Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Contents

# 1 General Synthetic Aspects

Reactions with air- and moisture-sensitive compounds were performed in round-bottom flasks or glass tubes equipped with valves with PTFE stems (Rettberg, Göttingen) under argon using Schlenk-line techniques.

# 2 Analytical Instruments and Details

$^{1}$H, $^{2}$H, $^{11}$B, $^{13}$C, $^{19}$F and $^{31}$P spectra were recorded at 25 °C in $(CD_3)_2CO$ on a Bruker Avance 500 NMR spectrometer, a Bruker Avance Neo I 600 or a Bruker Avance Neo 400 spectrometer. NMR signals were referenced against $(CH_3)_4Si$ ($^{1}$H and $^{13}$C) with $\Xi(^{13}C) = 25.145020$ MHz, $(CD_3)_4Si$ with $\Xi(^{2}H) = 15.350609$ MHz, $BF_3{\cdot}OEt_2$ in $CDCl_3$ with $\Xi(^{11}B) = 32.083974$ MHz, $CFCl_3$ with $\Xi(^{19}F) = 94.094011$ MHz, $H_3PO_4$ with $\Xi(^{31}P) = 40.480742$ as external standard.[1] $^{1}$H and $^{13}$C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively ($\delta(^{1}H)$: $(CD_2H)(CD_3)CO$ 2.05 ppm; $\delta(^{13}C)$: $(CD_3)_2CO$ 206.26 and 29.84 ppm.[2] IR spectra were recorded at room temperature with a Bruker Alpha FT IR spectrometer with an apodized resolution of 4 cm$^{-1}$ in the attenuated total reflection (ATR) mode in the region of 4000−400 cm$^{-1}$ using a setup with a diamond crystal. Raman spectra were recorded at room temperature with a Bruker MultiRAM FT Raman spectrometer with an apodized resolution of 4 cm$^{-1}$ using the 1064 nm line of a Nd/YAG laser for excitation of the crystalline samples contained in melting point capillaries.

Elemental analyses (C, H, N) were performed either with a Euro EA3000 instrument (HEKA-Tech, Germany) or with an Elementar Vario MICRO cube instrument (Elementar Analysensysteme, Germany). Thermal analyses were performed with a DSC 204 F1 Phoenix (Netzsch) in the temperature range of −175 to 580 °C with a heating rate of 10 K·min$^{-1}$. Viscosities and densities were measured with a rolling-ball viscosimeter Lovis 2000 ME combined with a DMA 4100 M density meter (Anton Paar) at different angles and temperatures. The water content of the ILs was determined by Karl-Kischer titration with a Metrohm 831 KF Coulometer. The water content of the ILs was <50 ppm.

# 3 Chemicals

All standard chemicals were obtained from commercial sources and used without further purification. Solvents were dried according to standard protocols[3] and stored under argon atmosphere in flasks with valves with PTFE stems (Rettberg, Göttingen).

$K[B(CN)_4]$[4], $K[BF_3(CN)]$[4], $K[BF_2(CN)_2]$[4], $K[BF(CN)_3]$[5], $K[BFH(CN)_2]$[6], $K[BH_2(CN)_2]$[7], and $K[BH(CN)_2]$[7] were prepared according to known procedures.

# 4 Syntheses and Analytics

## 4.1 [EMIm] salts

### 4.1.1 $[EMIm][BF_4]$

$[EMIm][BF_4]$ was purchased from Sigma-Aldrich.

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta = 8.91$ (s, 1H, NC*H*N), 7.73 (dd, 1H, $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.8$ Hz, N−CH=C*H*−N), 7.65 (dd, 1H $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.8$ Hz, N−C*H*=CH−N), 4.35 (q, 2H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$), 4.00 (s, 3H, $CH_3$), 1.53 ppm (t, 3H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 137.2$ (s, 1C, *C*H), 124.6 (s, 1C, *C*H), 122.9 (s, 1C, *C*H), 45.6 (s, 1C, $CH_2CH_3$), 36.4 (s, 1C, $CH_3$), 15.5 ppm (s, 1C, $CH_2CH_3$).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -0.9$ ppm (s, 1B, $BF_4$).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -0.9$ ppm (s, 1B, $BF_4$).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -150.88$ (s, 4F, (~20%) $^{10}BF_4$) −150.94 ppm (q, 4F (~80%), $^1J(^{19}F,^{11}B) = 0.7$ Hz, $^{11}BF_4$).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -150.88$ (s, 4F, (~20%) $^{10}BF_4$) −150.94 ppm (s, 4F (~80%), $^{11}BF_4$).

Elemental analysis calcd (%) for $C_6H_{11}BF_4N_2$: C 36.40, H 5.60, N 14.15; found: C 35.65, H 5.86, N 14.51.

### 4.1.2 $[EMIm][BF_3(CN)]$

$K[BF_3CN]$ (2.66 g, 20.0 mmol) was dissolved in water (25 ml) and a solution of [EMIm]Cl (3.0 g, 20.46 mmol) in water (4.3 mL) was added. The solution was then extracted with $CH_2Cl_2$ (5×4 mL) and the combined organic layers were dried with $MgSO_4$, filtered and the $CH_2Cl_2$ was removed in vacuum. The remaining ionic liquid was dissolved in $CH_2Cl_2$ (2.5 mL) and the solution was washed with deionized water (3×0.5 mL) and with bidistilled water (3×0.5 mL) and then dried in a fine vacuum.

Yield: 2.91 g, 14.20 mmol [EMIm][$BF_3$(CN)] (71%).

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 8.97 (s, 1H, NC*H*N), 7.75 (dd, 1H, $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.8$ Hz, N−CH=C*H*−N), 7.68 (dd, 1H $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.8$ Hz, N−C*H*=CH−N), 4.39 (q, 2H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$), 4.04 (s, 3H, $CH_3$), 1.56 ppm (t, 3H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 137.1 (s *C*H), 132.2 (m, $BF_3$(*C*N)) 124.7 (s, *C*H), 123.0 (s, *C*H), 45.7 (s, $CH_2CH_3$), 36.6 (s, $CH_3$), 15.6 ppm (s $CH_2CH_3$).

$^{13}C\{^{19}F\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 137.1 (d, $^1J(^{13}C,^1H) = 224.8$ Hz, *C*H), 132.2 (q, $^1J(^{13}C,^{11}B) = 88.7$ Hz, $BF_3$(*C*N)) 124.7 (d, $^1J(^{13}C,^1H) = 206.6$ Hz, *C*H), 123.0 (d, $^1J(^{13}C,^1H) = 209.9$ Hz, *C*H), 45.7 (t, $^1J(^{13}C,^1H) = 144.5$ Hz, $CH_2CH_3$), 36.6 (q, $^1J(^{13}C,^1H)$= 143.8 Hz, $CH_3$), 15.6 ppm (qt, $^1J(^{13}C,^1H) = 128.8$ Hz, $^2J(^{13}C,^1H) = 3.8$ Hz, $CH_2CH_3$).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −3.55 ppm (q, 1B, $^1J(^{19}F,^{11}B) = 27.0$ Hz, $BF_3$(CN)).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −3.55 ppm (s, 1B, $BF_3$(CN)), $^1J(^{13}C,^{11}B) = 88.7$ Hz, ($^{13}C$-satelites).

$^{19}F$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −137.57 (spt, $^1J(^{19}F,^{10}B) = 9.1$ Hz, $^{10}BF_3$(CN)), (−137.63 ppm (q, 3F, $^1J(^{19}F,^{11}B) = 26.9$ Hz, $^{11}BF_3$(CN)).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −137.57 (spt, $^1J(^{19}F,^{10}B) = 9.1$ Hz, $^{10}BF_3$(CN)), −137.63 ppm (s, 3F, $^{11}BF_3$(CN)).

IR (ATR): 2209 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2211 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_7H_{11}BF_3N_3$: C 41.01, H 5.41, N 20.50; found: C 40.81, H 5.37, N 21.30.

### 4.1.3 [EMIm][$BF_2(CN)_2$]

Na[$BF_2(CN)_2$] (4.7 g, 37.96 mmol) was treated with [EMIm]Cl (5.9 g, 40.24 mmol) in water (15 mL). The suspension was then extracted with $CH_2Cl_2$ (60 mL) and the $CH_2Cl_2$ phase was washed with bidistilled water (5×1 mL). All volatiles were removed in a vacuum and the remaining ionic liquid was dried in a fine vacuum.

Yield: 4.9 g, 23.11 mmol [EMIm][$BF_2(CN)_2$] (61%).

$^1H$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta = 8.94$ (s, 1H, NC*H*N), 7.71 (dd, 1H, $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.8$ Hz, N−CH=C*H*−N), 7.64 (dd, 1H $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.8$ Hz, N−C*H*=CH−N), 4.37 (q, 2H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$), 4.03 (s, 3H, $CH_3$), 1.56 ppm (t, 3H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.9$ (s, *C*H), 130.5 (qt, $^1J(^{13}C,^{11}B) = 80.7$ Hz, $^2J(^{19}F,^{13}C) = 50.4$ Hz, $BF_2(CN)_2$), 124.6 (s, *C*H), 122.9 (s, *C*H), 45.6 (s, $CH_2CH_3$), 36.5 (s, $CH_3$), 15.4 ppm (s, $CH_2CH_3$).

$^{13}C\{^{19}F\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.9$ (d, $^1J(^{13}C,^1H) = 221.1$ Hz, *C*H), 130.5 (q, $^1J(^{13}C,^{11}B) = 80.6$ Hz, $BF_2(CN)_2$) 124.6 (d, $^1J(^{13}C,^1H) = 206.2$ Hz, *C*H), 122.9 (d, $^1J(^{13}C,^1H) = 209.0$ Hz, *C*H), 45.6 (t, $^1J(^{13}C,^1H) = 144.4$ Hz, $CH_2CH_3$), 36.5 (q, 1C, $^1J(^{13}C,^1H) = 143.9$ Hz, $CH_3$), 15.4 ppm (qt, 1C, $^1J(^{13}C,^1H) = 128.8$ Hz, $^2J(^{13}C,^1H) = 3.7$ Hz, $CH_2CH_3$).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -7.3$ ppm (t, 1B, $^1J(^{19}F,^{11}B) = 41.1$ Hz, $BF_2(CN)_2$).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -7.3$ ppm (s, 1B, $BF_2(CN)_2$).

$^{19}F$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -153.9$ (spt, 1F (~20%), $^1J(^{19}F,^{10}B) = 13.8$ Hz, $^{10}BF_2(CN)_2$), −154.0 ppm (q, 1F (~80%), $^1J(^{19}F,^{11}B) = 41.2$ Hz, $^{11}BF_2(CN)_2$).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -153.9$ (spt, 1F (~20%), $^1J(^{19}F,^{10}B) = 13.8$ Hz, $^{10}BF_2(CN)_2$), −154.0 ppm (s, 1F (~80%), $^{11}BF_2(CN)_2$).

IR (ATR): 2210 $cm^{-1}$ ($\nu$(C≡N)).

Raman: 2212 $cm^{-1}$ ($\nu$(C≡N)).

Elemental analysis calcd (%) for $C_8H_{11}BF_2N_4$: C 45.32, H 5.23, N 26.43; found: C 44.96, H 5.35, N 26.72.

### 4.1.4 [EMIm][$BF(CN)_3$]

K[$BF(CN)_3$] (75 g, 0.51 mol) was dissolved in water (150 mL) and [EMIm]Cl (76 g, 0.52 mol) and $CH_2Cl_2$ (100 mL) were added. The organic layer was separated and washed with deionized water (5×10 mL) and then with bidistilled water (5×5 mL). The $CH_2Cl_2$ was removed with a rotary evaporator and the remained ionic liquid was dried in a fine vacuum.

Yield: 110.1 g, 0.503 mol [EMIm][$BF(CN)_3$] (98%)

$^1H$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta = 8.97$ (s, 1H, NC*H*N), 7.72 (dd, 1H, $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.6$ Hz, N−CH=C*H*−N), 7.65 (dd, 1H $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.6$ Hz, N−C*H*=CH−N), 4.38 (q, 2H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$), 4.04 (s, 3H, $CH_3$), 1.57 ppm (t, 3H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.9$ (s, *C*H), 127.6 (qd, $^1J(^{13}C,^{11}B) = 74.7$ Hz, $^2J(^{19}F,^{13}C) = 37.1$ Hz, $BF(CN)_3$), 124.6 (s, *C*H), 122.9 (s, *C*H), 45.7 (s, $CH_2CH_3$), 36.5 (s, $CH_3$), 15.5 ppm (s, $CH_2CH_3$).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -17.8$ ppm (d, 1B, $^1J(^{19}F,^{11}B) = 44.6$ Hz, $BF(CN)_3$).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -17.8$ ppm (s, 1B, $BF(CN)_3$).

$^{19}F$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -211.9$ ppm (q, 1F, $^1J(^{19}F,^{11}B) = 44.6$ Hz, $BF(CN)_3$).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -211.9$ ppm (s, 1F, $BF(CN)_3$).

IR (ATR): 2214 $cm^{-1}$ ($\nu$(C≡N)).

Raman: 2217 $cm^{-1}$ ($\nu$(C≡N)).

Elemental analysis calcd (%) for $C_9H_{11}BFN_5$: C 49.35, H 5.06, N 31.98; found: C 48.85, H 5.07, N 32.05.

### 4.1.5 [EMIm][$BFH(CN)_2$]

K[$BFH(CN)_2$] (4.00 g, 28.0 mmol) was treated with a solution of [EMIm]Cl (5.05 g, 34.4 mmol) in water (15 mL). The mixture was stirred for 15 min and then extracted with $CH_2Cl_2$ (100 mL). The organic layer was washed with bidistilled water (5×3 mL) and all volatiles were removed in a vacuum. The remaining ionic liquid was dried in a fine vacuum, washed again with bidistilled water (5×1 mL) and finally dried in a fine vacuum.

Yield: 4.92 g, 25.36 mmol [EMIm][$BFH(CN)_2$] (77%).

$^1H$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta = 8.94$ (s, 1H, NC*H*N), 7.72 (dd, 1H, $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.7$ Hz, N−CH=C*H*−N), 7.65 (dd, 1H $^3J(^1H,^1H) \approx {}^4J(^1H,^1H) \approx 1.7$ Hz, N−C*H*=CH−N), 4.38 (q, 2H, $^3J(^1H,^1H) = 7.3$ Hz, $CH_2CH_3$), 4.03 (s, 3H, $CH_3$), 2.73 (qd, 1H,

$^{1}J(^{11}\mathrm{B},^{1}\mathrm{H})$ = 109.6 Hz, $^{2}J(^{19}\mathrm{F},^{1}\mathrm{H})$ = 40.8 Hz, BF*H*(CN)$_2$), 1.56 ppm (t, 3H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ = 7.3 Hz, CH$_2$C*H*$_3$).

$^{1}$H{$^{11}$B} NMR (500.1 MHz, (CD$_3$)$_2$CO) $\delta$ = 8.94 (s, 1H, NC*H*N), 7.72 (dd, 1H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx {}^{4}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx$ 1.7 Hz, N−CH=C*H*−N), 7.65 (dd, 1H $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx {}^{4}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx$ 1.7 Hz, N−C*H*=CH−N), 4.38 (q, 2H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ = 7.3 Hz, C*H*$_2$CH$_3$), 4.03 (s, 3H, C*H*$_3$), 2.73 (d, 1H, $^{2}J(^{19}\mathrm{F},^{1}\mathrm{H})$ = 40.8 Hz, BF*H*(CN)$_2$), 1.56 ppm (t, 3H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ = 7.3 Hz, CH$_2$C*H*$_3$).

$^{1}$H{$^{19}$F} NMR (400.3 MHz, (CD$_3$)$_2$CO) $\delta$ = 8.94 (s, 1H, NC*H*N), 7.72 (dd, 1H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx {}^{4}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx$ 1.7 Hz, N−CH=C*H*−N), 7.65 (dd, 1H $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx {}^{4}J(^{1}\mathrm{H},^{1}\mathrm{H}) \approx$ 1.7 Hz, N−C*H*=CH−N), 4.38 (q, 2H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ = 7.3 Hz, C*H*$_2$CH$_3$), 4.03 (s, 3H, C*H*$_3$), 2.73 (q, 1H, $^{1}J(^{11}\mathrm{B},^{1}\mathrm{H})$ = 109.7 Hz, BF*H*(CN)$_2$), 1.56 ppm (t, 3H, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ = 7.3 Hz, CH$_2$C*H*$_3$).

$^{13}$C{$^{1}$H} NMR (125.7 MHz, (CD$_3$)$_2$CO) $\delta$ = 136.9 (s, *C*H), 132.6 (qd, $^{1}J(^{13}\mathrm{C},^{11}\mathrm{B})$ = 64.8 Hz, $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C})$ = 35.3 Hz, BFH(*C*N)$_2$), 124.6 (s, *C*H), 122.9 (s, *C*H), 45.6 (s, *C*H$_2$CH$_3$), 36.5 (s, *C*H$_3$), 15.5 ppm (s, CH$_2$*C*H$_3$).

$^{13}$C{$^{19}$F} NMR (125.7 MHz, (CD$_3$)$_2$CO) $\delta$ = 136.9 (d, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 222.2 Hz *C*H), 132.6 (q, $^{1}J(^{13}\mathrm{C},^{11}\mathrm{B})$ = 64.8 Hz, BFH(*C*N)$_2$), 124.7 (d, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 206.0 Hz, *C*H), 123.0 (d, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 203.1 Hz, *C*H), 45.7 (t, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 144.3 Hz, *C*H$_2$CH$_3$), 36.6 (q, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 143.8 Hz, *C*H$_3$), 15.5 ppm (qt, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 128.8 Hz, $^{2}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 3.7 Hz, CH$_2$*C*H$_3$).

$^{11}$B NMR (160.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −14.2 ppm (dd, 1B, $^{1}J(^{11}\mathrm{B},^{1}\mathrm{H})$ = 109.8 Hz, $^{1}J(^{19}\mathrm{F},^{11}\mathrm{B})$ = 56.0 Hz, *B*FH(CN)$_2$).

$^{11}$B{$^{1}$H} NMR (160.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −14.2 ppm (d, 1B, $^{1}J(^{19}\mathrm{F},^{11}\mathrm{B})$ = 56.0 Hz, *B*FH(CN)$_2$).

$^{11}$B{$^{19}$F} NMR (160.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −14.2 ppm (d, 1B, $^{1}J(^{11}\mathrm{B},^{1}\mathrm{H})$ = 109.8 Hz, *B*FH(CN)$_2$).

$^{19}$F NMR (470.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −233.9 ppm (qd, 1F, $^{1}J(^{19}\mathrm{F},^{11}\mathrm{B})$ = 56.0 Hz, $^{2}J(^{19}\mathrm{F},^{1}\mathrm{H})$ = 40.8 Hz B*F*H(CN)$_2$).

$^{19}$F{$^{11}$B} NMR (470.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −233.9 ppm (d, 1F, $^{2}J(^{19}\mathrm{F},^{1}\mathrm{H})$ = 40.8 Hz B*F*H(CN)$_2$).

$^{19}$F{$^{1}$H} NMR (377 MHz, (CD$_3$)$_2$CO) $\delta$ = −234.1 ppm (q, 1F, $^{1}J(^{19}\mathrm{F},^{11}\mathrm{B})$ = 56.0 Hz, B*F*H(CN)$_2$).

IR (ATR): 2375 ($\nu$(B−H), 2189 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2383 ($\nu$(B−H), 2201 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_8H_{12}BFN_4$: C 49.52, H 6.23, N 28.88; found: C 49.84, H 5.96, N 28.82.

## 4.2 [BMPL] salts

### 4.2.1 [BMPL][$BF_3$(CN)]

K[$BF_3$CN] (1.33 g, 10.0 mmol) was dissolved in water (25 ml) and a solution of [BMPL]Cl (1.78 g, 10.03 mmol) was added. The solution was extracted with $CH_2Cl_2$ (5×4 mL) and the combined organic layers were dried with $MgSO_4$, filtered and the $CH_2Cl_2$ was removed in vacuum. The remaining ionic liquid was dried in a fine vacuum.

Yield: 1.21 g, 5.125 mmol [BMPL][$BF_3$(CN)] (51%).

$^{1}$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 3.75-3.65 (m, 4H, $CH_2$), 3.54-3.51 (m, 2H, $CH_2$), 3.23 (s, 3H, $CH_3$), 2.35-2.27 (m, 4H, $CH_2$), 1.93-1.86 (m, 2H, $CH_2$), 1.47-1.40 (m, 2H, $CH_2CH_3$), 0.98 ppm (t, 3H, $^{3}J(^{1}H,^{1}H)$ = 7.41 Hz, $CH_2CH_3$).

$^{13}C\{^{1}H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 132.2 (m, $BF_3$(CN)), 65.2 (t, $^{1}J(^{14}N,^{13}C)$ = 3.1 Hz, N$CH_2$), 65.0 (t, $^{1}J(^{14}N,^{13}C)$ = 3.0 Hz, N$CH_2$), 48.9 (t, $^{1}J(^{14}N,^{13}C)$ = 4.1 Hz, N$CH_3$), 26.3 (s, $CH_2$), 22.3 (s, $CH_2$), 20.4 (t, $J(^{14}N,^{13}C)$ = 1.60 Hz,$CH_2CH_3$) 13.8 ppm (s, $CH_2CH_3$).

$^{13}C\{^{19}F\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 132.2 (q, $^{1}J(^{13}C,^{11}B)$ = 89.5 Hz, $BF_3$(CN)), 65.2 (t, $^{1}J(^{13}C,^{1}H)$ = 145.0 Hz, N$CH_2$), 65.0 (t, $^{1}J(^{13}C,^{1}H)$ = 142.2 Hz, N$CH_2$), 48.9 (qm, $^{1}J(^{13}C,^{1}H)$ = 143.6 Hz, N$CH_3$), 26.3 (t, $^{1}J(^{13}C,^{1}H)$ = 129.3 Hz, $CH_2$), 22.3 (t, $^{1}J(^{13}C,^{1}H)$ = 135.5 Hz $CH_2$), 20.6 (t,$^{1}J(^{13}C,^{1}H)$ = 127.5 Hz, $CH_2CH_3$) 15.8 ppm (qm, 1C,$^{1}J(^{13}C,^{1}H)$ = 125.6 Hz, $CH_2CH_3$).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −3.56 ppm (q, 1B, $^{1}J(^{19}F,^{11}B)$ = 26.9 Hz, $BF_3$(CN)).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −3.56 ppm (s, 1B, $BF_3$(CN)), $^{1}J(^{13}C,^{11}B)$ = 89.6 Hz, ($^{13}$C-satelites).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −137.68 (spt, $^{1}J(^{19}F,^{10}B)$ = 8.8 Hz, $^{10}BF_3$(CN)), −137.75 ppm (q, 3F, $^{1}J(^{19}F,^{11}B)$ = 27.1 Hz, $^{11}BF_3$(CN)).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −137.68 (spt, $^{1}J(^{19}F,^{10}B)$ = 8.8 Hz, $^{10}BF_3$(CN)), −137.75 ppm (s, 3F, $^{11}BF_3$(CN)).

IR (ATR): 2207 $cm^{-1}$ ( $\nu$(C≡N)).

Raman: 2209 $cm^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{10}H_{20}BF_3N_2$: C 50.87, H 8.54, N 11.87; found: C 50.70, H 8.36, N 12.70.

### 4.2.2 [BMPL][$BF_2(CN)_2$]

Na[$BF_2(CN)_2$] (3.2 g, 25.85 mmol) was treated with [BMPL]Cl (4.75 g, 26.7 mmol) in water (15 mL). The suspension was then extracted with $CH_2Cl_2$ (60 mL) and the $CH_2Cl_2$ phase was washed with bidistilled water (5×1 mL). All volatiles were removed in a vacuum and the resulting ionic liquid was dried in a fine vacuum.

Yield: 4.65 g, 19.13 mmol [BMPL][$BF_2(CN)_2$] (74%).

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 3.74-3.63 (m, 4H, $CH_2$), 3.54-3.48 (m, 2H, $CH_2$), 3.22 (s, 3H, $CH_3$), 2.36-2.27 (m, 4H, $CH_2$), 1.93-1.86 (m, 2H, $CH_2$), 1.47-1.39 (m, 2H, $CH_2CH_3$), 0.98 ppm (t, 3H, $^3J(^1H,^1H)$ = 7.41 Hz, $CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 130.7 (qt, $^1J(^{13}C,^{11}B)$ = 80.6 Hz, $^2J(^{19}F,^{13}C)$ = 50.3 Hz, $BF_2(CN)_2$), 65.1 (t, $^1J(^{14}N,^{13}C)$ = 3.3 Hz, $NCH_2$), 65.0 (t, $^1J(^{14}N,^{13}C)$ = 3.0 Hz, $NCH_2$), 48.9 (t, $^1J(^{14}N,^{13}C)$ = 4.0 Hz, $NCH_3$), 26.2 (s, $CH_2$), 22.3 (s, $CH_2$), 20.3 (t, $J(^{14}N,^{13}C)$ = 1.54 Hz,$CH_2CH_3$) 13.7 ppm (s, $CH_2CH_3$).

$^{13}C\{^{19}F\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 130.7 (q, $^1J(^{13}C,^{11}B)$ = 80.6 Hz, $^{11}BF_2(CN)_2$), 130.6 (spt, $^1J(^{13}C,^{10}B)$ = 27.3 Hz, $^{10}BF_2(CN)_2$), 65.1 (t, $^1J(^{13}C,^1H)$ = 148.0 Hz, $NCH_2$), 64.9 (t, $^1J(^{13}C,^1H)$ = 143.3 Hz, $NCH_2$), 48.9 (qm, $^1J(^{13}C,^1H)$ = 143.8 Hz, $NCH_3$), 26.2 (t, $^1J(^{13}C,^1H)$ = 127.6 Hz, $CH_2$), 22.3 (t, $^1J(^{13}C,^1H)$ = 137.6 Hz $CH_2$), 20.3 (t,$^1J(^{13}C,^1H)$ = 127.5 Hz, $CH_2CH_3$) 13.7 ppm (qm, 1C,$^1J(^{13}C,^1H)$ = 125.4 Hz, $CH_2CH_3$).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −7.3 ppm (t, 1B, $^1J(^{19}F,^{11}B)$ = 41.2 Hz, $BF_2(CN)_2$).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −7.3 ppm (s, 1B, $BF_2(CN)_2$).

$^{19}F$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −153.8 ppm (spt, 1F, (~20%), $^1J(^{19}F,^{10}B)$ = 13.8 Hz, $^{10}BF_2(CN)_2$), −153.9 ppm (q, 1F (~80%), $^1J(^{19}F,^{11}B)$ = 41.2 Hz, $^{11}BF_2(CN)_2$).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −153.8 ppm (spt, 1F, (~20%), $^1J(^{19}F,^{10}B)$ = 13.8 Hz, $^{10}BF_2(CN)_2$), −153.9 ppm (s, 1F (~80%), $^{11}BF_2(CN)_2$).

IR (ATR): 2209 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2211 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{11}H_{20}BF_2N_3$: C 54.35, H 8.29, N 17.28; found: C 53.92, H 8.40, N 18.09.

### 4.2.3 [BMPL][BF(CN)$_3$]

K[BF(CN)$_3$] (75 g, 0.51 mol) was dissolved in water (150 mL) and [BMPL]Cl (92 g, 0.52 mol) and $\mathrm{CH_2Cl_2}$ (100 mL) were added. The organic layer was separated and washed with deionized water (5×10 mL) and then with bidistilled water (5×5 mL). The $\mathrm{CH_2Cl_2}$ was removed with a rotary evaporator and the remained ionic liquid was dried in a fine vacuum.

Yield: 123.8 g, 0.495 mol [BMPL][BF(CN)$_3$] (97%).

$^1$H NMR (500.1 MHz, $\mathrm{(CD_3)_2CO}$) $\delta$ = 3.73-3.64 (m, 4H, $\mathrm{C}\mathit{H}_2$), 3.53-3.49 (m, 2H, $\mathrm{C}\mathit{H}_2$), 3.23 (s, 3H, $\mathrm{C}\mathit{H}_3$), 2.34-2.27 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.93-1.85 (m, 2H, $\mathrm{C}\mathit{H}_2$), 1.47-1.39 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 0.98 ppm (t, 3H, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.41 Hz, $\mathrm{CH_2C}\mathit{H}_3$).

$^{13}$C{$^1$H} NMR (125.7 MHz, $\mathrm{(CD_3)_2CO}$) $\delta$ = 127.7 (qd, $^1J(^{13}\mathrm{C},^{11}\mathrm{B})$ = 75.1 Hz, $^2J(^{19}\mathrm{F},^{13}\mathrm{C})$ = 37.1 Hz, $\mathrm{BF(}\mathit{C}\mathrm{N)_3}$), 65.1 (t, 2C, $^1J(^{14}\mathrm{N},^{13}\mathrm{C})$ = 3.4 Hz, $\mathrm{N}\mathit{C}\mathrm{H_2}$), 65.0 (t, 1C, $^1J(^{14}\mathrm{N},^{13}\mathrm{C})$ = 3.0 Hz, $\mathrm{N}\mathit{C}\mathrm{H_2}$), 48.9 (t, 1C, $^1J(^{14}\mathrm{N},^{13}\mathrm{C})$ = 4.0 Hz, $\mathrm{N}\mathit{C}\mathrm{H_3}$), 26.2 (s, 1C, $\mathit{C}\mathrm{H_2}$), 22.3 (s, 2C, $\mathrm{CH_2}$), 20.3(t, 1C, $\mathit{C}\mathrm{H_2CH_3}$) 13.7 ppm (s, 1C $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$).

$^{11}$B NMR (160.5 MHz, $\mathrm{(CD_3)_2CO}$) $\delta$ = −17.8 ppm (d, 1B, $^1J(^{19}\mathrm{F},^{11}\mathrm{B})$ = 44.6 Hz, $\mathit{B}\mathrm{F(CN)_3}$).

$^{11}$B{$^{19}$F} NMR (160.5 MHz, $\mathrm{(CD_3)_2CO}$) $\delta$ = −17.8 ppm (s, 1B, $\mathit{B}\mathrm{F(CN)_3}$).

$^{19}$F NMR (470.5 MHz, $\mathrm{(CD_3)_2CO}$) $\delta$ = −211.9 ppm (q, 1F, $^1J(^{19}\mathrm{F},^{11}\mathrm{B})$ = 44.7 Hz, $\mathrm{B}\mathit{F}\mathrm{(CN)_3}$).

$^{19}$F{$^{11}$B} NMR (470.5 MHz, $\mathrm{(CD_3)_2CO}$) $\delta$ = −211.9 ppm (s, 1F, $\mathrm{B}\mathit{F}\mathrm{(CN)_3}$).

IR (ATR): 2212 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2216 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $\mathrm{C_{12}H_{20}BFN_4}$: C 57.62, H 8.06, N 22.40; found: C 57.46, H 8.03, N 23.48.

### 4.2.4 [BMPL][BFH(CN)$_2$]

K[BFH(CN)$_2$] (3.00 g, 24.6 mmol) was dissolved in water (15 mL) and a solution of [BMPL]Cl (5.33 g, 30.0 mmol) in water (15 mL) was added. The mixture was extracted with $\mathrm{CH_2Cl_2}$ (1×30 mL,5×15 mL) and the combined organic layers were concentrated to 25 mL with a rotary evaporator and washed with bidistilled water (5×2 mL). All volatiles were removed in vacuum and the remaining ionic liquid was dried in a fine vacuum.

Yield: 4.088 g, 18.490 mmol [BMPL][BFH(CN)$_2$] (75%).

$^1$H{$^{11}$B} NMR (500.1 MHz, (CD$_3$)$_2$CO) $\delta$ = 3.68-3.56 (m, 4H, C*H*$_2$), 3.46-3.41 (m, 2H, C*H*$_2$), 3.14 (s, 3H, C*H*$_3$), 2.73 (qd, 1H,$^1J$($^{11}$B,$^1$H) = 110.0 Hz, $^2J$($^{19}$F,$^1$H) = 40.7 Hz, BF*H*(CN)$_2$) 2.30-2.23 (m, 4H, C*H*$_2$), 1.88-1.80 (m, 2H, C*H*$_2$), 1.45-1.37 (m, 2H, C*H*$_2$CH$_3$), 0.96 ppm (t, 3H, $^3J$($^1$H,$^1$H) = 7.48 Hz, CH$_2$C*H*$_3$).

$^1$H{$^{11}$B} NMR (500.1 MHz, (CD$_3$)$_2$CO) $\delta$ = 3.68-3.56 (m, 4H, C*H*$_2$), 3.46-3.41 (m, 2H, C*H*$_2$), 3.14 (s, 3H, C*H*$_3$), 2.73 (d, 1H, $^2J$($^{19}$F,$^1$H) = 40.7 Hz, BF*H*(CN)$_2$) 2.30-2.23 (m, 4H, C*H*$_2$), 1.88-1.80 (m, 2H, C*H*$_2$), 1.45-1.37 (m, 2H, C*H*$_2$CH$_3$), 0.96 ppm (t, 3H, $^3J$($^1$H,$^1$H) = 7.48 Hz, CH$_2$C*H*$_3$).

$^1$H{$^{19}$F} NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ = 3.68-3.56 (m, 4H, C*H*$_2$), 3.46-3.41 (m, 2H, C*H*$_2$), 3.14 (s, 3H, C*H*$_3$), 2.73 (q, 1H, $^1J$($^{11}$B,$^1$H) = 110.0 Hz, BF*H*(CN)$_2$) 2.30-2.23 (m, 4H, C*H*$_2$), 1.88-1.80 (m, 2H, C*H*$_2$), 1.45-1.37 (m, 2H, C*H*$_2$CH$_3$), 0.96 ppm (t, 3H, $^3J$($^1$H,$^1$H) = 7.48 Hz, CH$_2$C*H*$_3$).

$^{13}$C{$^1$H} NMR (125.7 MHz, (CD$_3$)$_2$CO) $\delta$ = 132.5 (qd, $^1J$($^{13}$C,$^{11}$B) = 65.2 Hz, $^2J$($^{19}$F,$^{13}$C) = 35.6 Hz, BFH(*C*N)$_2$), 64.8 (t, 2C, $^1J$($^{14}$N,$^{13}$C) = 3.2 Hz, N*C*H$_2$), 64.6 (t, 1C, $^1J$($^{14}$N,$^{13}$C) = 3.0 Hz, N*C*H$_2$), 48.7 (t, 1C, $^1J$($^{14}$N,$^{13}$C) = 4.1 Hz, N*C*H$_3$), 25.9 (s, 1C, *C*H$_2$), 22.0 (s, 2C, CH$_2$), 20.0 (t, 1C, *C*H$_2$CH$_3$) 13.6 ppm (s, 1C CH$_2$*C*H$_3$).

$^{13}$C{$^{19}$F} NMR (125.7 MHz, (CD$_3$)$_2$CO) $\delta$ = 132.5 (q, $^1J$($^{13}$C,$^{11}$B) = 65.2 Hz, BFH(*C*N)$_2$), 64.9 (t, 2C, $^1J$($^{13}$C,$^1$H) = 148.1 Hz, N*C*H$_2$), 64.7 (t, 1C, $^1J$($^{13}$C,$^1$H) = 143.8 Hz, N*C*H$_2$), 48.7 (qm, 1C, $^1J$($^{13}$C,$^1$H) = 143.9 Hz, N*C*H$_3$), 26.0 (t, 1C, $^1J$($^{13}$C,$^1$H) = 128.3 Hz, *C*H$_2$), 22.1 (t, 2C, $^1J$($^{13}$C,$^1$H) = 136.7 Hz CH$_2$), 20.1 (t, 1C,$^1J$($^{13}$C,$^1$H) = 127.0 Hz, *C*H$_2$CH$_3$) 13.6 ppm (qm, 1C,$^1J$($^{13}$C,$^1$H) = 125.4 Hz, CH$_2$*C*H$_3$).

$^{11}$B NMR (160.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −14.2 ppm (dd, 1B, $^1J$($^{11}$B,$^1$H) = 110.0 Hz, $^1J$($^{19}$F,$^{11}$B) = 56.2 Hz, *B*FH(CN)$_2$).

$^{11}$B{$^{19}$F} NMR (160.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −14.2 ppm (d, 1B, $^1J$($^{11}$B,$^1$H) = 110.0 Hz, *B*FH(CN)$_2$).

$^{11}$B{$^1$H} NMR (160.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −14.2 ppm (d, 1B, $^1J$($^{19}$F,$^{11}$B) = 56.2 Hz, *B*FH(CN)$_2$).

$^{19}$F NMR (470.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −233.6 ppm (qd, 1F, $^1J$($^{19}$F,$^{11}$B) = 56.0 Hz, $^2J$($^{19}$F,$^1$H) = 40.7 Hz, B*F*H(CN)$_2$).

$^{19}$F{$^{11}$B} NMR (470.5 MHz, (CD$_3$)$_2$CO) $\delta$ = −233.6 ppm (d, 1F, $^2J$($^{19}$F,$^1$H) = 40.7 Hz, B*F*H(CN)$_2$).

$^{19}$F{$^1$H} NMR (377 MHz, (CD$_3$)$_2$CO) $\delta$ = -233.6 ppm (q, 1F, $^1J$($^{19}$F,$^{11}$B) = 56.0 Hz, B*F*H(CN)$_2$).

IR (ATR): 2371 ($\nu$(B−H), 2198 cm$^{-1}$ ($\nu$(C≡N)).

Raman: 2379 ($\nu$(B−H), 2200 cm$^{-1}$ ($\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{11}H_{21}BFN_3$: C 58.69, H 9.40, N 18.67; found: C 58.46, H 9.33, N 19.66.

### 4.2.5 [BMIm][$BH_2(CN)_2$]

K[$BH_2(CN)_2$] (2.2 g, 21.2 mmol) was dissolved in water (5 mL) and a solution of [BMPL]Cl (5.84 g, 33.43 mmol) in water (15 mL) was added. The mixture was extracted with $CH_2Cl_2$ (5×5 mL) and the combined organic layers were washed with bidistilled water (5×3 mL). All volatiles were removed in a vacuum and the remaining ionic liquid was dried in a fine vacuum.

Yield: 2.87 g, 14.07 mmol [BMPL][$BFH(CN)_2$] (67%).

## 4.3 [$BnPh_3P$] salts

[$BnPh_3P$]Cl was dissolved in ethanol (20-30 mL) and an equimolar solution of the respective potassium or sodium borate in ethanol was added (10-15 mL). The mixture was stirred for 15 minutes. After adding water (150-200 mL) dropwise for 30 minutes, the resulting precipitate was filtered off and washed with water and diethyl ether. The colourless product was dried in vacuo.

### 4.3.1 [$BnPh_3P$][$BF_4$]

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.99−7.91 (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.38−7.33 (m, 1H, P−$CH_2$−Ph-$H_p$), 7.28−7.24 (m, 2H, P−$CH_2$−Ph-$H_m$), 7.12−7.09 (m, 2H, P−$CH_2$−Ph-$H_o$), 5.09 ppm (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.1 Hz, P−Ph-$C_p$), 135.2 (d, $^3J(^{31}P,^{13}C)$ = 9.8 Hz, P−Ph-$C_o$), 132.0 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−$CH_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-$C_m$), 129.9 (d, $^4J(^{31}P,^{13}C)$ = 3.3 Hz, P−$CH_2$−Ph-$C_m$), 129.6 (d, $^5J(^{31}P,^{13}C)$ = 3.8 Hz, P−$CH_2$−Ph-$C_p$), 128.5 (d, $^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−$CH_2$−Ph-$C_i$), 118.8 (d, $^1J(^{31}P,^{13}C)$ = 86.1 Hz, P−Ph-$C_i$), 30.3 ppm (d, $^1J(^{31}P,^{13}C)$ = 53.1 Hz, P−$CH_2$−Ph).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −0.86 ppm (s, 1B, $BF_4$).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −0.86 ppm (s, 1B, $BF_4$).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -151.54$ (s, 4F (~20%), $^{10}$B$F_4$) −151.59 ppm (s, 4F (~80%), $^{11}$B$F_4$).

$^{19}$F{$^{11}$B} NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -151.54$ (s, 4F (~20%), $^{10}$B$F_4$) −151.59 ppm (s, 4F (~80%), $^{11}$B$F_4$).

$^{31}$P NMR (202.5 MHz,$(CD_3)_2CO$) $\delta = 23.0$ ppm (s, BzPh$_3$$P$).

$^{31}$P{$^{1}$H} NMR (202.5 MHz,$(CD_3)_2CO$) $\delta = 23.0$ ppm (s, BzPh$_3$$P$).

Elemental analysis calcd (%) for $C_{25}H_{22}BF_4P$: C 68.21, H 5.04; found: C 68.15, H 5.04.

K[BF$_4$]: 300 mg, 2.38 mmol.

[BnPh$_3$P]Cl: 930 mg, 2.38 mmol.

yield: 710 mg, 1.61 mmol [BnPh$_3$P][BF$_4$] (68 %).

### 4.3.2 [BnPh$_3$P][BF$_3$(CN)]

$^{1}$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta = 7.98{-}7.94$ (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.38−7.34 (m, 1H, P−CH$_2$−Ph-$H_p$), 7.29−7.24 (m, 2H, P−CH$_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−CH$_2$−Ph-$H_o$), 5.09 ppm (d, 2H, $^{2}J(^{31}P,^{1}H) = 15.0$ Hz, P−C$H_2$−Ph).

$^{13}$C{$^{1}$H} NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.2$ (d, $^{4}J(^{31}P,^{13}C) = 3.1$ Hz, P−Ph-$C_p$), 135.2 (d, $^{3}J(^{31}P,^{13}C) = 9.7$ Hz, P−Ph-$C_o$), 132.4 (m, BF$_3$($C$N)), 132.0 (d, $^{3}J(^{31}P,^{13}C) = 5.5$ Hz, P−CH$_2$−Ph-$C_o$), 131.1 (d, $^{3}J(^{31}P,^{13}C) = 12.6$ Hz, P−Ph-$C_m$), 129.9 (d, $^{4}J(^{31}P,^{13}C) = 3.2$ Hz, P−CH$_2$−Ph-$C_m$), 129.6 (d, $^{5}J(^{31}P,^{13}C) = 3.8$ Hz, P−CH$_2$−Ph-$C_p$), 128.5 (d, $^{2}J(^{31}P,^{13}C) = 8.5$ Hz, P−CH$_2$−Ph-C$_i$), 118.8 (d, $^{1}J(^{31}P,^{13}C) = 86.1$ Hz, P−Ph-$C_i$), 30.4 ppm (d, $^{1}J(^{31}P,^{13}C) = 48.4$ Hz, P−$C$H$_2$−Ph).

$^{13}$C{$^{19}$F} NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.2$ (m, P−Ph-$C_p$), 135.2 (m, P−Ph-$C_o$), 132.4 (q, $^{1}J(^{13}C,^{11}B) = 89.3$ Hz, BF$_3$($C$N)), 132.0 (m, P−CH$_2$−Ph-$C_o$), 131.1 (m, P−Ph-$C_m$), 129.9 (m, P−CH$_2$−Ph-$C_m$), 129.6 (m, P−CH$_2$−Ph-$C_p$), 128.5 (m, P−CH$_2$−Ph-C$_i$), 118.8 (m, P−Ph-$C_i$) 30.3 ppm (m, P−$C$H$_2$−Ph).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -3.47$ ppm (t, 1B, $^{1}J(^{19}F,^{11}B) = 26.8$ Hz, $B$F$_3$(CN)).

$^{11}$B{$^{19}$F} NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -3.47$ ppm (s, 1B, $B$F$_3$(CN)).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -137.6$ (spt, 3F (~20%), $^{1}J(^{19}F,^{10}B) = 8.7$ Hz, $^{10}$B$F_3$(CN)), −137.7 ppm (q, 3F (~80%), $^{1}J(^{19}F,^{11}B) = 26.8$ Hz, $^{11}$B$F_3$(CN)).

$^{19}$F{$^{11}$B} NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −137.6 (spt, 3F (~20%), $^1J(^{19}F,^{10}B)$ = 8.7 Hz, $^{10}BF_3(CN)$), −137.7 ppm (s, 3F (~80%), $^{11}BF_3(CN)$).

$^{31}$P NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, BzPh$_3$*P*).

$^{31}$P{$^1$H} NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, BzPh$_3$*P*).

IR (ATR): 2207 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2209 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{26}H_{22}BF_3NP$: C 69.82, H 4.96, N 3.13; found: C 69.80, H 5.01, N 3.12.

K[BF$_3$(CN)]: 200 mg, 1.50 mmol.

[BnPh$_3$P]Cl: 590 mg, 1.50 mmol.

yield: 511 mg, 1.14 mmol [BnPh$_3$P][BF$_3$(CN)] (76 %).

### 4.3.3 [BnPh$_3$P][BF$_2$(CN)$_2$]

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.98−7.94 (m, 3H, P−Ph-$H_p$), 7.82−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.38−7.34 (m, 1H, P−CH$_2$−Ph-$H_p$), 7.29−7.24 (m, 2H, P−CH$_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−CH$_2$−Ph-$H_o$), 5.08 ppm (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C*H*$_2$−Ph).

$^{13}$C{$^1$H} NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.0 Hz, P−Ph-$C_p$), 135.1 (d, $^3J(^{31}P,^{13}C)$ = 9.8 Hz, P−Ph-$C_o$), 130.8 (qd, BF$_2$(*C*N)$_2$), 131.9 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−CH$_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-$C_m$), 129.9 (d, $^4J(^{31}P,^{13}C)$ = 3.2 Hz, P−CH$_2$−Ph-$C_m$), 129.6 (d, $^5J(^{31}P,^{13}C)$ = 3.8 Hz, P−CH$_2$−Ph-$C_p$), 128.4 (d, $^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−CH$_2$−Ph-C$_i$), 118.7 (d, $^1J(^{31}P,^{13}C)$ = 86.1 Hz, P−Ph-$C_i$), 30.4 ppm (d, $^1J(^{31}P,^{13}C)$ = 48.4 Hz, P−*C*H$_2$−Ph).

$^{13}$C{$^{19}$F} NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (m, P−Ph-$C_p$), 135.2 (m, P−Ph-$C_o$), 135.1 (m, P−CH$_2$−Ph-$C_o$), 130.8 (q, $^1J(^{13}C,^{11}B)$ = 80.6 Hz, BF$_2$(*C*N)$_2$), 131.9 (m, P−CH$_2$−Ph-$C_o$), 131.1 (m, P−Ph-$C_m$), 129.9 (m, P−CH$_2$−Ph-$C_m$), 129.6 (m, P−CH$_2$−Ph-$C_p$), 128.4 (m, P−CH$_2$−Ph-C$_i$), 118.7 (m, P−Ph-$C_i$), 30.4 ppm (m, P−*C*H$_2$−Ph).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −7.2 ppm (t, 1B,$^1J(^{19}F,^{11}B)$ = 41.2 Hz) *B*F$_2$(CN)$_2$).

$^{11}$B{$^{19}$F} NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −7.2 ppm (s, 1B, *B*F$_2$(CN)$_2$).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −153.9 (spt, 2F (~20%), $^1J(^{19}F,^{10}B)$ = 13.8 Hz, $^{10}BF_2(CN)_2$), −154.0 ppm (q, 4F (~80%), $^1J(^{19}F,^{11}B)$ = 41.2 Hz, $^{11}BF_2(CN)_2$).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta = -153.9$ (spt, 2F (~20%), $^1J(^{19}F,^{10}B) = 13.8$ Hz, $^{10}BF_2(CN)_2$), −154.0 ppm (s, 4F (~80%), $^{11}BF_4$).

$^{31}P$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta = 22.9$ ppm (s, $BzPh_3P$).

$^{31}P\{^1H\}$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta = 22.9$ ppm (s, $BzPh_3P$).

IR (ATR): 2208 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2211 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{27}H_{22}BF_2N_2P$: C 71.39, H 4.88, N 6.17; found: C 71.40, H 5.01, N 6.29.

$Na[BF_2(CN)_2]$: 2.40 g, 19.4 mmol.

$[BnPh_3P]Cl$: 8.0 g, 20.6 mmol.

yield: 8.43 g, 18.56 mmol $[BnPh_3P][BF_2(CN)_2]$ (95.5 %).

### 4.3.4 $[BnPh_3P][BF(CN)_3]$

$^1H$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta = 7.99–7.92$ (m, 3H, P−Ph-$H_p$), 7.82−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.39−7.34 (m, 1H, P−$CH_2$−Ph-$H_p$), 7.30−7.25 (m, 2H, P−$CH_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−$CH_2$−Ph-$H_o$), 5.09 ppm (d, 2H, $^2J(^{31}P,^1H) = 15.0$ Hz, P−C$H_2$−Ph).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.2$ (d, $^4J(^{31}P,^{13}C) = 3.0$ Hz, P−Ph-$C_p$), 135.2 (d, $^3J(^{31}P,^{13}C) = 9.8$ Hz, P−Ph-$C_o$), 131.9 (d, $^3J(^{31}P,^{13}C) = 5.5$ Hz, P−$CH_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C) = 12.6$ Hz, P−Ph-$C_m$), 129.9 (d, $^4J(^{31}P,^{13}C) = 3.3$ Hz, P−$CH_2$−Ph-$C_m$), 129.6 (d, $^5J(^{31}P,^{13}C) = 3.8$ Hz, P−$CH_2$−Ph-$C_p$), 128.4 (d, $^2J(^{31}P,^{13}C) = 8.5$ Hz, P−$CH_2$−Ph-$C_i$), 127.9 (qd, $^1J(^{13}C,^{11}B) = 74.6$ Hz, $^2J(^{19}F,^{13}C) = 37.4$ Hz, BF($C$N)$_3$), 118.7 (d, $^1J(^{31}P,^{13}C) = 86.1$ Hz, P−Ph-$C_i$), 30.4 ppm (d, $^1J(^{31}P,^{13}C) = 48.5$ Hz, P−$CH_2$−Ph).

$^{13}C\{^{19}F\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta = 136.2$ (m, P−Ph-$C_p$), 135.2 (m, P−Ph-$C_o$), 132.0 (m, P−$CH_2$−Ph-$C_o$), 131.1 (m, P−Ph-$C_m$), 129.9 (m, P−$CH_2$−Ph-$C_m$), 129.6 (m, P−$CH_2$−Ph-$C_p$), 128.5 (m, P−$CH_2$−Ph-$C_i$), 127.9 (q, $^1J(^{13}C,^{11}B) = 74.7$ Hz, BF($C$N)$_3$), 118.7 (m, P−Ph-$C_i$), 30.4 ppm (m, P−$CH_2$−Ph).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -17.7$ ppm (d, 1B, $^1J(^{19}F,^{11}B) = 44.5$ Hz, $B$F(CN)$_3$).

$^{11}B\{^{19}F\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta = -17.7$ ppm (s, 1B, $B$F(CN)$_3$).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −211.8 (spt, 1F (~20%), $^1J(^{19}F,^{10}B)$ = 14.9 Hz, $^{10}BF(CN)_3$), −211.9 ppm (q, 1F (~80%), $^1J(^{19}F,^{11}B)$ = 44.5 Hz, $^{11}BF(CN)_3$).

$^{19}F\{^{11}B\}$ NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −211.8 (spt, 1F (~20%), $^1J(^{19}F,^{10}B)$ = 14.9 Hz, $^{10}BF(CN)_3$) −211.9 ppm (s, 4F (~80%), $^{11}BF(CN)_3$).

$^{31}$P NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, $BzPh_3P$).

$^{31}P\{^1H\}$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, $BzPh_3P$).

IR (ATR): 2213 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2217 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{28}H_{22}BFN_3P$: C 72.91, H 4.81, N 9.11; found: C 72.81, H 4.77, N 9.15.

K[BF(CN)$_3$]: 200 mg, 1.50 mmol.

[BnPh$_3$P]Cl: 590 mg, 1.50 mmol.

yield: 546 mg, 1.18 mmol [BnPh$_3$P][BF(CN)$_3$] (87 %).

### 4.3.5 [BnPh$_3$P][B(CN)$_4$]

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.99−7.93 (m, 3H, P−Ph-$H_p$), 7.82−7.74 (m, 12H, P−Ph-$H_o/H_m$), 7.39−7.34 (m, 1H, P−$CH_2$−Ph-$H_p$), 7.30−7.25 (m, 2H, P−$CH_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−$CH_2$−Ph-$H_o$), 5.09 ppm (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.0 Hz, P−Ph-$C_p$), 135.1 (d, $^3J(^{31}P,^{13}C)$ = 9.8 Hz, P−Ph-$C_o$), 131.9 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−$CH_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-$C_m$), 129.9 (d, $^4J(^{31}P,^{13}C)$ = 3.2 Hz, P−$CH_2$−Ph-$C_m$), 129.6 (d, $^5J(^{31}P,^{13}C)$ = 3.8 Hz, P−$CH_2$−Ph-$C_p$), 128.4 (d, $^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−$CH_2$−Ph-$C_i$), 123.1 (q, $^1J(^{13}C,^{11}B)$ = 70.8 Hz, B($C$N)$_4$), 118.7 (d, $^1J(^{31}P,^{13}C)$ = 86.1 Hz, P−Ph-$C_i$), 30.4 ppm (d, $^1J(^{31}P,^{13}C)$ = 48.3 Hz, P−$CH_2$−Ph).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −38.5 ppm (s, 1B, $B(CN)_4$).

$^{31}$P NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 25.2−21.1 ppm (m, $BzPh_3P$).

$^{31}P\{^1H\}$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, $BzPh_3P$).

IR (ATR): 2221 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2224 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{29}H_{22}BN_4P$: C 74.38, H 4.74, N 11.96; found: C 74.36, H 4.75, N 12.01.

$K[B(CN)_4]$: 200 mg, 1.45 mmol.

$[BnPh_3P]Cl$: 565 mg, 1.45 mmol.

yield: 580 mg, 1.24 mmol $[BnPh_3P][B(CN)_4]$ (85 %).

### 4.3.6 $[BnPh_3P][BFH(CN)_2]$

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.98−7.93 (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.38−7.33 (m, 1H, $PCH_2Ph$-$H_p$), 7.28−7.24 (m, 2H, $PCH_2Ph$-$H_m$), 7.12−7.09 (m, 2H, $PCH_2Ph$-$H_o$), 5.08 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph), 2.82 ppm (qd, 1H, $^1J(^{11}B,^1H)$ = 109.3 Hz, $^2J(^{19}F,^1H)$ = 40.7 Hz, BF$H$(CN)$_2$).

$^1$H{$^{11}$B} NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.98−7.93 (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.38−7.33 (m, 1H, $PCH_2Ph$-$H_p$), 7.28−7.24 (m, 2H, $PCH_2Ph$-$H_m$), 7.12−7.09 (m, 2H, $PCH_2Ph$-$H_o$), 5.08 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph), 2.82 ppm (d, 1H, $^2J(^{19}F,^1H)$ = 40.7 Hz, BF$H$(CN)$_2$).

$^1$H{$^{19}$F} NMR (400 MHz, $(CD_3)_2CO$) $\delta$ = 7.98−7.93 (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.38−7.33 (m, 1H, $PCH_2Ph$-$H_p$), 7.28−7.24 (m, 2H, $PCH_2Ph$-$H_m$), 7.12−7.09 (m, 2H, $PCH_2Ph$-$H_o$), 5.08 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph), 2.82 ppm (q, 1H, $^1J(^{11}B,^1H)$ = 109.3 Hz, BF$H$(CN)$_2$).

$^{13}$C{$^1$H} NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.0 Hz, P−Ph-$C_p$), 135.1 (d, $^3J(^{31}P,^{13}C)$ = 9.7 Hz, P−Ph-$C_o$), 132.8 (qd, $^1J(^{13}C,^{11}B)$ = 65.3 Hz, $^2J(^{19}F,^{13}C)$ = 34.7 Hz, BFH($C$N)$_2$), 131.9 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−$CH_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-$C_m$), 129.9 (d, $^4J(^{31}P,^{13}C)$ = 3.2 Hz, P−$CH_2$−Ph-$C_m$), 129.5 (d, $^5J(^{31}P,^{13}C)$ = 3.8 Hz, P−$CH_2$−Ph-$C_p$), 128.4 (d, $^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−$CH_2$−Ph-$C_i$), 118.6 (d, $^1J(^{31}P,^{13}C)$ = 86.1 Hz, P−Ph-$C_i$), 30.3 ppm (d, $^1J(^{31}P,^{13}C)$ = 48.0 Hz, P−$C$H$_2$−Ph).

$^{13}$C{$^{19}$F} NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (m, P−Ph-$C_p$), 135.1 (m, P−Ph-$C_o$), 132.8 (q, $^1J(^{13}C,^{11}B)$ = 65.3 Hz, BFH($C$N)$_2$), 131.9 (m, P−$CH_2$−Ph-$C_o$), 131.1 (m, P−Ph-$C_m$), 129.9 (m, P−$CH_2$−Ph-$C_m$), 129.5 (m, P−$CH_2$−Ph-$C_p$), 128.4 (m, P−$CH_2$−Ph-$C_i$), 118.6 (m, P−Ph-$C_i$), 30.3 ppm (m, P−$C$H$_2$−Ph).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −14.1 ppm (dd, 1B, $^1J(^{11}B,^1H)$ = 109.4 Hz, $^1J(^{19}F,^{11}B)$ = 56.0 Hz, $BH_3(CN)$).

$^{11}$B{$^1$H} NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −14.1 ppm (d, 1B, $^1J(^{19}F,^{11}B)$ = 56.0 Hz, $BH_3(CN)$).

$^{11}$B{$^{19}$F} NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −14.1 ppm (d, 1B, $^1J(^{11}B,^1H)$ = 109.4 Hz, $BH_3(CN)$).

$^{19}$F NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −234.0 ppm (qd, 1F, $^1J(^{19}F,^{11}B)$ = 55.9 Hz,
$^2J(^{19}F,^1H)$ = 40.7 Hz, $B\mathit{F}H(CN)_2$).

$^{19}$F{$^{11}$B} NMR (470.5 MHz, $(CD_3)_2CO$) $\delta$ = −234.0 ppm (d, 1F, $^2J(^{19}F,^1H)$ = 40.7 Hz, $B\mathit{F}H(CN)_2$).

$^{19}$F{$^1$H} NMR (377 MHz, $(CD_3)_2CO$) $\delta$ = −234.0 ppm (q, 1F, $^1J(^{19}F,^{11}B)$ = 55.9 Hz, $B\mathit{F}H(CN)_2$).

$^{31}$P NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, $BzPh_3\mathit{P}$).

$^{31}$P{$^1$H} NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, $BzPh_3\mathit{P}$).

IR (ATR): 2401 ($\nu$(B−H), 2201 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2403 ($\nu$(B−H), 2202 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{27}H_{23}BFN_2P$: C 74.33, H 5.31, N 6.42; found: C 74.51, H 5.41, N 6.53.

K[BFH(CN)$_2$]: 1.34 g, 11.0 mmol.

[BnPh$_3$P]Cl: 4.3 g, 11.0 mmol.

yield: 3.54 g, 8.37 mmol [BnPh$_3$P][BFH(CN)$_2$] (77 %).

### 4.3.7 [BnPh$_3$P][BH$_3$(CN)]

$^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.99−7.91 (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.37−7.32 (m, 1H, PCH$_2$Ph-$H_p$), 7.28−7.23 (m, 2H, PCH$_2$Ph-$H_m$), 7.13−7.09 (m, 2H, PCH$_2$Ph-$H_o$), 5.12 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph), 0.51 ppm (q, 3H, $^1J(^{11}B,^1H)$ = 88.3 Hz, B$H_3$(CN)).

$^1$H{$^{11}$B} NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = $^1$H NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.99−7.91 (m, 3H, P−Ph-$H_p$), 7.81−7.74 (m, 12H, P−Ph-$H_o$/$H_m$), 7.37−7.32 (m, 1H, P−CH$_2$−Ph-$H_p$), 7.28−7.23 (m, 2H, P−CH$_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−CH$_2$−Ph-$H_o$), 5.12 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C$H_2$−Ph), 0.51 ppm (s, 3H, B$H_3$(CN)).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.0 Hz, P−Ph-$C_p$), 135.2 (d, $^3J(^{31}P,^{13}C)$ = 9.8 Hz, P−Ph-$C_o$), 132.0 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−$CH_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-$C_m$), 129.8 (d, $^4J(^{31}P,^{13}C)$ = 3.3 Hz, P−$CH_2$−Ph-$C_m$), 129.5 (d, $^5J(^{31}P,^{13}C)$ = 3.9 Hz, P−$CH_2$−Ph-$C_p$), 128.5 (d, $^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−$CH_2$−Ph-$C_i$), 118.8 (d, $^1J(^{31}P,^{13}C)$ = 86.0 Hz, P−Ph-$C_i$), 30.3 ppm (d, $^1J(^{31}P,^{13}C)$ = 54.1 Hz, P−$CH_2$−Ph).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −41.8 ppm (q, 1B, $^1J(^{11}B,^1H)$ = 88.3 Hz, $BH_3(CN)$).

$^{11}B\{^1H\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −41.8 ppm (s, 1B, $BH_3(CN)$).

$^{31}P$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 23.0 ppm (s, $BzPh_3P$).

$^{31}P\{^1H\}$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 23.0 ppm (s, $BzPh_3P$).

IR (ATR): 2310 ($\nu$(B−H), 2161 cm$^{-1}$ ( $\nu$(C≡N)).

Raman: 2334 ($\nu$(B−H), 2167 cm$^{-1}$ ( $\nu$(C≡N)).

Elemental analysis calcd (%) for $C_{27}H_{24}BN_2P$: C 79.41, H 6.41, N 3.59; found: C 79.18, H 6.27, N 3.50.

$K[BH_3(CN)]$: 200 mg, 3.18 mmol.

$[BnPh_3P]Cl$: 1.24 g, 3.18 mmol.

yield: 846 mg, 2.15 mmol $[BnPh_3P][BH_3(CN)]$ (68 %).

### 4.3.8 $[BnPh_3P][BH_2(CN)_2]$

$^1H$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.99−7.92 (m, 3H, P−Ph-$H_p$), 7.82−7.74 (m, 12H, P−Ph-$H_o/H_m$), 7.38−7.33 (m, 1H, P−$CH_2$−Ph-$H_p$), 7.29−7.24 (m, 2H, P−$CH_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−$CH_2$−Ph-$H_o$), 5.10 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−$CH_2$−Ph), 1.12 ppm (q, 2H, $^1J(^{11}B,^1H)$ = 93.7 Hz, $BH_2(CN)_2$).

$^1H\{^{11}B\}$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.99−7.92 (m, 3H, P−Ph-$H_p$), 7.82−7.74 (m, 12H, P−Ph-$H_o/H_m$), 7.38−7.33 (m, 1H, P−$CH_2$−Ph-$H_p$), 7.29−7.24 (m, 2H, P−$CH_2$−Ph-$H_m$), 7.13−7.09 (m, 2H, P−$CH_2$−Ph-$H_o$), 5.10 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−$CH_2$−Ph), 1.12 ppm (s, 2H, $BH_2(CN)_2$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.0 Hz, P−Ph-$C_p$), 135.1 (d, $^3J(^{31}P,^{13}C)$ = 9.8 Hz, P−Ph-$C_o$), 134.6 (q, 2C, $^1J(^{13}C,^{11}B)$ = 58.6 Hz, $BH_2(CN)_2$), 131.9 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−$CH_2$−Ph-$C_o$), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-$C_m$), 129.9 (d, $^4J(^{31}P,^{13}C)$ = 3.3 Hz, P−$CH_2$−Ph-$C_m$), 129.5 (d, $^5J(^{31}P,^{13}C)$ = 3.8 Hz, P−$CH_2$−Ph-$C_p$), 128.4 (d,

$^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−CH$_2$−Ph-C$_i$), 118.7 (d, $^1J(^{31}P,^{13}C)$ = 86.1 Hz, P−Ph-*C$_i$*), 30.3 ppm (d, $^1J(^{31}P,^{13}C)$ = n.b., P−*C*H$_2$−Ph).

$^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −41.6 ppm (t, 1B, $^1J(^{11}B,^1H)$ = 93.7 Hz, *B*H$_2$(CN)$_2$).

$^{11}B\{^1H\}$ NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −41.6 ppm (s, 1B, *B*H$_2$(CN)$_2$).

$^{31}P$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 23.0 ppm (s, BzPh$_3$*P*).

$^{31}P\{^1H\}$ NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 23.0 ppm (s, BzPh$_3$*P*).

IR (ATR): 2385 (*ν*(B−H), 2184 cm$^{-1}$ ( *ν*(C≡N)).

Raman: 2389 (*ν*(B−H), 2191 cm$^{-1}$ ( *ν*(C≡N)).

Elemental analysis calcd (%) for $C_{27}H_{24}BN_2P$: C 77.53, H 5.78, N 6.70; found: C 77.65, H 5.79, N 6.70.

K[BH$_2$(CN)$_2$]: 200 mg, 1.92 mmol.

[BnPh$_3$P]Cl: 750 mg, 1.92 mmol.

yield: 717 mg, 1.71 mmol [BnPh$_3$P][BH$_2$(CN)$_2$] (89 %).

### 4.3.9 [BnPh$_3$P][BH(CN)$_3$]

$^1H$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.98−7.93 (m, 3H, P−Ph-*H$_p$*), 7.82−7.73 (m, 12H, P−Ph-*H$_o$*/*H$_m$*), 7.38−7.34 (m, 1H, P−CH$_2$−Ph-*H$_p$*), 7.30−7.25 (m, 2H, P−CH$_2$−Ph-*H$_m$*), 7.11−7.09 (m, 2H, P−CH$_2$−Ph-*H$_o$*), 5.09 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C*H$_2$*−Ph), 1.81 ppm (q, 1H, $^1J(^{11}B,^1H)$ = 96.7 Hz, B*H*(CN)$_3$).

$^1H\{^{11}B\}$ NMR (500.1 MHz, $(CD_3)_2CO$) $\delta$ = 7.98−7.93 (m, 3H, P−Ph-*H$_p$*), 7.82−7.73 (m, 12H, P−Ph-*H$_o$*/*H$_m$*), 7.38−7.34 (m, 1H, P−CH$_2$−Ph-*H$_p$*), 7.30−7.25 (m, 2H, P−CH$_2$−Ph-*H$_m$*), 7.11−7.09 (m, 2H, P−CH$_2$−Ph-*H$_o$*), 5.09 (d, 2H, $^2J(^{31}P,^1H)$ = 15.0 Hz, P−C*H$_2$*−Ph), 1.81 ppm (s, 1H, B*H*(CN)$_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $(CD_3)_2CO$) $\delta$ = 136.2 (d, $^4J(^{31}P,^{13}C)$ = 3.0 Hz, P−Ph-*C$_p$*), 135.1 (d, $^3J(^{31}P,^{13}C)$ = 9.8 Hz, P−Ph-*C$_o$*), 131.9 (d, $^3J(^{31}P,^{13}C)$ = 5.5 Hz, P−CH$_2$−Ph-*C$_o$*), 131.1 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz, P−Ph-*C$_m$*), 129.9 (d, $^4J(^{31}P,^{13}C)$ = 3.3 Hz, P−CH$_2$−Ph-*C$_m$*), 129.6 (d, $^5J(^{31}P,^{13}C)$ = 3.8 Hz, P−CH$_2$−Ph-*C$_p$*), 128.4 (d, $^2J(^{31}P,^{13}C)$ = 8.5 Hz, P−CH$_2$−Ph-C$_i$), 128.0 (q, 3C, $^1J(^{13}C,^{11}B)$ = 66.0 Hz, BH(*C*N)$_3$), 118.7 (d, $^1J(^{31}P,^{13}C)$ = 86.1 Hz, P−Ph-*C$_i$*), 30.4 ppm (d, $^1J(^{31}P,^{13}C)$ = 48.4 Hz, P−*C*H$_2$−Ph).

$^{11}$B NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −40.0 ppm (d, 1B, $^1J(^{11}B,^1H)$ = 96.7 Hz, *B*H(CN)$_3$).

$^{11}$B{$^1$H} NMR (160.5 MHz, $(CD_3)_2CO$) $\delta$ = −40.0 ppm (s, 1B, *B*H(CN)$_3$).

$^{31}$P NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, BzPh$_3$*P*).

$^{31}$P{$^1$H} NMR (202.5 MHz,$(CD_3)_2CO$) $\delta$ = 22.9 ppm (s, BzPh$_3$*P*).

IR (ATR): 2394 (*ν*(B−H), 2213 cm$^{-1}$ ( *ν*(C≡N)).

Raman: 2397 (*ν*(B−H), 2214 cm$^{-1}$ ( *ν*(C≡N)).

Elemental analysis calcd (%) for $C_{28}H_{23}BN_3P$: C 75.87, H 5.23, N 9.48; found: C 75.89, H 5.28, N 9.51.

K[BH(CN)$_3$]: 200 mg, 1.55 mmol.

[BnPh$_3$P]Cl: 603 mg, 1.55 mmol.

yield: 470 mg, 1.06 mmol [BnPh$_3$P][BH(CN)$_3$] (68 %).

