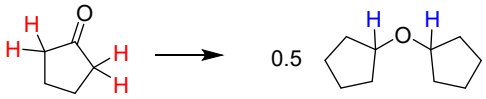
Reductive Etherification of Hexanal

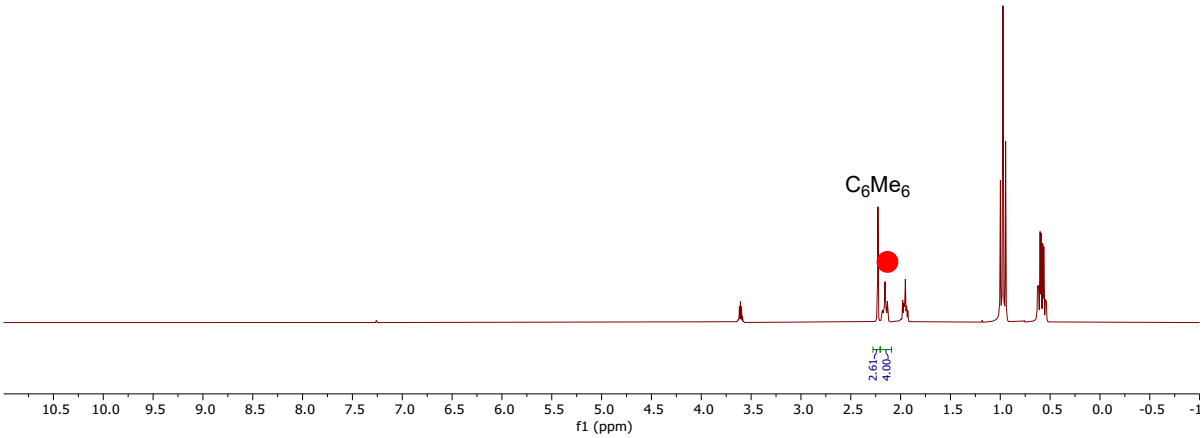
Performed according to the representative procedure using hexanal (10.0 mg, 100 µmol) and 1,2-dichloroethane instead of hexamethylbenzene as the internal standard. Reaction time: 2.5 h. Yield: 99%. The compound was identified by comparison to its literature reported ^{1}H NMR spectrum.[4]

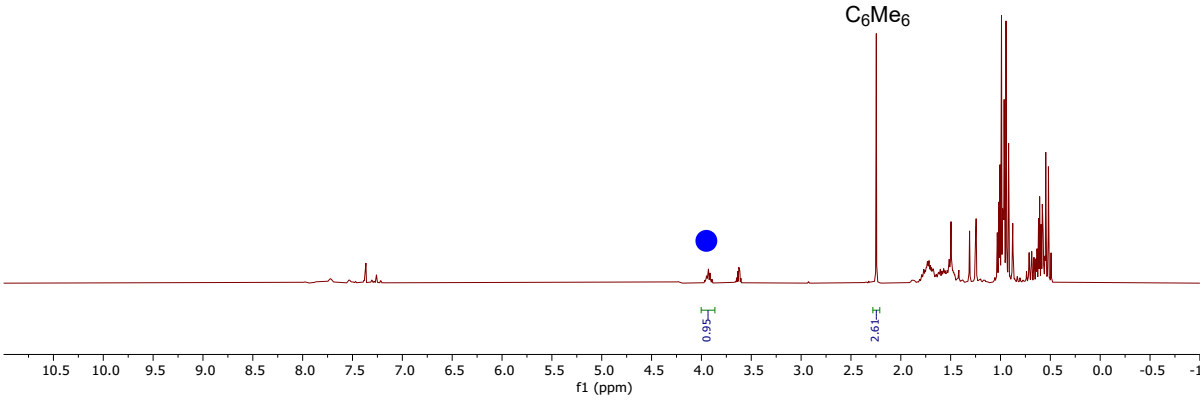


Reductive Etherification of Cyclopentanone

Performed according to the representative procedure using cyclopentanone (8.4 mg, 0.10 mmol). Reaction time: 2.5 h. Yield: 95%. The compound was identified by comparison to its literature reported ^{1}H NMR spectrum.[4]







Single crystal X-ray diffraction analysis

General Information

Data collection was done on two dual source equipped *Bruker D8 Venture* four-circle-diffractometer from *Bruker AXS GmbH*; used X-ray sources: microfocus *IμS 2.0* Cu/Mo and microfocus *IμS 3.0* Ag/Mo from *Incoatec GmbH* with mirror optics *HELIOS* and single-hole collimator from *Bruker AXS GmbH;* used detector: *Photon III CE14* (Cu/Mo) and *Photon III HE* (Ag/Mo) from *Bruker AXS GmbH*.

Used programs: *APEX4 Suite* (v2022.1-1) for data collection and therein integrated programs *SAINT* V8.40A (Integration) und *SADABS* 2016/2 (Absorption correction) from *Bruker AXS GmbH*; structure solution was done with *SHELXT*, refinement with *SHELXL*-2018/3;[7] OLEX^2 and FinalCif were used for data finalization.[8]

Special Utilities: *SMZ1270* stereomicroscope from *Nikon Metrology GmbH* was used for sample preparation; crystals were mounted on *MicroMounts* or *MicroLoops* from *MiTeGen* in NVH oil; crystals were cooled to given temperature with *Cryostream 800* from *Oxford Cryosystems.*

The crystallization conditions are individually stated for each compound. The solvent vapor diffusion method refers to the methodology described in the literature.[9]

This supplement contains in the following the refinement details tables, a figure of the complete asymmetric unit and a picture of the crystal used for data collection. Further details can be obtained from the crystallographic information files (CIFs) uploaded to the *Cambridge Crystallographic Data Centre* (CCDC), where they can be obtained free of charge.

Identifier	CCDC number	Identifier	CCDC number
2	2353322	**6**	2353326
3	2353323	**7**	2353327
4	2353324	**8**	2353328
5	2353325	**9**	2353329

Refinement details

Compound **2**

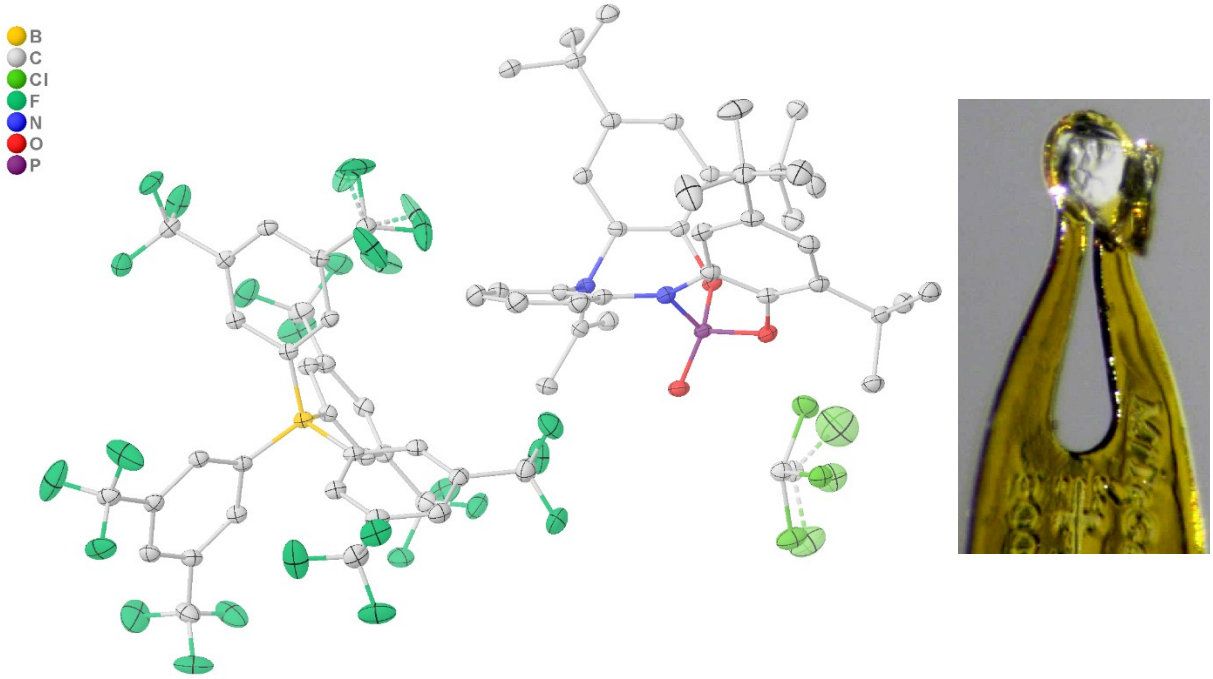


Figure S 1: Asymmetric unit of **2**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. One CF_3 group of the BArF anion exhibits rotational disorder (occupancy 0.503:0.497), the co-crystalized chloroform positional disorder (occupancy 0.92:0.08). Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained from chloroform by slow evaporation.

CCDC number	2353322
Empirical formula	$C_{70}H_{63}BCl_3F_{24}N_2O_3P$
Formula weight	1584.35
Temperature [K]	100.00
Crystal system	Triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	12.6492(9)
b [Å]	13.6605(10)
c [Å]	21.8343(14)
α [°]	81.400(2)
β [°]	78.136(2)
γ [°]	78.970(2)

Volume [Å^3]	3600.1(4)
Z	2
ρ_{calc} [gcm^{-3}]	1.462
μ [mm^{-1}]	0.259
F(000)	1616
Crystal size [mm^3]	0.3×0.287×0.132
Crystal color	Colorless
Crystal shape	Block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.84 to 57.48 (0.74 Å)
Index ranges	−17 ≤ h ≤ 16 −18 ≤ k ≤ 18 −29 ≤ l ≤ 29
Reflections	91367

collected	
Independent reflections	18627 R_{int} = 0.0369 R_{sigma} = 0.0283
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	18627/108/1016

Goodness-of-fit on F^2	1.034
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0461 wR_2 = 0.1145
Final R indexes [all data]	R_1 = 0.0574 wR_2 = 0.1227
Largest peak/hole [eÅ^{-3}]	0.74/-0.48

Compound **3**

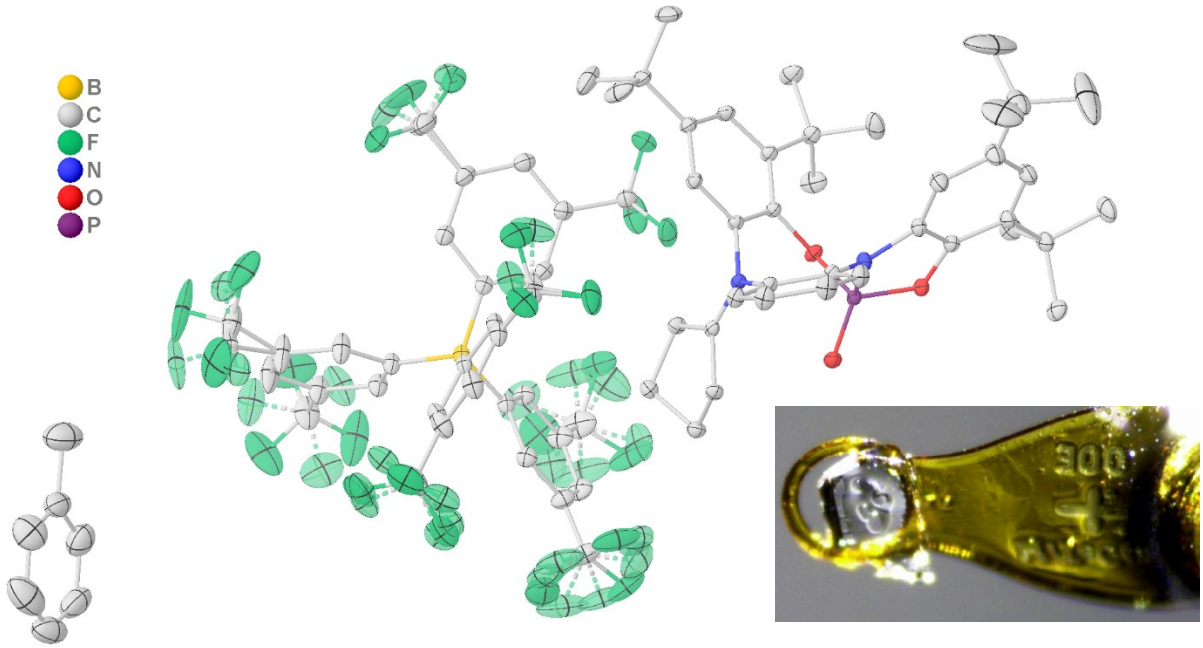


Figure S 2 Asymmetric unit of **3**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Seven CF_3 groups of the BArF anion exhibit rotational disorder in various degrees that were modelled over two or three positions (occupancies: 0.764:0.236, 0.534:0.466; 0.446:0.246:0.308, 0.585:0.240:0.176, 0.420:0.351:0.229; the remining two are refined with occupancies constrained to 0.5:0.5). The co-crystalized toluene is located on a symmetry center. Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained by solvent vapor diffusion method using toluene and pentane.

CCDC number	2353323
Empirical formula	$C_{149}H_{136}B_2F_{48}N_4O_6P_2$
Formula weight	3074.17
Temperature [K]	100.00
Crystal system	Triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	13.6399(13)
b [Å]	16.8477(13)
c [Å]	19.2953(16)
α [°]	115.857(3)
β [°]	102.316(2)
γ [°]	98.273(2)

Volume [Å^3]	3754.1(6)
Z	1
ρ_{calc} [gcm^{-3}]	1.360
μ [mm^{-1}]	0.143
F(000)	1578
Crystal size [mm^3]	0.418×0.271×0.084
Crystal color	Colorless
Crystal shape	Plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.15 to 63.18 (0.68 Å)
Index ranges	−20 ≤ h ≤ 20 −24 ≤ k ≤ 24 −28 ≤ l ≤ 28

Reflections collected	150191
Independent reflections	25097 R_{int} = 0.0373 R_{sigma} = 0.0234
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	25097/464/1285

Goodness-of-fit on F^2	1.047
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0531 wR_2 = 0.1336
Final R indexes [all data]	R_1 = 0.0683 wR_2 = 0.1474
Largest peak/hole [eÅ^{-3}]	0.73/-0.77

Compound **4**

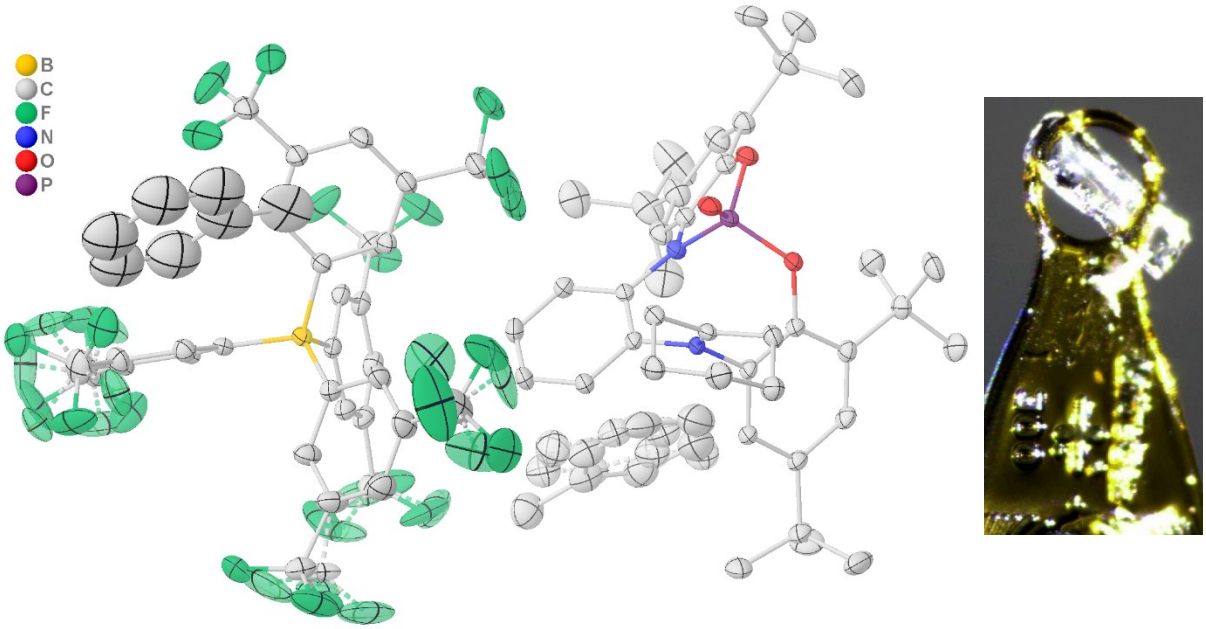


Figure S 3: Asymmetric unit of **4**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Six CF_3 groups of the BArF anion exhibit rotational disorder in various degrees that were modelled over two positions (occupancies: 0.679:0.321, 0.679:0.321, 0.621:0.379, 0.607:0.393, 0.599:0.401, 0.572:0.428). The two molecules of co-crystalized toluene are located each on a symmetry center and both exhibit positional disorder (occupancy for the first one: 0.345:0.155). However, for one toluene no satisfactory second position could be modelled and due to refinement instability, the occupancy was fixed at a value of 0.380 because it produced the best agreement indices. A mixed position disorder with other solvent molecules were considered but could not be discerned. Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained by solvent vapor diffusion method using toluene and pentane.

CCDC number	2353324
Empirical formula	$C_{79}H_{74}BF_{24}N_2O_3P$
Formula weight	1597.18
Temperature [K]	100.00
Crystal system	Triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	13.9743(17)
b [Å]	16.814(2)
c [Å]	19.335(3)
α [°]	115.292(3)

β [°]	106.112(3)
γ [°]	94.371(4)
Volume [Å^3]	3845.6(9)
Z	2
ρ_{calc} [gcm^{-3}]	1.379
μ [mm^{-1}]	0.143
F(000)	1644
Crystal size [mm^3]	0.527×0.166×0.1
Crystal color	Colorless
Crystal shape	Needle
Radiation	MoK_α (λ=0.71073 Å)

2θ range [°]	3.94 to 58.41 (0.73 Å)
Index ranges	−19 ≤ h ≤ 18 −23 ≤ k ≤ 23 −26 ≤ l ≤ 26
Reflections collected	197941
Independent reflections	20799 R_{int} = 0.0412 R_{sigma} = 0.0208
Completeness to	100.0 %

θ = 25.242°	
Data / Restraints / Parameters	20799/662/1295
Goodness-of-fit on F^2	1.018
Final R indexes [I≥2σ(I)]	R_1 = 0.0543 wR_2 = 0.1369
Final R indexes [all data]	R_1 = 0.0691 wR_2 = 0.1494
Largest peak/hole [eÅ^{-3}]	1.60/-0.59

Compound **5**

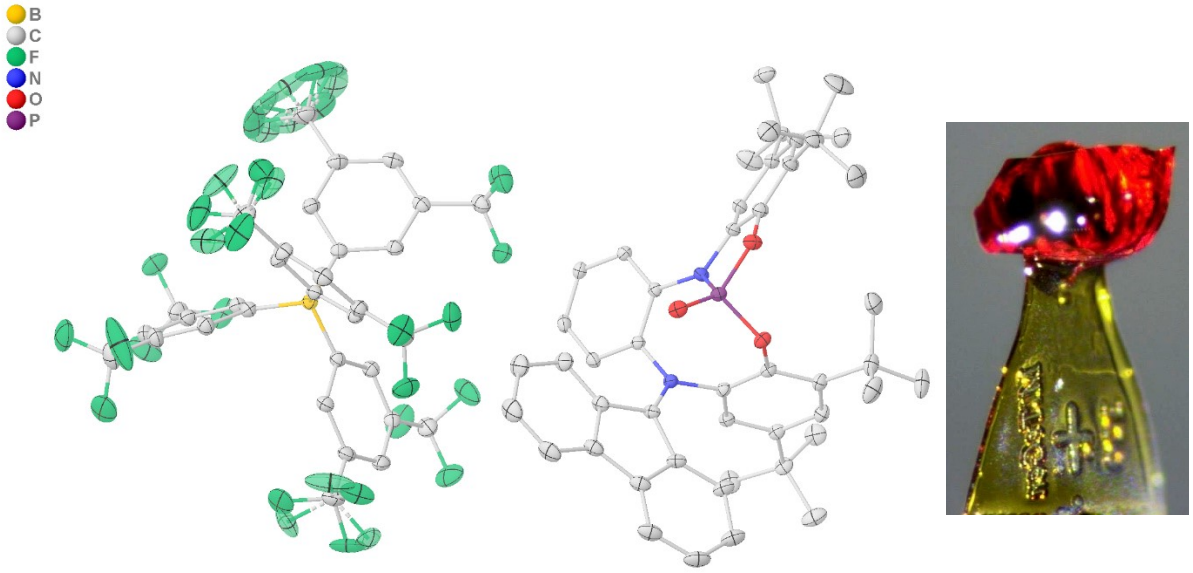


Figure S 4: Asymmetric unit of **5**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Three CF_3 groups of the BArF anion exhibit rotational disorder of which one was split on three positions (occupancies: 0.815:0.185, 0.695:0.305, 0.368:0.358:0.275). Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained from DCM/toluene by slow evaporation.

CCDC number	2353325
Empirical formula	$C_{79}H_{64}BF_{24}N_2O_3P$
Formula weight	1587.10
Temperature [K]	100.00
Crystal system	Monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	12.3660(8)
b [Å]	20.9073(15)
c [Å]	29.743(2)
α [°]	90
β [°]	97.228(2)
γ [°]	90
Volume [Å^3]	7628.7(9)
Z	4

ρ_{calc} [gcm^{-3}]	1.382
μ [mm^{-1}]	0.144
F(000)	3248
Crystal size [mm^3]	0.626×0.574×0.328
Crystal color	Red
Crystal shape	Block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.85 to 63.11 (0.68 Å)
Index ranges	−18 ≤ h ≤ 14 −30 ≤ k ≤ 30 −43 ≤ l ≤ 43
Reflections collected	173402
Independent reflections	25477 R_{int} = 0.0324 R_{sigma} = 0.0199
Completeness to	100.0 %

θ = 25.242°	
Data / Restraints / Parameters	25477/47/1116
Goodness-of-fit on F^2	1.022

Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0434 wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.0560 wR_2 = 0.1199
Largest peak/hole [eÅ^{-3}]	0.48/-0.56

Compound **6**

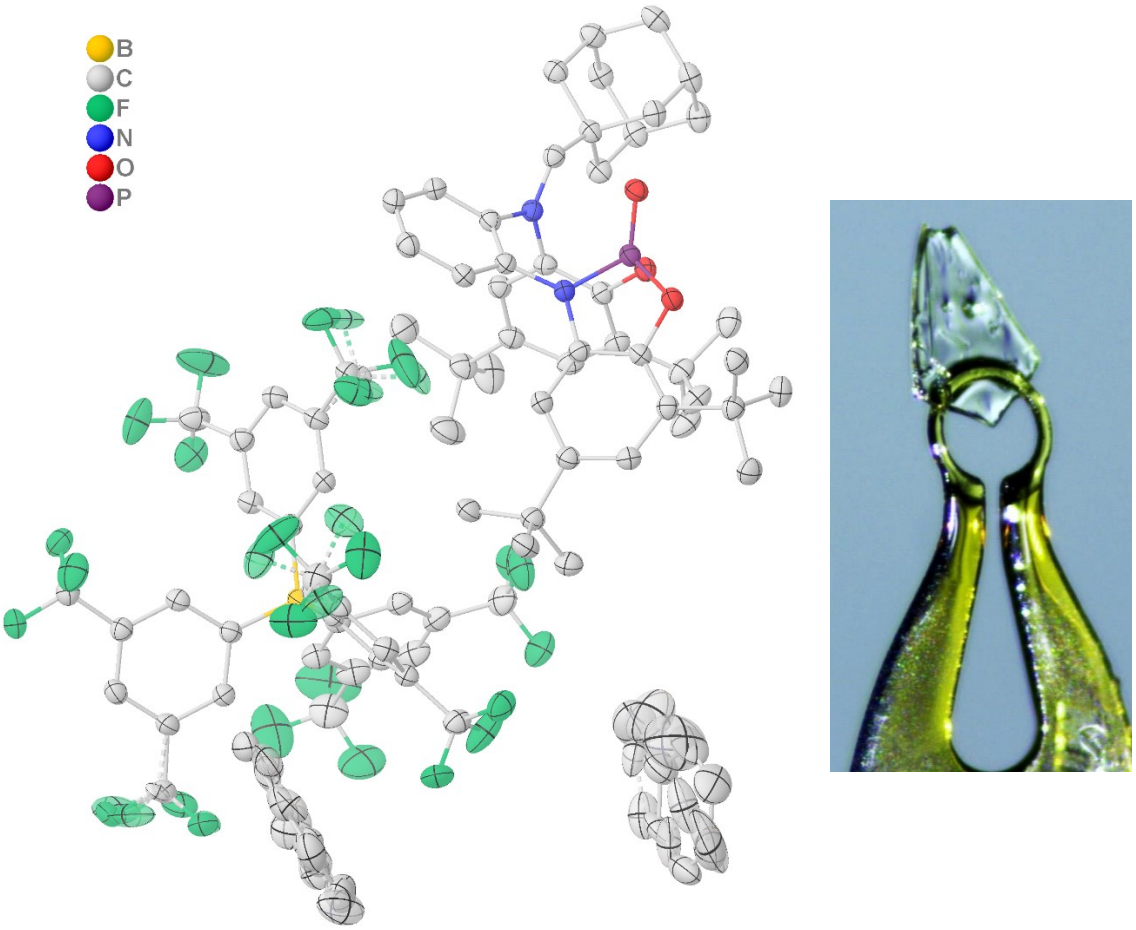


Figure S 5: Asymmetric unit of **6**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Three CF_3 groups of the BArF anion exhibit rotational disorder in various degrees that were modelled over two positions (occupancies: 0.90:0.10, 0.78:0.22, 0.68:0.32). The two molecules of co-crystalized toluene both exhibit positional disorder (occupancies: 0.81:0.19, 0.71:0.29). Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained from warm toluene by slow cooling.

