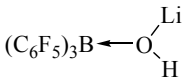
Experimental Section

All reactions were performed in the strict absence of oxygen and water under a purified argon atmosphere using glove-box or vacuum-line techniques. Solvents were dried by usual procedures and degassed before use. ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on Bruker spectrometers. Chemical shifts are given relative to external references (^{1}H, ^{13}C: TMS at 0; ^{19}F: $CFCl_3$ at 0; ^{11}B: $BF_3.OEt_2$ at 0). $B(C_6F_5)_3$, Cp_2ZrMe_2 and the phosphonium chlorides were purchased from commercial sources. The imidazolium and pyrrolidinium chlorides were prepared according to literature methods.

Preparation of (**1**) 

A mixture of $B(C_6F_5)_3$ (200 mg, 0.39 mmol, 1 eq) and anhydrous LiOH (11 mg, 0.39 mmol, 1 eq) was stirred at room temperature overnight. A white precipitate was filtered off and the yellow filtrate obtained as a white powder after removal of the volatile solvent was analyzed.
^{19}F NMR [282.4 MHz, C_6D_6] (δ, ppm): -133.7 (bs, o-F); -151.2 (bs, p-F); -162.0 (m, m-F). ^{1}H NMR [300.1 MHz, C_6D_6] (δ, ppm): 4.52 (s, 1H, OH). ^{13}C NMR [75.5 MHz, C_6D_6] (δ, ppm): 136.0, 139.48, 141.16, 144.64, 146.60; 149.88 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% C_6D_6)] (δ, ppm): 40.36 (s). IR [KBr]: ν(OH) = 3443 cm^{-1}.

General procedure :
Preparation of $[BMIM^+][B(C_6F_5)_3Cl^-]$ (**2**)
A solution of 1-butyl-3-methyl imidazolium chloride (80 mg, 0.46 mmol, 1 eq) in dichloromethane was added dropwise via a canula to a solution of $B(C_6F_5)_3$ (234 mg, 0.46 mmol, 1 eq) in dichloromethane at room temperature. After stirring at room temperature for several hours, the solvent was evaporated and **2** was obtained as a pale yellow oil.
^{19}F NMR [282.4 MHz, C_6D_6] (δ, ppm): -132.4 (dd, 6F, $^{3}J_{FF}$ = 7.9 Hz, $^{3}J_{FF}$ = 7.5 Hz, o-F); -160.8 (t, 3F, $^{3}J_{FF}$ = 20.9 Hz, p-F); -166.2 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, C_6D_6] (δ, ppm): 0.67 (t, 3H, $^{3}J_{HH}$ = 7.3 Hz, CH_3); 0.80 (sextet, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2); 0.99 (quintet, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2); 2.63 (s, 3H, CH_3); 3.05 (t, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2); 5.59 (m, 1H, CH); 5.66 (m, 1H, CH); 7.25 (s, 1H, CH). ^{13}C NMR [75.5 MHz, C_6D_6] (δ, ppm): 13.08 (CH_3); 19.34 (CH_2); 31.53 (CH_2); 35.28 (CH_3); 49.45 (CH_2); 121.10 (CH ($BMIm^+$)); 122.61 (CH ($BMIm^+$)); 134.72 (CH ($BMIm^+$)); 135.73, 137.92, 139.18, 141.28, 147.33, 150.61 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% C_6D_6)] (δ, ppm): -7.34 (s). ES-MS: positive mode [M = 139, $BMIm^+$]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$].

The same procedure as for (**2**) was used for the synthesis of (**4-9**).

$[BMMIM^+][B(C_6F_5)_3Cl^-]$ (**4**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.2 (dd, 6F, $^{3}J_{FF}$ = 8.0 Hz, $^{3}J_{FF}$ = 7.9 Hz, o-F); -162.4 (t, 3F, $^{3}J_{FF}$ = 20.5 Hz, p-F); -167.4 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.96 (t, 3H, $^{3}J_{HH}$ = 7.3 Hz, CH_3); 1.36 (sextet, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2); 1.78 (quintet, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2); 2.58 (s, 3H, CH_3); 3.78 (s, 3H, CH_3); 4.03 (t, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2); 7.17 (d, 1H, $^{3}J_{HH}$ = 2.4 Hz, CH); 7.18 (d, 1H, $^{3}J_{HH}$ = 2.4 Hz, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 10.25 (CH_3); 13.50 (CH_3); 20.53 (CH_2); 32.01 (CH_2); 36.18 (CH_3); 49.47 (CH_2); 121.60 (CH ($BMMIm^+$)); 123.11 (CH ($BMMIm^+$)); 135.45, 137.62, 138.70, 140.91 (CF); 143.87 (C(CH_3) ($BMMIm^+$));146.75, 150.0 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -7.49 (s). ES-MS: positive mode [M = 153, $BMMIm^+$]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$].

$[EMIM^+][B(C_6F_5)_3Cl^-]$ (**5**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.1 (dd, 6F, $^{3}J_{FF}$ = 7.7 Hz, $^{3}J_{FF}$ = 7.2 Hz, o-F); -161.8 (t, 3F, $^{3}J_{FF}$ = 20.6 Hz, p-F); -167.0 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 1.52 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_3); 3.93 (s, 3H, CH_3); 4.23 (quartet, 2H, $^{3}J_{HH}$ = 7.4 Hz, CH_2); 7.26 (m, 1H, CH); 7.29 (m, 1H, CH); 8.84 (s, 1H, CH). ^{13}C NMR [75.5 MHz, C_6D_6] (δ, ppm): 15.29 (CH_3); 37.01 (CH_3); 46.06 (CH_2); 122.48 (CH ($EMIm^+$)); 124.15 (CH ($EMIm^+$)); 135.42 (CH ($EMIm^+$)); 135.78, 137.81, 138.90, 141.03, 146.86, 150.03 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -7.17 (s). ES-MS: positive mode [M = 111, $EMIm^+$]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$].