# 5 NMR spectra

## 5.1 [EMIm] salts

### 5.1.1 [EMIm][BF$_4$]

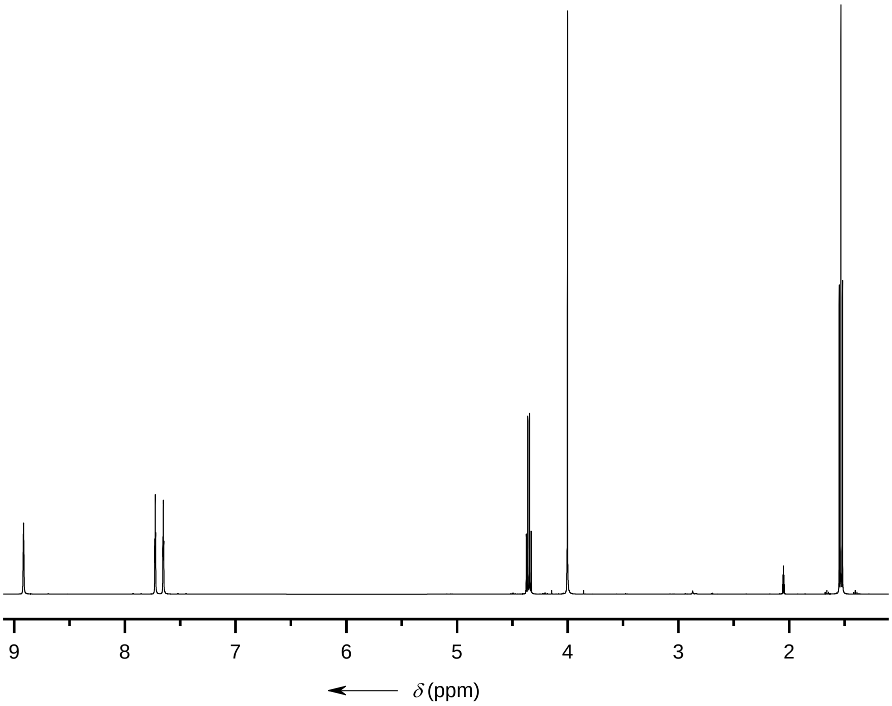


**Figure S1: $^1$H NMR spectrum of [EMIm][BF$_4$].**

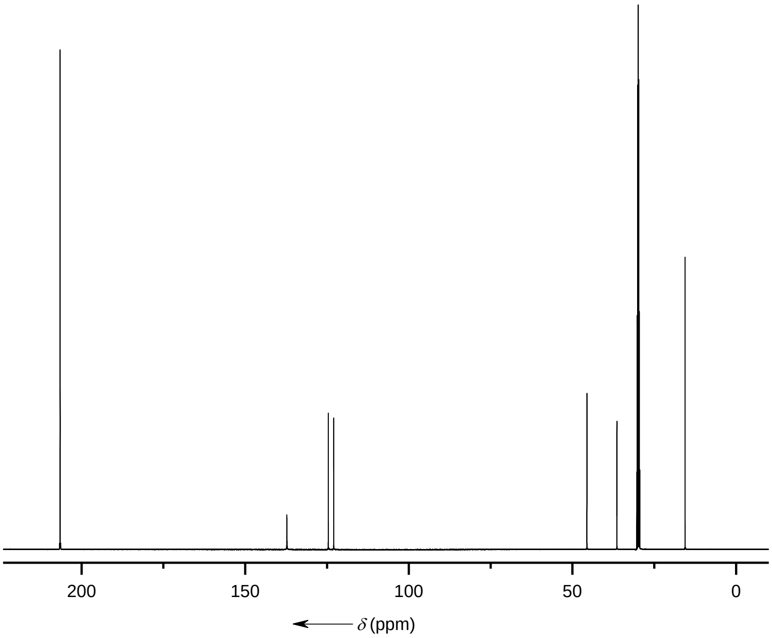


**Figure SS2: $^{13}$C{$^1$H} NMR spectrum of [EMIm][BF$_4$].**

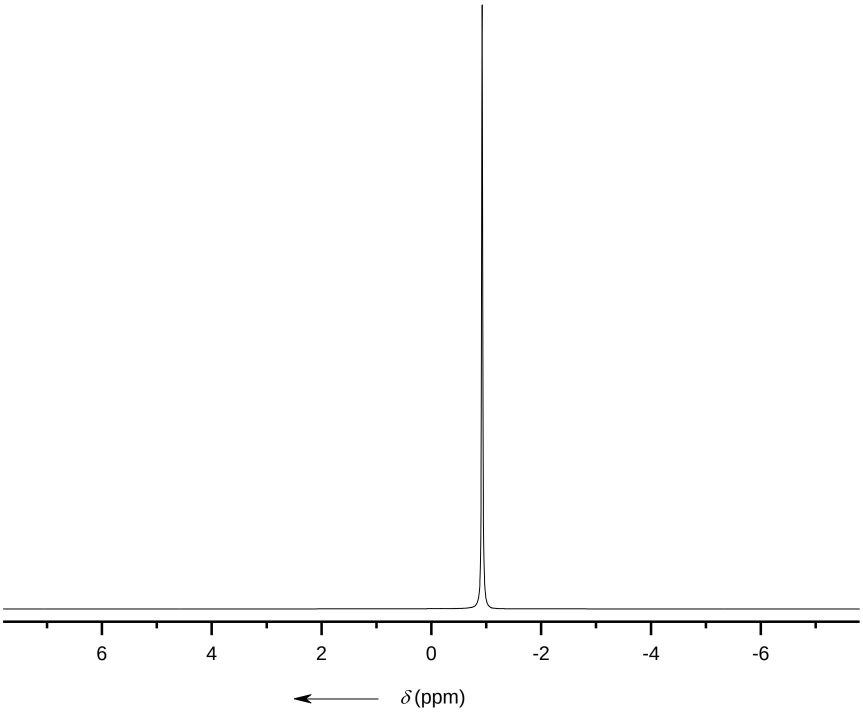


**Figure S3:** $^{11}$B NMR spectrum of [EMIm][BF$_4$].

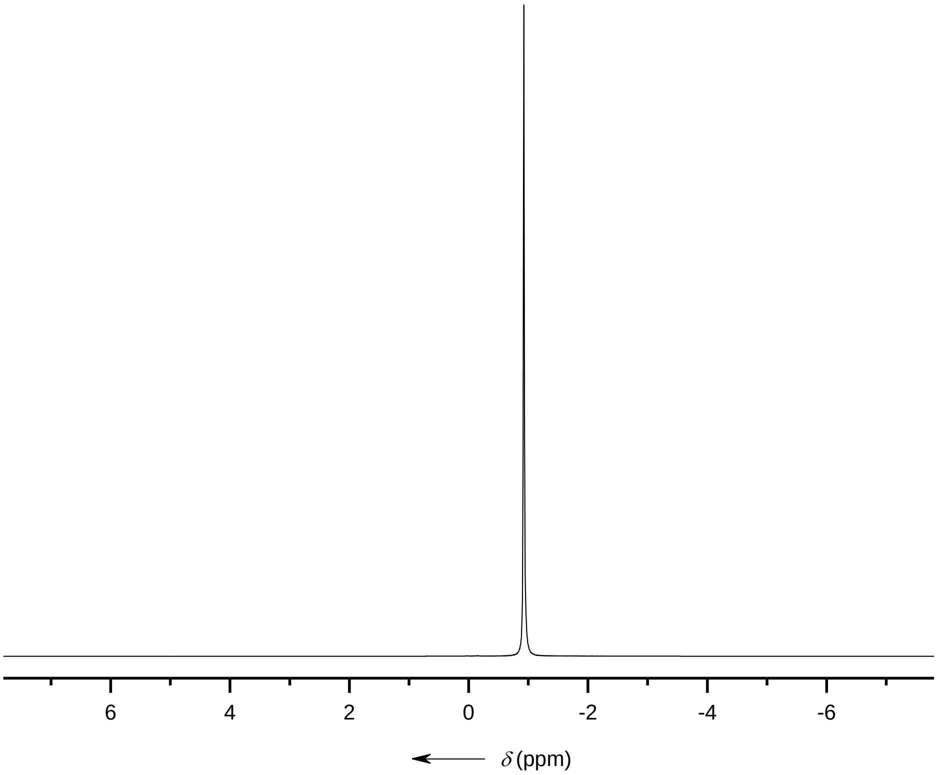


**Figure S4:** $^{11}$B{$^{19}$F} NMR spectrum of [EMIm][BF$_4$].

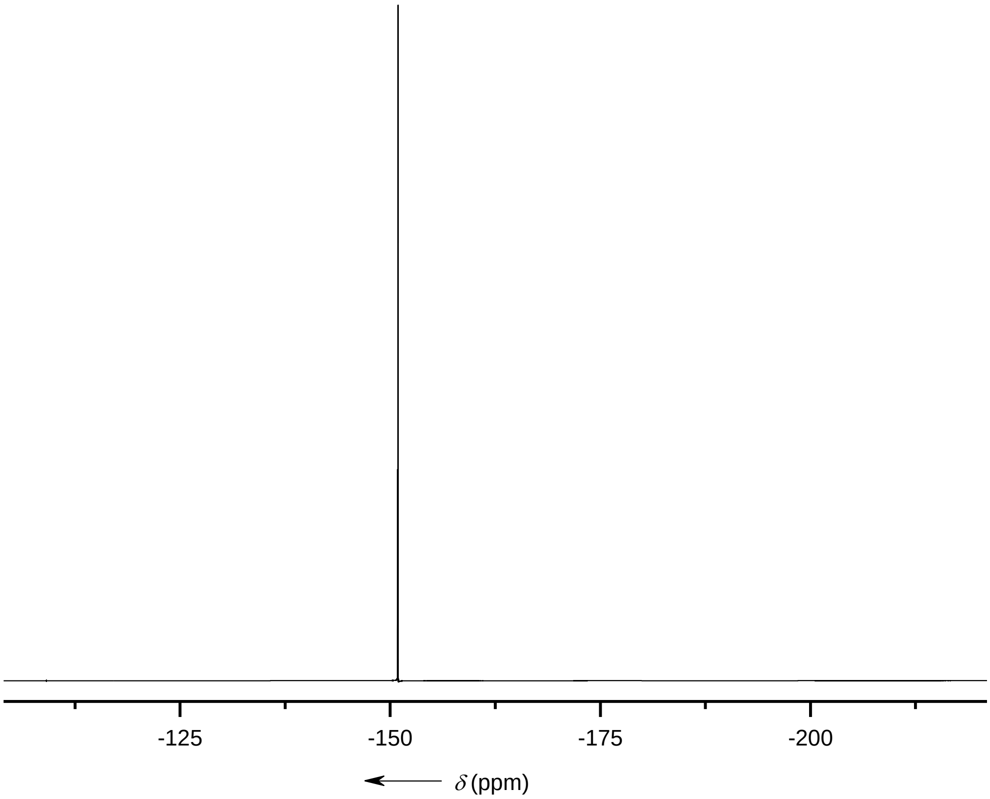


Figure S5: $^{19}$F NMR spectrum of [EMIm][BF$_4$].

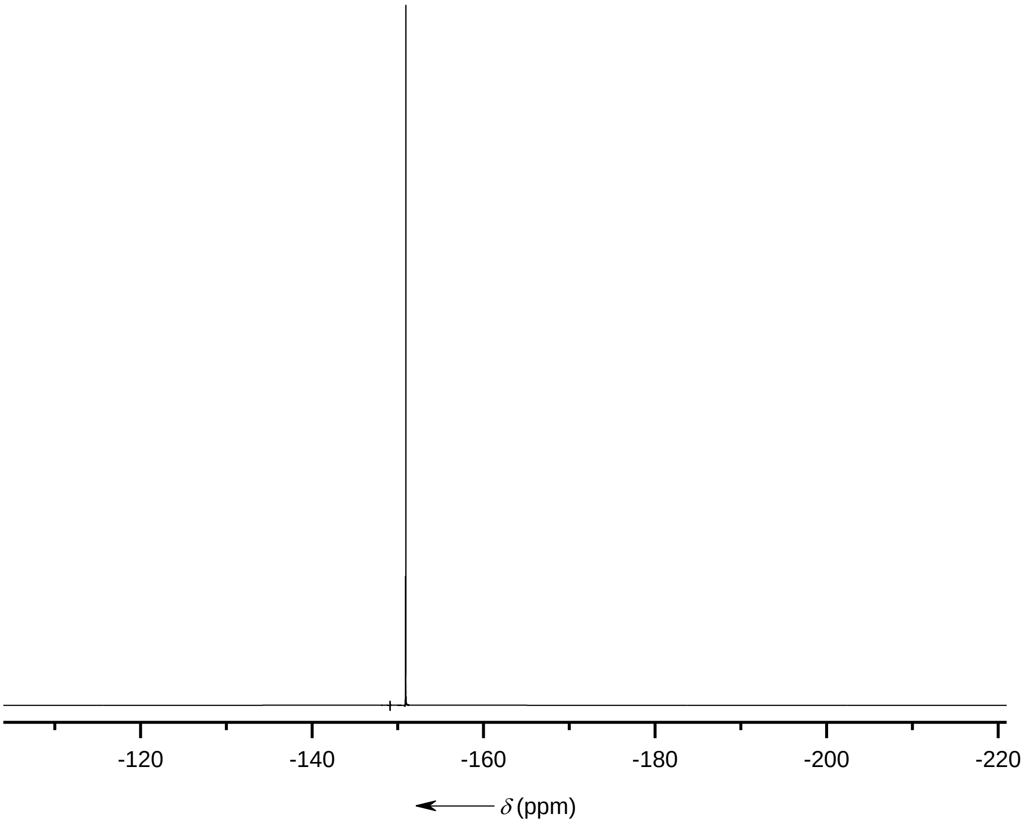


Figure S6: $^{19}$F{$^{11}$B} NMR spectrum of [EMIm][BF4].

### 5.1.2 [EMIm][BF$_3$(CN)]

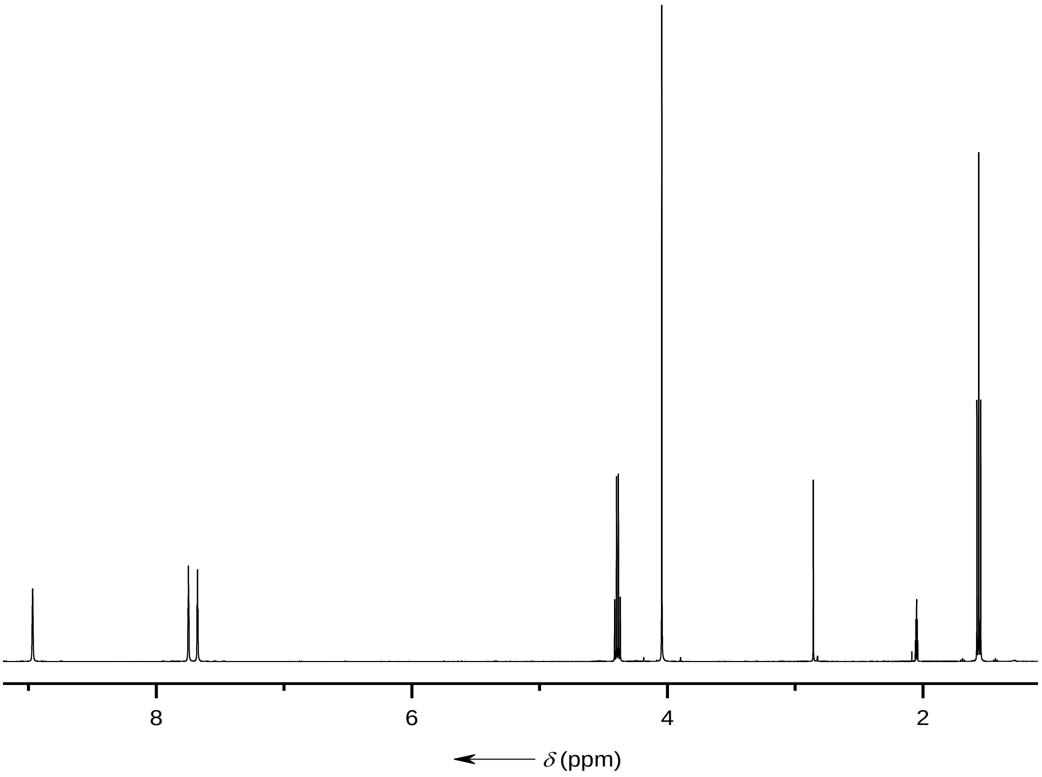


**Figure S7: $^1$H NMR spectrum of [EMIm][BF$_3$(CN)].**

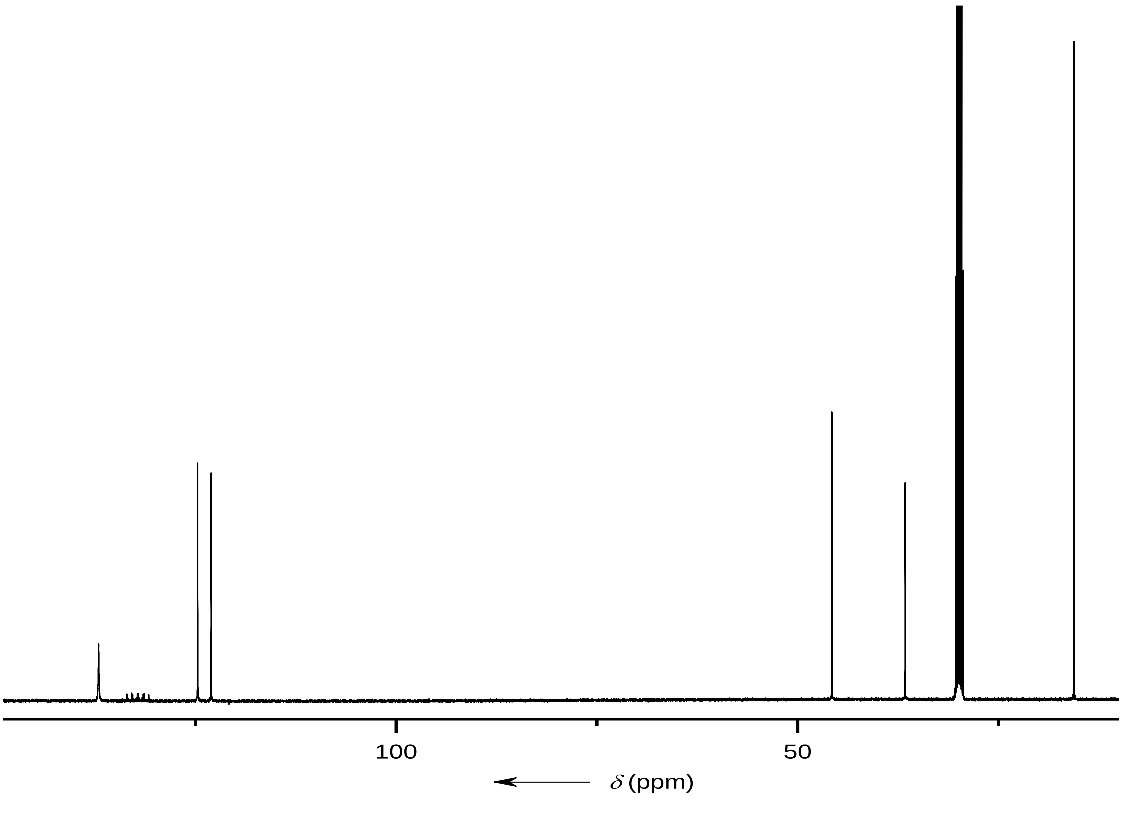


**Figure S8: $^{13}$C{$^1$H} NMR spectrum of [EMIm][BF$_3$(CN)].**

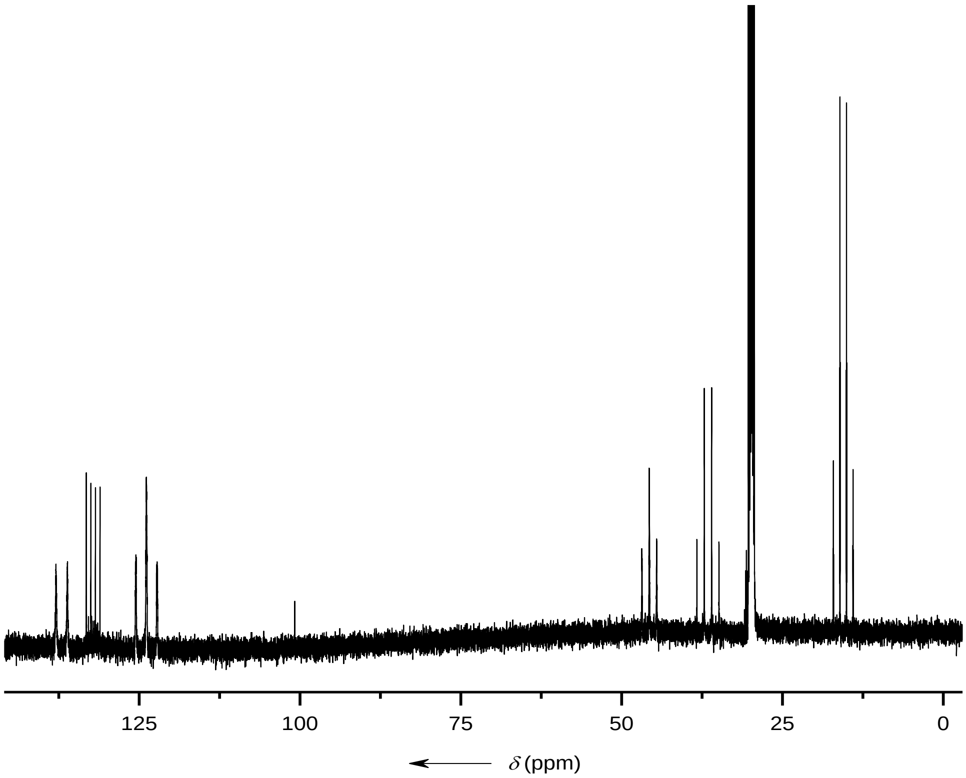


Figure S8: $^{13}C\{^{19}F\}$ NMR spectrum of [EMIm][$BF_3(CN)$].

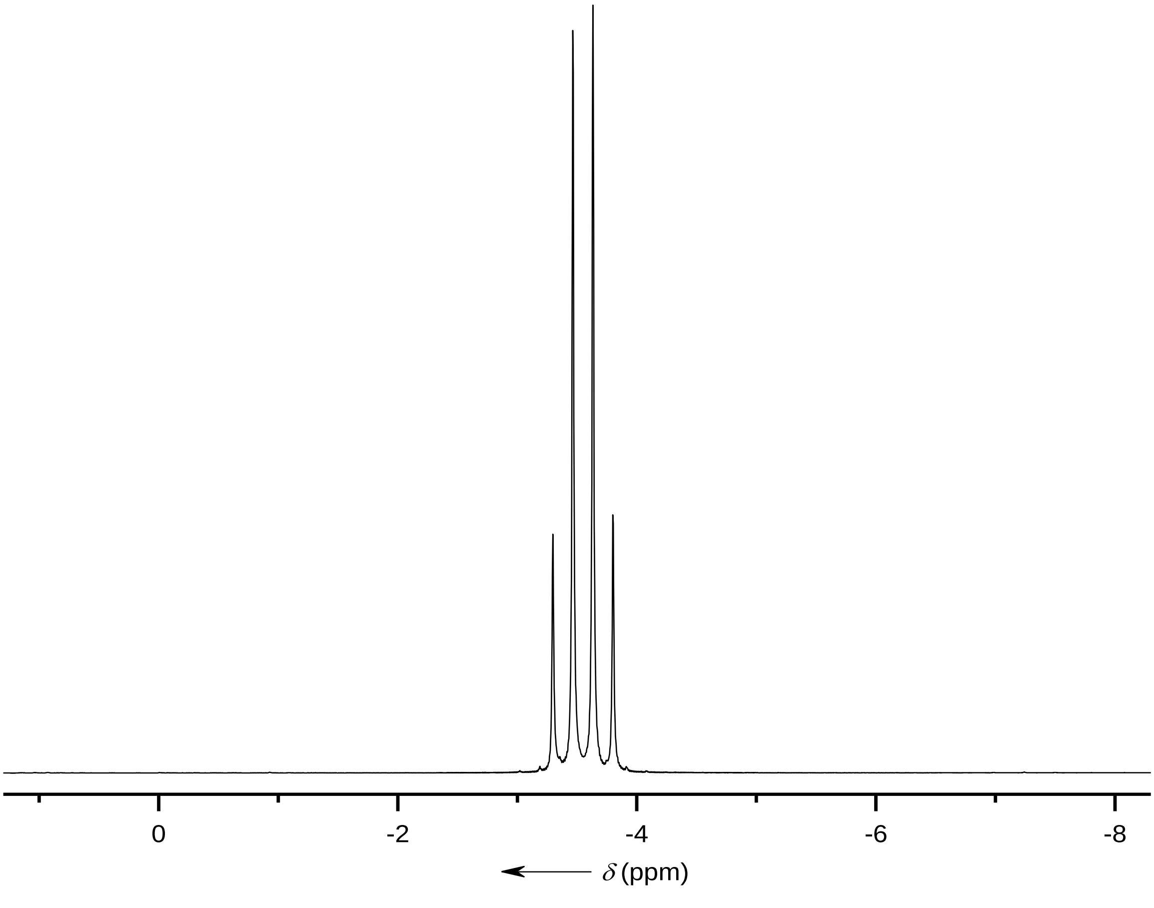


Figure S9: $^{11}B$ NMR spectrum of [EMIm][$BF_3(CN)$].

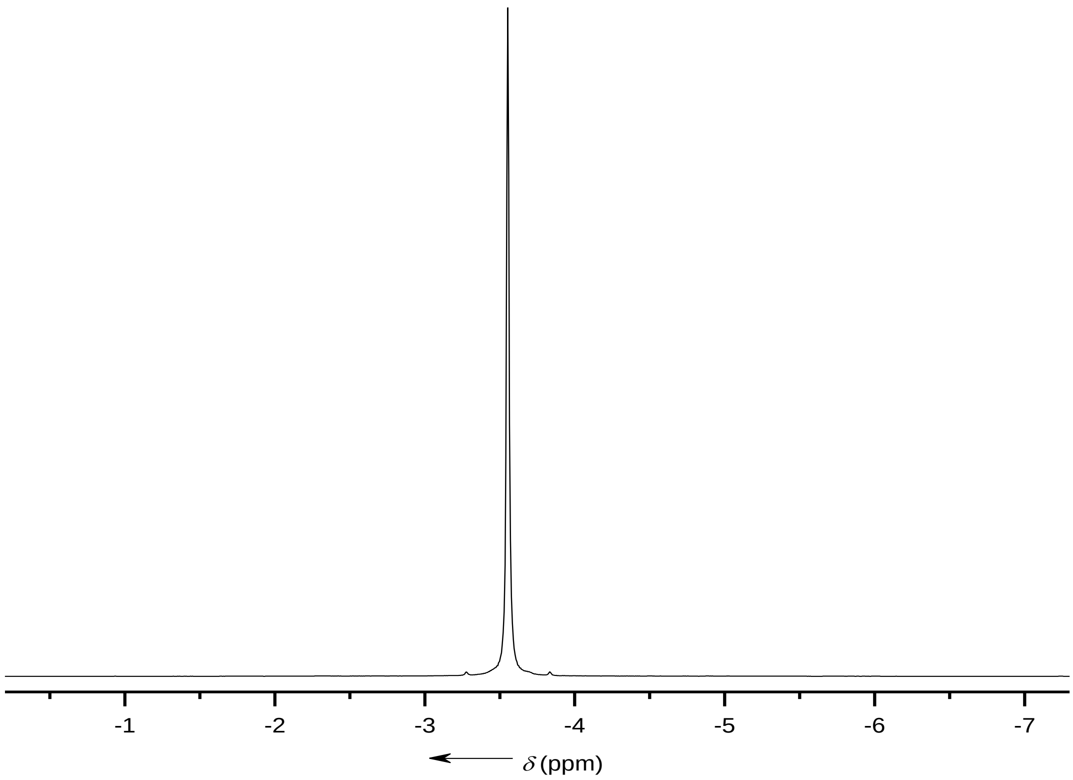


**Figure S10:** $^{11}B\{^{19}F\}$ **NMR spectrum of [EMIm][BF$_3$(CN)].**

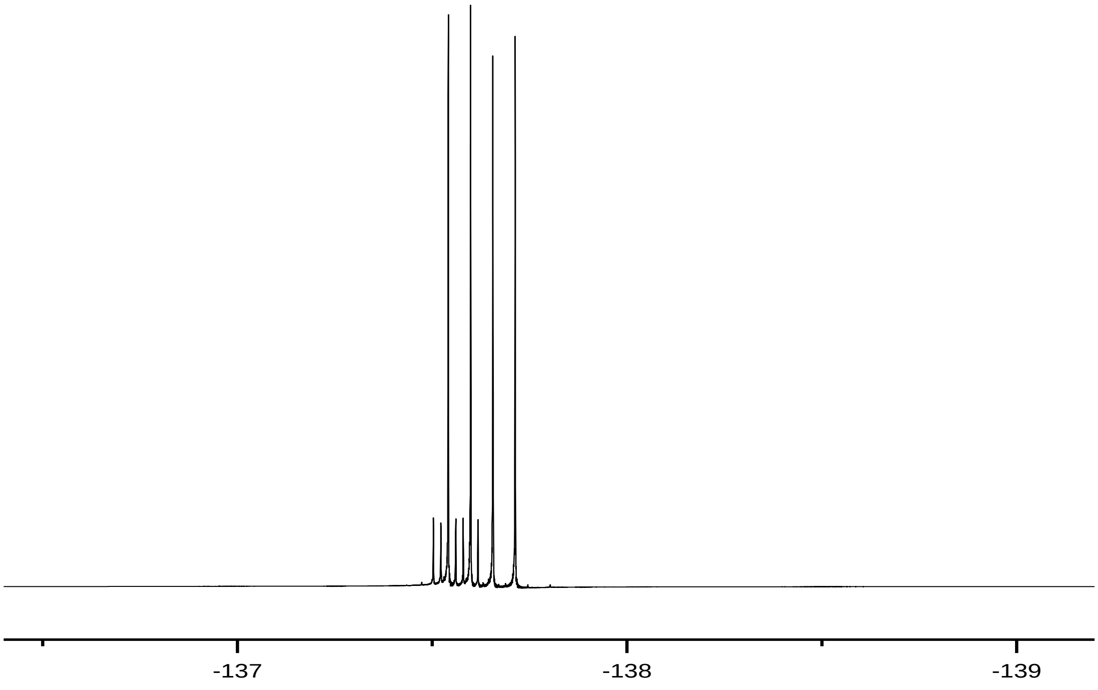


**Figure S11:** $^{19}F$ **NMR spectrum of [EMIm][BF$_3$(CN)].**

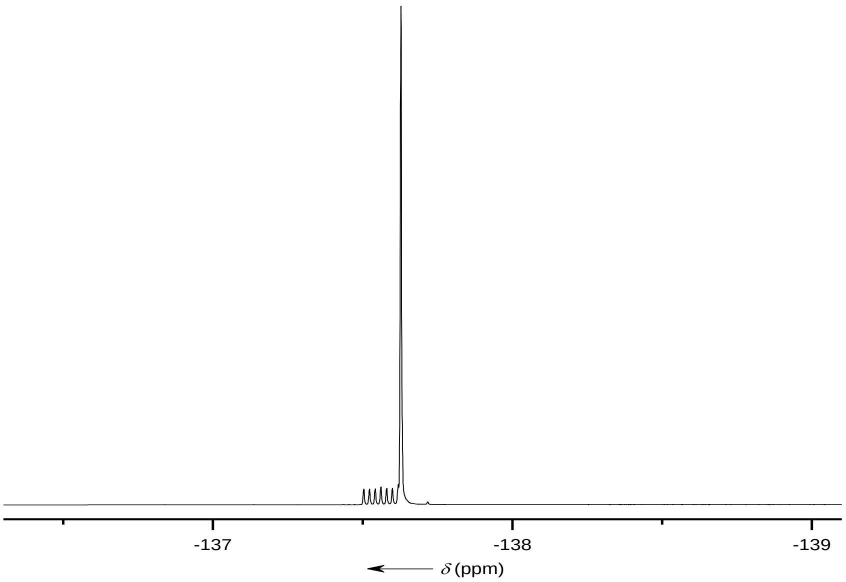


Figure S12: $^{19}F\{^{11}B\}$ NMR spectrum of [EMIm][BF$_3$(CN)].

### 5.1.3 [EMIm][BF$_2$(CN)$_2$]

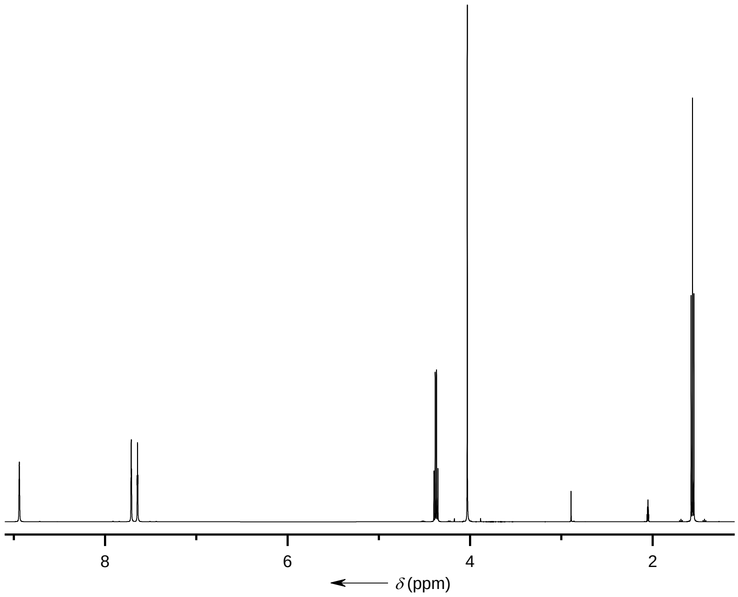


Figure S13: $^1H$ NMR spectrum of [EMIm][BF$_2$(CN)$_2$].

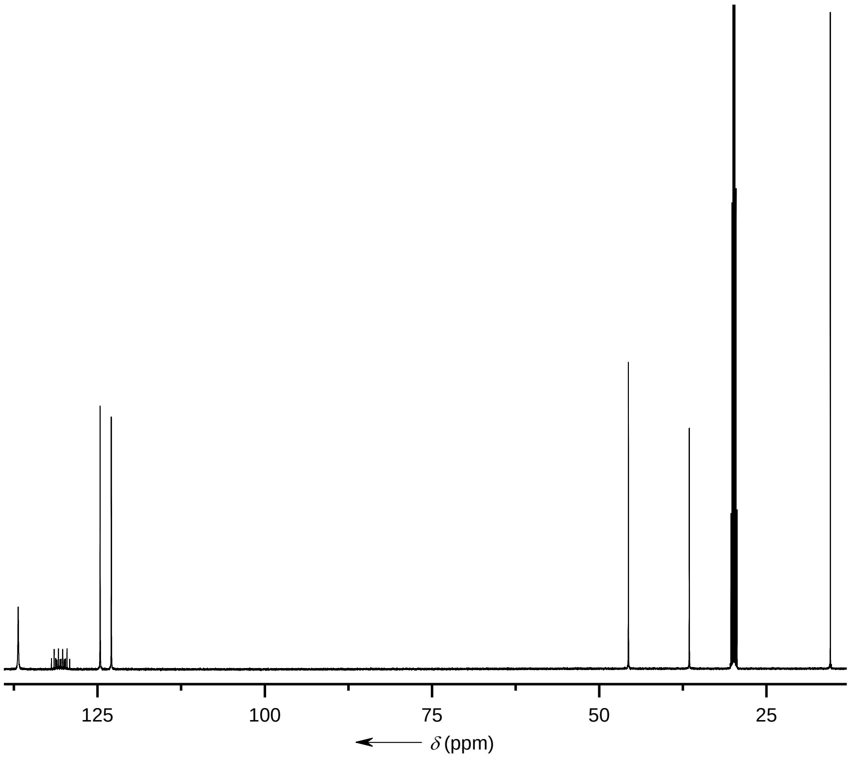


Figure S14: $^{13}C\{^1H\}$ NMR spectrum of [EMIm][BF$_2$(CN)$_2$].

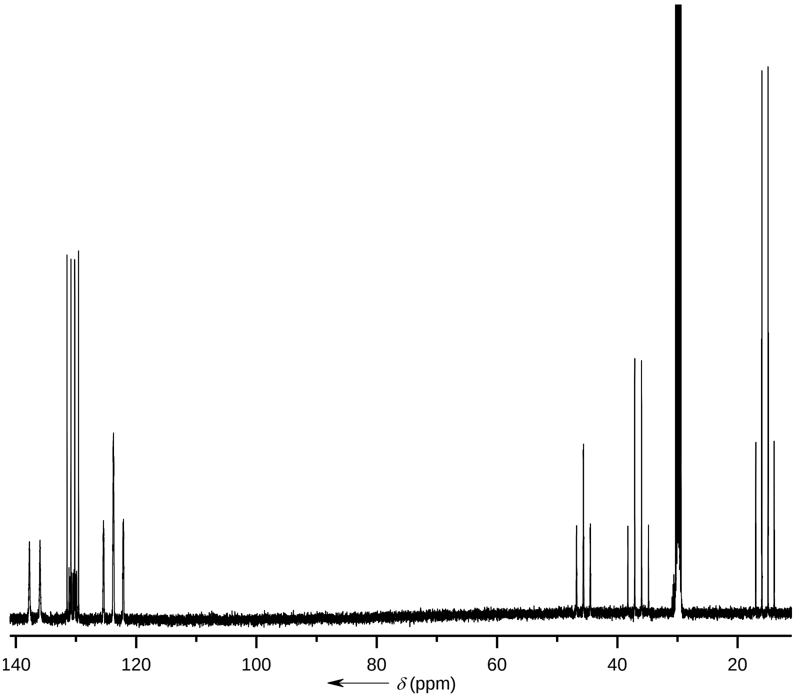


Figure S15: $^{13}C\{^{19}F\}$ NMR spectrum of [EMIm][BF$_2$(CN)$_2$].

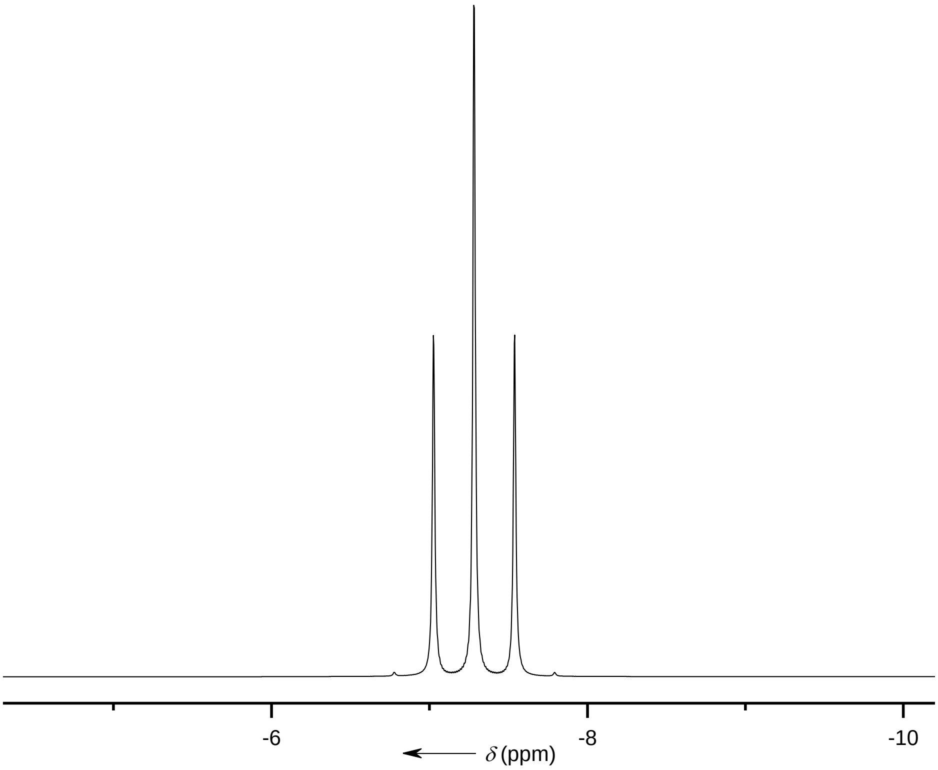


**Figure S16:** $^{11}$B NMR spectrum of [EMIm][BF$_2$(CN)$_2$].

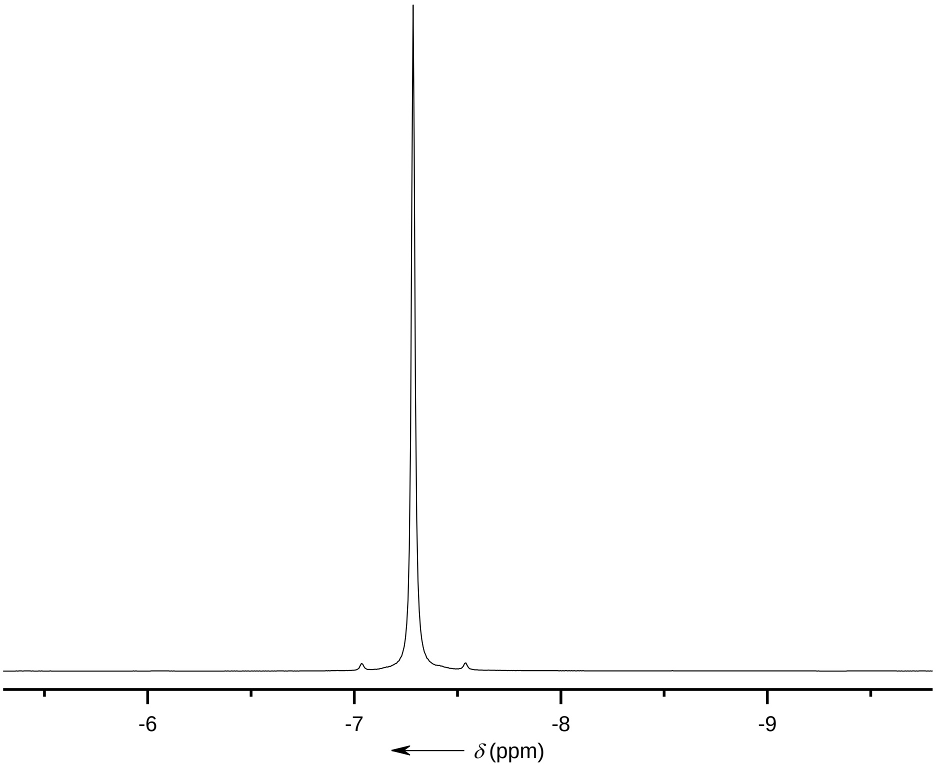


**Figure S17:** $^{11}$B{$^{19}$F} NMR spectrum of [EMIm][BF$_2$(CN)$_2$].

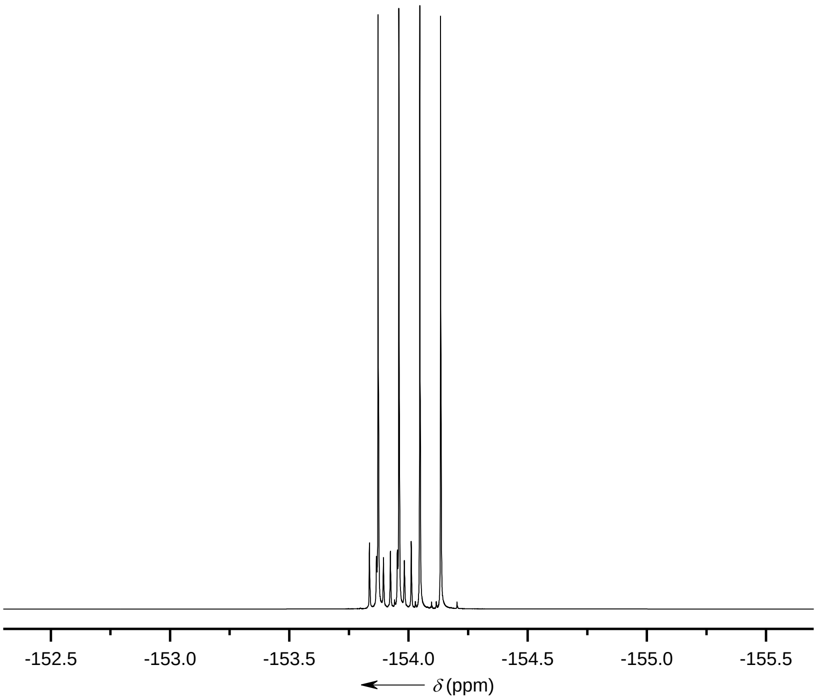


**Figure S18:** $^{19}F$ **NMR spectrum of [EMIm][BF$_2$(CN)$_2$].**

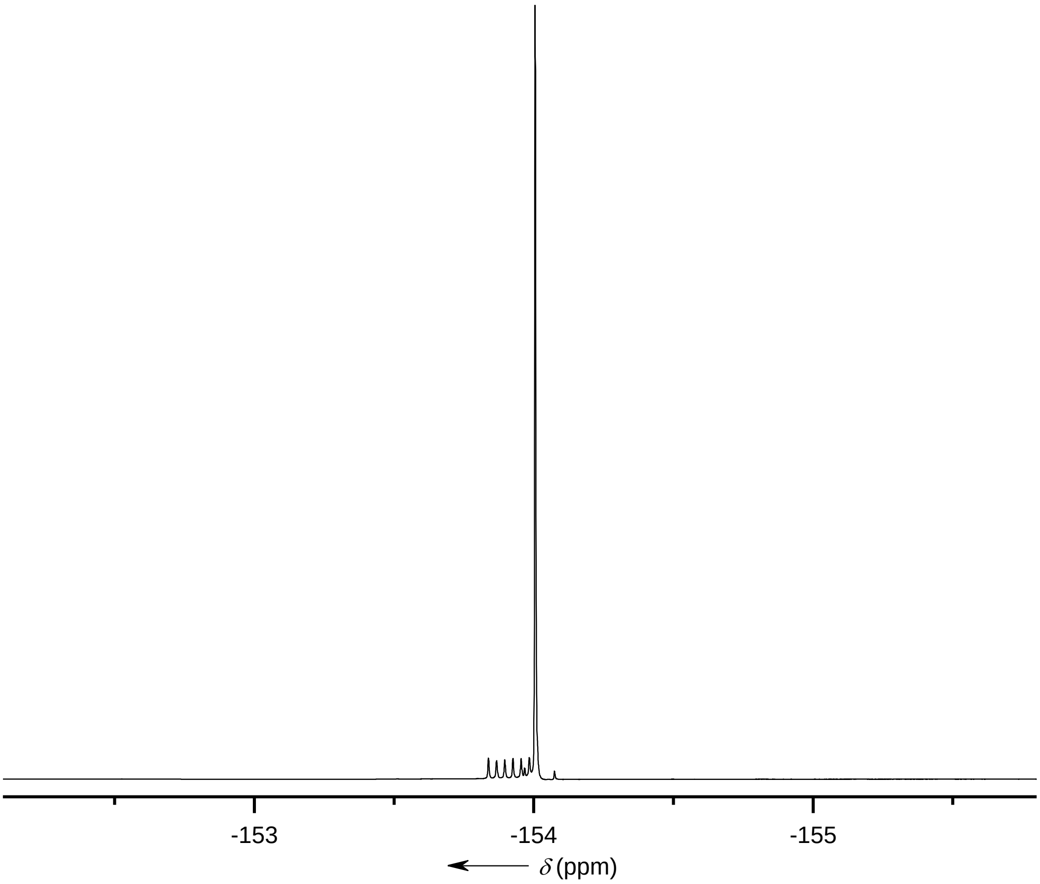


**Figure S19:** $^{19}F\{^{11}B\}$ **NMR spectrum of [EMIm][BF$_2$(CN)$_2$].**

## 5.1.4 [EMIm][BF(CN)$_3$]

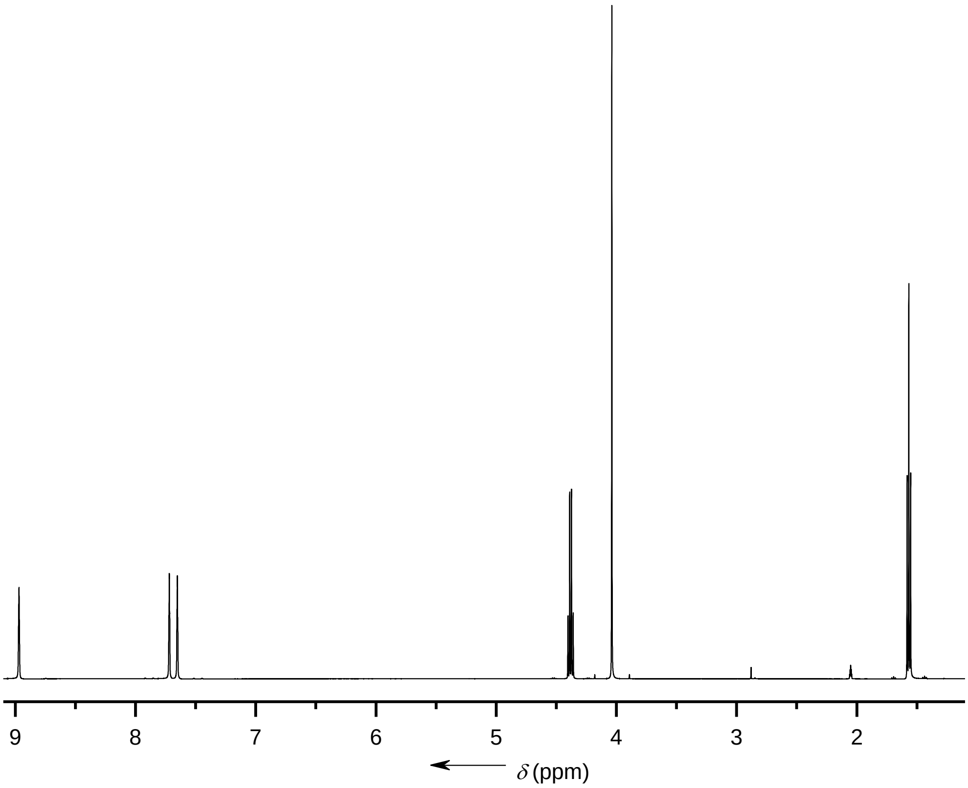


**Figure S20: $^1$H NMR spectrum of [EMIm][BF(CN)$_3$].**

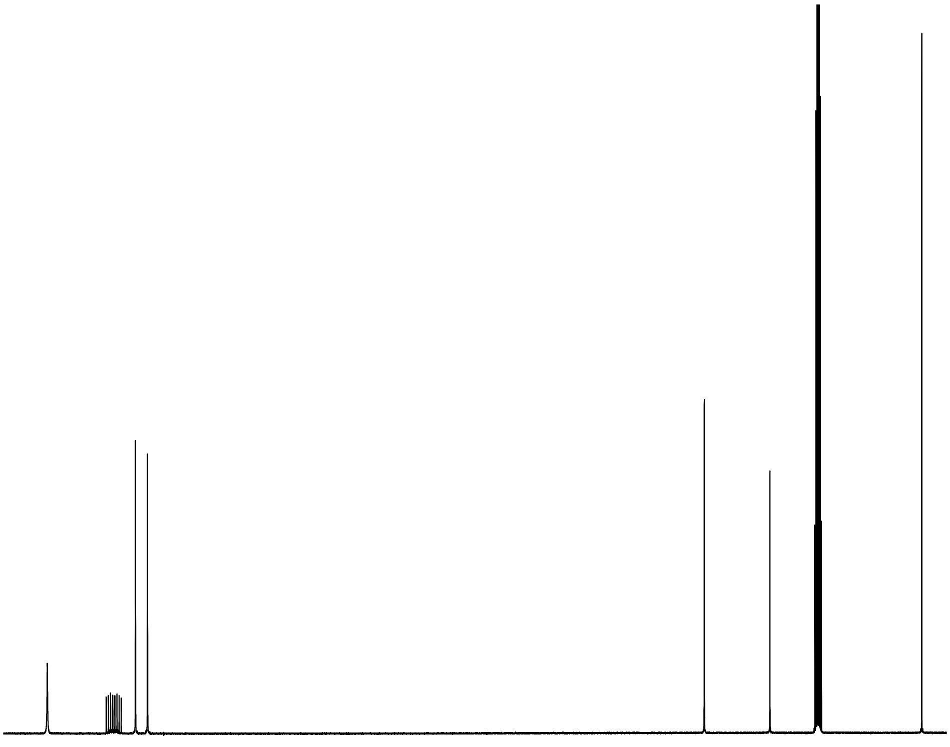


**Figure S21: $^{13}$C{$^1$H} NMR spectrum of [EMIm][BF(CN)$_3$].**

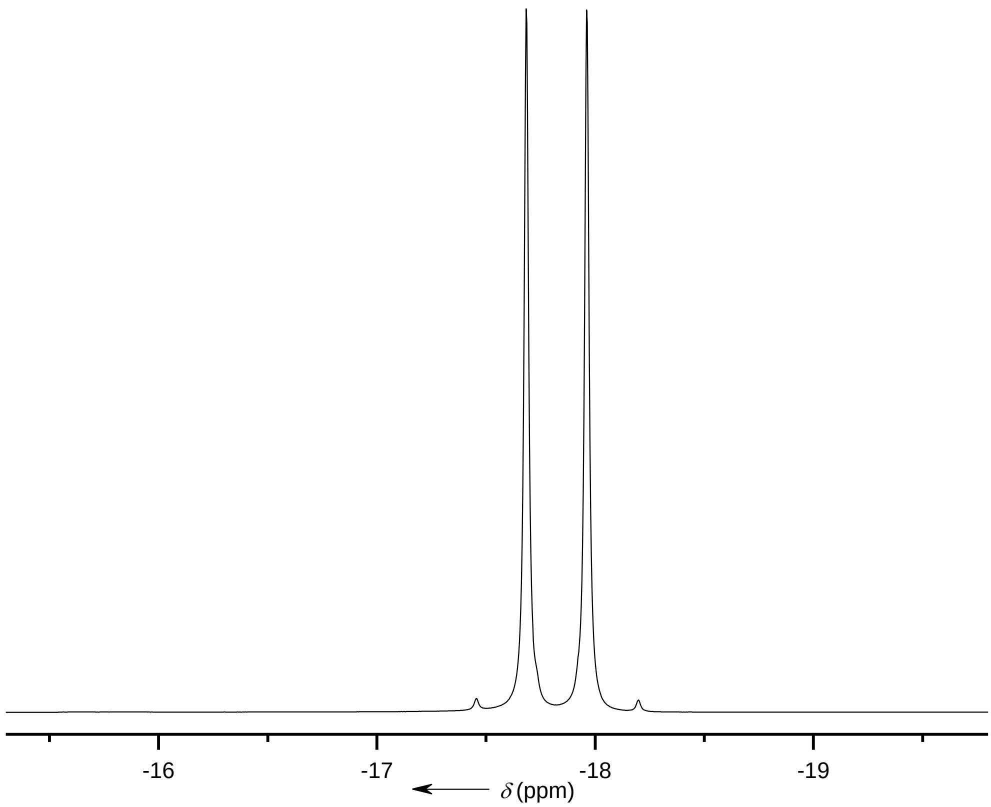


**Figure S22: $^{11}$B NMR spectrum of [EMIm][BF(CN)$_3$].**

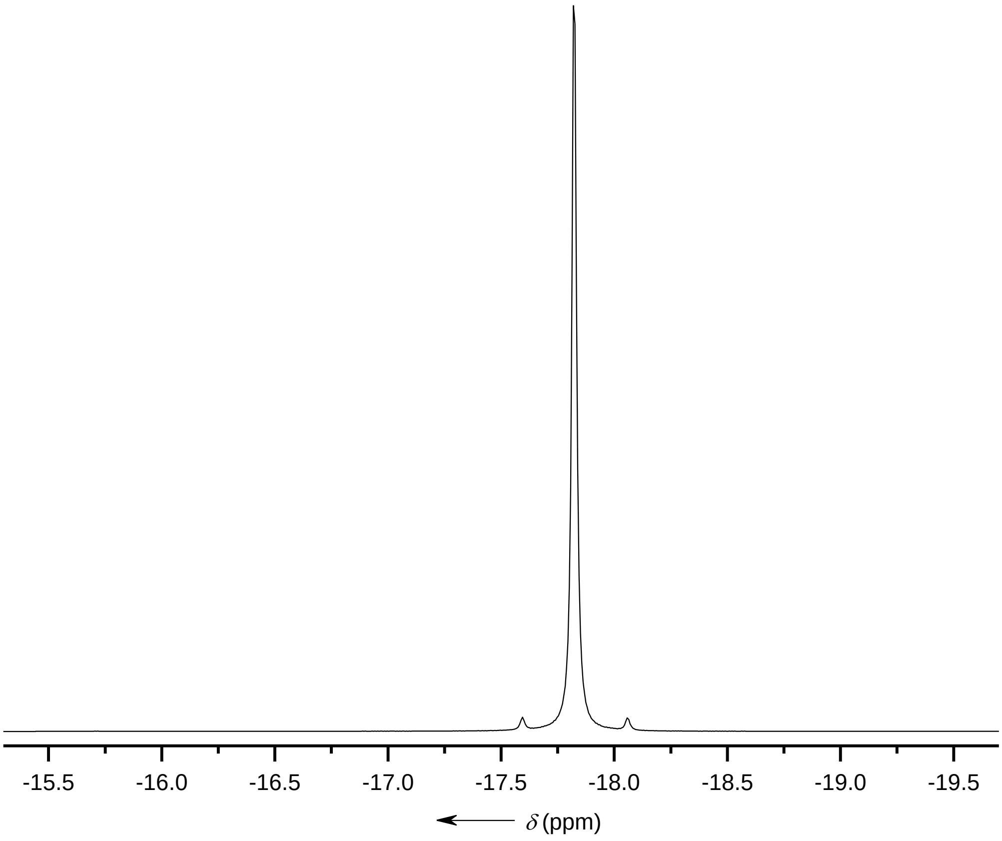


**Figure S23: $^{11}$B{$^{19}$F} NMR spectrum of [EMIm][BF(CN)$_3$].**

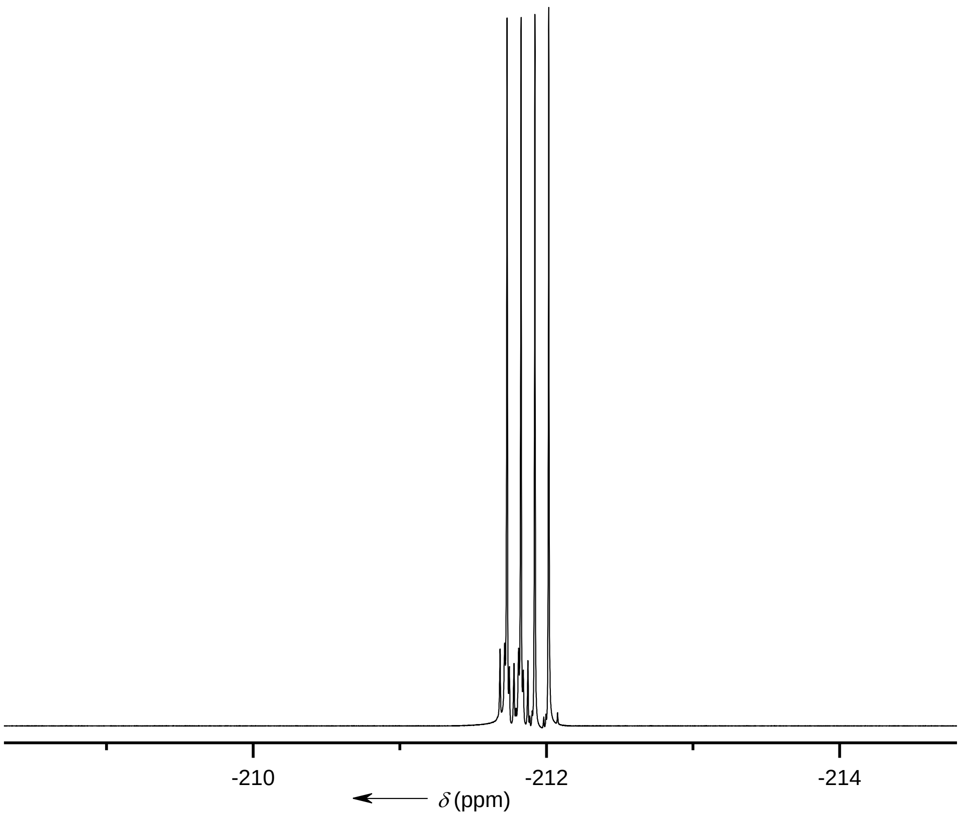


**Figure S24: $^{19}$F NMR spectrum of [EMIm][BF(CN)$_3$].**

**Figure S25: $^{19}$F{$^{11}$B} NMR spectrum of [EMIm][BF(CN)$_3$].**

### 5.1.5 [EMIm][BFH(CN)$_2$]

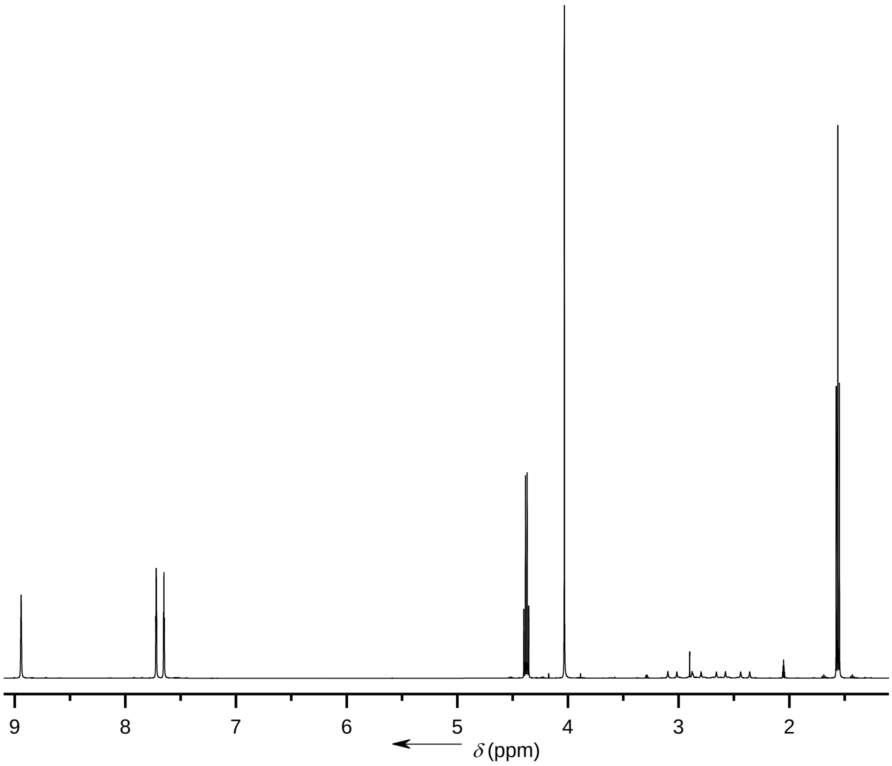


**Figure S26: $^1$H NMR spectrum of [EMIm][BFH(CN)$_2$].**

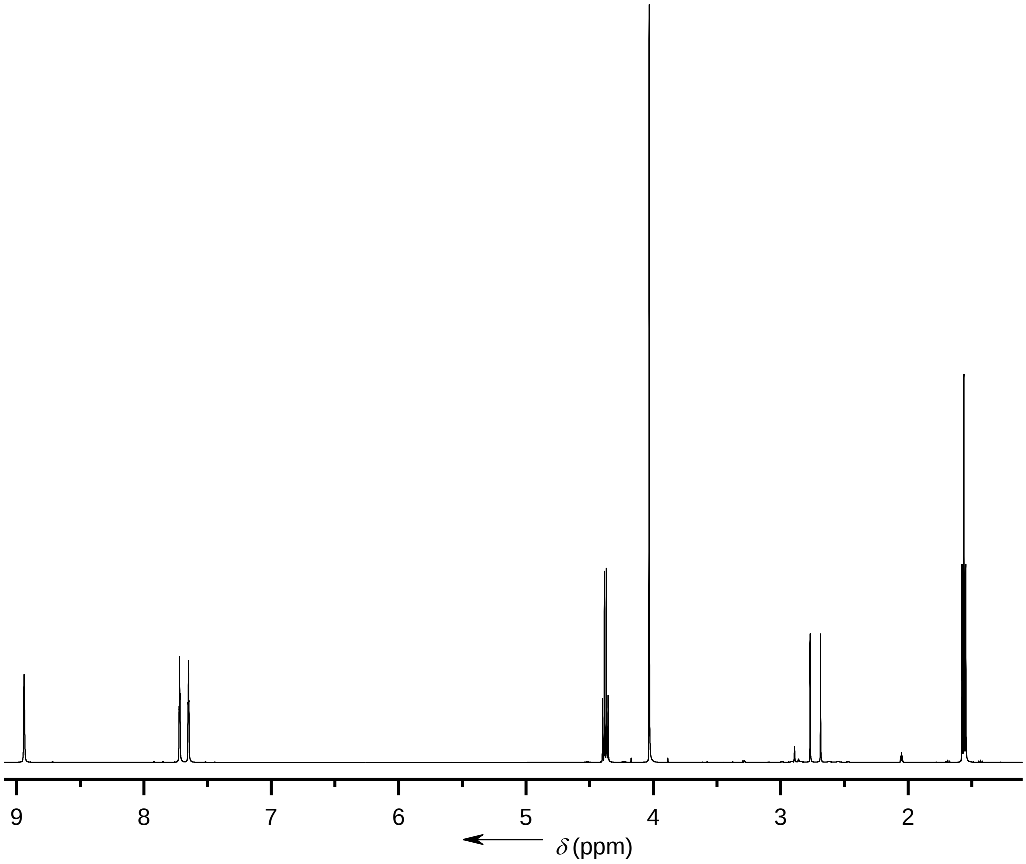


**Figure S27: $^1$H{$^{11}$B} NMR spectrum of [EMIm][BFH(CN)$_2$].**

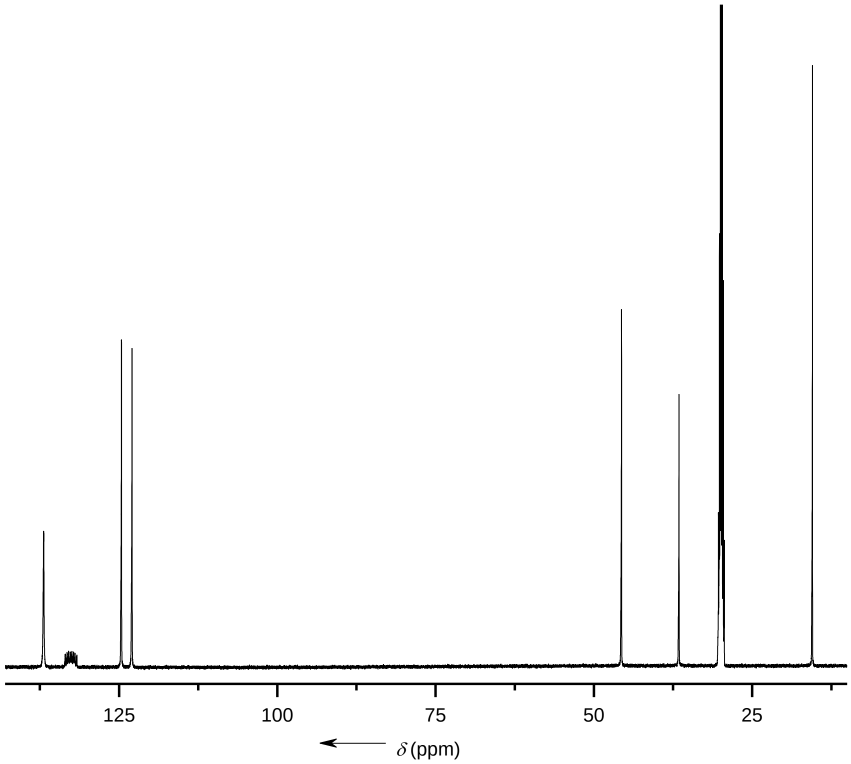


**Figure S28:** $^{13}C\{^1H\}$ **NMR spectrum of [EMIm][BFH(CN)$_2$].**

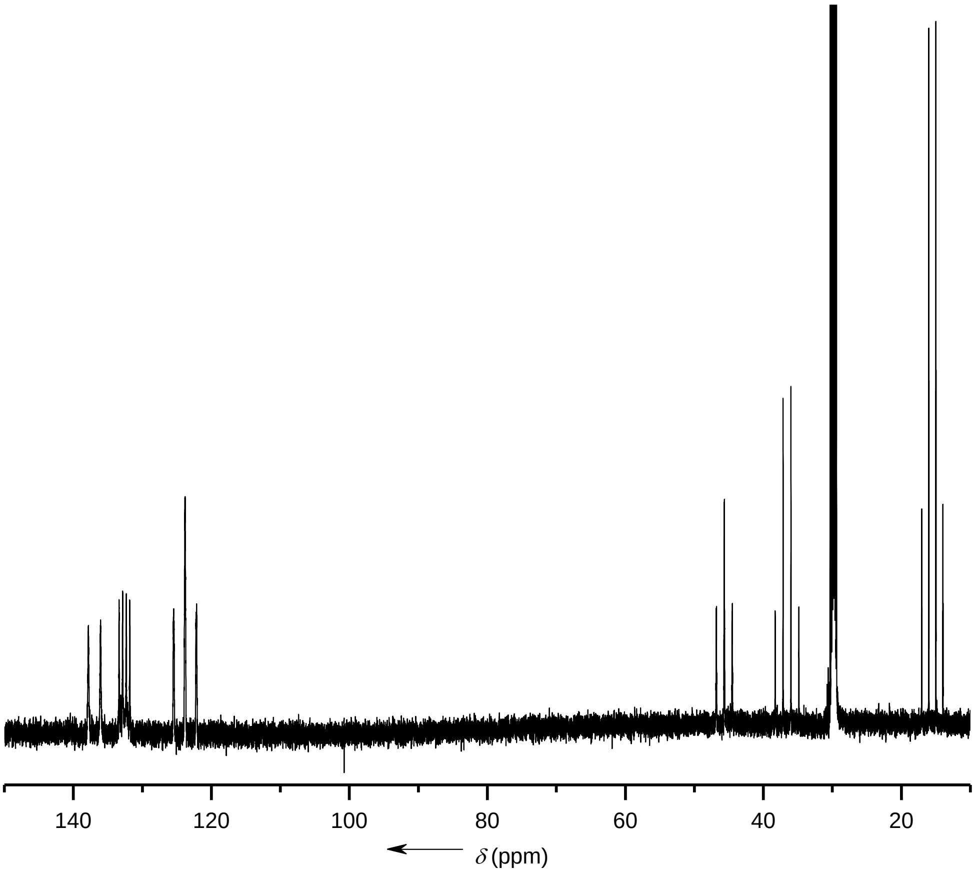


**Figure S29:** $^{13}C\{^{19}F\}$ **NMR spectrum of [EMIm][BFH(CN)$_2$].**

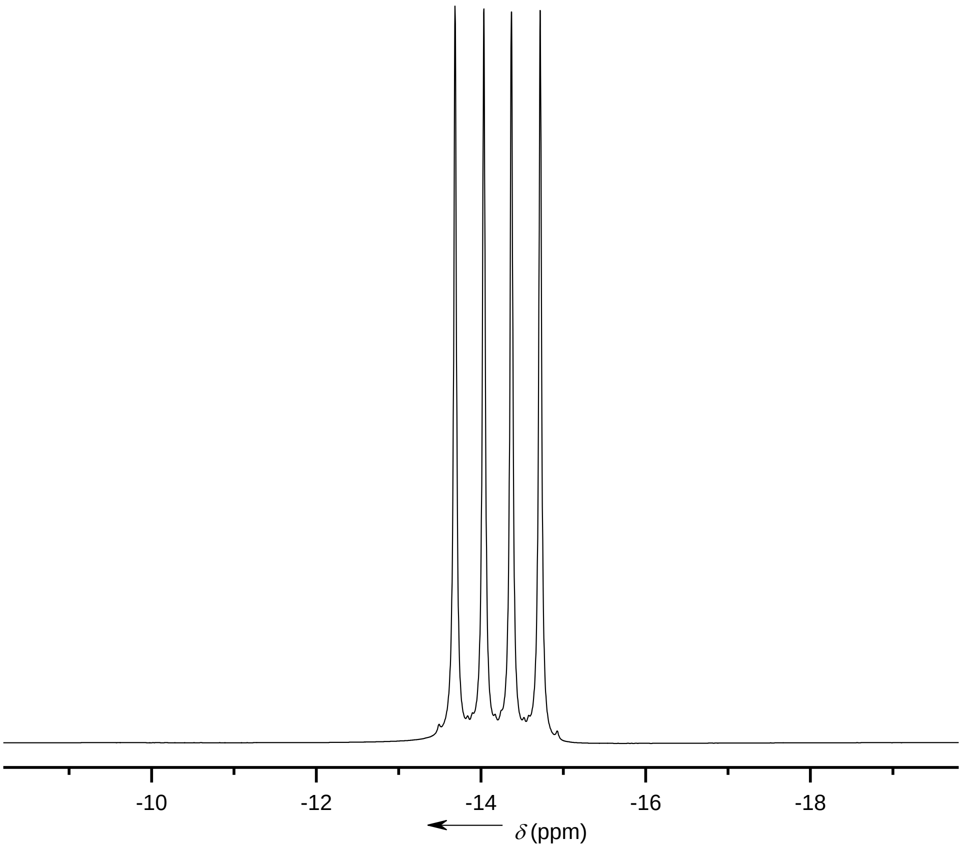


Figure S30: $^{11}$B NMR spectrum of [EMIM][BFH(CN)$_2$].

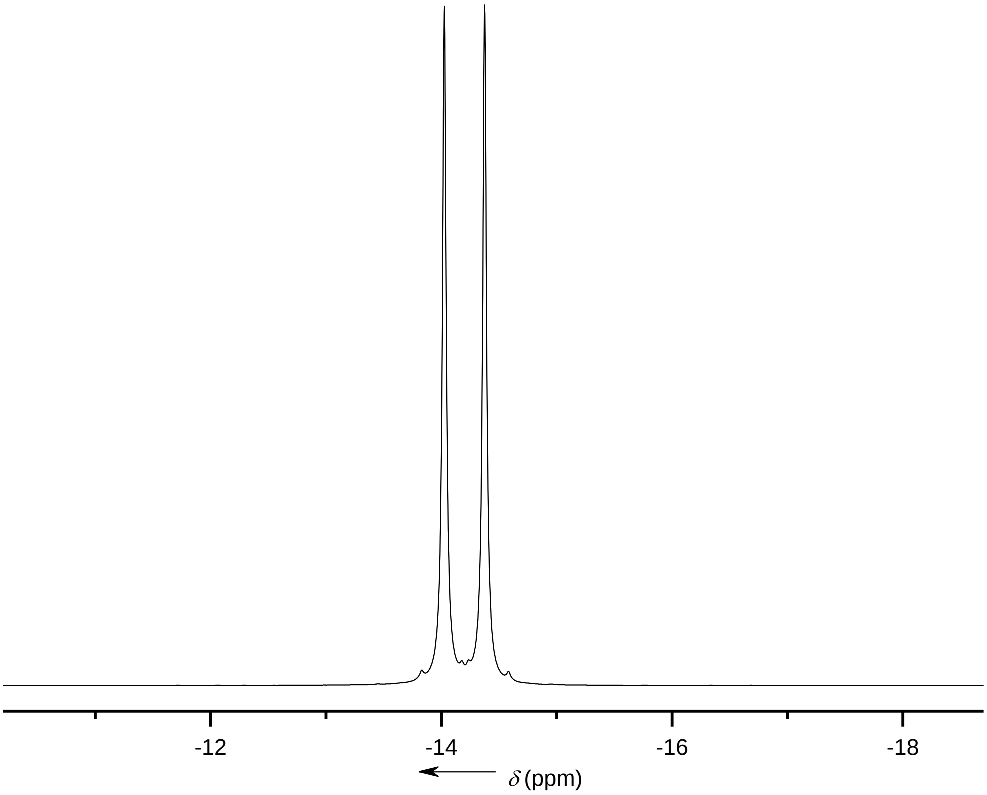


Figure S31: $^{11}$B{$^1$H} NMR spectrum of [EMIm][BFH(CN)$^2$].

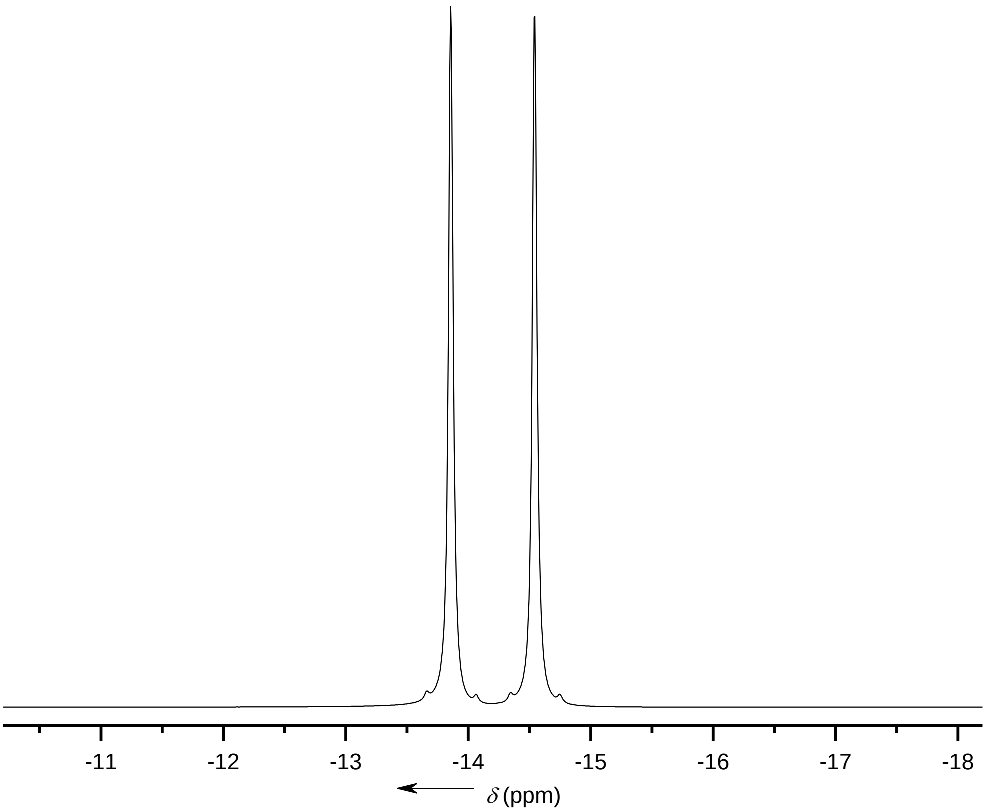


Figure S32: $^{11}B\{^{19}F\}$ NMR spectrum of $[EMIm][BFH(CN)_2]$.