CCDC number	2353326
Empirical formula	$C_{91}H_{88}BF_{24}N_2O_3P$
Formula weight	1755.41
Temperature [K]	100.00
Crystal system	Monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	13.9705(8)
b [Å]	31.6393(19)

c [Å]	19.2626(12)
α [°]	90
β [°]	93.898(2)
γ [°]	90
Volume [Å^3]	8494.7(9)
Z	4
ρ_{calc} [gcm^{-3}]	1.373
μ [mm^{-1}]	0.136
F(000)	3632

Crystal size [mm^3]	0.458×0.277×0.03
Crystal color	Colorless
Crystal shape	Plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.89 to 55.01 (0.77 Å)
Index ranges	−18 ≤ h ≤ 18 −41 ≤ k ≤ 41 −24 ≤ l ≤ 24
Reflections collected	200748
Independent reflections	19461 R_{int} = 0.0620 R_{sigma} = 0.0332

Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	19461/446/1354
Absorption correction T_{min}/T_{max} (method)	0.9302/1.0000 (numerical)
Goodness-of-fit on F^2	1.092
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0613 wR_2 = 0.1155
Final R indexes [all data]	R_1 = 0.0776 wR_2 = 0.1228
Largest peak/hole [$eÅ^{-3}$]	0.44/−0.37

Compound **7**

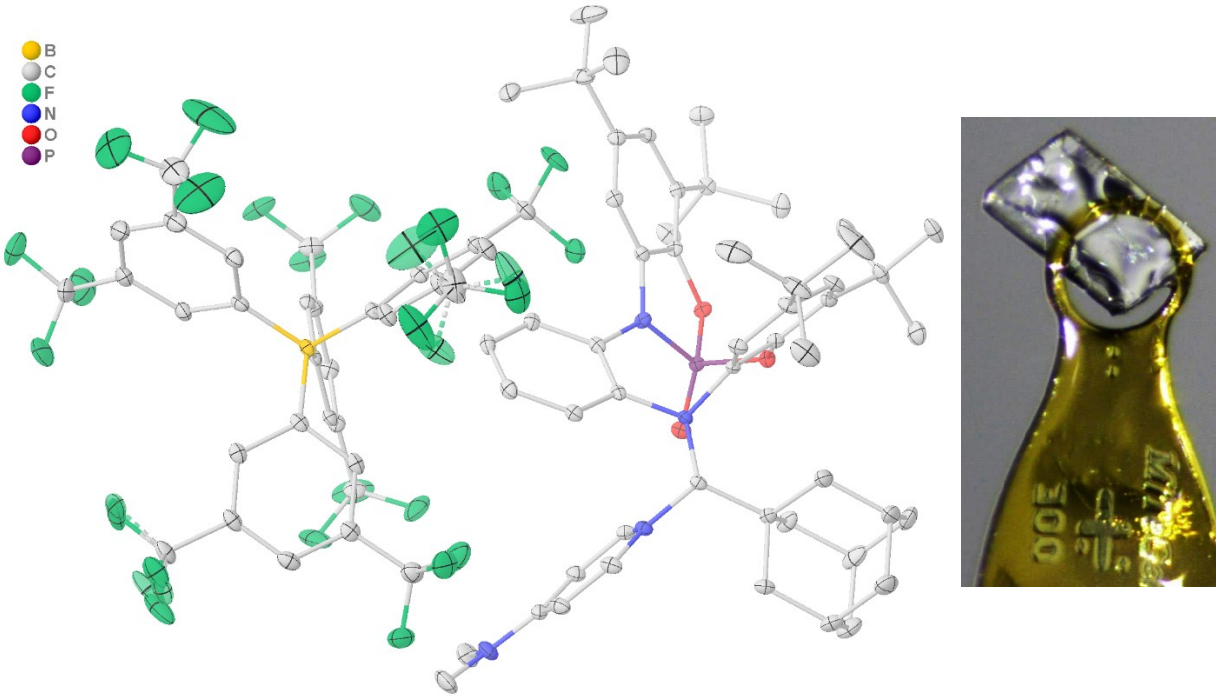


Figure S 6: Asymmetric unit of **7**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Two CF_3 groups of the BArF anion exhibit rotational disorder in various degrees that were modelled over two positions (occupancies: 0.686:0.314, 0.593:0.407). Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained by solvent vapor diffusion method using chloroform and pentane.

CCDC number	2353327
Empirical formula	$C_{86}H_{85}BF_{24}N_5O_3P$
Formula weight	1734.36
Temperature [K]	100.00
Crystal system	Triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	12.1449(17)
b [Å]	18.623(3)
c [Å]	20.405(3)
α [°]	70.624(3)
β [°]	73.911(4)
γ [°]	75.970(4)

Volume [Å^3]	4125.2(10)
Z	2
ρ_{calc} [gcm^{-3}]	1.396
μ [mm^{-1}]	0.140
F(000)	1792
Crystal size [mm^3]	0.578×0.29×0.05
Crystal color	Colorless
Crystal shape	Plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.91 to 57.77 (0.74 Å)
Index ranges	−16 ≤ h ≤ 16 −24 ≤ k ≤ 25 −27 ≤ l ≤ 27

Reflections collected	89259
Independent reflections	21505 R_{int} = 0.0523 R_{sigma} = 0.0469
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	21505/127/1133

Goodness-of-fit on F^2	1.087
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0576 wR_2 = 0.1441
Final R indexes [all data]	R_1 = 0.0766 wR_2 = 0.1551
Largest peak/hole [eÅ^{-3}]	0.76/-0.61

Compound **8**

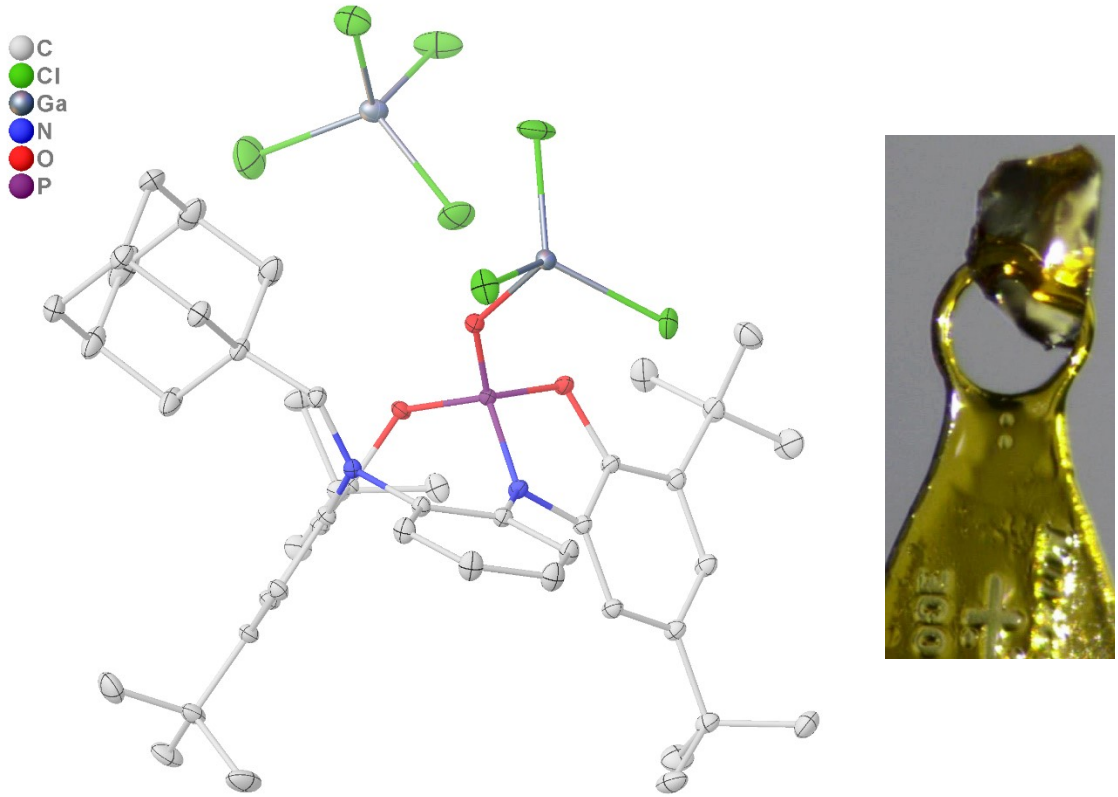


Figure S 7: Asymmetric unit of **8**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Single crystals were obtained by solvent vapor diffusion method using toluene and pentane.

CCDC number	2353328
Empirical formula	$C_{45}H_{60}Cl_7Ga_2N_2O_3P$
Formula weight	1095.51
Temperature [K]	100.00
Crystal system	Monoclinic
Space group (number)	Cc (9)
a [Å]	20.9640(7)
b [Å]	12.2176(3)
c [Å]	20.1457(7)
α [°]	90
β [°]	93.7430(10)
γ [°]	90

Volume [Å^3]	5148.9(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.413
μ [mm^{-1}]	1.480
F(000)	2256
Crystal size [mm^3]	0.464×0.255×0.254
Crystal color	Yellow
Crystal shape	Block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.86 to 69.62 (0.62 Å)
Index ranges	−33 ≤ h ≤ 33 −19 ≤ k ≤ 19 −32 ≤ l ≤ 32

Reflections collected	149799
Independent reflections	20805 R_{int} = 0.0397 R_{sigma} = 0.0218
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	20805/2/553

Goodness-of-fit on F^2	1.027
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0224 wR_2 = 0.0580
Final R indexes [all data]	R_1 = 0.0231 wR_2 = 0.0583
Largest peak/hole [eÅ^{-3}]	0.56/-0.48
Flack X parameter	0.006(2)

Compound **9**

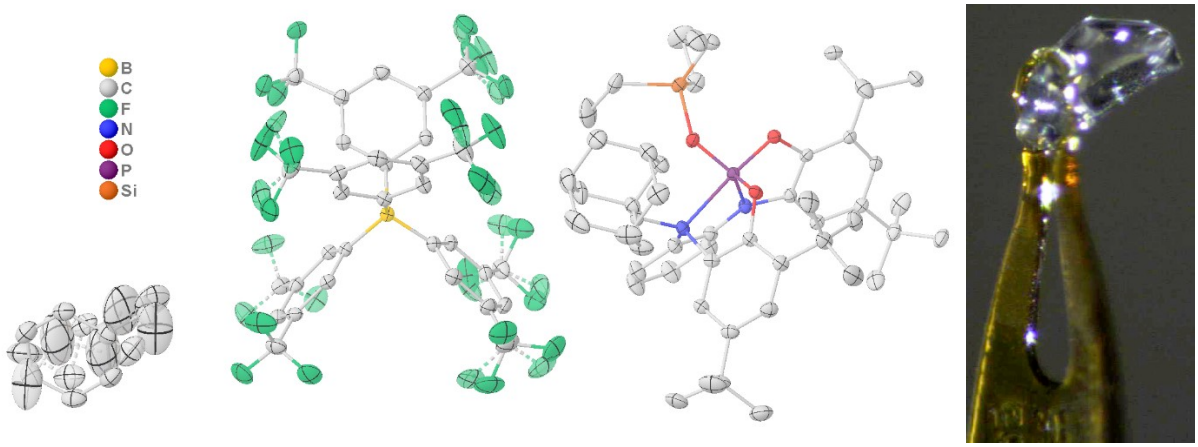


Figure S 8: Asymmetric unit of **9**; hydrogen atoms omitted for clarity, anisotropic displacement ellipsoids drawn at 50% probability level. Five CF_3 groups of the BArF anion exhibit rotational disorder in various degrees that were modelled over two positions (occupancies: 0.864:0.136, 0.842:0.158, 0.721:0.279, 0.716:0.287, 0.605:0.395). The co-crystalized solvent molecule was modelled as positional disorder between toluene and pentane, the latter split over two positions (occupancy: 0.682:0.198.0.120). Minor disorder parts are drawn translucent with stippled bonds. Single crystals were obtained by solvent vapor diffusion method using toluene and pentane.

CCDC number	2353329
Empirical formula	$C_{89.36}H_{97.27}BF_{24}N_2O_3PSi$
Formula weight	1773.21
Temperature [K]	100.00
Crystal system	Triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	13.1456(7)
b [Å]	17.6698(12)
c [Å]	20.0734(15)
α [°]	95.272(2)
β [°]	103.875(2)
γ [°]	91.260(2)
Volume [Å^3]	4502.8(5)
Z	2
ρ_{calc} [gcm^{-3}]	1.308

μ [mm^{-1}]	0.142
F(000)	1843
Crystal size [mm^3]	0.539×0.25×0.171
Crystal color	Colorless
Crystal shape	Plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.03 to 59.30 (0.72 Å)
Index ranges	−15 ≤ h ≤ 18 −24 ≤ k ≤ 24 −27 ≤ l ≤ 27
Reflections collected	159746
Independent reflections	25342 R_{int} = 0.0603 R_{sigma} = 0.0406
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	25342/373/1339

Goodness-of-fit on F^2	1.072
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0534 wR_2 = 0.1375

Final R indexes [all data]	R_1 = 0.0714 wR_2 = 0.1511
Largest peak/hole [eÅ^{-3}]	0.73/-0.51

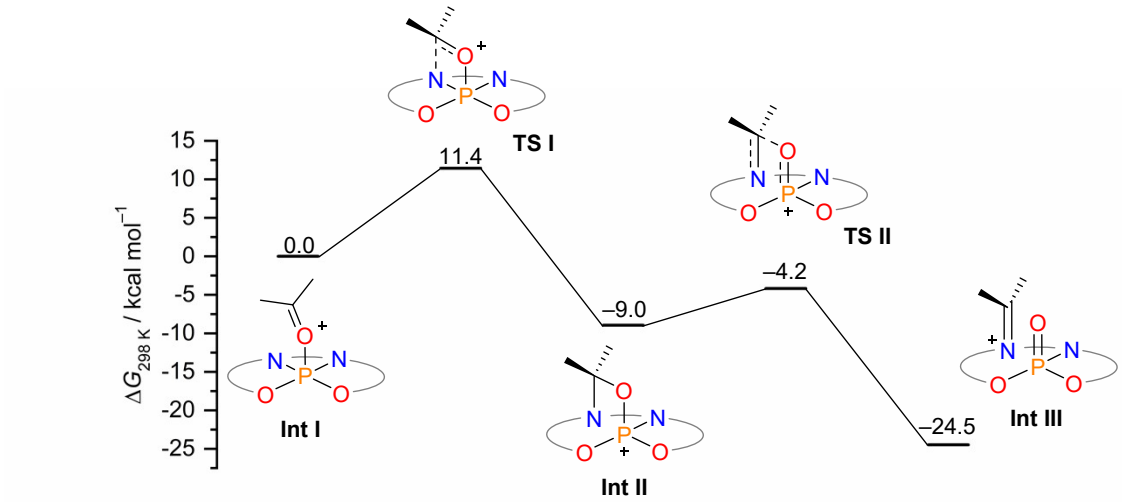
Computational Details

General Information

Geometry optimization and frequency calculations were done with Gaussian16, Revision A.03.[10] For the creation of input files, analysis of calculation outcomes and visualization of molecular orbitals and spin densities GaussView 6.0 was used. Stationary points were characterized by frequency evaluation.

Computation of Free Energy Landscape and Intrinsic Bond Orbitals

Geometry optimization and frequency calculations were performed using the PBE-D3(BJ)[11] functional in combination with the def2-SVP[12] basis set. Single point energies of the optimized structures were obtained at the B3LYP[13]-D3(BJ)/def2-TZVP level including implicit solvation using the C-PCM model (dichloromethane). Relative free energies were determined at standard molarity (1 M) and the reaction temperature of 298 K. For computational efficiency, truncated geometries were used in which the four *tert*-butyl groups of the bisamidophenolate moiety were replaced by methyl groups. Intrinsic Bond Orbitals (IBOs) were calculated at the PBE/def2-TZVP level of theory and visualized using the IboView program suite.[14]



Scheme S1: Free Energy landscape with schematic representations of intermediates and transition states at the B3LYP-D3(BJ)/def2-TZVP(C-PCM)//PBE-D3(BJ)/def2-SVP level.

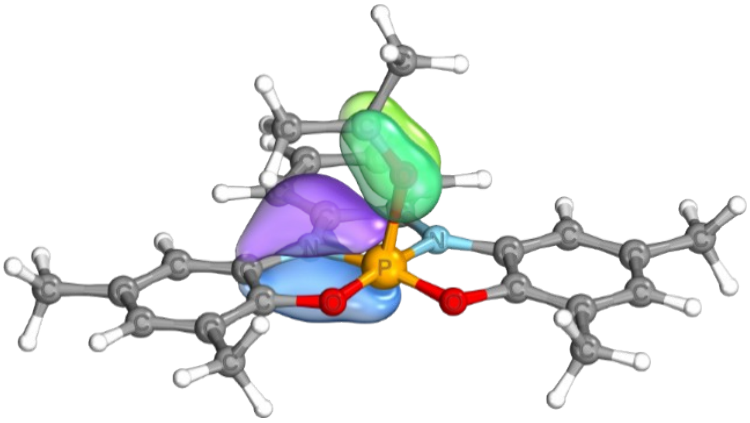
Table S1: Overview of single point energies SPE_{B3LYP} (B3LYP-D3(BJ)(C-PCM:CH_2Cl_2)/def2-TZVP), SPE_{PBE} (PBE-D3(BJ)/def2-SVP), correction terms for Gibbs free energy G_{corr} (PBE-D3(BJ)/def2-SVP) and imaginary frequencies $\tilde{\nu}_i$ for transition states (PBE-D3(BJ)/def2-SVP).

	SPE_{B3LYP} / E_h	SPE_{PBE} / E_h	G_{corr} / E_h	$\tilde{\nu}_i$ / cm^{-1}
Int I	–1645.405625	–1641.99873	0.382844	
TS I	–1645.389287	–1641.97989	0.384727	*i*127.05
Int II	–1645.427657	–1642.00865	0.390607	
TS II	–1645.418559	–1641.99390	0.389113	*i*275.24
Int III	–1645.449151	–1642.01455	0.387363	

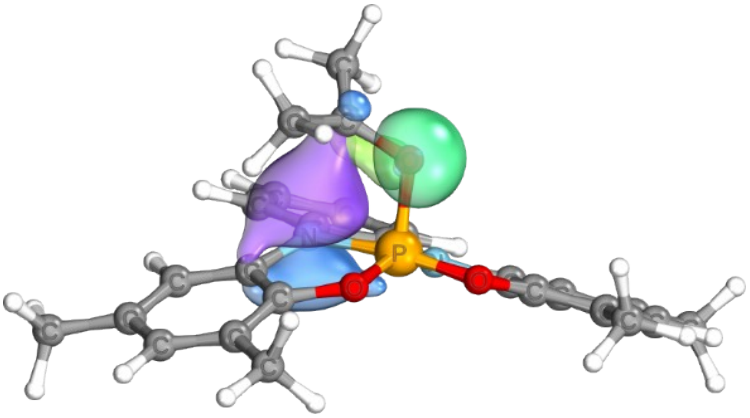
Visualization of Intrinsic Bond Orbitals

π-Bond Activation

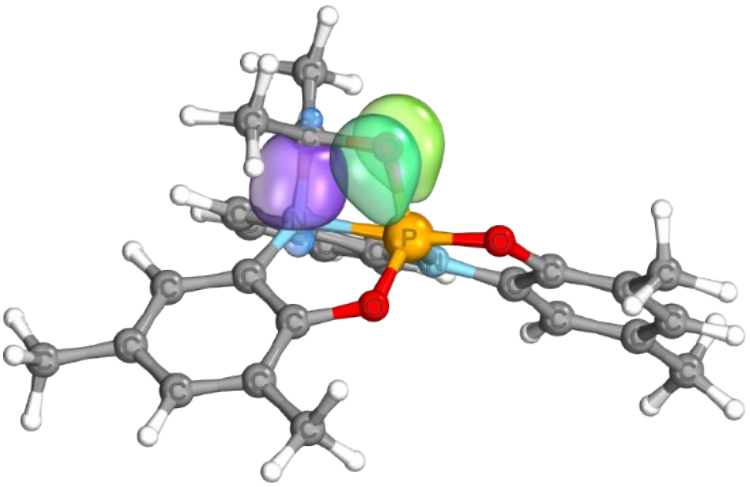
Int I



TS I

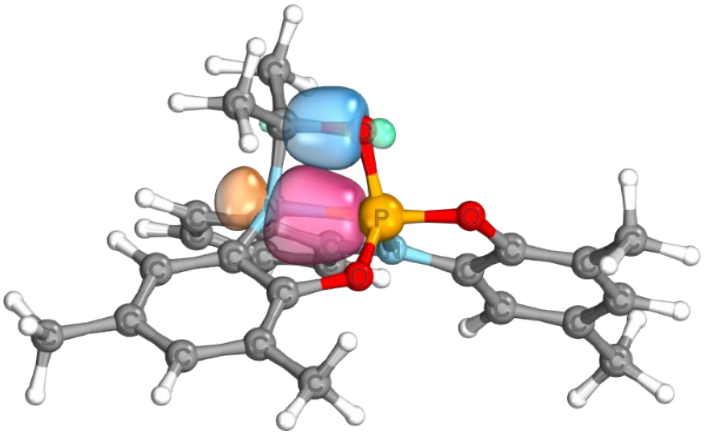


Int II

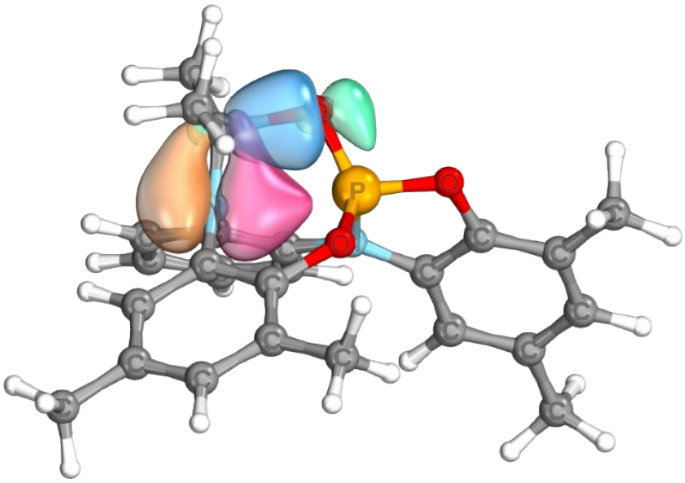


σ -Bond Activation

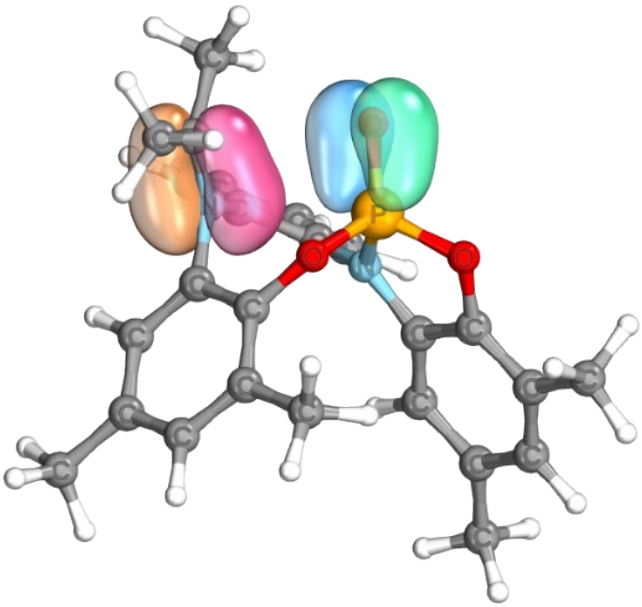
Int II



TS II



Int III



Cartesian Coordinates of Optimized Geometries

Int I

P	0.07209500	-0.49779400	-0.23996400
O	0.36665000	-0.78327700	1.76547700
O	-1.10974100	-1.67146600	-0.40350900
O	1.21986700	-1.66531800	-0.52223100
N	-1.14276300	0.74604900	-0.29908800
N	1.28504100	0.74296100	-0.27035800
C	-2.38356300	-1.16354500	-0.52130400
C	-3.51359300	-1.97796900	-0.68602700
C	-4.74053100	-1.29702700	-0.78841700
H	-5.65692800	-1.89517800	-0.91194900
C	-4.84615400	0.11251000	-0.75013700
C	-3.68345100	0.89310300	-0.59140700
H	-3.76934100	1.98473500	-0.57668600
C	-2.44422400	0.24334900	-0.47281700
C	-0.36025400	-0.66587200	2.78153000
C	-1.83646100	-0.45463700	2.70667000
H	-2.02964400	0.57616500	2.33828900
H	-2.32029800	-0.56827000	3.69251800
H	-2.30122500	-1.13710800	1.96719700
C	0.30464700	-0.73624700	4.11424600
H	0.02310200	0.15014500	4.72176800
H	1.40136000	-0.81280500	4.01573000
H	-0.09102100	-1.61667200	4.66624400
C	-0.63884300	2.04992200	-0.23938300
C	-1.34608600	3.26343400	-0.19827800
H	-2.44043200	3.28397400	-0.19965100
C	-0.62530000	4.46344000	-0.14279400
H	-1.17203300	5.41641000	-0.10496400
C	0.78087900	4.45974400	-0.13542700
H	1.33118500	5.41061400	-0.09538000
C	1.49782100	3.25734300	-0.17577700
H	2.59208400	3.27282800	-0.16866500
C	0.78803500	2.04496900	-0.22211500
C	2.58777800	0.22284800	-0.36204700
C	2.50790700	-1.17555500	-0.51380600
C	3.63124000	-1.99796100	-0.67563400
C	4.87225600	-1.33681100	-0.65393000
H	5.78484500	-1.94293500	-0.76707500
C	4.99902500	0.06271300	-0.49429500
C	3.84251700	0.85338100	-0.35025100
H	3.94615200	1.93684100	-0.22883700
C	6.36704700	0.69669200	-0.48277600
H	6.99452900	0.27988700	0.33161600