$[BBIM^+][B(C_6F_5)_3Cl^-]$ (**6**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.3 (dd, 6F, $^{3}J_{FF}$ = 7.4 Hz, $^{3}J_{FF}$ = 7.5 Hz, o-F); -162.1 (t, 3F, $^{3}J_{FF}$ = 20.2 Hz, p-F); -167.2 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.95 (t, 6H, $^{3}J_{HH}$ = 7.4 Hz, CH_3); 1.34 (sextet, 4H, $^{3}J_{HH}$ = 7.4 Hz, CH_2); 1.84 (quintet, 4H, $^{3}J_{HH}$ = 7.4 Hz, CH_2); 4.15 (t, 4H, $^{3}J_{HH}$ = 7.4 Hz, CH_2); 7.28 (bs, 2H, CH); 8.64 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.38 (CH_3); 19.80 (CH_2); 32.31 (CH_2);

50.79 (CH_2); 122.84 (CH ($BBIm^+$)); 134.76 (CH ($BBIm^+$)); 135.55, 137.68, 138.66, 140.97, 146.67, 150.12 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -7.18 (s). ES-MS: positive mode [M = 181, $BBIm^+$]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$], [M = 1275, $[2\times B(C_6F_5)_3Cl^- + BBIm^+]^-$].

$[BMpy^+][B(C_6F_5)_3Cl^-]$ (**7**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.2 (dd, 6F, $^3J_{FF}$ = 6.9 Hz, $^3J_{FF}$ = 7.5 Hz, o-F); -162.2 (t, 3F, $^3J_{FF}$ = 20.7 Hz, p-F); -167.3 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.98 (t, 3H, $^3J_{HH}$ = 7.7 Hz, CH_3); 1.40 (sextet, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2); 1.73 (quintet, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2); 2.25 (bs, 4H, CH_2); 3.0 (s, 3H, CH_3); 3.23 (m, 2H, CH_2); 3.44 (m, 4H, CH_2). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.53 (CH_3); 20.02 (CH_2); 22.11 (CH_2); 26.19 (CH_2); 49.37 (CH_3); 65.50 (CH_2); 65.62 (CH_2); 135.48, 137.70, 138.76, 141.02, 146.84, 150.01 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -7.27 (s). ES-MS: positive mode [M = 142, $BMpy^+$]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$].

$[Bu_4P^+][B(C_6F_5)_3Cl^-]$ (**8**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.0 (dd, 6F, $^3J_{FF}$ = 7.7 Hz, $^3J_{FF}$ = 7.7 Hz, o-F); -162.5 (t, 3F, $^3J_{FF}$ = 20.4 Hz, p-F); -167.4 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.96 (t, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3); 1.47-1.50 (m, 16H, CH_2); 1.98-2.07 (m, 8H, PCH_2). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.32 (CH_3); 19.04 (d, $^1J_{PC}$ = 49.8 Hz, PCH_2); 23.74 (d, $^2J_{PC}$ = 4.6 Hz, CH_2); 24.20 (d, $^3J_{PC}$ = 14.9 Hz, CH_2); 135.61, 137.59, 138.75, 140.91, 146.79, 149.98 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -7.45 (s). ^{31}P NMR [121.5 MHz, CD_2Cl_2] (δ, ppm): 33.39 (s) ($^1J_{PC}$ = 48.1 Hz, $^2J_{PC}$ = 14.7 Hz). ES-MS: positive mode [M = 259, Bu_4P^+]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$], [M = 1353, $[2\times B(C_6F_5)_3Cl^- + Bu_4P^+]^-$].

$[Ph_4P^+][B(C_6F_5)_3Cl^-]$ (**9**)
White powder. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.0 (dd, 6F, $^3J_{FF}$ = 7.8 Hz, $^3J_{FF}$ = 7.2 Hz, o-F); -162.8 (t, 3F, $^3J_{FF}$ = 20.1 Hz, p-F); -167.5 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 7.58-7.93 (m, 20H, Ph). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 117.88 (d, $^1J_{PC}$ = 90.2 Hz, PC); 130.90 (d, $^3J_{PC}$ = 12.9 Hz, m-CH); 134.74 (d, $^2J_{PC}$ = 10.6 Hz, o-CH); 136.04 (bs, p-CH); 135.46, 137.56, 138.61, 140.79, 146.79, 149.98 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -7.60 (s). ^{31}P NMR [121.5 MHz, CD_2Cl_2] (δ, ppm): 23.43 (s) ($^1J_{PC}$ = 89.0 Hz, $^2J_{PC}$ = 10.3 Hz). ES-MS: positive mode [M = 339, Ph_4P^+]; negative mode [M = 547, $B(C_6F_5)_3Cl^-$], [M = 1433, $[2\times B(C_6F_5)_3Cl^- + Ph_4P^+]^-$].

Preparation of $[BMIM^+][B(C_6F_5)_3OH^-]$ (**3**)
A solution of **2** (0.46 mmol, 1 eq) in dichloromethane was added dropwise via a canula to a suspension of anhydrous LiOH (11 mg, 0.46 mmol, 1 eq) in dichloromethane at room temperature. The reaction mixture was stirred overnight and the white precipitate of LiCl was filtered. Solvent was removed under vacuum to leave **3** as a pale yellow oil.
^{19}F NMR [282.4 MHz, C_6D_6] (δ, ppm): -135.9 (d, 6F, $^3J_{FF}$ = 21.3 Hz, o-F); -161.7 (t, 3F, $^3J_{FF}$ = 20.7 Hz, p-F); -165.8 (m, 6F, m-F). ^1H NMR [300.1 MHz, C_6D_6] (δ, ppm): 0.64 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3); 0.75 (sextet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 0.94 (quintet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 2.09 (s, 1H, OH); 2.56 (s, 3H, CH_3); 3.04 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 5.32 (m, 1H, CH); 5.43 (m, 1H, CH); 9.19 (s, 1H, CH). ^{13}C NMR [75.5 MHz, C_6D_6] (δ, ppm): 13.07 (CH_3); 19.30 (CH_2); 31.63 (CH_2); 34.72 (CH_3); 49.08 (CH_2); 120.42 (CH ($BMIm^+$)); 121.84 (CH ($BMIm^+$)); 135.72 (CH ($BMIm^+$)); 137.57, 137.87, 139.11, 140.90, 147.25, 150.39 (CF).
^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -137.0 (d, 6F, $^3J_{FF}$ = 21.3 Hz, o-F); -163.1 (t, 3F, $^3J_{FF}$ = 20.7 Hz, p-F); -167.0 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.92 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3); 1.29 (sextet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 1.78 (quintet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 1.84 (s, 1H, OH); 3.84 (s, 3H, CH_3); 4.07 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 7.21 (m, 2H, CH); 9.45 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.32 (CH_3); 19.71 (CH_2); 32.29 (CH_2); 36.65 (CH_3); 50.47 (CH_2); 122.60 (CH ($BMIm^+$)); 123.89 (CH ($BMIm^+$)); 135.49 (CF); 136.97 (CH ($BMIm^+$)); 137.27, 138.69, 140.47, 146.73, 149.86 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% C_6D_6)] (δ, ppm): -4.69 (s). ES-MS: positive mode [M = 139, $BMIm^+$], [M = 806, $[2\times BMIm^+ + B(C_6F_5)_3OH^-]^+$]; negative mode [M = 529, $B(C_6F_5)_3OH^-$], [M = 1196, $[2\times B(C_6F_5)_3OH^- + BMIm^+]^-$]. IR [KBr]: ν(OH) = 3679 cm^{-1}.