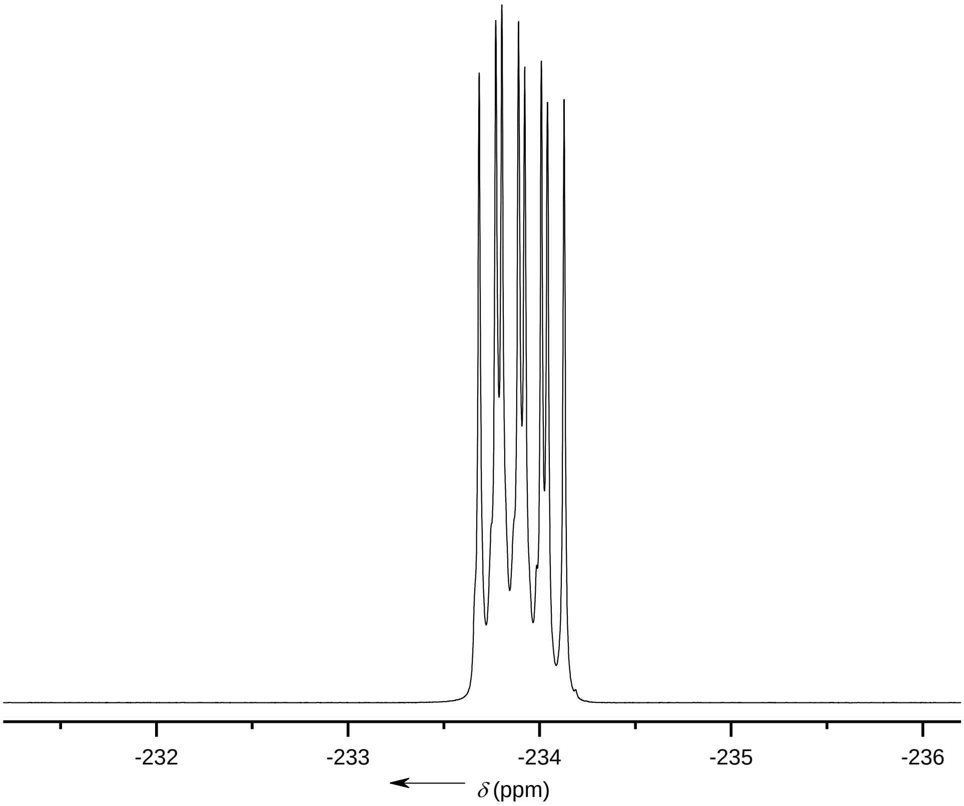


Figure S33: $^{19}F$ NMR spectrum of $[EMIm][BFH(CN)_2]$.

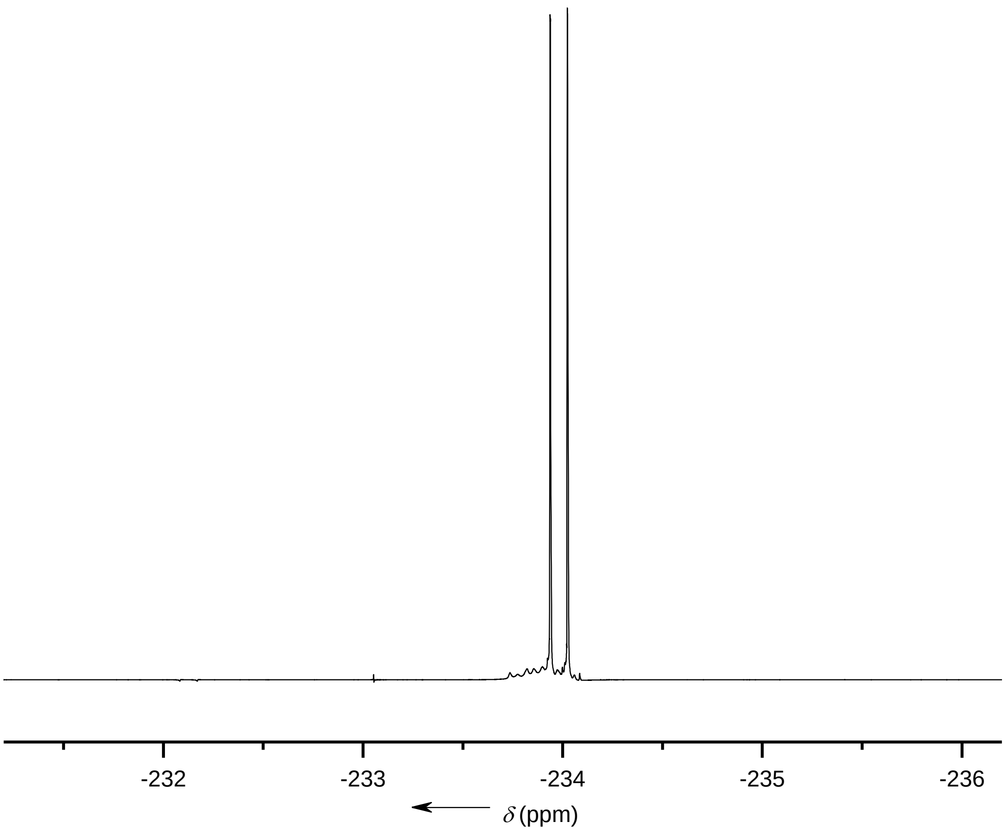


**Figure S34: $^{19}F\{^{11}B\}$ NMR spectrum of [EMIm][BFH(CN)$_2$].**

## 5.2 [BMPL] salts

### 5.2.1 [BMPL][BF$_3$(CN)]

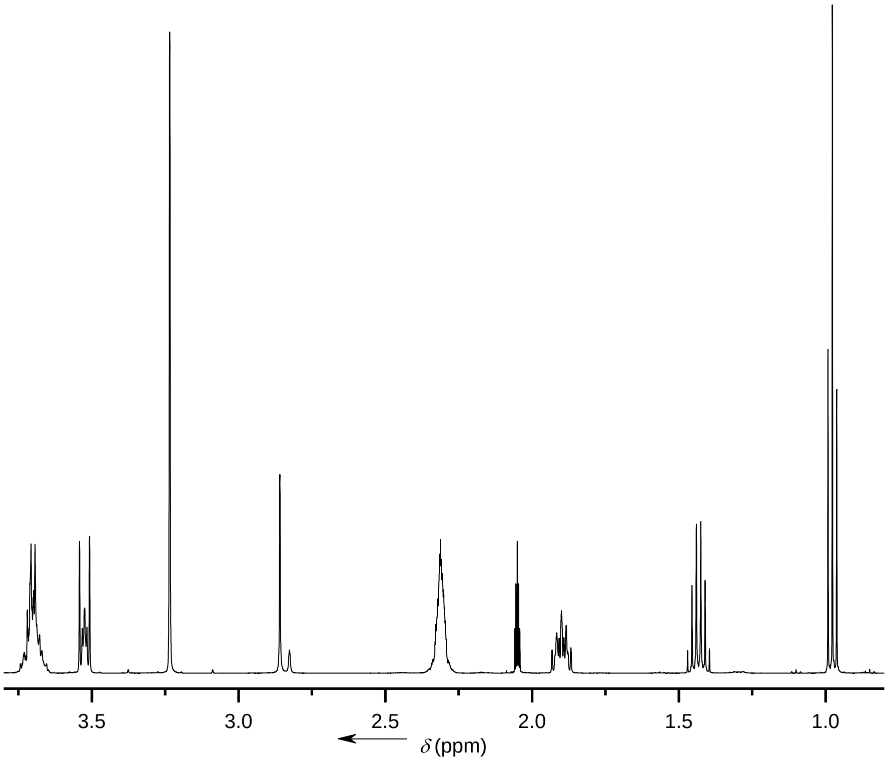


**Figure S35: $^1$H NMR spectrum of [BMPL][BF$_3$(CN)].**

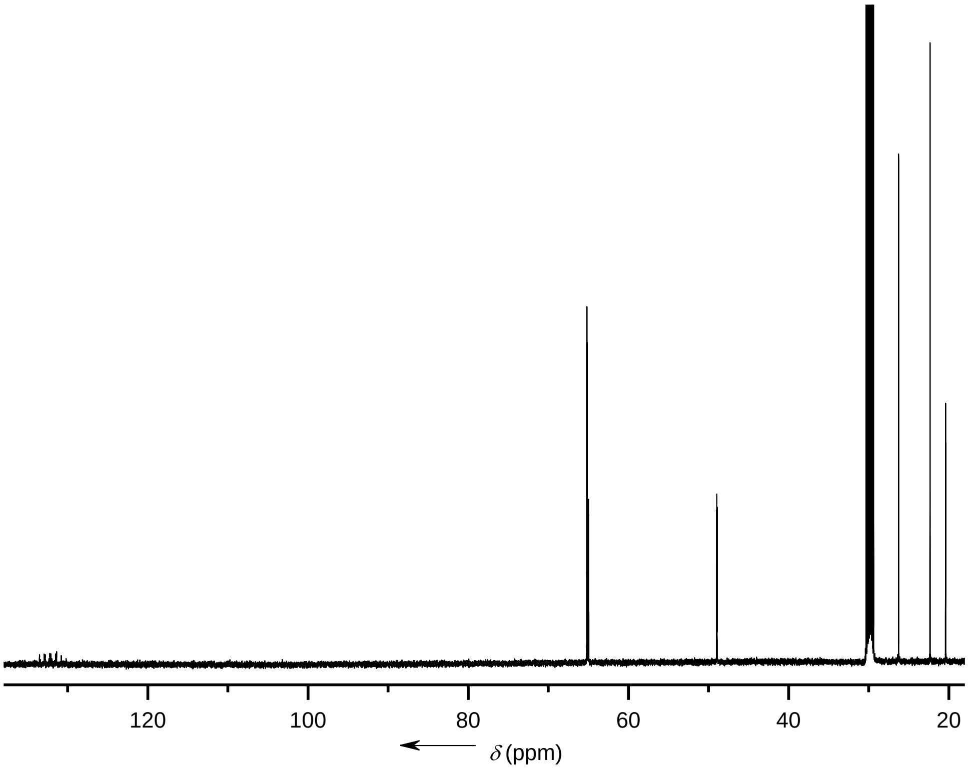


**Figure S36: 13C{$^1$H} NMR spectrum of [BMPL][BF$_3$(CN)].**

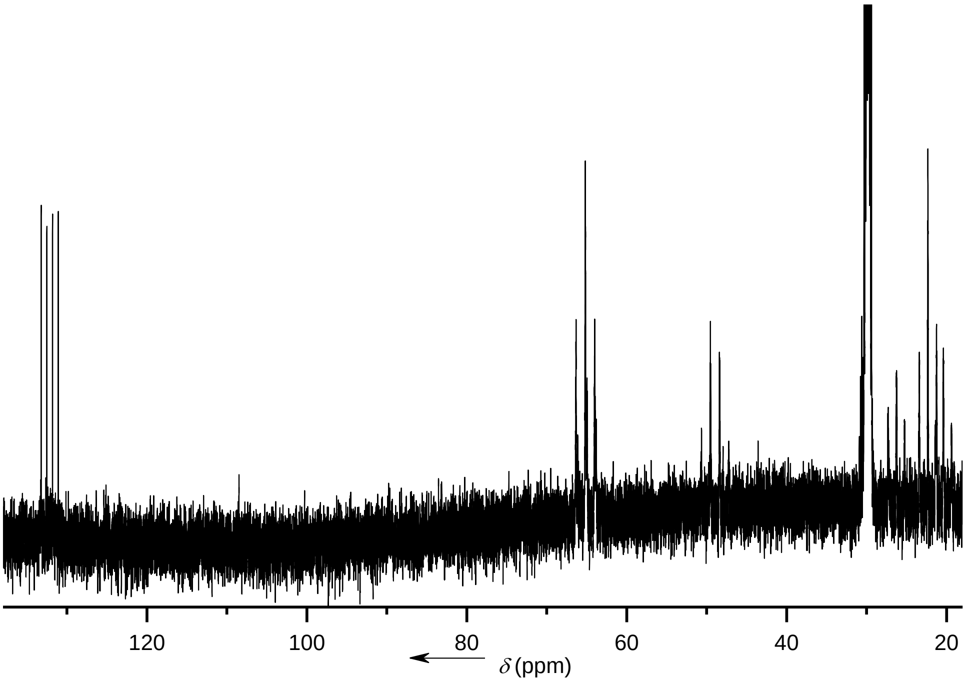


**Figure S37:** $^{13}C\{^{19}F\}$ **NMR spectrum of [BMPL][BF$_3$(CN)].**

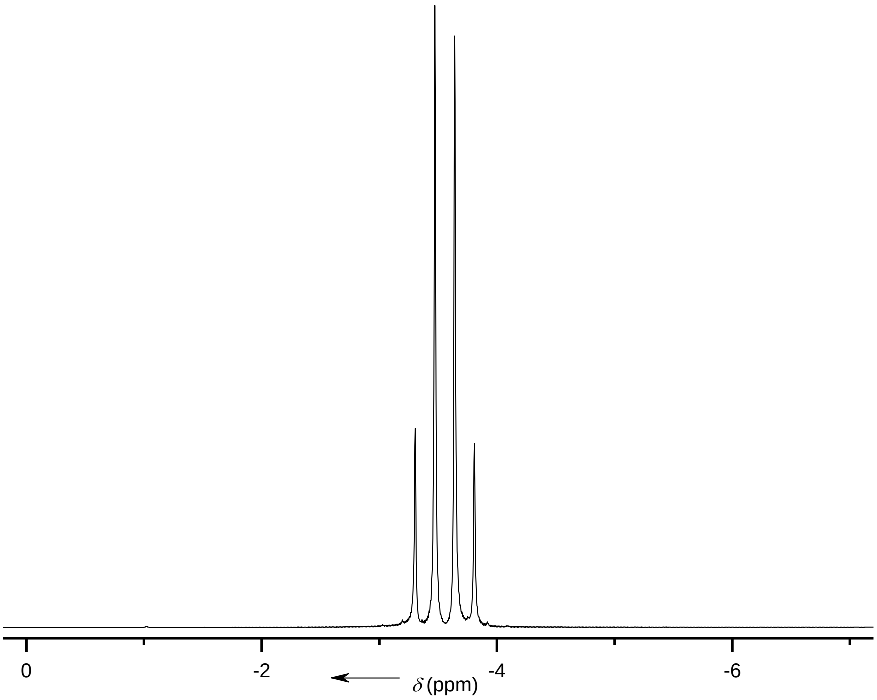


**Figure S38:** $^{11}B$ **NMR spectrum of [BMPL][BF$_3$(CN)].**

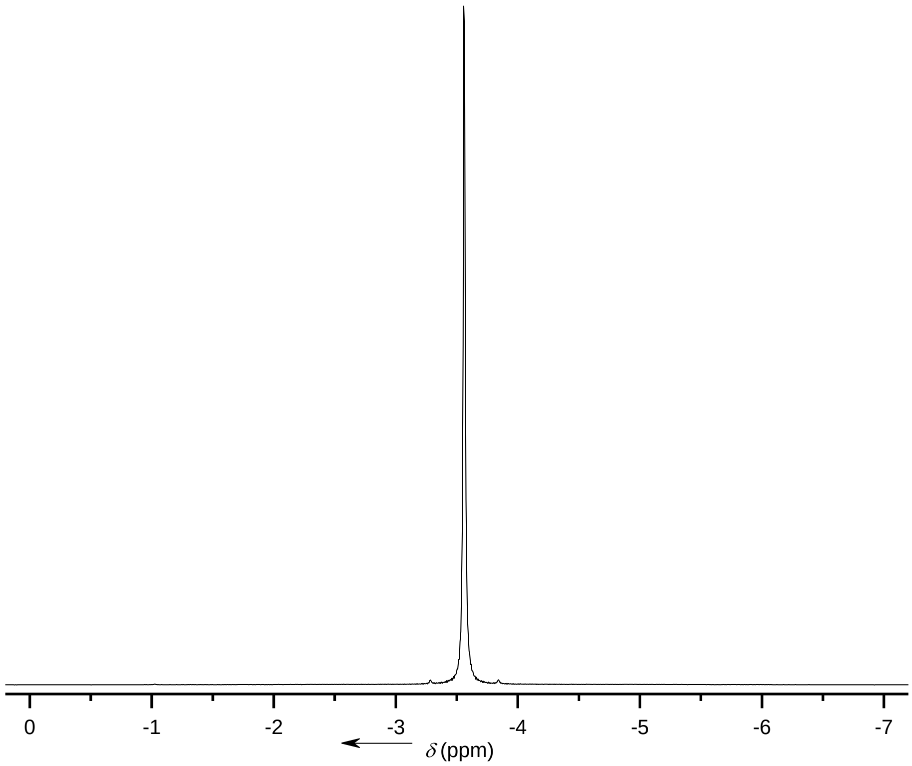


**Figure S39: $^{11}B\{^{1}H\}$ NMR spectrum of [BMPL][$BF_3$(CN)].**

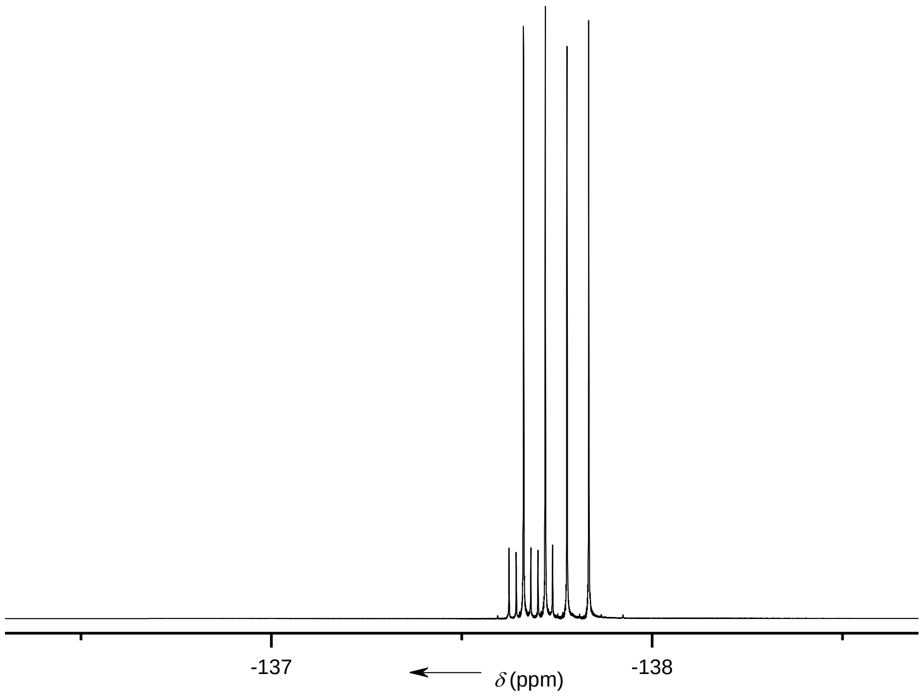


**Figure S40: $^{19}F$ NMR spectrum of [BMPL][$BF_3$(CN)].**

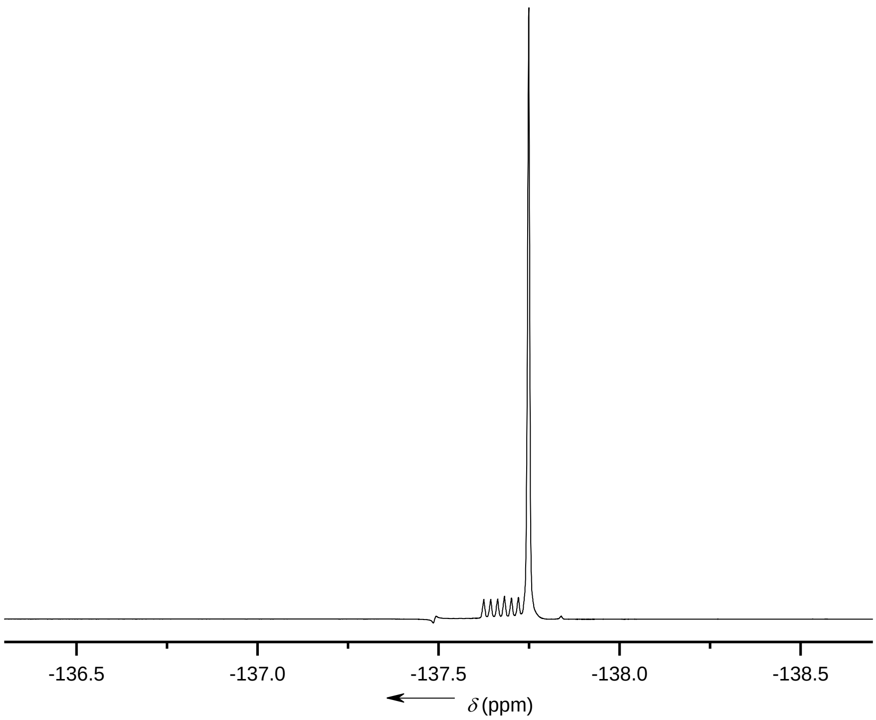


**Figure S41: $^{19}F\{^{11}B\}$ NMR spectrum of [BMPL][$BF_3(CN)$].**

### 5.2.2 [BMPL][$BF_2(CN)_2$]

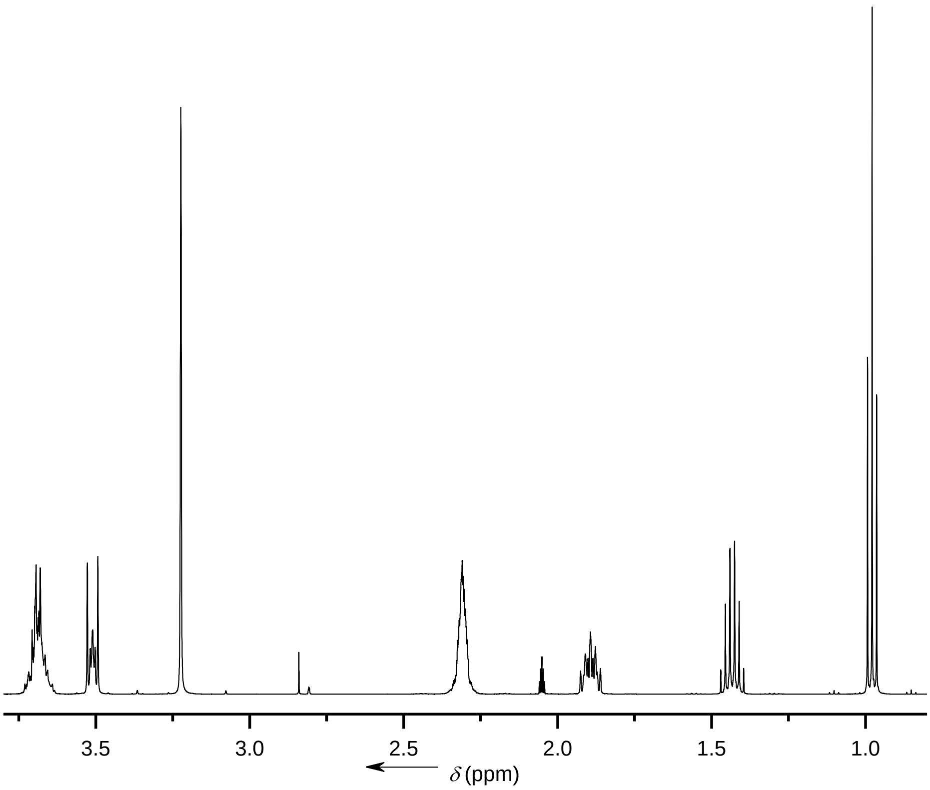


**Figure S42: 1H NMR spectrum of [BMPL][$BF_2(CN)_2$].**

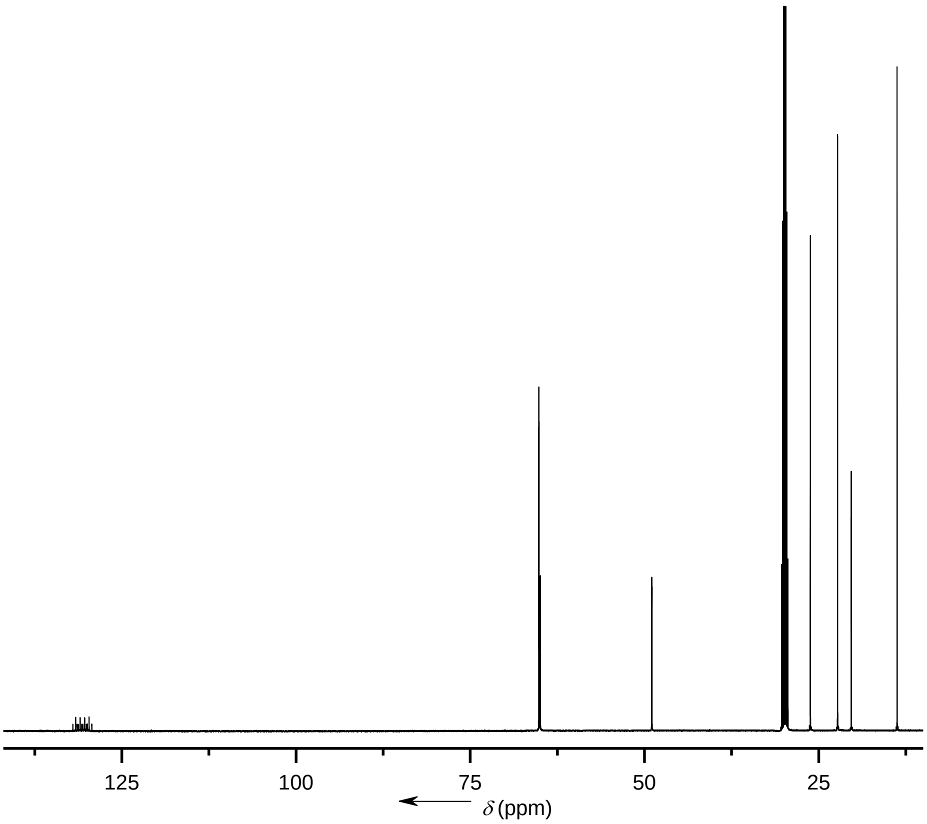


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum of [BMPL][$BF_2(CN)_2$].

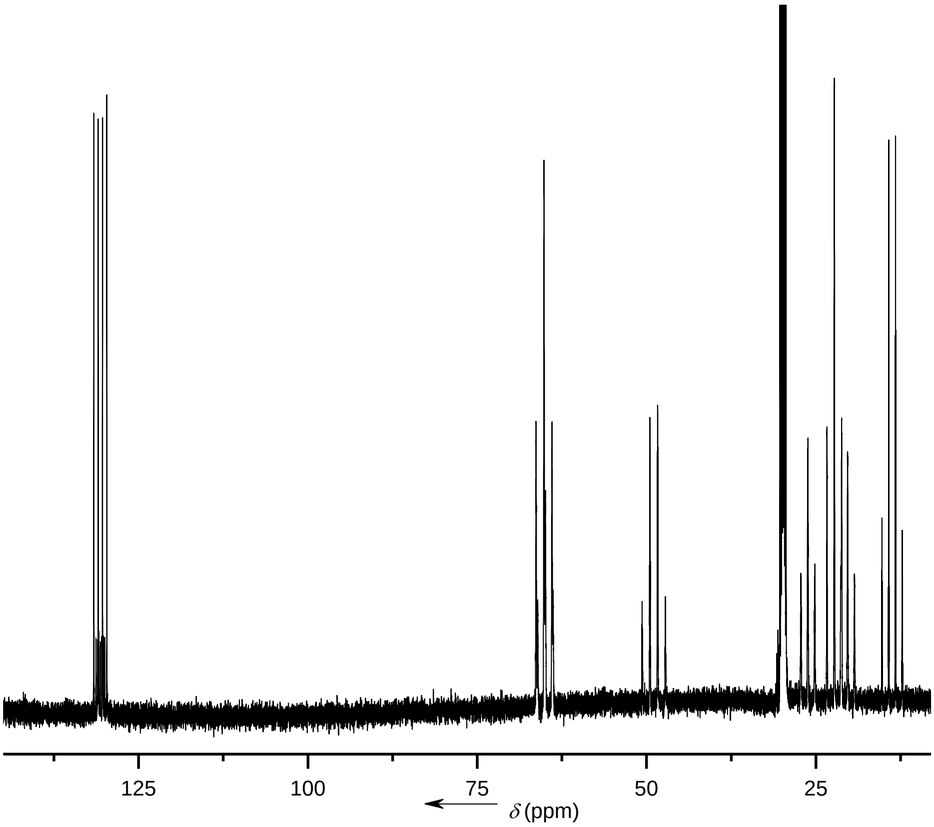


Figure S44: $^{13}C\{^{19}F\}$ NMR spectrum of [BMPL][$BF_2(CN)_2$].

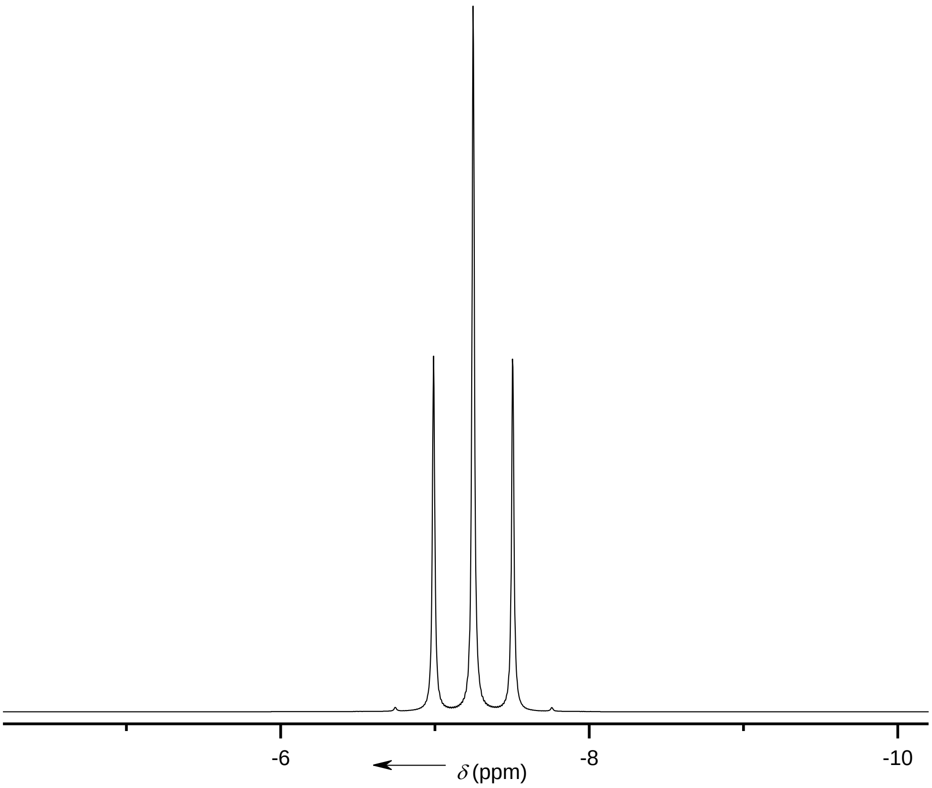


**Figure S45: $^{11}$B NMR spectrum of [BMPL][BF$_2$(CN)$_2$].**

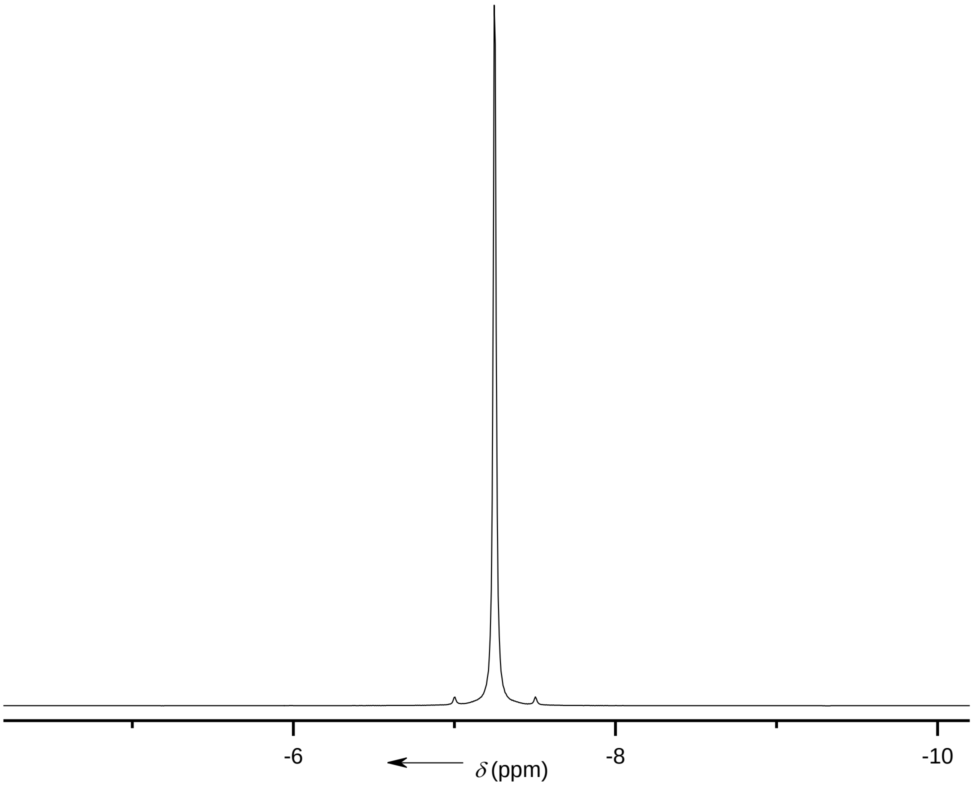


**Figure S46: $^{11}$B{$^{19}$F} NMR spectrum of [BMPL][BF$_2$(CN)$_2$].**

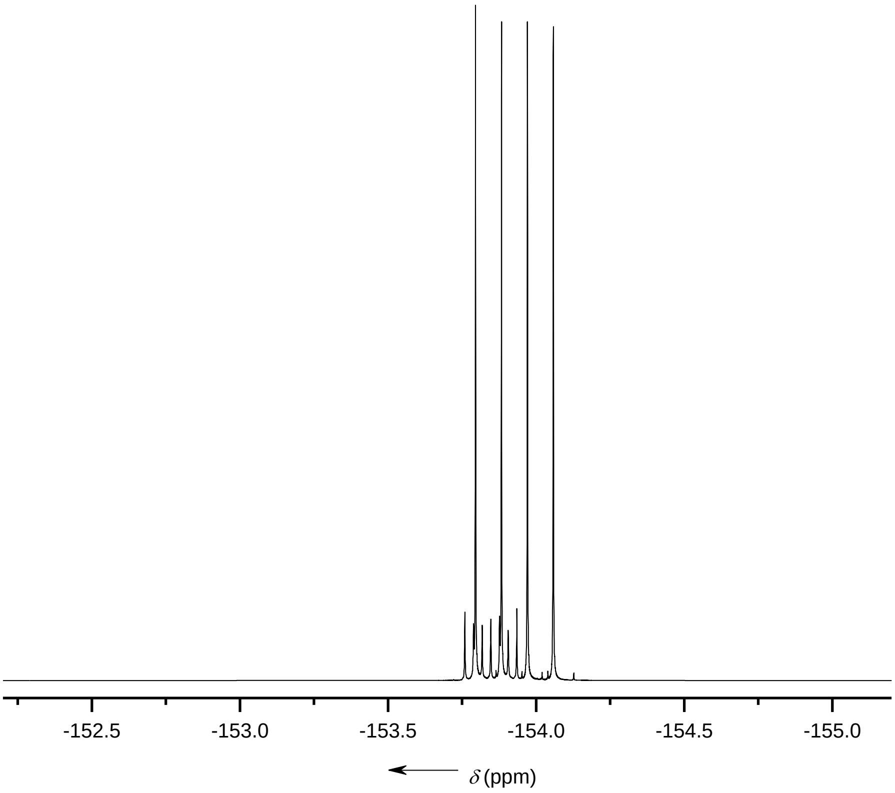


**Figure S47: $^{19}$F NMR spectrum of [BMPL][BF$_2$(CN)$_2$].**

**Figure S48: $^{19}$F{$^{11}$B} NMR spectrum of [BMPL][BF$_2$(CN)$_2$].**

## 5.2.3 [BMPL][BF(CN)$_3$]

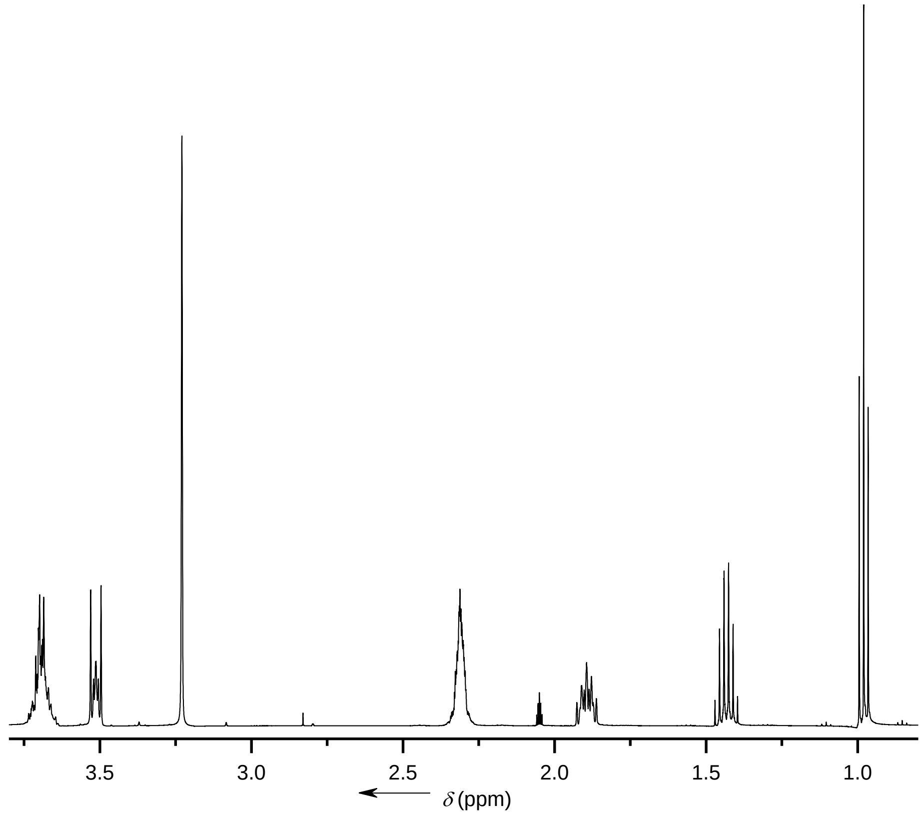


**Figure S49: $^1$H NMR spectrum of [BMPL][BF(CN)$_3$].**

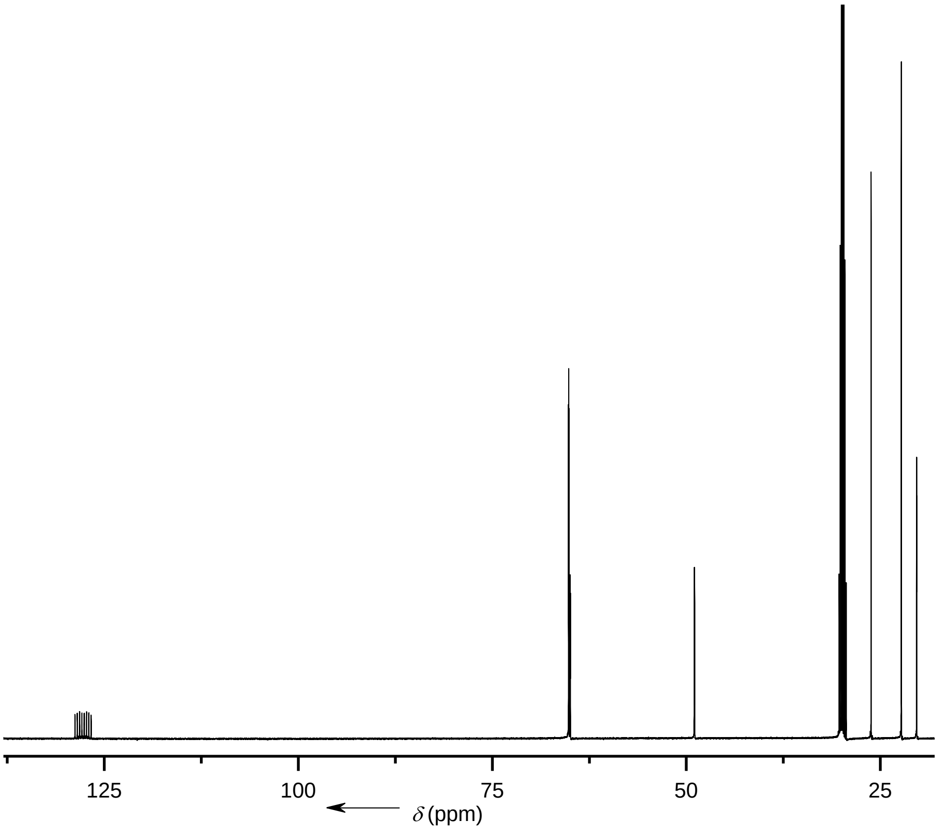


**Figure S50: $^{13}$C{$^1$H} NMR spectrum of [BMPL][BF(CN)$_3$].**

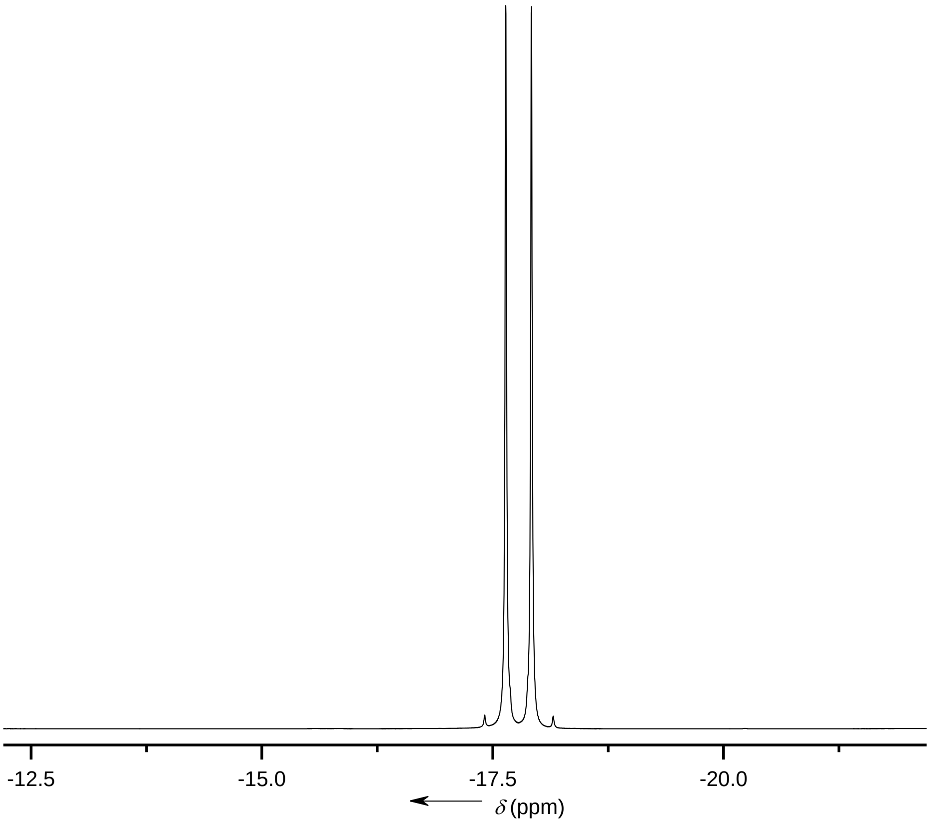


**Figure S51:** $^{11}$B NMR spectrum of [BMPL][BF(CN)$_3$].

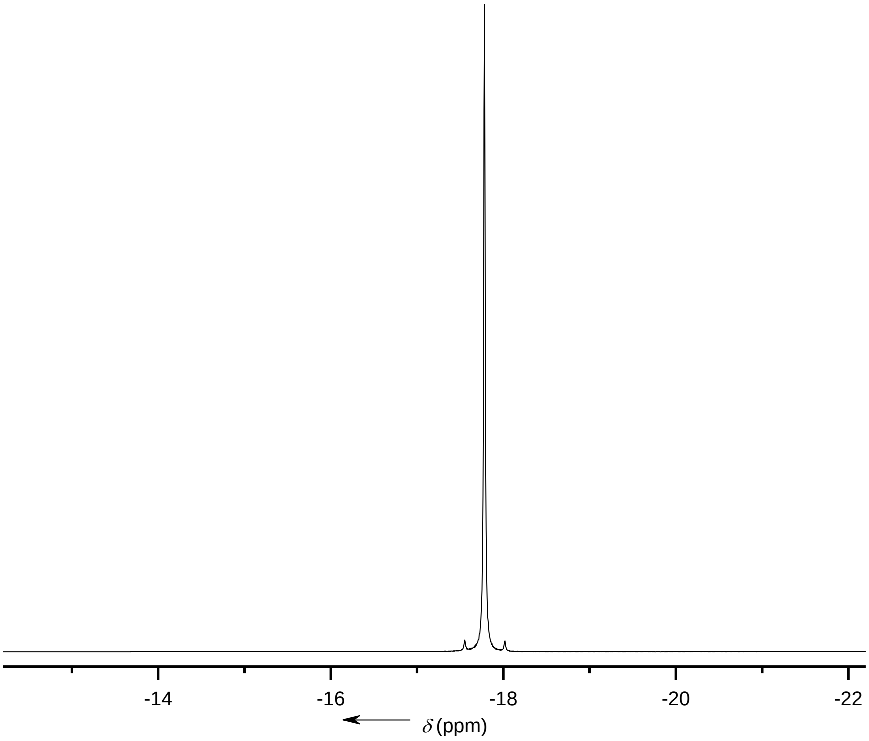


**Figure S52:** $^{11}$B{$^{19}$F} NMR spectrum of [BMPL][BF(CN)$_3$].

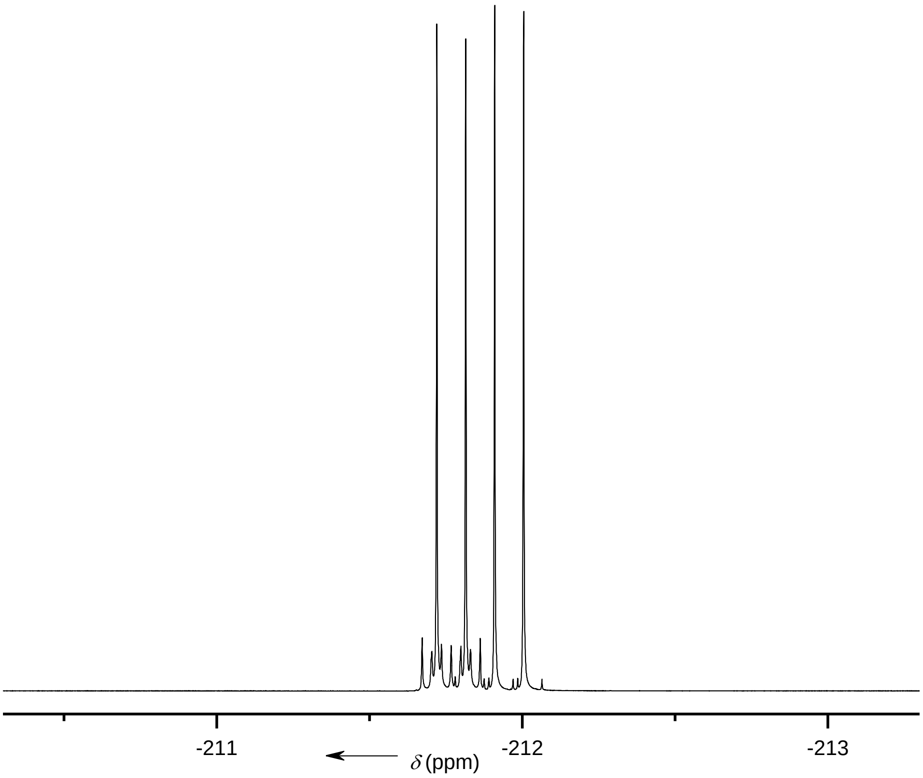


**Figure S53: $^{19}$F NMR spectrum of [BMPL][BF(CN)$_3$].**

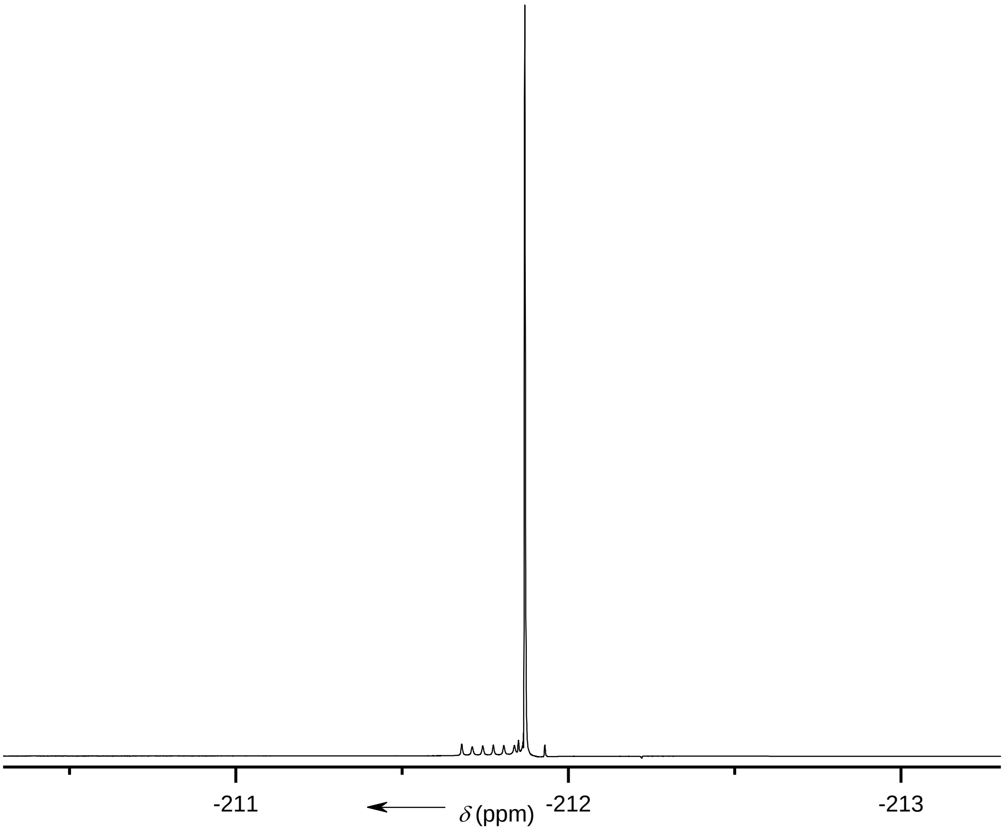


**Figure S54: $^{19}$F{$^{11}$B} NMR spectrum of [BMPL][BF(CN)$_3$].**

### 5.2.4 [BMPL][BFH(CN)$_2$]

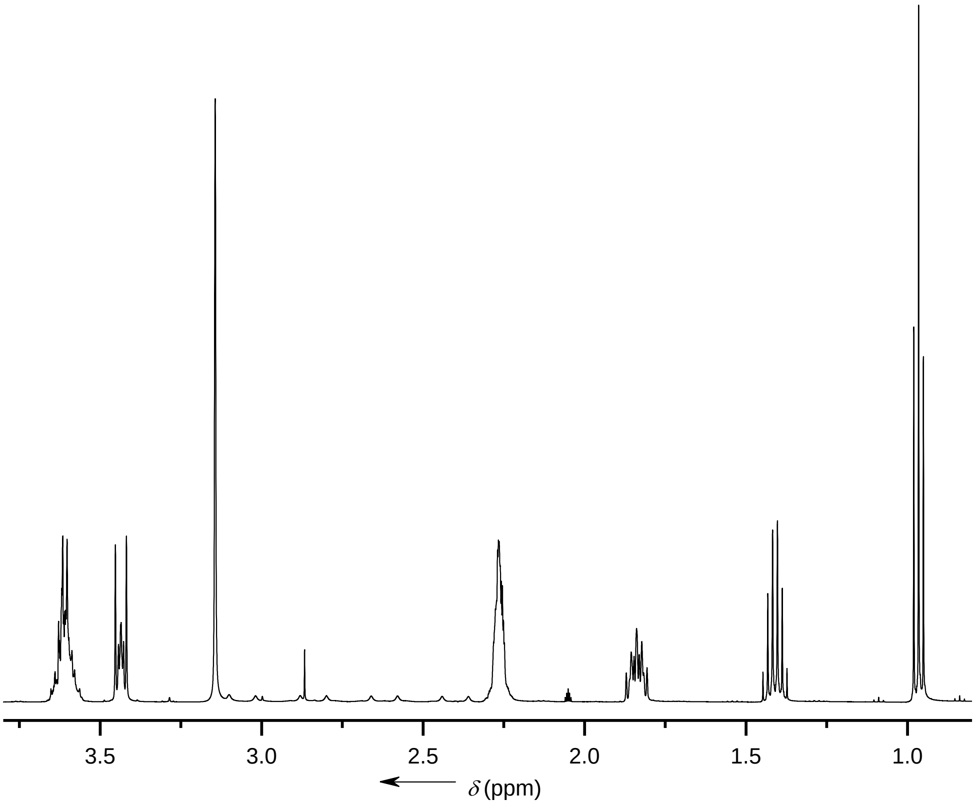


**Figure S55: $^1$H NMR spectrum of [BMPL][BFH(CN)$_2$].**

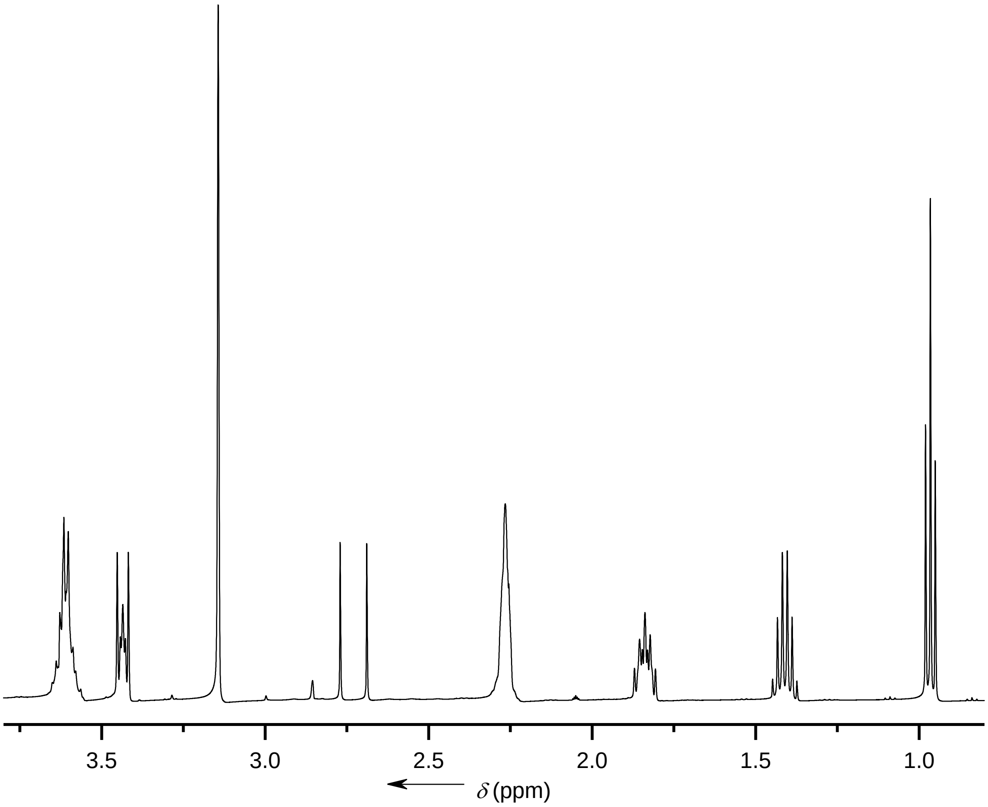


**Figure S56: $^1$H{$^{11}$B} NMR spectrum of [BMPL][BFH(CN)2].**

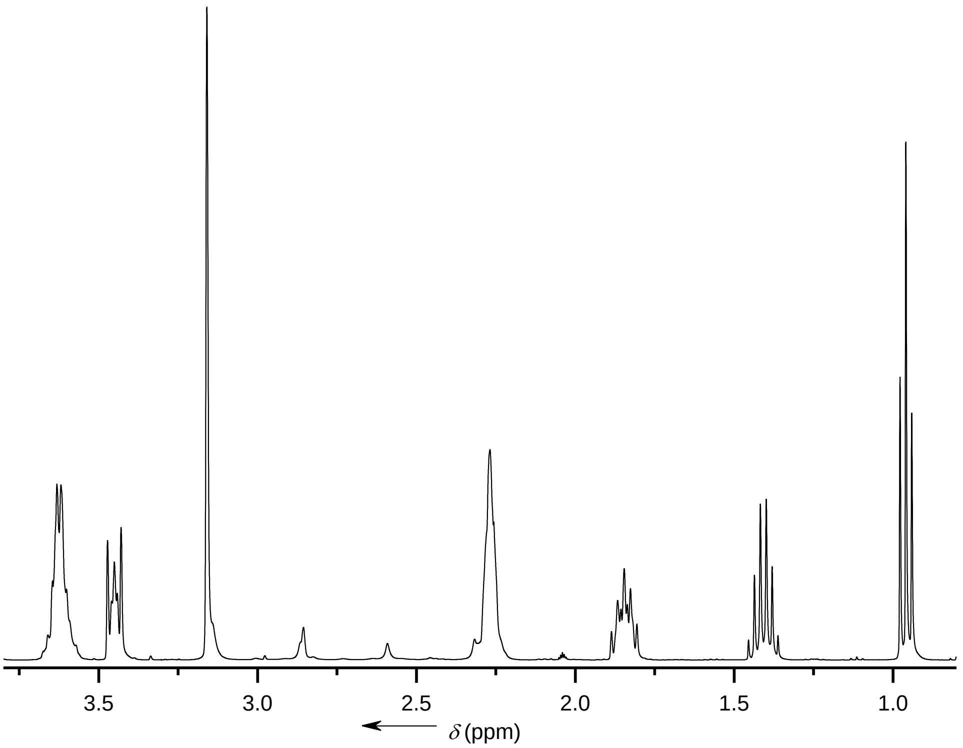


**Figure S57: $^{1}H\{^{19}F\}$ NMR spectrum of [BMPL][BFH(CN)$_2$].**

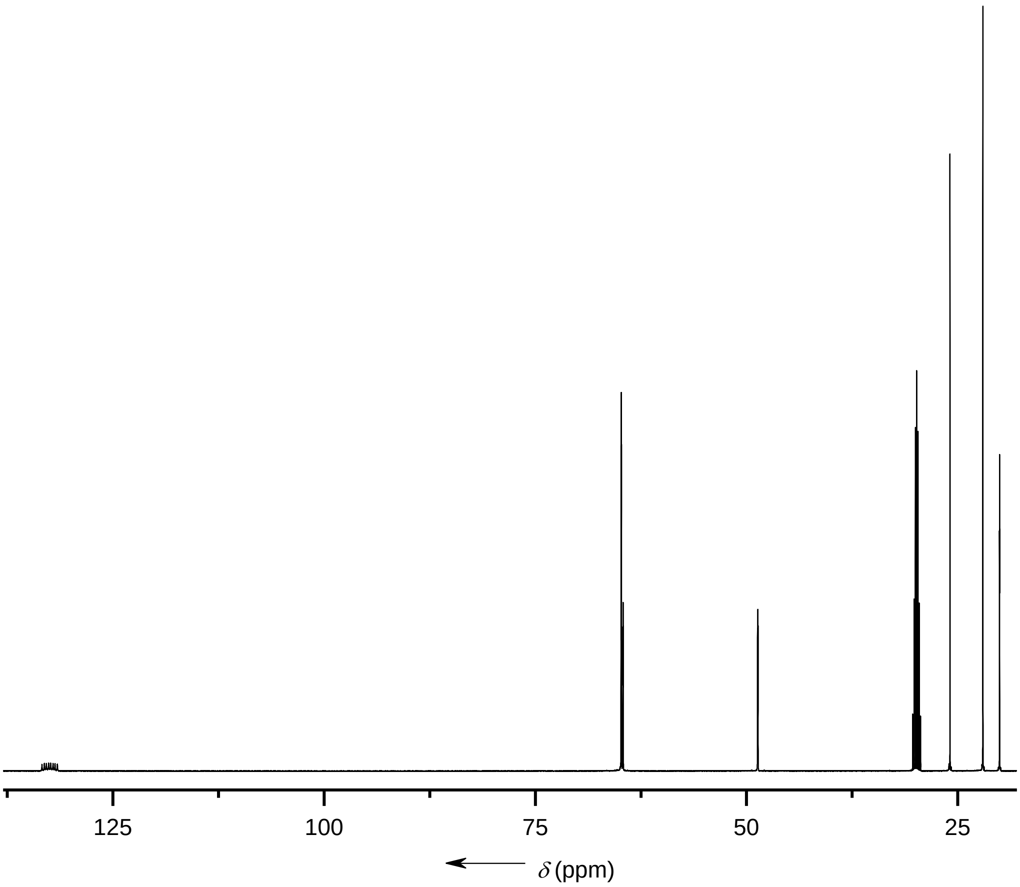


**Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of [BMPL][BFH(CN)$_2$].**

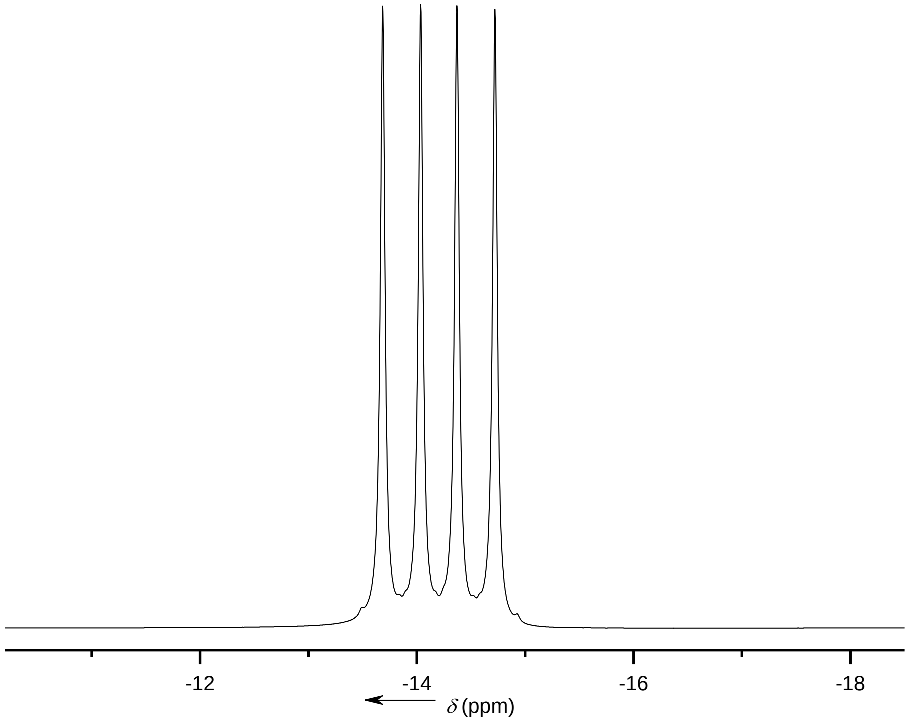


**Figure S59: $^{11}$B NMR spectrum of [BMPL][BFH(CN)$_2$].**

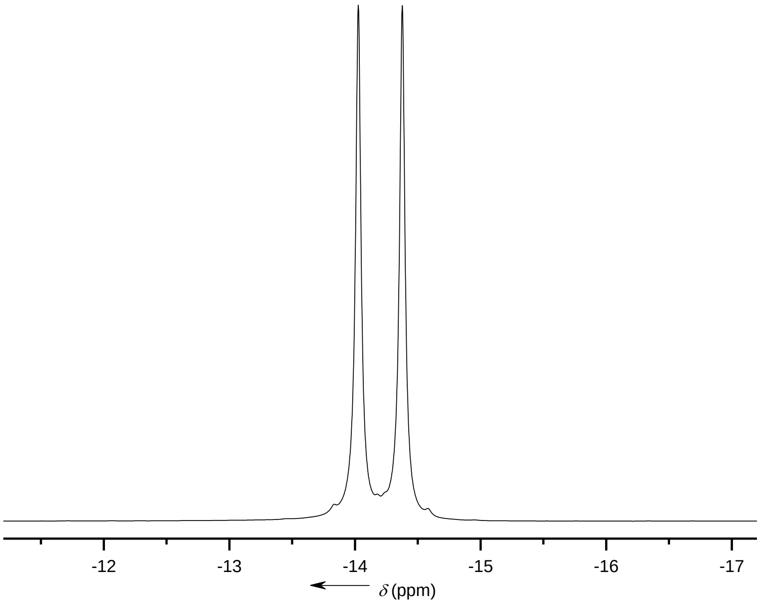


**Figure S60: $^{11}$B{$^1$H} NMR spectrum of [BMPL][BFH(CN)$_2$].**

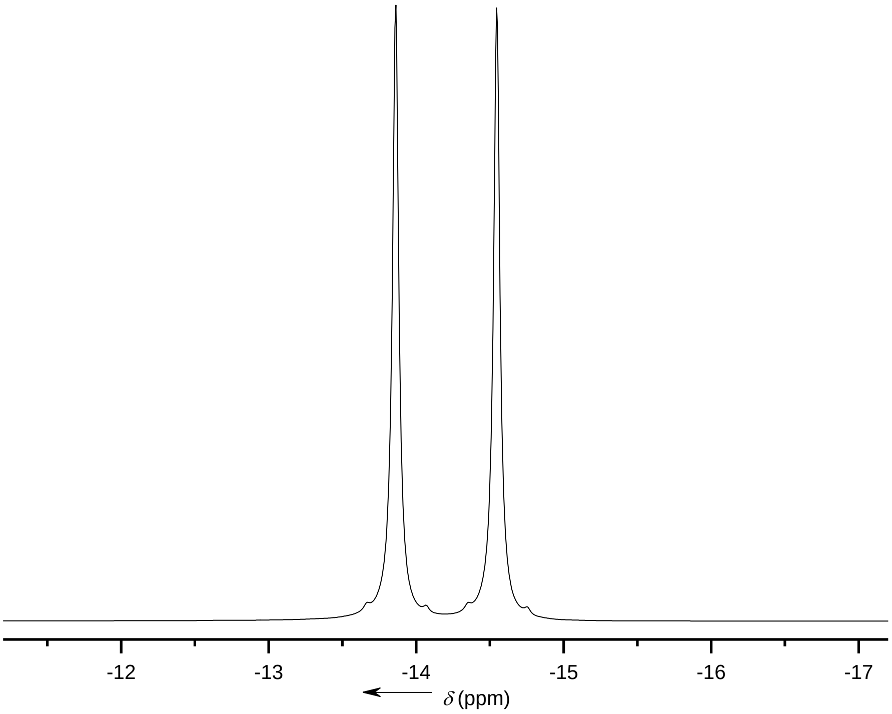


**Figure S61: $^{11}B\{^{19}F\}$ NMR spectrum of [BMPL][BFH(CN)$_2$].**

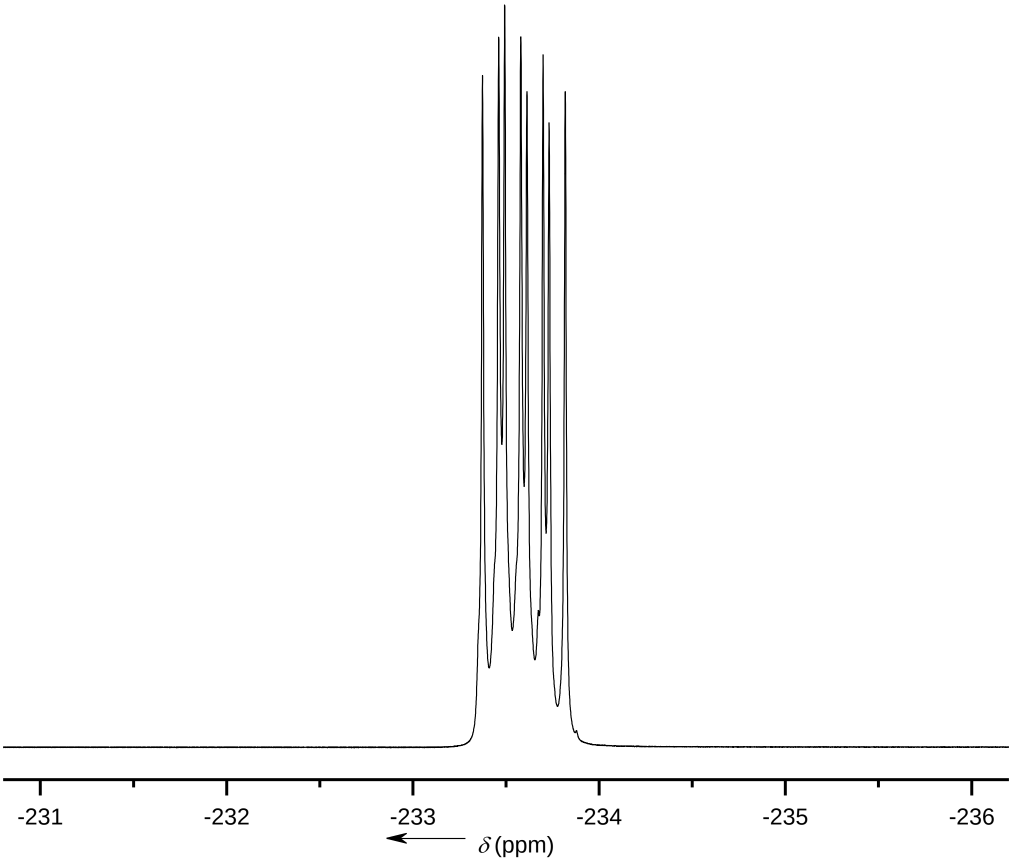


**Figure S62: $^{19}F$ NMR spectrum of [BMPL][BFH(CN)$_2$].**

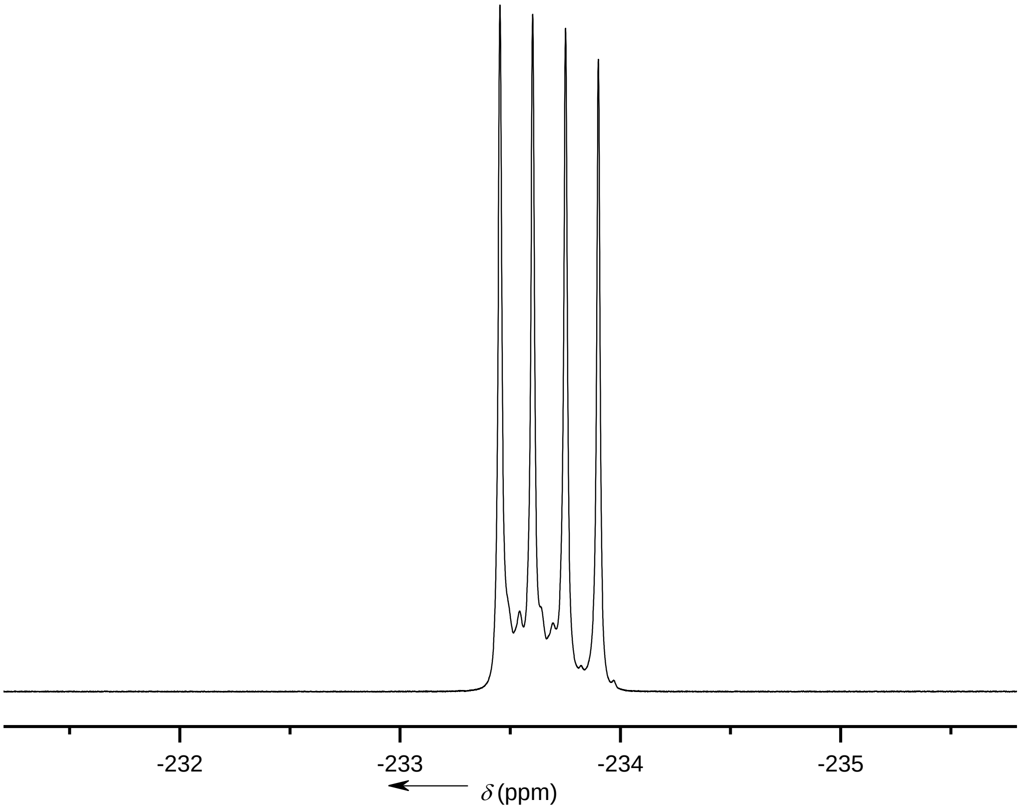


Figure S63: $^{19}F\{^{1}H\}$ NMR spectrum of [BMPL][BFH(CN)$_2$].