H	6.90448900	0.50063700	-1.43334400
H	6.31397100	1.79303900	-0.34386300
C	3.48354000	-3.48222500	-0.85513200
H	2.95467200	-3.94082700	0.00544100
H	2.88212200	-3.71735700	-1.75728700
H	4.46944600	-3.97125200	-0.95868300
C	-3.38517800	-3.47356400	-0.75099400
H	-4.37586500	-3.95571400	-0.83934900
H	-2.76997700	-3.78148100	-1.62152300
H	-2.87817200	-3.87807500	0.14901900
C	-6.19400500	0.77099300	-0.90107900
H	-6.14932000	1.85759800	-0.69743200
H	-6.58472200	0.63836400	-1.93167700
H	-6.94084800	0.32258500	-0.21547900

TS I

P	0.16543700	-0.59991700	0.36379000
O	0.17613800	-0.42848100	2.08160400
O	-0.97826100	-1.81114600	0.08276100
O	1.36534300	-1.74466500	0.29247900
N	-1.17627700	0.63355100	0.19512300
N	1.26493400	0.61607600	-0.20760800
C	-2.20848900	-1.35370200	-0.33084000
C	-3.21060900	-2.21006200	-0.81042400
C	-4.39478200	-1.58116900	-1.23826100
H	-5.21531700	-2.21838400	-1.60403600
C	-4.57579000	-0.17584000	-1.23261600
C	-3.53679400	0.65050200	-0.76832500
H	-3.65721100	1.74015400	-0.78253400
C	-2.34891100	0.05289700	-0.30577000
C	-0.90741300	0.18313300	2.57682300
C	-2.14248200	-0.59547800	2.78387800
H	-2.79555700	-0.55222700	1.87132100
H	-2.74101400	-0.19321200	3.62239500
H	-1.90469900	-1.66647600	2.93346300
C	-0.69406200	1.51180400	3.18750100
H	-1.63777500	2.08419300	3.26552000
H	0.08140300	2.08991900	2.65075600
H	-0.32411000	1.35239100	4.22947700
C	-0.68041600	1.92716700	-0.08185800
C	-1.39788500	3.12804500	-0.08241100
H	-2.47050400	3.13910700	0.14804100
C	-0.71593500	4.32955700	-0.34903600
H	-1.27120300	5.27820000	-0.35156500
C	0.66193300	4.31803700	-0.59906100
H	1.19206300	5.25973100	-0.80124800

C	1.39272200	3.11516000	-0.58100200
H	2.47218400	3.13599200	-0.75809700
C	0.72284100	1.91382700	-0.31495100
C	2.57882000	0.13830500	-0.36044200
C	2.59943400	-1.23622700	-0.04154300
C	3.75452100	-2.02664800	-0.10803500
C	4.92295300	-1.35563900	-0.50996200
H	5.85871200	-1.93321500	-0.57058500
C	4.94714000	0.01851700	-0.84718100
C	3.76019100	0.77329200	-0.77805800
H	3.78429800	1.83040300	-1.06223200
C	6.24049500	0.66290000	-1.27634100
H	6.98774500	0.63986100	-0.45606100
H	6.69074000	0.12316900	-2.13427900
H	6.09823800	1.71879700	-1.57454600
C	3.70984000	-3.48954300	0.23060900
H	3.36337200	-3.64986500	1.27218200
H	2.99769900	-4.02973300	-0.42652000
H	4.70637500	-3.95492000	0.12023500
C	-2.99892800	-3.69668100	-0.85018200
H	-3.86492900	-4.21202800	-1.30412400
H	-2.09150400	-3.95248400	-1.43432200
H	-2.84320200	-4.10903000	0.16808600
C	-5.87134200	0.41616900	-1.72450200
H	-5.85309800	1.52210400	-1.70834800
H	-6.08695200	0.09337400	-2.76352000
H	-6.72597900	0.07994900	-1.10171900

Int II

P	0.29911700	-0.59338100	0.80045700
O	-0.20916500	-0.41603300	2.33948500
O	-0.50099000	-1.76273900	-0.04982800
O	1.64967100	-1.46931900	1.08776900
N	-1.34180900	0.57647300	0.64205200
N	1.13879400	0.63814700	-0.04454500
C	-1.78565600	-1.45799200	-0.48418100
C	-2.52457600	-2.38009800	-1.24315500
C	-3.81907100	-1.97023400	-1.61440000
H	-4.42904300	-2.66992500	-2.20744800
C	-4.37140000	-0.71622600	-1.26687000
C	-3.59057200	0.17825100	-0.50936400
H	-3.99793400	1.15736900	-0.22462400
C	-2.30005400	-0.20452500	-0.12838100
C	-1.38644000	0.45047500	2.19583800
C	-2.61458000	-0.27908400	2.69300500
H	-2.74586000	-1.25418900	2.18998400

H	-3.52391500	0.33067800	2.53388900
H	-2.49533300	-0.45825800	3.77842100
C	-1.11623300	1.76229600	2.90050400
H	-1.97004600	2.45623000	2.78703800
H	-0.20226100	2.25373700	2.51981900
H	-0.97573700	1.55009400	3.97746100
C	-0.91279800	1.83903100	0.06070000
C	-1.72336800	2.96219200	-0.11255500
H	-2.77687800	2.94189100	0.19696200
C	-1.16761200	4.12503500	-0.66893400
H	-1.79289800	5.01713700	-0.81242300
C	0.18887300	4.14221100	-1.02565100
H	0.63143200	5.05659900	-1.44701300
C	1.00773200	3.01526700	-0.84881800
H	2.06933200	3.06916100	-1.10879100
C	0.45545700	1.84022500	-0.31058600
C	2.49045300	0.24977100	-0.27652900
C	2.75020200	-0.95905500	0.39694100
C	3.98344300	-1.61283500	0.35704900
C	4.97828500	-0.98357200	-0.41992600
H	5.96781300	-1.46267200	-0.48038800
C	4.75496300	0.21220700	-1.13225600
C	3.48743300	0.83299900	-1.06875200
H	3.30559300	1.73793600	-1.65910300
C	5.86257300	0.84143000	-1.93942600
H	6.46636800	1.53119300	-1.31173100
H	6.55551200	0.07777400	-2.34207900
H	5.46839800	1.43139400	-2.78963900
C	4.20115900	-2.90326400	1.09514400
H	4.05008100	-2.77098600	2.18623400
H	3.47906600	-3.67875700	0.76701200
H	5.22432100	-3.28797900	0.93112400
C	-1.94091400	-3.71263000	-1.61731000
H	-2.65812300	-4.31138600	-2.20759600
H	-1.01461100	-3.58753100	-2.21469000
H	-1.65809100	-4.29283600	-0.71525400
C	-5.76485200	-0.35062600	-1.70822800
H	-6.08049000	0.63179800	-1.30951200
H	-5.83081400	-0.30420900	-2.81487100
H	-6.50234100	-1.10867000	-1.37477800

TS II

P	0.41768200	-0.38959100	1.30431600
O	-0.29119300	0.12946400	2.58431700
O	-0.33084800	-1.66404700	0.62420400
O	1.86568100	-1.00239700	1.66193700

N	-1.77546300	0.72437800	0.64690800
N	0.94374800	0.72793400	0.14101600
C	-1.47855600	-1.55810400	-0.17126800
C	-1.84092000	-2.67692500	-0.94268600
C	-3.00705400	-2.55295800	-1.71877300
H	-3.31124800	-3.41456300	-2.33387600
C	-3.79553100	-1.38153000	-1.74643200
C	-3.39633600	-0.29215200	-0.95154200
H	-3.98401500	0.63708300	-0.94415300
C	-2.23970000	-0.37788900	-0.16248100
C	-1.86273500	0.70182200	2.05449900
C	-2.78976100	-0.33340900	2.63535500
H	-2.61612100	-1.34110700	2.21916500
H	-3.83325600	-0.04262300	2.39694800
H	-2.67050200	-0.36845100	3.73250300
C	-1.86777300	2.04241200	2.74257800
H	-2.84414100	2.53315300	2.55269500
H	-1.06830600	2.70591000	2.36871100
H	-1.74623100	1.90328600	3.83131200
C	-1.20270500	1.86486400	-0.02896600
C	-1.98646000	2.95919400	-0.41869700
H	-3.06845200	2.93589400	-0.22440000
C	-1.39149600	4.06942700	-1.03314300
H	-2.00813500	4.92459600	-1.34360800
C	-0.00192200	4.08506900	-1.22807800
H	0.48006500	4.96328700	-1.68203300
C	0.79421400	2.99781300	-0.84103300
H	1.88232700	3.04233900	-0.96979100
C	0.19725500	1.86251800	-0.26121800
C	2.26650800	0.34041900	-0.24436100
C	2.77565400	-0.62611400	0.64367700
C	4.03880400	-1.20507100	0.52103200
C	4.79656600	-0.76141600	-0.58338100
H	5.80108200	-1.18931200	-0.72503100
C	4.31637900	0.17776100	-1.51996600
C	3.02602300	0.72836600	-1.35499800
H	2.62958900	1.42981200	-2.09968000
C	5.17854900	0.60929200	-2.67905300
H	5.84985000	1.44271500	-2.38084700
H	5.82492000	-0.21666500	-3.03358600
H	4.57137200	0.96513400	-3.53359300
C	4.52718100	-2.23288100	1.50196700
H	4.59274600	-1.80968300	2.52540100
H	3.83273900	-3.09584600	1.55833300
H	5.52750800	-2.60788300	1.21875900
C	-1.00225500	-3.92432000	-0.92211200
H	-1.41176000	-4.69037900	-1.60534700

H	0.04280300	-3.70809100	-1.22464900
H	-0.95224700	-4.35773700	0.09791200
C	-5.02842400	-1.31075300	-2.60914600
H	-5.57391500	-0.35826700	-2.47200600
H	-4.76607400	-1.39985800	-3.68366300
H	-5.72597000	-2.14182900	-2.37998500

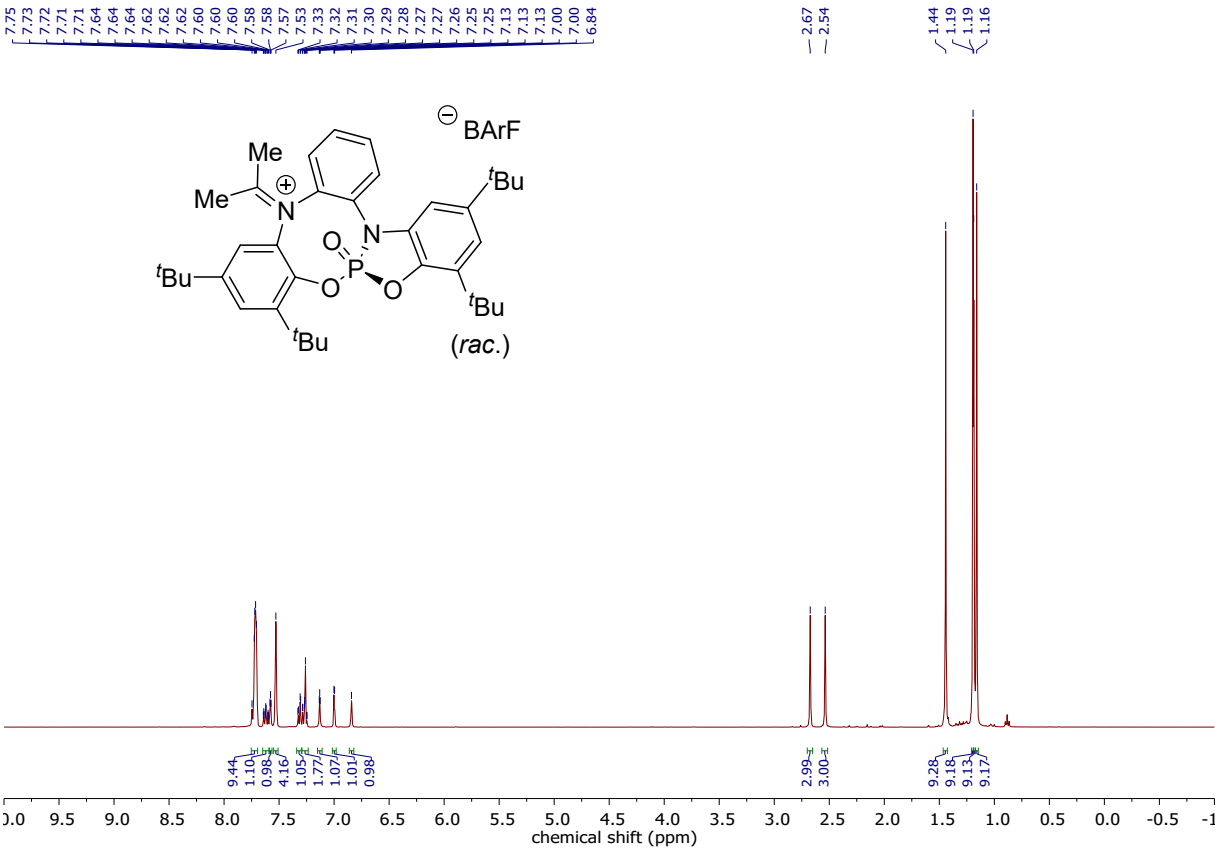
Int III

P	0.14688800	-0.57264500	-1.82173900
O	-0.77511800	-1.29460100	-2.73684100
O	-0.21477900	1.05568800	-1.73383400
O	1.75323200	-0.55481300	-2.14282300
N	-2.30536700	-0.07188000	-0.22847500
N	0.31874300	-1.07607300	-0.18346200
C	-0.58496200	1.66131100	-0.54862500
C	0.11570900	2.80669400	-0.11564400
C	-0.30310800	3.40416400	1.08505400
H	0.23437700	4.30096900	1.43180800
C	-1.35907500	2.89605800	1.87574500
C	-2.02011900	1.73827400	1.43283400
H	-2.83523700	1.29463900	2.02326800
C	-1.64440300	1.14332100	0.21869400
C	-3.08393000	-0.09808400	-1.30378700
C	-3.36956200	1.15907000	-2.03927200
H	-3.33656000	2.05403000	-1.39096000
H	-4.33506200	1.08825400	-2.57332500
H	-2.57138000	1.27290000	-2.80822600
C	-3.64983700	-1.37144600	-1.81577200
H	-4.72936500	-1.42338700	-1.55235700
H	-3.13702100	-2.26509400	-1.42299300
H	-3.58861300	-1.36281200	-2.92137900
C	-2.00956200	-1.25208100	0.55700400
C	-3.02046100	-1.88166300	1.30002100
H	-4.04713900	-1.48967000	1.25747600
C	-2.70376100	-2.98219400	2.10420600
H	-3.48898600	-3.47202100	2.69712300
C	-1.37881400	-3.45080600	2.14905700
H	-1.12646400	-4.32311200	2.76953500
C	-0.37329000	-2.83302900	1.39642000
H	0.65442500	-3.22127900	1.41135900
C	-0.67091200	-1.71612200	0.58929700
C	1.67907200	-0.88314200	0.19215100
C	2.46581700	-0.57460000	-0.93463700
C	3.82948000	-0.27907500	-0.85289700
C	4.38298000	-0.31862500	0.44445900
H	5.45552100	-0.09493700	0.55493000

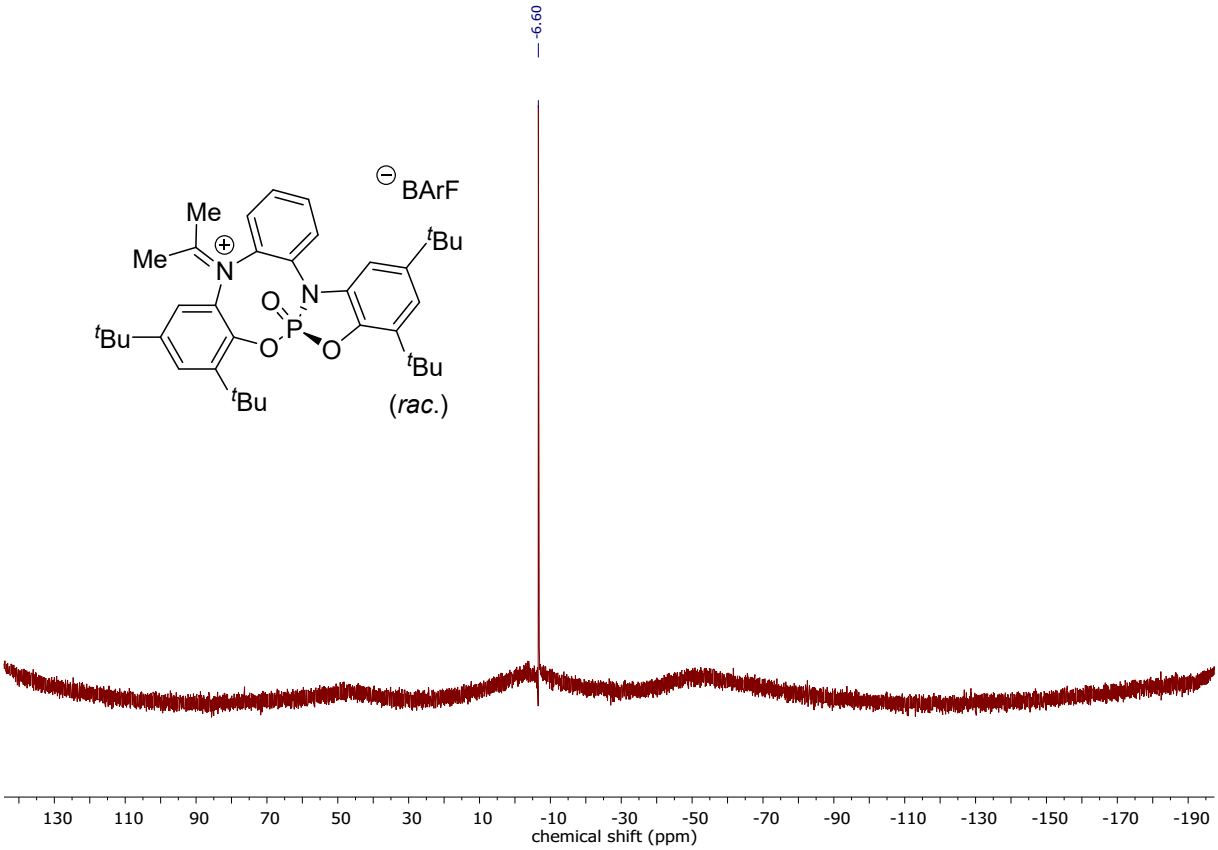
C	3.62660000	-0.61626500	1.59910500
C	2.24818100	-0.89186400	1.47060500
H	1.63473700	-1.09890400	2.35865400
C	4.28780800	-0.65871000	2.95361200
H	4.76555800	-1.64631400	3.12857800
H	5.08500400	0.10502200	3.04067900
H	3.56073500	-0.49523300	3.77229800
C	4.62619200	0.05274300	-2.08287500
H	4.65408400	-0.80691800	-2.78381200
H	4.17243900	0.89773600	-2.64020800
H	5.66672500	0.32144400	-1.82427200
C	1.28505000	3.31205300	-0.91344400
H	1.67951800	4.25410500	-0.49115200
H	2.10603700	2.56382000	-0.91776200
H	1.00846400	3.48457800	-1.97261600
C	-1.75873000	3.58458000	3.15416400
H	-2.50349900	2.99801100	3.72412900
H	-0.87986700	3.75460400	3.80822600
H	-2.20024400	4.58135300	2.94577700

NMR Spectra

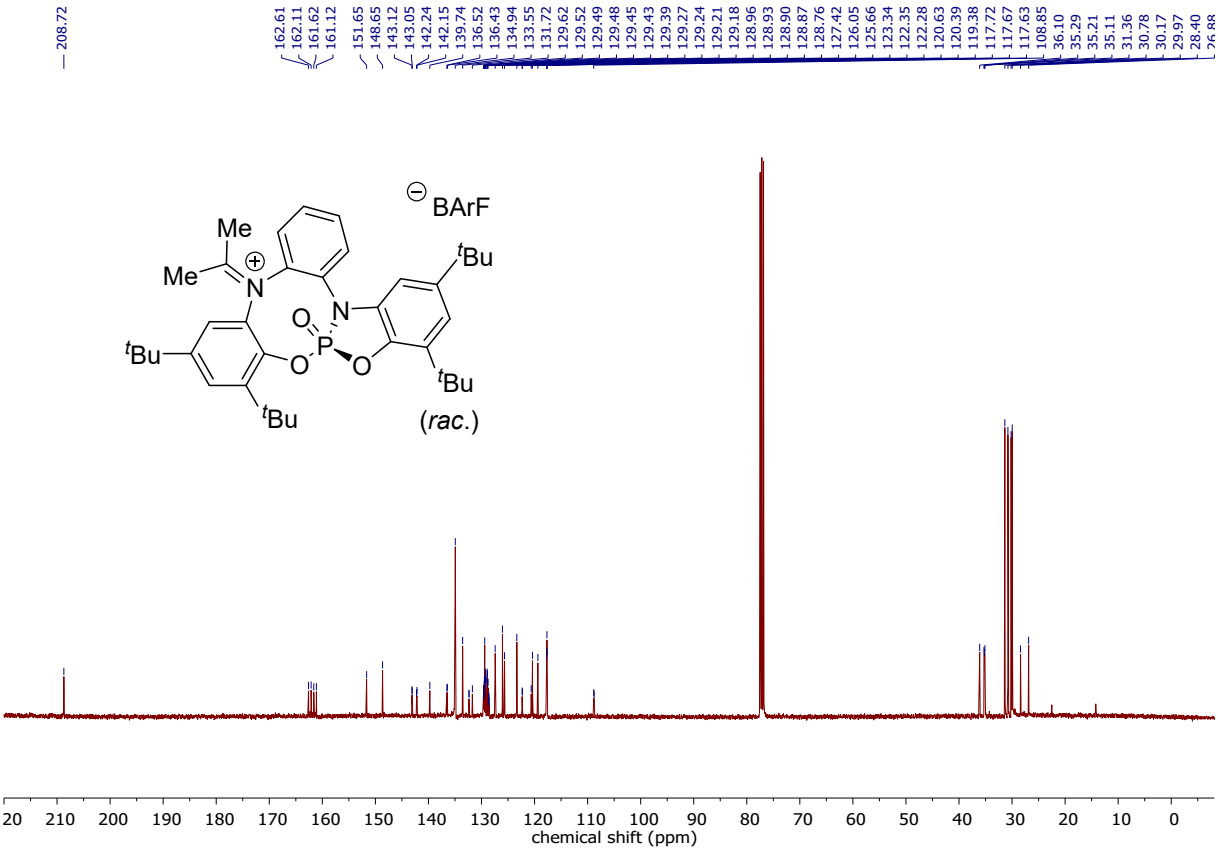
^{1}H NMR (400 MHz, $CDCl_3$) of **2**



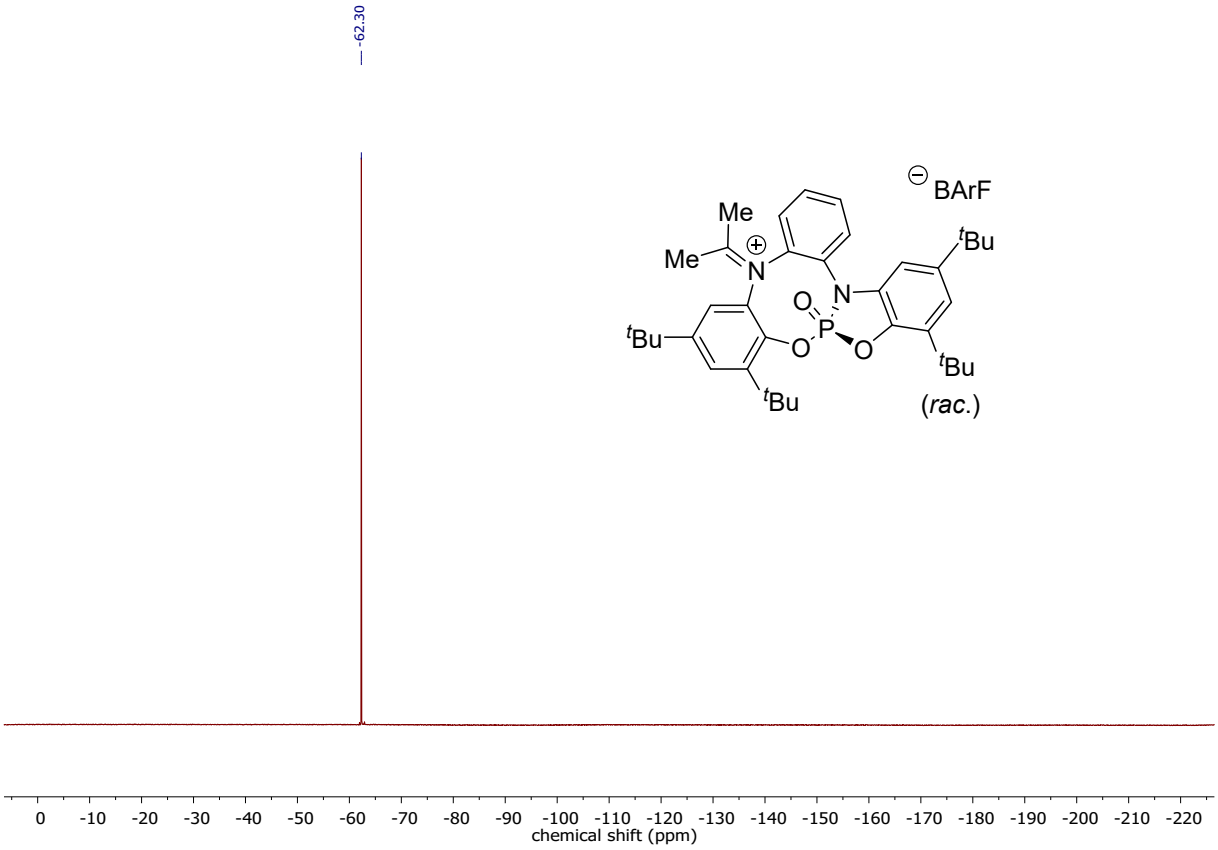
^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$) of **2**