The same procedure as for (**3**) was used for the synthesis of (**10**-**15**).
$[BMMIM^+][B(C_6F_5)_3OH^-]$ (**10**)
Colorless liquid. Yield: 81 %. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -136.8 (d, 6F, $^3J_{FF}$ = 21.5 Hz, o-F); -163.7 (t, 3F, $^3J_{FF}$ = 20.3 Hz, p-F); -167.4 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.95 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3); 1.35 (sextet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 1.67 (s, 1H, OH); 1.75 (quintet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 2.58 (s, 3H, CH_3); 3.78 (s, 3H, CH_3); 4.03 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 7.21 (d, 1H, $^3J_{HH}$ = 2.1 Hz, CH); 7.27 (d, 1H, $^3J_{HH}$ = 2.1 Hz, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 9.86 (CH_3); 13.41 (CH_3); 19.88 (CH_2); 31.98 (CH_2); 35.76 (CH_3); 49.24 (CH_2); 121.53 (CH ($BMMIm^+$)); 123.14 (CH ($BMMIm^+$)); 135.32, 137.24, 138.63, 140.48 (CF); 143.80 (C(CH_3) ($BMMIm^+$));146.80, 149.96 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -4.52 (s). ES-MS: positive mode [M = 153, $BMMIm^+$]; negative mode [M = 529, $B(C_6F_5)_3OH^-$]. IR [KBr]: ν(OH) = 3689 cm^{-1}.

$[EMIM^+][B(C_6F_5)_3OH^-]$ (**11**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -136.7 (d, 6F, $^3J_{FF}$ = 22.1 Hz, o-F); -163.0 (t, 3F, $^3J_{FF}$ = 20.1 Hz, p-F); -167.0 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 1.48 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3); 1.90 (s, 1H, OH); 3.86 (s, 3H, CH_3); 4.16 (quartet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 7.21 (m, 1H, CH); 7.25 (m, 1H, CH); 9.46 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 15.32 (CH_3); 36.57 (CH_3); 45.82 (CH_2); 122.13 (CH ($EMIm^+$)); 123.91 (CH ($EMIm^+$)); 135.35 (CF); 137.0 (CH ($EMIm^+$)); 137.20, 138.63, 140.47, 146.72, 149.88 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -4.45 (s). ES-MS: positive mode [M = 751, $[2\times EMIm^+ + B(C_6F_5)_3OH^-]^+$]; negative mode [M = 529, $B(C_6F_5)_3OH^-$], [M = 1169, $[2\times B(C_6F_5)_3OH^- + EMIm^+]^-$]. IR [KBr]: ν(OH) = 3685 cm^{-1}.

$[BBIM^+][B(C_6F_5)_3OH^-]$ (**12**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -136.8 (d, 6F, $^3J_{FF}$ = 21.8 Hz, o-F); -163.2 (t, 3F, $^3J_{FF}$ = 20.3 Hz, p-F); -167.1 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.93 (t, 6H, $^3J_{HH}$ = 7.5 Hz, CH_3); 1.29 (sextet, 4H, $^3J_{HH}$ = 7.5 Hz, CH_2); 1.77 (quintet, 4H, $^3J_{HH}$ = 7.5 Hz, CH_2); 1.81 (s, 1H, OH); 4.09 (t, 4H, $^3J_{HH}$ = 7.5 Hz, CH_2); 7.23 (bs, 1H, CH); 7.24 (bs, 1H, CH); 9.47 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.35 (CH_3); 19.75 (CH_2); 32.34 (CH_2); 50.35 (CH_2); 122.52 (CH ($BBIm^+$)); 135.38 (CF); 136.63 (CH ($BBIm^+$)); 137.17, 138.64, 140.43, 146.72, 149.98 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -4.43 (s). ES-MS: [M = 181, $BBIm^+$], [M = 891, $[2\times BBIm^+ + B(C_6F_5)_3OH^-]^+$]; negative mode [M = 529, $B(C_6F_5)_3OH^-$], [M = 1239, $[2\times B(C_6F_5)_3OH^- + BBIm^+]^-$]. IR [KBr]: ν(OH) = 3683 cm^{-1}.

$[BMpy^+][B(C_6F_5)_3OH^-]$ (**13**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -136.8 (d, 6F, $^3J_{FF}$ = 21.9 Hz, o-F); -163.5 (t, 3F, $^3J_{FF}$ = 20.0 Hz, p-F); -167.2 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.98 (t, 3H, $^3J_{HH}$ = 7.7 Hz, CH_3); 1.38 (sextet, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2); 1.68 (s, 1H, OH); 1.70 (quintet, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2); 2.23 (bs, 4H, CH_2); 3.0 (s, 3H, CH_3); 3.25 (m, 2H, CH_2); 3.44 (m, 4H, CH_2). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.53 (CH_3); 20.02 (CH_2); 22.05 (CH_2); 26.16 (CH_2); 49.19 (CH_3); 65.29 (CH_2); 65.38 (CH_2); 135.27, 137.22, 138.63, 140.40, 146.76, 149.94 (CF). ^{11}B NMR [96.3 MHz, (CH_2Cl_2, 10% CD_2Cl_2)] (δ, ppm): -4.44 (s). ES-MS: positive mode [M = 142, $BMpy^+$]; negative mode [M = 529, $B(C_6F_5)_3OH^-$]. IR [KBr]: ν(OH) = 3688 cm^{-1}.