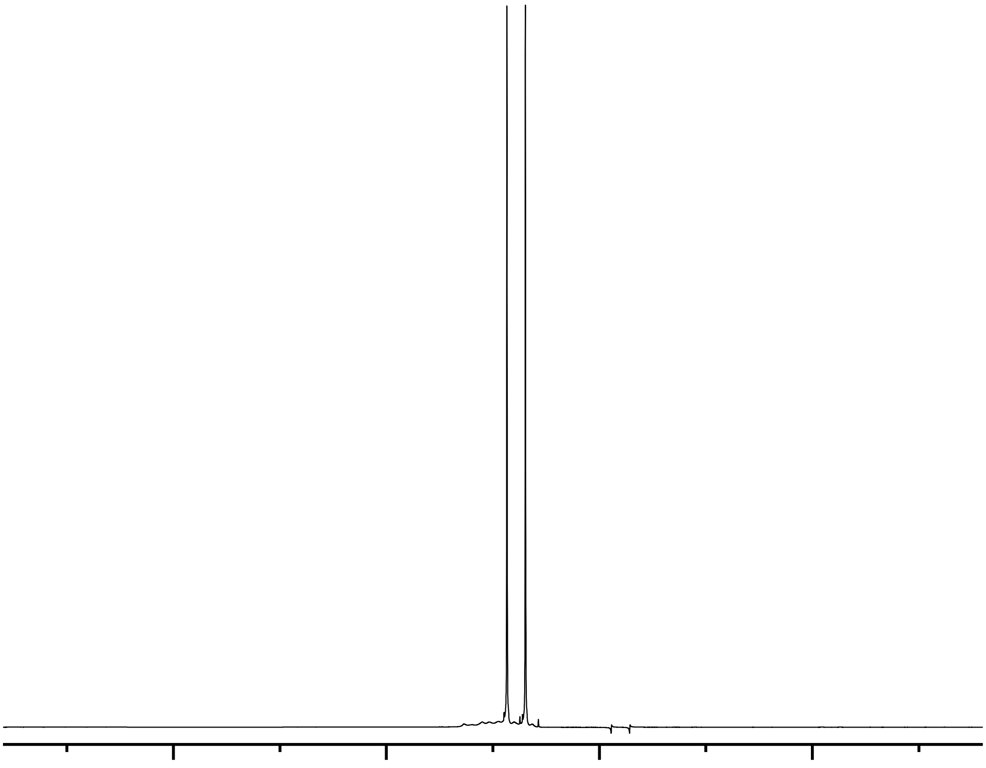


Figure S64: $^{19}F\{^{11}B\}$ NMR spectrum of [BMPL][BFH(CN)$_2$].

## 5.3 Phosphonium salts

### 5.3.1 [BnPh$_3$P][BF$_4$]

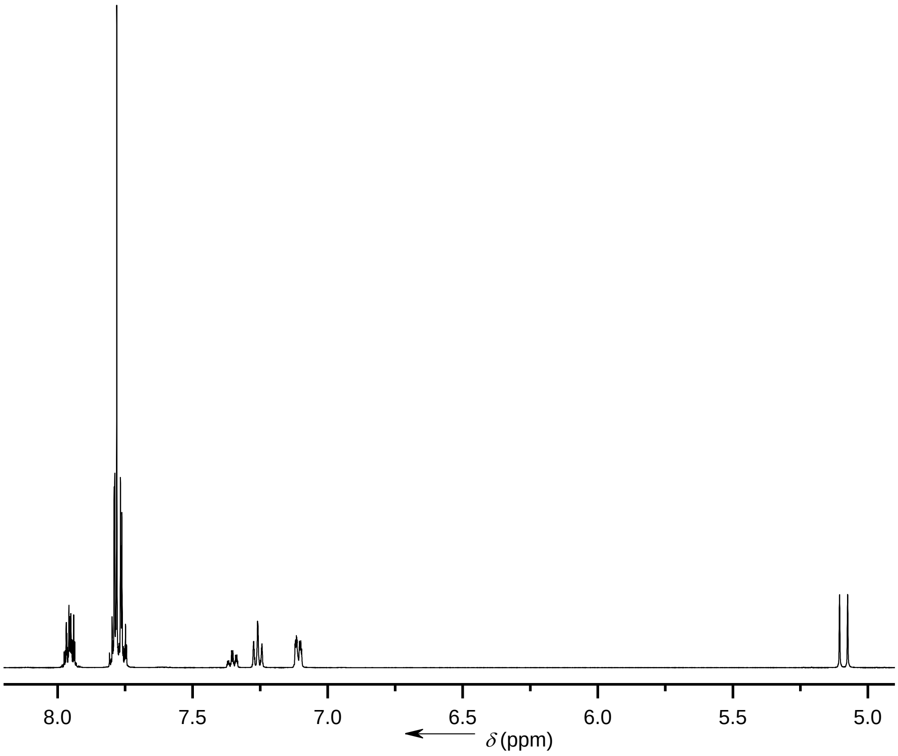


Figure S65: $^1$H NMR spectrum of [BnPh$_3$P][BF$_4$].

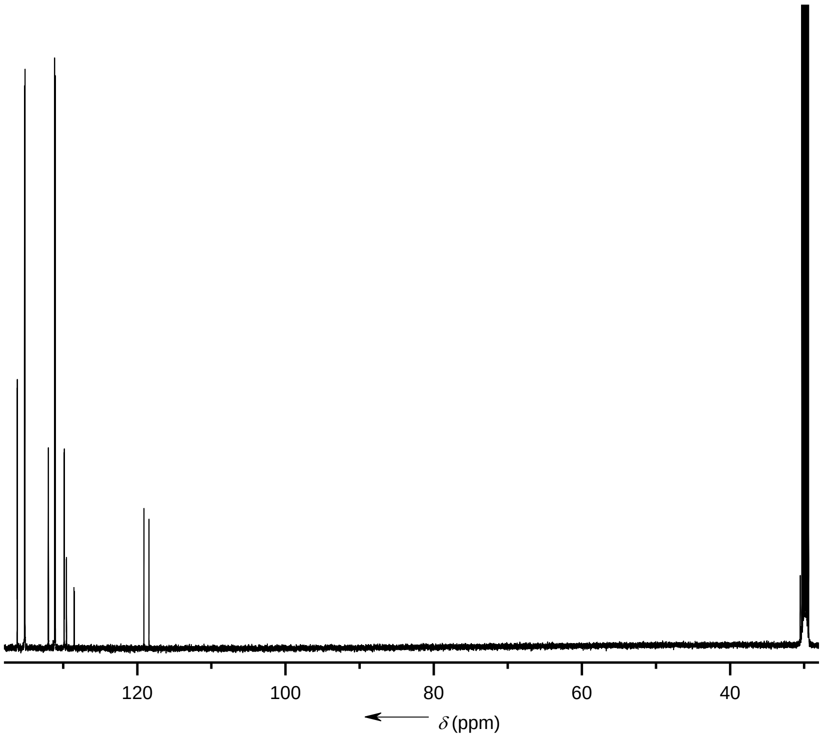


Figure S66: $^{13}$C{$^1$H} NMR spectrum of [BnPh$_3$P][BF$_4$].

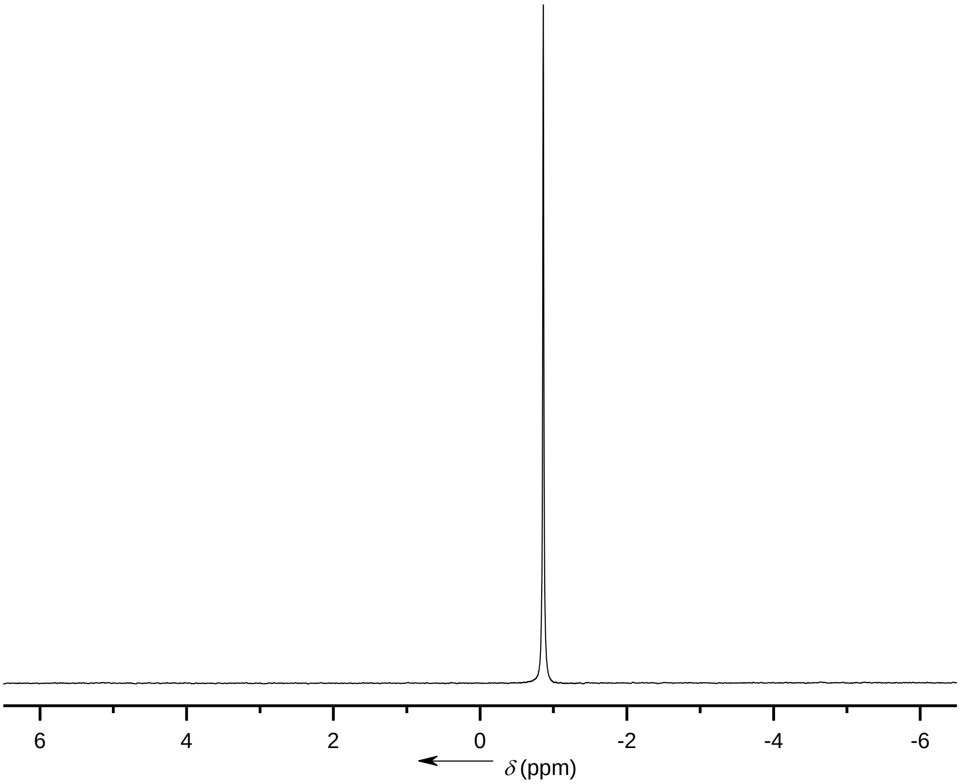


Figure S67: $^{11}B$ NMR spectrum of $[BnPh_3P][BF_4]$.

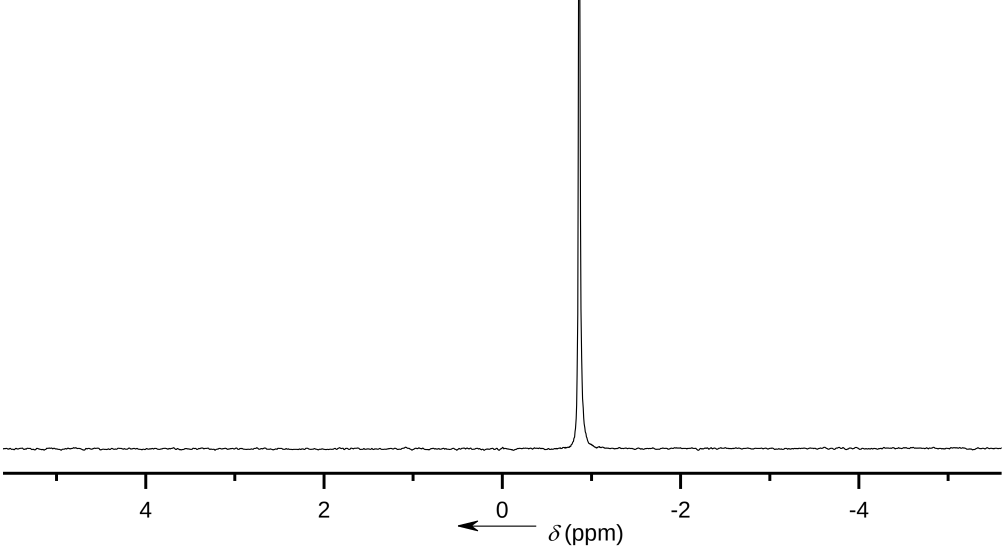


Figure S68: $^{11}B\{^1H\}$ NMR spectrum of $[BnPh_3P][BF_4]$.

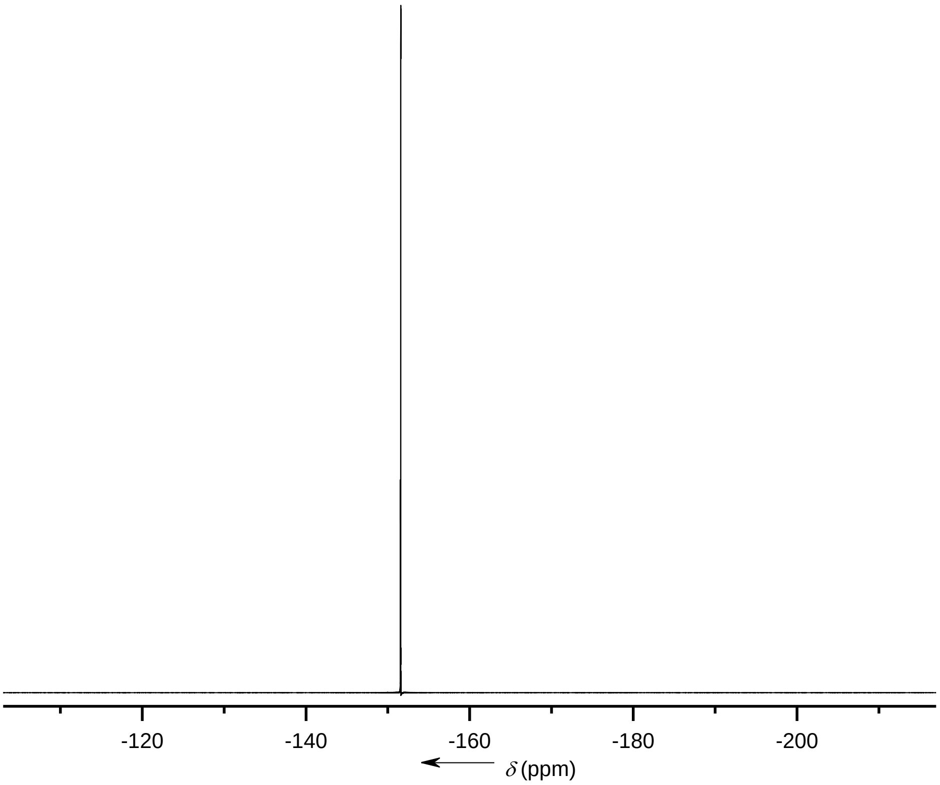


**Figure S69: $^{19}$F NMR spectrum of [BnPh$_3$P][BF$_4$].**

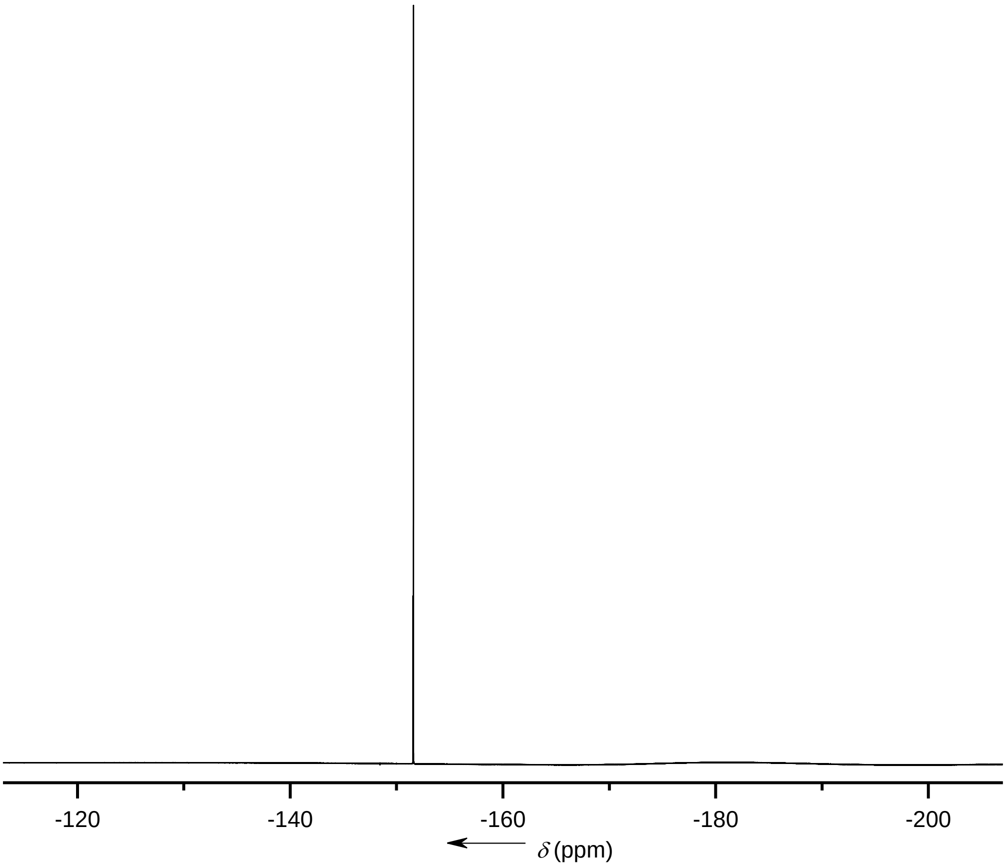


**Figure S70: $^{19}$F{$^{11}$B} NMR spectrum of [BnPh$_3$P][BF$_4$].**

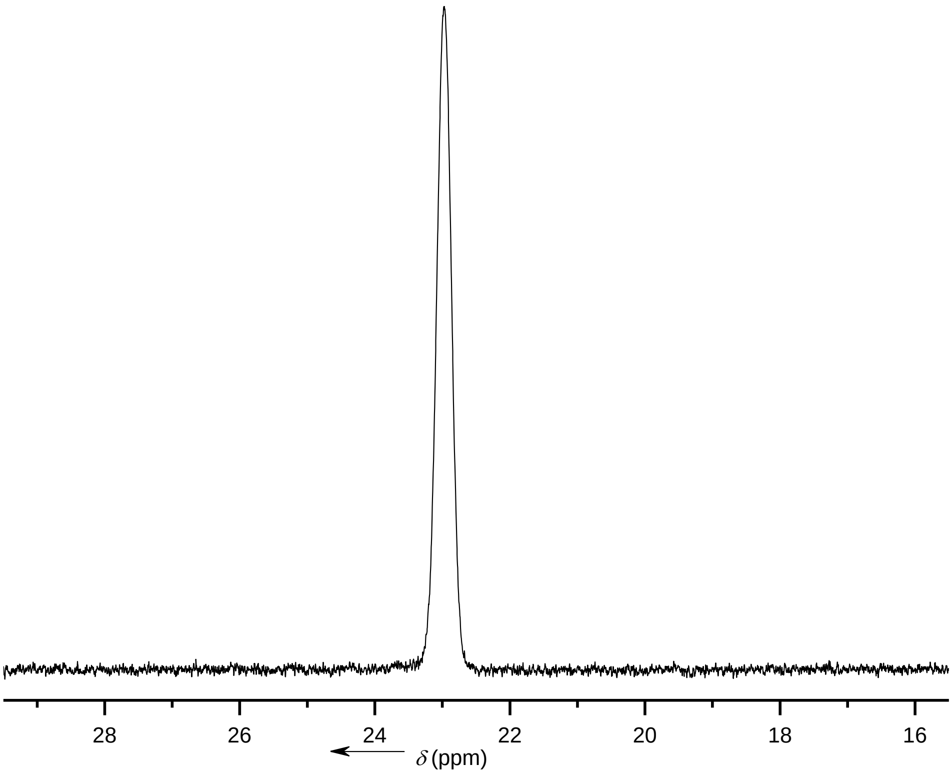


Figure S71: $^{31}$P NMR spectrum of [BnPh$_3$P][BF$_4$].

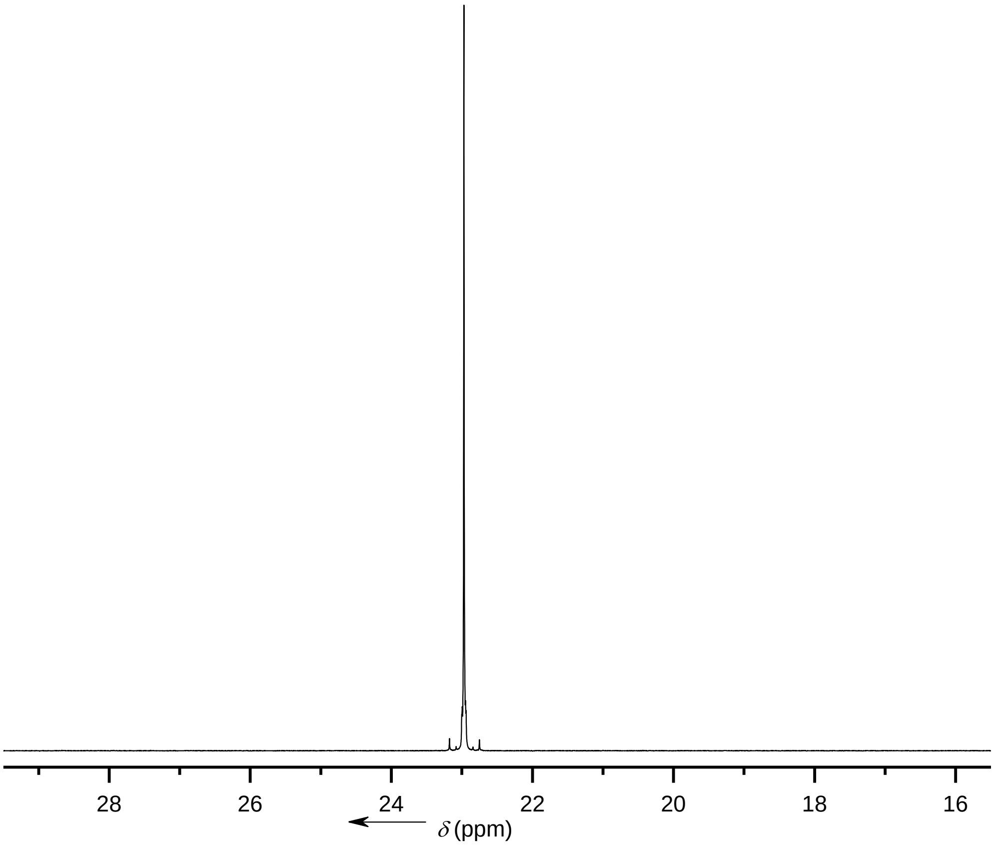


Figure S72: $^{31}$P{$^{1}$H} NMR spectrum of [BnPh$_3$P][BF$_4$].

## 5.3.2 [BnPh$_3$P][BF$_3$(CN)]

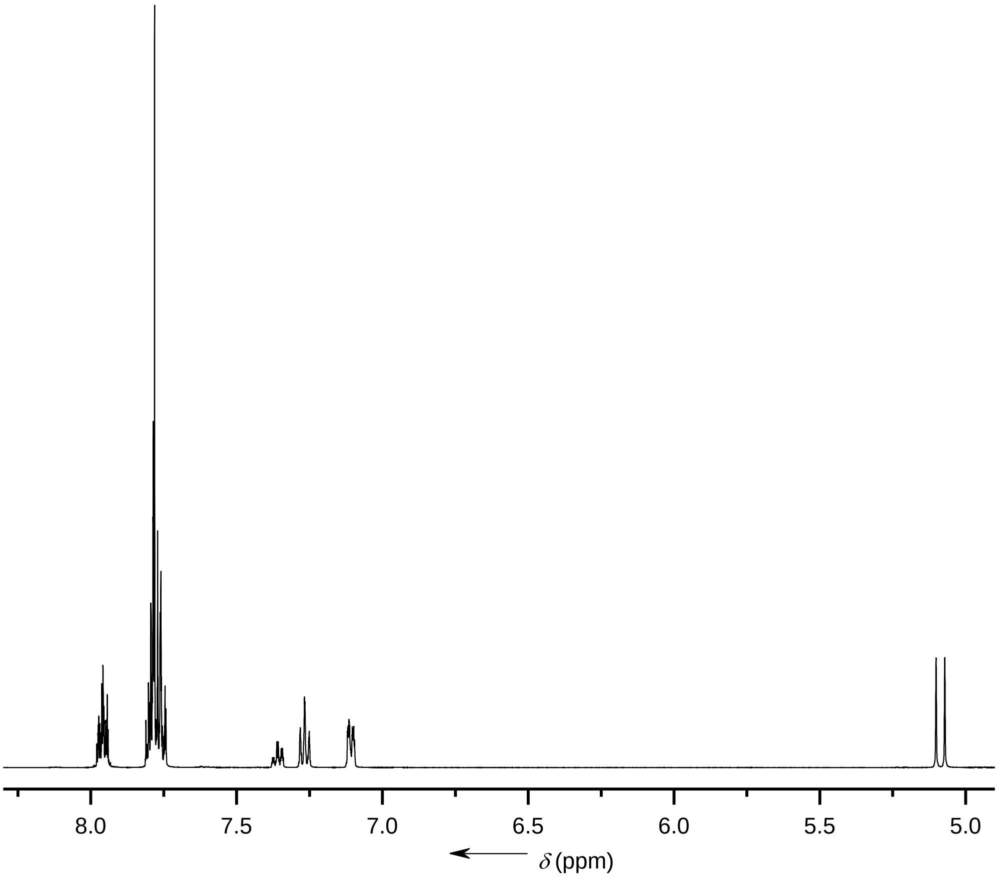


**Figure S73: $^1$H NMR spectrum of [BnPh$_3$P][BF$_3$(CN)].**

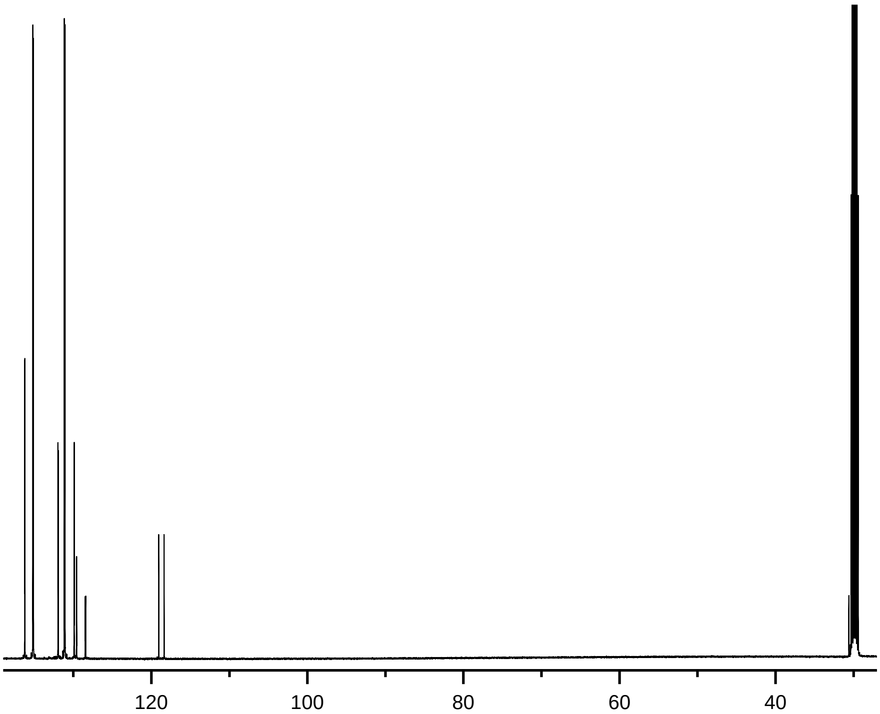


**Figure S74: $^{13}$C{$^1$H} NMR spectrum of [BnPh$_3$P][BF$_3$(CN)].**

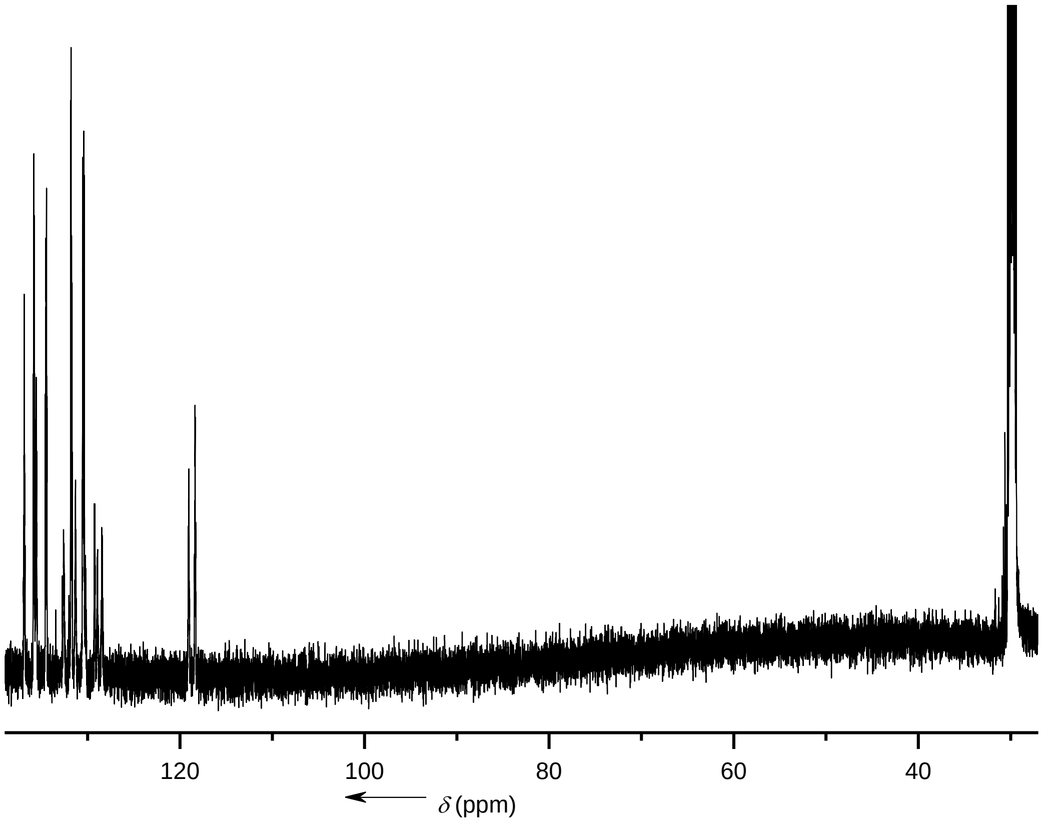


Figure S75: $^{13}C\{^{19}F\}$ NMR spectrum of [BnPh$_3$P][BF$_3$(CN)].

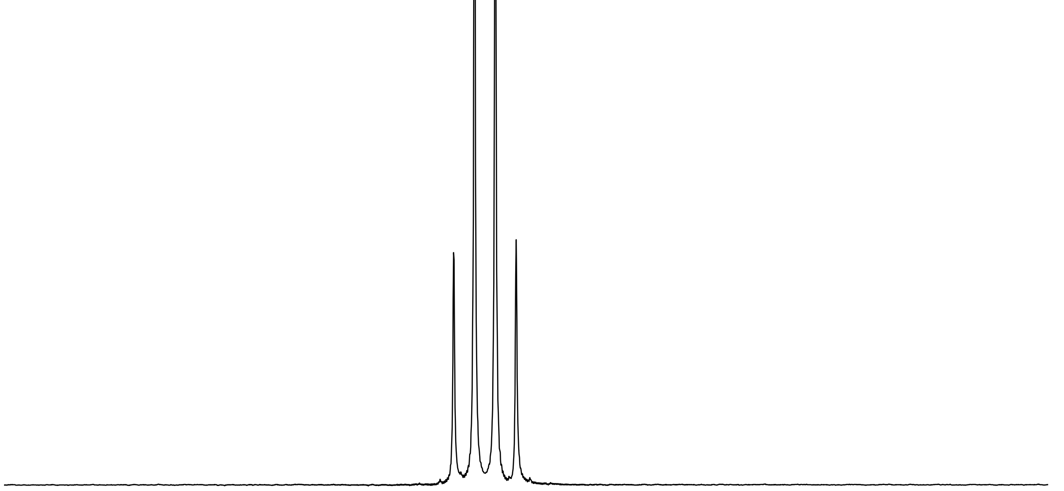


Figure S76: $^{11}B$ NMR spectrum of [BnPh$_3$P][BF$_3$(CN)].

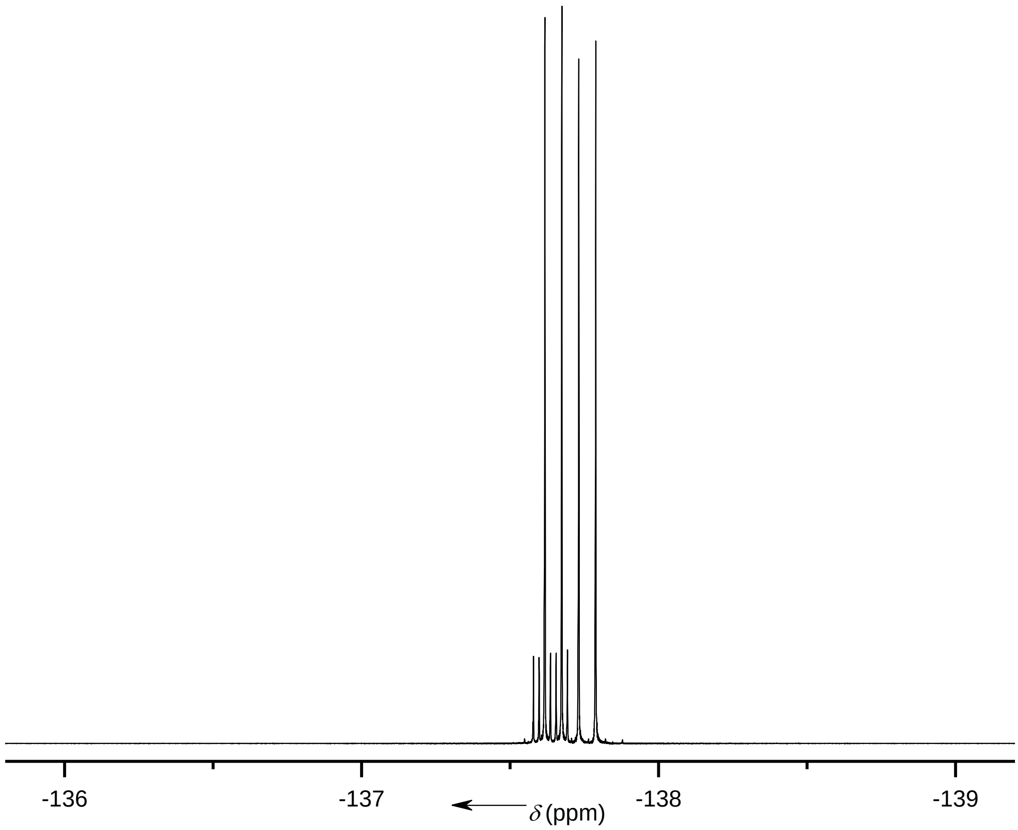


**Figure S77: $^{19}$F NMR spectrum of [BnPh$_3$P][BF$_3$(CN)].**

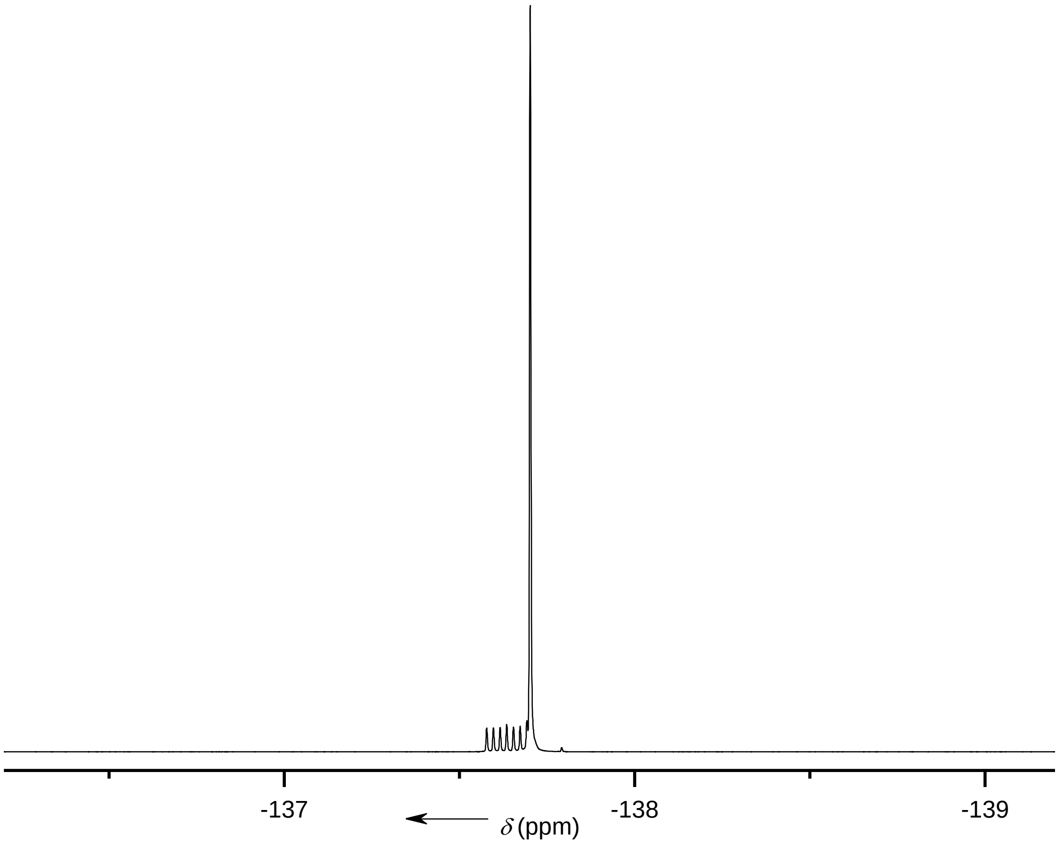


**Figure S78: $^{19}$F{$^{11}$B} NMR spectrum of [BnPh$_3$P][BF$_3$(CN)].**

## 5.3.3 [$BnPh_3P$][$BF_2(CN)_2$]

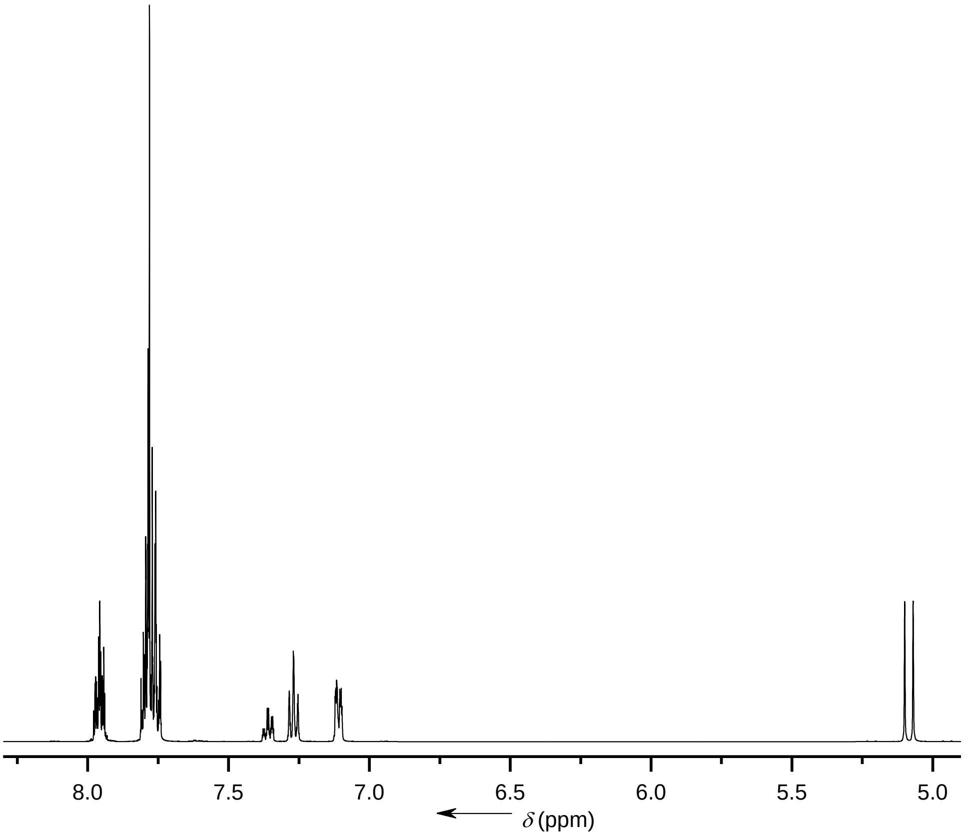


**Figure S79: $^1H$ NMR spectrum of [$BnPh_3P$][$BF_2(CN)_2$].**

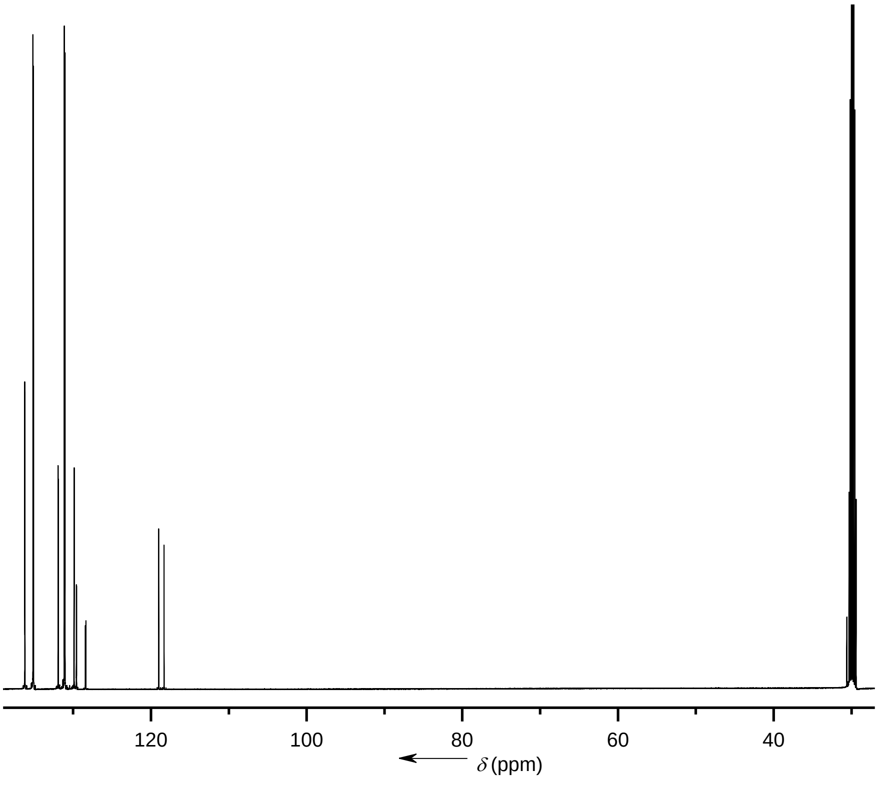


**Figure S80: $^{13}C\{^1H\}$ NMR spectrum of [$BnPh_3P$][$BF_2(CN)_2$].**

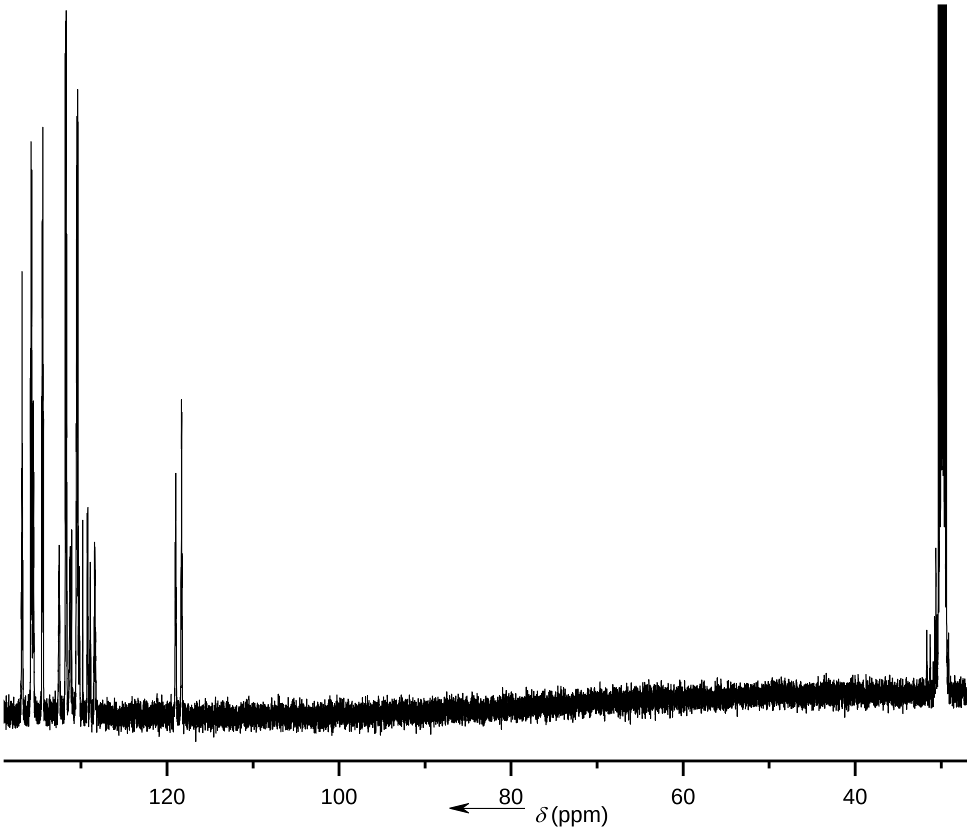


Figure S81: $^{13}C\{^{19}F\}$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.

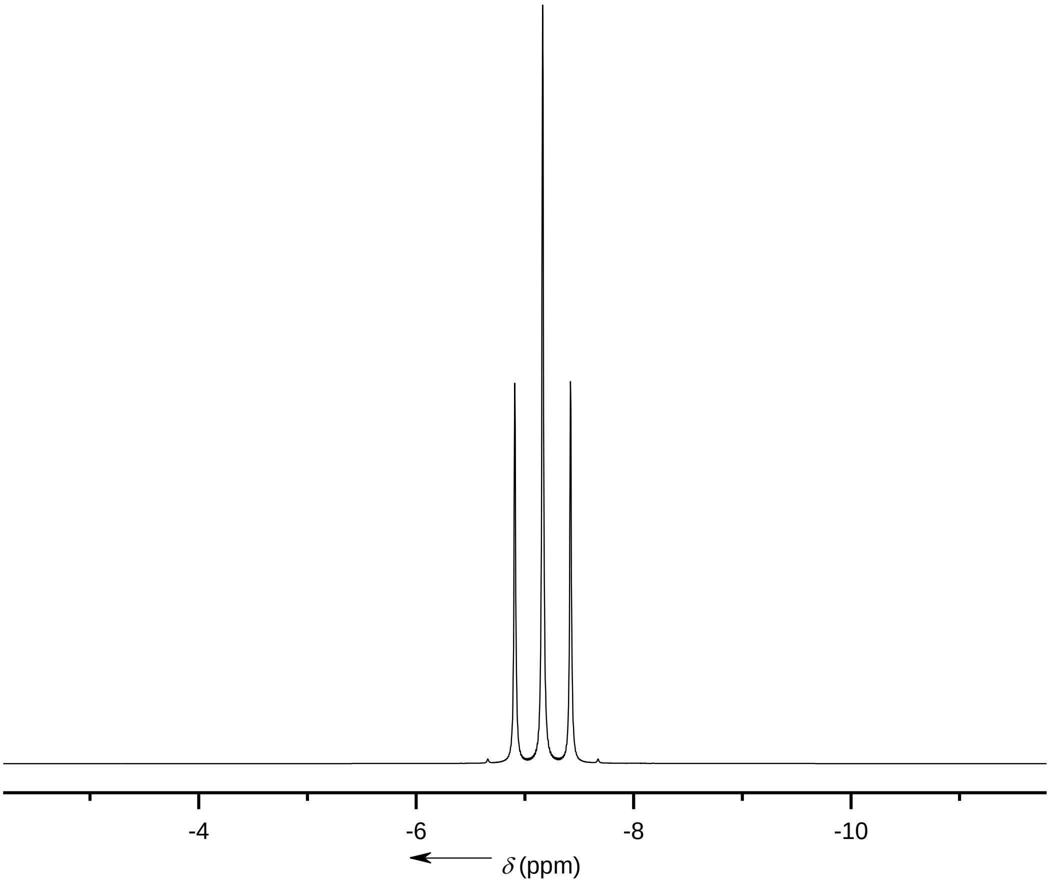


Figure S82: $^{11}B$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.

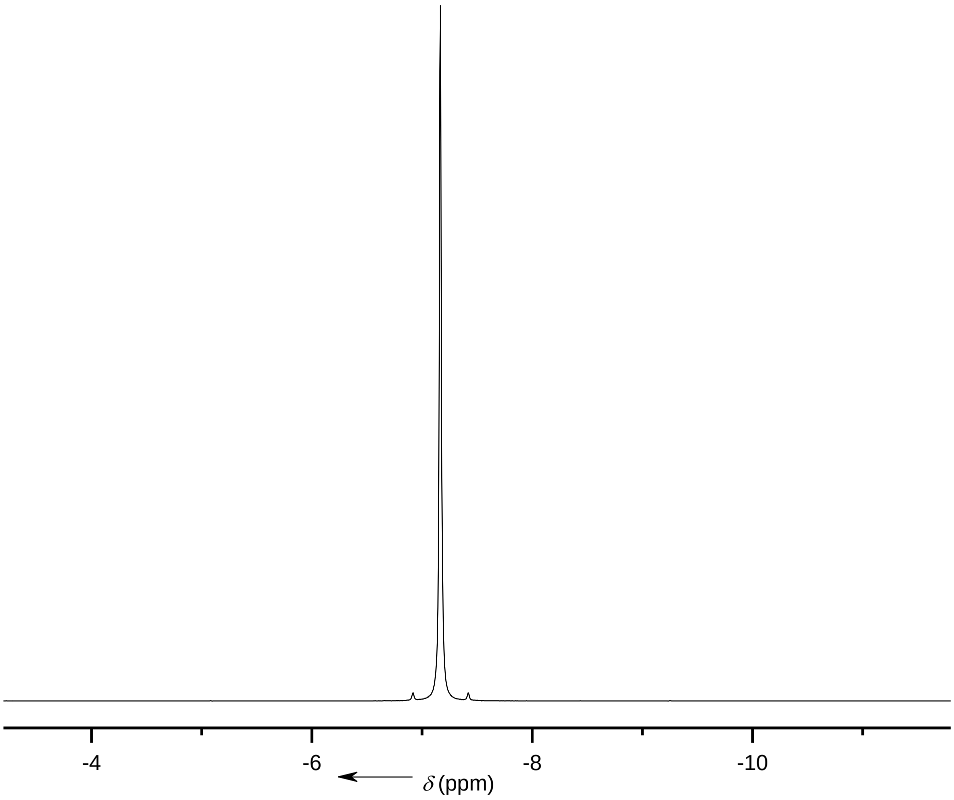


**Figure S83: $^{11}B\{^{1}H\}$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.**

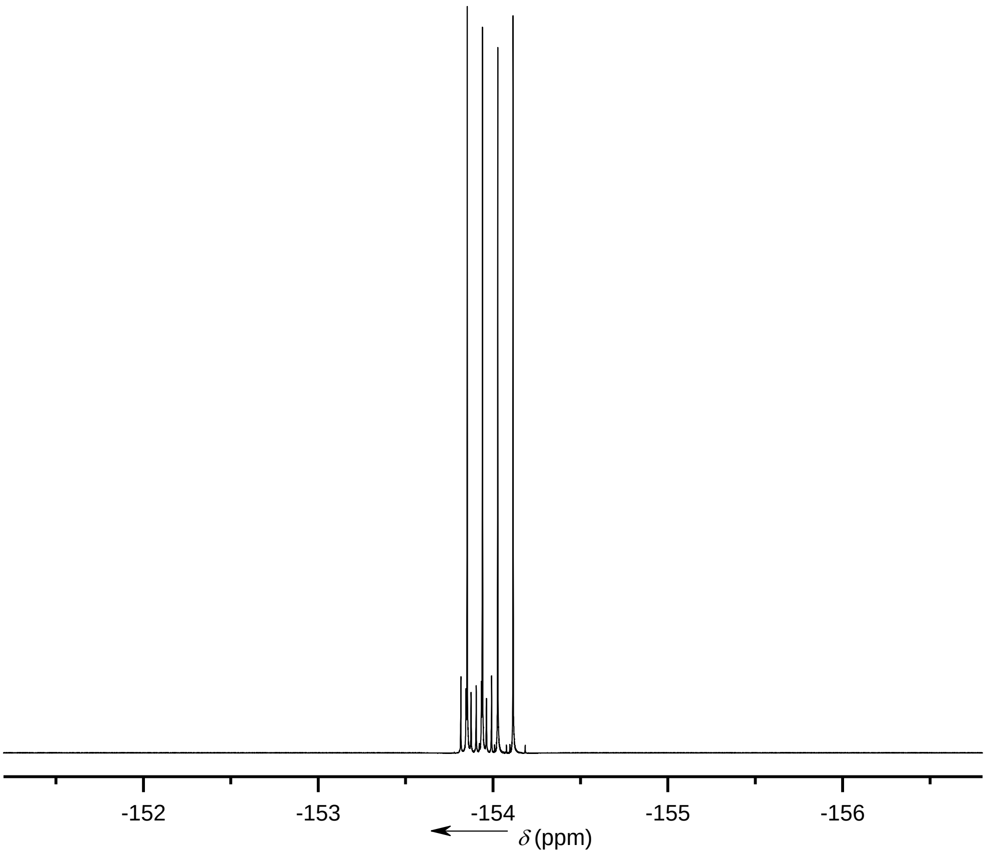


**Figure S84: $^{19}F$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.**

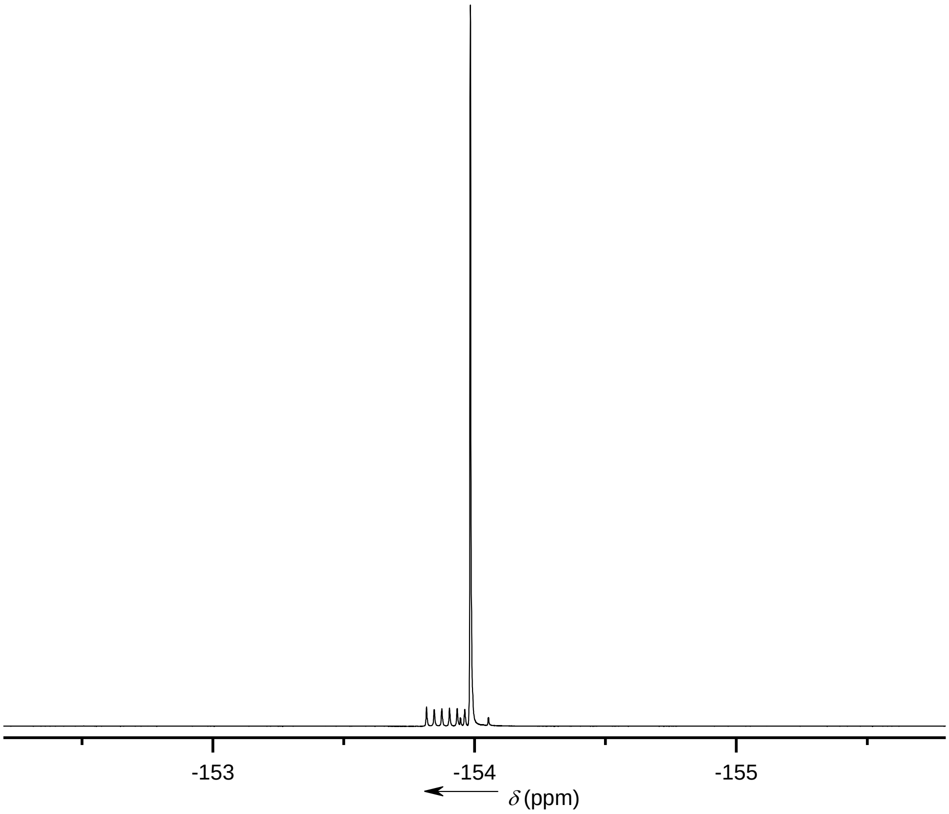


**Figure S85: $^{19}F\{^{11}B\}$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.**

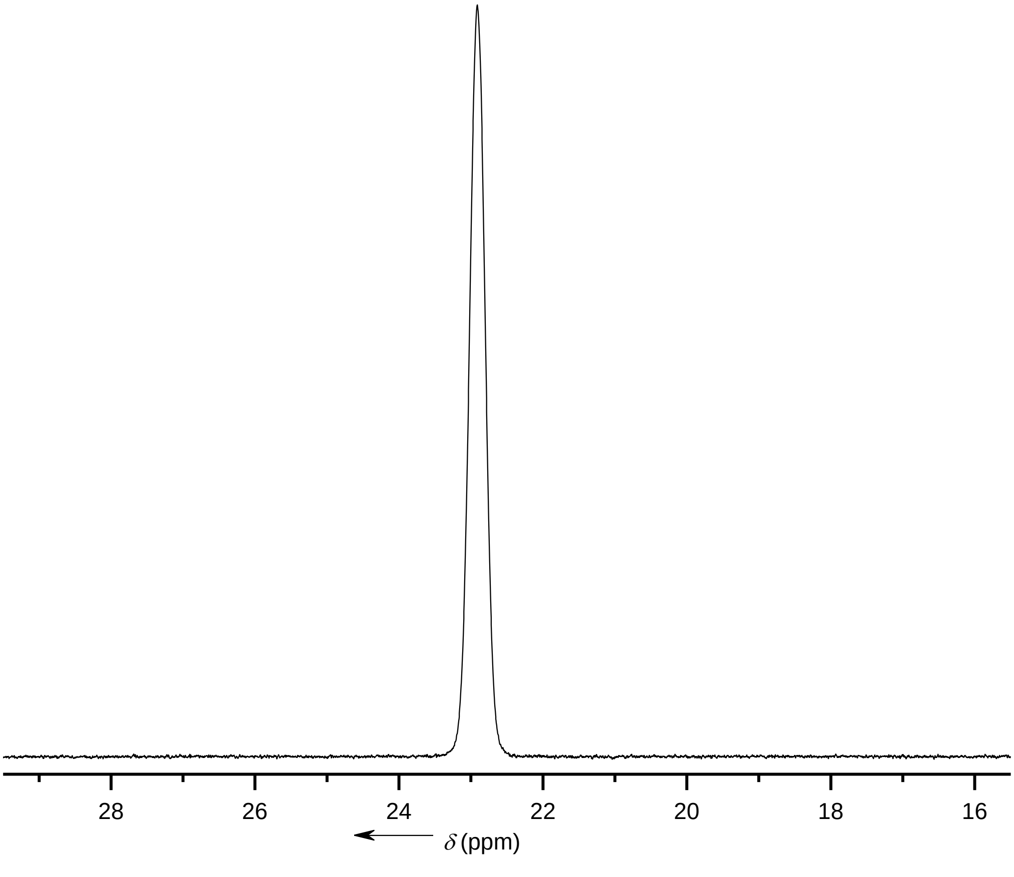


**Figure S86: $^{31}P$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.**

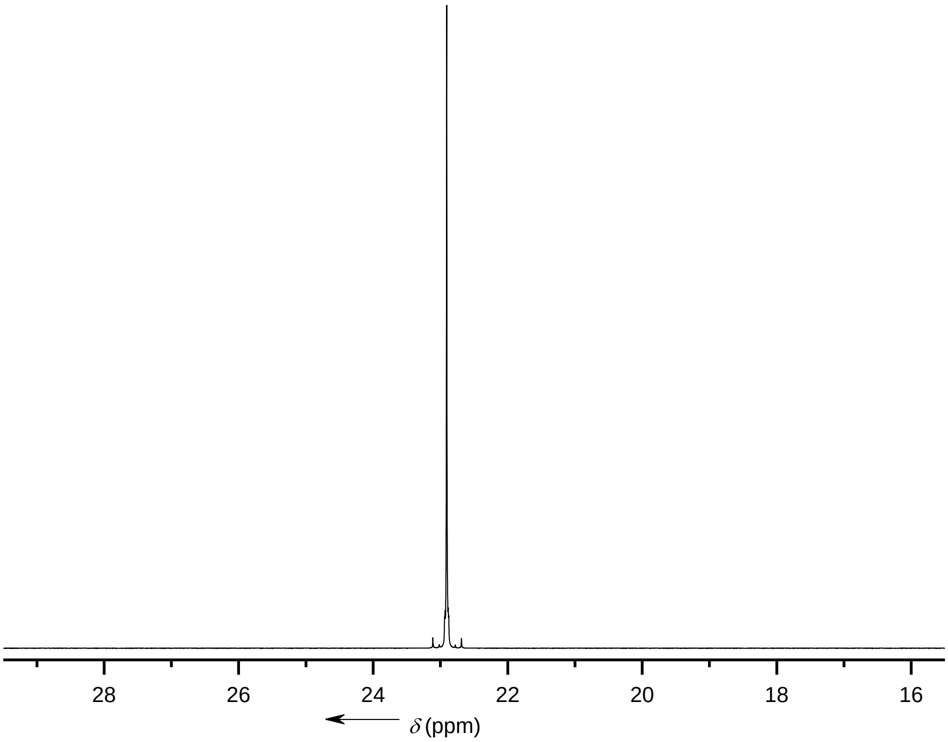


Figure S87: $^{31}P\{^1H\}$ NMR spectrum of $[BnPh_3P][BF_2(CN)_2]$.

### 5.3.4 $[BnPh_3P][BF(CN)_3]$

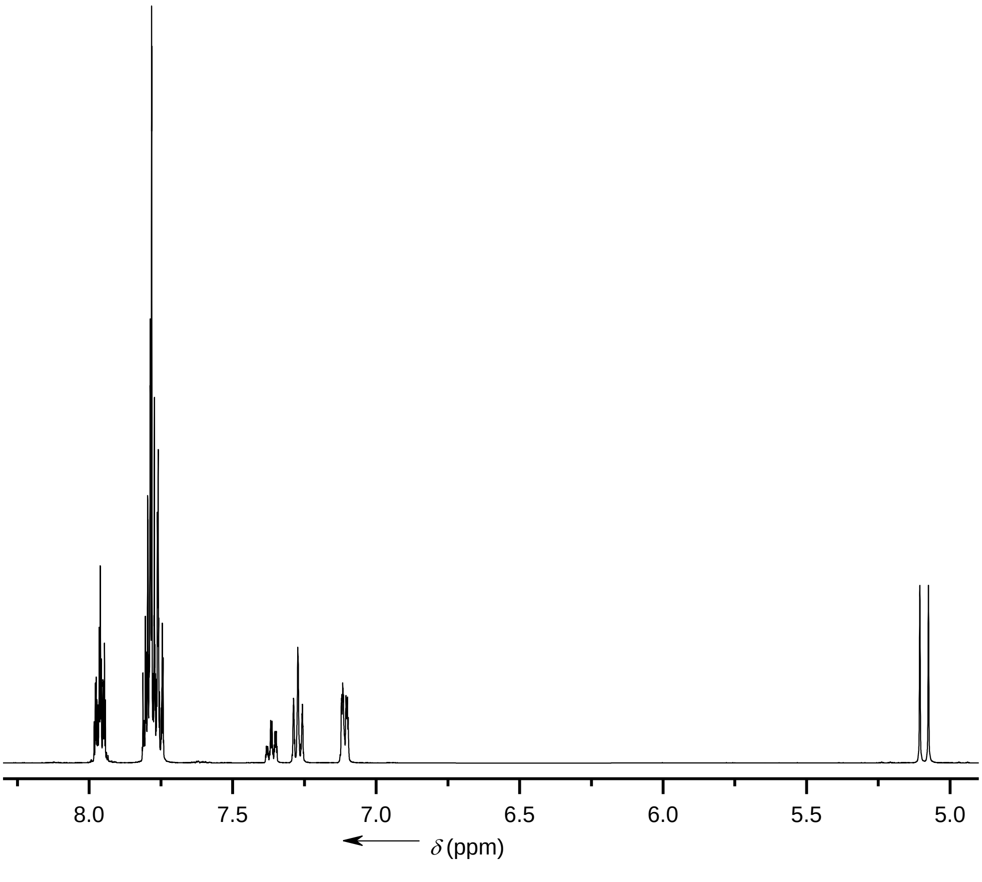


Figure S88: $^1H$ NMR spectrum of $[BnPh_3P][BF(CN)_3]$.

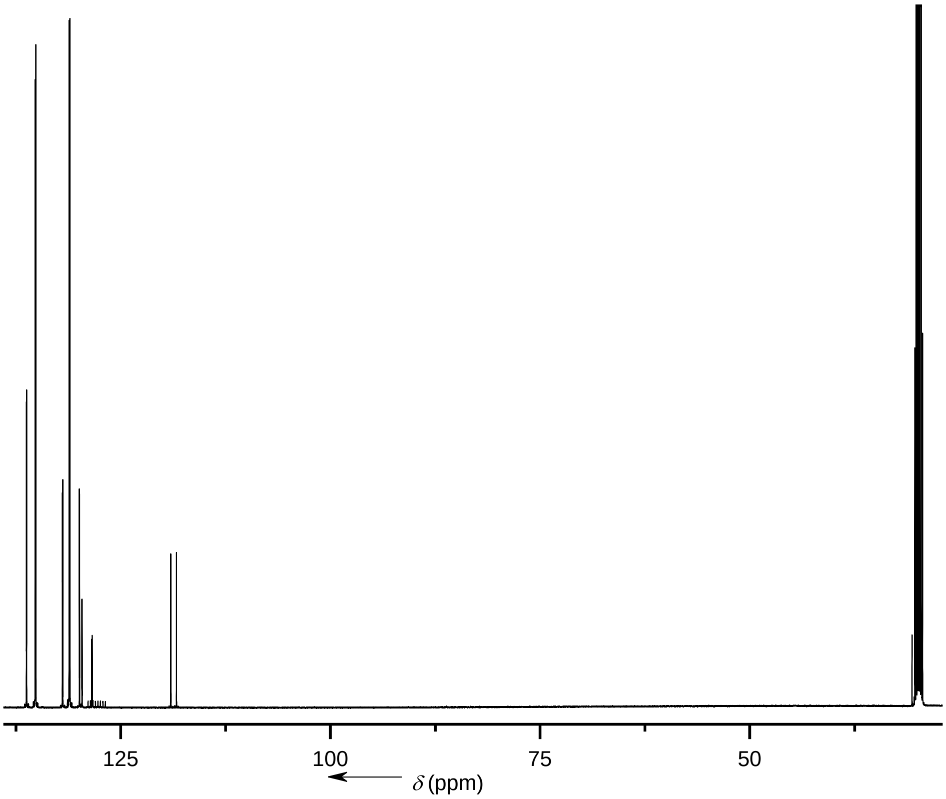


Figure S89: $^{13}C\{^{1}H\}$ NMR spectrum of $[BnPh_3P][BF(CN)_3]$.

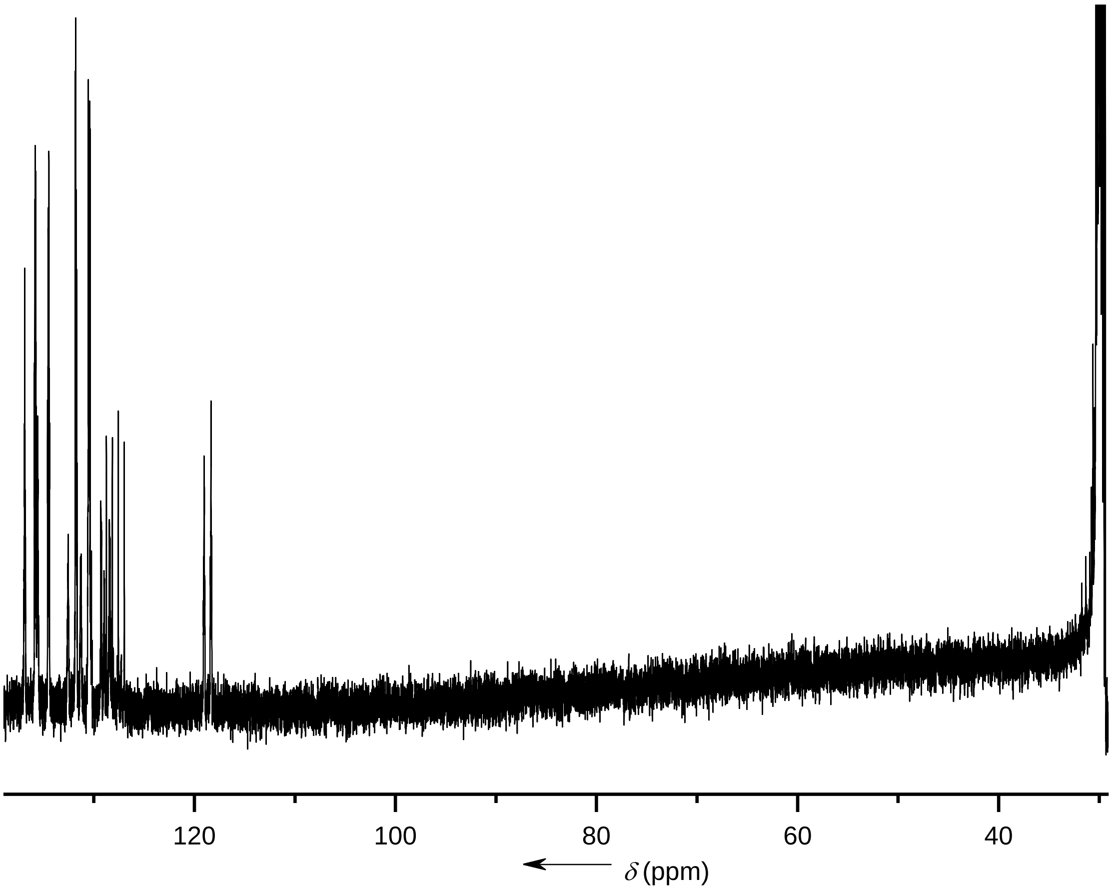


Figure S90: $^{13}C\{^{19}F\}$ NMR spectrum of $[BnPh_3P][BF(CN)_3]$.

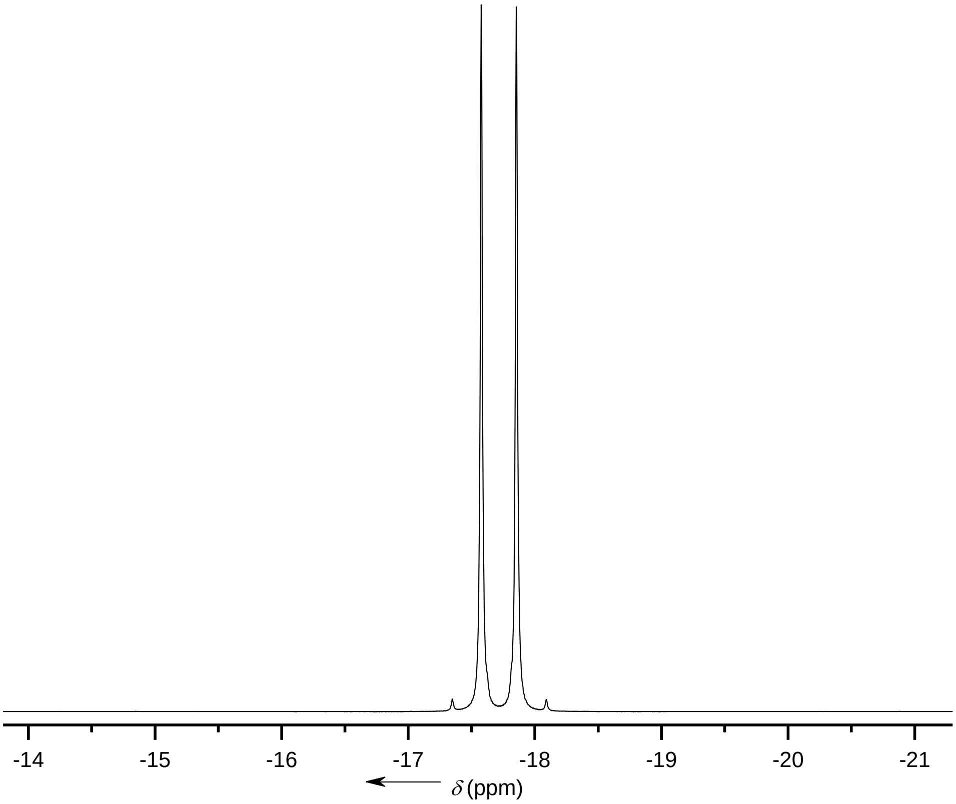


Figure S91: $^{11}B$ NMR spectrum of $[BnPh_3P][BF(CN)_3]$.

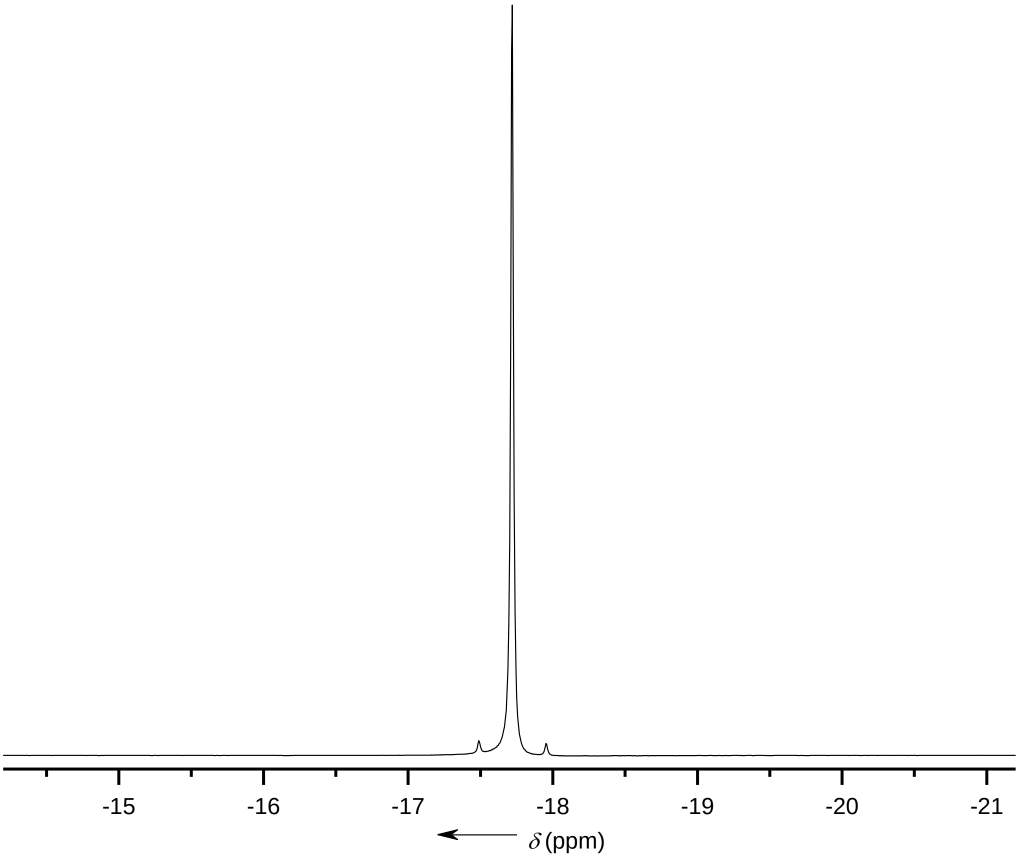


Figure S92: $^{11}B\{^{19}F\}$ NMR spectrum of $[BnPh_3P][BF(CN)_3]$.