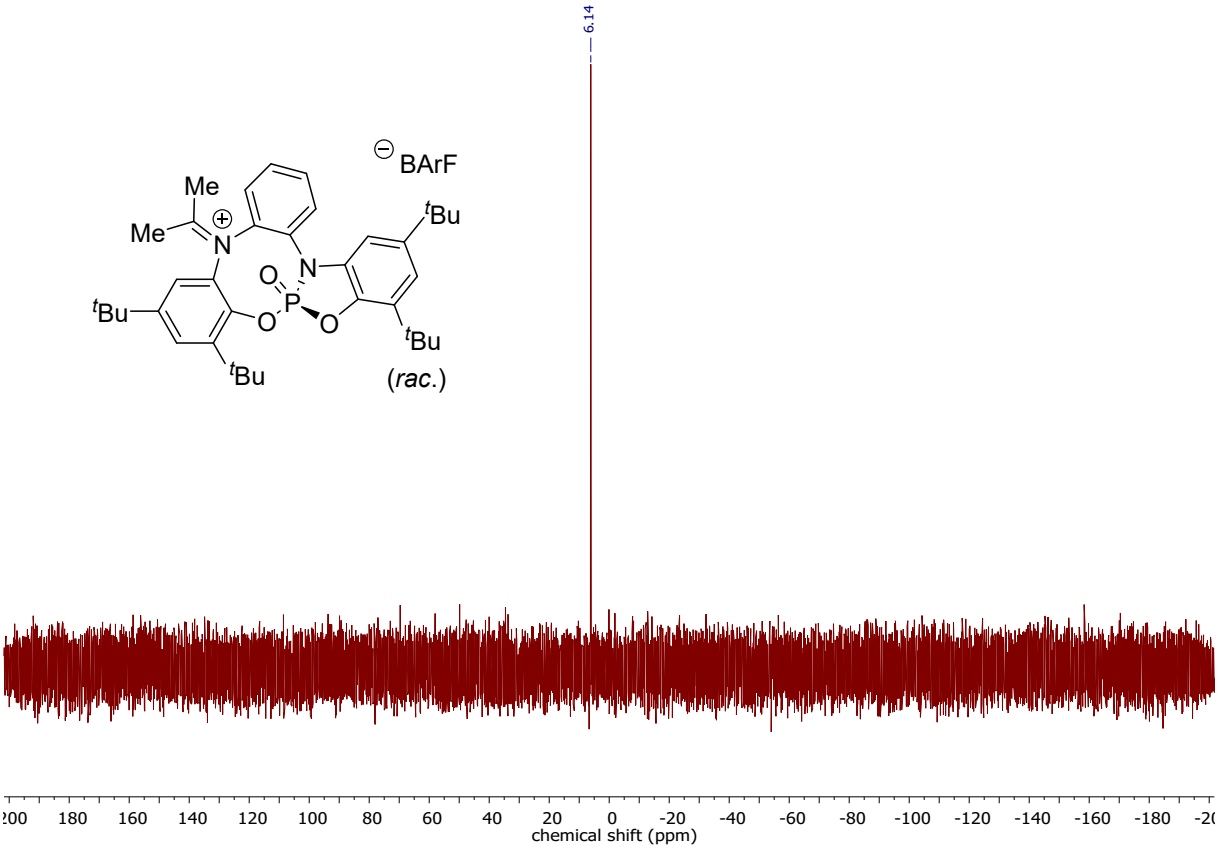
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) of **2**



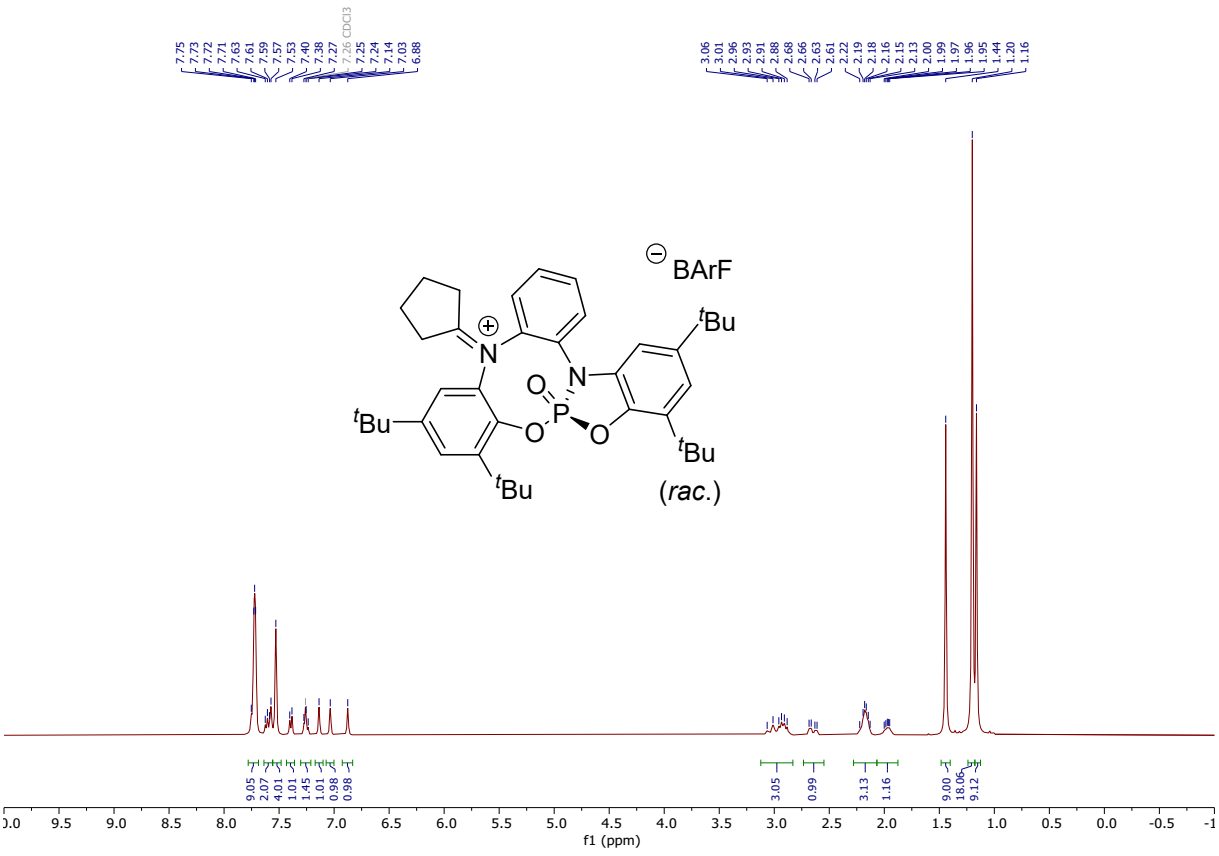
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of **2**



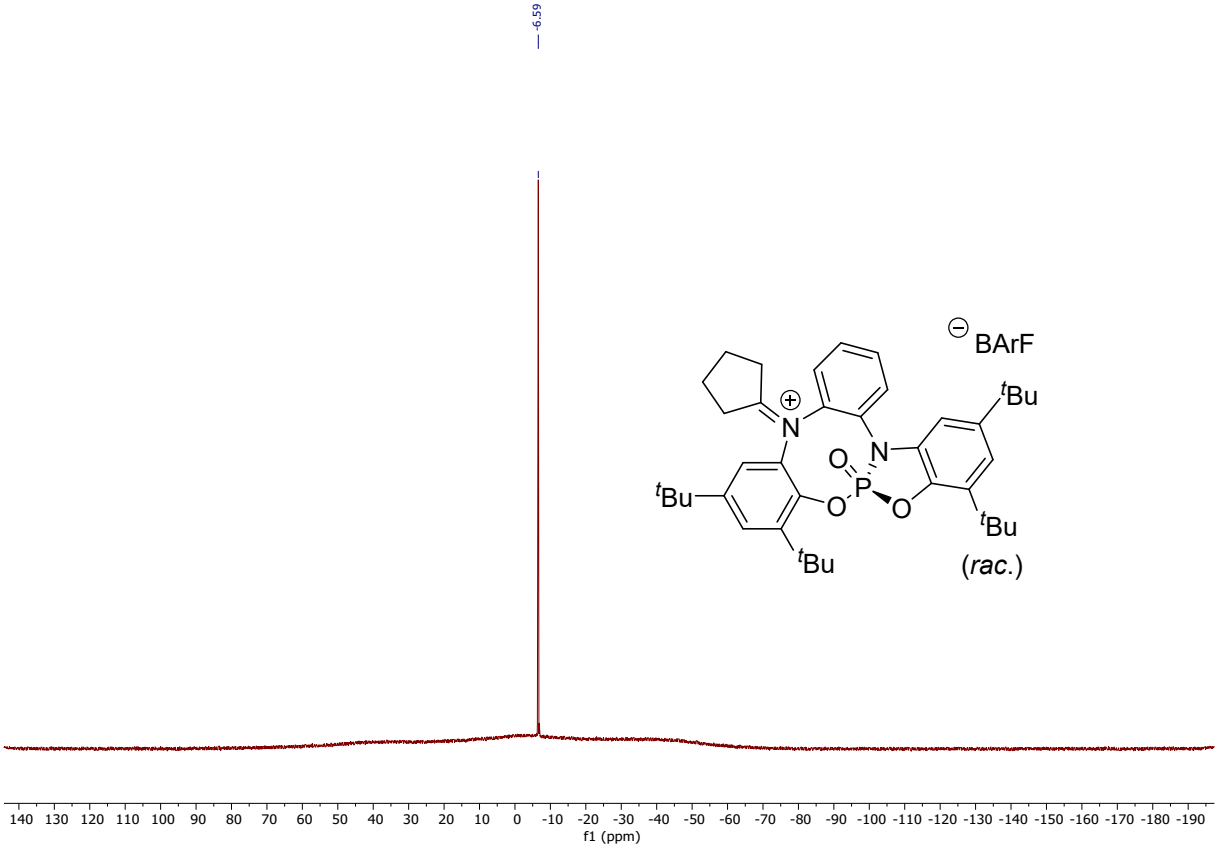
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **2**



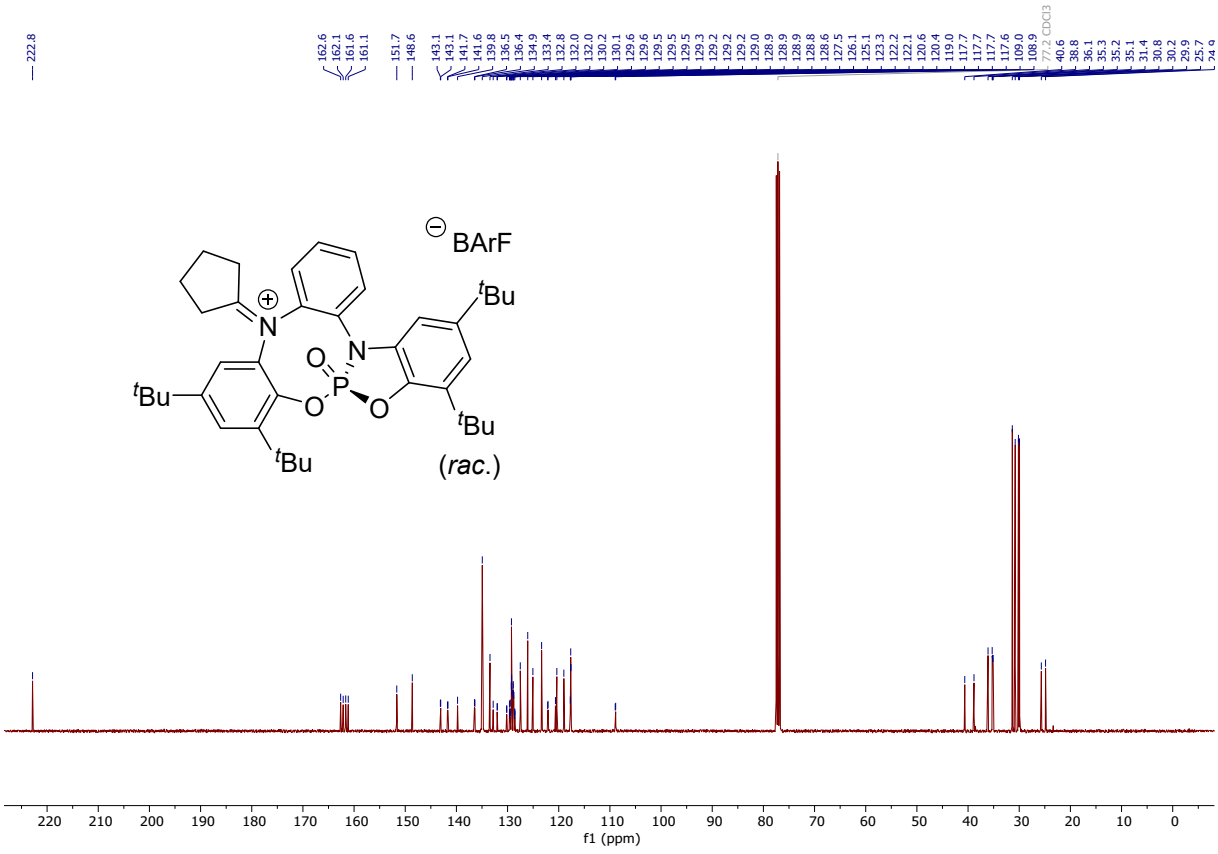
^{1}H NMR (400 MHz, $CDCl_3$) of **3**


7.75
7.73
7.72
7.71
7.63
7.61
7.59
7.57
7.53
7.40
7.38
7.27
CDCl3
7.26
7.25
7.24
7.14
7.03
6.88
3.06
3.01
2.96
2.93
2.91
2.88
2.68
2.66
2.63
2.61
2.22
2.19
2.18
2.16
2.15
2.13
2.00
1.99
1.97
1.96
1.95
1.44
1.20
1.16
BArF
tBu
tBu
tBu
tBu
(rac.)
9.05
2.07
4.01
1.01
1.45
1.01
0.98
0.98
3.05
0.99
3.13
1.16
9.00
18.06
9.12
f1 (ppm)

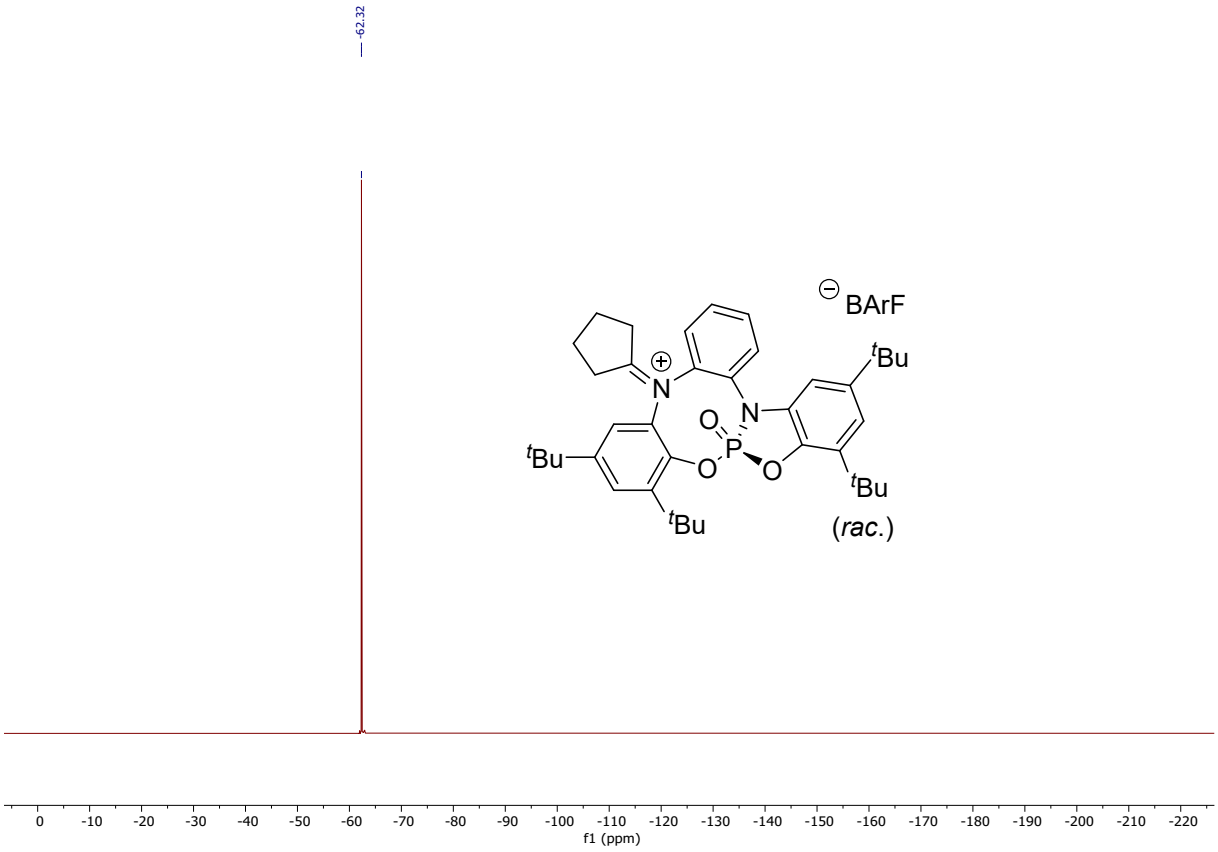
$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$) of **3**



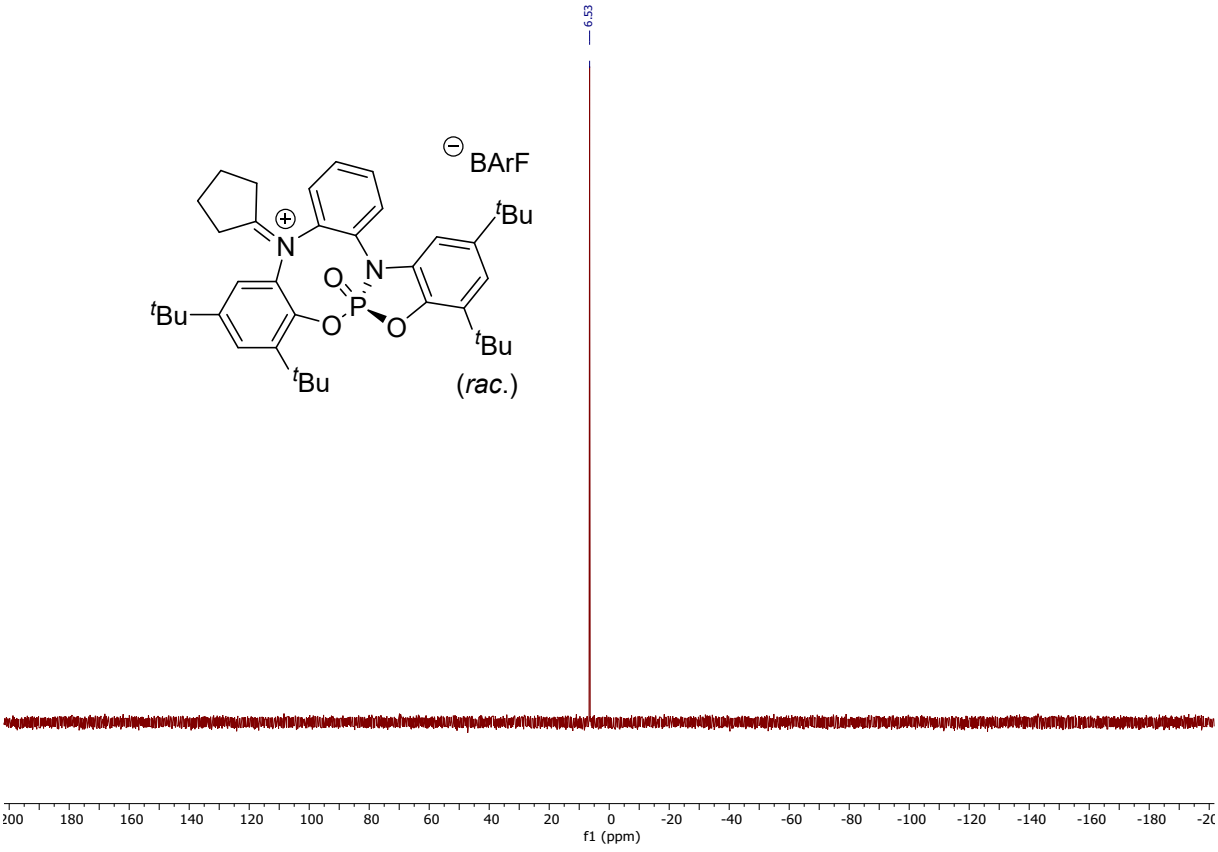
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **3**


222.8
162.6
162.1
161.6
161.1
151.7
148.6
143.1
143.1
141.7
141.6
139.8
136.5
136.4
134.9
133.4
132.8
132.0
132.0
130.2
130.1
129.6
129.6
129.5
129.5
129.5
129.3
129.2
129.2
129.2
129.0
128.9
128.9
128.9
128.8
128.6
127.5
126.1
125.1
123.3
122.2
122.1
120.6
120.4
119.0
117.7
117.7
117.7
117.6
108.9
77.2 CDCl3
40.6
38.8
36.1
35.3
35.2
35.1
31.4
30.8
30.2
29.9
25.7
24.9
BArF
tBu
tBu
tBu
tBu
(rac.)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