$[Bu_4P^+][B(C_6F_5)_3OH^-]$ (**14**)
Colorless liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -136.8 (d, 6F, $^3J_{FF}$ = 21.7 Hz, o-F); -163.8 (t, 3F, $^3J_{FF}$ = 20.4 Hz, p-F); -167.3 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.96 (t, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3); 1.44-1.52 (m, 16H, CH_2); 1.64 (s, 1H, OH); 1.97-2.07 (m, 8H, PCH_2). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.34 (CH_3); 19.01 (d, $^1J_{PC}$ = 48.0 Hz, PCH_2); 23.73 (d, $^2J_{PC}$ = 4.6 Hz, CH_2); 24.22 (d, $^3J_{PC}$ = 15.1 Hz, CH_2); 135.45, 137.03, 138.71, 140.30, 146.53, 146.90 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -4.50 (s). ^{31}P NMR [121.5 MHz, CD_2Cl_2] (δ, ppm): 33.41 (s) ($^1J_{PC}$ = 47.7 Hz, $^2J_{PC}$ = 15.2 Hz). ES-MS: positive mode [M = 259, Bu_4P^+]; negative mode [M = 529, $B(C_6F_5)_3OH^-$]. IR [KBr]: ν(OH) = 3689 cm^{-1}.

$[Ph_4P^+][B(C_6F_5)_3OH^-]$ (**15**)
In this case, 4 days of stirring were necessary to complete the anion exchange.
White foam. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -136.6 (d, 6F, $^3J_{FF}$ = 21.8 Hz, o-F); -164.1 (t, 3F, $^3J_{FF}$ = 20.6 Hz, p-F); -167.5 (m, 6F, m-F). ^1H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 1.56 (s, 1H, OH); 7.56-7.93 (m, 20H, Ph). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 117.92 (d, $^1J_{PC}$ = 88.9 Hz, PC); 130.89 (d, $^3J_{PC}$ = 12.7 Hz, m-CH); 134.74 (d, $^2J_{PC}$ = 10.3 Hz, o-CH); 136.01 (bs, p-CH); 135.26, 136.99, 138.35, 140.16, 146.73, 149.86 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -4.48 (s). ^{31}P NMR [121.5 MHz, CD_2Cl_2] (δ, ppm): 23.43 (s) ($^1J_{PC}$ = 90.6 Hz, $^2J_{PC}$ = 11.3 Hz). ES-MS: positive mode [M = 339, Ph_4P^+]; negative mode [M = 529, $B(C_6F_5)_3OH^-$], [M = 1397, $[2\times B(C_6F_5)_3OH^- + Ph_4P^+]^-$]. IR [KBr]: ν(OH) = 3693 cm^{-1}.

Preparation of

A solution of [BMIM$^+$][B(C_6F_5)$_3$OH$^-$] (0.54 mmol) in toluene (8 ml) was added dropwise to a solution of Cp_2ZrMe_2 (0.54 mmol, 137 mg, 1 eq) in toluene (8 ml) at low temperature. After stirring 1h, the yellow solution settled to a red phase isolated and identified to [BMIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$]. The yellow upper solution was also analyzed and mainly contained $Cp_2Zr(Me)OZr(Me)Cp_2$ (**23**).

[BMIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**16**) ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.9 (d, 6F, $^3J_{FF}$ = 22.5 Hz, o-F); -164.4 (t, 3F, $^3J_{FF}$ = 20.8 Hz, p-F); -167.8 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.19 (s, 3H, Zr-CH_3), 0.97 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_3); 1.34 (sextet, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 1.81 (quintet, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 3.85 (s, CH_3); 4.1 (t, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 5.77 (s, 10H, Cp); 7.15 (s, 2H, CH); 8.17 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.39 (CH_3); 17.66 (Zr-CH_3); 19.68 (CH_2); 32.25 (CH_2); 36.66 (CH_3); 50.43 (CH_2); 109.69 (Cp); 122.41 (CH (BMIM$^+$)); 123.76 (CH (BMIM$^+$)); 135.06, 136.85 (CF), 138.34 (CH (BMIM$^+$)); 138.35, 139.92, 146.58, 149.79 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.93 (s). ES-MS: positive mode [M = 139, BMIM$^+$]; negative mode [M = 763, $Cp_2Zr(Me)OB(C_6F_5)_3^-$].

$Cp_2Zr(Me)OZr(Me)Cp_2$ (**23**)

White powder. ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.014 (s, 6H, Zr-CH_3), 5.97 (s, 20H, Cp). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 19.86 (Zr-CH_3); 110.95 (Cp).EI (m/z, int): 471 ([$M^{+\bullet}$ – CH_3], 100); 391 ([$M^{+\bullet}$ – 2CH_3 – Cp], 24).

Preparation of [BMMIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**17**)

A solution of [BMMIM$^+$][B(C_6F_5)$_3$OH$^-$] (0.46 mmol) in dichloromethane (8 ml) was added dropwise to a solution of Cp_2ZrMe_2 (0.46 mmol, 116 mg, 1 eq) in dichloromethane (8 ml) at low temperature. After stirring 1h, the yellow solution was analyzed and the compounds [BMMIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**17**), $Cp_2Zr(Me)OZr(Me)Cp_2$ (**23**) were identified.

[BMMIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**17**)

^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.9 (d, 6F, $^3J_{FF}$ = 22.8 Hz, o-F); -164.6 (t, 3F, $^3J_{FF}$ = 20.8 Hz, p-F); -167.9 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.23 (s, 3H, Zr-CH_3), 0.97 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_3); 1.35 (sextet, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 1.77 (quintet, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 2.53 (s, CH_3); 3.73 (s, CH_3); 3.99 (t, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 5.74 (s, 10H, Cp); 7.12 (s, 2H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 9.82 (CH_3); 13.41 (CH_2); 17.52 (Zr-CH_3); 19.89 (CH_2); 31.94 (CH_2); 35.76 (CH_3); 49.27 (CH_2); 109.66 (Cp); 121.52 (CH (BMMIM$^+$)); 122.98 (CH (BMMIM$^+$)); 135.10, 136.74, 138.37; 139.95 (CF), 143.68 (C(CH_3) (BMMIM$^+$)), 146.70, 149.89 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.97 (s).