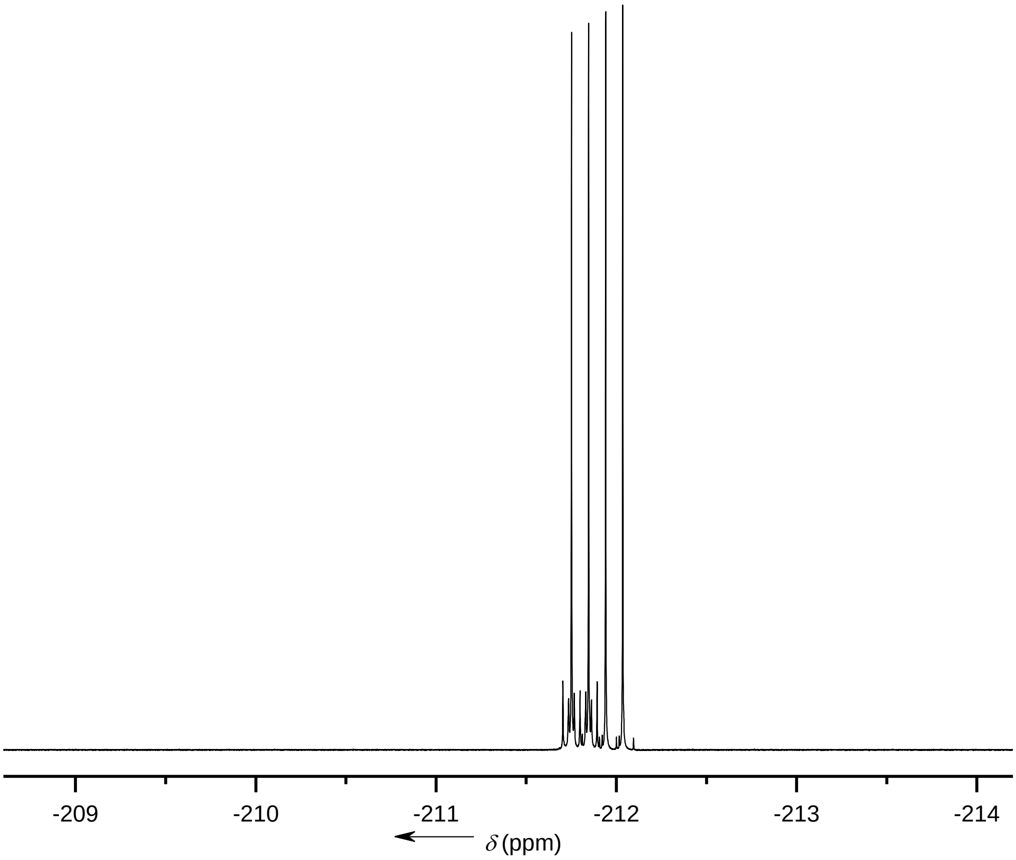


Figure S93: $^{19}F$ NMR spectrum of [BnPh$_3$P][BF(CN)$_3$].

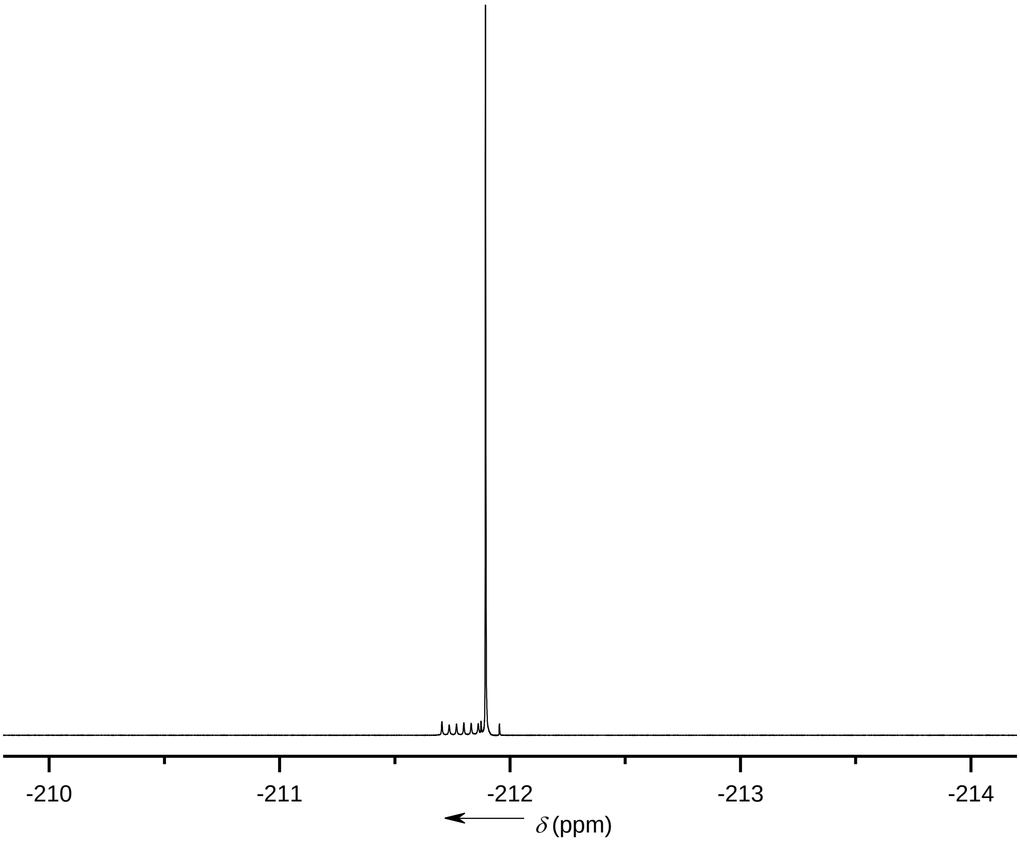


Figure S94: $^{19}F\{^{11}B\}$ NMR spectrum of [BnPh$_3$P][BF(CN)$_3$].

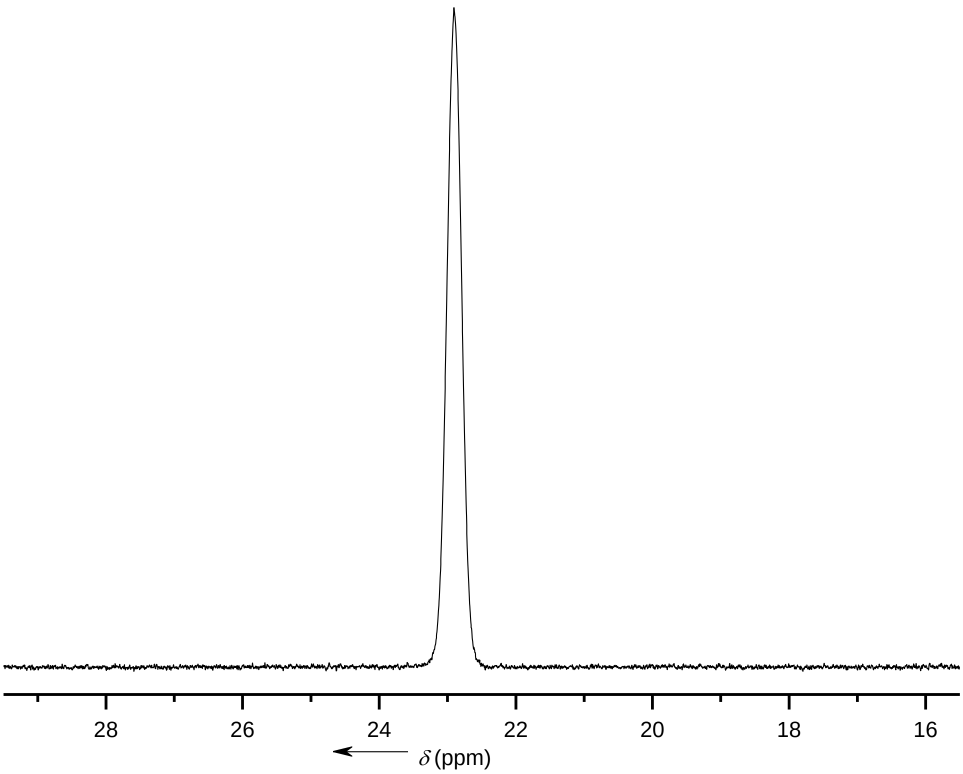


**Figure S95: $^{31}$P NMR spectrum of [BnPh$_3$P][BF(CN)$_3$].**

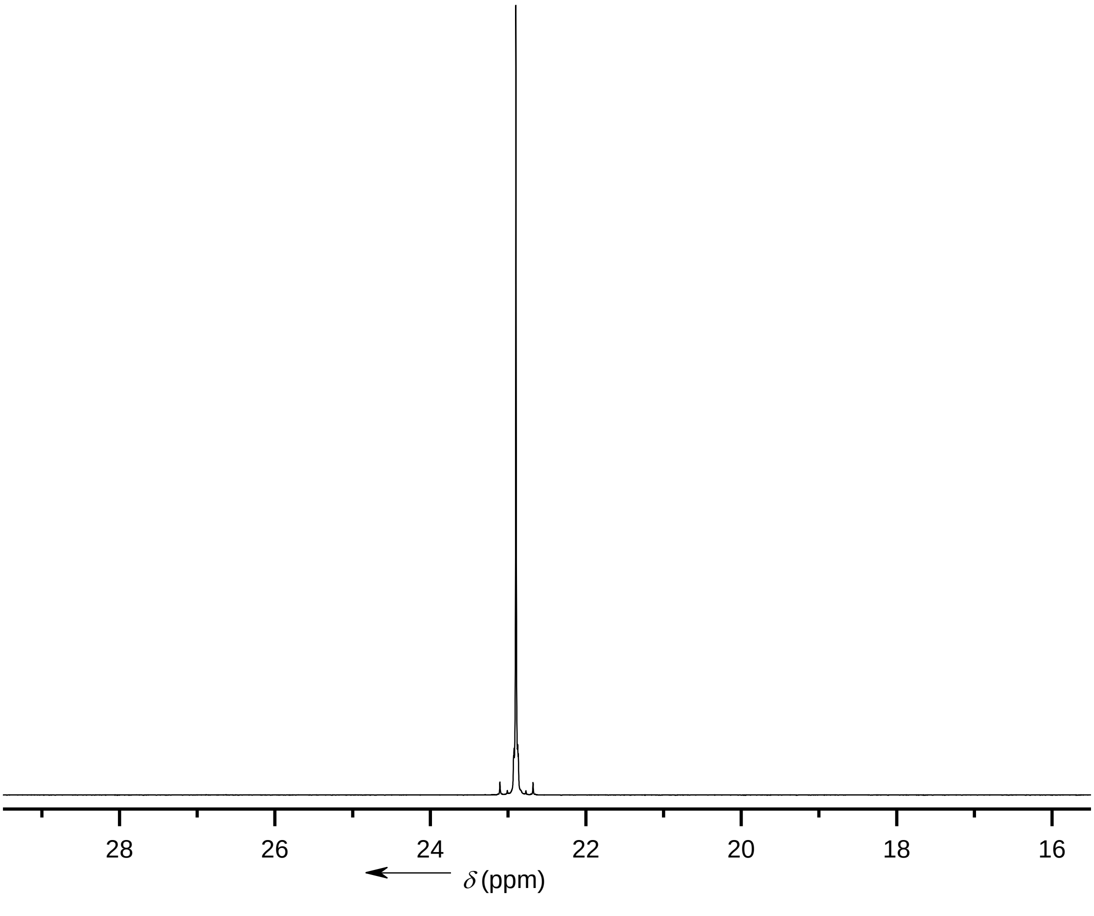


**Figure S96: $^{31}$P{$^{1}$H} NMR spectrum of [BnPh$_3$P][BF(CN)$_3$].**

### 5.3.5 [$BnPh_3P$][$B(CN)_4$]

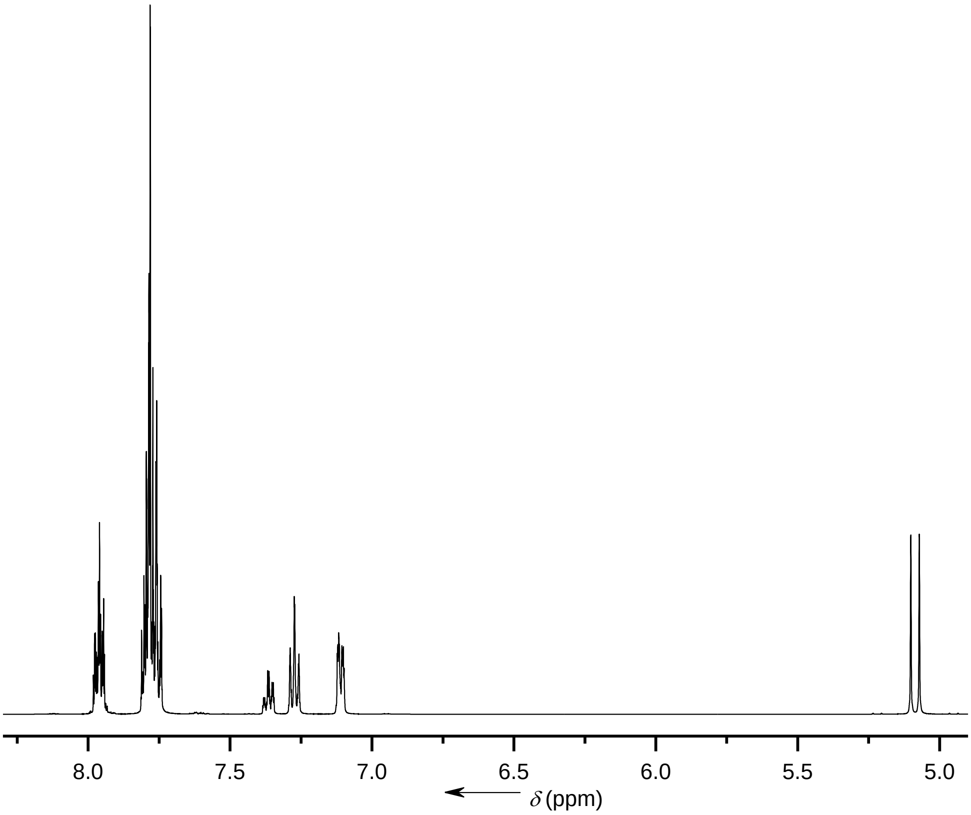


**Figure S97: $^1H$ NMR spectrum of [$BnPh_3P$][$B(CN)_4$].**

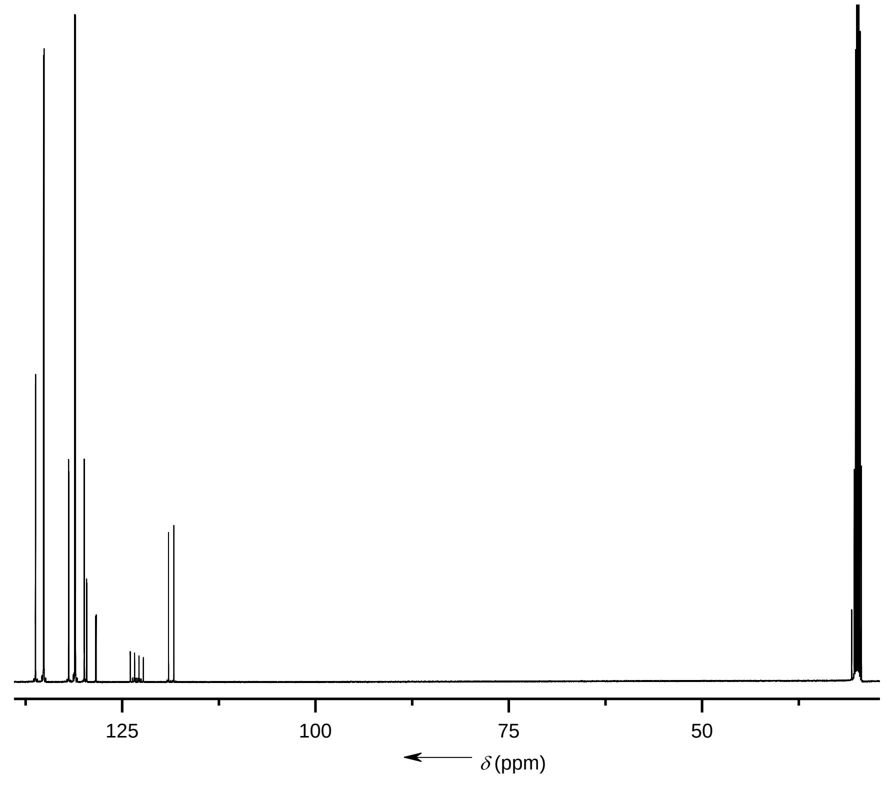


**Figure S98: $^{13}C\{^1H\}$ NMR spectrum of [$BnPh_3P$][$B(CN)_4$].**

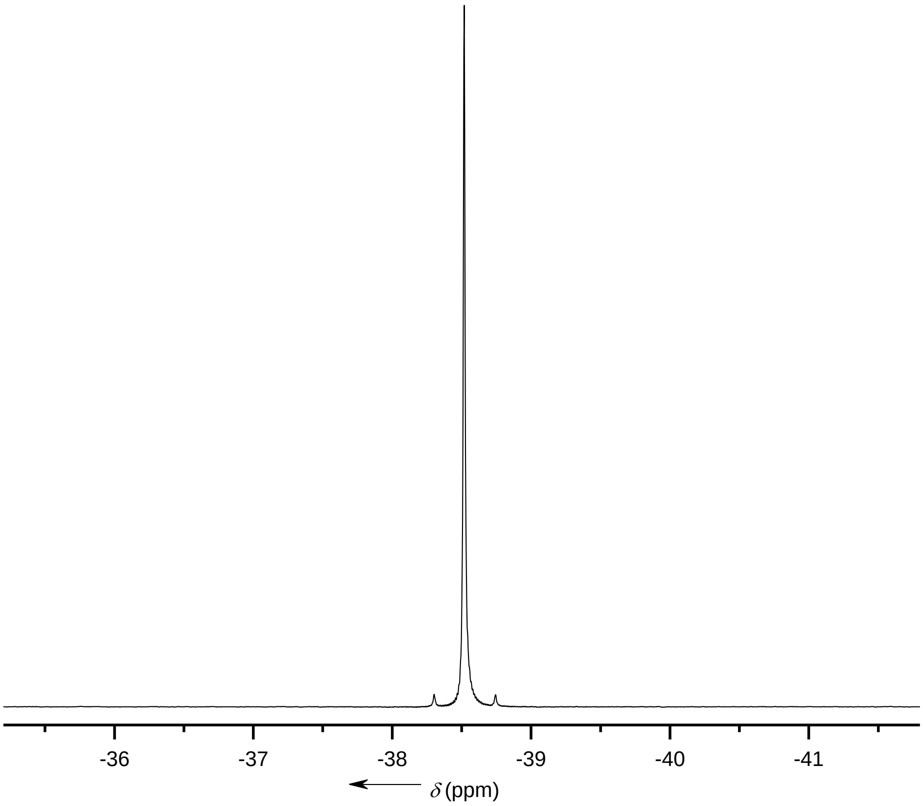


**Figure S99: $^{11}B$ NNR of [$BnPh_3P$][$B(CN)_4$].**

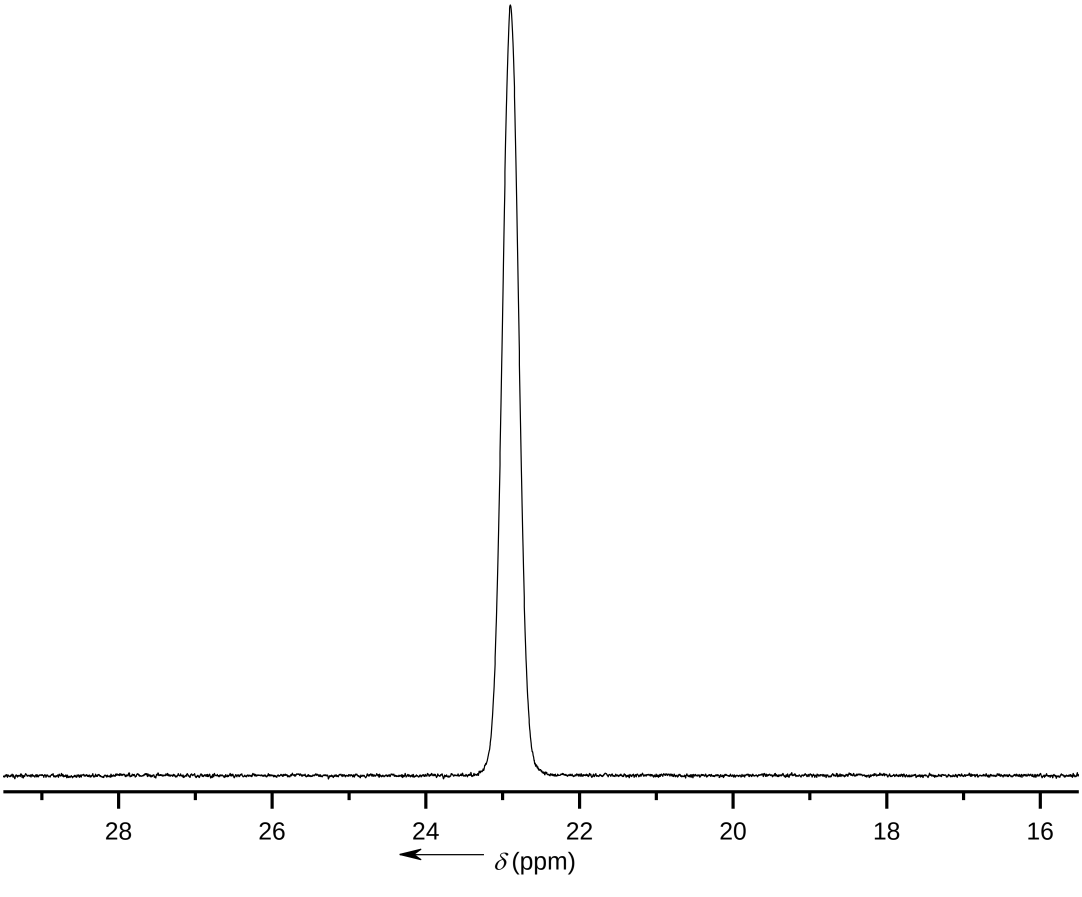


**Figure S100: $^{31}P$ NMR spectrum of [$BnPh_3P$][$B(CN)_4$].**

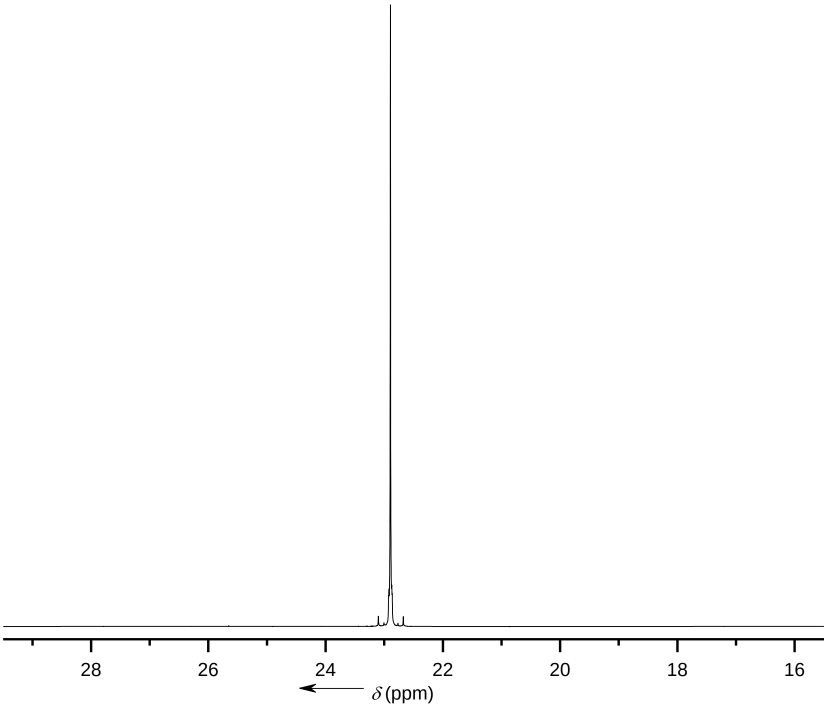


Figure S101: $^{31}P\{^1H\}$ NMR spectrum of $[BnPh_3P][B(CN)_4]$.

### 5.3.6 $[BnPh_3P][BFH(CN)_2]$

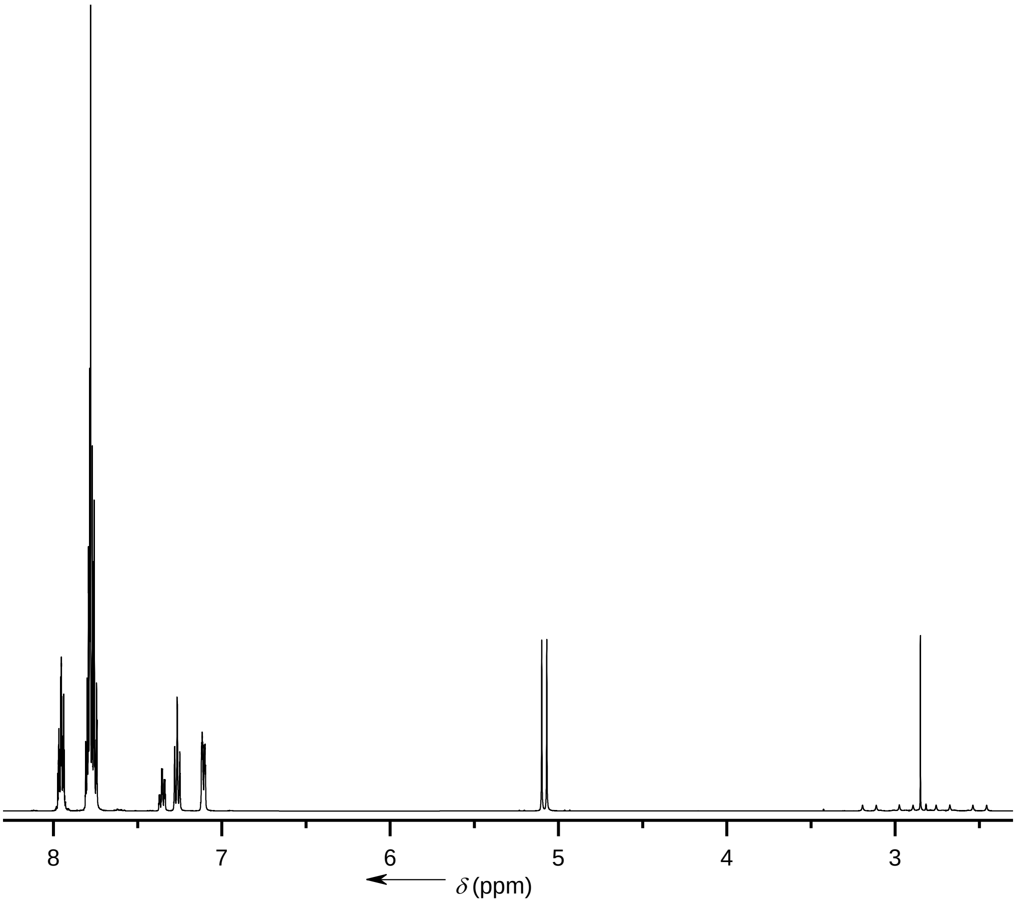


Figure S102: $^1H$ NMR spectrum of $[BnPh_3P][BFH(CN)_2]$.

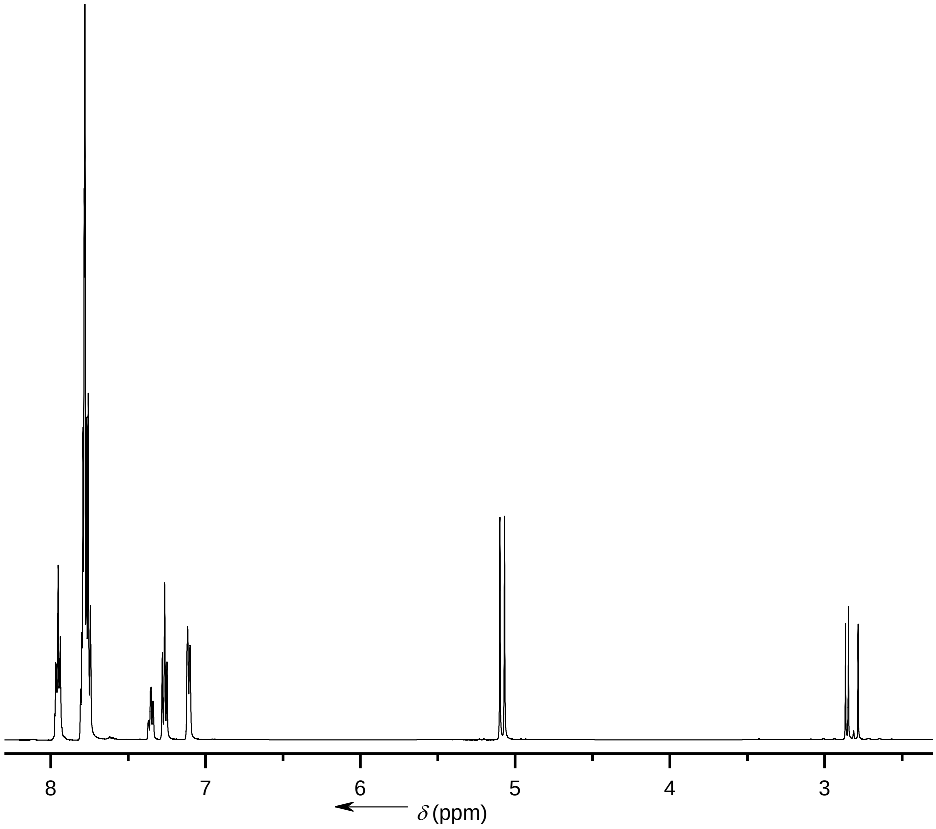


**Figure S103:** $^{1}H\{^{11}B\}$ **NMR spectrum of** $[BnPh_3P][BFH(CN)_2]$**.**

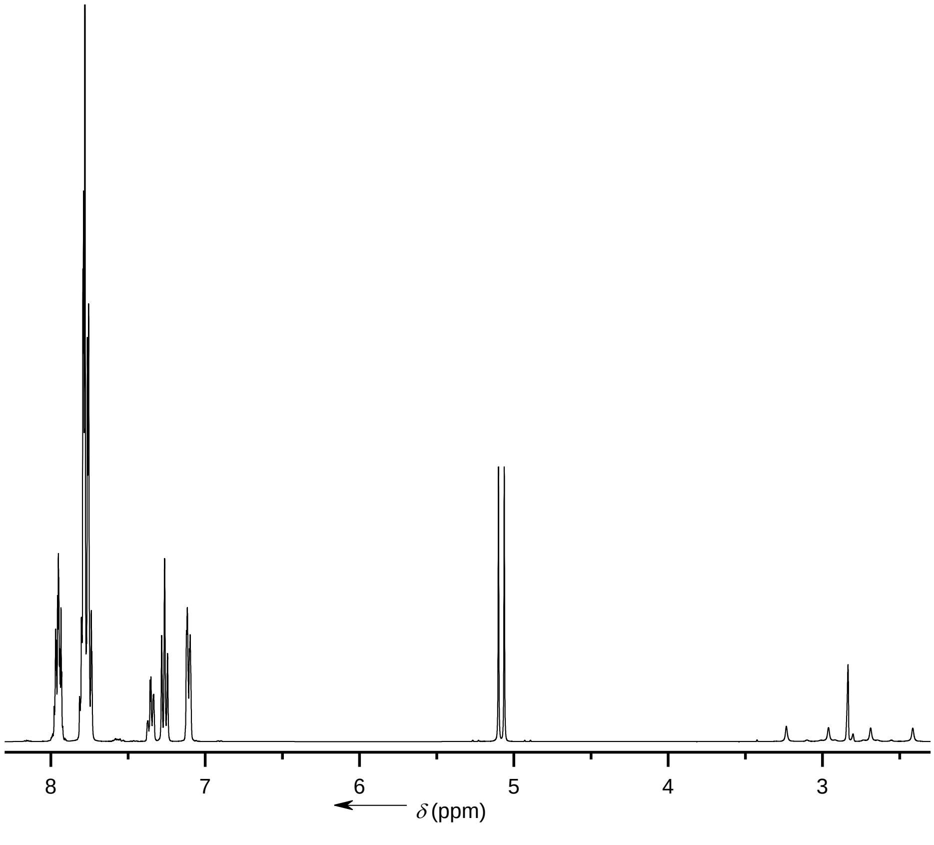


**Figure S104:** $^{1}H\{^{19}F\}$ **NMR spectrum of** $[BnPh_3P][BFH(CN)_2]$**.**

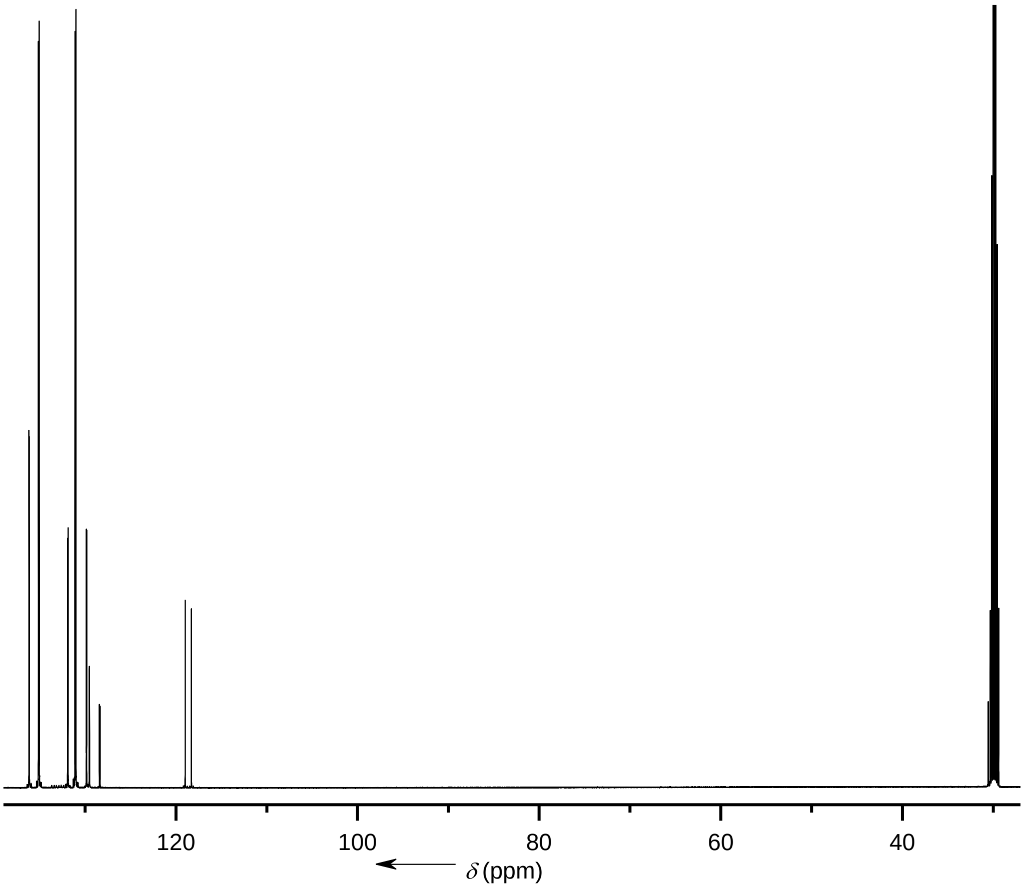


Figure S105: $^{13}C\{^{1}H\}$ NMR spectrum of $[BnPh_3P][BFH(CN)_2]$.

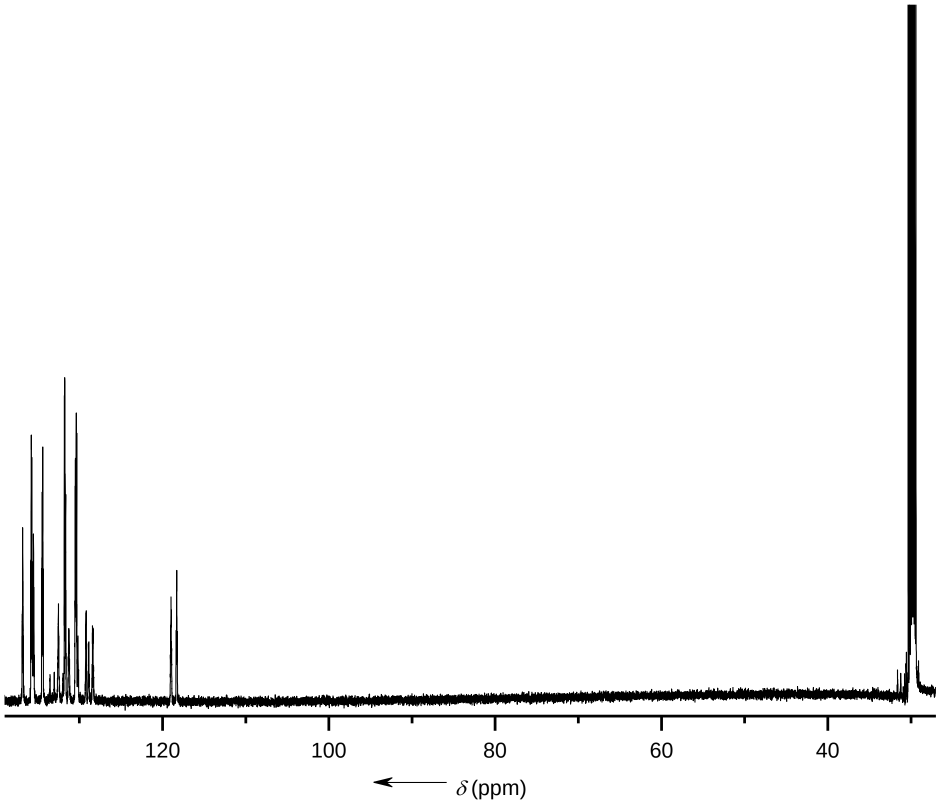


Figure S106: $^{13}C\{^{19}F\}$ NMR spectrum of [BnPh3P]$[BFH(CN)_2]$.

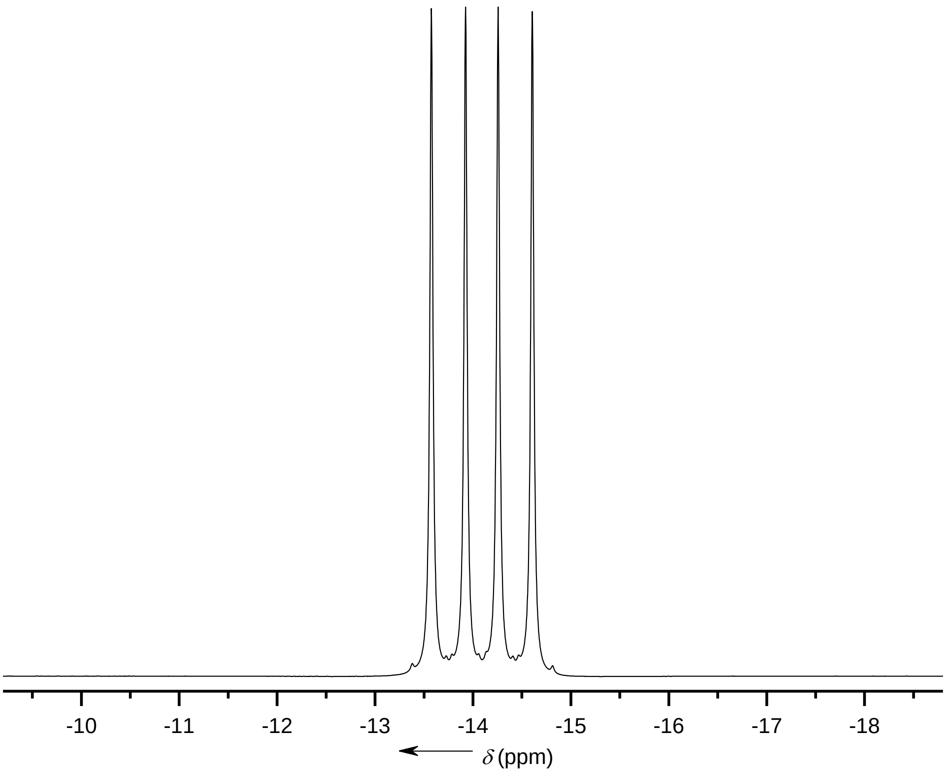


**Figure S107: $^{11}B$ NMR spectrum of [$BnPh_3P$][$BFH(CN)_2$].**

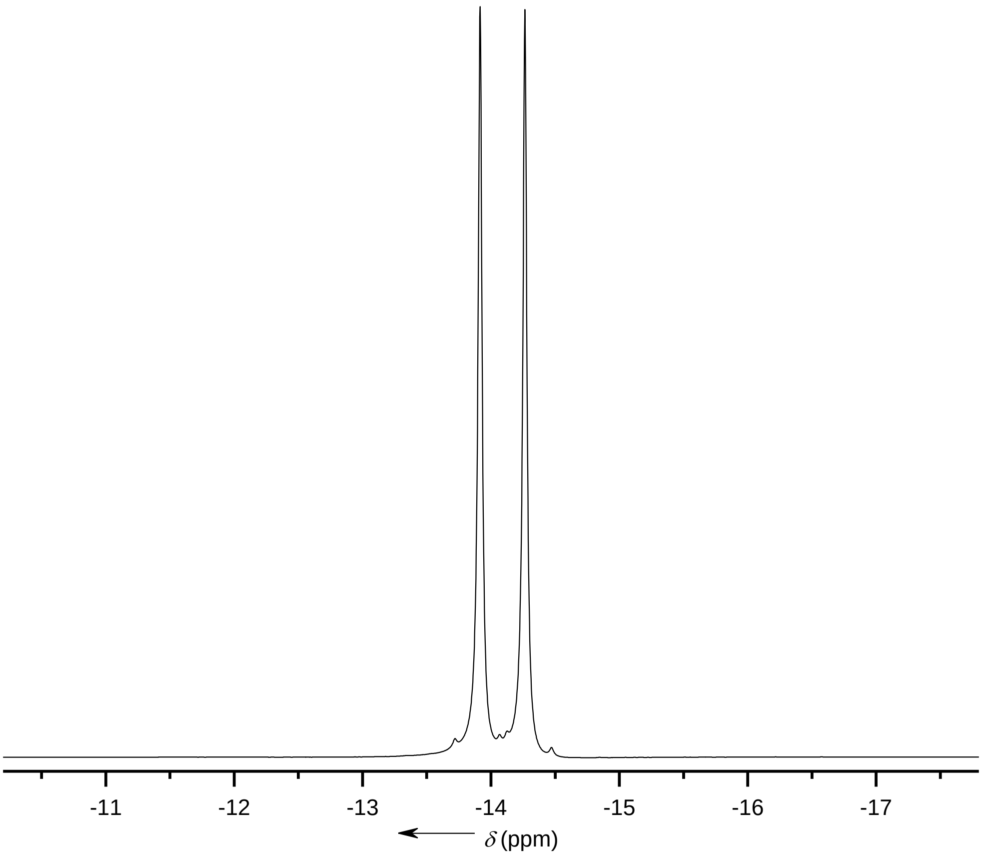


**Figure S108: $^{11}B\{^1H\}$ NMR spectrum of [$BnPh_3P$][$BFH(CN)_2$].**

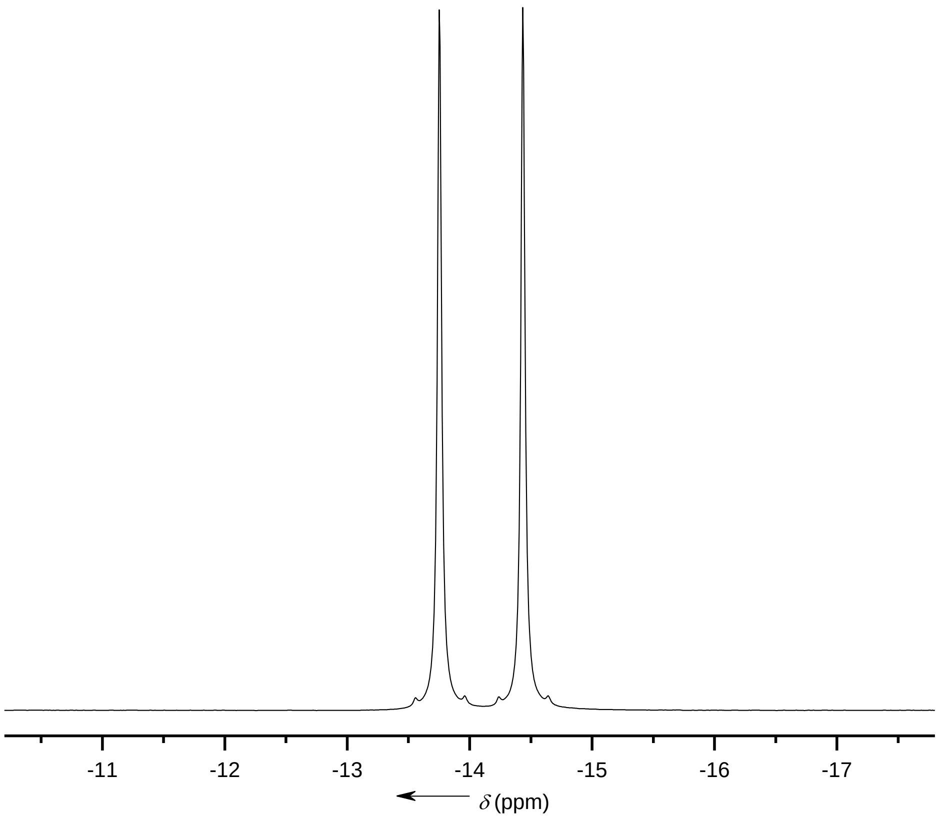


Figure S109: $^{11}B\{^{19}F\}$ NMR spectrum of $[BnPh_3P][BFH(CN)_2]$.

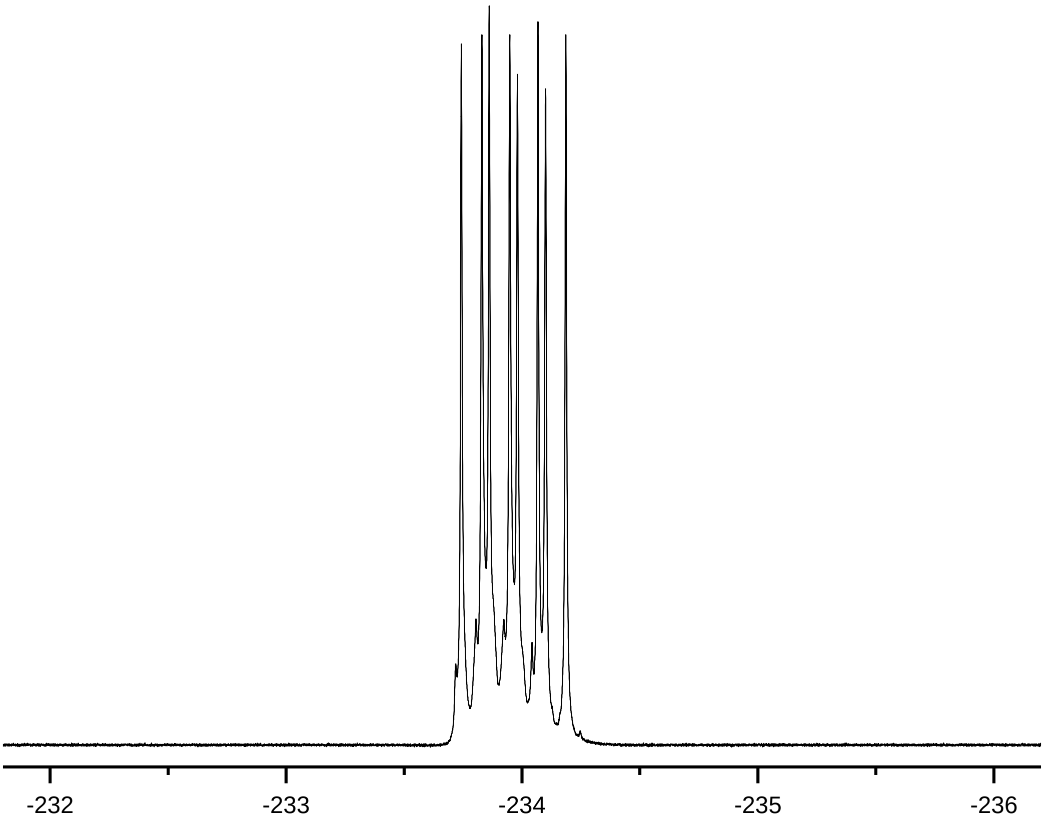


Figure S110: $^{19}F$ NMR spectrum of $[BnPh_3P][BFH(CN)_2]$.

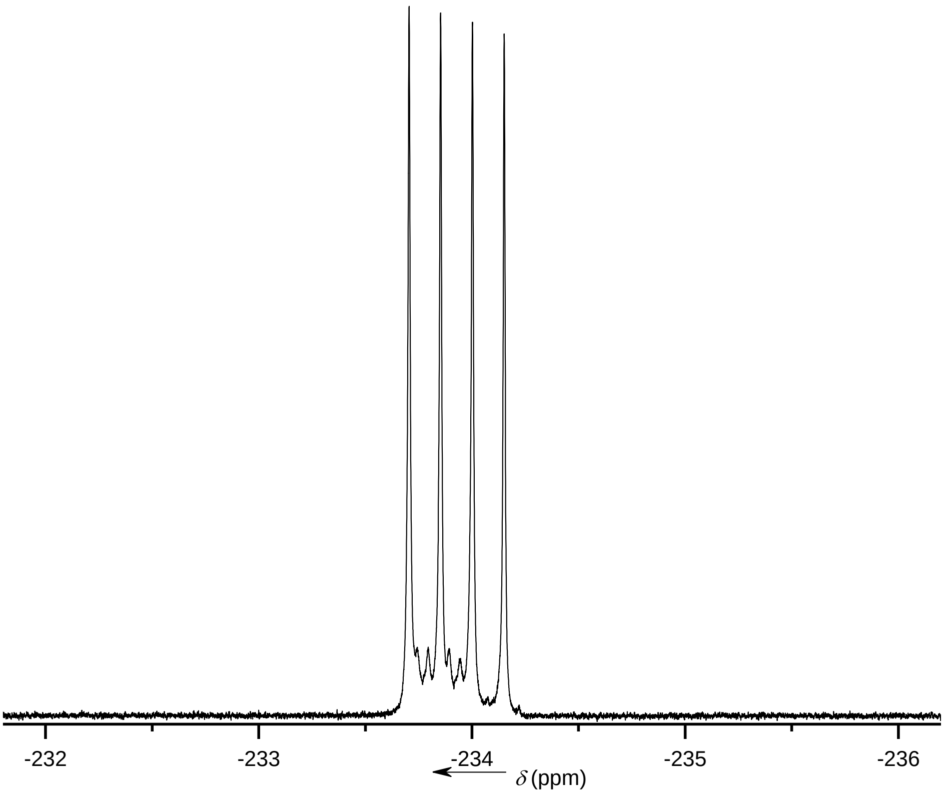


**Figure S111:** $^{19}F\{^1H\}$ **NMR spectrum of [BnPh$_3$P][BFH(CN)$_2$].**

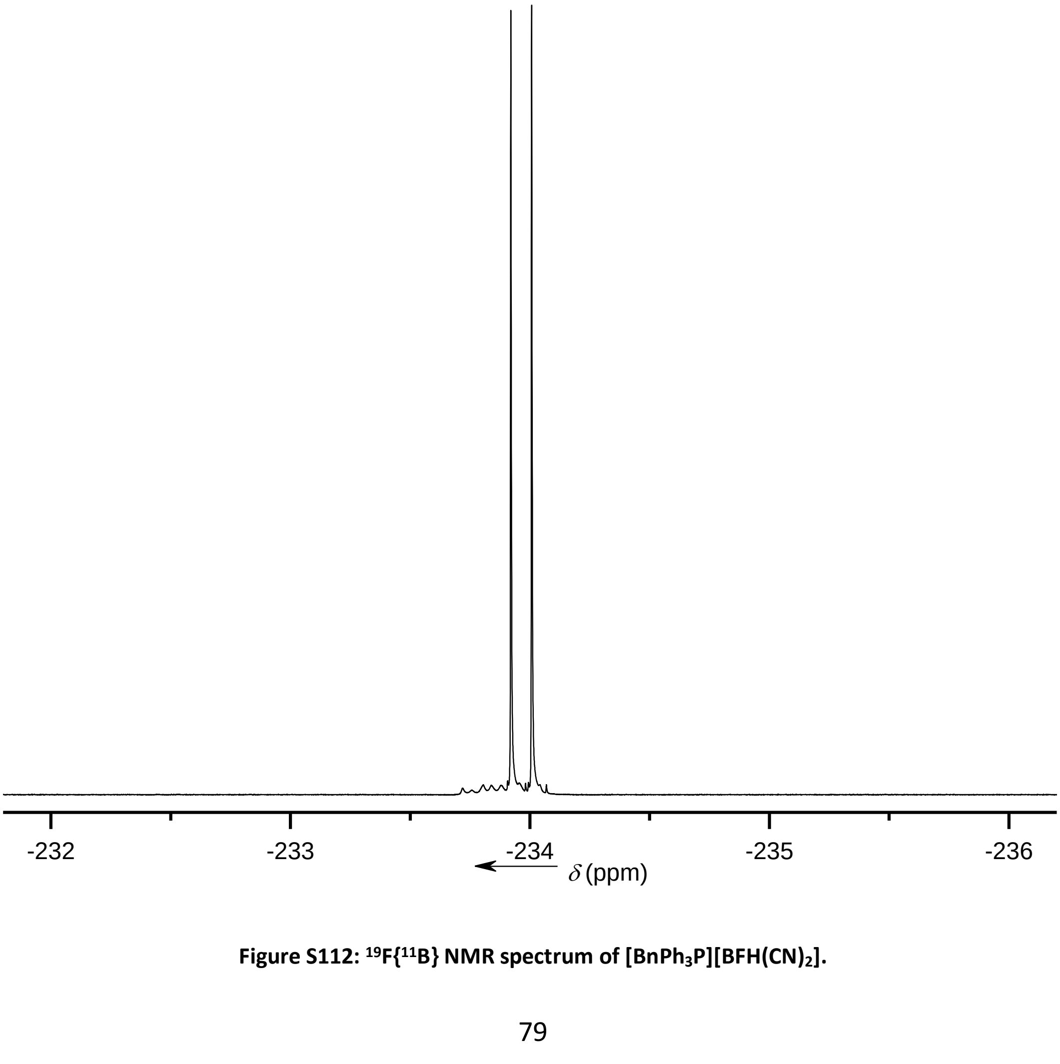


**Figure S112:** $^{19}F\{^{11}B\}$ **NMR spectrum of [BnPh$_3$P][BFH(CN)$_2$].**

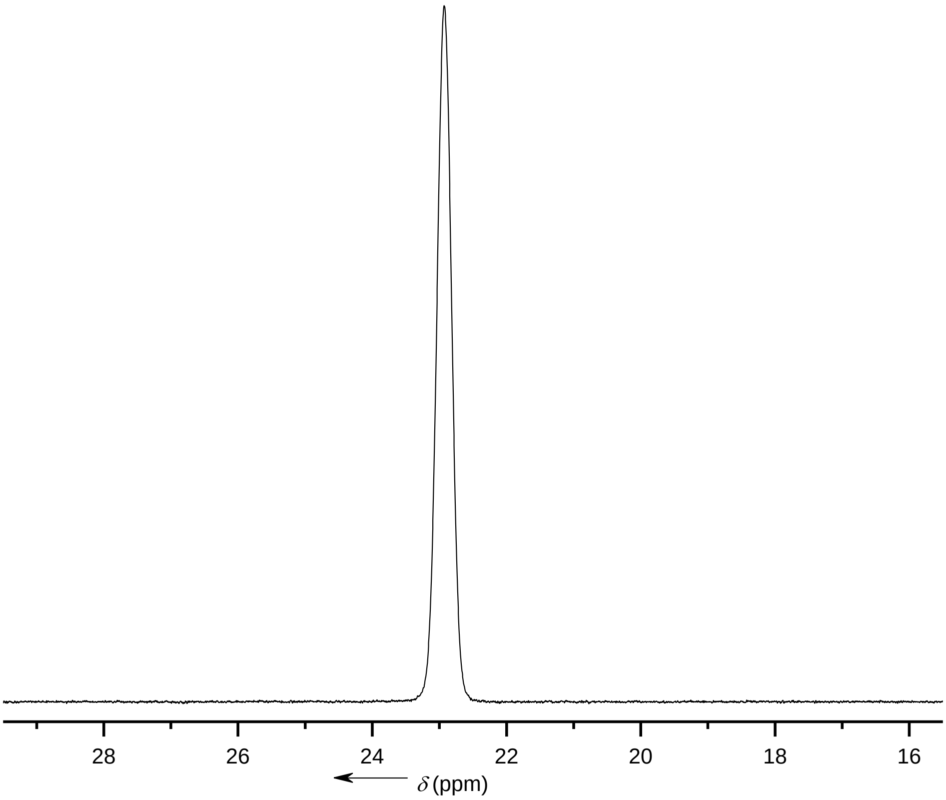


**Figure S113:** $^{31}$P NMR spectrum of [BnPh$_3$P][BFH(CN)$_2$].

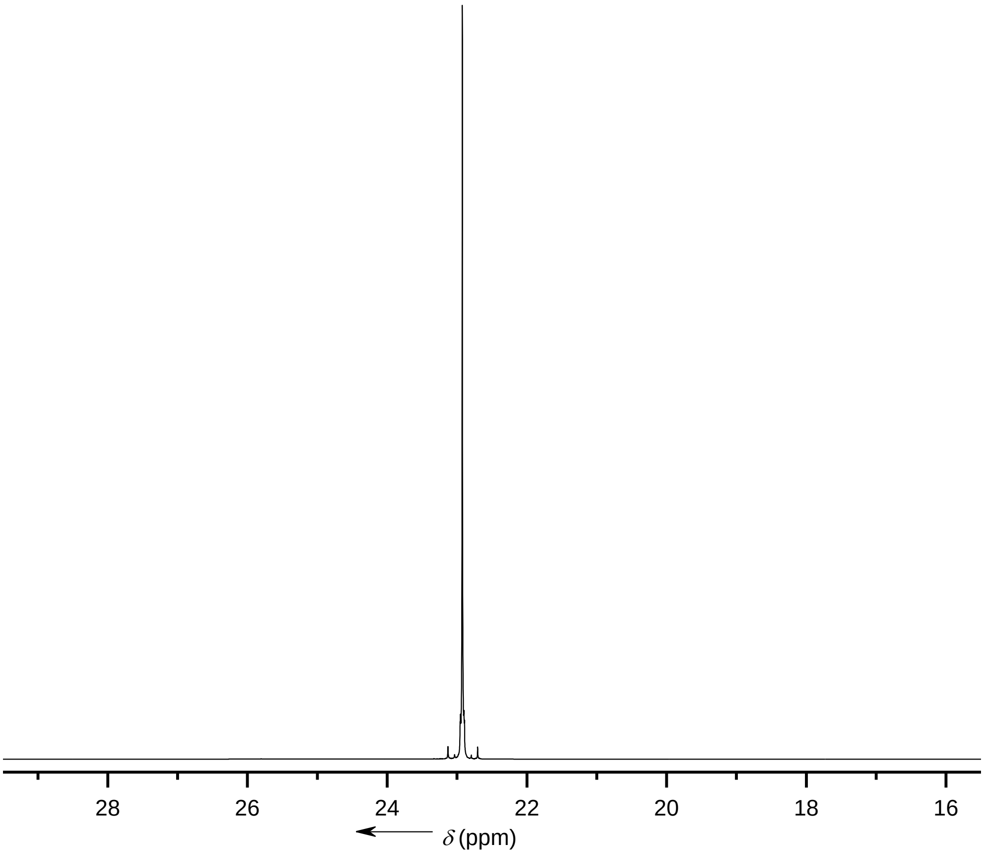


**Figure S114:** $^{31}$P{$^1$H} NMR spectrum of [BnPh$_3$P][BFH(CN)$_2$].

### 5.3.7 [$BnPh_3P$][$BH_3(CN)$]

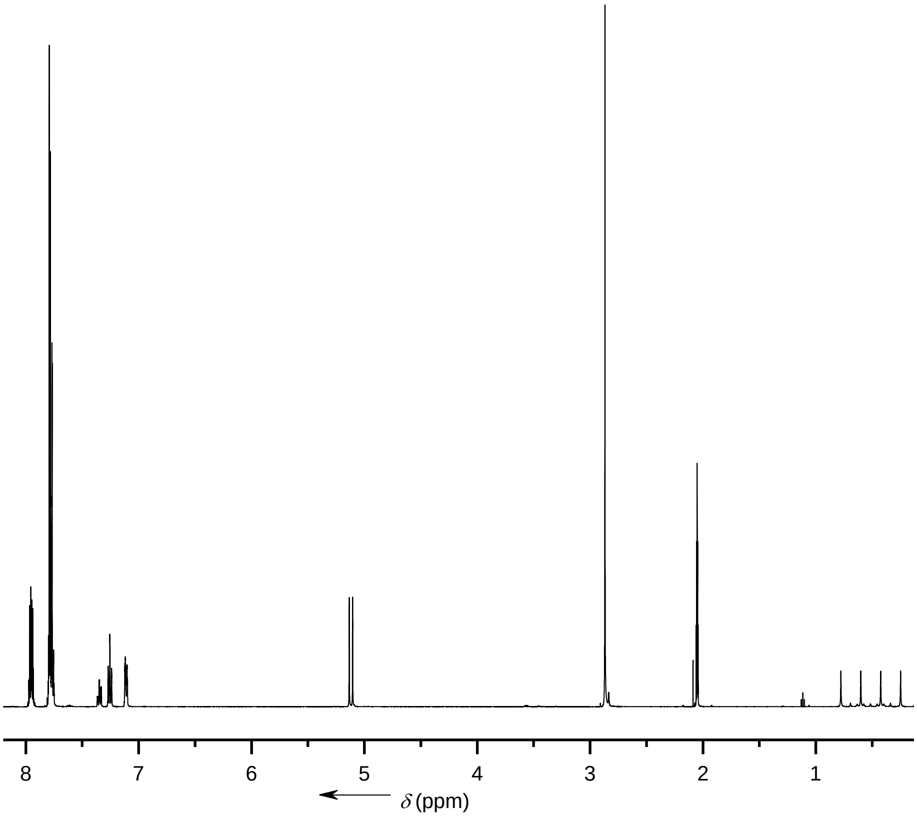


**Figure S115: $^1H$ NMR spectrum of [$BnPh_3P$][$BH_3(CN)$].**

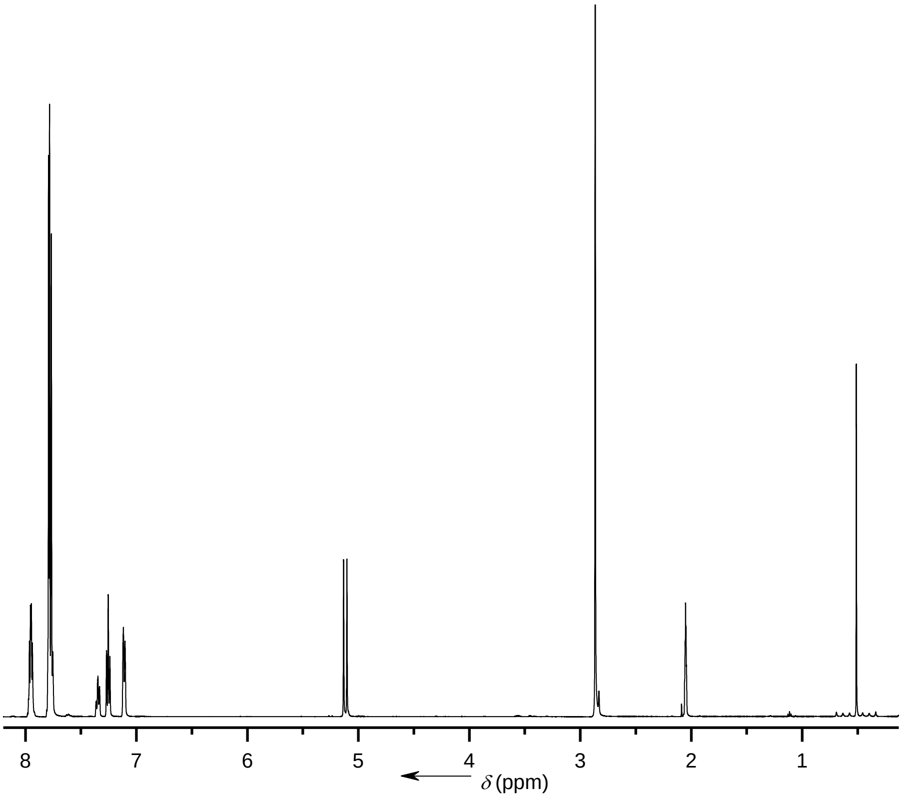


**Figure S116: $^1H\{^{11}B\}$ NMR spectrum of [$BnPh_3P$][$BH_3(CN)$].**

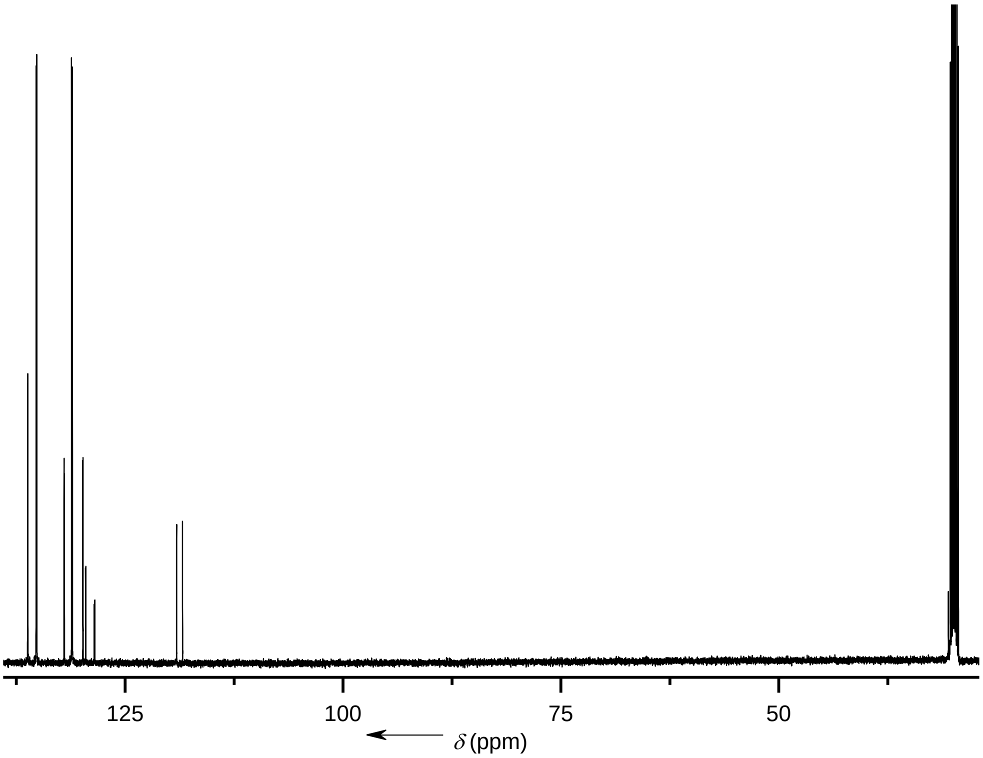


**Figure S117: $^{13}C\{^{1}H\}$ NMR spectrum of $[BnPh_3P][BH_3(CN)]$.**

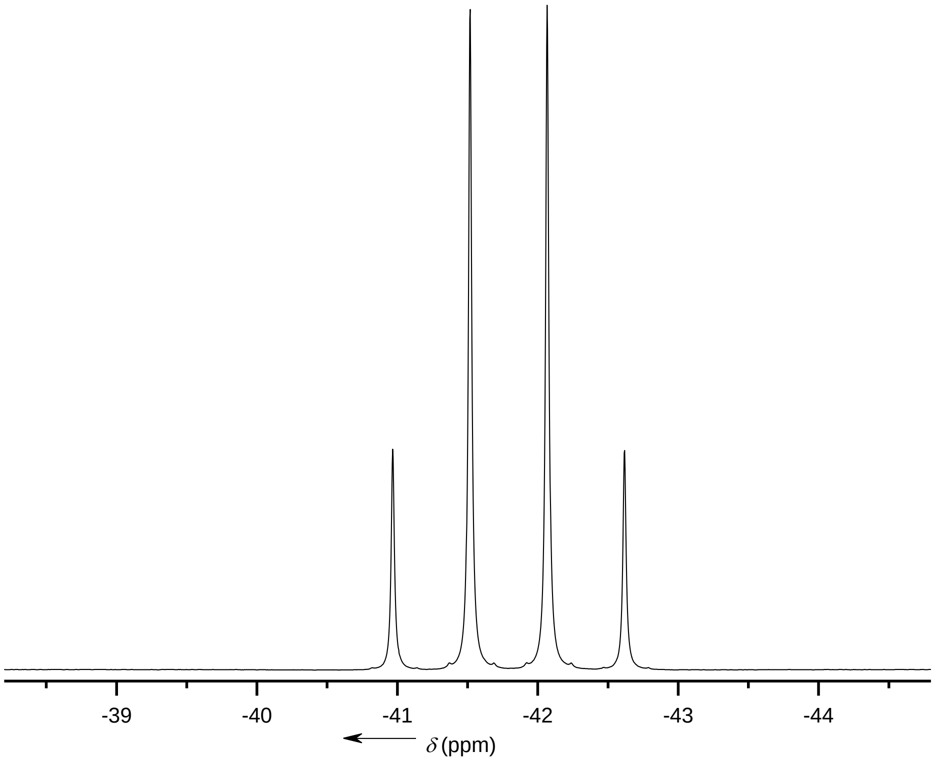


**Figure S118: $^{11}B$ NMR spectrum of $[BnPh_3P][BH_3(CN)]$.**

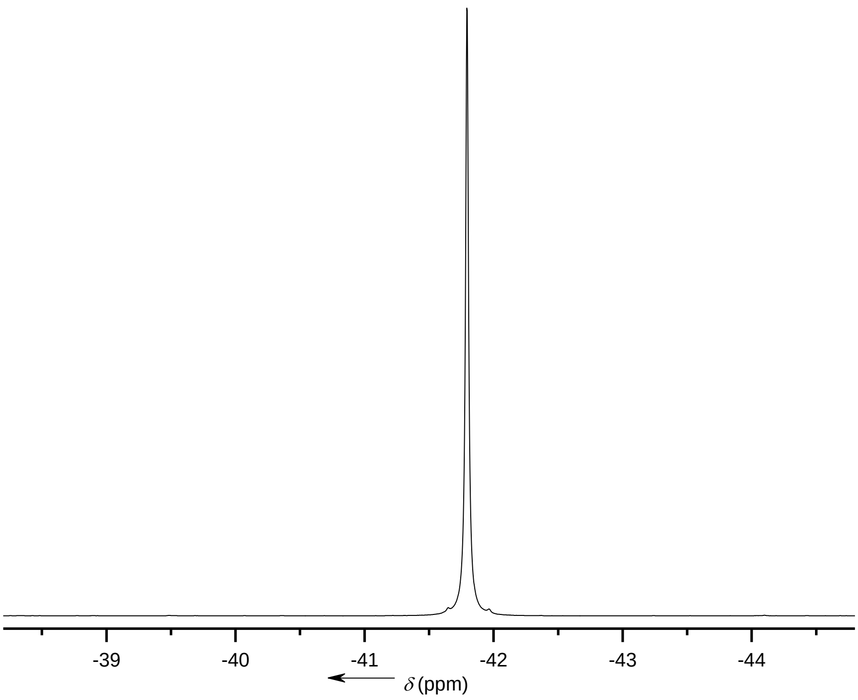


**Figure S119: $^{11}B\{^1H\}$ NMR spectrum of [BnPh$_3$P][BH$_3$(CN)].**

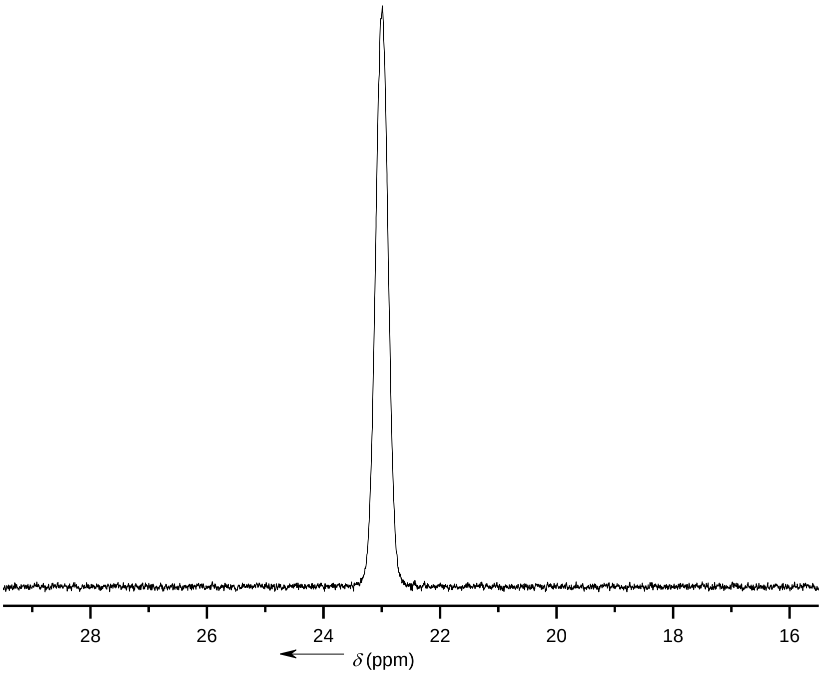


**Figure S120: $^{31}P$ NMR spectrum of [BnPh$_3$P][BH$_3$(CN)].**

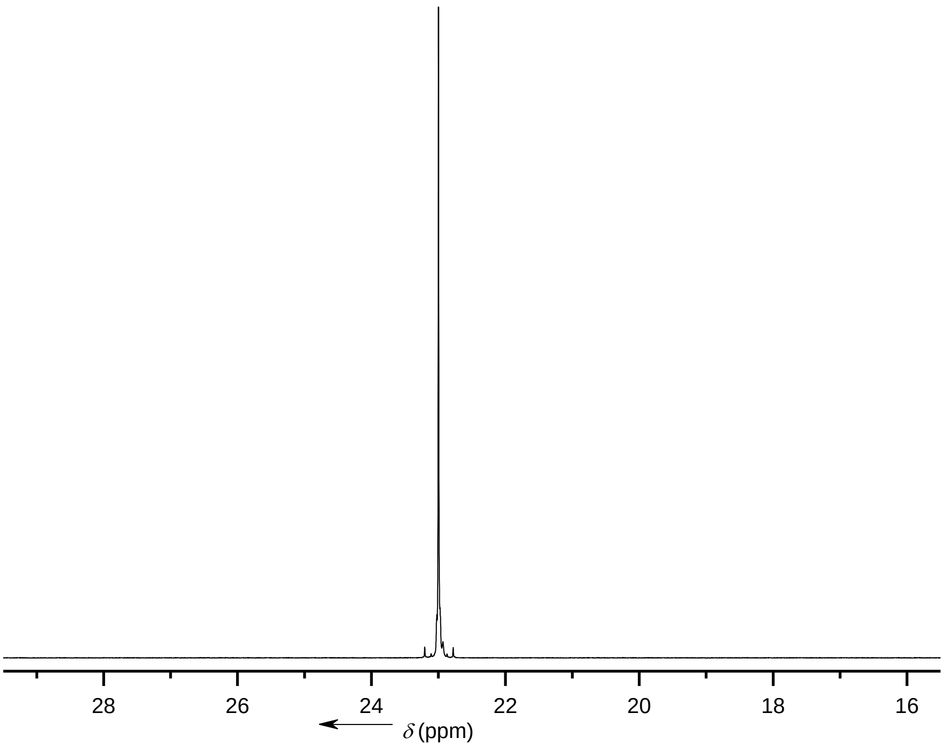


Figure S121: $^{31}P\{^1H\}$ NMR spectrum of $[BnPh_3P][BH_3(CN)]$.