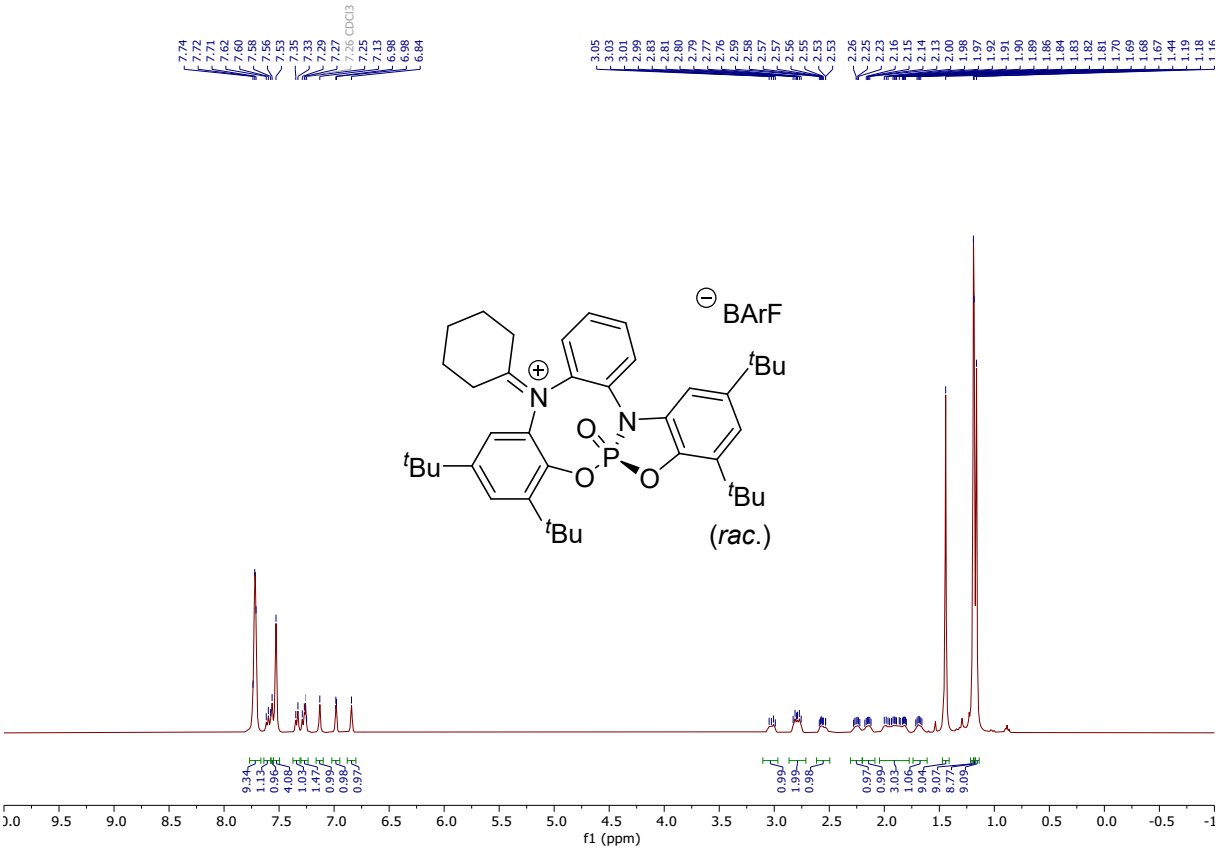
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of **3**



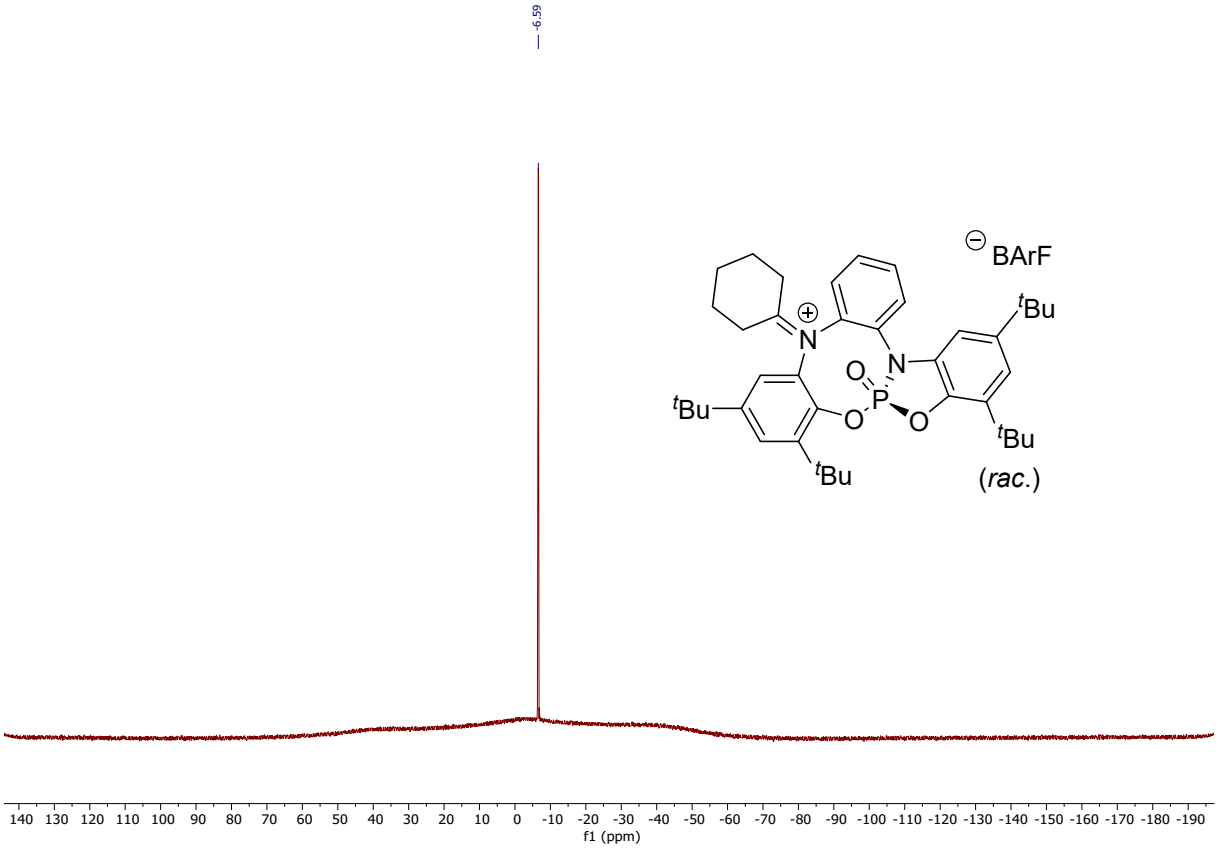
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **3**


6.53
BArF
tBu
tBu
tBu
tBu
(rac.)
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

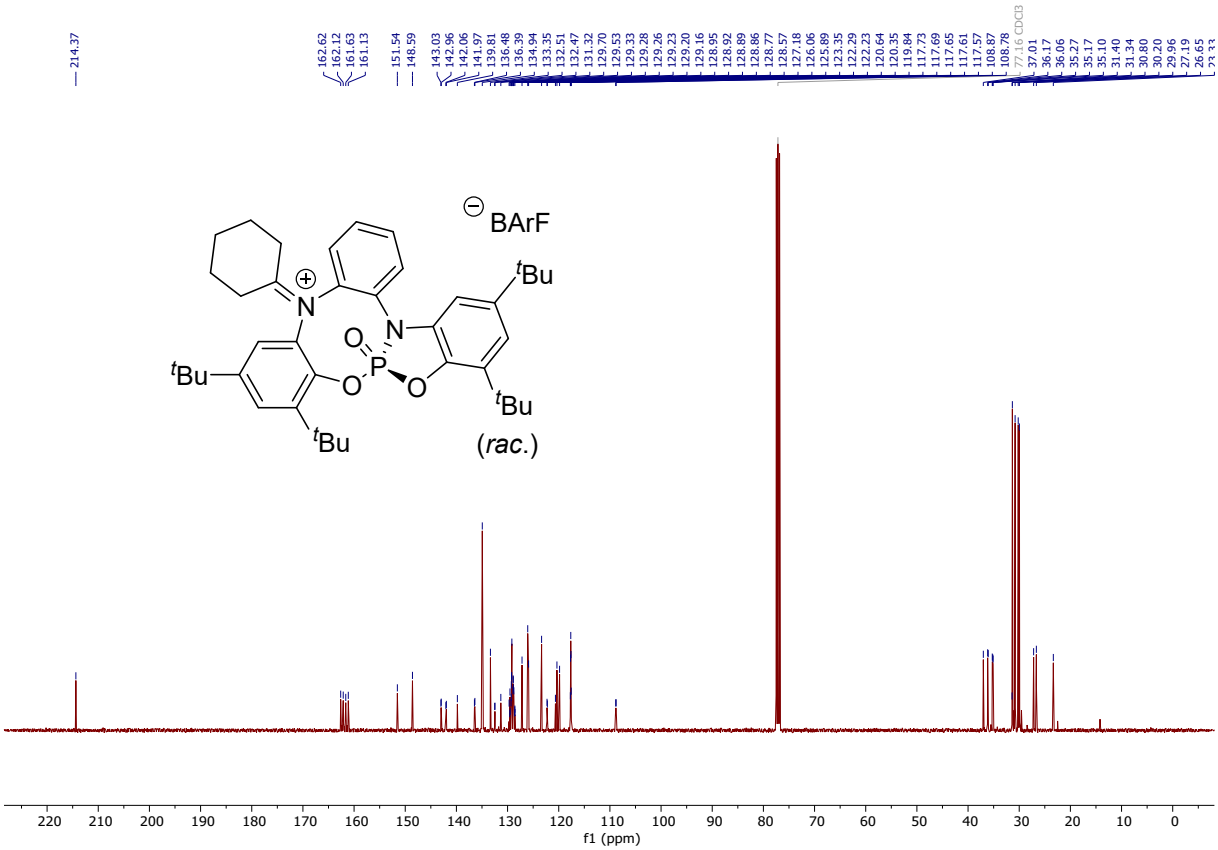
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



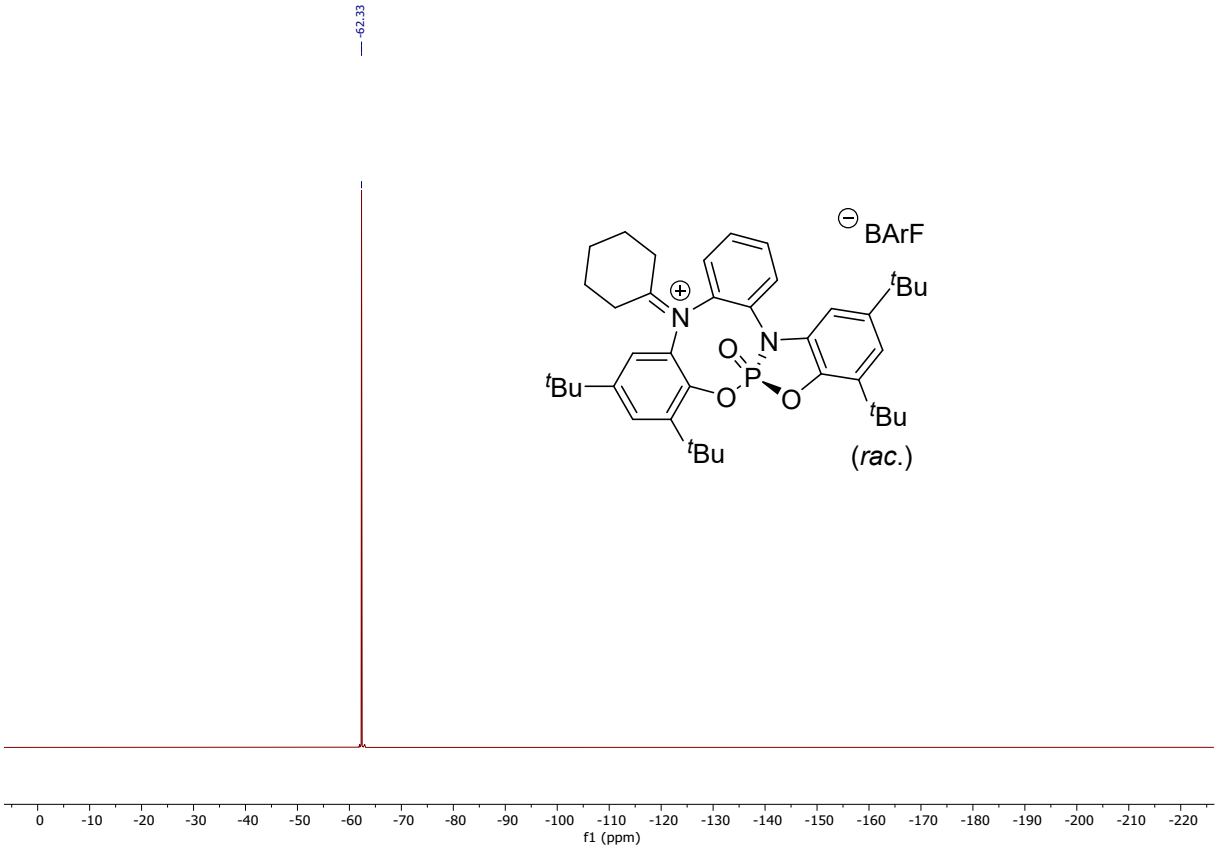
^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$) of **4**


-6.59
BArF
tBu
tBu
tBu
tBu
(rac.)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

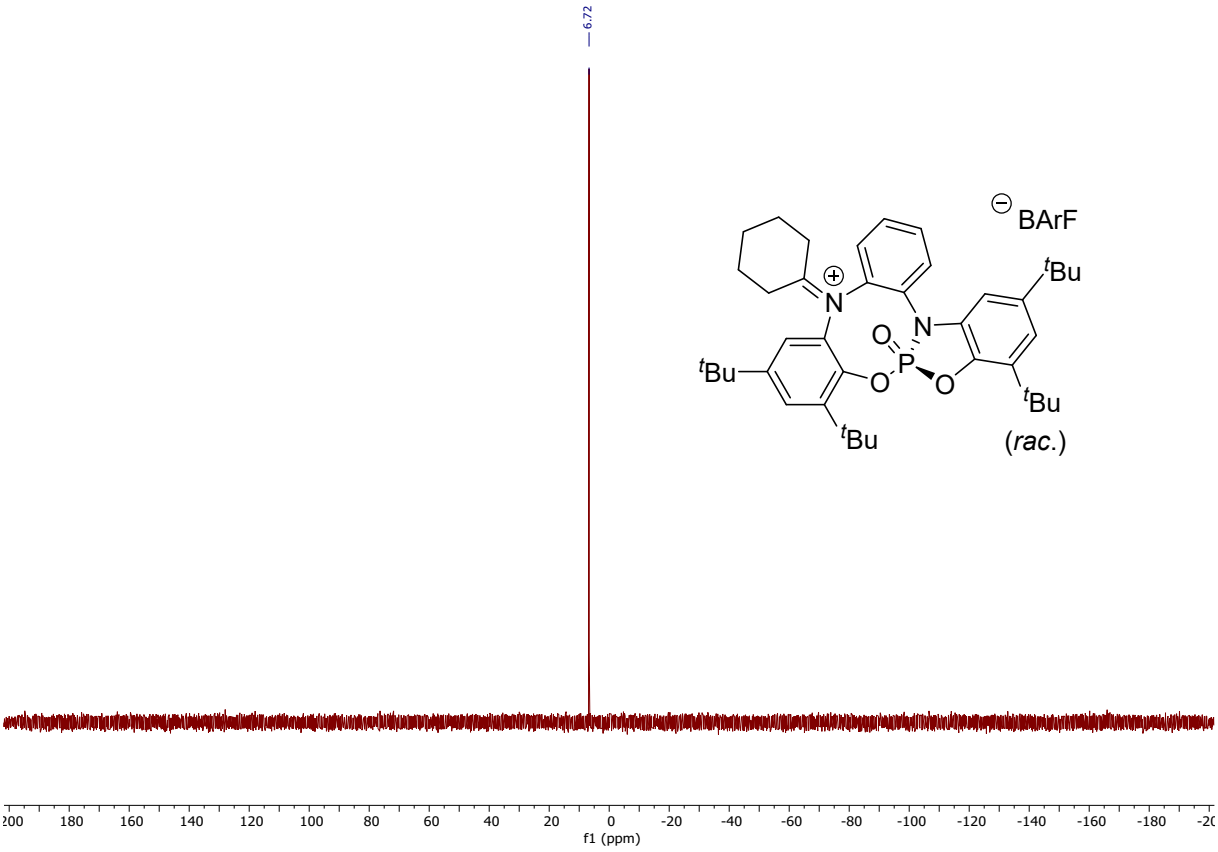
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **4**



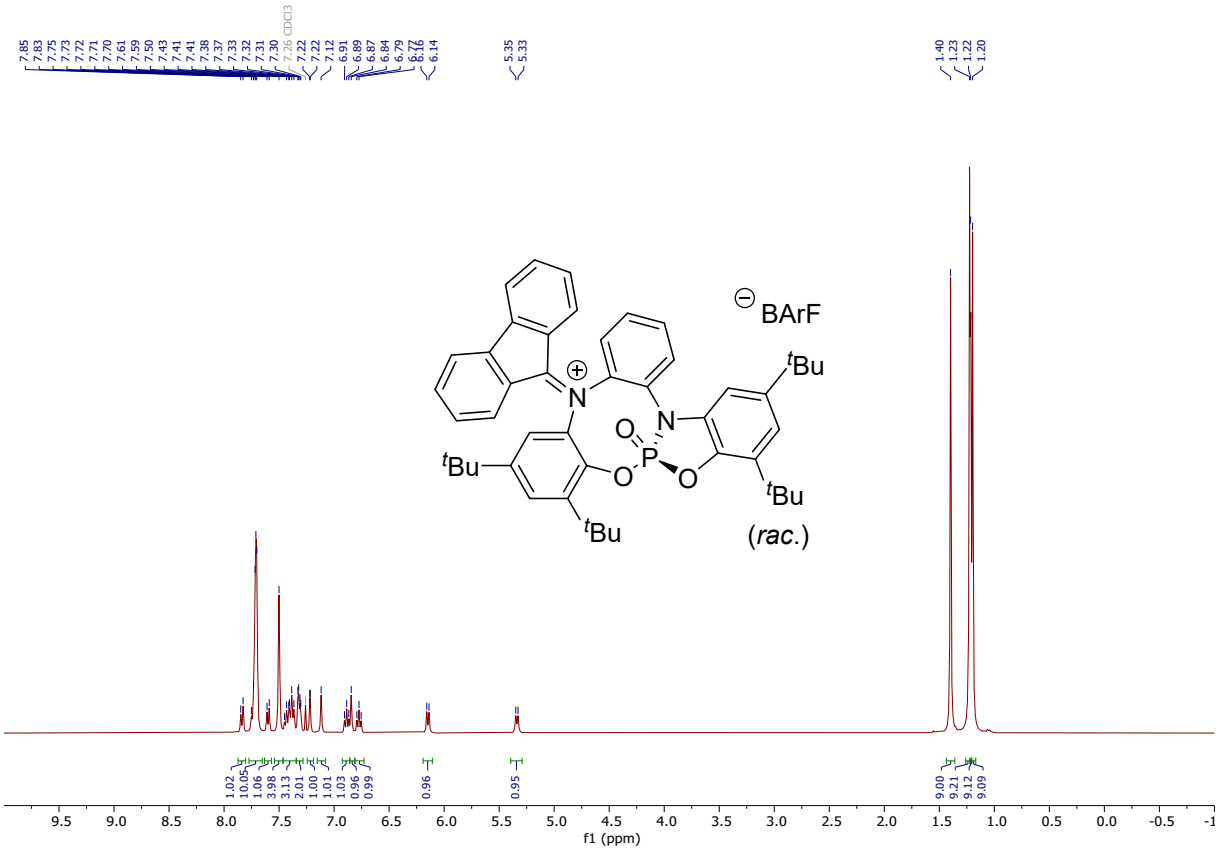
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of **4**



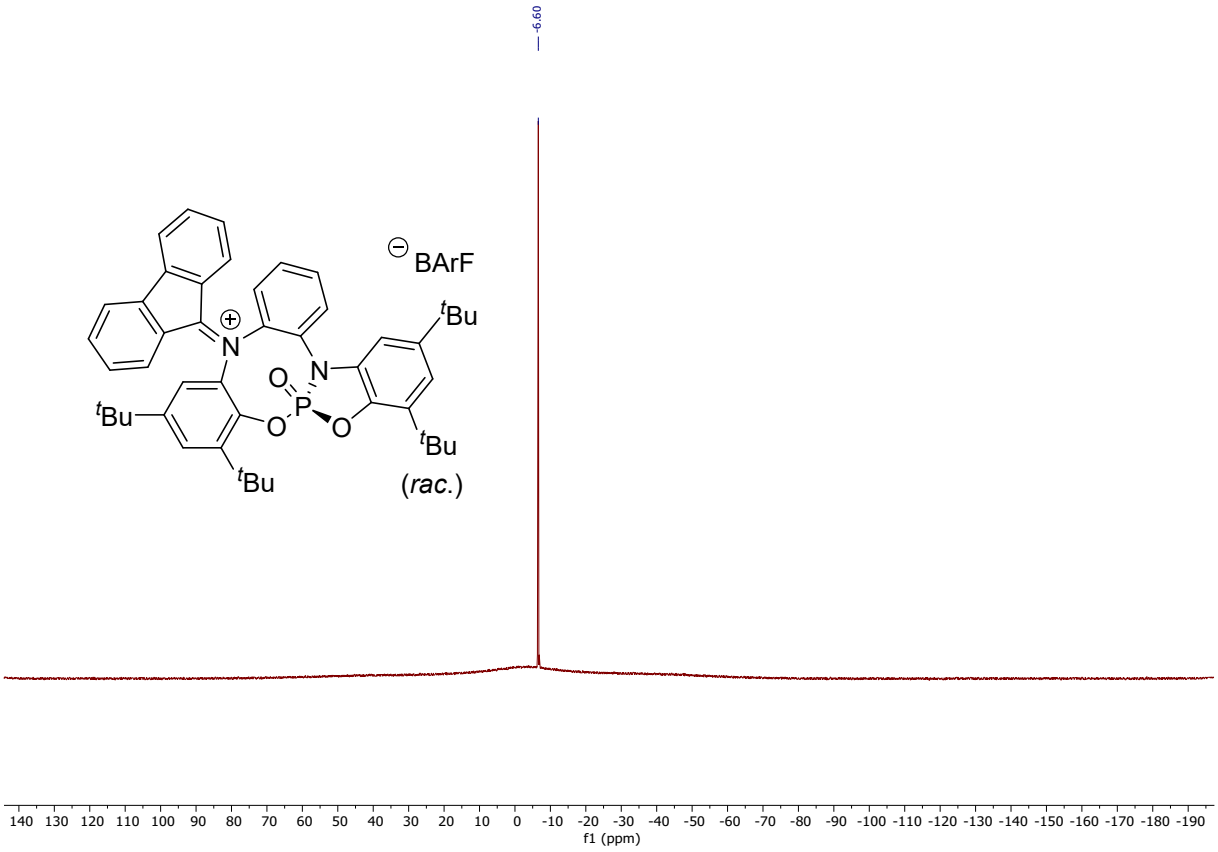
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **4**



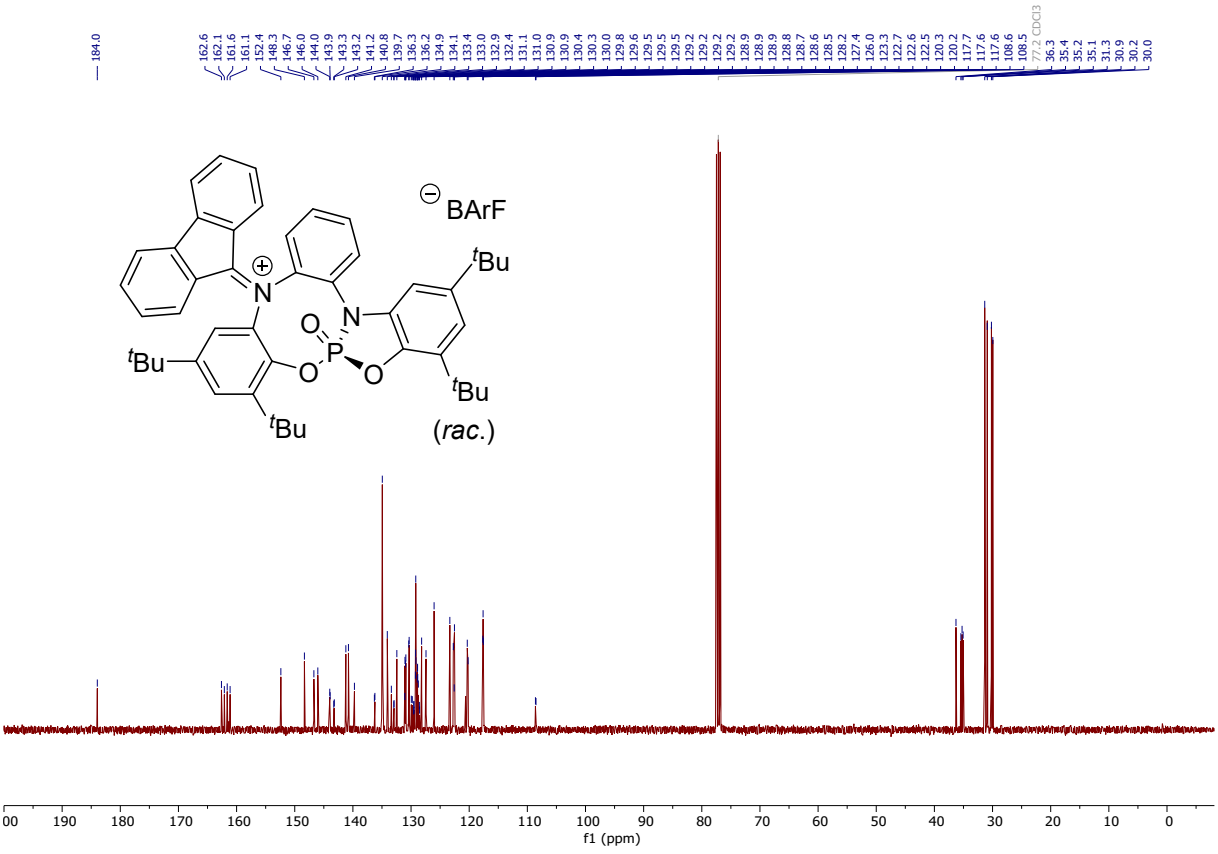
^{1}H NMR (400 MHz, $CDCl_3$) of **5**


7.85
7.83
7.75
7.73
7.72
7.71
7.70
7.61
7.59
7.50
7.43
7.41
7.38
7.37
7.33
7.32
7.31
7.30
7.26 CDCl3
7.22
7.22
7.12
6.91
6.89
6.87
6.84
6.79
6.77
6.16
6.14
5.35
5.33
1.40
1.23
1.22
1.20
BArF
tBu
tBu
tBu
tBu
(rac.)
1.02
10.05
1.06
3.98
3.13
2.01
1.00
1.01
1.03
0.96
0.99
0.96
0.95
9.00
9.21
9.12
9.09
f1 (ppm)