The same procedure as for (**16**) was used for the synthesis of (**18-22**).

[EMIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**18**)

Red liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -134.0 (d, 6F, $^3J_{FF}$ = 28.5 Hz, o-F); -164.5 (t, 3F, $^3J_{FF}$ = 21.0 Hz, p-F); -167.9 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.18 (s, 3H, Zr-CH_3), 1.50 (t, 6H, $^3J_{HH}$ = 7.6 Hz, CH_3); 3.84 (s, 3H, CH_3); 4.14 (quartet, 4H, $^3J_{HH}$ = 7.6 Hz, CH_2); 5.77 (s, 10H, Cp); 7.16 (s, 1H, CH), 7.20 (s, 1H, CH), 8.67 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 15.19 (CH_3); 17.82 (Zr-CH_3); 36.62 (CH_2); 49.94 (CH_2); 109.80 (Cp); 122.35 (CH (EMIM$^+$)); 124.0 (CH (EMIM$^+$)); 135.23, 136.99 (CF); 138.44 (CH (EMIM$^+$)), 138.71, 140.30, 146.84, 150.02 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.92 (s).

[BBIM$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**19**)

Red liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -134.0 (d, 6F, $^3J_{FF}$ = 23.9 Hz, o-F); -164.4 (t, 3F, $^3J_{FF}$ = 20.3 Hz, p-F); -167.8 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.17 (s, 3H, Zr-CH_3), 0.97 (t, 6H, $^3J_{HH}$ = 7.3 Hz, CH_3); 1.35 (sextet, 4H, $^3J_{HH}$ = 7.3 Hz, CH_2); 1.82 (quintet, 4H, $^3J_{HH}$ = 7.3 Hz, CH_2); 4.1 (t, 4H, $^3J_{HH}$ = 7.3 Hz, CH_2); 5.78 (s, 10H, Cp); 7.19 (s, 2H, CH), 8.33 (s, 1H, CH). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.31 (CH_3); 17.80 (Zr-CH_3); 19.76 (CH_2); 32.24 (CH_2); 50.53 (CH_2); 109.78 (Cp); 122.73 (CH (BBIM$^+$)); 135.03 (CH (BBIM$^+$), 135.03 (CF); 136.76, 138.36, 139.93, 146.74, 149.78 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.88 (s).

[BMpy$^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**20**)

Red liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -134.0 (d, 6F, $^3J_{FF}$ = 25.2 Hz, o-F); -164.7 (t, 3F, $^3J_{FF}$ = 20.2 Hz, p-F); -167.9 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.22 (s, 3H, Zr-CH_3); 0.96 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_3); 1.37 (sextet, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2); 1.68 (quintet, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2); 2.2 (bs, 4H, CH_2); 3.07 (s, 3H, CH_3); 3.31 (m, 2H, CH_2); 3.49-3.57 (m, 4H, CH_2); 5.74 (s, 10H, Cp). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 13.64 (CH_3); 17.50 (Zr-CH_3); 20.07 (CH_2); 22.0 (CH_2); 26.11 (CH_2); 48.99 (CH_3); 64.59 (CH_2); 64.86 (CH_2); 109.68 (Cp); 134.99, 136.85, 138.38, 139.99, 146.67, 149.79 (CF). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.95 (s).

[Bu_4P^+][$Cp_2Zr(Me)OB(C_6F_5)_3^-$] (**21**)

Yellow powder. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -133.9 (d, 6F, $^3J_{FF}$ = 24.3 Hz, o-F); -164.6 (t, 3F, $^3J_{FF}$ = 20.2 Hz, p-F); -167.9 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.21 (s, 3H, Zr-CH_3); 0.98 (t, 12H, $^3J_{HH}$ = 6.9 Hz, CH_3); 1.46-1.51 (m, 16H, CH_2); 1.93-2.03 (m, 8H, PCH_2); 5.75 (s, 10H, Cp). ^{13}C NMR [75.5 MHz, CD_2Cl_2]

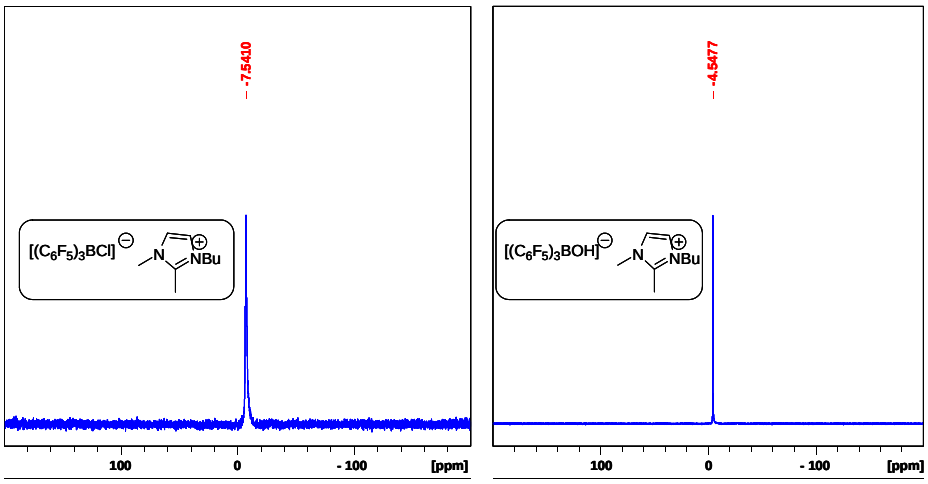
(δ, ppm): 13.32 (CH_3); 17.58 (Zr-CH_3); 18.99 (d, $^1J_{PC}$ = 48.3 Hz, PCH_2); 23.70 (d, $^2J_{PC}$ = 4.7 Hz, CH_2); 24.21 (d, $^3J_{PC}$ = 15.5 Hz, CH_2); 109.65 (Cp); 135.12, 136.78, 138.33, 139.99, 146.65, 149.81 (CF). ^{31}P NMR [121.5 MHz, CD_2Cl_2] (δ, ppm): 33.40 (s) ($^1J_{PC}$ = 47.6 Hz, $^2J_{PC}$ = 14.9 Hz). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.95 (s).