## 5.3.8 $[BnPh_3P][BH_2(CN)_2]$

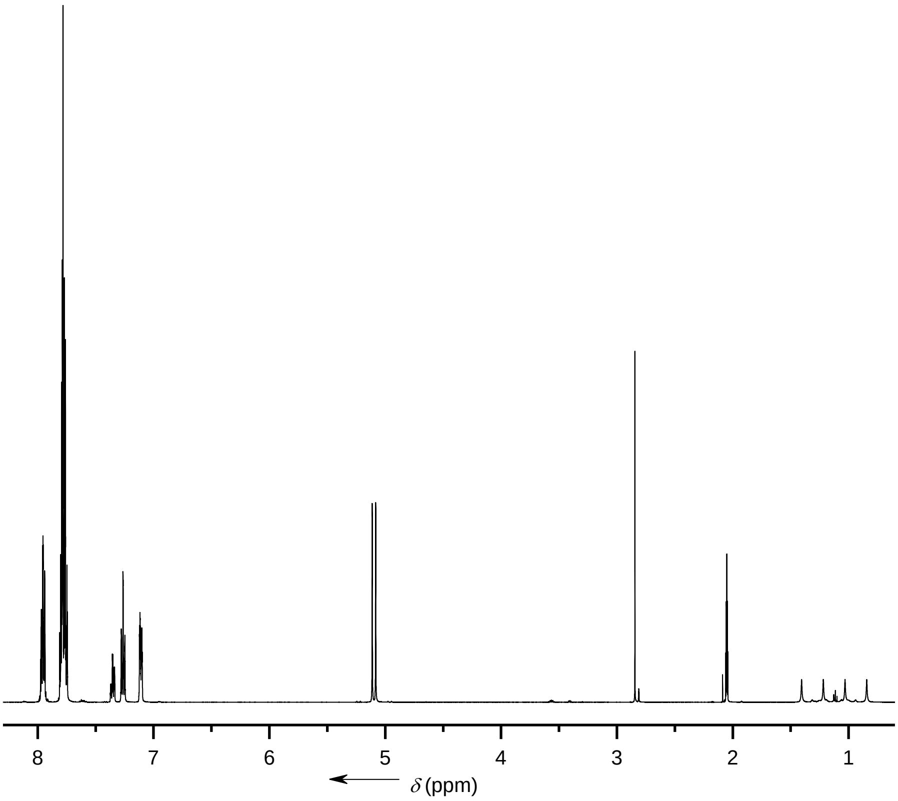


Figure S122: $^1H$ NMR spectrum of $[BnPh_3P][BH_2(CN)_2]$.

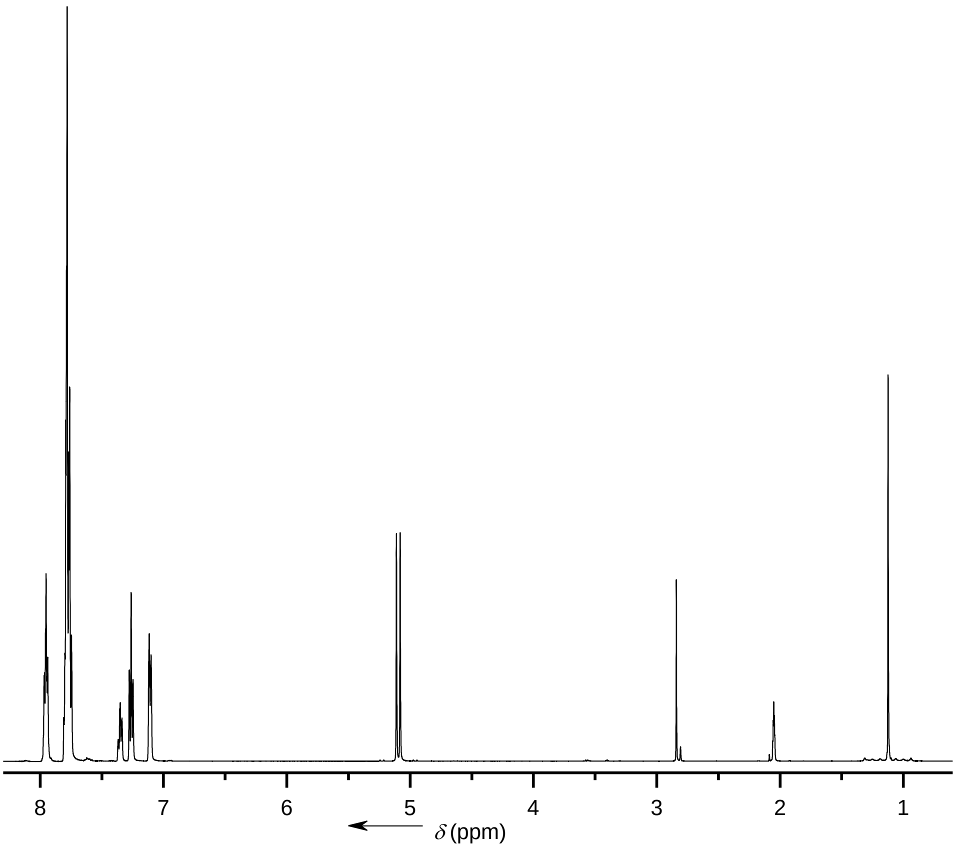


Figure S123: $^{1}H\{^{11}B\}$ NMR spectrum of $[BnPh_3P][BH_2(CN)_2]$.

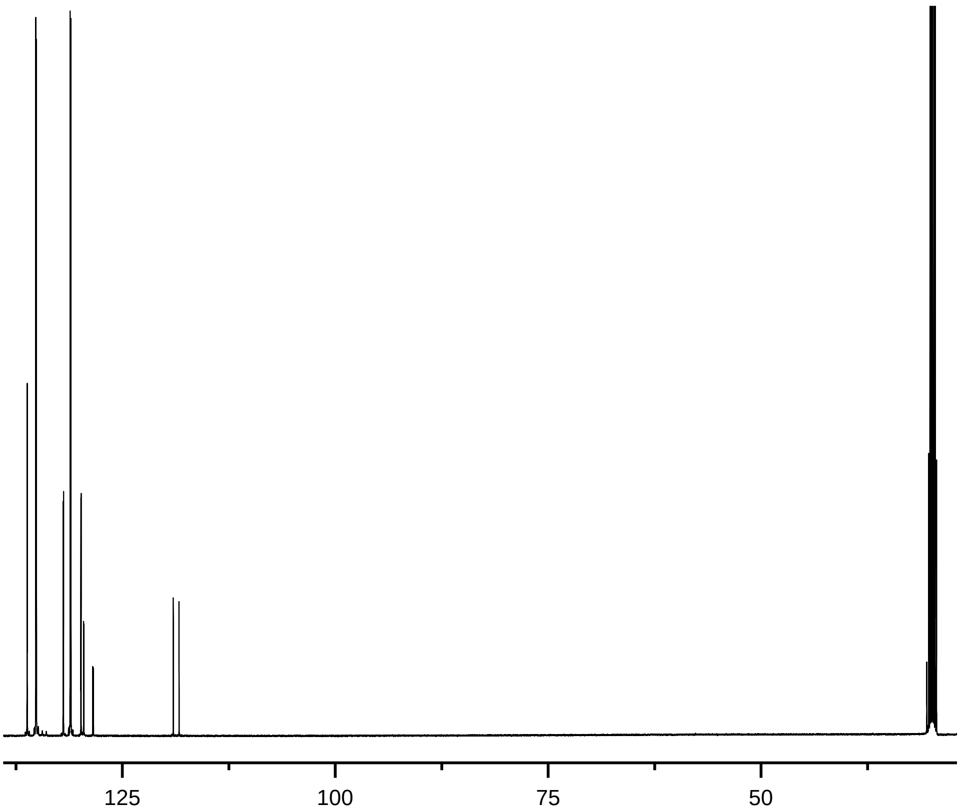


Figure S124: $^{13}C\{^{1}H\}$ NMR spectrum of $[BnPh_3P][BH_2(CN)_2]$.

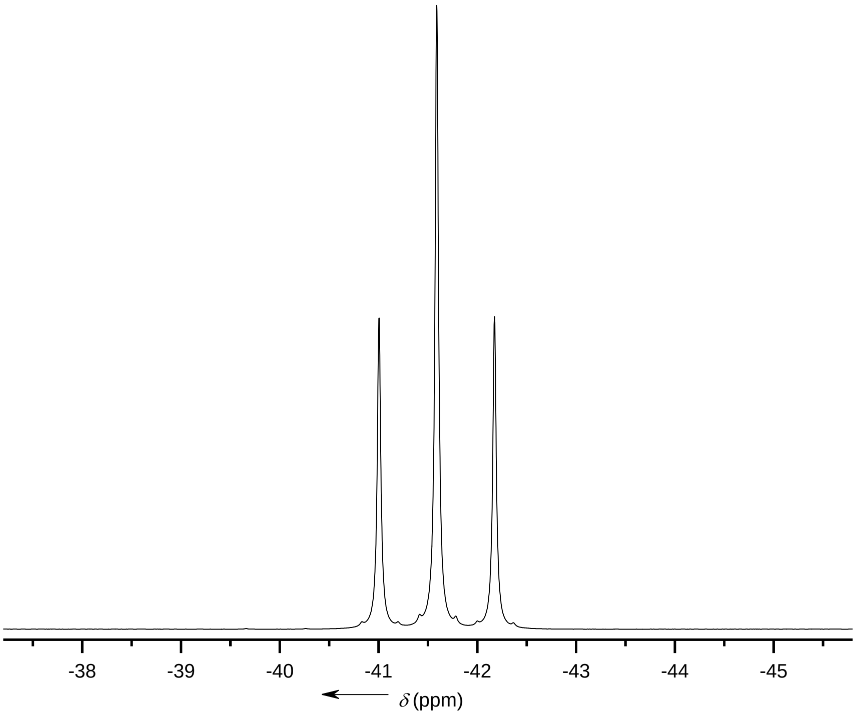


**Figure S125: $^{11}$B NMR spectrum of [BnPh$_3$P][BH$_2$(CN)$_2$].**

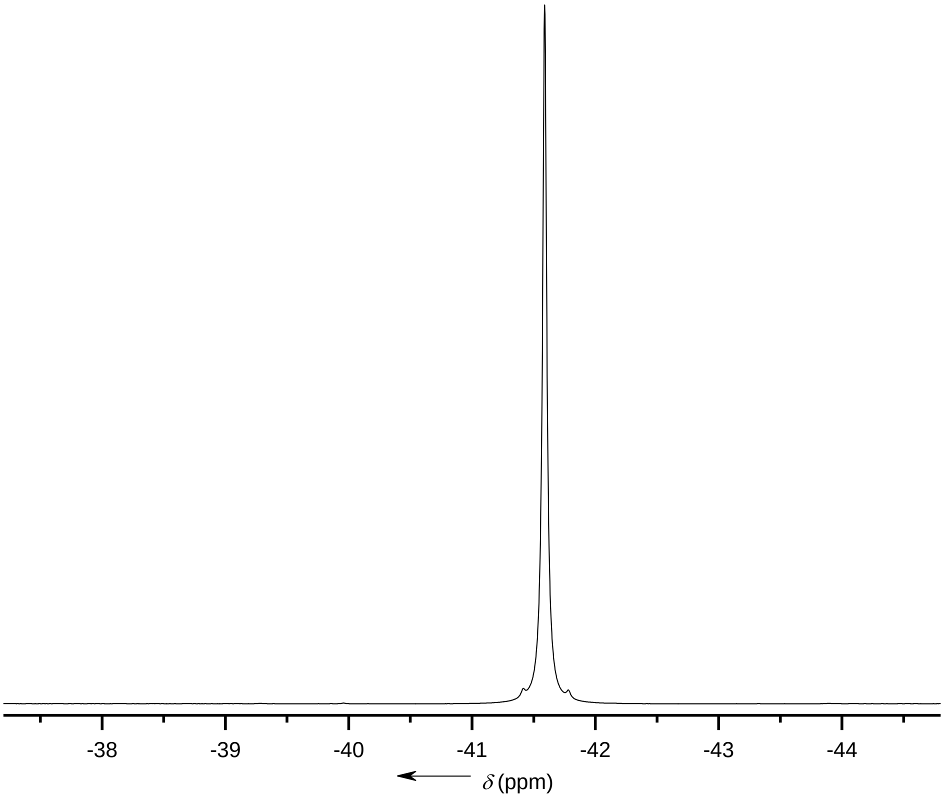


**Figure S126:$^{11}$B{$^1$H} NMR spectrum of [BnPh$_3$P][BH$_2$(CN)$_2$].**

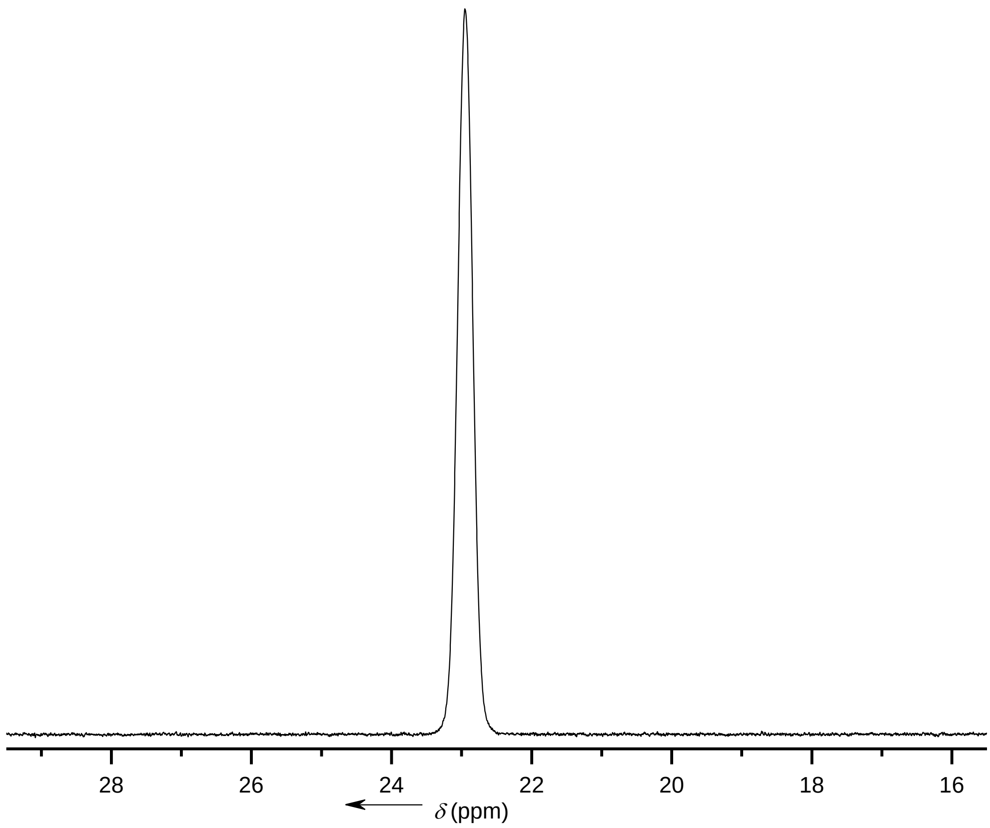


**Figure S127: $^{31}$P NMR spectrum of [BnPh$_3$P][BH$_2$(CN)$_2$].**

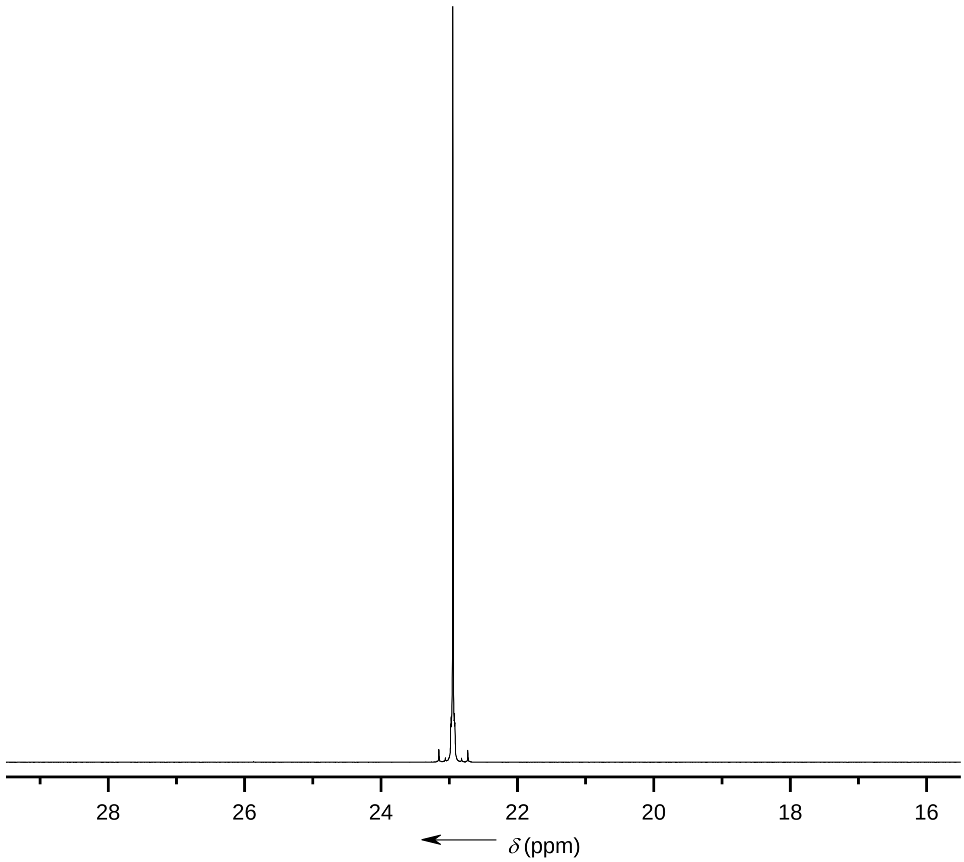


**Figure S128: $^{31}$P{$^1$H} NMR spectrum of [BnPh$_3$P][BH$_2$(CN)$_2$].**

## 5.3.9 [BnPh$_3$P][BH(CN)$_3$]

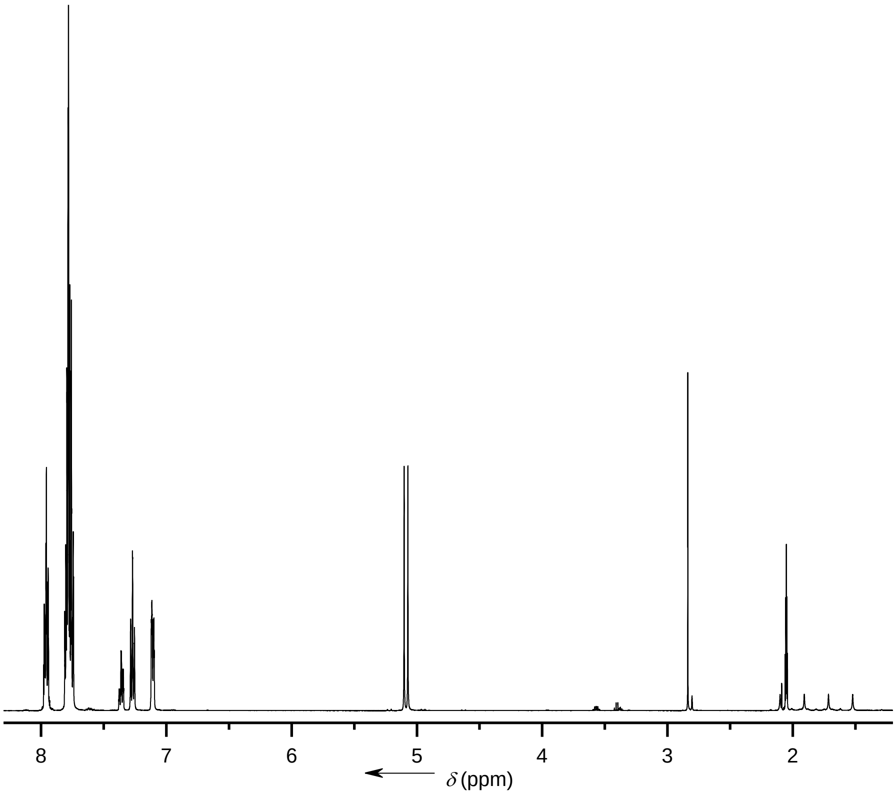


**Figure S129: $^1$H NMR spectrum of [BnPh$_3$P][BH(CN)$_3$].**

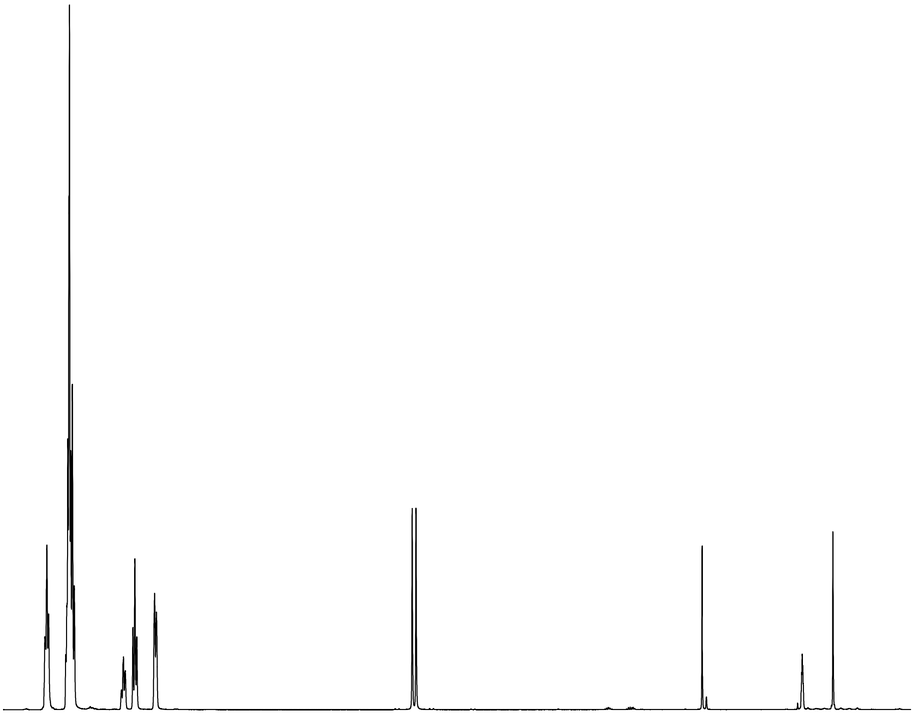


**Figure S130: $^1$H{$^{11}$B} NMR spectrum of [BnPh$_3$P][BH(CN)$_3$].**

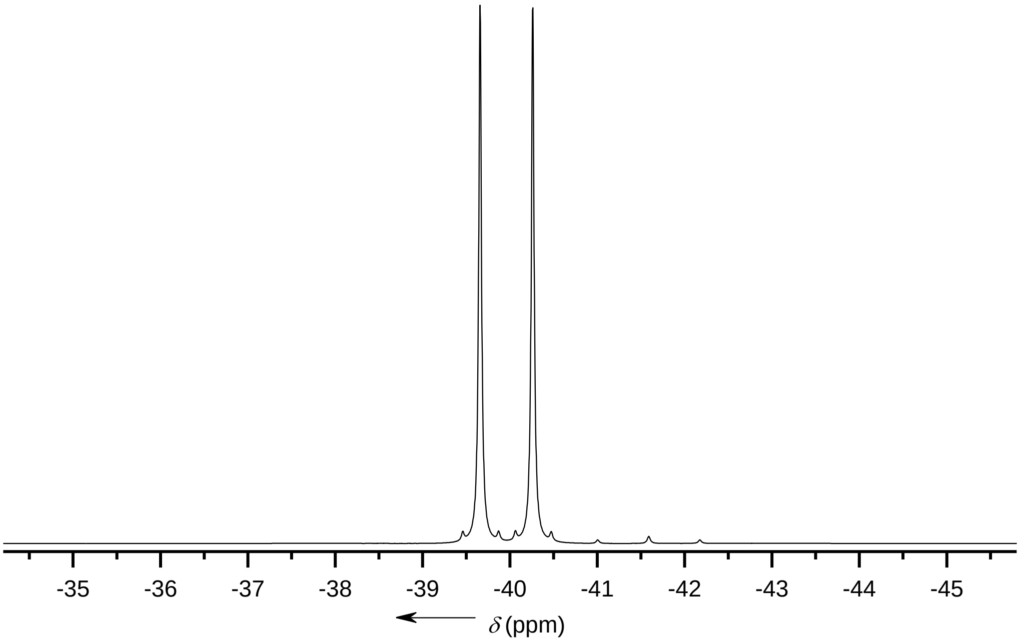


**Figure S131:** $^{11}$B NMR spectrum of [BnPh$_3$P][BH(CN)$_3$].

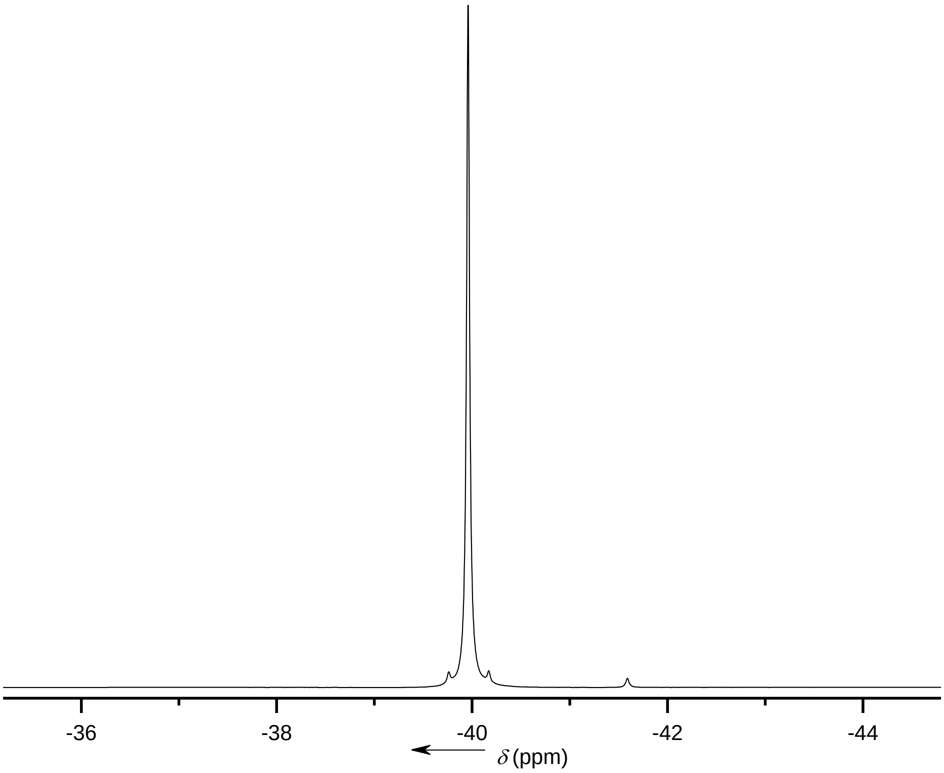


**Figure S132:** $^{11}$B{$^1$H} NMR spectrum of [BnPh$_3$P][BH(CN)$_3$].

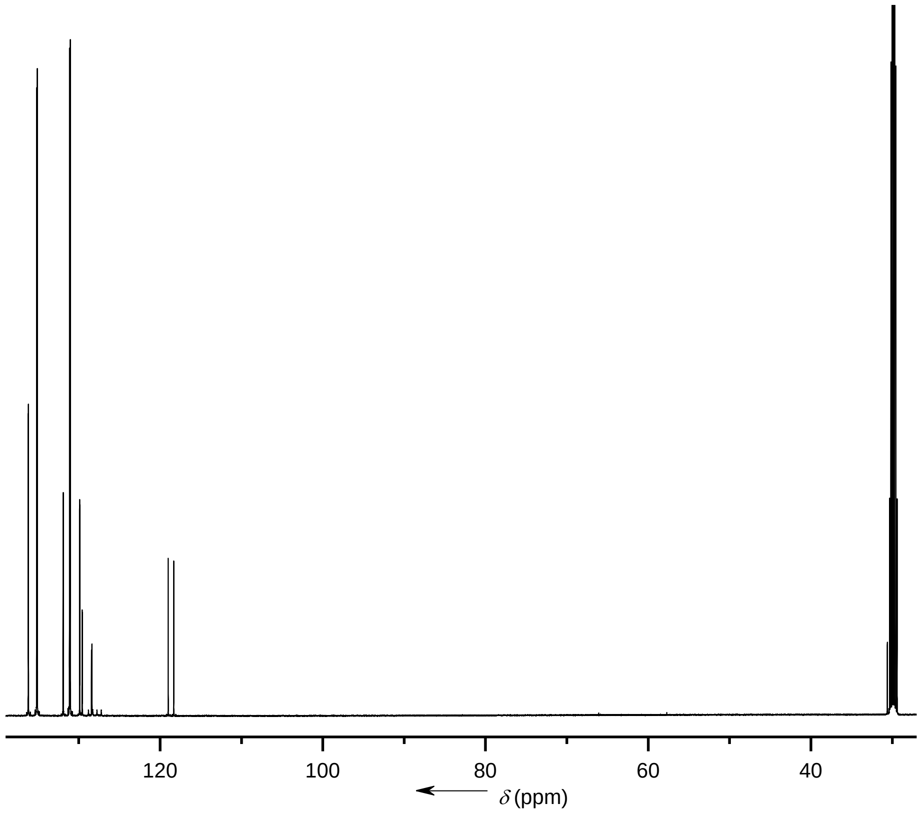


Figure S133: $^{13}C\{^{1}H\}$ NMR spectrum of $[BnPh_3P][BH(CN)_3]$.

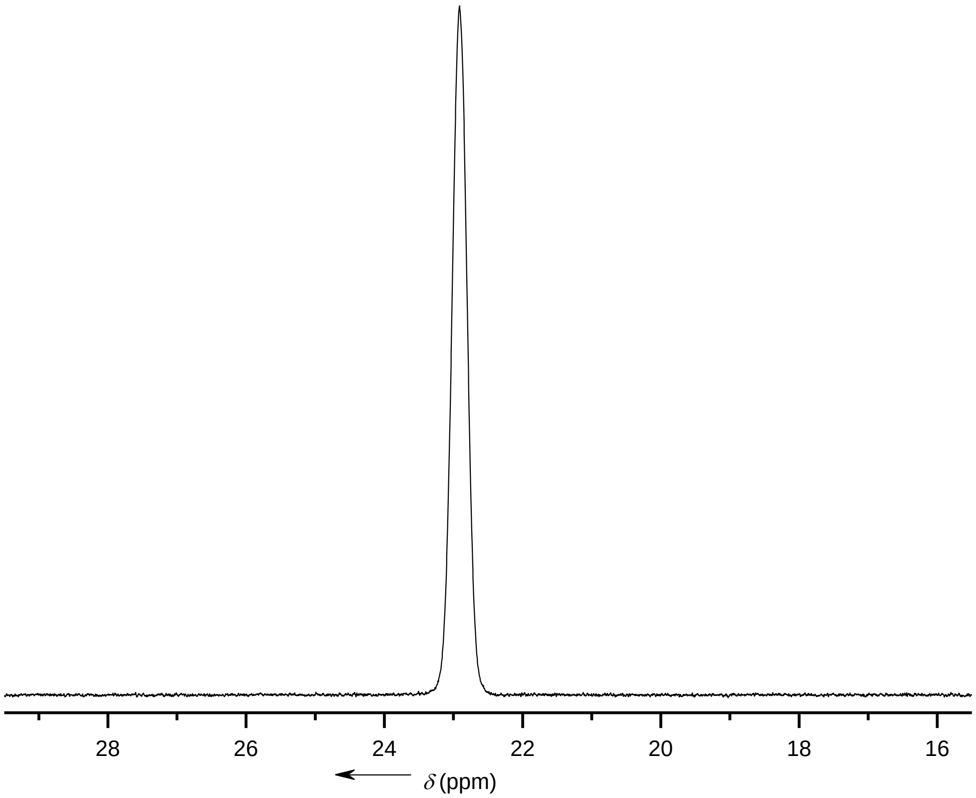


Figure S134: $^{31}P$ NMR spectrum of $[BnPh_3P][BH(CN)_3]$.

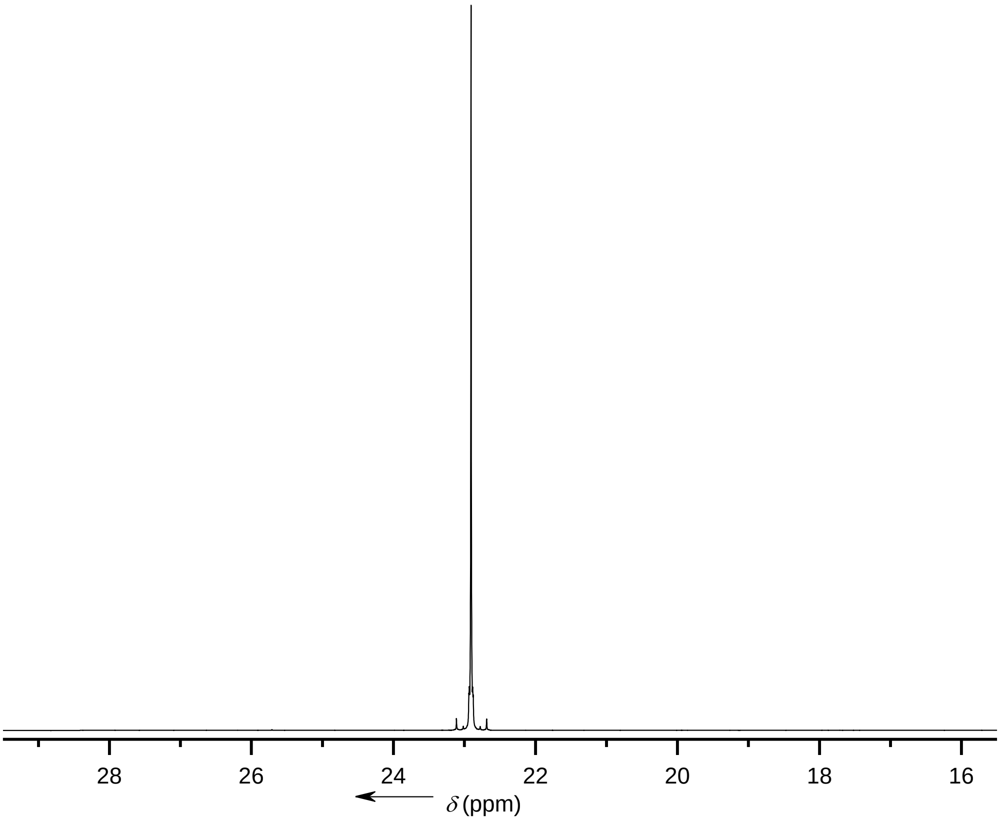


**Figure S135: $^{31}P\{^{1}H\}$ NMR spectrum of [BnPh$_3$P][BH(CN)$_3$].**

# 6 IR and Raman Spectra

## 6.1 [EMIm] salts

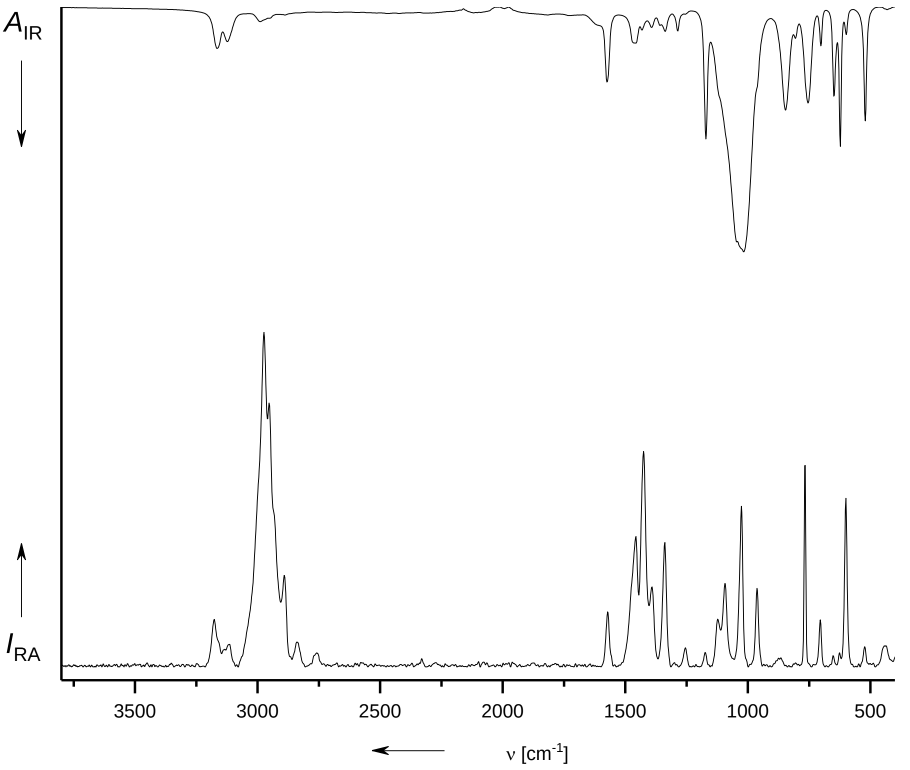


**Figure S136: IR and Raman spectra of [EMIm][BF$_4$].**

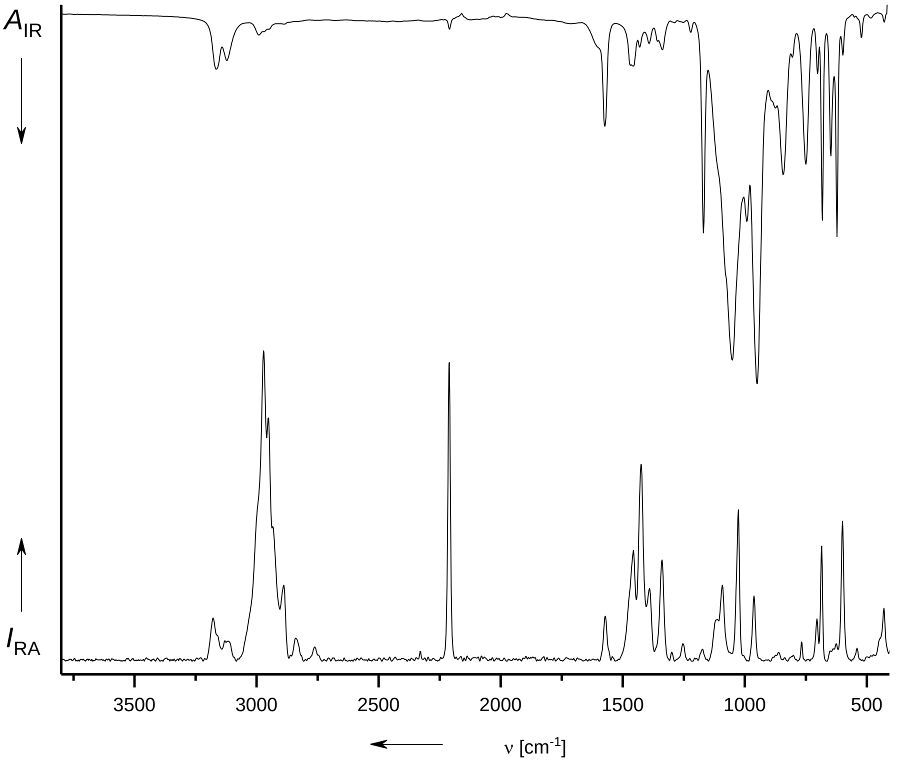


**Figure S137: IR and Raman spectra of [EMIm][BF$_3$(CN)].**

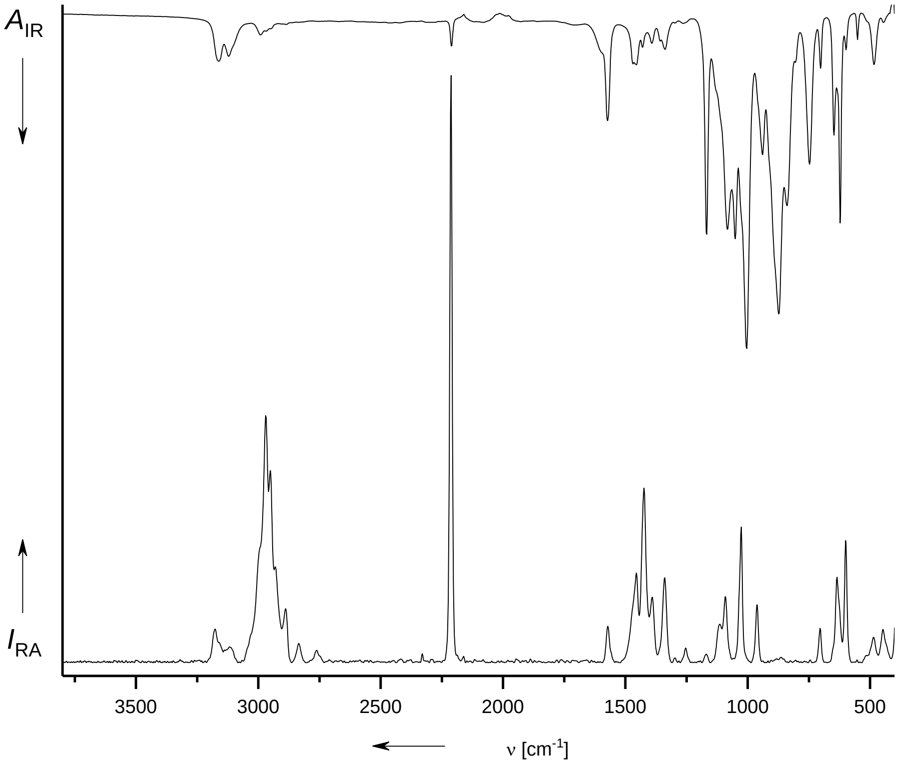


Figure S138: IR and Raman spectra of [EMIm][$BF_2(CN)_2$].

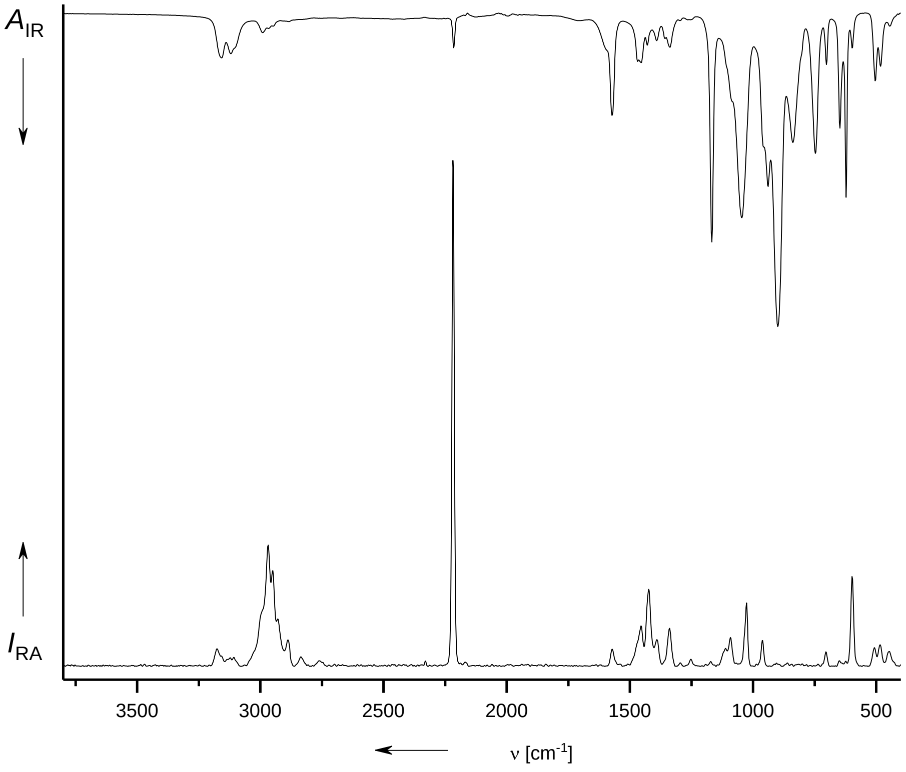


Figure S139: IR and Raman spectra of [EMIm][$BF(CN)_3$].

## 6.2 [BMPL] salts

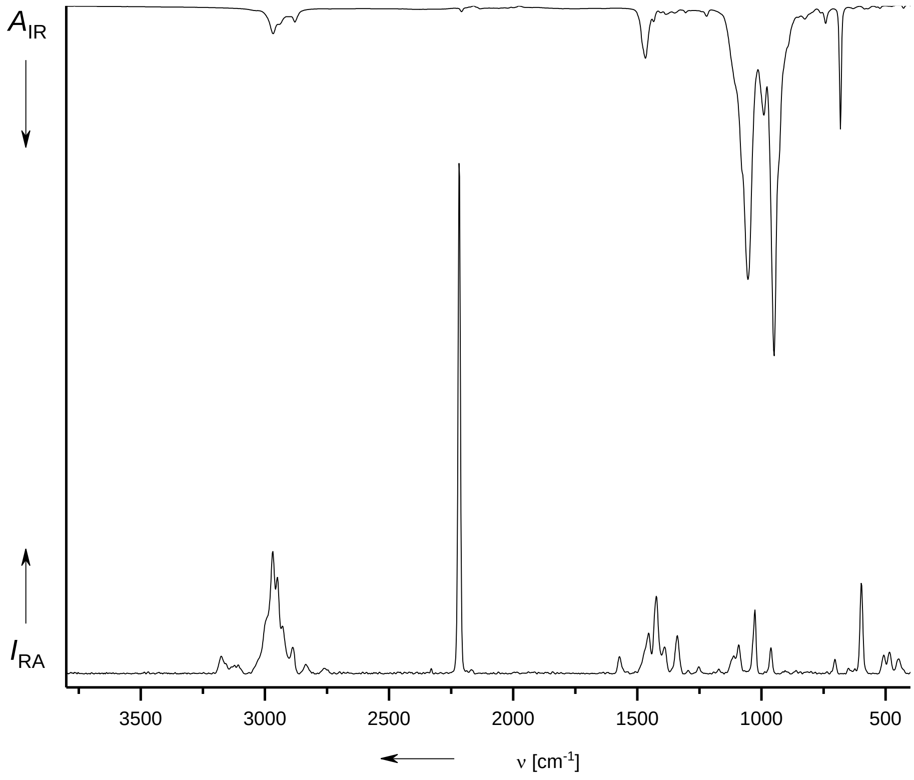


**Figure S140: IR and Raman spectra of [BMPL][$BF_3$(CN)].**

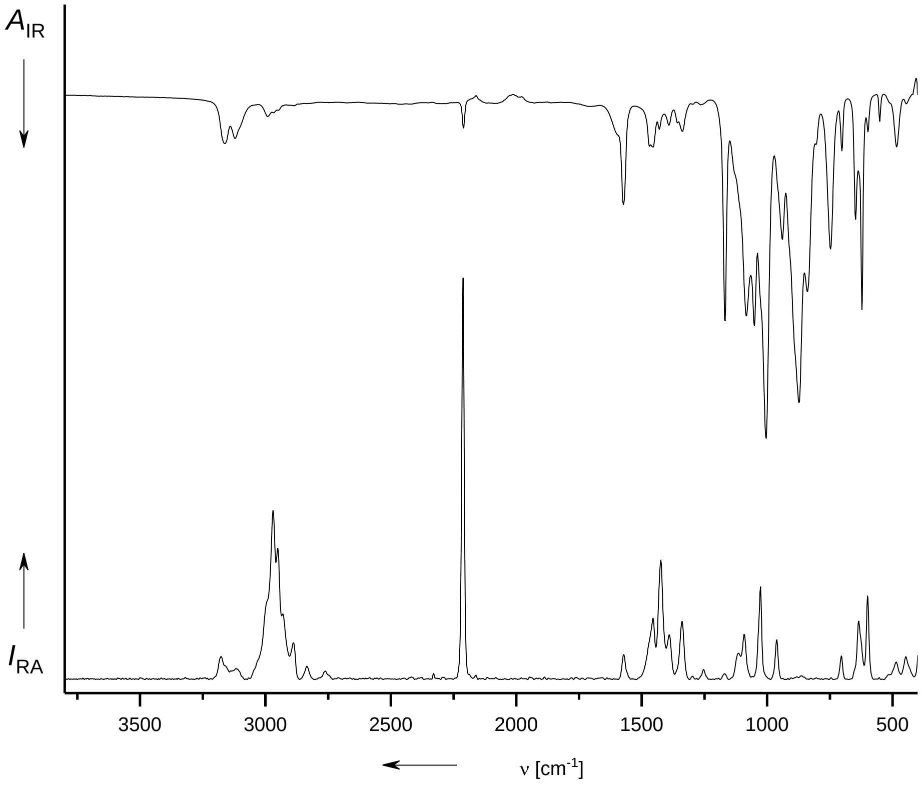


**Figure S141: IR and Raman spectra of [BMPL][$BF_2(CN)_2$].**

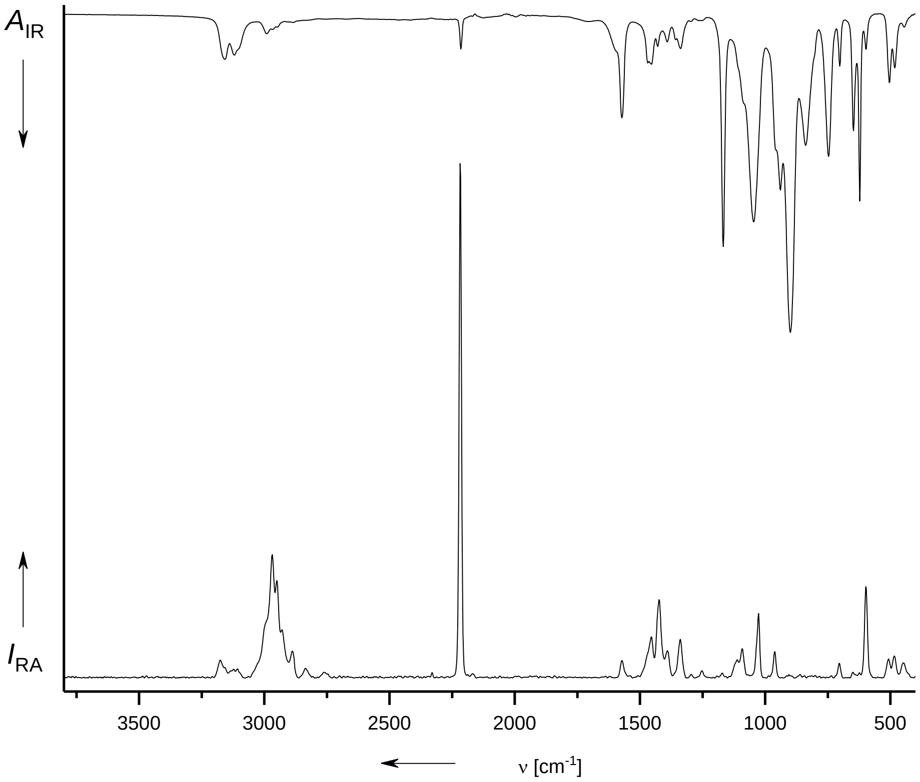


Figure S142: IR and Raman spectra of [BMPL][BF(CN)$_3$].

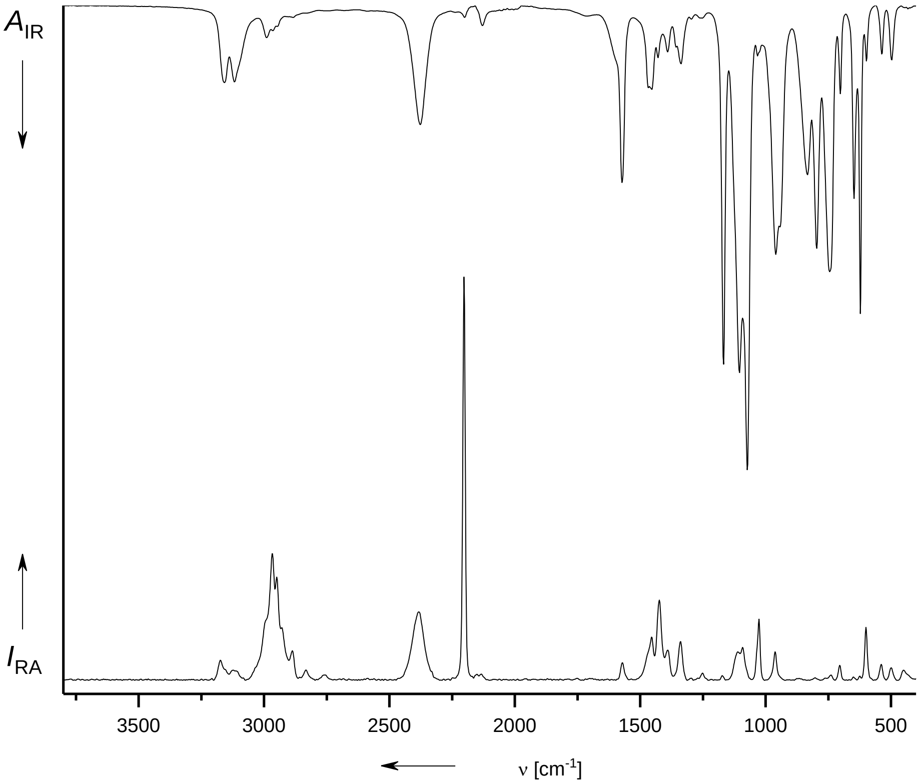


Figure S143: IR and Raman spectra of [BMPL][BFH(CN)$_2$].

## 6.3 Phosphonium salts

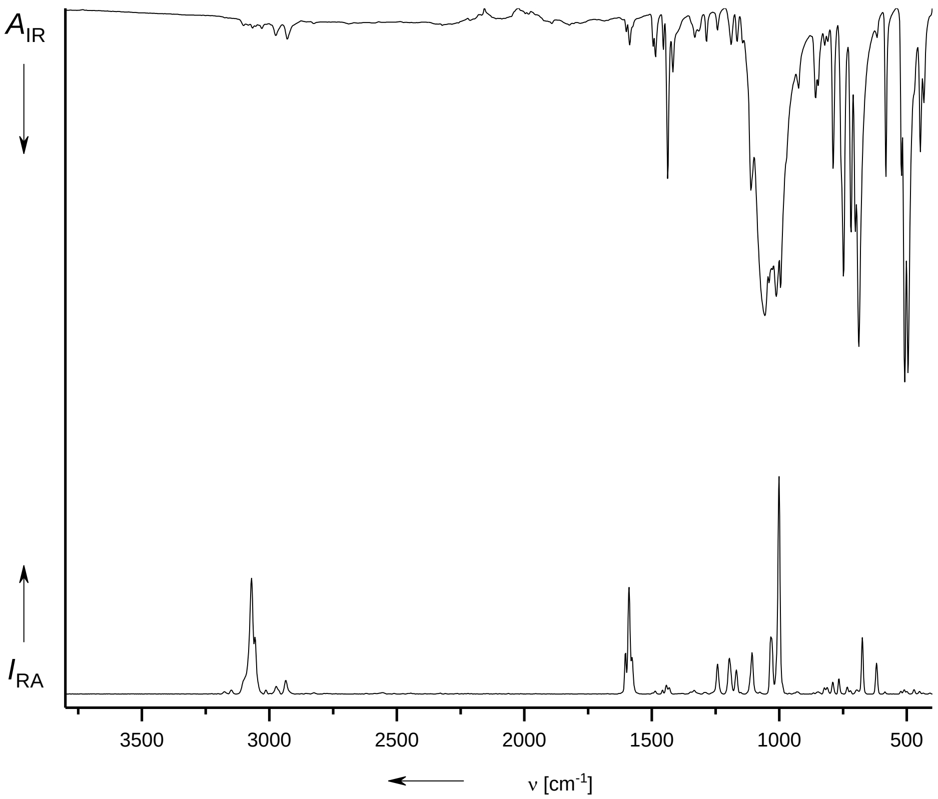


**Figure S144: IR and Raman spectra of [BnPh$_3$P][BF$_4$].**

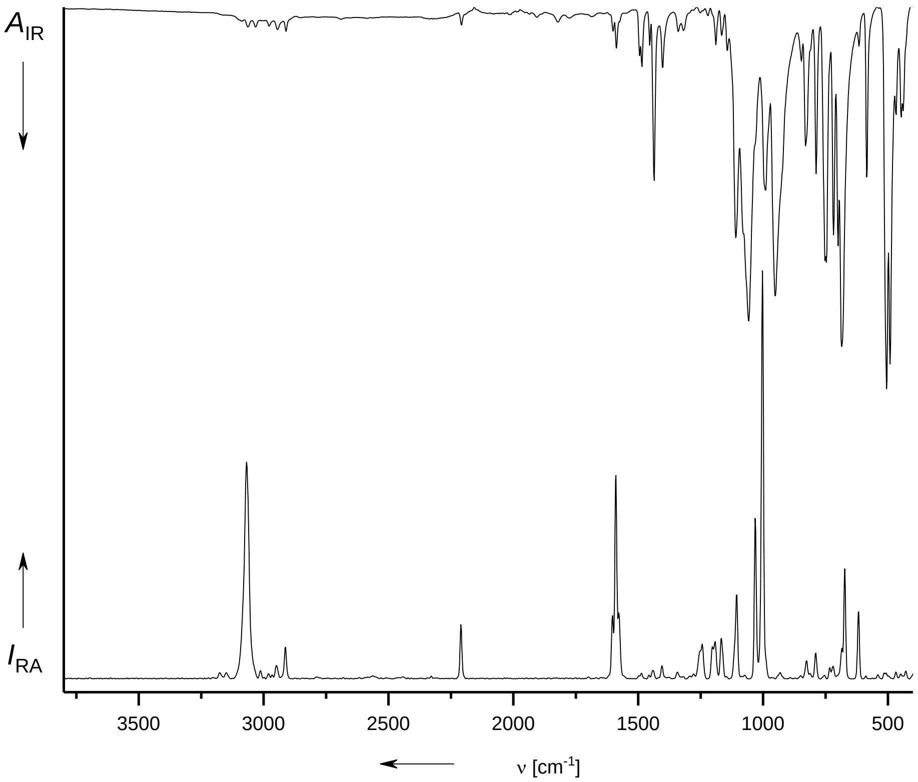


**Figure S145: IR and Raman spectra of [BnPh$_3$P][BF$_3$(CN)].**

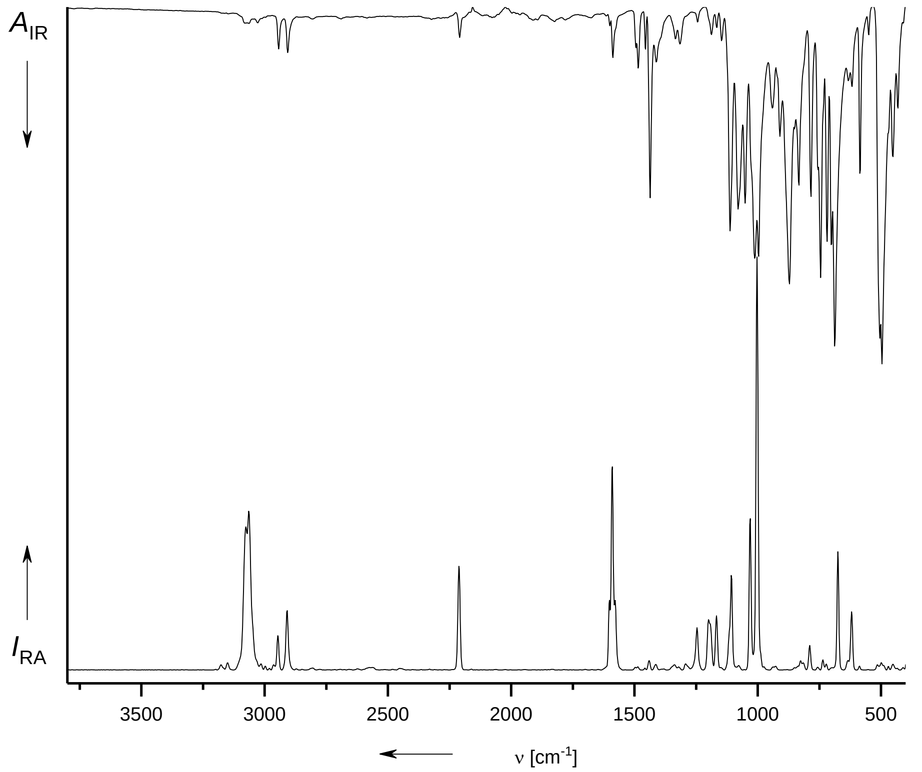


Figure S146: IR and Raman spectra of [BnPh$_3$P][BF$_2$(CN)$_2$].

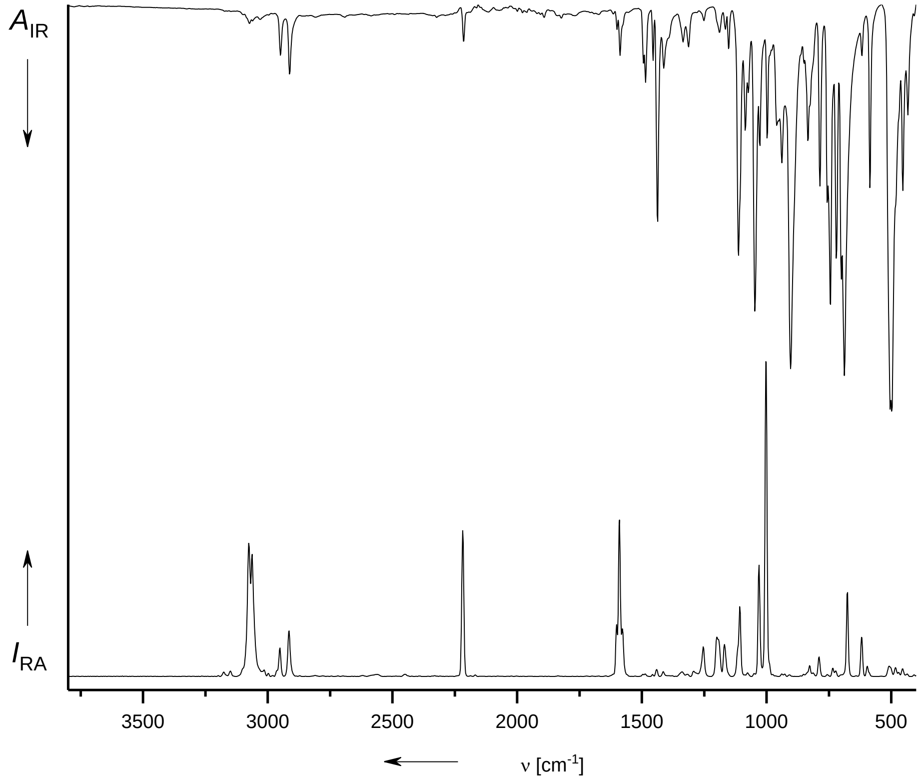


Figure S147: IR and Raman spectra of [BnPh$_3$P][BF(CN)$_3$].

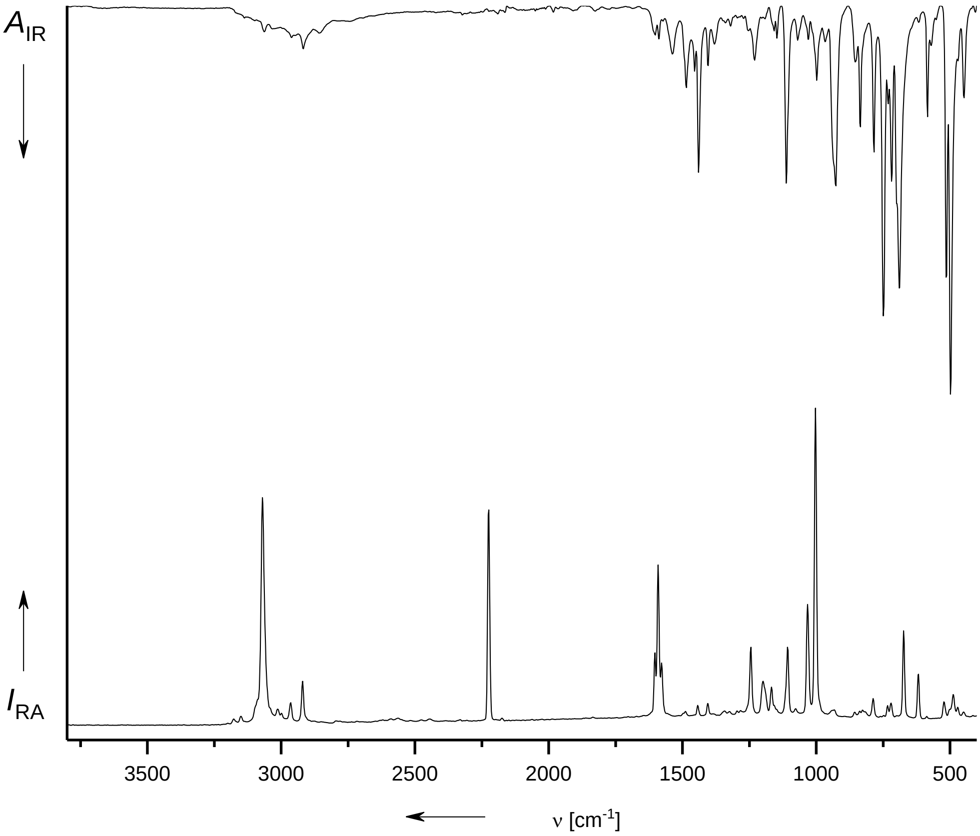


Figure S148: IR and NMR spectra of [BnPh$_3$P][B(CN)$_4$].

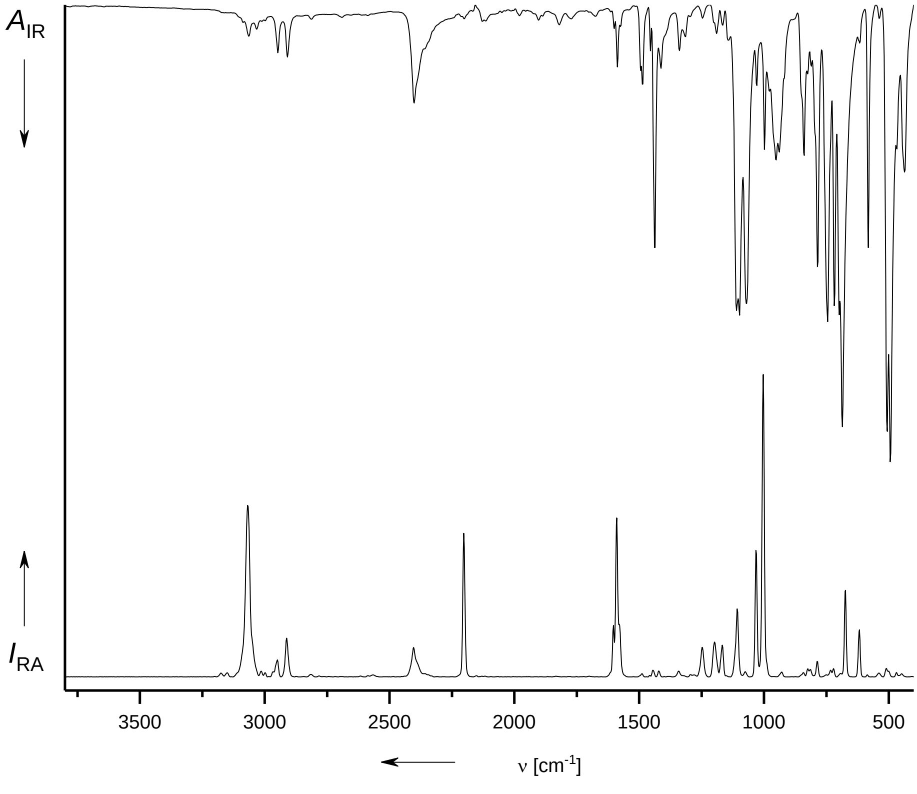


Figure S149: IR and NMR spectra of [BnPh$_3$P][BFH(CN)$_2$].

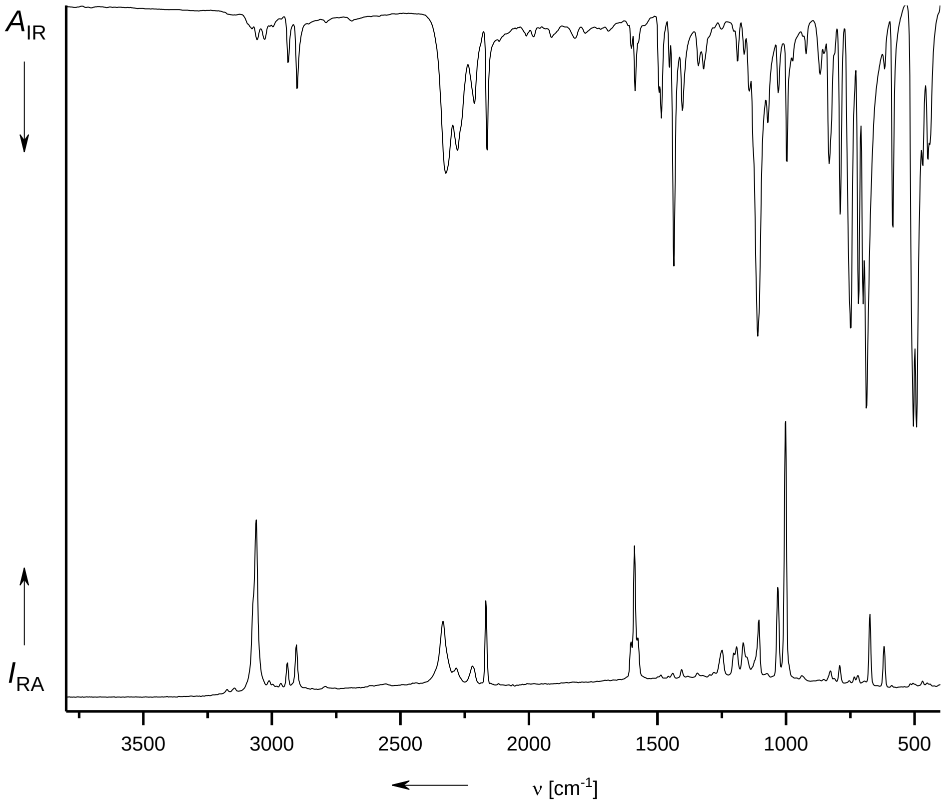


**Figure S150: IR and Raman spectra of [BnPh$_3$P][BH$_3$(CN)].**

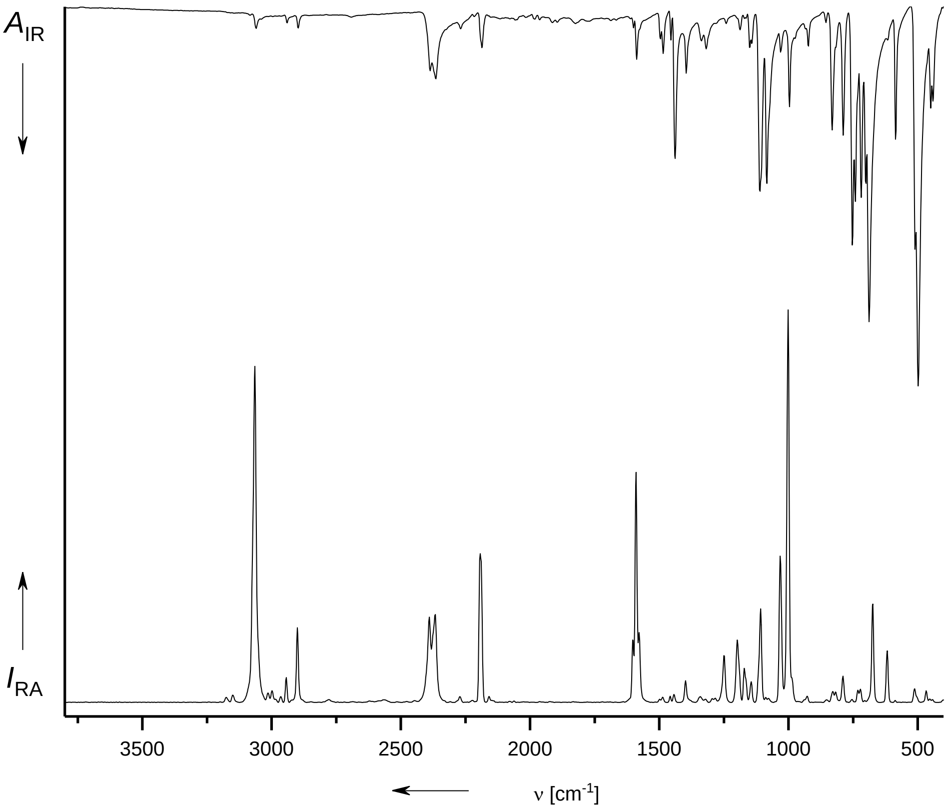


**Figure S151: IR and Raman spectra of [BnPh$_3$P][BH$_2$(CN)$_2$].**

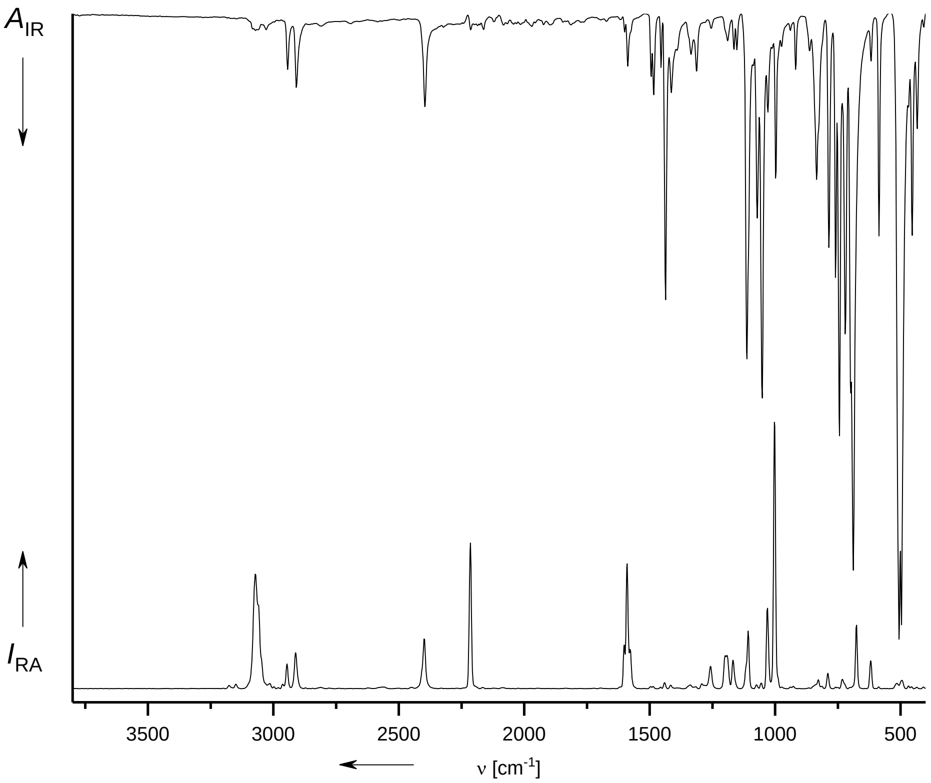


**Figure S152: IR and Raman spectra of [BnPh$_3$P][BH(CN)$_3$]**

# 7 Electrochemical Measurements

All electrochemical studies were performed with the neat ILs under an Ar atmosphere with a Metrohm PGSTAT30 potentiostat and a Microcell HC set-up with a Eurotherm temperature controller (rhd instruments). A 0.1 mL Pt-cell TSC-70 closed (rhd instruments) served as counter electrode and was equipped with a glassy carbon working electrode (surface area: $3.14 \cdot 10^{-2}$ cm$^2$). Specific conductivities (σ) were determined at different temperatures (20, 40, 60, 70, 80 °C) by impedance spectroscopy from $500 \cdot 10^3$ to 800 Hz. The cell constant was determined on a 1413 µS·cm$^{-1}$ conductivity solution HI 70031 (HANNA instruments).