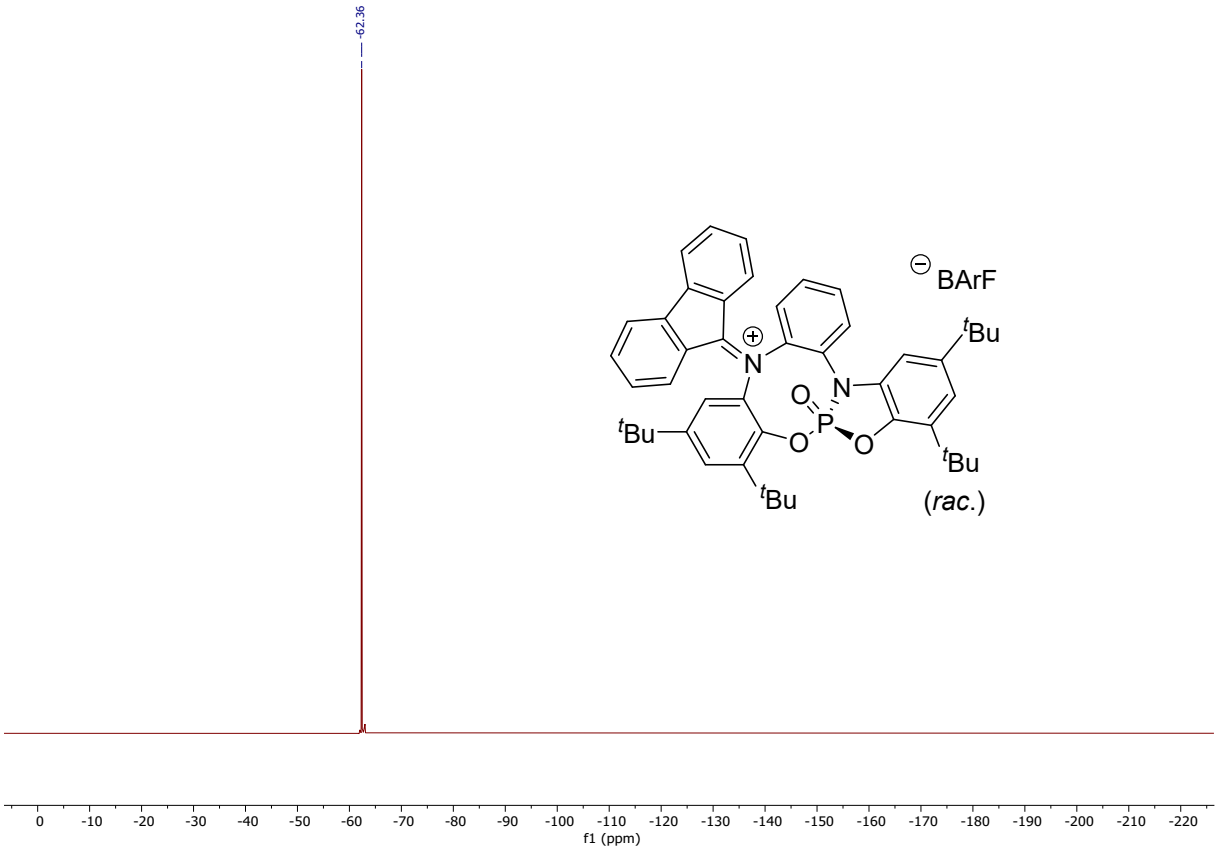
$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$) of **5**



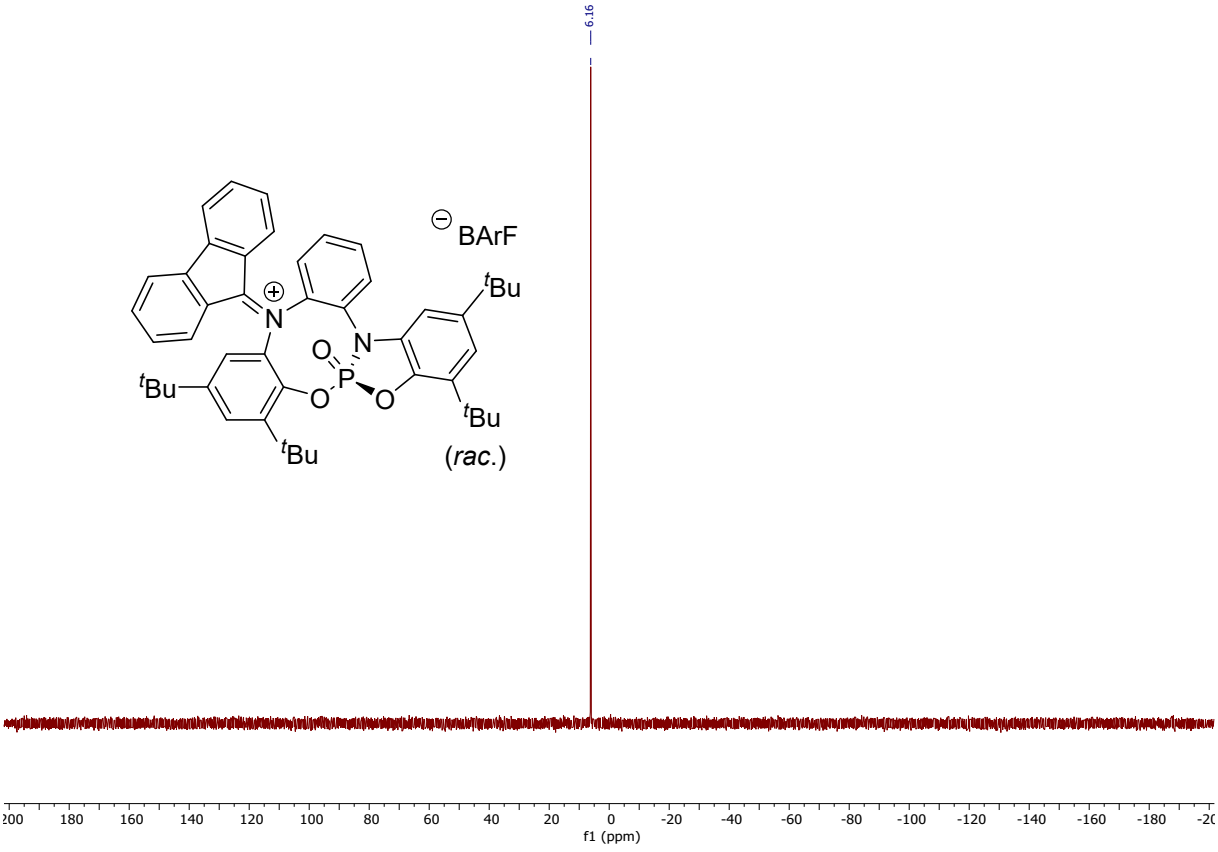
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **5**


184.0
162.6
162.1
161.6
161.1
152.4
148.3
146.7
146.0
144.0
143.9
143.3
143.2
141.2
140.8
139.7
136.3
136.2
134.9
134.1
133.4
133.0
132.9
132.4
131.1
131.0
130.9
130.9
130.4
130.3
130.0
129.8
129.6
129.5
129.5
129.5
129.2
129.2
129.2
129.2
128.9
128.9
128.9
128.8
128.7
128.6
128.5
128.2
127.4
126.0
123.3
122.7
122.6
122.5
120.3
120.2
117.7
117.6
117.6
108.6
108.5
77.2 CDCl3
36.3
35.4
35.2
35.1
31.3
30.9
30.2
30.0
BArF
tBu
tBu
tBu
tBu
N
N
O
P
O
O
(rac.)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

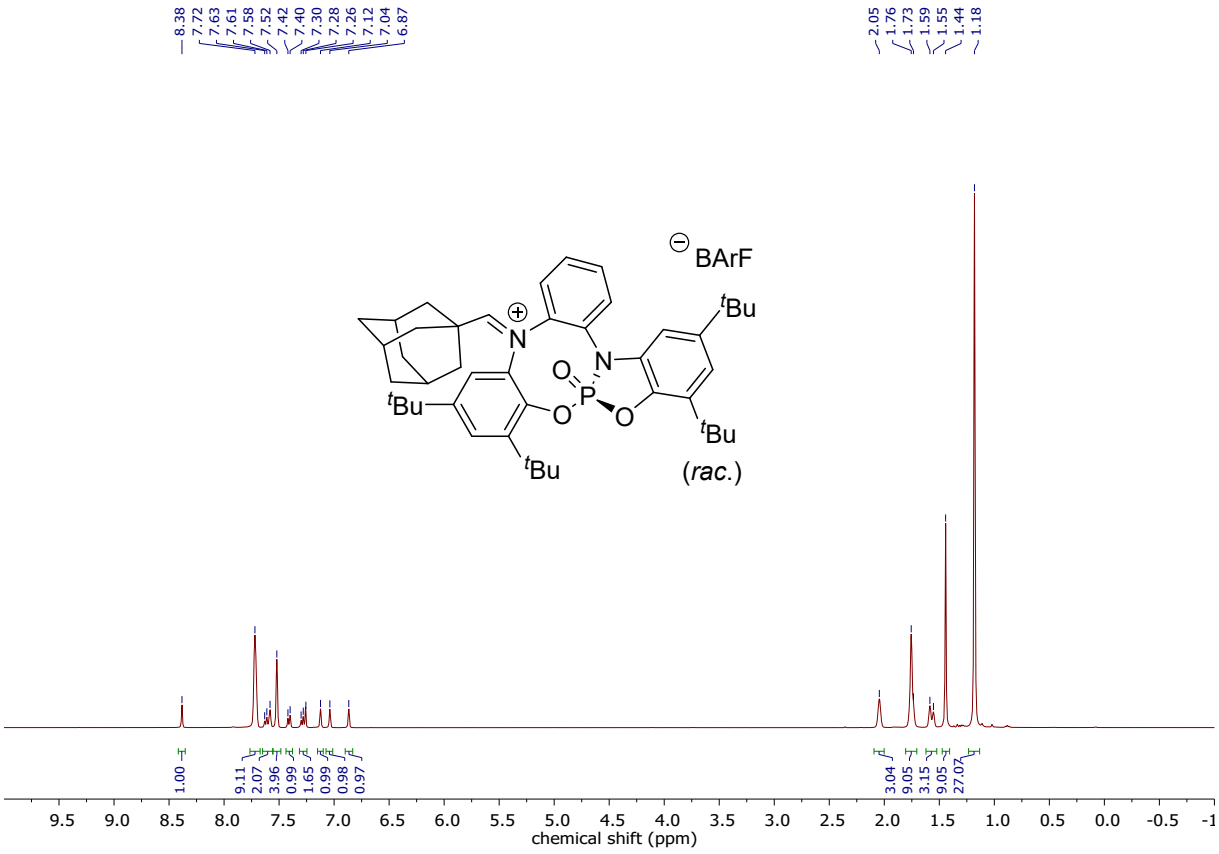
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of **5**



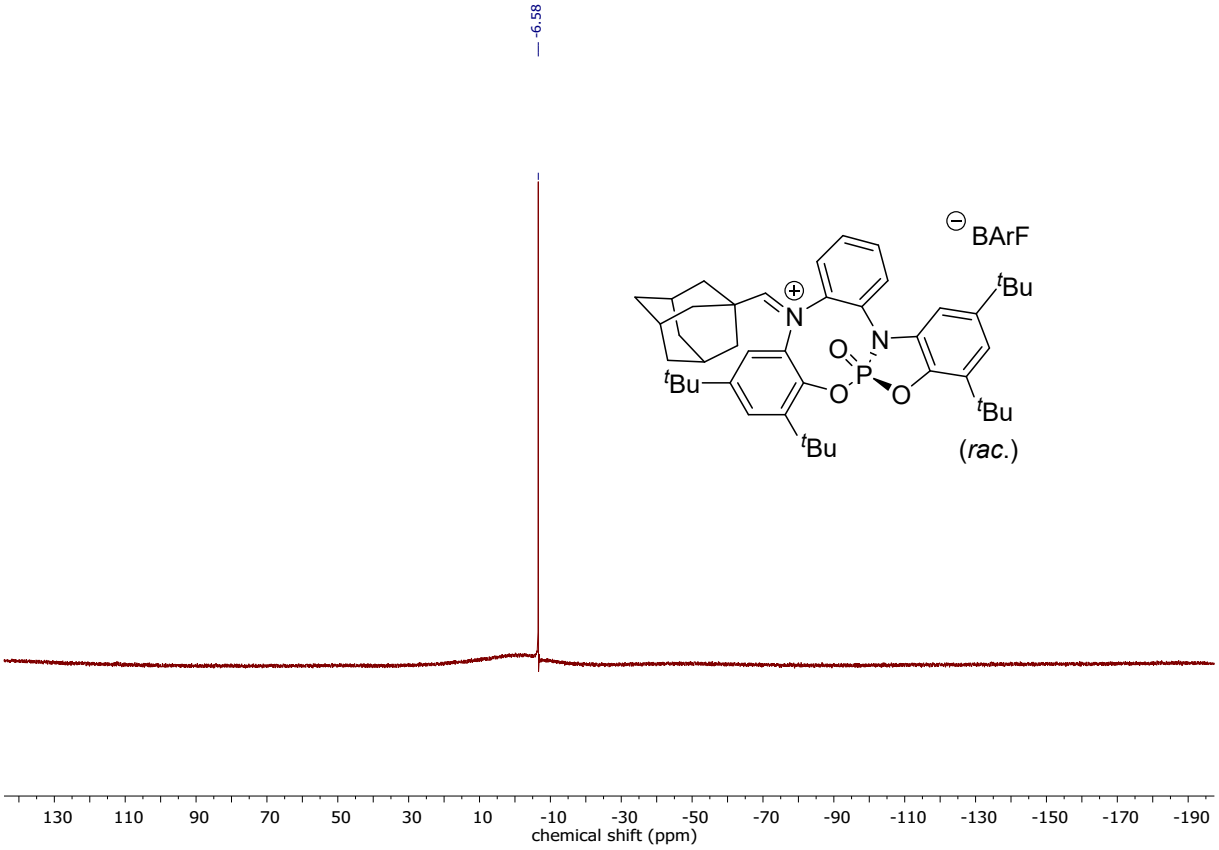
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **5**



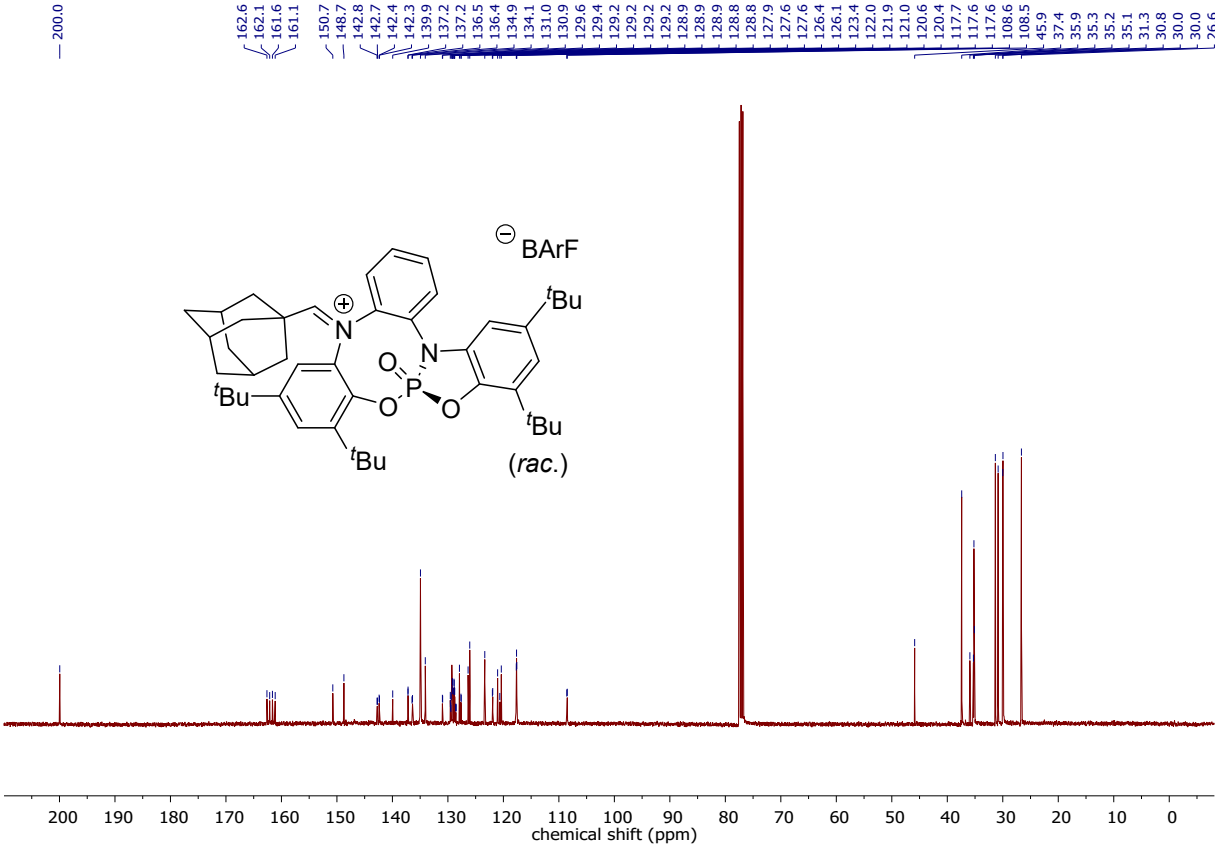
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



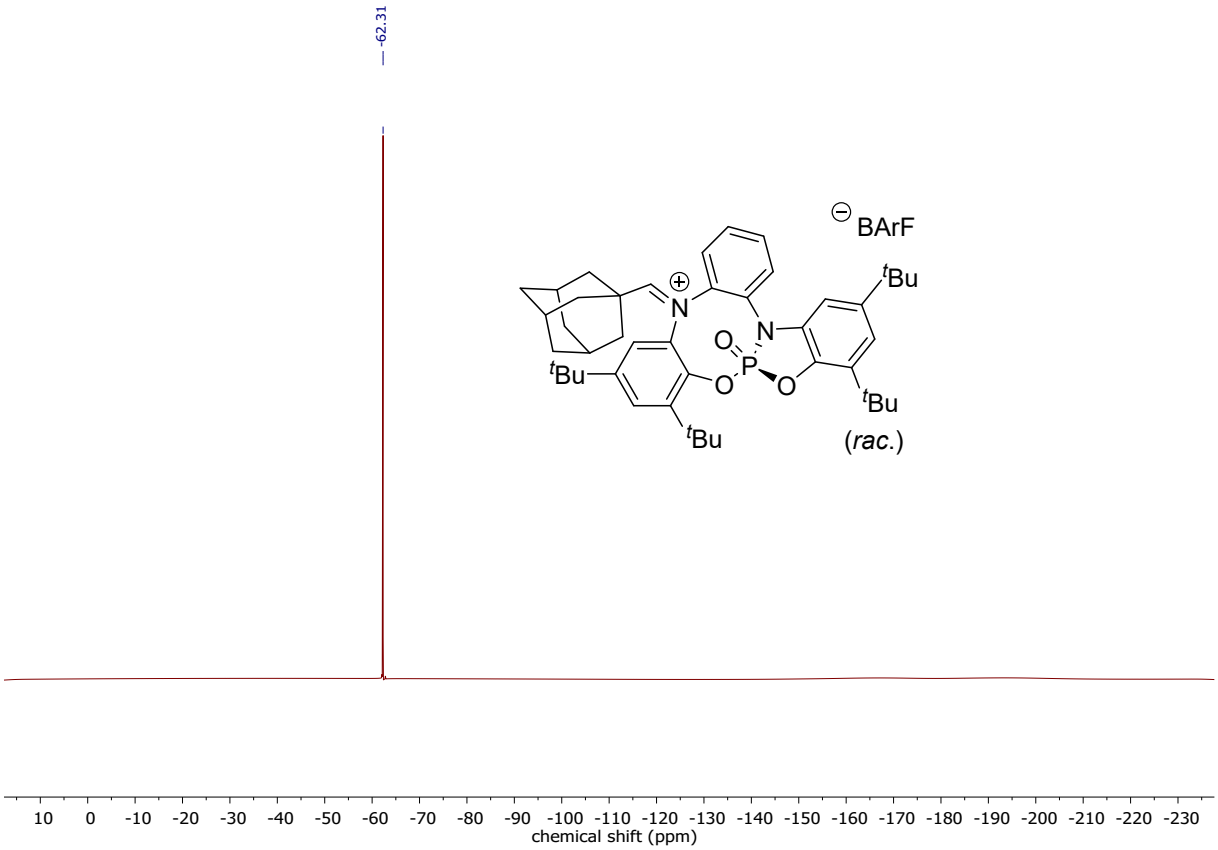
$^{11}B\{^{1}H\}$ NMR (96 MHz, $CDCl_3$) of **6**



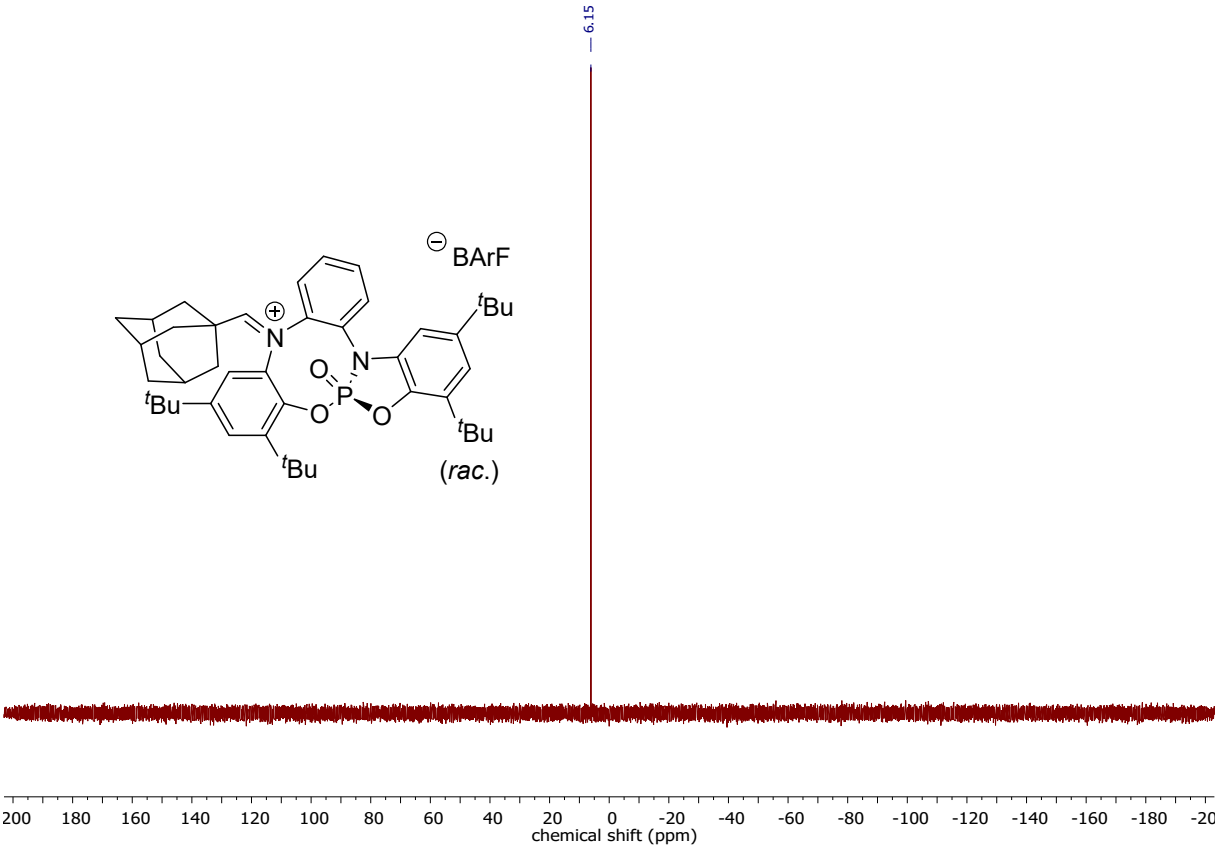
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **6**