$[Ph_4P^+][Cp_2Zr(Me)OB(C_6F_5)_3^-]$ (**22**)
Yellow liquid. ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -134.0 (d, 6F, $^3J_{FF}$ = 21.7 Hz, o-F); -164.7 (t, 3F, $^3J_{FF}$ = 20.2 Hz, p-F); -167.9 (m, 6F, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): -0.23 (s, 3H, Zr-CH_3); 5.72 (s, 10H, Cp); 7.56-7.76 (m, 20H, Ph). ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 17.47 (Zr-CH_3); 109.63 (Cp); 117.92 (d, $^1J_{PC}$ = 90.3 Hz, PC); 130.98 (d, $^3J_{PC}$ = 13.1 Hz, m-CH); 134.76 (d, $^2J_{PC}$ = 10.0 Hz, o-CH); 136.01 (d, $^4J_{PC}$ = 2.8 Hz, p-CH); 135.24, 136.73, 138.54, 139.89, 146.65, 149.91 (CF). ^{31}P NMR [121.5 MHz, CD_2Cl_2] (δ, ppm): 23.43 (s) ($^1J_{PC}$ = 90.2 Hz, $^2J_{PC}$ = 11.4 Hz). ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -3.98 (s).

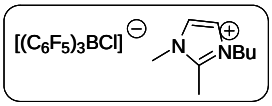
Reaction of $[BBIM]^+[Cp_2Zr(Me)OB(C_6F_5)_3]^-$ (**19**) with $B(C_6F_5)_3$
A stoichiometric amount of $B(C_6F_5)_3$ (23 mg, 0.045 mmol) was added to a solution of $[BBIM]^+[Cp_2Zr(Me)OB(C_6F_5)_3]^-$ (43 mg, 0.045 mmol) in dichloromethane. The immediate formation of the anion $[MeB(C_6F_5)_3]^-$ was checked by ^{11}B, ^{19}F, ^{13}C, ^{1}H NMR :
$[MeB(C_6F_5)_3]^-$: ^{19}F NMR [282.4 MHz, CD_2Cl_2] (δ, ppm): -134.2 (m, o-F); -165.7 (m, p-F); -168.1 (m, m-F). ^{1}H NMR [300.1 MHz, CD_2Cl_2] (δ, ppm): 0.48. ^{13}C NMR [75.5 MHz, CD_2Cl_2] (δ, ppm): 10.12. ^{11}B NMR [96.3 MHz, CD_2Cl_2] (δ, ppm): -15.35.
Several zirconium complexes that contain the $-OB(C_6F_5)_3^-$ fragment around the chemical shift of –2.9 ppm in ^{11}B NMR were identified by Cp resonances at 5.96, 6.14, 6.16, 6.34 ppm in ^{1}H NMR and at 113.75, 114.01, 114.19, 115.55 ppm in ^{13}C NMR.

Reaction of $[Bu_4P]^+[Cp_2Zr(Me)OB(C_6F_5)_3]^-$ (**21**) with $B(C_6F_5)_3$ in the presence of the ionic liquid $[BMpy]^+[N(Tf)_2]^-$
This reaction was followed by ^{11}B NMR: the complex $[Bu_4P]^+[Cp_2Zr(Me)OB(C_6F_5)_3]^-$ (108 mg, 0.11 mmol) soluble in the mixture of CD_2Cl_2 (0.7 mL) and the added ionic liquid $[BMpy]^+[NTf_2]^-$ (0.1 mL) presents a signal at -3.94 ppm. In the NMR Young-tube, $B(C_6F_5)_3$ (54 mg, 0.11 mmol) was then added. Two new resonances appeared on the ^{11}B NMR spectrum. The signal at –15.39 ppm was unambiguitely attributed to the anion $[MeB(C_6F_5)_3]^-$whereas the second resonance at –3.09 ppm corresponds to a zirconium complex with a Cp resonance at 6.19 ppm in ^{1}H NMR and at 114.02 ppm in ^{13}C NMR. This product containing the $-OB(C_6F_5)_3^-$ part is observed in ^{19}F NMR with the following resonances : -134.3 (dd, 6F, $^3J_{FF}$ = 9.7 Hz, $^3J_{FF}$ = 9.9 Hz, o-F), -162.9 (t, 3F, $^3J_{FF}$ = 20.4 Hz, p-F), -167.2 (m, 6F, m-F).

NMR ^{11}B (CH_2Cl_2, 10% CD_2Cl_2)

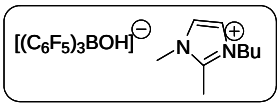


NMR ^{19}F (CD_2Cl_2)



δ ^{19}F (ppm) :

➡ **-133.2 (m, *o*-F)**
-162.4 (m, *p*-F)
-167.4 (m, *m*-F)



δ ^{19}F (ppm) :