Cyclic voltammetry was conducted at 20 °C with a scan rate of 50 mV·s$^{-1}$ using the same set-up as employed for the conductivity measurements and an additional Ag/Ag$^+$ micro reference electrode (acetonitrile, rhd instruments). Cathodic ($E_c$) and anodic ($E_a$) limits of stability have been assessed via linear fits below and above the onset of electrolyte decomposition and determination of the intersection point of both lines in analogy to a method described in the literature.[19,20]

**Table S1: Specific conductivity[a] *σ* determined via impedance spectroscopy at different temperatures.**

| $T$ / K | 293.1 | 313.1 | 333.1 | 343.1 | 353.1 |
|---|---|---|---|---|---|
| [EMIm][B(CN)$_4$] | 12.1 | 20.7 | 31.0 | 36.6 | 42.4 |
| [EMIm][BF(CN)$_3$] | 20.2 | 29.7 | 41.4 | 47.5 | 54.0 |
| [EMIm][BF$_2$(CN)$_2$] | 25.0 | 35.0 | 45.9 | 51.7 | 58.2 |
| [EMIm][BF$_3$(CN)] | 22.9 | n.d. | n.d. | n.d. | n.d. |
| [EMIm][BF$_4$] | 12.3 | 20.9 | 30.7 | 36.1 | 41.7 |
| [EMIm][BH(CN)$_3$] | 20.1 | 30.6 | 42.5 | 49.0 | 55.7 |
| [EMIm][BH$_2$(CN)$_2$] | 32.6 | 46.4 | 61.1 | 69.5 | n.d. |
| [EMIm][BH$_3$(CN)] | 26.6 | 40.2 | 54.2 | 62.8 | n.d. |
| [EMIm][BFH(CN)$_2$] | 27.6 | 38.8 | 50.1 | 55.6 | 61.6 |
| [BMPL][B(CN)$_4$] | 4.1 | 7.6 | 12.4 | 15.2 | 18.2 |
| [BMPL][BF(CN)$_3$] | 7.7 | 12.1 | 17.4 | 20.2 | 23.0 |
| [BMPL][BF$_2$(CN)2] | 8.3 | 13.5 | 20.0 | 23.6 | 27.5 |
| [BMPL][BF$_3$(CN)] | 6.3 | n.d. | n.d. | n.d. | n.d. |
| [BMPL][BFH(CN)$_2$] | 11.2 | 17.0 | 23.8 | 27.3 | 31.1 |

[a] Specific conductivity *σ* in mS·cm$^{-1}$. n.d.: not determined

# 8 Viscosity and Density

**Table S2: Dynamic viscosity and density of ILs in the temperature range of 293–353 K at 60° angle.**

| Species | $\rho$ / g·cm$^{-3}$ | | | | | | | $\eta$ / mPa·s | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$ / K | 293 | 303 | 313 | 323 | 333 | 343 | 353 | 293 | 303 | 313 | 323 | 333 | 343 | 353 |
| [EMIm][B(CN)$_4$] | 1.040 | 1.033 | 1.025 | 1.017 | 1.009 | 1.002 | 0.994 | 22.6 | 15.7 | 11.4 | 8.7 | 7.0 | 5.7 | 4.7 |
| [EMIm][BF(CN)$_3$] | 1.073 | 1.065 | 1.057 | 1.050 | 1.042 | 1.035 | 1.028 | 12.6 | 9.3 | 7.5 | 6.0 | 5.0 | 4.2 | 3.5 |
| [EMIm][BF$_2$(CN)$_2$] | 1.120 | 1.112 | 1.104 | 1.097 | 1.090 | 1.082 | 1.075 | 10.8 | 8.5 | 6.8 | 5.7 | 4.8 | 4.1 | 3.5 |
| [EMIm][BF$_3$(CN)] | 1.191 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 14.6 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| [EMIm][BF$_4$] | 1.286 | 1.278 | 1.271 | 1.263 | 1.256 | 1.248 | 1.241 | 43.7 | 29.9 | 22.2 | 16.7 | 13.0 | 10.4 | 8.5 |
| [EMIm][BH(CN)$_3$] | 1.013 | 1.006 | 0.999 | 0.992 | 0.985 | 0.979 | 0.972 | 12.3 | 9.2 | 7.2 | 5.8 | 4.7 | 3.9 | 3.4 |
| [EMIm][BH$_2$(CN)$_2$] | 0.981 | 0.975 | 0.969 | 0.969 | 0.957 | 0.950 | 0.945 | 10.2 | 7.9 | 6.4 | 5.3 | 4.4 | 3.8 | 3.3 |
| [EMIm][BH$_3$(CN)] | 0.948 | 0.943 | 0.937 | 0.932 | 0.926 | 0.921 | 0.916 | 15.7 | 11.8 | 9.2 | 7.4 | 6.0 | 5.0 | 4.3 |
| [EMIm][BFH(CN)$_2$] | 1.056 | 1.049 | 1.042 | 1.035 | 1.028 | 1.022 | 1.015 | 10.6 | 8.3 | 6.7 | 5.5 | 4.6 | 3.9 | 3.4 |
| [BMPL][B(CN)$_4$] | 0.979 | 0.973 | 0.966 | 0.959 | 0.952 | 0.946 | 0.939 | 60.2 | 39.8 | 27.4 | 19.9 | 15.1 | 11.7 | 9.3 |
| [BMPL][BF(CN)$_3$] | 1.004 | 0.998 | 0.991 | 0.984 | 0.978 | 0.972 | 0.965 | 30.7 | 22.1 | 16.6 | 13.0 | 10.6 | 8.6 | 7.1 |
| [BMPL][BF$_2$(CN)$_2$] | 1.039 | 1.033 | 1.026 | 1.020 | 1.013 | 1.007 | 1.001 | 28.2 | 21.6 | 16.6 | 13.0 | 10.6 | 8.7 | 7.3 |
| [BMPL][BF$_3$(CN)] | 1.089 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 57.7 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| [BMPL][BFH(CN)$_2$] | 0.987 | 0.981 | 0.975 | 0.969 | 0.963 | 0.957 | 0.952 | 25.2 | 19.1 | 14.8 | 11.7 | 9.5 | 7.9 | 6.6 |
| [BMIm][BH$_2$(CN)$_2$] | 0.962 | 0.956 | 0.950 | 0.944 | 0.938 | 0.932 | 0.926 | 18.3 | 13.3 | 10.1 | 8.0 | 6.4 | 5.3 | 4.5 |

n.d.: not determined.

# 9 Vogel-Fulcher-Tammann (VFT), Arrhenius, and Litovitz Fits

The dynamic viscosity ($\eta$) and the specific conductivity ($\sigma$) at different temperatures ($T$) were fitted to the following equations (fitting parameters see below).

**Vogel-Fulcher-Tammann (VFT)**:[8]

$$\eta = \eta_0 \exp\left(\frac{k_\eta}{T - T_0}\right) \qquad (1)$$

with $\eta_0$ = viscosity at infinite temperature; $k_\eta$ = constant; $T_0$ $T_0$ = Vogel temperature.

$$\sigma = \sigma_0 \exp\left(\frac{-k_\sigma}{T - T_0{}'}\right) \qquad (2)$$

With $\sigma_0$ = conductivity at infinite temperature; $k_\sigma$ = constant.

**Arrhenius**:[9]

$$\sigma = \sigma_0\, exp\left(\frac{-E_\sigma}{R\,T}\right) \qquad (3)$$

with $E_\sigma$ = activation energy of conductivity; R = universal gas constant.

**Litovitz**:[10]

$$\sigma = \sigma_0 \exp\left(\frac{-B}{R\,T^3}\right) \qquad (4)$$

with $B$ = constant.

**Table S3: Fitting parameters for Vogel-Fulcher-Tammann (VFT), Arrhenius and Litovitz equations describing the behaviour of $[EMIm]^+$ and $[BMPL]^+$ salts of fluorocyanoborate anions in the temperature range of 293–353 K.**

| | | VFT parameters ($\eta$)[a] | | | VFT parameters ($\sigma$) with variable $T_0'$ [b] | | | VFT parameters ($\sigma$) fixed $T_0'$ [c] | | Arrhenius parameters ($\eta$)[d] | | Arrhenius parameters ($\sigma$)[e] | | Litovitz parameters ($\eta$)[f] | | Litovitz parameters ($\sigma$)[g] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\eta_0$ | $k_\eta$ | $T_0$ | $\sigma_0$ | $k_\sigma$ | $T_0'$ | $\sigma_0$ | $k_\sigma$ | $\eta_0$ | $E_\eta$ | $\sigma_0$ | $E_\sigma$ | $\eta_0$ | $B$ | $\sigma_0$ | $B$ |
| | | [$10^{-3}$mPa·s] | [K] | [K] | [mS·cm$^{-1}$] | [K] | [K] | [mS·cm$^{-1}$] | K | [$10^{-3}$mPa·s] | [kJ·mol$^{-1}$] | [mS·cm$^{-1}$] | [kJ·mol$^{-1}$] | [$10^{-3}$mPa·s] | [$10^{-6}$J·K$^2$·mol$^{-1}$] | [mS·cm$^{-1}$] | [$10^{-6}$J·K$^2$·mol$^{-1}$] |
| [EMIm] | $[BF_4]$ | 264 ± 76 | 658 ± 84 | 164 ± 9 | 467 ± 29 | 433 ± 19 | 174 ± 3 | | | 2 ± 0.4 | 24 ± 0.5 | 12975 ± 2042 | 17 ± 0.4 | 973 ± 2 | 796 ± 6 | 210 ± 2 | 592 ± 3 |
| | $[BF_2(CN)_2]$ | 180 ± 50 | 657 ± 101 | 133 ± 14 | 3961 ± 433 | 1481 ± 37 | 0 ± 0 | 607 ± 50 | 514 ± 16 | 13 ± 1 | 16 ± 0.3 | 3961 ± 395 | 12 ± 0.3 | 709 ± 19 | 597 ± 6 | 189 ± 10 | 428 ± 16 |
| | $[BF(CN)_3]$ | 134 ± 56 | 720 ± 150 | 134±19 | 806±88 | 564 ± 41 | 139 ± 7 | | | 7 ± 1 | 18 ± 0.3 | 7967 ± 697 | 14 ± 0.2 | 709 ± 19 | 597 ± 6 | 228 ± 2 | 505 ± 3 |
| | $[BFH(CN)_2]$ | 138 ± 25 | 730 ± 68 | 125±9 | 354±24 | 334 ± 22 | 162 ± 5 | | | 11 ± 1 | 17 ± 0.2 | 2869 ± 257 | 11 ± 0.2 | 768 ± 14 | 550 ± 4 | 178 ± 1 | 391 ± 1 |
| [BMPL] | $[BF_2(CN)_2]$ | 44 ± 35 | 1440 ± 382 | 70 ± 33 | 680 ± 31 | 708 ± 18 | 132 ± 2 | | | 8 ± 1 | 20 ± 0.2 | 8455 ± 787 | 17 ± 0.3 | 1277 ± 59 | 651 ± 11 | 137 ± 2 | 590 ± 4 |
| | $[BF(CN)_3]$ | 318 ± 62 | 592 ± 58 | 163 ± 7 | 273 ± 27 | 479 ± 33 | 159 ± 6 | | | 4 ± 1 | 21 ± 0.5 | 4449 ± 538 | 15 ± 0.3 | 1041 ± 18 | 708 ± 4 | 101 ± 1 | 541 ± 2 |
| | $[BFH(CN)_2]$ | 88 ± 40 | 1084 ± 192 | 101 ± 19 | 289 ± 24 | 526 ± 22 | 145 ± 4 | | | 8 ± 1 | 20 ± 0.2 | 4190 ± 391 | 14 ± 0.2 | 1167 ± 39 | 646 ± 8 | 122 ± 1 | 503 ± 2 |

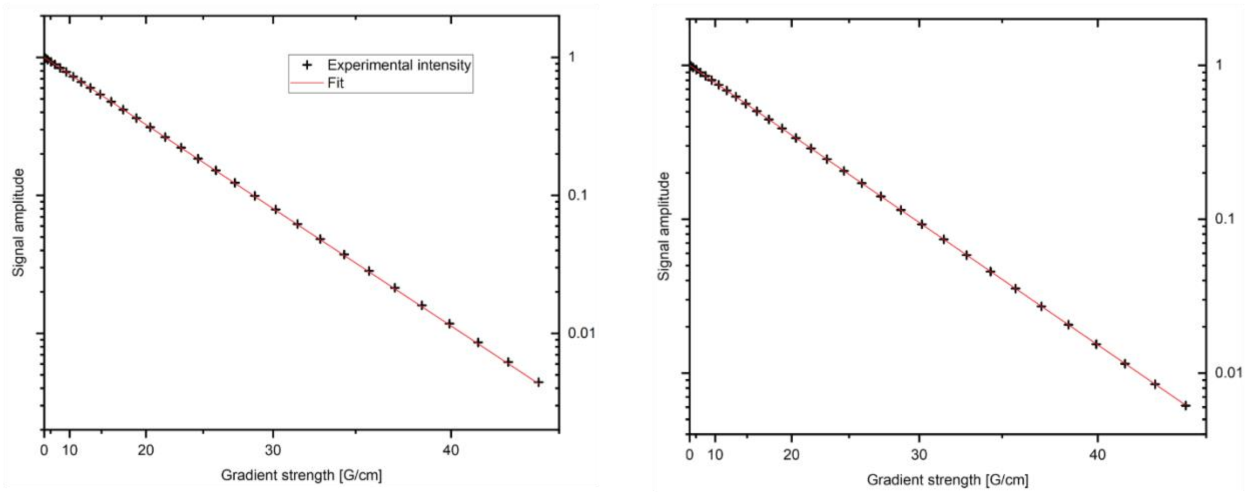
[a] $R^2 \geq 99.96\%$. [b] $R^2 \geq 99.99\%$. [c] $T_0'$ was taken from the VFT($\eta$) fit (4th column) and was used as an invariable constant ($T_0'=T_0$); $R^2 = 99.47$. [d] $R^2 \geq 99.86\%$. [e] $R^2 \geq 99.67\%$. [f] $R^2 \geq 99.93\%$. [g] $R^2 \geq 99.27\%$.

# 10 Diffusion NMR

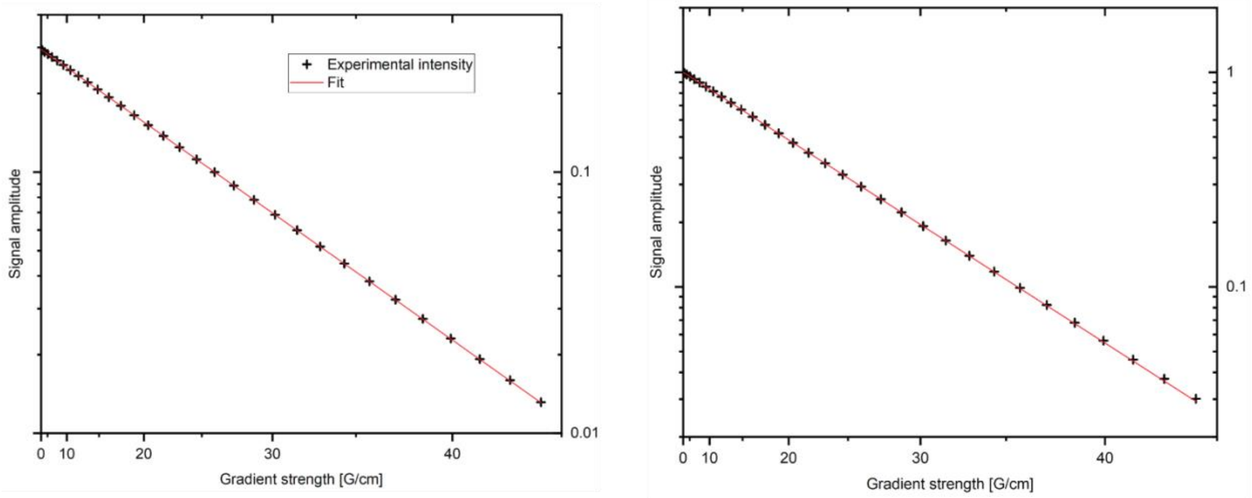
All diffusion (DOSY) NMR measurements were performed on a 14.1 T Bruker Avance III Spectrometer with a BCU 2 cooling unit using a BBFO probe equipped with a z-gradient (max. gradient strength of 50 G $cm^{-1}$). The ionic liquids were filled into coaxial insert tubes with the insert being filled with DMSO-$d_6$. No sample rotation was employed.

Each sample was measured at three different temperatures, 293.1 K, 313.1 K and 333.1 K, which were calibrated prior to the measurement series. $^{1}H$, $^{11}B$ and $^{19}F$ 90° pulses were calibrated for each sample and temperature. Furthermore, diffusion times $\Delta$ and durations of the bipolar gradient pulse $\delta$ were estimated based on the known viscosities and existing data in literature[11] and subsequently optimized for each sample prior to the experiment. The DOSY measurements were done using both the stimulated echo BPP-LED pulse (ledbpgp2s) sequence and the double stimulated echo pulse (dstebpgp3s) sequence. By comparison of the two datasets, convection effects could be excluded. Signals had decayed to below 10 % or, if possible, to below 5 % of the initial signal area. The analysis of the DOSY data was done using the Topspin T1/T2 module with the area option yielding the temperature dependent diffusion coefficients for each nucleus and thus for the different components of the ionic liquid.

[EMIm][BF(CN)$_3$]



[EMIm][BF$_2$(CN)$_2$]



[EMIm][BF$_3$(CN)]

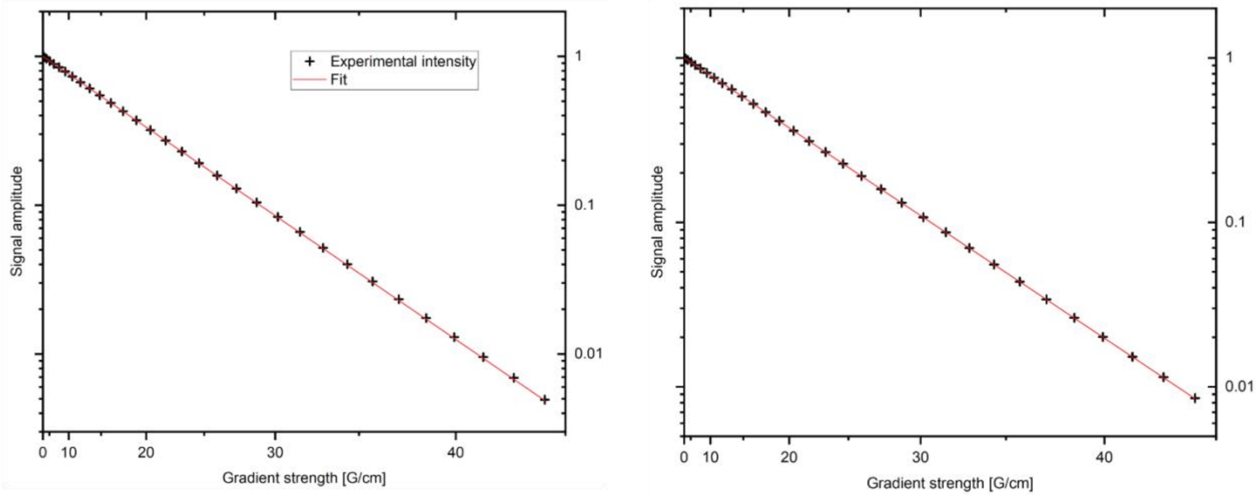
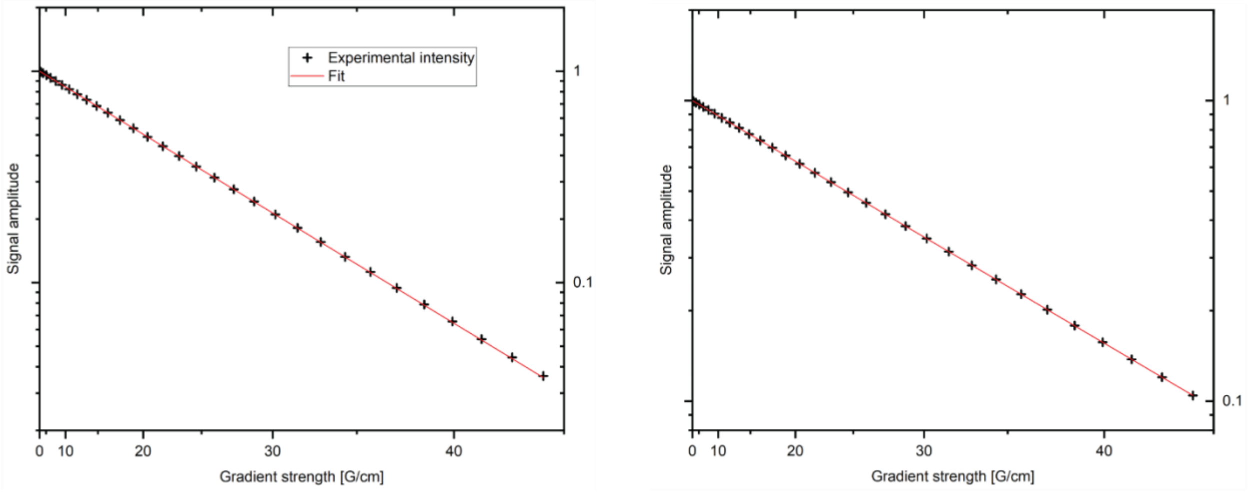


**Figure S153: Signal decay as function of gradient strength *G* for $^1$H (left) and $^{19}$F (right) DOSY NMR experiments for [EMIm][BF(CN)$_3$], [EMIm][BF$_2$(CN)$_2$] and [EMIm][BF$_3$(CN)].**

[EMIm][BF$_4$]



[EMIm][BFH(CN)$_2$]

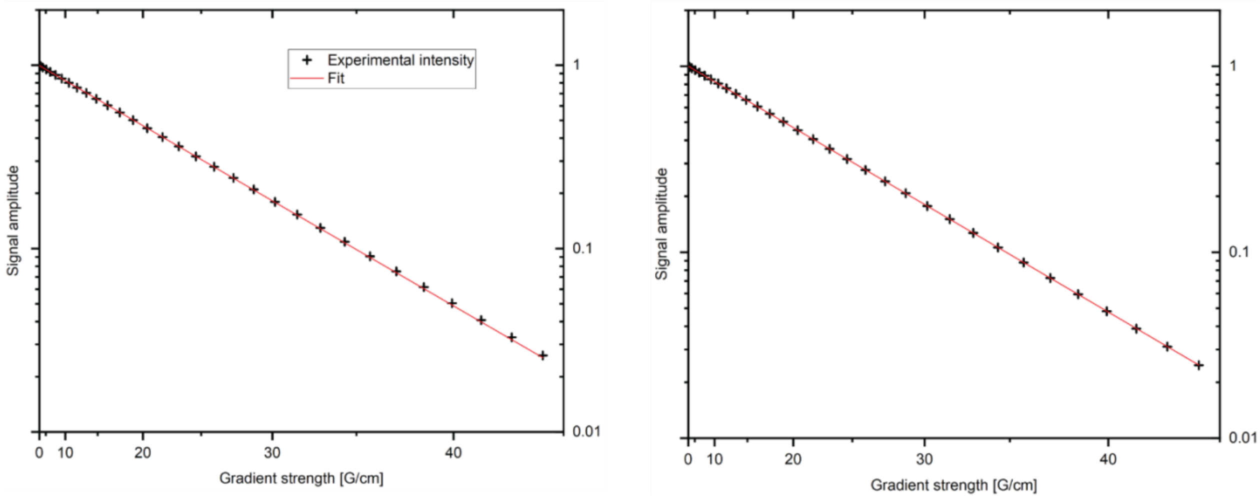
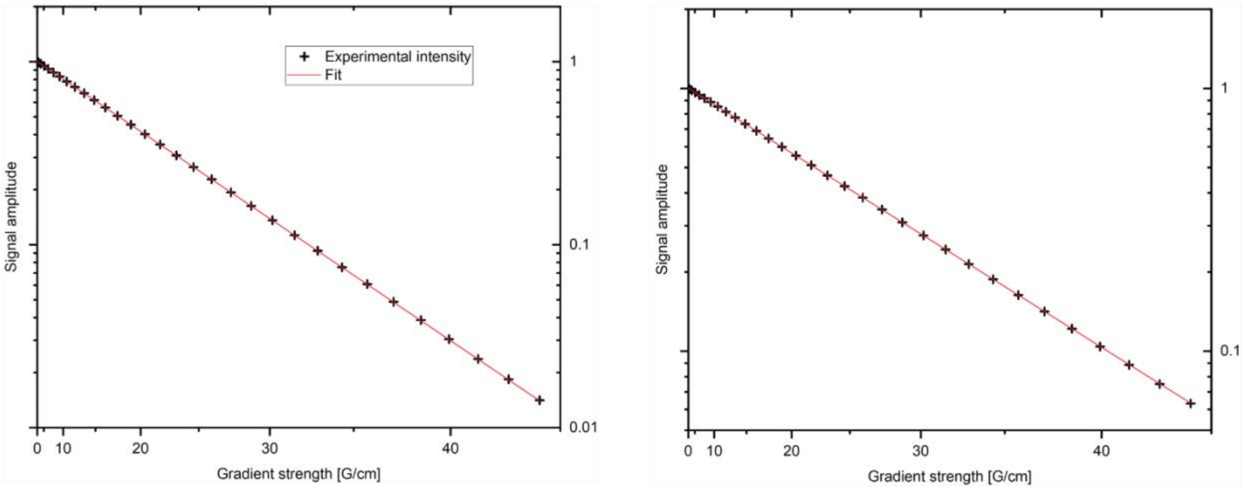
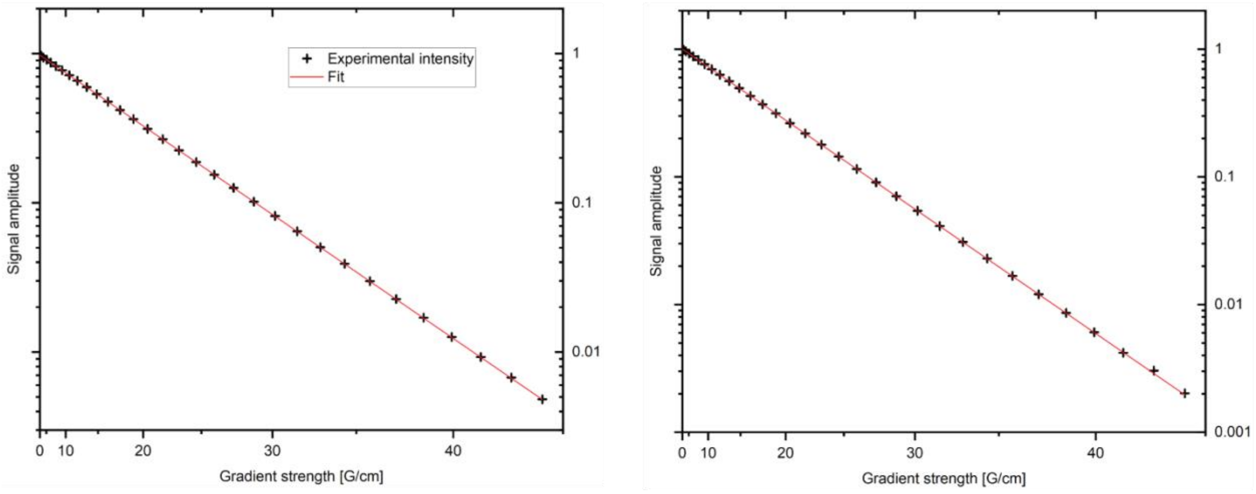


**Figure S154: Signal decay as function of gradient strength *G* for $^1$H (left) and $^{19}$F (right) DOSY NMR experiments for [EMIm][BF$_4$] and [EMIm][BFH(CN)$_2$].**

[BMPL][B(CN)$_4$]



[BMPL][BF(CN)$_3$]



[BMPL][BF$_2$(CN)$_2$]

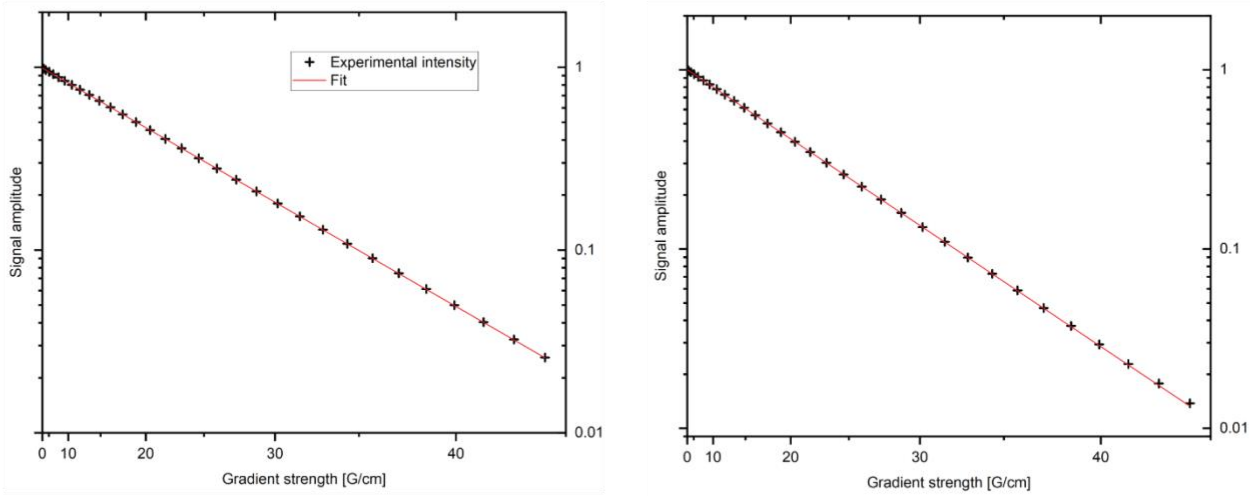
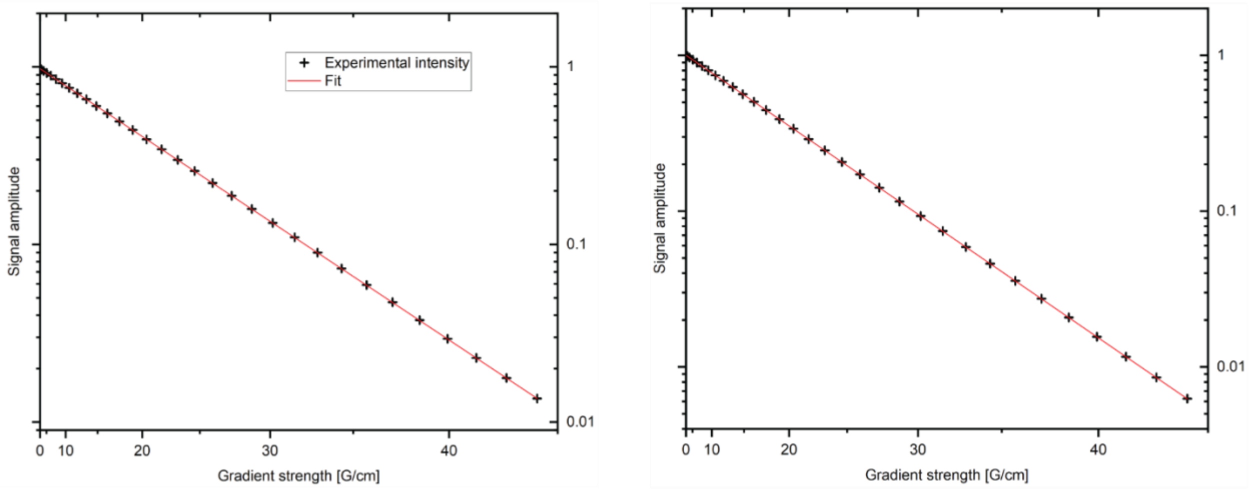


**Figure S155: Signal decay as function of gradient strength *G* for $^1$H (left) and $^{19}$F (right) DOSY NMR experiments for [BMPL][B(CN)$_4$], [BMPL][BF(CN)$_3$] and [BMPL][BF$_2$(CN)$_2$].**

[BMPL][$BF_3$(CN)]



[BMPL][BFH$(CN)_2$]

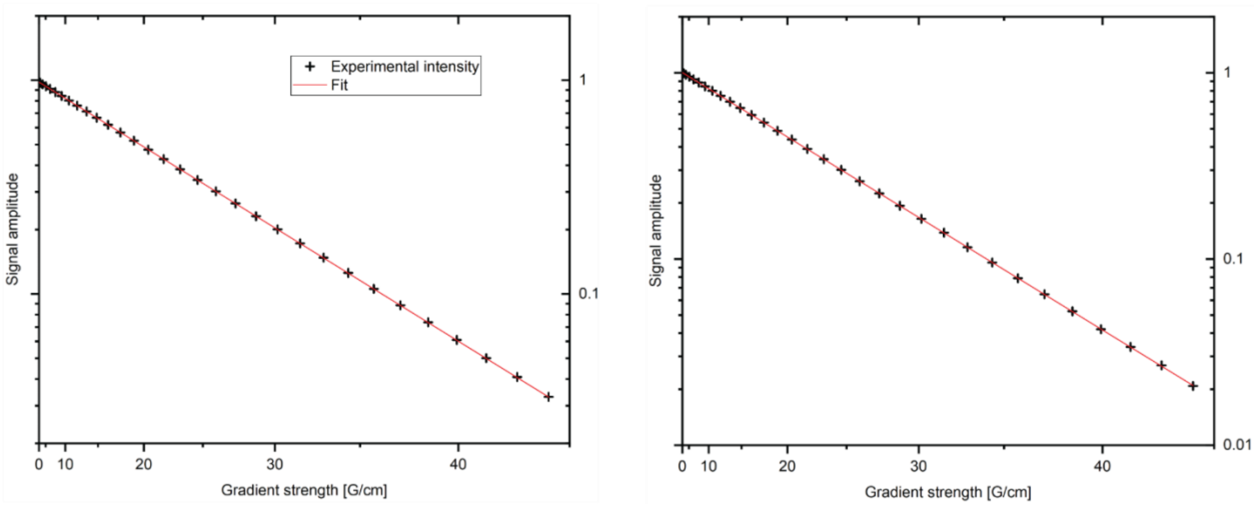


**Figure S156: Signal decay as function of gradient strength *G* for $^1$H (left) and $^{19}$F (right) DOSY NMR experiments for [BMPL][$BF_3$(CN)] and [BMPL][BFH$(CN)_2$].**

**Table S4: Diffusion coefficients[a] $D^+$ and $D^-$ determined via DOSY NMR at different temperatures.**

| $T$ / K | 293.1 | | | | 313.1 | | | | 333.1 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $D^+$ | $D^-$ | | | $D^+$ | $D^-$ | | | $D^+$ | $D^-$ | | |
| nucleus | $^{1}H$ | $^{1}H$ | $^{19}F$ | $^{11}B$ | $^{1}H$ | $^{1}H$ | $^{19}F$ | $^{11}B$ | $^{1}H$ | $^{1}H$ | $^{19}F$ | $^{11}B$ |
| [EMIm][B(CN)$_4$] | 6.3 | | | 5.4 | 13.3 | | | 11.8 | 22.5 | | | 20.1 |
| [EMIm][BF(CN)$_3$] | 10.26$^{b}$ | | 9.62$^{b}$ | n.d. | 18.96$^{b}$ | | 17.78$^{b}$ | n.d. | 29.53$^{b}$<br>29.30$^{c}$ | | 27.69$^{b}$<br>27.73$^{c}$ | 27.76$^{b}$ |
| [EMIm][BF$_2$(CN)$_2$] | 12.21$^{b}$ | | 11.73$^{b}$ | n.d. | 21.13$^{b}$<br>21.31$^{c}$ | | [22.22]$^{bd}$<br>20.42$^{c}$ | n.d. | 31.71$^{b}$<br>32.17$^{c}$ | | 30.15$^{b}$<br>30.36$^{c}$ | 30.24$^{b}$<br>30.45$^{c}$ |
| [EMIm][BF$_3$(CN)] | 10.04$^{b}$ | | 9.03$^{b}$ | n.d. | 17.50$^{b}$<br>17.58$^{c}$ | | 15.93$^{b}$<br>16.07$^{c}$ | n.d. | 26.47$^{b}$<br>26.61$^{c}$ | | 24.30$^{b}$<br>24.48$^{c}$ | 24.37$^{b}$<br>24.46$^{c}$ |
| [EMIm][BF$_4$] | 3.86$^{b}$ | | 2.95$^{b}$ | n.d. | 8.21$^{b}$<br>8.35$^{c}$ | | 6.58$^{b}$<br>6.60$^{c}$ | n.d. | 14.13$^{b}$<br>14.22$^{c}$ | | 11.64$^{b}$<br>11.63$^{c}$ | 11.67$^{b}$<br>11.56$^{c}$ |
| [EMIm][BH(CN)$_3$] | 1.05$^{b}$ | 1.03$^{b}$ | | | 1.94$^{b}$ | 1.91$^{b}$ | | | 3.06$^{b}$<br>3.06$^{c}$ | 2.94$^{b}$<br>2.93$^{c}$ | | |
| [EMIm][BH$_2$(CN)$_2$] | 1.33$^{b}$ | 1.28$^{b}$ | | | 2.30$^{b}$ | 2.23$^{b}$ | | | 3.44$^{b}$<br>3.42$^{c}$ | 3.36$^{b}$<br>3.38$^{c}$ | | |
| [EMIm][BH$_3$(CN)] | 0.94$^{b}$ | 0.89$^{b}$ | | | 1.73$^{b}$ | 1.66$^{b}$ | | | 2.71$^{b}$<br>2.70$^{c}$ | 2.63$^{b}$<br>2.66$^{c}$ | | |
| [EMIm][BFH(CN)$_2$] | 12.53$^{b}$ | 12.39$^{b}$ | 12.29$^{b}$ | n.d. | 21.70$^{b}$<br>21.80$^{c}$ | 21.25$^{b}$<br>21.25$^{c}$ | 21.25$^{b}$<br>21.30$^{c}$ | 21.34$^{b}$<br>21.48$^{c}$ | 32.64$^{b}$<br>33.05$^{c}$ | 31.93$^{b}$<br>32.06$^{c}$ | 31.79$^{b}$<br>31.81$^{c}$ | 31.85$^{b}$<br>32.00$^{c}$ |
| [BMPL][B(CN)$_4$] | 1.96$^{b}$ | | | 2.21$^{b}$<br>2.23$^{c}$ | 4.81$^{b}$<br>4.84$^{c}$ | | | 5.40$^{b}$<br>5.43$^{c}$ | 9.01$^{b}$<br>9.05$^{c}$ | | | 10.04$^{b}$<br>10.00$^{c}$ |
| [BMPL][BF(CN)$_3$] | 3.79$^{b}$ | | 4.46$^{b}$ | n.d. | 7.75$^{b}$ | | 9.41$^{b}$ | n.d. | 13.02$^{b}$<br>13.13$^{c}$ | | 15.59$^{b}$<br>15.66$^{c}$ | n.d. |
| [BMPL][BF$_2$(CN)$_2$] | 4.21$^{b}$ | | 5.11$^{b}$ | n.d. | 8.01$^{b}$<br>8.04$^{c}$ | | 9.71$^{b}$<br>9.78$^{c}$ | n.d. | 12.89$^{b}$<br>12.96$^{c}$ | | 15.52$^{b}$<br>15.62$^{c}$ | 15.55$^{b}$<br>15.58$^{c}$ |
| [BMPL][BF$_3$(CN)] | 2.42$^{b}$ | | 2.88$^{b}$ | n.d. | 5.01$^{b}$<br>5.01$^{c}$ | | 5.99$^{b}$<br>6.04$^{c}$ | n.d. | 8.62$^{b}$<br>8.65$^{c}$ | | 10.30$^{b}$<br>10.33$^{c}$ | 10.32$^{b}$<br>10.37$^{c}$ |
| [BMPL][BFH(CN)$_2$] | 4.57$^{b}$ | 5.52$^{b}$ | 5.62$^{b}$ | n.d | 8.69$^{b}$<br>8.81$^{c}$ | 10.67$^{b}$<br>9.967$^{c}$ | 10.59$^{b}$<br>10.68$^{c}$ | n.d. | 14.97$^{b}$<br>14.07$^{c}$ | 16.98$^{b}$<br>17.31$^{c}$ | 17.02$^{b}$<br>17.04$^{c}$ | 17.03$^{b}$<br>17.20$^{c}$ |

[a] Diffusion coefficients $D^+$ and $D^-$ in $10^{-11} m^2 \cdot s^{-1}$. [b] ledbpgp2s pulse sequence. [c] dstebpgp3s pulse sequence. [d] Unexpectedly high value; thus, omitted from discussion. n.d.: not determined.

# 11 Overview physical propterties of RTILs

**Table S5: Selected physical properties[a] of $[\mathrm{EMIm}]^+$ and $[\mathrm{BMPL}]^+$ RTILs in the temperature range of 293–333 K.**

| *T* | salt | *M* | *ρ* | σ | *D*⁺ | *D*⁻ | $\Lambda_{\mathrm{NMR}}$ | $\Lambda_{\mathrm{imp}}$ | *I* |
|---|---|---|---|---|---|---|---|---|---|
| K | | $\mathrm{g{\cdot}mol^{-1}}$ | $\mathrm{g{\cdot}cm^{-3}}$ | $\mathrm{mS{\cdot}cm^{-1}}$ | $\mathrm{10^{-11}m^{2}{\cdot}s^{-1}}$ | $\mathrm{cm^{2}{\cdot}S\ mol^{-1}}$ | $\mathrm{cm^{2}{\cdot}S{\cdot}mol^{-1}}$ | $\mathrm{cm^{2}{\cdot}S{\cdot}mol^{-1}}$ | |
| 293.17 | $\mathrm{[EMIm][B(CN)_4]}$ | 226.05 | 1.040 | 12.1 | 6.3 | 5.4 | 4.45 | 2.63 | 0.59 |
| | $\mathrm{[EMIm][BF(CN)_3]}$ | 219.03 | 1.073 | 20.2 | 10.26 | 9.62 | 7.56 | 4.12 | 0.54 |
| | $\mathrm{[EMIm][BF_2(CN)_2]}$ | 212.01 | 1.120 | 25.0 | 12.21 | 11.73 | 9.10 | 4.73 | 0.52 |
| | $\mathrm{[EMIm][BF_3(CN)]}$ | 204.99 | 1.191 | 22.9 | 10.04 | 9.03 | 7.25 | 3.94 | 0.54 |
| | $\mathrm{[EMIm][BF_4]}$ | 197.97 | 1.286 | 12.3 | 3.86 | 2.95 | 2.59 | 1.89 | 0.73 |
| | $\mathrm{[EMIm][BH(CN)_3]}$ | 201.04 | 1.013 | 20.1 | 10.5 | 10.3 | 7.91 | 3.99 | 0.50 |
| | $\mathrm{[EMIm][BH_2(CN)_2]}$ | 176.03 | 0.981 | 32.6 | 13.3 | 12.8 | 9.93 | 5.85 | 0.59 |
| | $\mathrm{[EMIm][BH_3(CN)]}$ | 151.02 | 0.948 | 26.6 | 9.4 | 8.9 | 6.96 | 4.24 | 0.61 |
| | $\mathrm{[EMIm][BFH(CN)_2]}$ | 194.02 | 1.056 | 27.6 | 12.53 | 12.34[b] | 9.46 | 5.07 | 0.54 |
| | $\mathrm{[BMPL][B(CN)_4]}$ | 257.15 | 0.979 | 4.1 | 1.96 | 2.21 | 1.59 | 1.08 | 0.68 |
| | $\mathrm{[BMPL][BF(CN)_3]}$ | 250.13 | 1.004 | 7.7 | 3.79 | 4.46 | 3.14 | 1.92 | 0.61 |
| | $\mathrm{[BMPL][BF_2(CN)_2]}$ | 243.11 | 1.039 | 8.3 | 4.21 | 5.11 | 3.54 | 1.94 | 0.55 |
| | $\mathrm{[BMPL][BF_3(CN)]}$ | 236.09 | 1.089 | 6.3 | 2.42 | 2.88 | 2.02 | 1.37 | 0.68 |
| | $\mathrm{[BMPL][BFH(CN)_2]}$ | 225.12 | 0.987 | 11.2 | 4.57 | 5.57[b] | 3.86 | 2.56 | 0.66 |
| 313.17 | $\mathrm{[EMIm][B(CN)_4]}$ | 226.05 | 1.025 | 20.7 | 13.3 | 11.8 | 8.94 | 4.57 | 0.51 |
| | $\mathrm{[EMIm][BF(CN)_3]}$ | 219.03 | 1.057 | 31.6 | 18.96 | 17.78 | 13.08 | 6.15 | 0.47 |
| | $\mathrm{[EMIm][BF_2(CN)_2]}$ | 212.01 | 1.104 | 35.0 | 21.13 | 20.42[c] | 14.79 | 6.72 | 0.45 |
| | $\mathrm{[EMIm][BF_3(CN)]}$ | 204.99 | n.d. | n.d. | 17.5 | 15.93 | 11.90 | n.d. | n.d. |
| | $\mathrm{[EMIm][BF_4]}$ | 197.97 | 1.271 | 20.9 | 8.21 | 6.58 | 5.27 | 3.26 | 0.62 |
| | $\mathrm{[EMIm][BH(CN)_3]}$ | 201.04 | 0.999 | 30.6 | 19.4 | 19.1 | 13.71 | 6.16 | 0.45 |
| | $\mathrm{[EMIm][BH_2(CN)_2]}$ | 176.03 | 0.969 | 46.4 | 23.0 | 22.3 | 16.13 | 8.43 | 0.52 |
| | $\mathrm{[EMIm][BH_3(CN)]}$ | 151.02 | 0.937 | 40.2 | 17.3 | 16.6 | 12.07 | 6.48 | 0.54 |
| | $\mathrm{[EMIm][BFH(CN)_2]}$ | 194.02 | 1.042 | 38.8 | 21.7 | 21.28[b] | 15.30 | 7.23 | 0.47 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | [BMPL][B(CN)$_4$] | 257.15 | 0.966 | 7.6 | 4.81 | 5.4 | 3.63 | 2.02 | 0.56 |
| | [BMPL][BF(CN)$_3$] | 250.13 | 0.991 | 12.1 | 7.75 | 9.41 | 6.11 | 3.05 | 0.50 |
| | [BMPL][BF$_2$(CN)$_2$] | 243.11 | 1.026 | 13.5 | 8.01 | 9.71 | 6.31 | 3.20 | 0.51 |
| | [BMPL][BF$_3$(CN)] | 236.09 | n.d. | n.d. | 5.01 | 5.99 | 3.92 | n.d. | n.d. |
| | [BMPL][BFH(CN)$_2$] | 225.12 | 0.975 | 17 | 8.69 | 10.63[b] | 6.88 | 3.93 | 0.57 |
| 333.17 | [EMIm][B(CN)$_4$] | 226.05 | 1.009 | 31 | 22.5 | 20.1 | 14.26 | 6.95 | 0.49 |
| | [EMIm][BF(CN)$_3$] | 219.03 | 1.042 | 41.4 | 29.53 | 27.73[b] | 19.16 | 8.70 | 0.45 |
| | [EMIm][BF$_2$(CN)$_2$] | 212.01 | 1.090 | 45.9 | 31.71 | 30.2[b] | 20.72 | 8.93 | 0.43 |
| | [EMIm][BF$_3$(CN)] | 204.99 | n.d. | n.d. | 26.47 | 24.34[b] | 17.00 | n.d. | n.d. |
| | [EMIm][BF$_4$] | 197.97 | 1.256 | 30.7 | 14.13 | 11.66[b] | 8.63 | 4.84 | 0.56 |
| | [EMIm][BH(CN)$_3$] | 201.04 | 0.985 | 44.5 | 30.6 | 29.4 | 20.08 | 8.67 | 0.43 |
| | [EMIm][BH$_2$(CN)$_2$] | 176.03 | 0.957 | 61.1 | 34.4 | 33.6 | 22.76 | 11.24 | 0.49 |
| | [EMIm][BH$_3$(CN)] | 151.02 | 0.926 | 54.2 | 27.1 | 26.3 | 17.87 | 8.84 | 0.49 |
| | [EMIm][BFH(CN)$_2$] | 194.02 | 1.028 | 50.1 | 32.64 | 31.86[b] | 21.58 | 9.45 | 0.44 |
| | [BMPL][B(CN)$_4$] | 257.15 | 0.952 | 12.4 | 9.01 | 10.04 | 6.38 | 3.35 | 0.53 |
| | [BMPL][BF(CN)$_3$] | 250.13 | 0.978 | 17.4 | 13.02 | 15.59 | 9.57 | 4.45 | 0.46 |
| | [BMPL][BF$_2$(CN)$_2$] | 243.11 | 1.013 | 20 | 12.89 | 15.54[b] | 9.51 | 4.80 | 0.50 |
| | [BMPL][BF$_3$(CN)] | 236.09 | n.d. | n.d. | 8.62 | 10.31[b] | 6.33 | n.d. | n.d. |
| | [BMPL][BFH(CN)$_2$] | 225.12 | 0.963 | 23.8 | 14.97 | 17.01[b] | 10.70 | 5.56 | 0.52 |

[a] molar mass $M$; density $\rho$; specific conductivity $\sigma$ measured via impedance spectroscopy; diffusion coefficients of cations ($D^+$) and anion ($D^-$) obtained with ledbpgp2 pulse sequence when not otherwise stated; molar conductivities calcd. by $\Lambda_{\mathrm{imp}} = (D^+ + D^-)\cdot N_A\cdot k^{-1}\cdot T^{-1}$ and $\Lambda_{\mathrm{imp}} = \sigma\cdot M\cdot \rho^{-1}$; ionicity $I = \Lambda_{\mathrm{imp}}\cdot\Lambda_{\mathrm{NMR}}^{-1}$. [b] mean values over all measured nuclei, see table S4 for details. [c] obtained with dstebpgp3s pulse sequence. n.d.: not determined.

# 12 Cytotoxicity

Cytotoxicity of selected $[EMIm]^+$ and $[BMPL]^+$ RTILs as well as cyano(fluoro)borate and cyano(hydrido)borate anions including the anion $[BFH(CN)_2]^-$ (FHB) with sodium and potassium as counterion was conducted by formazan assay. The number of viable cells is determined by the cleavage of a tetrazolium salt into formazan by cellular enzymes. A decrease in the number of viable cells leads to a decrease in mitochondrial dehydrogenase and thus to lower formazan values. Cyano(fluoro)borate, cyano(hydrido)borate and FHB salts were dissolved in cell culture medium (DMEM + 10% FCS + 1% P/S) to a final concentration of 100 mM. EMIm- and BMPL-RTILs were dissolved in cell culture medium (DMEM + 10% FCS + 1% P/S) containing 2% DMSO to a final concentration of 100 mM. HEK 293 (4x104 cells/mL, 100 µL per well) and NIH3T3 (3x104 cells/mL, 100 µL per well) were seeded in a 96-well plate. Dilution series of each salt/RTIL ranging from 100 µM to 256 nM were prepared in growth medium and added (1:1 [V/V]) to the cells. A dilution series with DMSO was used as a solvent control for RTILs. Cells were incubated for 24 h at 37 °C and 5% $CO_2$, respectively. After incubation, 10 µL WST-1 reagent was added to each well and cells were incubated for up to four hours at 37 °C according to manufacturer instructions. Every 60 minutes, cells were analyzed and the absorbance of the soluble formazan product at 450 nm as well as background noise at 630 nm was determined using an Infinite M Plex microplate reader (Tecan Group Ltd., Männedorf, Switzerland). Relative cell viability (proliferation) with respect to untreated sample is expressed.

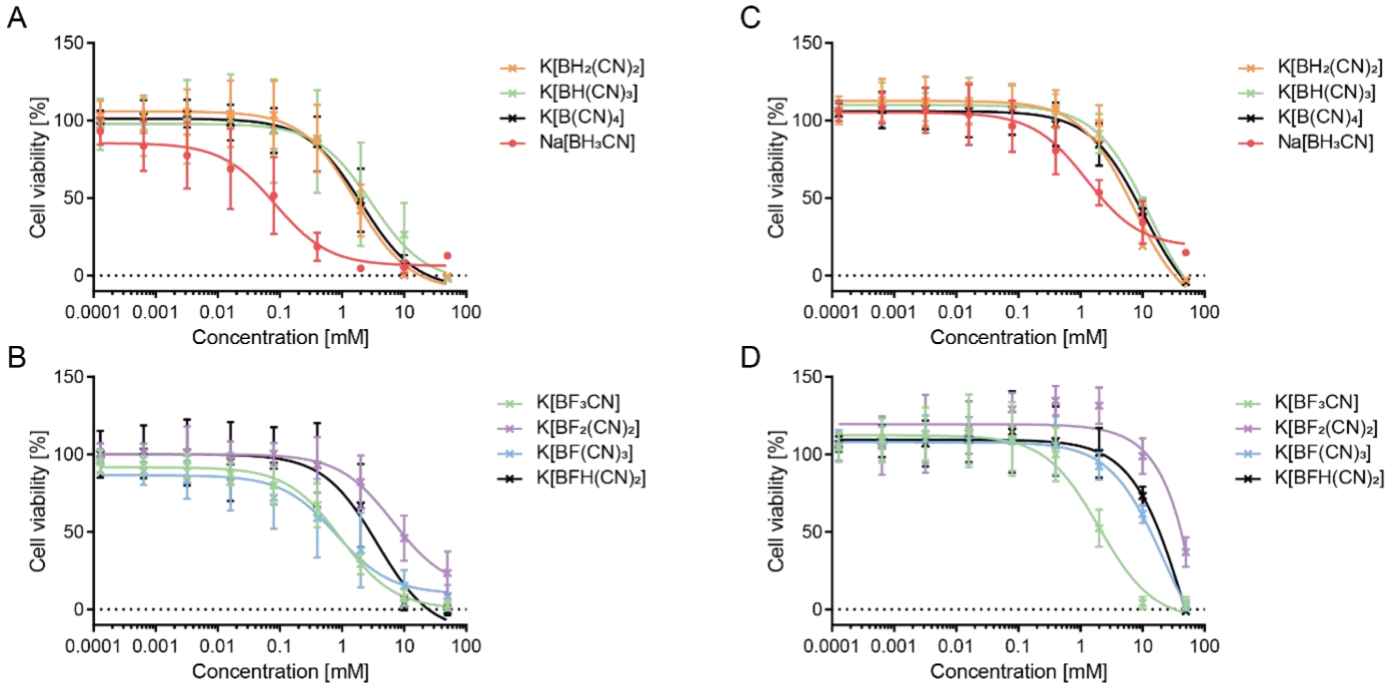


**Figure S157**: **Cytotoxic evaluation using NIH3T3 (A,B) and HEK293 (C,D) cells of selected cyano(fluoro)borate and cyano(hydrido)borate anions including the anion [BFH(CN)$_2$] (FHB) with sodium and potassium as counterion.**

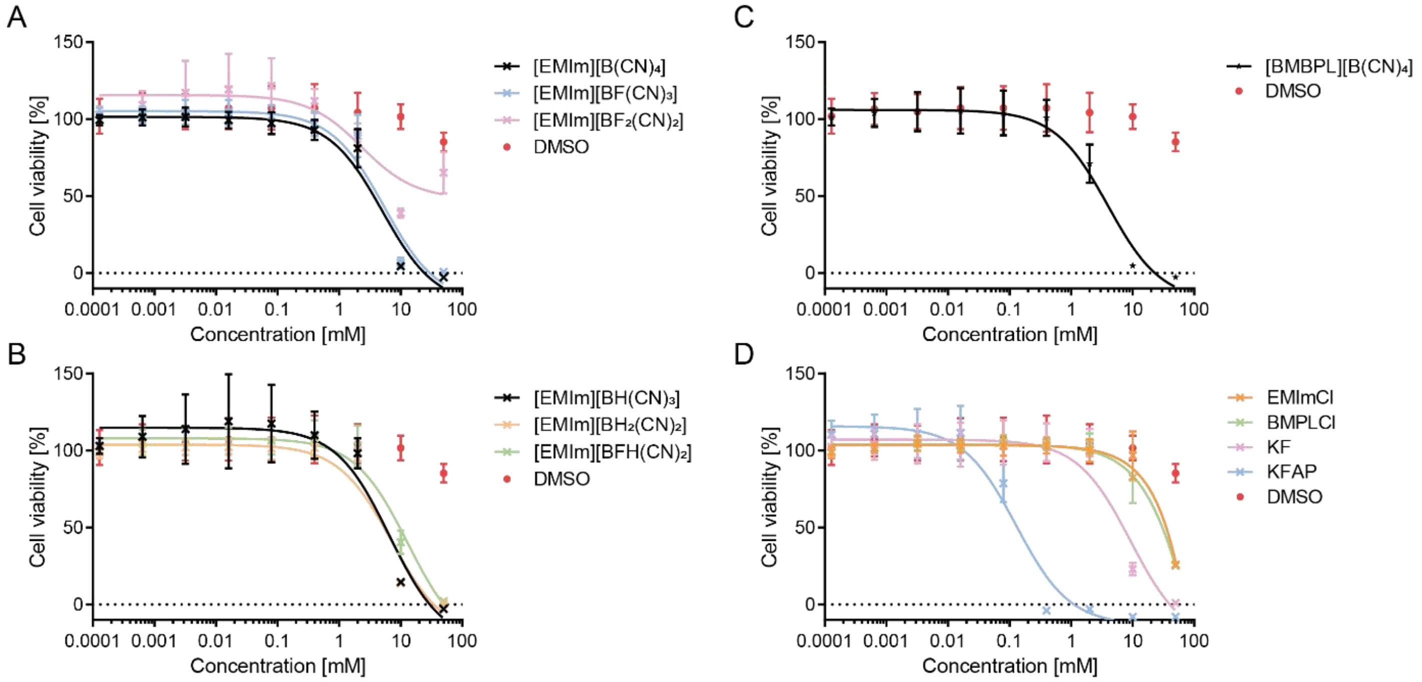
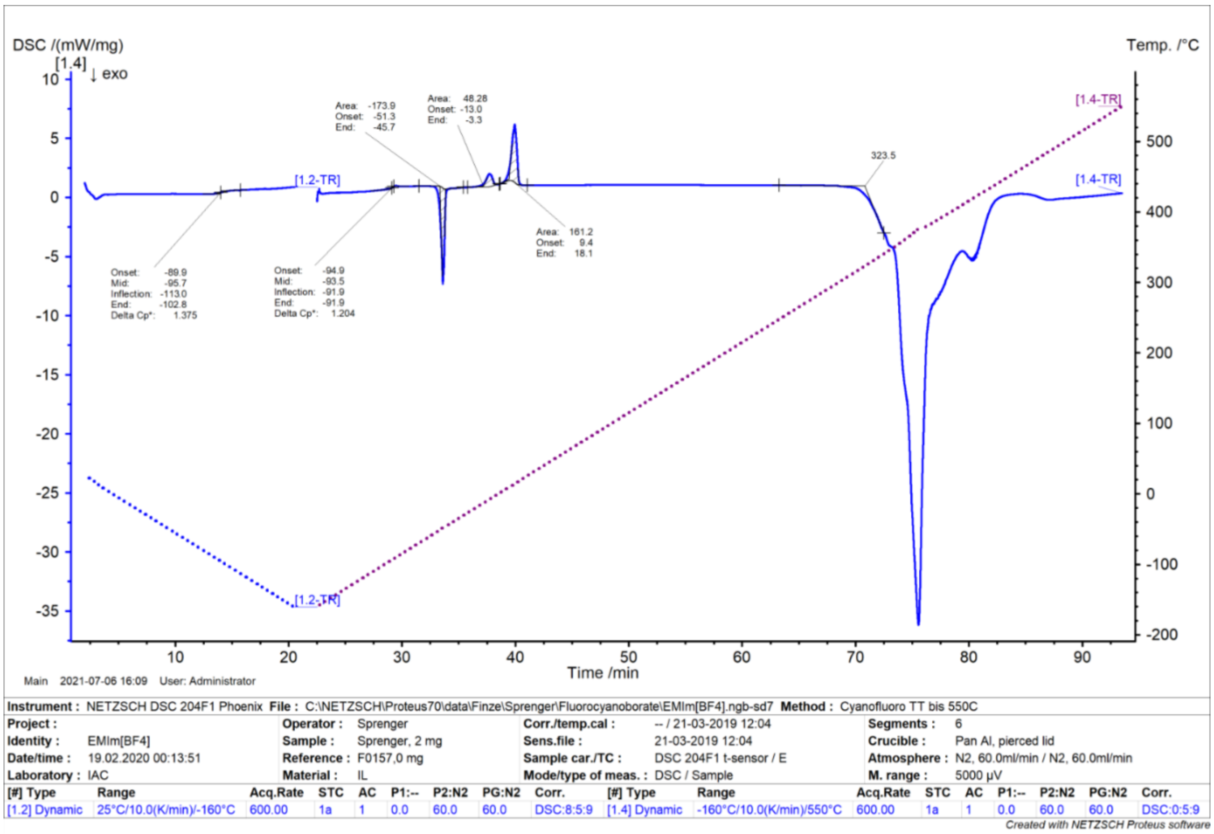


**Figure S158**: **Cytotoxic evaluation using HEK293 cells of selected EMIm- and BMPL-RTILs.**

# 13 Thermal Properties

## 13.1 [EMIm] salts



Main 2021-07-06 16:09 User: Administrator

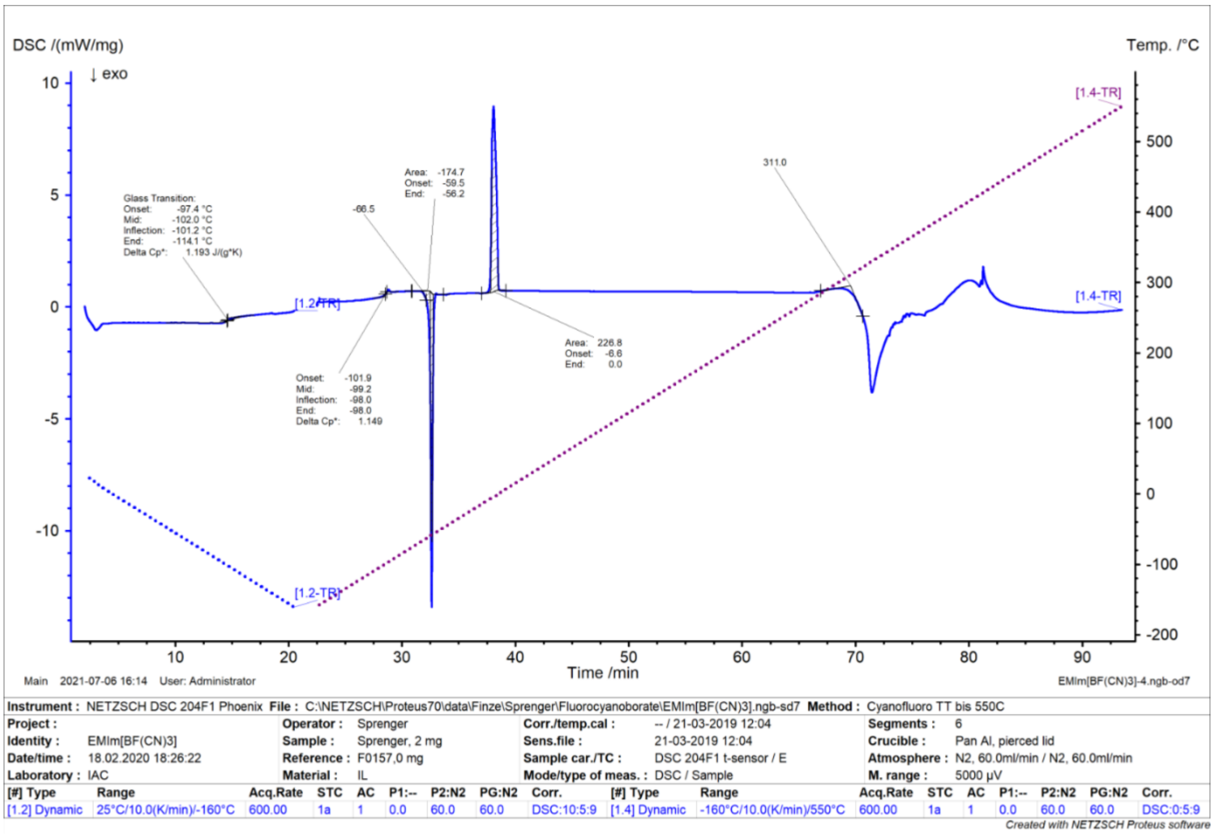
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\EMIm[BF4].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | EMIm[BF4] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 19.02.2020 00:13:51 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:8:5:9 |
| [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:0:5:9 |

*Created with NETZSCH Proteus software*

**Figure S159: DSC curve of [EMIm][BF$_4$].**



Main 2021-07-06 16:14 User: Administrator EMIm[BF(CN)3]-4.ngb-od7

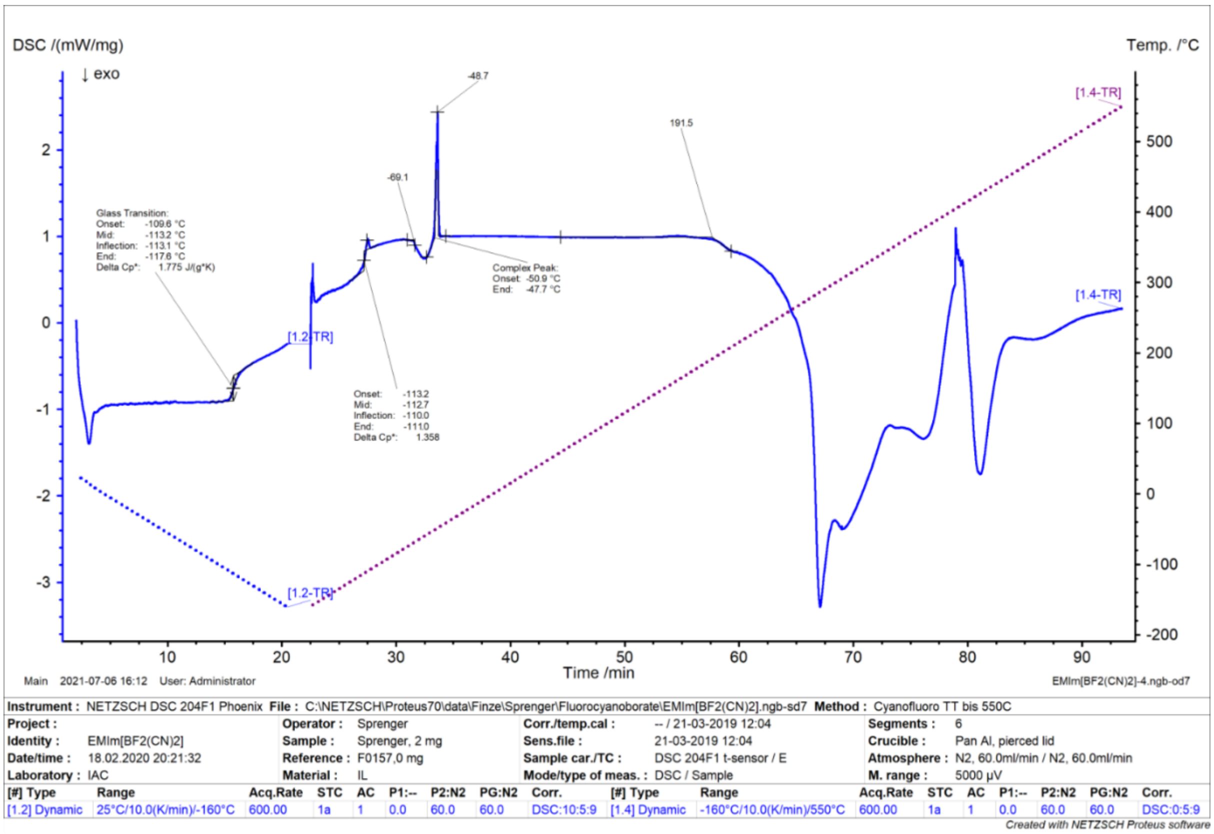
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\EMIm[BF(CN)3].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | EMIm[BF(CN)3] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 18.02.2020 18:26:22 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:10:5:9 |
| [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:0:5:9 |

*Created with NETZSCH Proteus software*

**Figure S160: DSC curve of [EMIm][BF$_3$(CN)].**



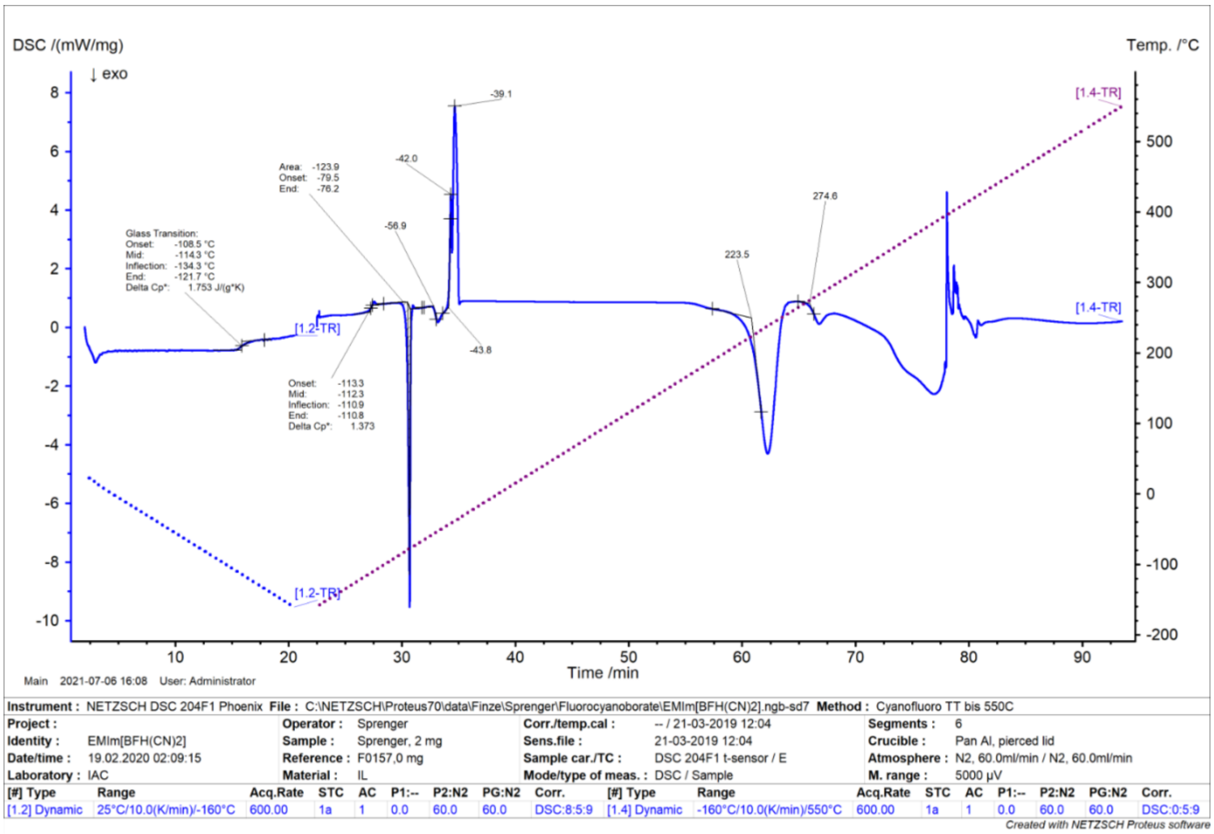
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\EMIm[BF2(CN)2].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | EMIm[BF2(CN)2] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 18.02.2020 20:21:32 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:10:5:9 | [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:0:5:9 |