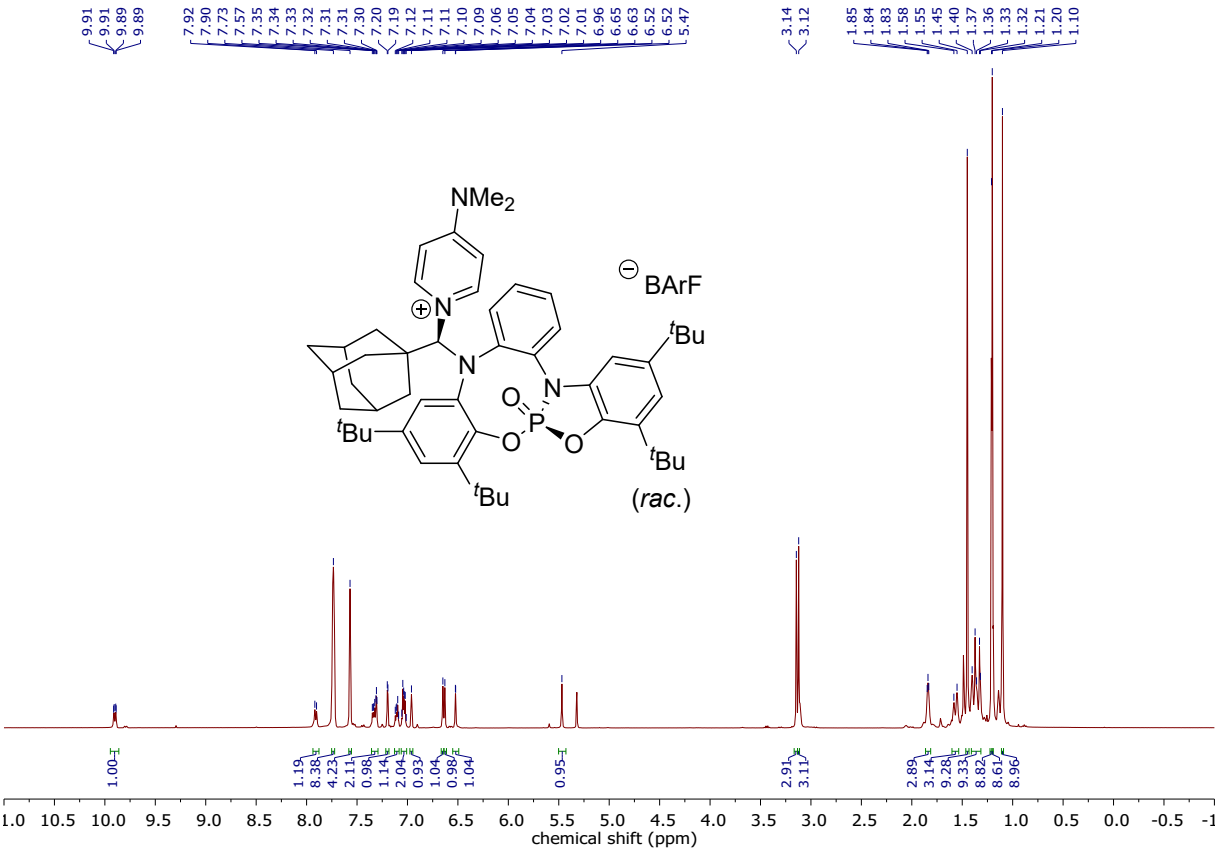
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of **6**


-62.31
BArF
tBu
tBu
tBu
tBu
(rac.)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
chemical shift (ppm)

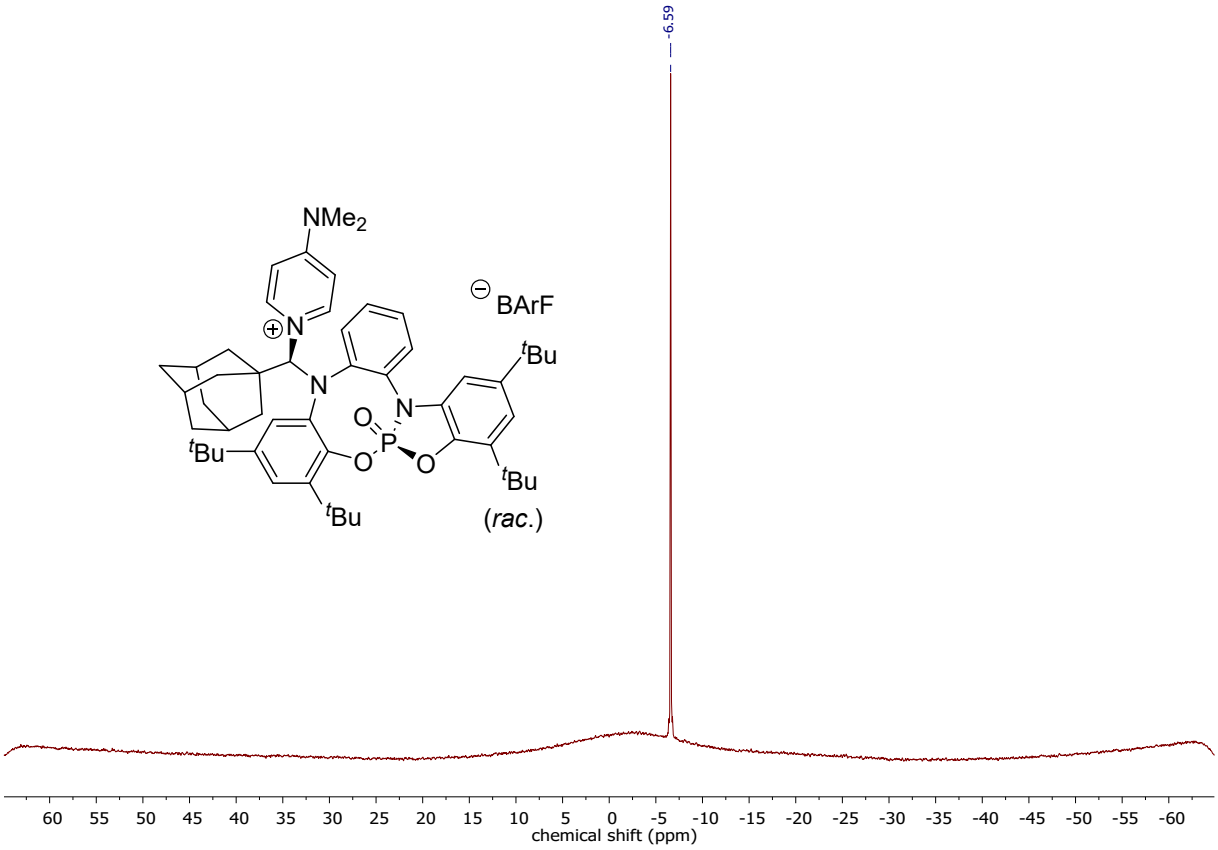
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of **6**



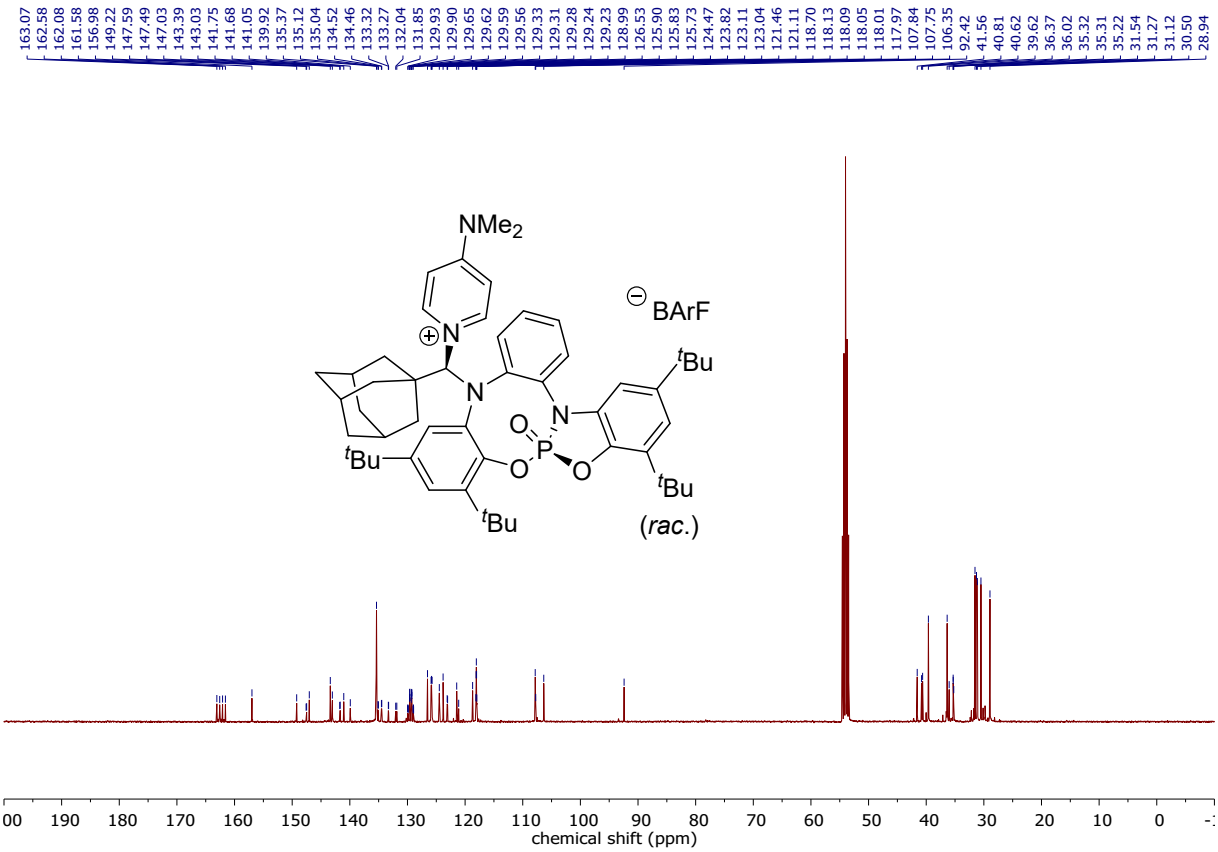
^{1}H NMR (400 MHz, CD_2Cl_2) of **7**


NMe2
BArF
tBu
tBu
tBu
tBu
(rac.)
chemical shift (ppm)

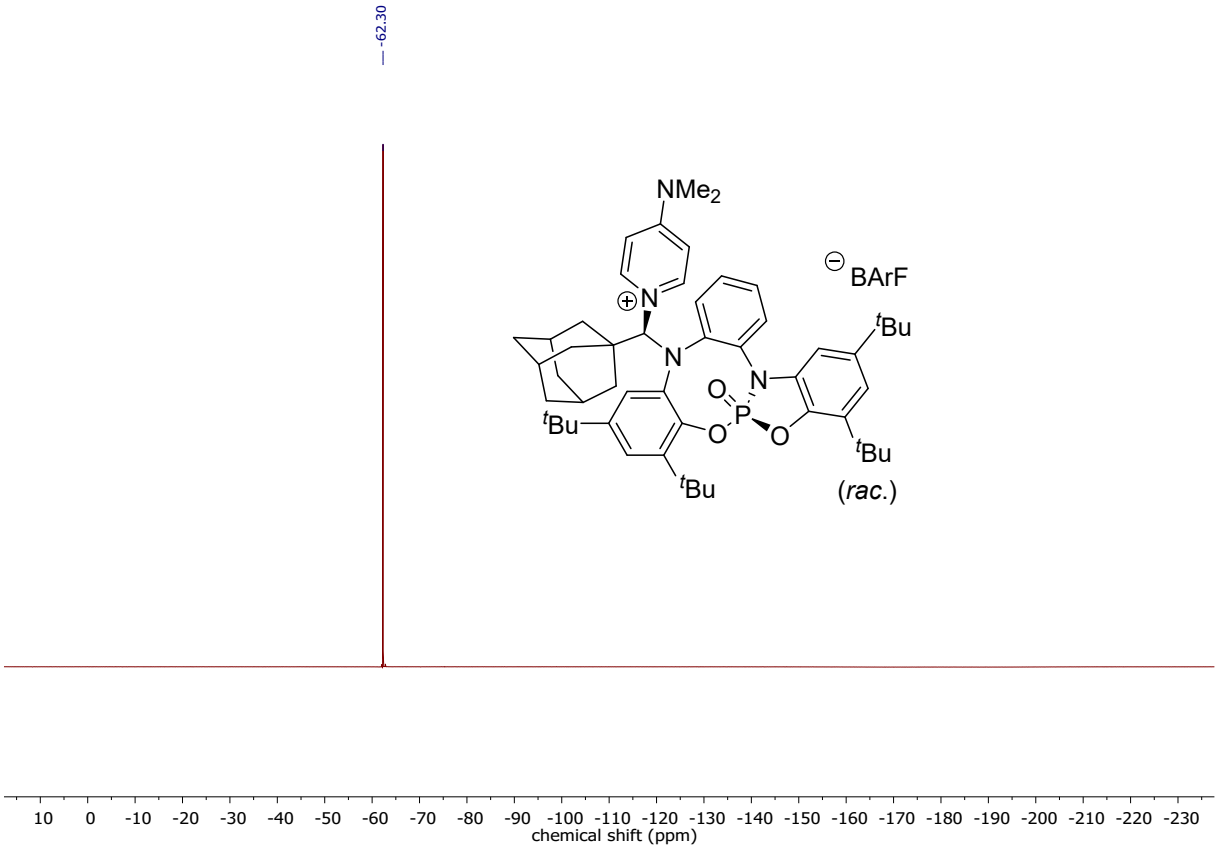
$^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2) of **7**



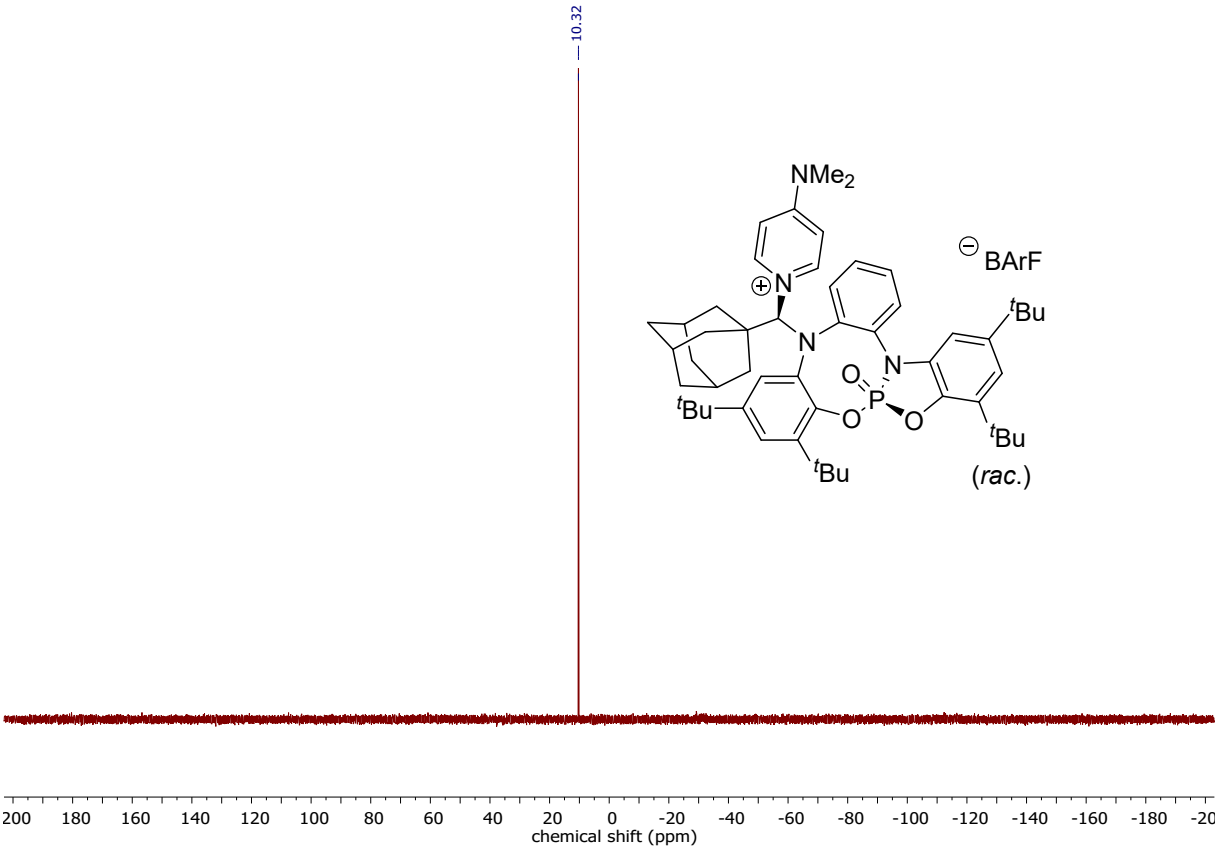
$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) of **7**


163.07
162.58
162.08
161.58
156.98
149.22
147.59
147.49
147.03
143.39
143.03
141.75
141.68
141.05
139.92
135.37
135.12
135.04
134.52
134.46
133.32
133.27
132.04
131.85
129.93
129.90
129.65
129.62
129.59
129.56
129.33
129.31
129.28
129.24
129.23
128.99
126.53
125.90
125.83
125.73
124.47
123.82
123.11
123.04
121.46
121.11
118.70
118.13
118.09
118.05
118.01
117.97
107.84
107.75
106.35
92.42
41.56
40.81
40.62
39.62
36.37
36.02
35.32
35.31
35.22
31.54
31.27
31.12
30.50
28.94
NMe2
BArF
tBu
tBu
tBu
tBu
(rac.)
chemical shift (ppm)

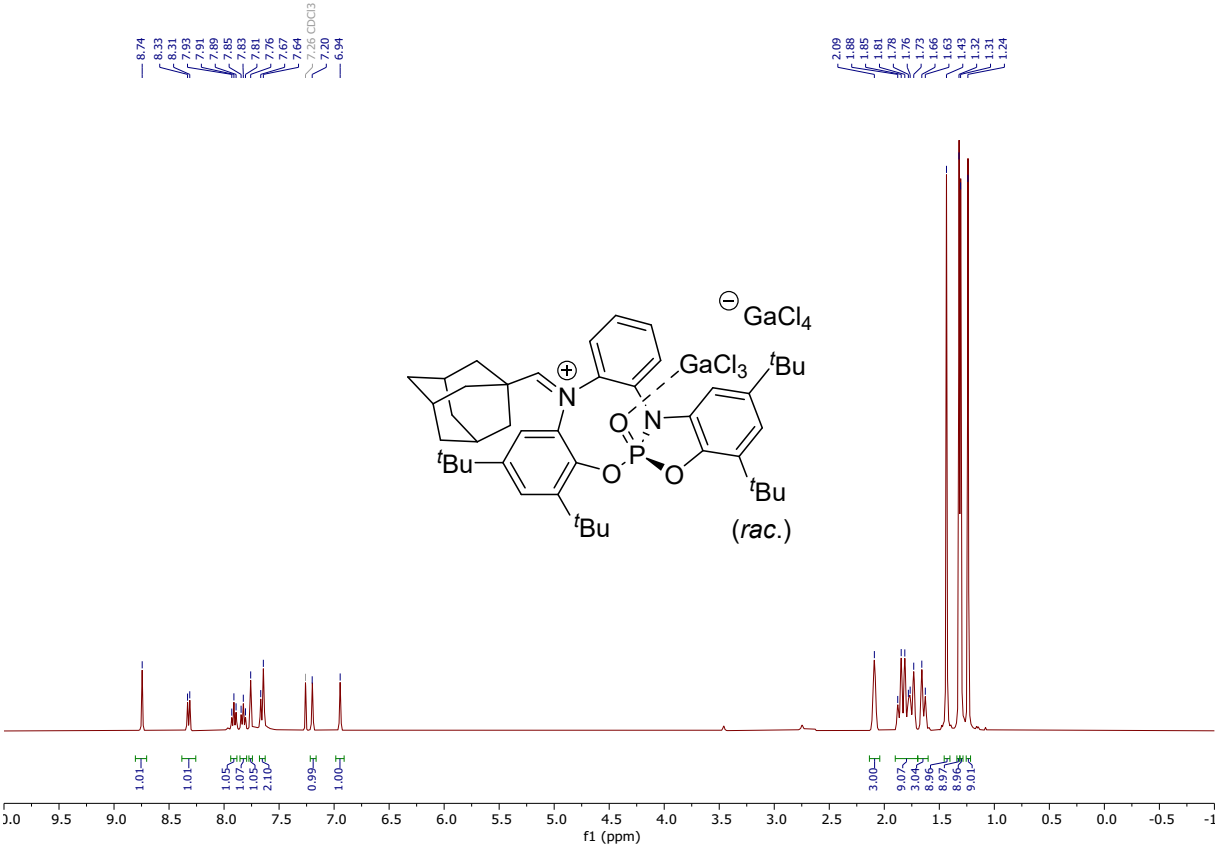
$^{19}F\{^{1}H\}$ NMR (377 MHz, CD_2Cl_2) of **7**



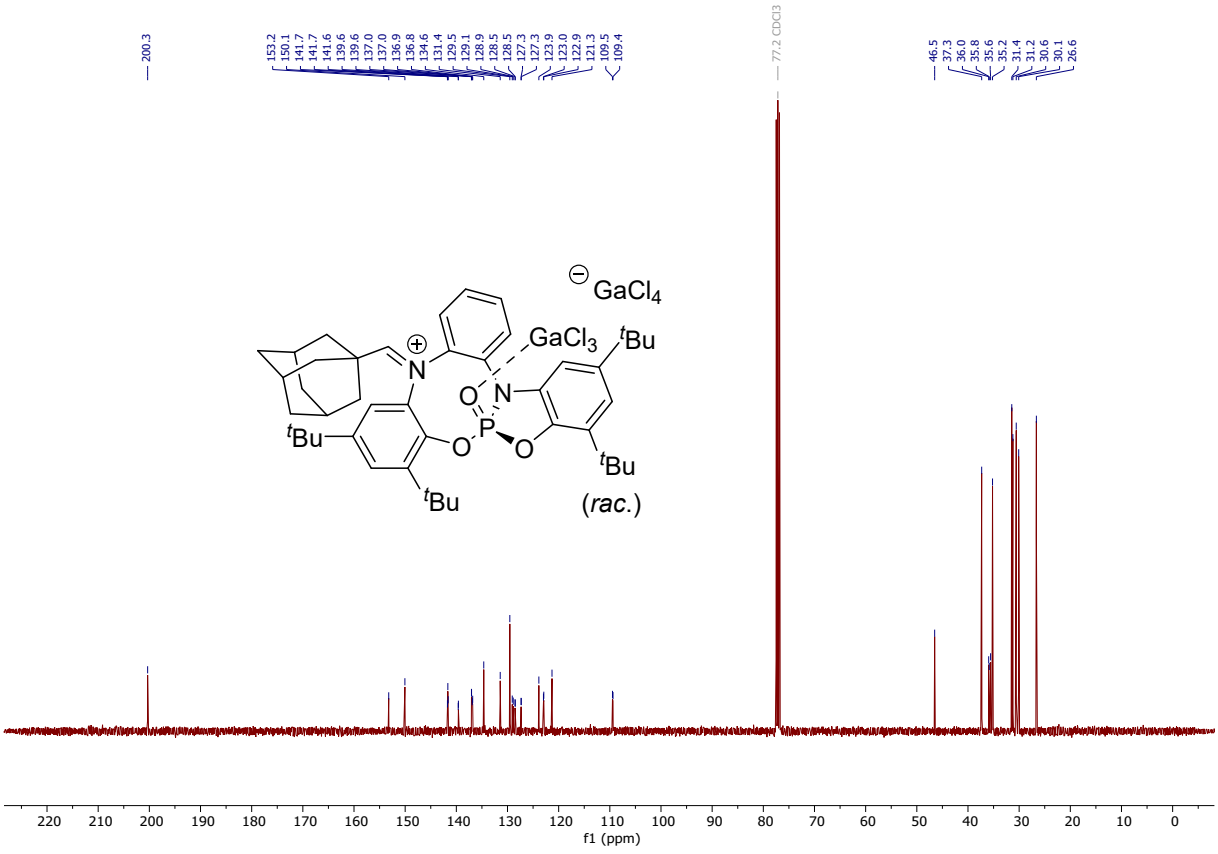
$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) of **7**