➡ **-136.8 (m, *o*-F)**
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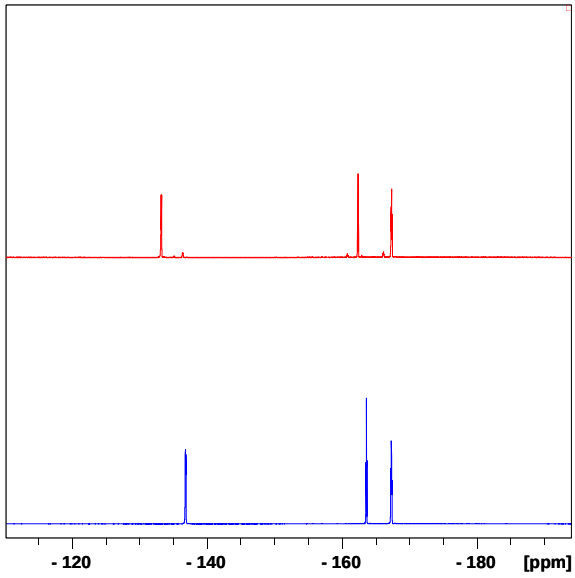
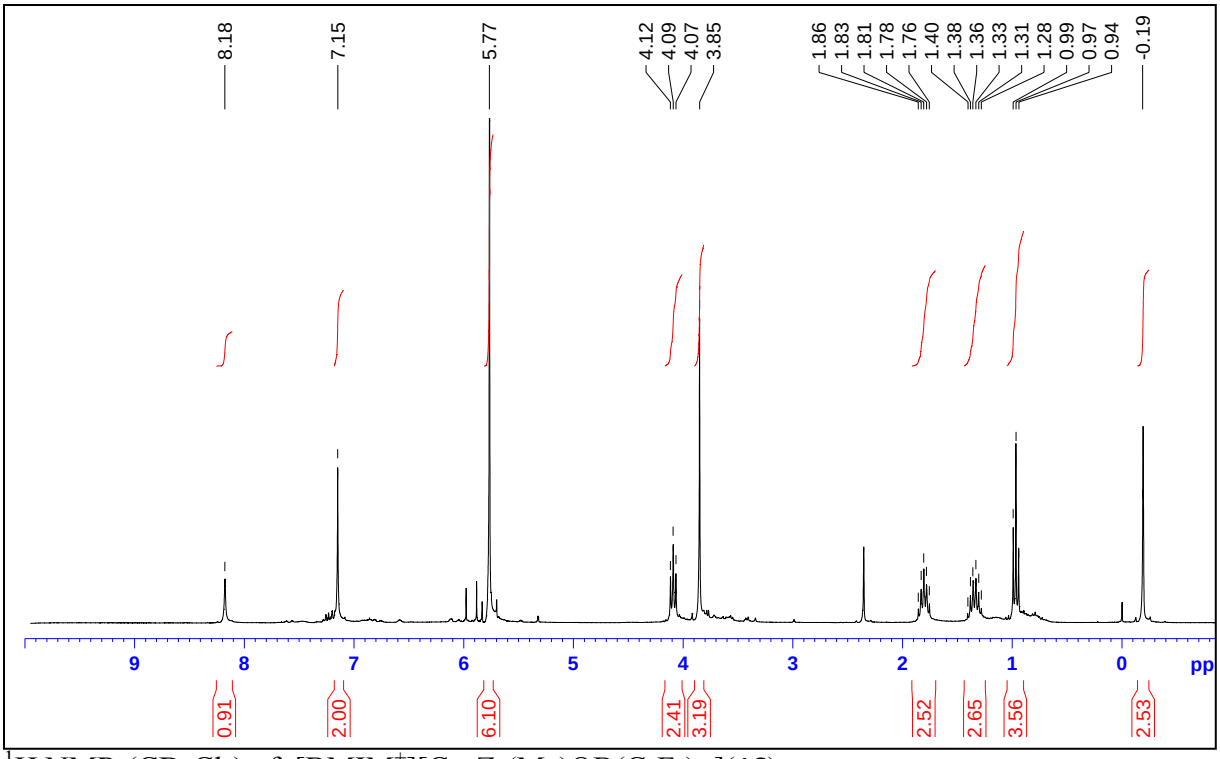
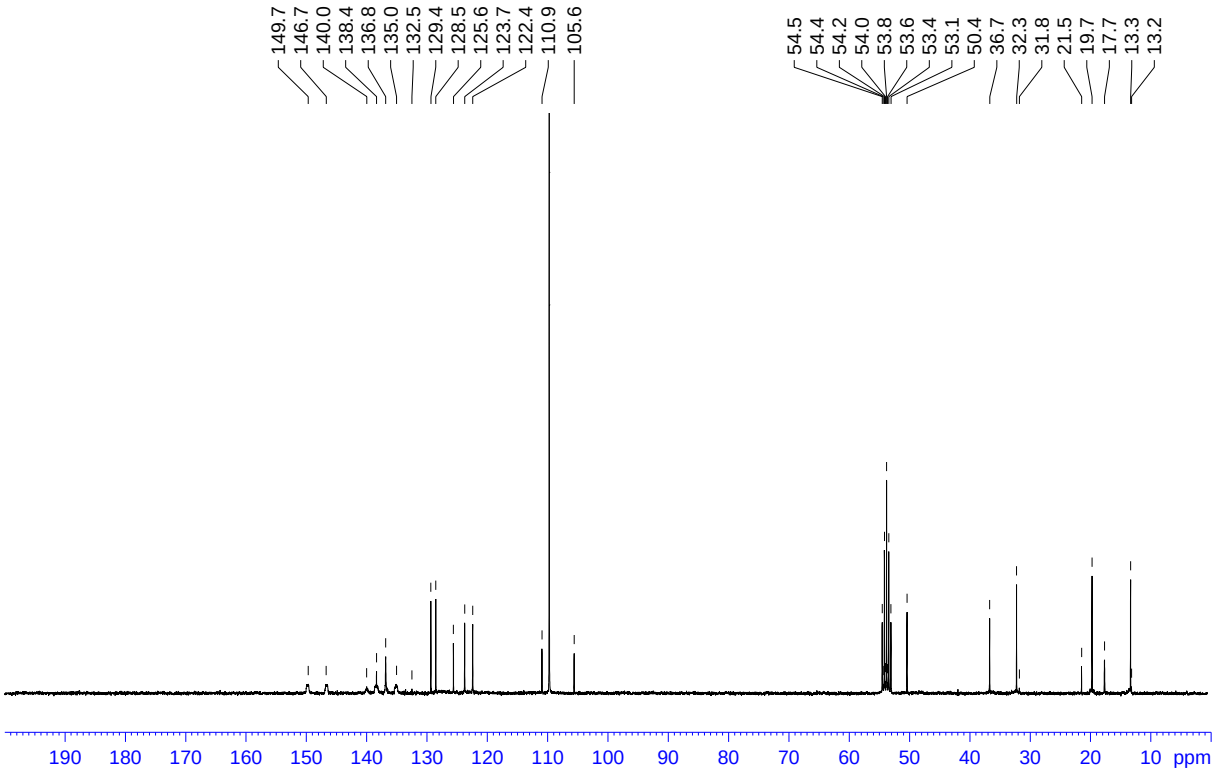
-167.4 (m, *m*-F)

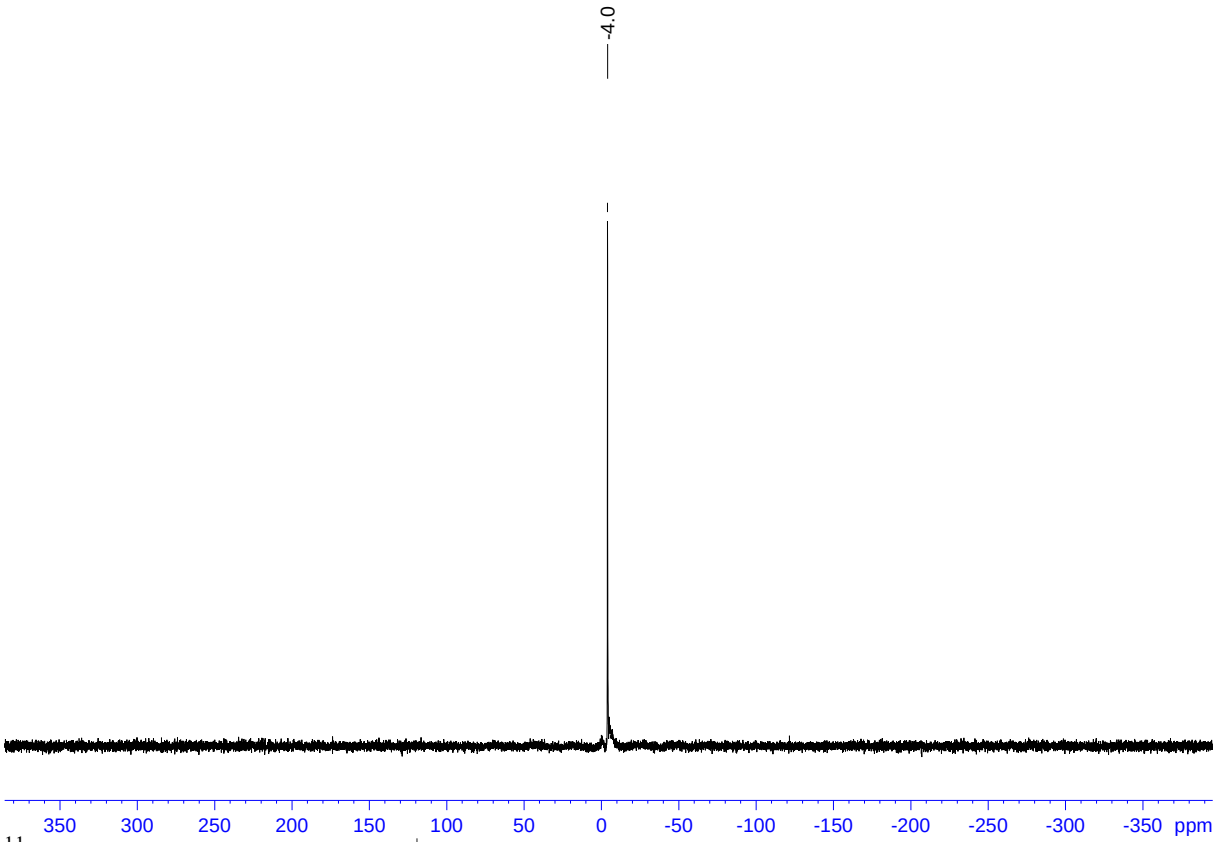




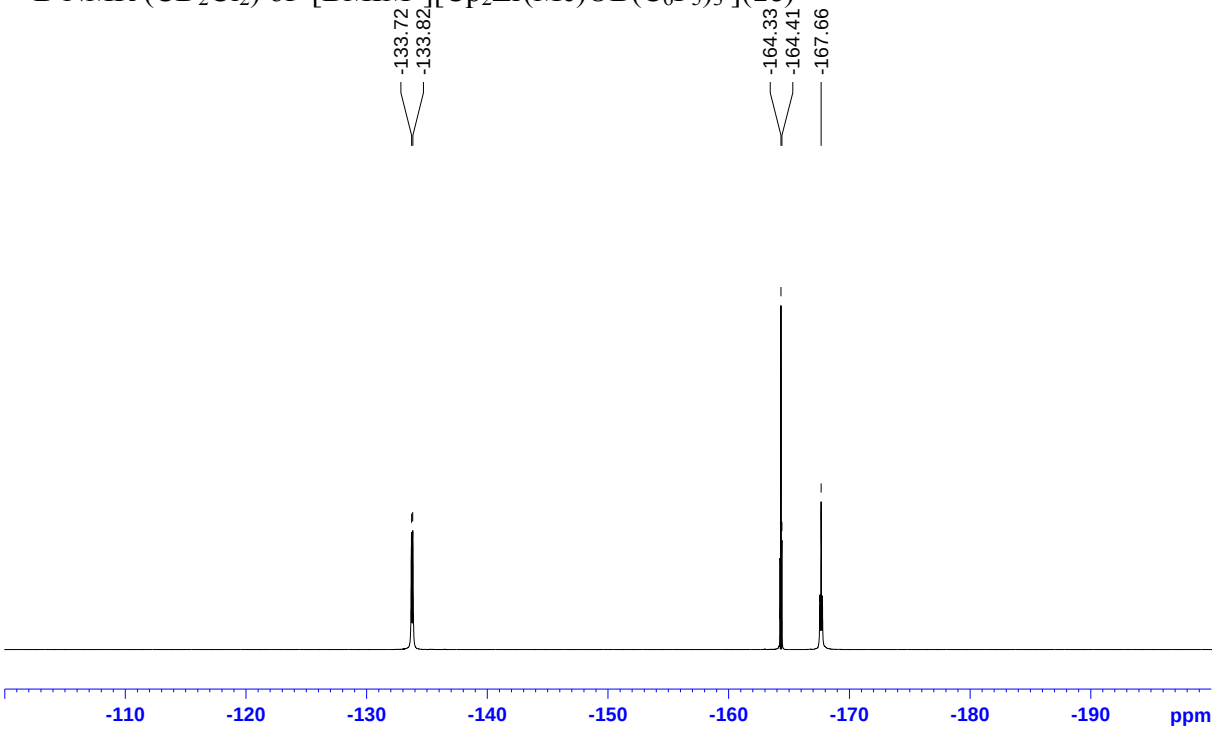
^{1}H NMR (CD_2Cl_2) of [$BMIM^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$](**16**)



^{13}C NMR (CD_2Cl_2) of [$BMIM^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$](**16**)



^{11}B NMR (CD_2Cl_2) of [$BMIM^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$](**16**)



^{19}F NMR (CD_2Cl_2) of [$BMIM^+$][$Cp_2Zr(Me)OB(C_6F_5)_3^-$](**16**)