10.32
NMe2
BArF
tBu
tBu
tBu
tBu
(rac.)
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
chemical shift (ppm)

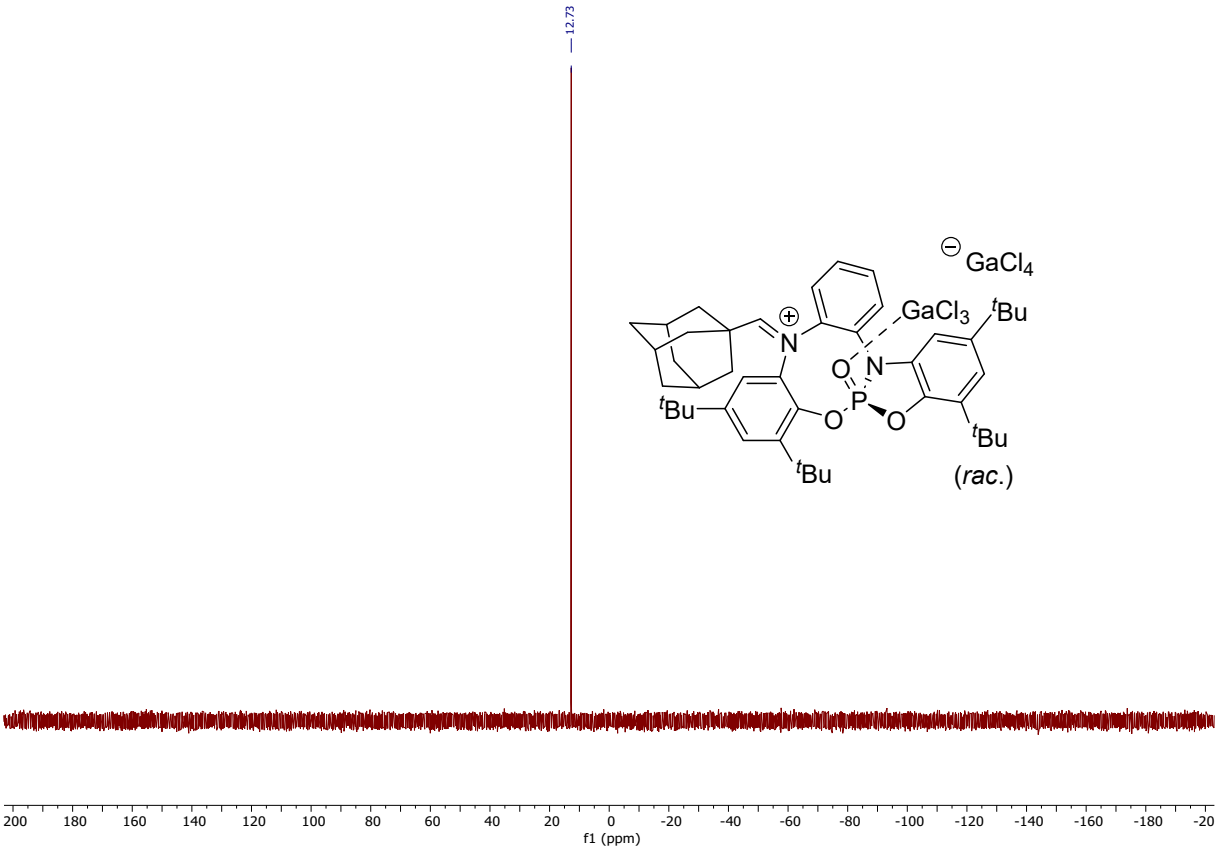
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



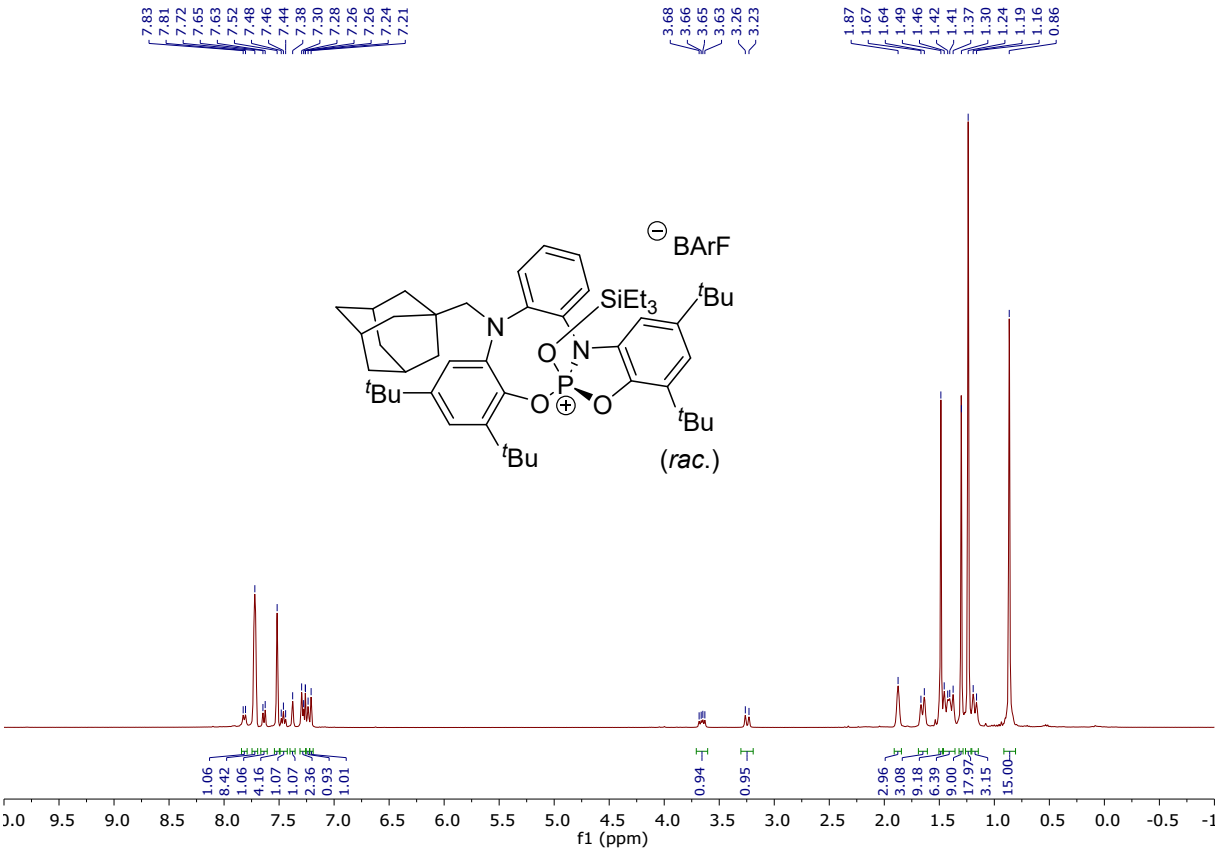
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **8**


200.3
153.2
150.1
141.7
141.7
141.6
139.6
139.6
137.0
137.0
136.9
136.8
134.6
131.4
129.5
129.1
128.9
128.5
128.5
127.3
127.3
123.9
123.0
122.9
121.3
109.5
109.4
77.2 CDCl3
46.5
37.3
36.0
35.8
35.6
35.2
31.4
31.2
30.6
30.1
26.6
GaCl4
GaCl3
tBu
tBu
tBu
tBu
(rac.)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

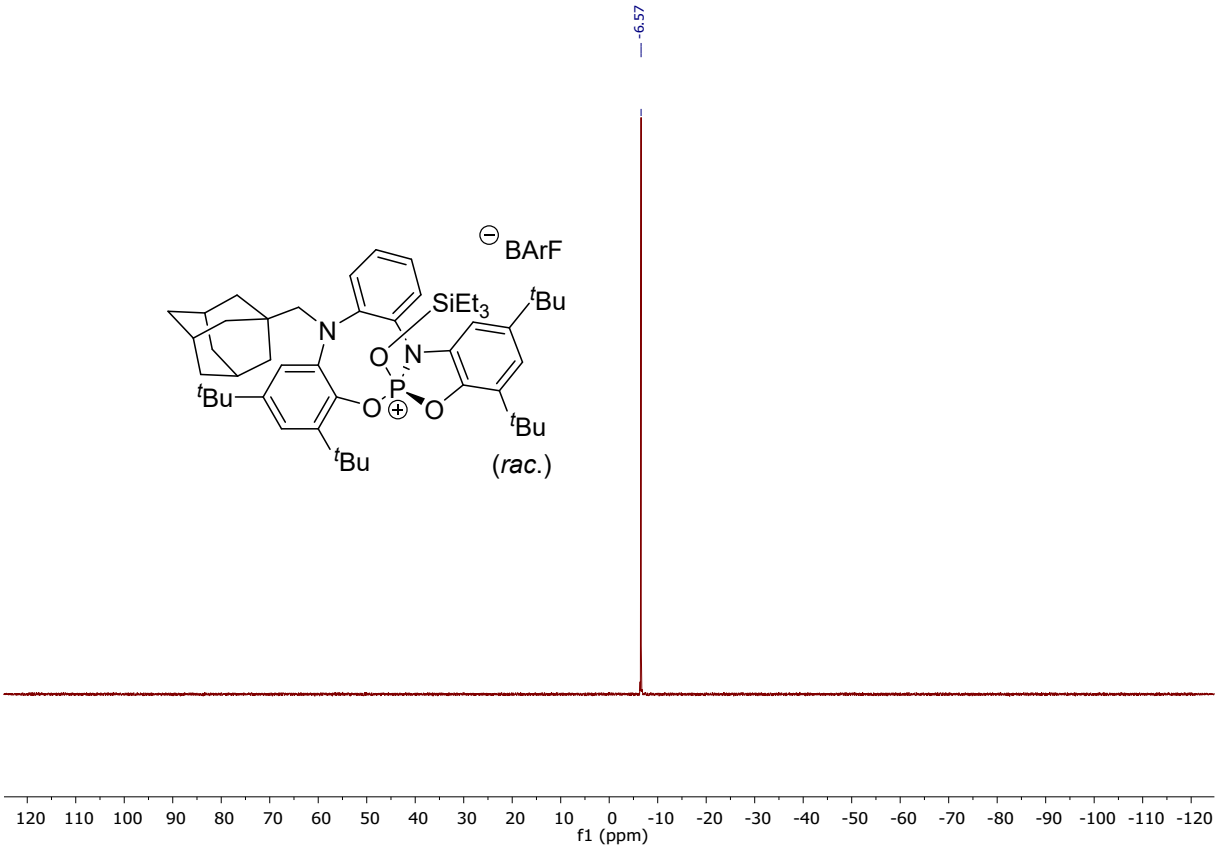
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **8**



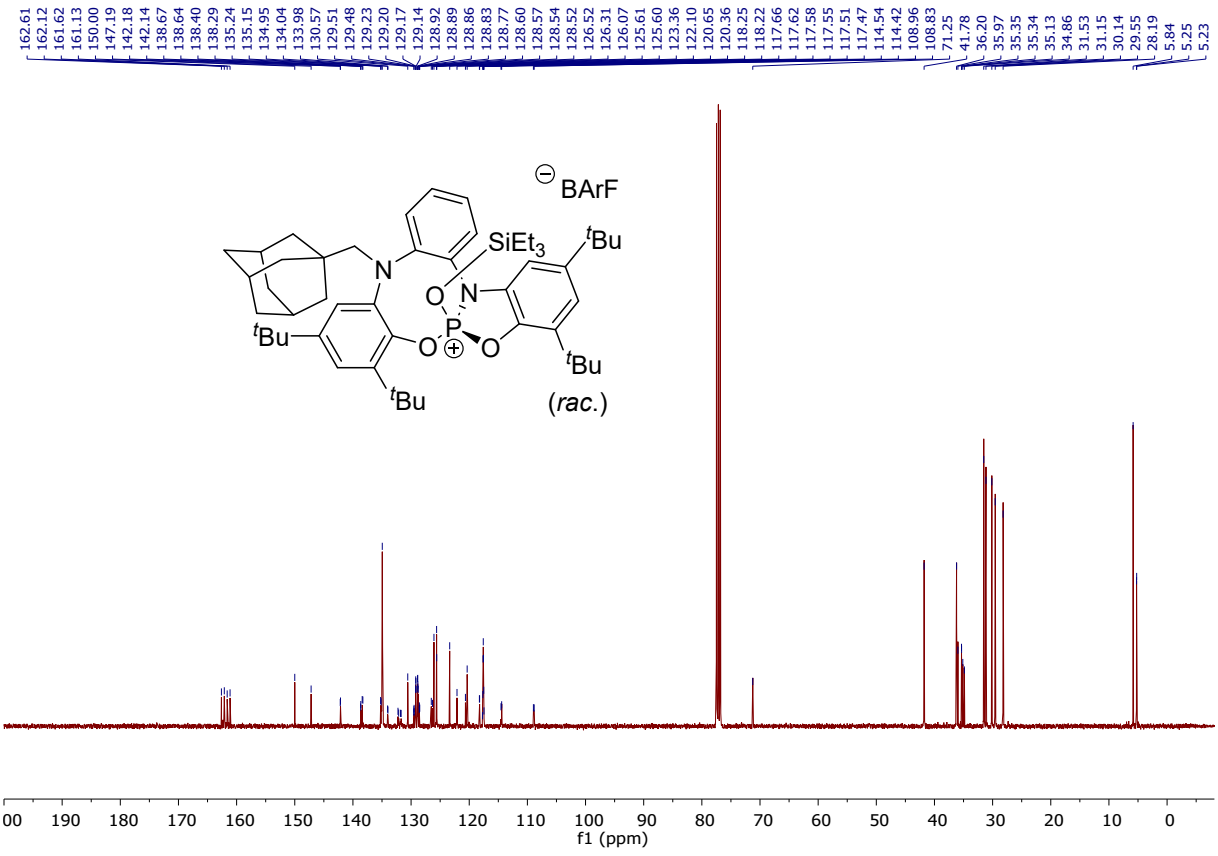
^{1}H NMR (400 MHz, $CDCl_3$) of **9**


7.83
7.81
7.72
7.65
7.63
7.52
7.48
7.46
7.44
7.38
7.30
7.28
7.26
7.26
7.24
7.21
3.68
3.66
3.65
3.63
3.26
3.23
1.87
1.67
1.64
1.49
1.46
1.42
1.41
1.37
1.30
1.24
1.19
1.16
0.86
BArF
SiEt3
tBu
tBu
tBu
tBu
N
O
N
O
P
O
(rac.)
1.06
8.42
1.06
4.16
1.07
1.07
2.36
0.93
1.01
0.94
0.95
2.96
3.08
9.18
6.39
9.00
17.97
3.15
15.00
f1 (ppm)

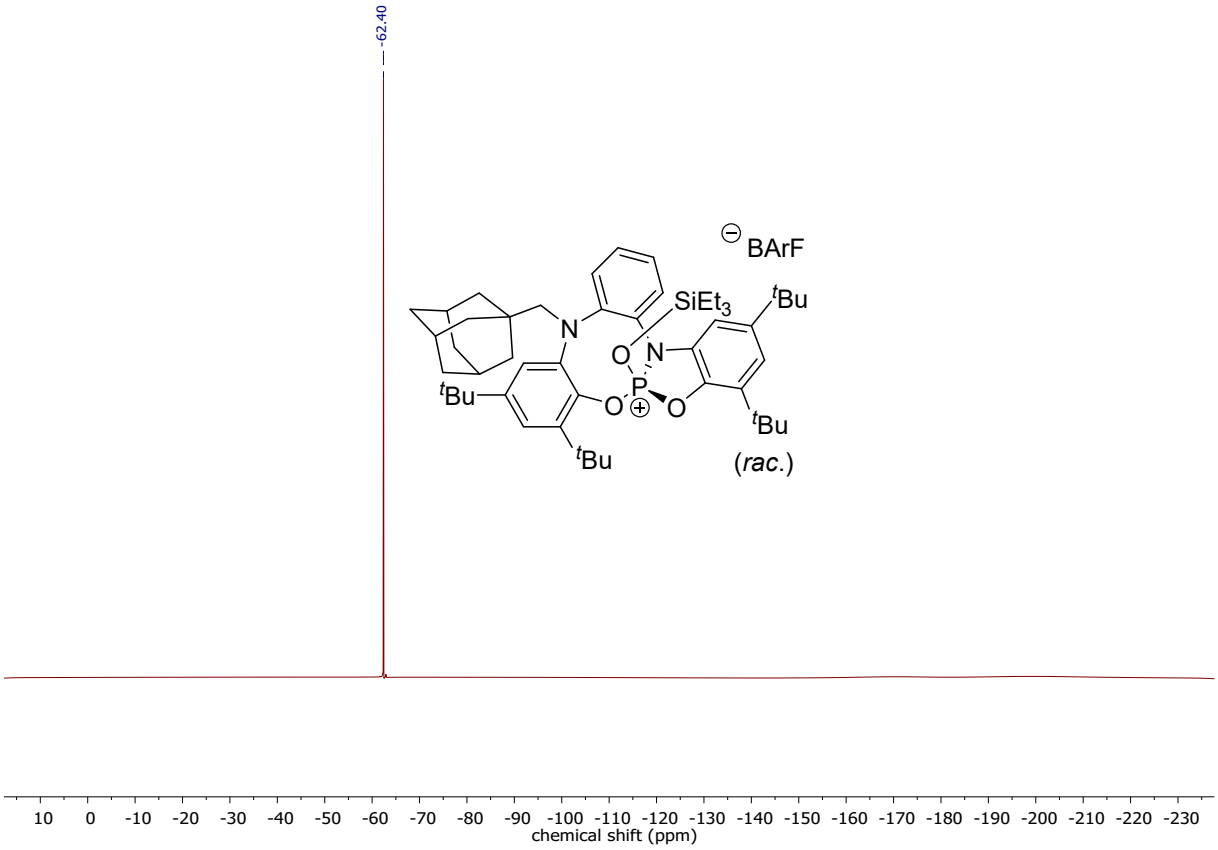
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) of **9**



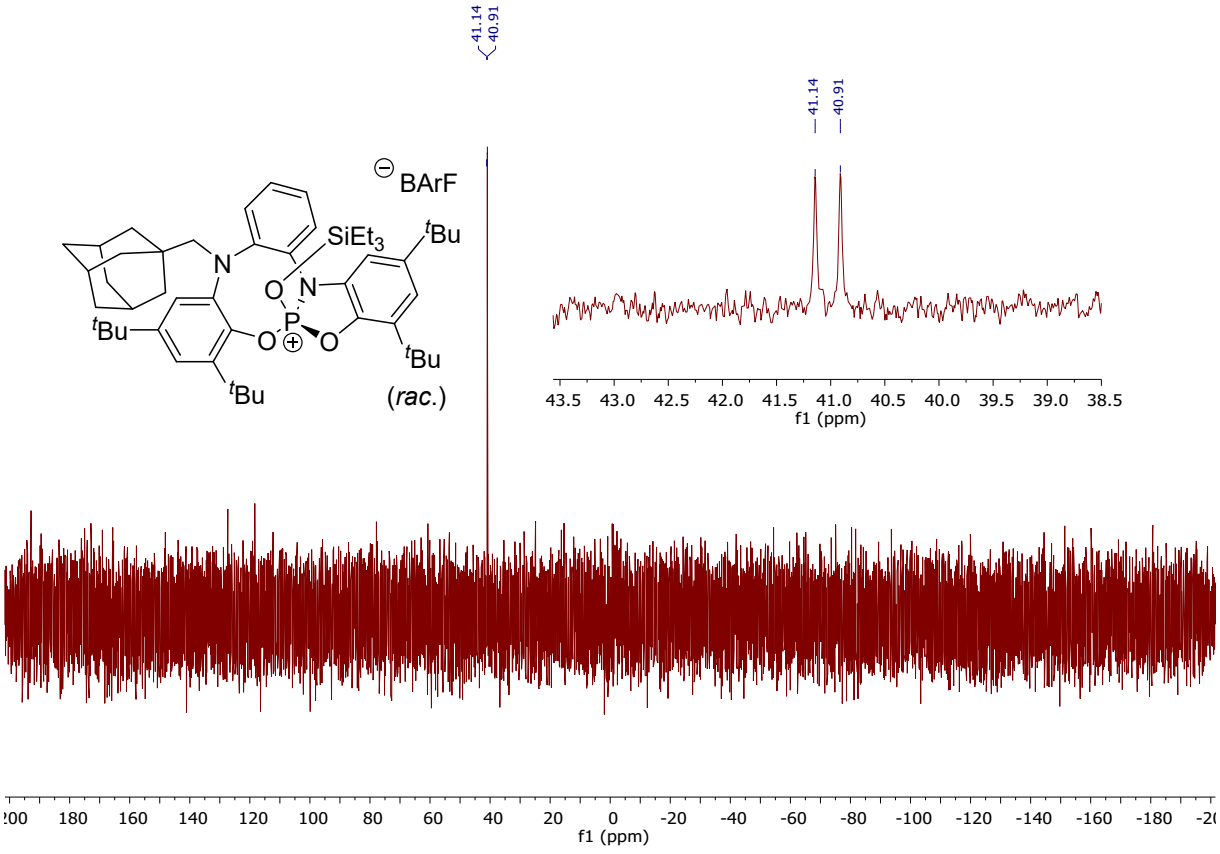
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **9**


162.61
162.12
161.62
161.13
150.00
147.19
142.18
142.14
138.67
138.64
138.40
138.29
135.24
135.15
134.95
134.04
133.98
130.57
129.51
129.48
129.23
129.20
129.17
129.14
128.92
128.89
128.86
128.83
128.77
128.60
128.57
128.54
128.52
126.52
126.31
126.07
125.61
125.60
123.36
122.10
120.65
120.36
118.25
118.22
117.66
117.62
117.58
117.55
117.51
117.47
114.54
114.42
108.96
108.83
71.25
41.78
36.20
35.97
35.35
35.34
35.13
34.86
31.53
31.15
30.14
29.55
28.19
5.84
5.25
5.23
⊖ BArF
SiEt3
tBu
tBu
tBu
tBu
(rac.)
N
O
N
O
P
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

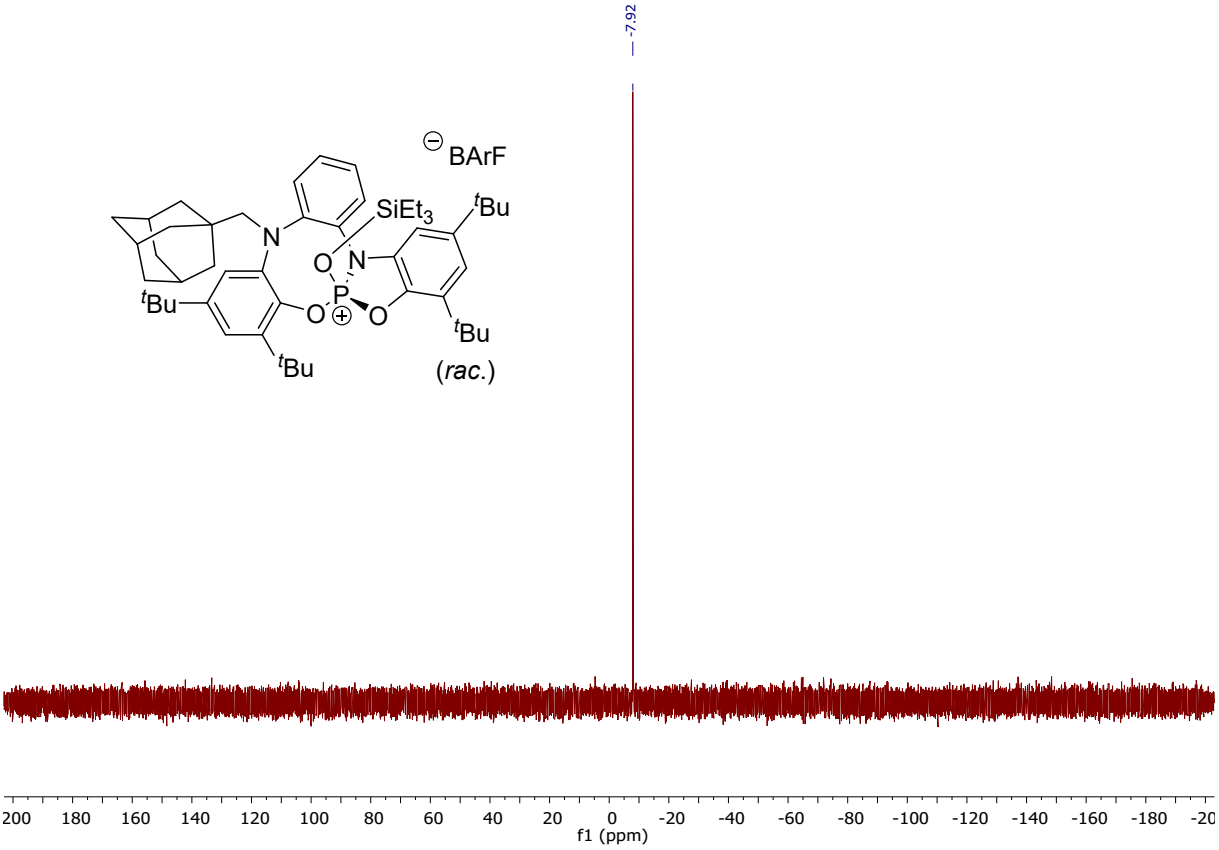
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of **9**



$^{29}Si\{^{1}H\}$-INEPT NMR (80 MHz, $CDCl_3$) of **9**


41.14
40.91
BArF
SiEt3
tBu
tBu
tBu
tBu
(rac.)
41.14
40.91
43.5 43.0 42.5 42.0 41.5 41.0 40.5 40.0 39.5 39.0 38.5
f1 (ppm)
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of **9**



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