*Created with NETZSCH Proteus software*

**Figure S161: DSC curve of [EMIm][$BF_2(CN)_2$].**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\EMIm[BFH(CN)2].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

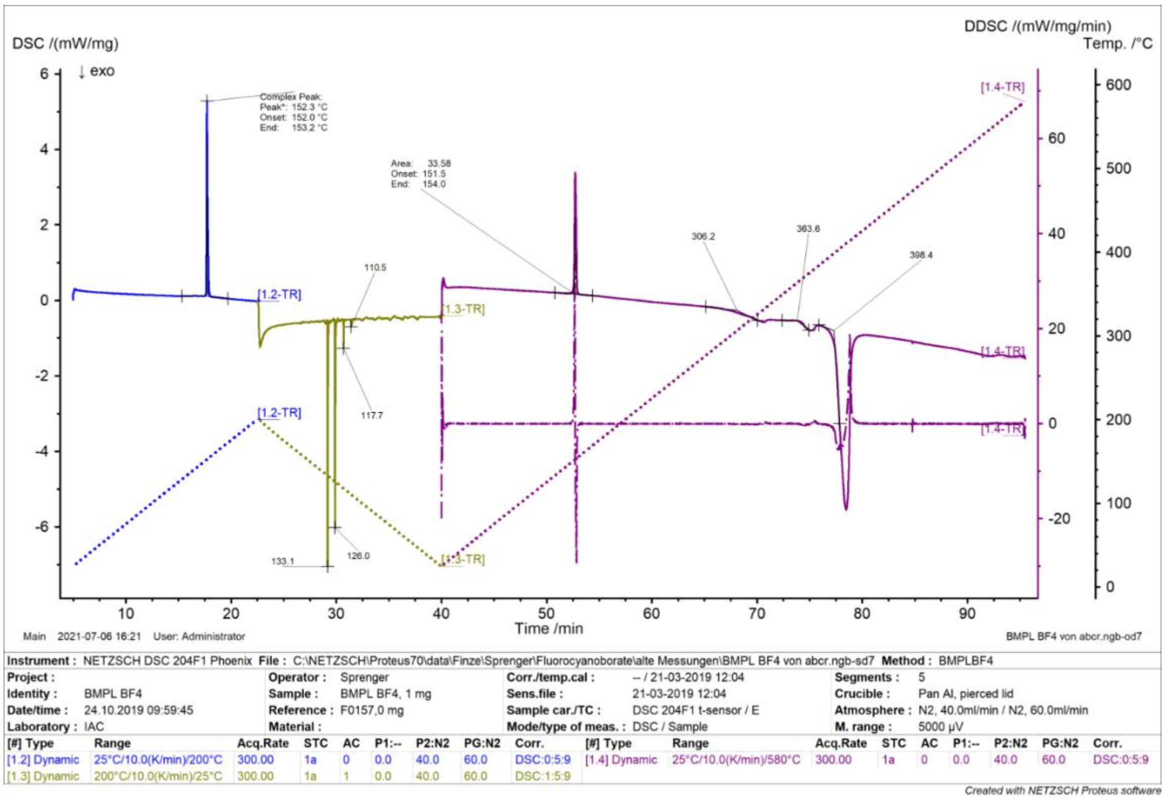
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | EMIm[BFH(CN)2] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 19.02.2020 02:09:15 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:8:5:9 | [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:0:5:9 |

*Created with NETZSCH Proteus software*

**Figure S162: DSC curve of [EMIm][$BFH(CN)_2$].**

## 13.2 [BMPL] salts



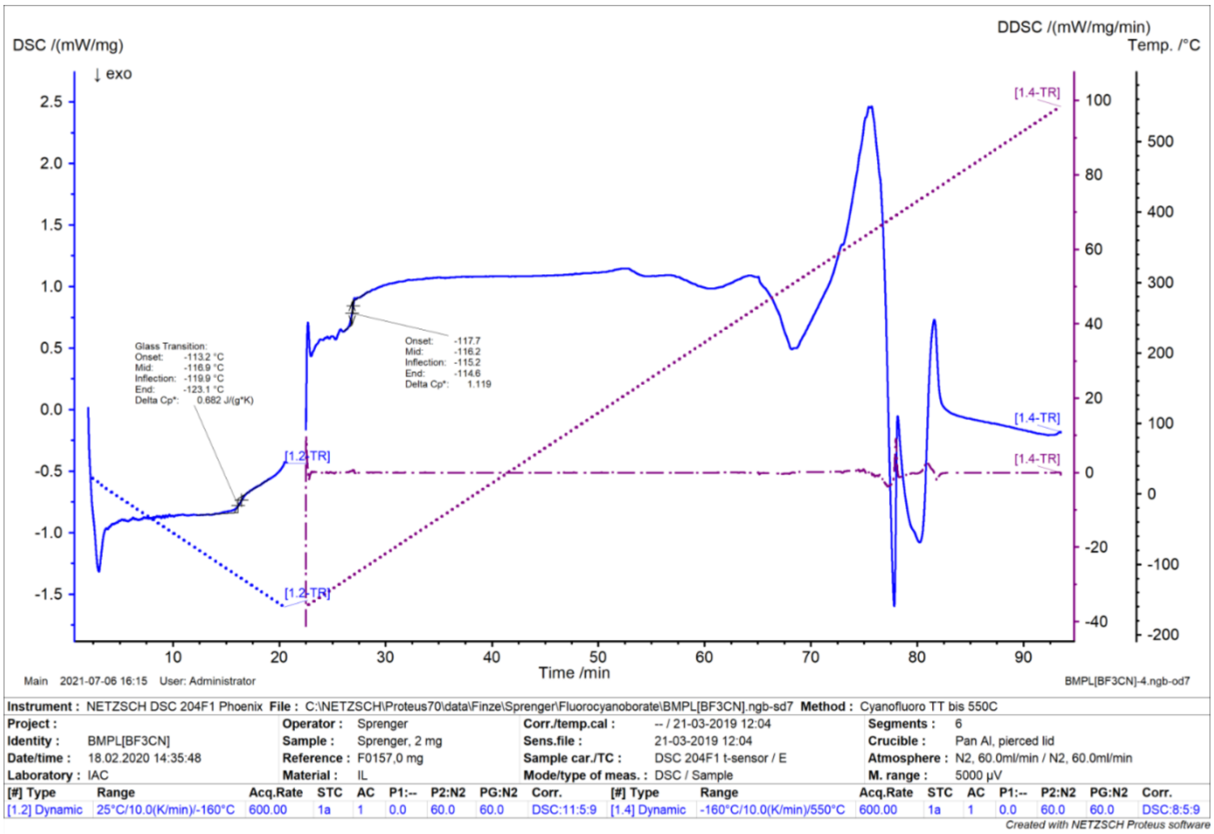
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\alte Messungen\BMPL BF4 von abcr.ngb-sd7 **Method :** BMPLBF4

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 5 |
| **Identity :** | BMPL BF4 | **Sample :** | BMPL BF4, 1 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 24.10.2019 09:59:45 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 40.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/200°C | 300.00 | 1a | 0 | 0.0 | 40.0 | 60.0 | DSC:0:5:9 | [1.4] Dynamic | 25°C/10.0(K/min)/580°C | 300.00 | 1a | 0 | 0.0 | 40.0 | 60.0 | DSC:0:5:9 |
| [1.3] Dynamic | 200°C/10.0(K/min)/25°C | 300.00 | 1a | 1 | 0.0 | 40.0 | 60.0 | DSC:1:5:9 | | | | | | | | | |

*Created with NETZSCH Proteus software*

**Figure S163: DSC curve of [BMPL][$BF_4$].**



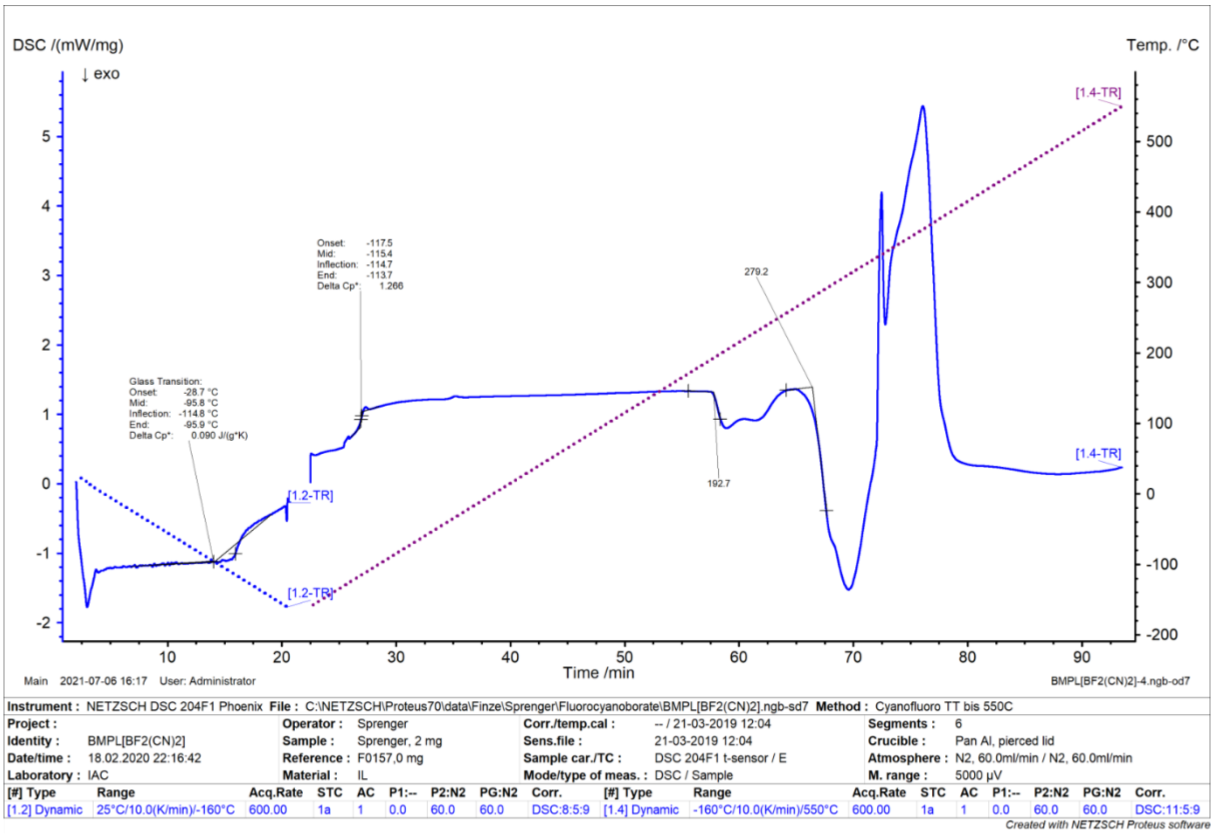
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\BMPL[BF3CN].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | BMPL[BF3CN] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 18.02.2020 14:35:48 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:11:5:9 | [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:8:5:9 |

*Created with NETZSCH Proteus software*

**Figure S164: DSC curve of [BMPL][$BF_3(CN)$].**



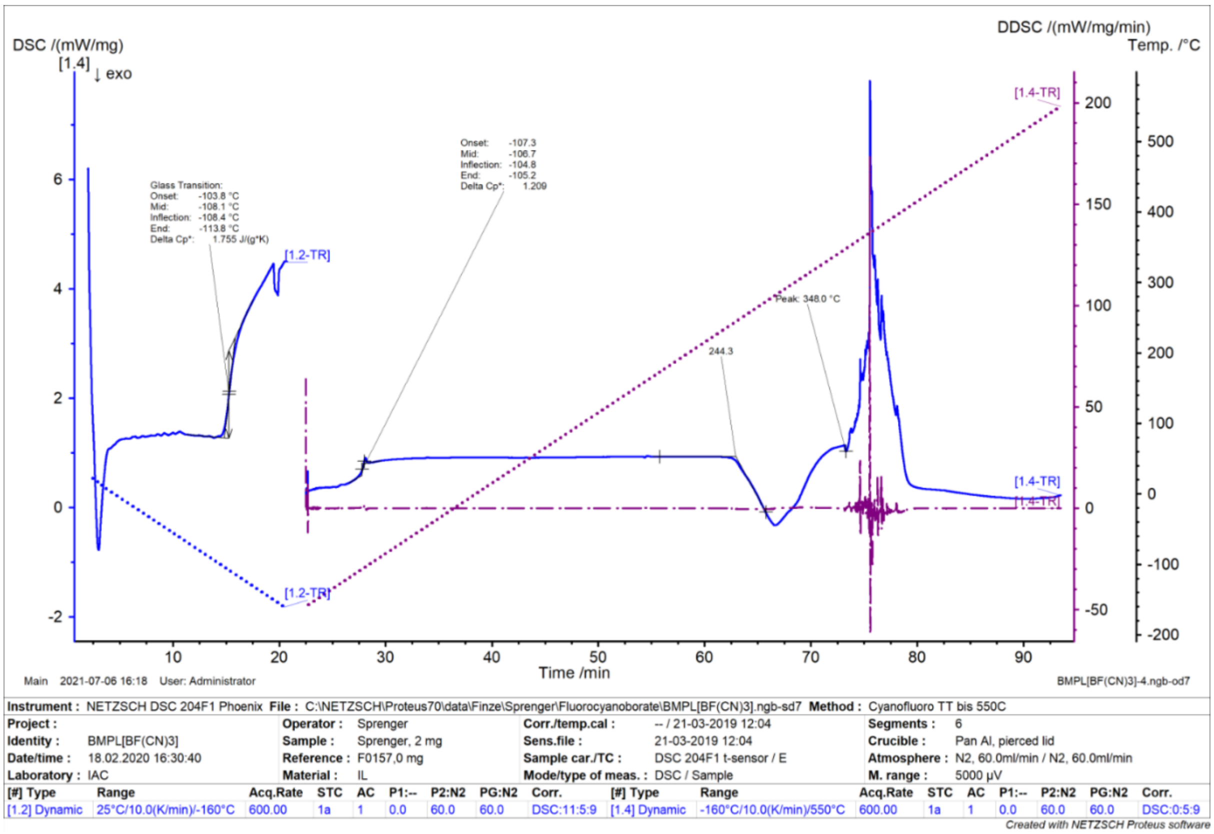
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\BMPL[BF2(CN)2].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | BMPL[BF2(CN)2] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 18.02.2020 22:16:42 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:8:5:9 | [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:11:5:9 |

*Created with NETZSCH Proteus software*

**Figure S165: DSC curve of [BMPL][$BF_2(CN)_2$].**



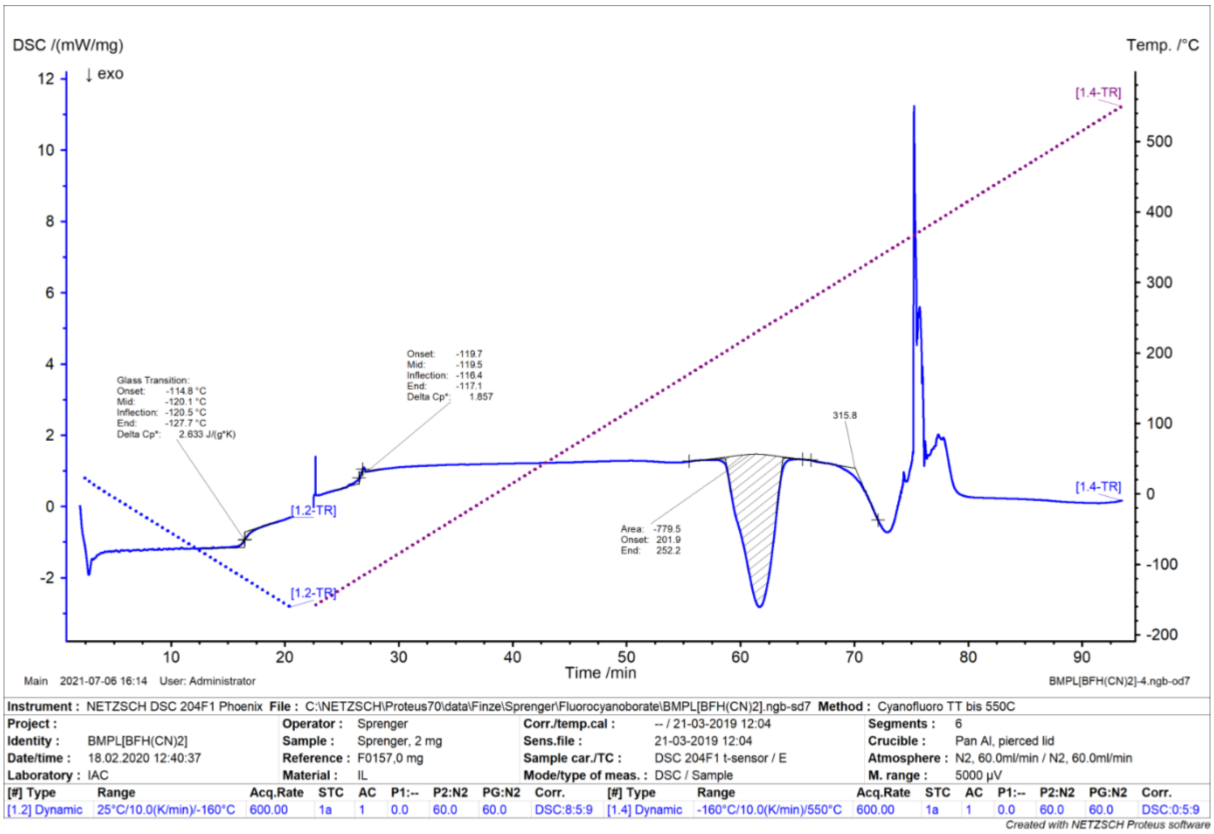
**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\BMPL[BF(CN)3].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | BMPL[BF(CN)3] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 18.02.2020 16:30:40 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:11:5:9 | [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:0:5:9 |

*Created with NETZSCH Proteus software*

**Figure S166: DSC curve of [BMPL][$BF(CN)_3$].**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Sprenger\Fluorocyanoborate\BMPL[BFH(CN)2].ngb-sd7 **Method :** Cyanofluoro TT bis 550C

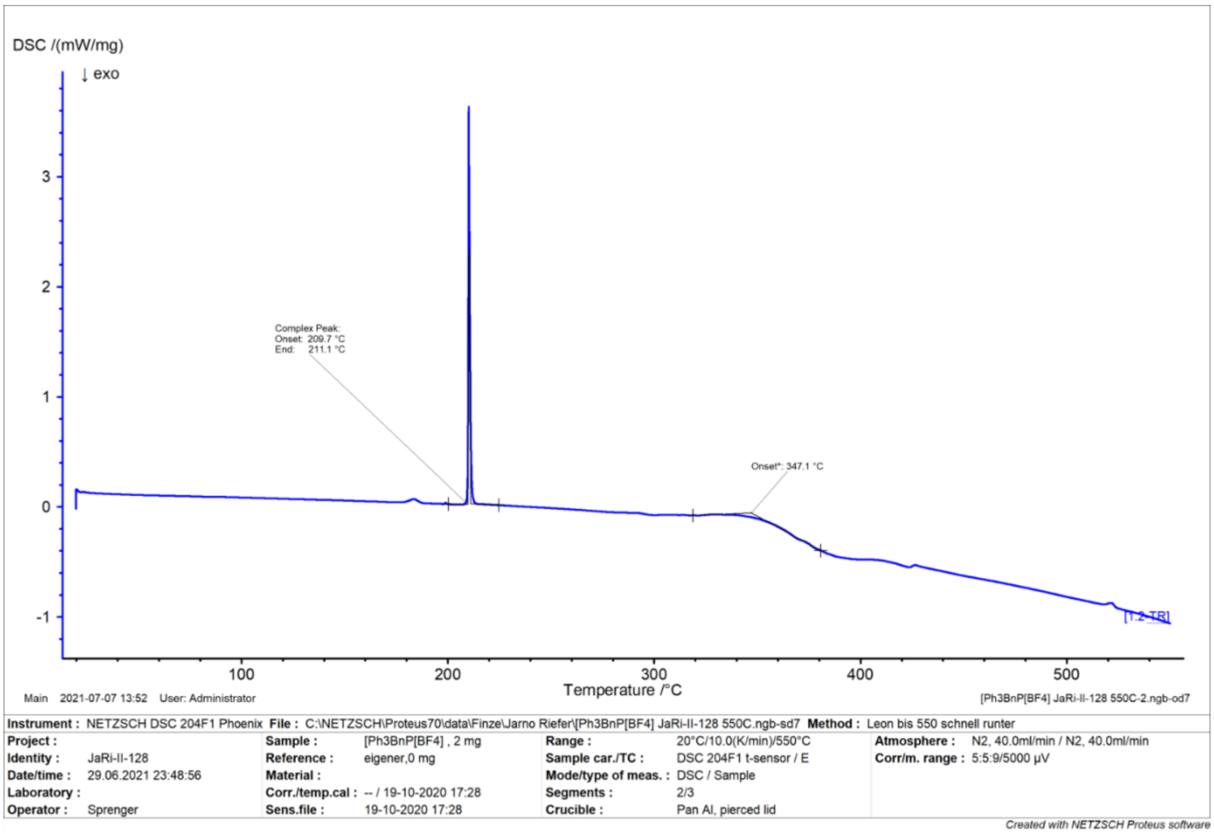
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 21-03-2019 12:04 | **Segments :** | 6 |
| **Identity :** | BMPL[BFH(CN)2] | **Sample :** | Sprenger, 2 mg | **Sens.file :** | 21-03-2019 12:04 | **Crucible :** | Pan Al, pierced lid |
| **Date/time :** | 18.02.2020 12:40:37 | **Reference :** | F0157,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 60.0ml/min / N2, 60.0ml/min |
| **Laboratory :** | IAC | **Material :** | IL | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV |

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/-160°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:8:5:9 | [1.4] Dynamic | -160°C/10.0(K/min)/550°C | 600.00 | 1a | 1 | 0.0 | 60.0 | 60.0 | DSC:0:5:9 |

*Created with NETZSCH Proteus software*

**Figure S167: DSC curve of [BMPL][BFH(CN)$_2$].**

## 13.3 [BnPh$_3$P] salts

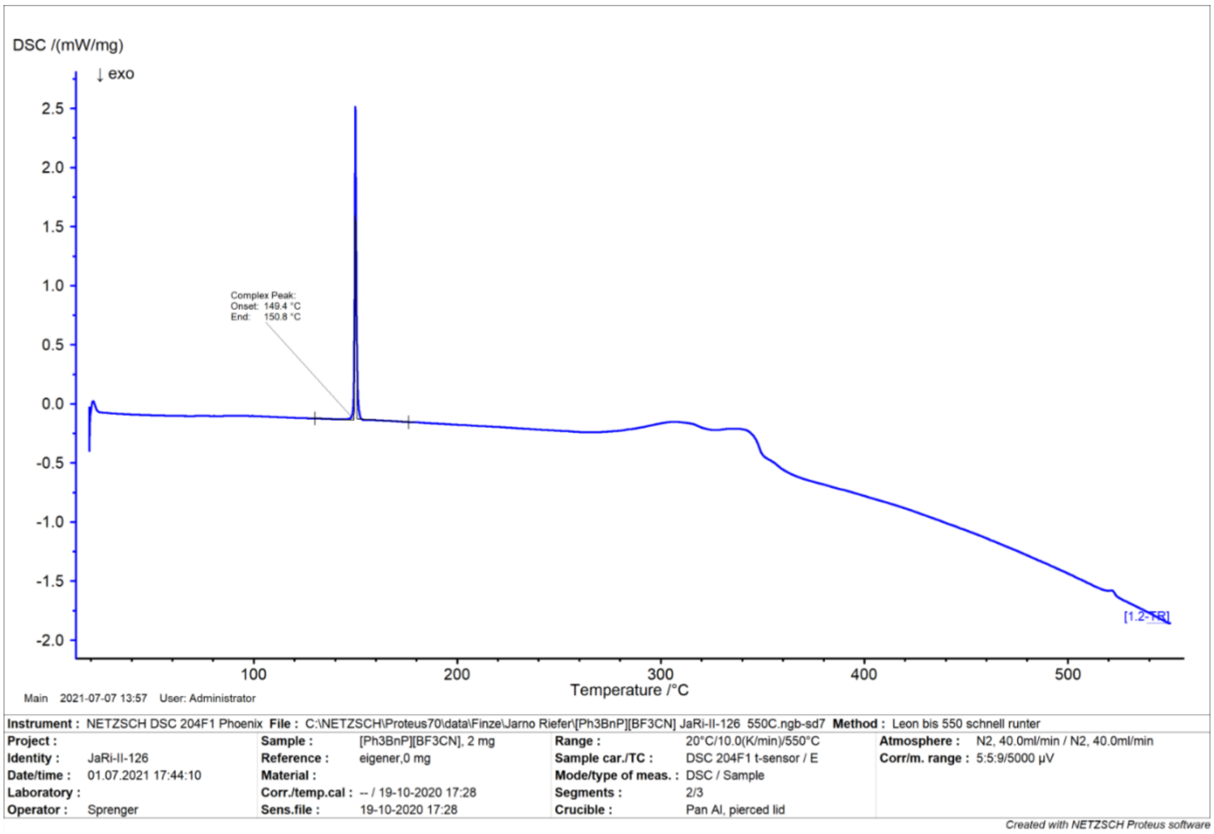


**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP[BF4] JaRi-II-128 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Sample :** | [Ph3BnP[BF4] , 2 mg | **Range :** | 20°C/10.0(K/min)/550°C | **Atmosphere :** | N2, 40.0ml/min / N2, 40.0ml/min |
| **Identity :** | JaRi-II-128 | **Reference :** | eigener,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Corr/m. range :** | 5:5:9/5000 µV |
| **Date/time :** | 29.06.2021 23:48:56 | **Material :** | | **Mode/type of meas. :** | DSC / Sample | | |
| **Laboratory :** | | **Corr./temp.cal :** | -- / 19-10-2020 17:28 | **Segments :** | 2/3 | | |
| **Operator :** | Sprenger | **Sens.file :** | 19-10-2020 17:28 | **Crucible :** | Pan Al, pierced lid | | |

*Created with NETZSCH Proteus software*

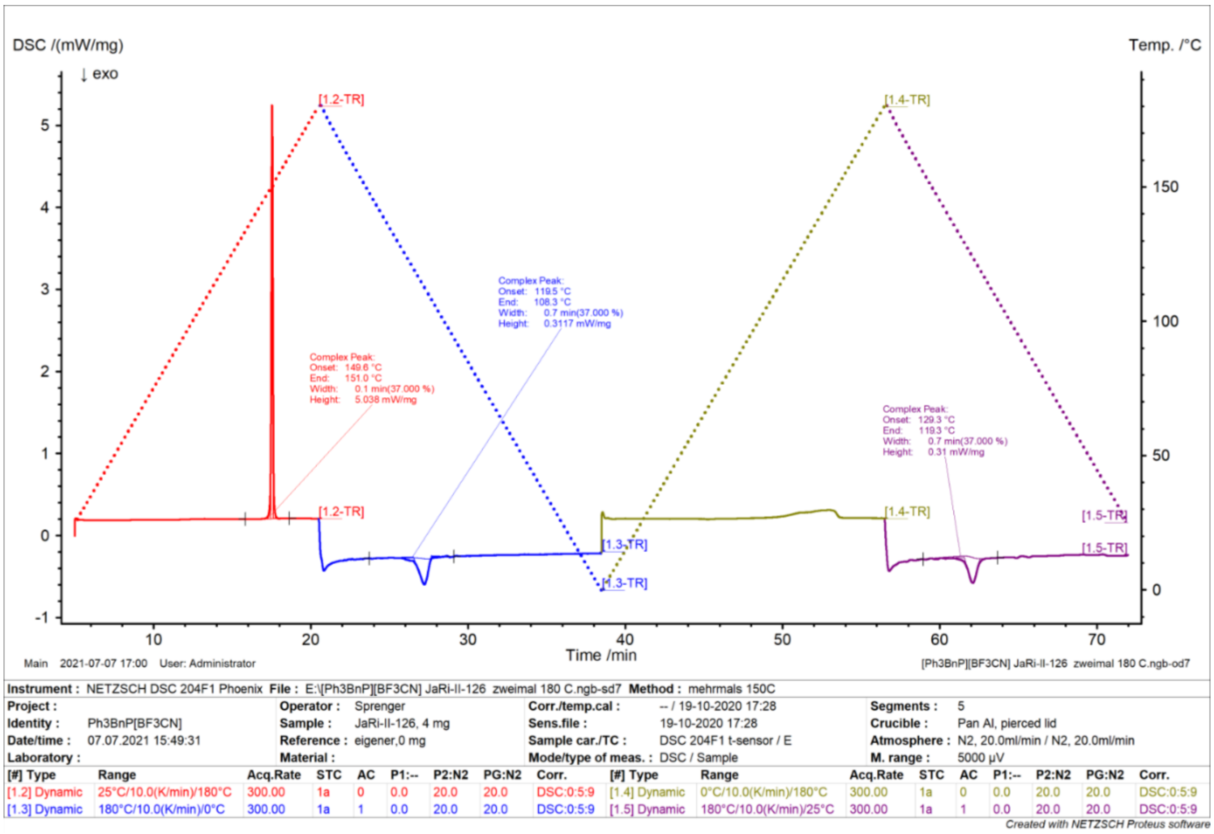
**Figure S168: DSC curve of [BnPh$_3$P][BF$_4$].**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP][BF3CN] JaRi-II-126 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

**Project :**
**Identity :** JaRi-II-126
**Date/time :** 01.07.2021 17:44:10
**Laboratory :**
**Operator :** Sprenger
**Sample :** [Ph3BnP][BF3CN], 2 mg
**Reference :** eigener,0 mg
**Material :**
**Corr./temp.cal :** -- / 19-10-2020 17:28
**Sens.file :** 19-10-2020 17:28
**Range :** 20°C/10.0(K/min)/550°C
**Sample car./TC :** DSC 204F1 t-sensor / E
**Mode/type of meas. :** DSC / Sample
**Segments :** 2/3
**Crucible :** Pan Al, pierced lid
**Atmosphere :** N2, 40.0ml/min / N2, 40.0ml/min
**Corr/m. range :** 5:5:9/5000 µV

**Figure S169: DSC curve of [$BnPh_3P$][$BF_3(CN)$].**

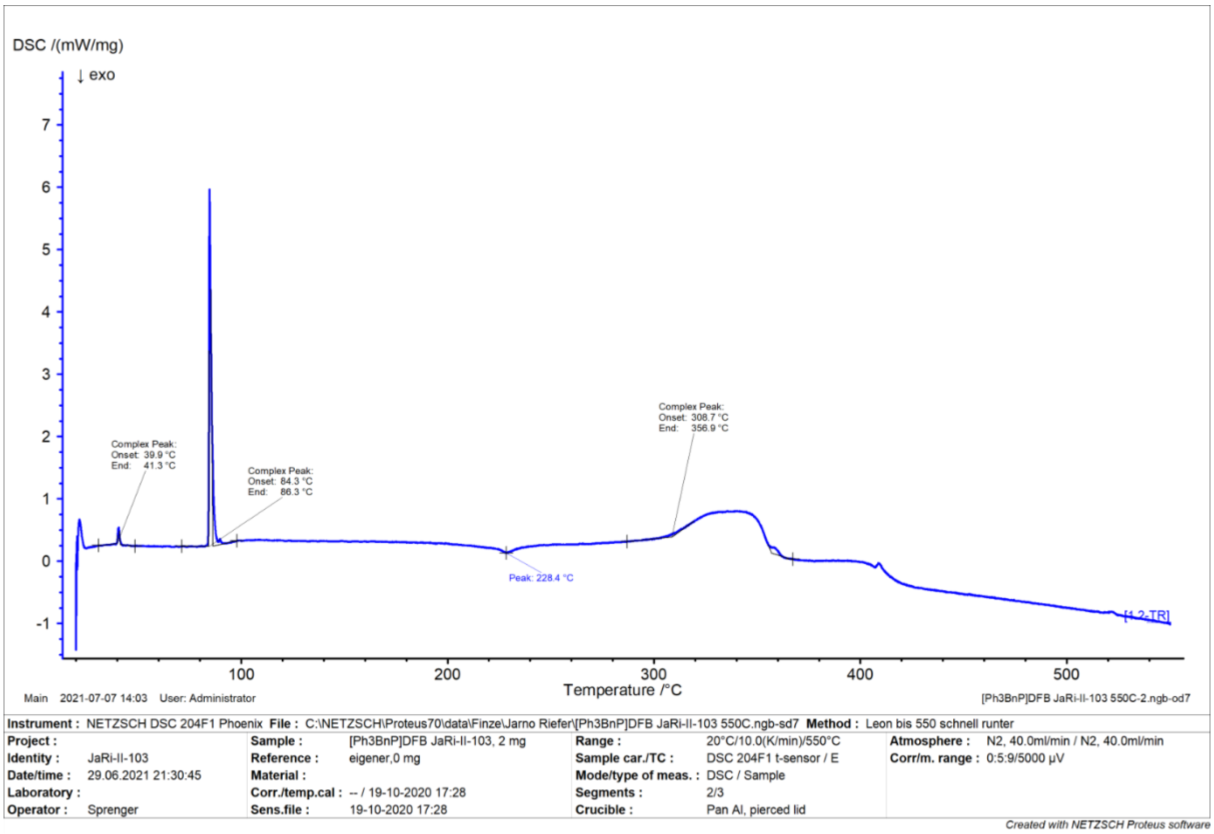


**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** E:\[Ph3BnP][BF3CN] JaRi-II-126 zweimal 180 C.ngb-sd7 **Method :** mehrmals 150C

**Project :**
**Identity :** Ph3BnP[BF3CN]
**Date/time :** 07.07.2021 15:49:31
**Laboratory :**
**Operator :** Sprenger
**Sample :** JaRi-II-126, 4 mg
**Reference :** eigener,0 mg
**Material :**
**Corr./temp.cal :** -- / 19-10-2020 17:28
**Sens.file :** 19-10-2020 17:28
**Sample car./TC :** DSC 204F1 t-sensor / E
**Mode/type of meas. :** DSC / Sample
**Segments :** 5
**Crucible :** Pan Al, pierced lid
**Atmosphere :** N2, 20.0ml/min / N2, 20.0ml/min
**M. range :** 5000 µV

| [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. | [#] Type | Range | Acq.Rate | STC | AC | P1:-- | P2:N2 | PG:N2 | Corr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [1.2] Dynamic | 25°C/10.0(K/min)/180°C | 300.00 | 1a | 0 | 0.0 | 20.0 | 20.0 | DSC:0:5:9 | [1.4] Dynamic | 0°C/10.0(K/min)/180°C | 300.00 | 1a | 0 | 0.0 | 20.0 | 20.0 | DSC:0:5:9 |
| [1.3] Dynamic | 180°C/10.0(K/min)/0°C | 300.00 | 1a | 1 | 0.0 | 20.0 | 20.0 | DSC:0:5:9 | [1.5] Dynamic | 180°C/10.0(K/min)/25°C | 300.00 | 1a | 1 | 0.0 | 20.0 | 20.0 | DSC:0:5:9 |

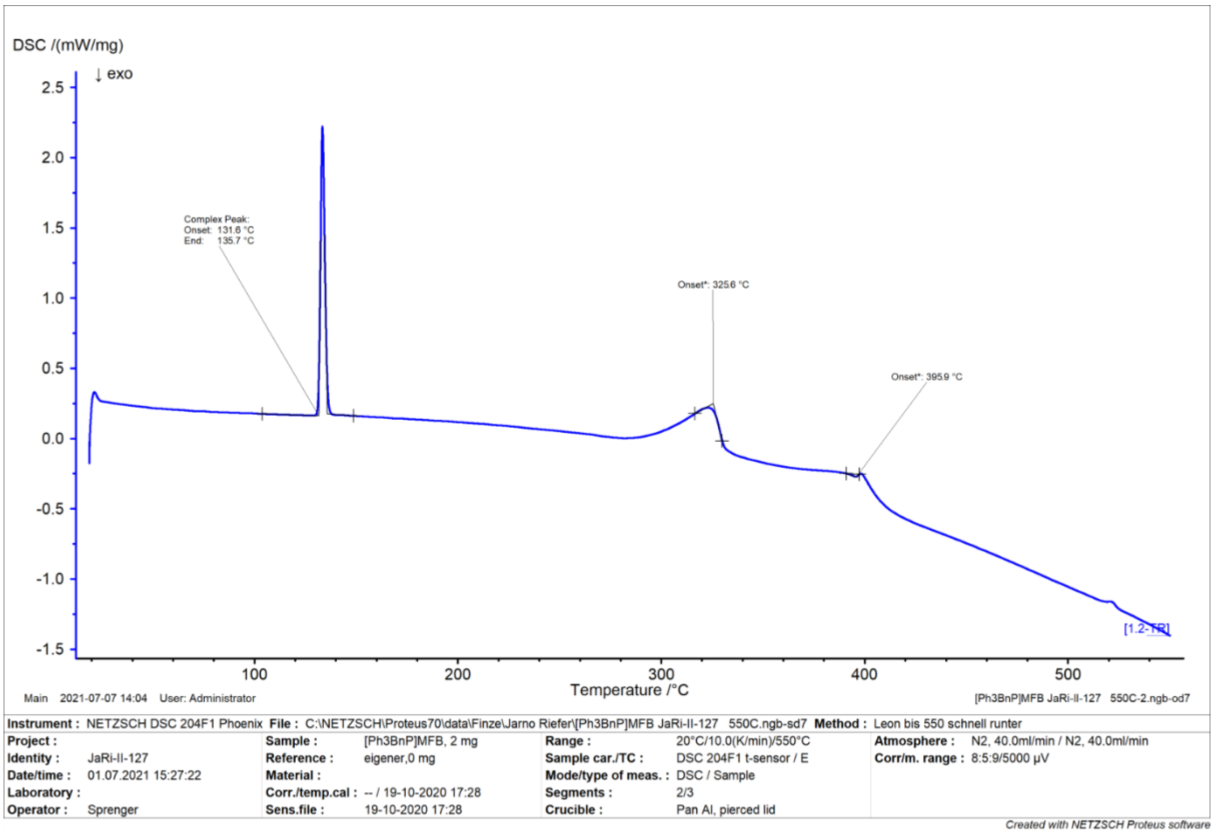
**Figure S170: DSC curve of [$BnPh_3P$][$BF_3(CN)$].**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP]DFB JaRi-II-103 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Sample :** | [Ph3BnP]DFB JaRi-II-103, 2 mg | **Range :** | 20°C/10.0(K/min)/550°C | **Atmosphere :** | N2, 40.0ml/min / N2, 40.0ml/min |
| **Identity :** | JaRi-II-103 | **Reference :** | eigener,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Corr/m. range :** | 0:5:9/5000 µV |
| **Date/time :** | 29.06.2021 21:30:45 | **Material :** | | **Mode/type of meas. :** | DSC / Sample | | |
| **Laboratory :** | | **Corr./temp.cal :** | -- / 19-10-2020 17:28 | **Segments :** | 2/3 | | |
| **Operator :** | Sprenger | **Sens.file :** | 19-10-2020 17:28 | **Crucible :** | Pan Al, pierced lid | | |

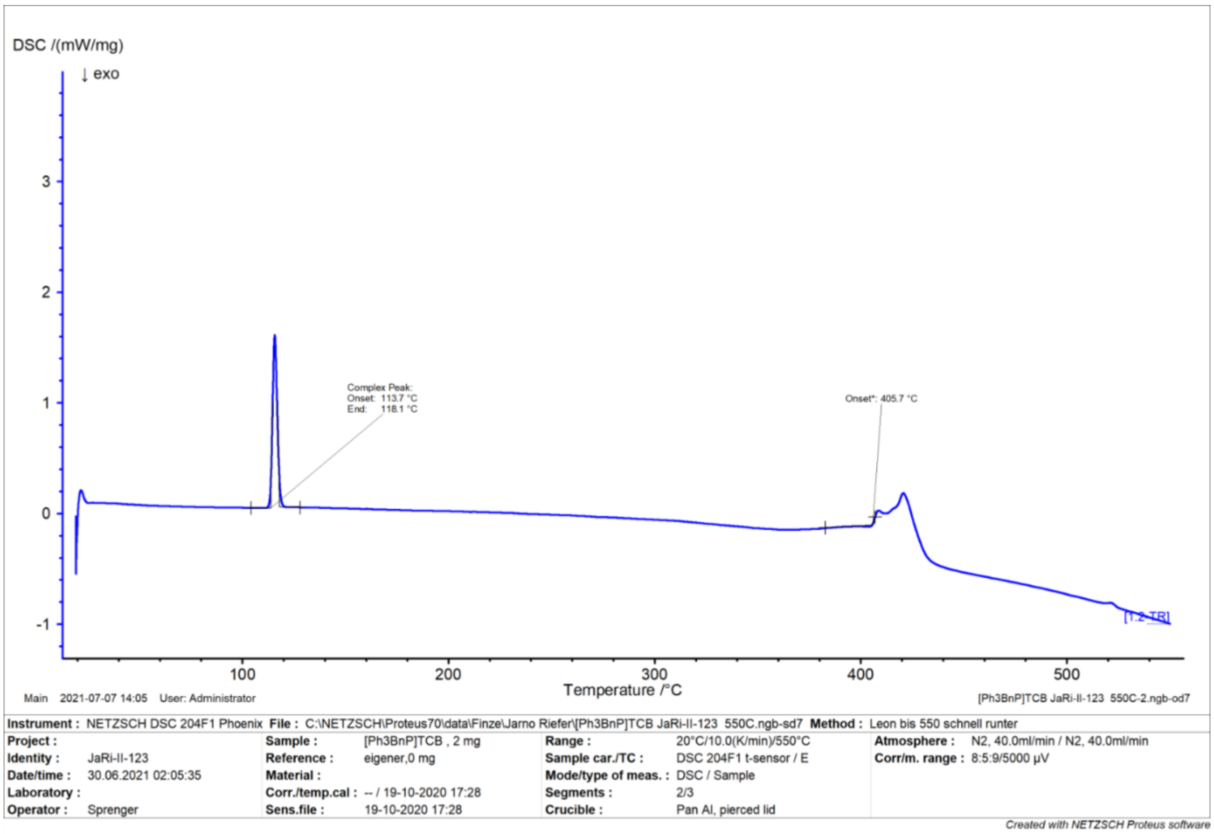
**Figure S171: DSC curve of [BnPh$_3$P][BF$_2$(CN)$_2$].**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP]MFB JaRi-II-127 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Sample :** | [Ph3BnP]MFB, 2 mg | **Range :** | 20°C/10.0(K/min)/550°C | **Atmosphere :** | N2, 40.0ml/min / N2, 40.0ml/min |
| **Identity :** | JaRi-II-127 | **Reference :** | eigener,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Corr/m. range :** | 8:5:9/5000 µV |
| **Date/time :** | 01.07.2021 15:27:22 | **Material :** | | **Mode/type of meas. :** | DSC / Sample | | |
| **Laboratory :** | | **Corr./temp.cal :** | -- / 19-10-2020 17:28 | **Segments :** | 2/3 | | |
| **Operator :** | Sprenger | **Sens.file :** | 19-10-2020 17:28 | **Crucible :** | Pan Al, pierced lid | | |

**Figure S172: DSC curve of [BnPh$_3$P][BF(CN)$_3$].**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP]TCB JaRi-II-123 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

**Project :**
**Identity :** JaRi-II-123
**Date/time :** 30.06.2021 02:05:35
**Laboratory :**
**Operator :** Sprenger

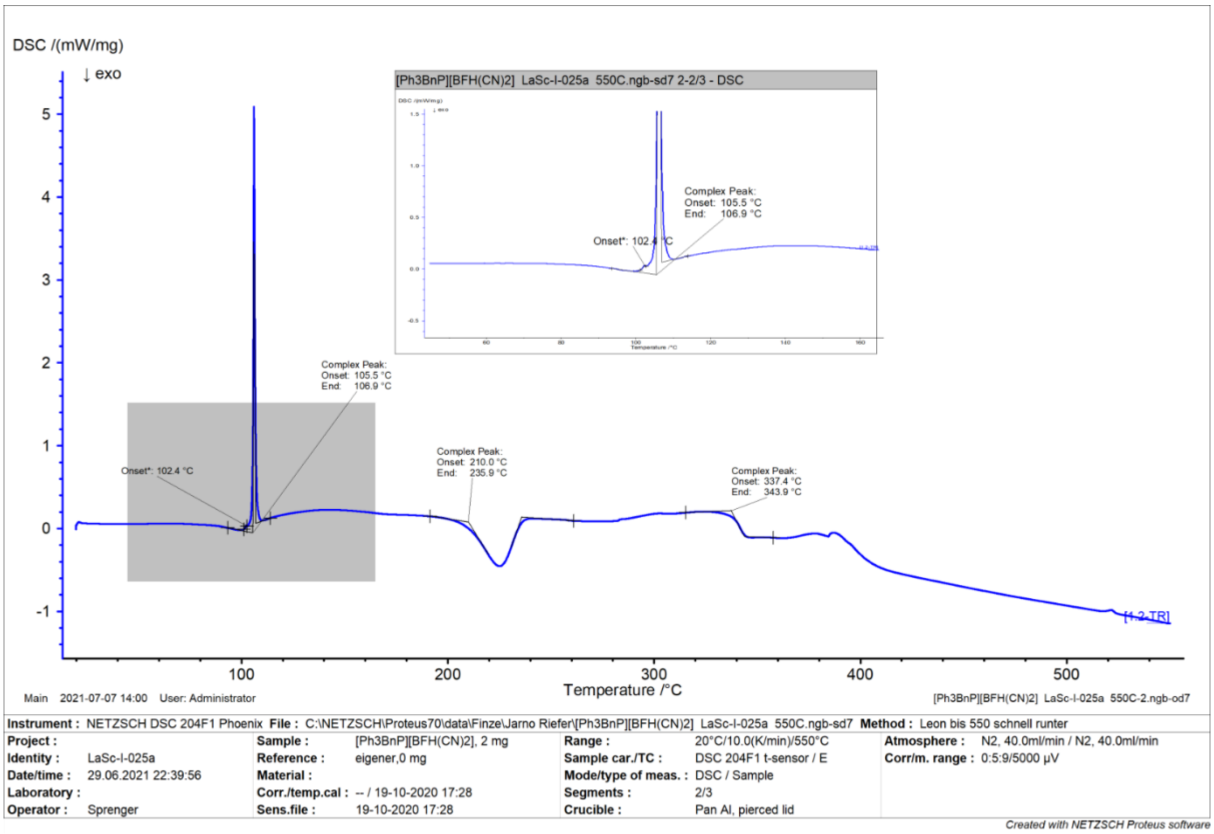
**Sample :** [Ph3BnP]TCB , 2 mg
**Reference :** eigener,0 mg
**Material :**
**Corr./temp.cal :** -- / 19-10-2020 17:28
**Sens.file :** 19-10-2020 17:28

**Range :** 20°C/10.0(K/min)/550°C
**Sample car./TC :** DSC 204F1 t-sensor / E
**Mode/type of meas. :** DSC / Sample
**Segments :** 2/3
**Crucible :** Pan Al, pierced lid

**Atmosphere :** N2, 40.0ml/min / N2, 40.0ml/min
**Corr/m. range :** 8:5:9/5000 µV

*Created with NETZSCH Proteus software*

**Figure S173: $[BnPh_3P][B(CN)_4]$.**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP][BFH(CN)2] LaSc-I-025a 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

**Project :**
**Identity :** LaSc-I-025a
**Date/time :** 29.06.2021 22:39:56
**Laboratory :**
**Operator :** Sprenger

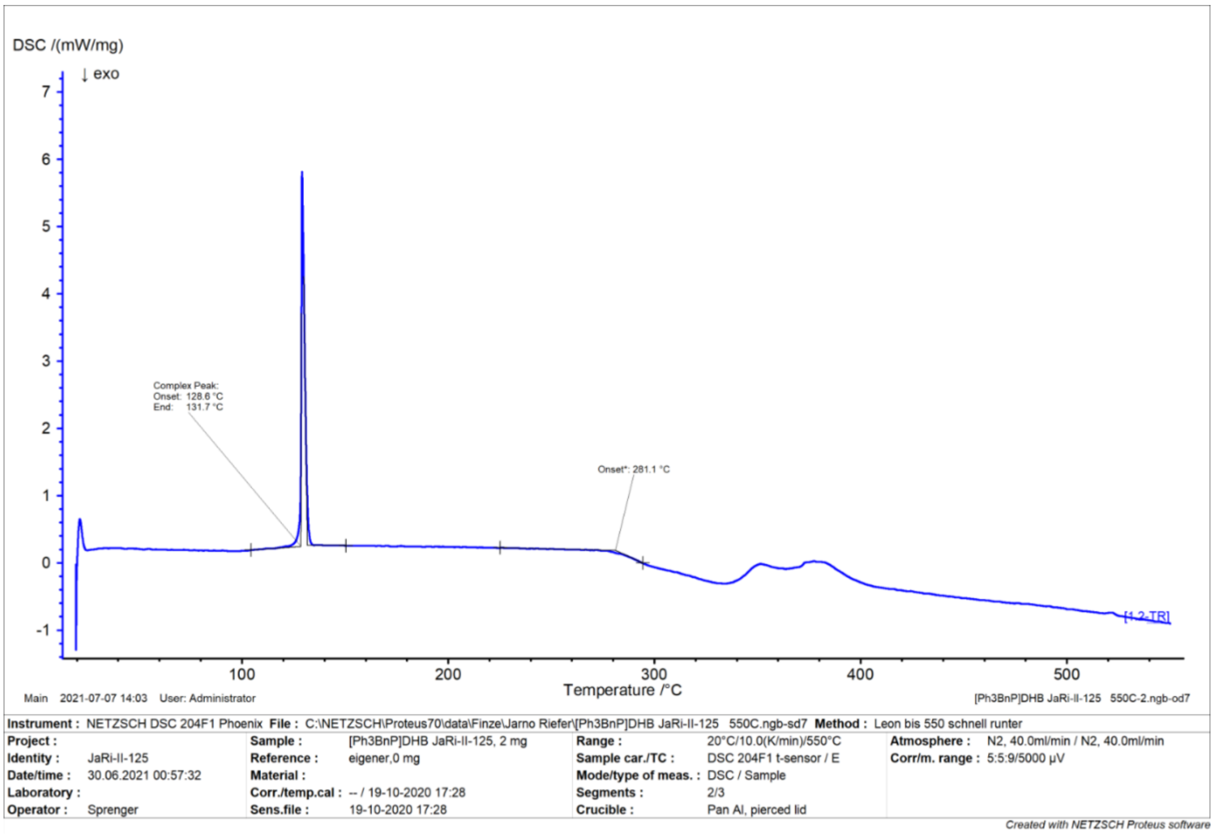
**Sample :** [Ph3BnP][BFH(CN)2], 2 mg
**Reference :** eigener,0 mg
**Material :**
**Corr./temp.cal :** -- / 19-10-2020 17:28
**Sens.file :** 19-10-2020 17:28

**Range :** 20°C/10.0(K/min)/550°C
**Sample car./TC :** DSC 204F1 t-sensor / E
**Mode/type of meas. :** DSC / Sample
**Segments :** 2/3
**Crucible :** Pan Al, pierced lid

**Atmosphere :** N2, 40.0ml/min / N2, 40.0ml/min
**Corr/m. range :** 0:5:9/5000 µV

*Created with NETZSCH Proteus software*

**Figure S174: DSC curve of $[BnPh_3P][BFH(CN)_2]$.**

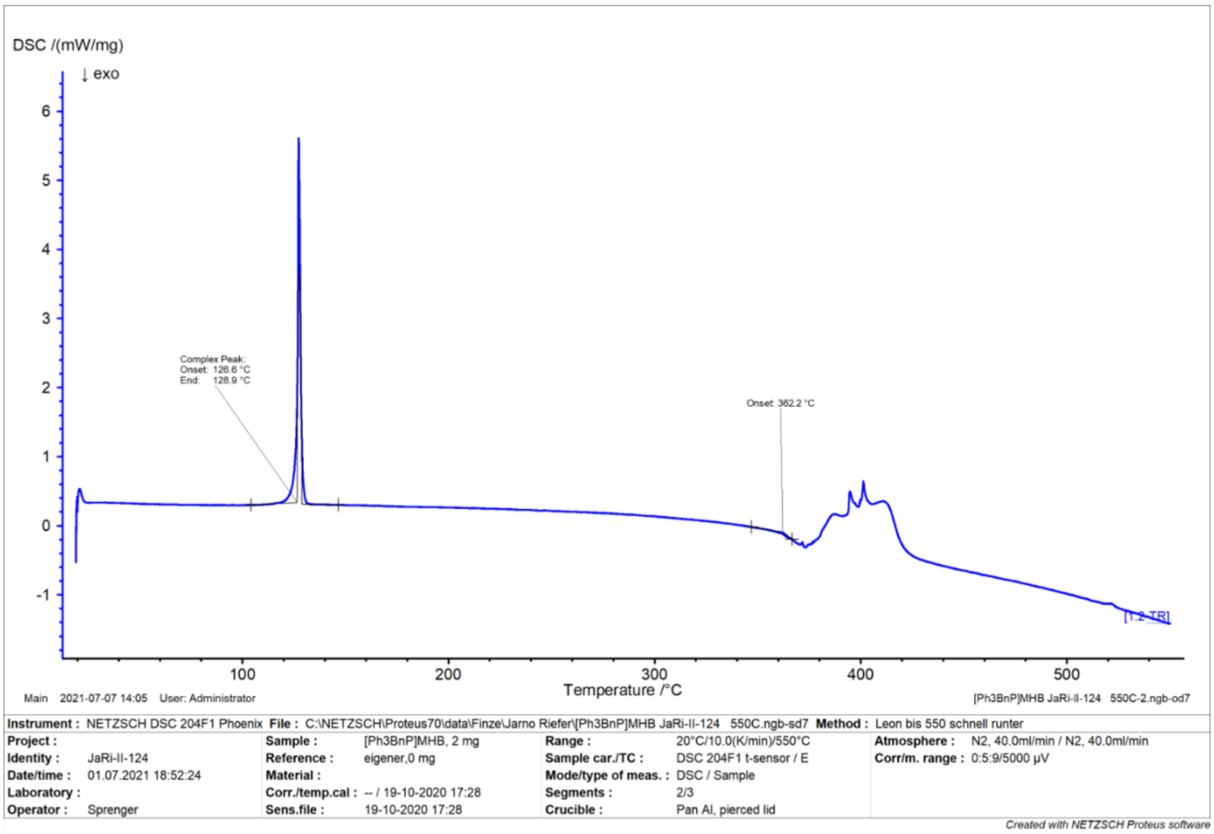


**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP]DHB JaRi-II-125 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Sample :** | [Ph3BnP]DHB JaRi-II-125, 2 mg | **Range :** | 20°C/10.0(K/min)/550°C | **Atmosphere :** | N2, 40.0ml/min / N2, 40.0ml/min |
| **Identity :** | JaRi-II-125 | **Reference :** | eigener,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Corr/m. range :** | 5:5:9/5000 µV |
| **Date/time :** | 30.06.2021 00:57:32 | **Material :** | | **Mode/type of meas. :** | DSC / Sample | | |
| **Laboratory :** | | **Corr./temp.cal :** | -- / 19-10-2020 17:28 | **Segments :** | 2/3 | | |
| **Operator :** | Sprenger | **Sens.file :** | 19-10-2020 17:28 | **Crucible :** | Pan Al, pierced lid | | |

*Created with NETZSCH Proteus software*

**Figure S175: DSC curve of $[BnPh_3P][BH_2(CN)_2]$.**



**Instrument :** NETZSCH DSC 204F1 Phoenix **File :** C:\NETZSCH\Proteus70\data\Finze\Jarno Riefer\[Ph3BnP]MHB JaRi-II-124 550C.ngb-sd7 **Method :** Leon bis 550 schnell runter

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project :** | | **Sample :** | [Ph3BnP]MHB, 2 mg | **Range :** | 20°C/10.0(K/min)/550°C | **Atmosphere :** | N2, 40.0ml/min / N2, 40.0ml/min |
| **Identity :** | JaRi-II-124 | **Reference :** | eigener,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Corr/m. range :** | 0:5:9/5000 µV |
| **Date/time :** | 01.07.2021 18:52:24 | **Material :** | | **Mode/type of meas. :** | DSC / Sample | | |
| **Laboratory :** | | **Corr./temp.cal :** | -- / 19-10-2020 17:28 | **Segments :** | 2/3 | | |
| **Operator :** | Sprenger | **Sens.file :** | 19-10-2020 17:28 | **Crucible :** | Pan Al, pierced lid | | |

*Created with NETZSCH Proteus software*

**Figure S176: DSC curve of $[BnPh_3P][BH(CN)_3]$.**

# 14 Quantum Chemical Calculations

Density functional calculations (DFT)[12] were carried out using the B3LYP functional[13] with the Gaussian16 program suite.[14] Geometries were optimized, and energies were calculated with the 6-311++G(d,p) or def2-TZVPP basis sets. Diffuse functions were incorporated because improved energies are obtained for anions.[15] All calculated structures represent true minima with no imaginary frequency on the respective hypersurface. Calculated energies are summarized in Tables S6a and S6b.

**Table S6*a*: Calculated electronic energies (EE), energies with zero-point corrections ($E_0$), enthalpies (H),and free energies(G) at the B3LYP/6-311+G(d,p) level of theory.**

| Species | Symmetry | *EE* / a.u. | $E_0$ / a.u. | *H* / a.u. | *G* / a.u. |
|---|---|---|---|---|---|
| $[BF_4]^-$ | $T_d$ | −424.679694 | −424.666025 | −424.660623 | −424.691361 |
| $[BF_3(CN)]^-$ | $C_{3v}$ | -417.636362 | -417.616753 | -417.610210 | -417.645096 |
| $[BF_2(CN)_2]^-$ | $C_{2v}$ | -410.588999 | -410.563414 | -410.555736 | -410.593802 |
| $[BF(CN)_3]^-$ | $C_{3v}$ | -403.545131 | -403.513328 | -403.504586 | -403.544877 |
| $[BFH(CN)_2]^-$ | $C_s$ | -311.247313 | -311.215304 | -311.208446 | -311.245063 |
| $[B(CN)_4]^-$ | $T_d$ | -396.509584 | -396.471239 | -396.461507 | -396.502909 |
| $[BH_3(CN)]^-$ | $C_{3v}$ | -119.605662 | -119.569409 | -119.564645 | -119.592633 |
| $[BH_2(CN)_2]^-$ | $C_{2v}$ | -211.920506 | -211.882496 | -211.876420 | -211.909823 |
| $[BH(CN)_3]^-$ | $C_{3v}$ | -304.221244 | -304.182611 | -304.174844 | -304.212768 |

**Table S7*b*: Calculated energies with zero-point corrections (E), enthalpies (H),and free energies(G) at the B3LYP/def2-TZVPP level of theory.**

| Species | Symmetry | *E* [au] | *H* [au] | *G* [au] |
|---|---|---|---|---|
| $BH_3$ | $D_{3h}$ | −26.595392 | −26.594448 | −26.615819 |
| $BF_3$ | $D_{3h}$ | −324.698335 | −324.697391 | −324.726320 |
| $[BF_4]^-$ | $T_d$ | −424.715786 | −424.714842 | −424.745480 |
| $BF_2(CN)$ | $C_{2v}$ | −317.620151 | −317.619207 | −317.652104 |
| $[BF_3(CN)]^-$ | $C_{3v}$ | −417.662672 | −417.661728 | −417.696568 |
| $BF(CN)_2$ | $C_{2v}$ | −310.538127 | −310.537183 | −310.573036 |
| $[BF_2(CN)_2]^-$ | $C_{2v}$ | −410.604844 | −410.603900 | −410.642603 |
| $B(CN)_3$ | $D_{3h}$ | −303.462308 | −303.461364 | −303.499016 |
| $[BF(CN)_3]^-$ | $C_{3v}$ | −403.550137 | −403.549193 | −403.589490 |
| $BH_2(CN)$ | $C_{2v}$ | −118.891448 | −118.890503 | −118.918544 |
| $[BFH_2(CN)]^-$ | $C_s$ | −218.924684 | −218.923740 | −218.955458 |
| $BH(CN)_2$ | $C_{2v}$ | −211.179866 | −211.178921 | −211.212376 |
| $[BFH(CN)_2]^-$ | $C_s$ | −311.243651 | −311.242706 | −311.279301 |
| $BFH(CN)$ | $C_s$ | −218.253804 | −218.252860 | −218.284207 |
| $[BF_2H(CN)]^-$ | $C_s$ | −318.289004 | −318.288060 | −318.322085 |
| $[B(CN)_4]^-$ | $T_d$ | −396.503680 | −396.502736 | −396.544123 |
| $[BH(CN)_3]^-$ | $C_{3v}$ | −304.207085 | −304.206141 | −304.245093 |
| $[BH_2(CN)_2]^-$ | $C_{2v}$ | −211.898844 | −211.897899 | −211.931289 |
| $[BH_3(CN)]^-$ | $C_{3v}$ | −119.577474 | −119.576530 | −119.604493 |
| $CN^-$ | $C_{3v}$ | −92.885370 | −92.884426 | −92.906762 |

# 15 Single Crystal X-Ray Diffraction

Single-crystals for $[BnPh_3P][BF_4]$, $[BnPh_3P][BF_3(CN)]$, $[BnPh_3P][BF_2(CN)_2]$, $[BnPh_3P][BF(CN)_3]$, $[BnPh_3P][B(CN)_4]$, $[BnPh_3P][BFH(CN)_2]$, $[BnPh_3P][BH_3(CN)]$, $[BnPh_3P][BH_2(CN)_2]$ and $[BnPh_3P][BH(CN)_3]$ were studied on a XtaLAB Synergy Dualflex, HyPix diffractometer using Cu-$K_\alpha$ radiation (micro-focus sealed X-ray tube, $\lambda = 1.54184$ Å).

All structures were solved by intrinsic phasing methods (SHELXT) and refinement is based on full-matrix least-squares calculations on $F^2$ (SHELXL).[16] All non-hydrogen atoms were refined anisotropically. For CH idealized bond lengths and angles were used. Calculations were carried out using the ShelXle graphical interface.[17] Molecular structure diagrams were drawn with the program Diamond 4.6.4.[18] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Experimental details, crystal data, and CCDC numbers are collected in Table S4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

**Table S8: Selected crystal data and details of the refinement of the crystal structures of [BnPh$_3$P][BF$_4$], [BnPh$_3$P][BF$_3$(CN)], [BnPh$_3$P][BF$_2$(CN)$_2$], [BnPh$_3$P][BF(CN)$_3$] and [BnPh$_3$P][BFH(CN)$_2$].**

| Compound | [BnPh$_3$P][BF$_4$] | [BnPh$_3$P][BF$_3$(CN)] | [BnPh$_3$P][BF$_2$(CN)$_2$] | [BnPh$_3$P][BF(CN)$_3$] | [BnPh$_3$P][BFH(CN)$_2$] |
|---|---|---|---|---|---|
| Chemical formula | $C_{25}H_{22}BF_4P$ | $C_{26}H_{22}BF_3NP$ | $C_{27}H_{22}BF_2N_2P$ | $C_{28}H_{22}BFN_3P$ | $C_{27}H_{23}BFN_2P$ |
| $M$ [g·mol$^{-1}$] | 440.20 | 447.22 | 454.24 | 461.26 | 436.25 |
| $T$ [K] | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal system | monoclinic | triclinic | monoclinic | orthorhombic | triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | $Pbca$ | $P\bar{1}$ |
| $a$ [Å] | 9.4958(1) | 10.1902(1) | 13.3421(1) | 13.4477(1) | 9.89780(10) |
| $b$ [Å] | 21.5696(2) | 13.3195(1) | 17.2505(2) | 17.6586(2) | 21.7519(2) |
| $c$ [Å] | 11.1131(1) | 18.9127(2) | 20.2011(2) | 20.6374(2) | 21.8961(3) |
| $\alpha$ [°] | 90 | 70.363(1) | 90 | 90 | 92.6690(10) |
| $\beta$ [°] | 107.745(1) | 83.801(1) | 93.974(1) | 90 | 90.0760(10) |
| $\gamma$ [°] | 90 | 69.417(1) | 90 | 90 | 92.7650(10) |
| Volume [Å$^3$] | 2167.90(4) | 2263.21(4) | 4638.26(8) | 4900.71(8) | 4703.52(9) |
| $Z$ | 4 | 4 | 8 | 8 | 8 |
| $D_{calc}$ [Mg·m$^{-3}$] | 1.349 | 1.313 | 1.301 | 1.250 | 1.232 |
| $\mu$ [mm$^{-1}$] | 1.508 | 1.403 | 1.329 | 1.219 | 1.226 |
| $F$(000) [e] | 912 | 928 | 1888 | 1920 | 1824 |
| Reflections collected | 23570 | 93511 | 17182 | 27804 | 98260 |
| Independent reflections, $R$(int) | 4549, 0.0397 | 9509, 0.0537 | 17182, –[d] | 5137, 0.0358 | 19628, 0.0464 |
| Parameters / data restraints | 280 / 0 | 577 / 0 | 596 / 0 | 307 / 0 | 1170 / 6 |
| $R1[I>2\sigma(I)]$[a] | 0.0355 | 0.0402 | 0.0351 | 0.0348 | 0.0664 |
| $wR2$ (all)[b] | 0.0903 | 0.1115 | 0.0931 | 0.0908 | 0.1749 |
| GooF on $F^2$[c] | 1.051 | 1.036 | 0.742 | 1.048 | 1.096 |
| Largest diff. peak / hole [e·Å$^{-3}$] | 0.288 / −0.362 | 0.535 −0.474 | 0.370 / −0.327 | 0.280 / −0.413 | 1.193 / −0.474 |
| CCDC no. | 2216851 | 2216850 | 2216854 | 2216856 | 2216852 |

[a] $R1 = (\Sigma\big||F_o| - |F_c|\big|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight scheme: $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0, F_o^2 + 2F_c^2]/3$ [BnPh$_3$P][BF$_4$]: $a = 0.0389, b = 1.058$; [BnPh$_3$P[BF$_3$(CN)]: $a = 0.0694, b = 0.7314$; [BnPh$_3$P][BF$_2$(CN)$_2$]: $a = 0.0625, b = 3.4393$; [BnPh$_3$P][BF(CN)$_3$]: $a = 0.044, b =$ 1.8917; [BnPh$_3$P][BFH(CN)$_2$]: $a = 0.045, b = 2.1091$. [c] GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(m-n)]^{0.5}$; ($m$ = reflections, $n$ = variables). [d] twin.

**Table S9**: **Selected crystal data and details of the refinement of the crystal structures of [BnPh$_3$P][B(CN)$_4$], [BnPh$_3$P][BH$_3$(CN)], [BnPh$_3$P][BH$_2$(CN)$_2$], [BnPh$_3$P][BH(CN)$_3$].**

| Compound | [BnPh$_3$P][B(CN)$_4$] | [BnPh$_3$P][BH$_3$(CN)] | [BnPh$_3$P][BH$_2$(CN)$_2$] | [BnPh$_3$P][BH(CN)$_3$] |
|---|---|---|---|---|
| Chemical formula | $C_{29}H_{22}BN_4P$ | $C_{26}H_{25}BNP$ | $C_{27}H_{24}BN_2P$ | $C_{28}H_{23}BN_3P$ |
| *M* [g·mol$^{-1}$] | 468.28 | 393.25 | 418.26 | 443.27 |
| *T* [K] | 100(2) | 100(2) | 100(2) | 95(2) |
| Crystal system | triclinic | triclinic | monoclinic | orthorhombic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | *P*2$_1$/n | *P*bca |
| *a* [Å] | 8.9003(1) | 9.9936(1) | 9.5349(2) | 13.4269(1) |
| *b* [Å] | 11.6360(2) | 13.0398(1) | 14.5833(3) | 17.4850(1) |
| *c* [Å] | 13.5576(2) | 18.8613(1) | 16.4465(3) | 20.6372(2) |
| *α* [°] | 111.524(1) | 70.179(1) | 90 | 90 |
| *β* [°] | 90.565(1) | 83.275(1) | 98.440(2) | 90 |
| *γ* [°] | 100.936(1) | 71.674(1) | 90 | 90 |
| Volume [Å$^3$] | 1277.58(3) | 2194.86(4) | 2262.12(8) | 4844.98(7) |
| *Z* | 2 | 4 | 4 | 8 |
| $D_{\text{calc}}$ [Mg·m$^{-3}$] | 1.217 | 1.190 | 1.228 | 1.215 |
| *μ* [mm$^{-1}$] | 1.133 | 1.175 | 1.187 | 1.151 |
| *F*(000) [e] | 488 | 832 | 880 | 1856 |
| Reflections collected | 26896 | 87588 | 24216 | 27306 |
| Independent reflections, *R*(int) | 5356, 0.0377 | 9218, 0.0434 | 4738, 0.0462 | 5067, 0.0366 |
| Parameters / data restraints | 316 / 0 | 547 / 0 | 288 / 0 | 302 / 0 |
| *R*1[*I*>2σ(*I*)][a] | 0.0362 | 0.0402 | 0.0382 | 0.0358 |
| *wR*2 (all)[b] | 0.0941 | 0.1095 | 0.1021 | 0.0921 |
| GooF on $F^2$[c] | 1.088 | 1.025 | 1.043 | 1.030 |
| Largest diff. peak / hole [e·Å$^{-3}$] | 0.374 / −0.469 | 0.623 / −0.414 | 0.352 / −0.373 | 0.310 / −0.461 |
| CCDC no. | 2216858 | 2216853 | 2216855 | 2216857 |

[a] $R1 = (\Sigma\big||F_o| - |F_c|\big|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight scheme: $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0, F_o^2 + 2F_c^2]/3$ [BnPh$_3$P][B(CN)$_4$]: $a = 0.044, b = 0.4619$; [BnPh$_3$P[BH$_3$(CN)]: $a = 0.0615, b = 0.9481$; [BnPh$_3$P][BH$_2$(CN)$_2$]: $a = 0.0514, b = 0.8377$; [BnPh$_3$P][BH(CN)$_3$]: $a = 0.045, b = 2.1091$. [c] GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(m-n)]^{0.5}$; (*m* = reflections, *n* = variables).

**Table S10: Experimental and calculated bonding parameters of $[BF_4]^-$, $[BF_3(CN)]^-$, $[BF_2(CN)_2]^-$, $[BF(CN)_3]^-$ and $[B(CN)_4]^-$.**

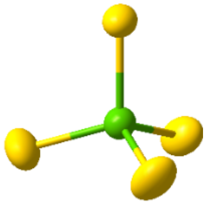
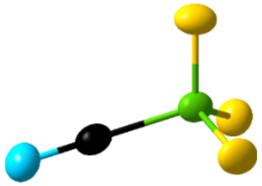
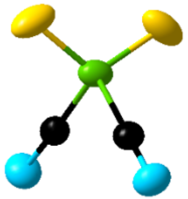
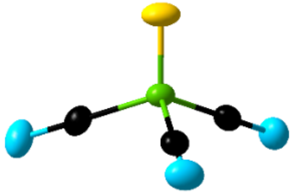
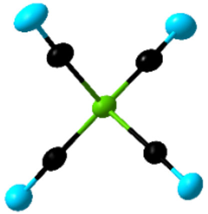
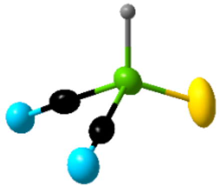
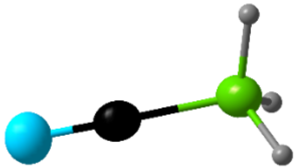
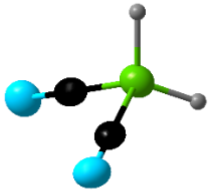
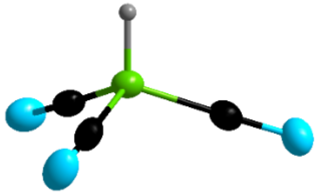
| Anion | | $[BF_4]^-$  | | | $[BF_3(CN)]^-$  | | | $[BF_2(CN)_2]^-$  | | | $[BF(CN)_3]^-$  | | | $[B(CN)_4]^-$  | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mean value | range | calc. | mean value | range | calc. | mean value | range | calc. | mean value | range | calc. | mean value | range | calc. |
| [Å] | *d*(B-C) | / | / | / | 1.643 | 1.641(2) - 1.645(2) | 1.63938 | 1.632 | 1.629(2) - 1.635(3) | 1.62565 | 1.609 | 1.6066(19) - 1.6121(19) | 1.60928 | 1.595 | 1.5910(19) - 1.5971(18) | 1.59558 |
| | *d*(B-F) | 1.393 | 1.3796(18) - 1.4117(17) | 1.41698 | 1.3833 | 1.3774(19) - 1.3969(17) | 1.41088 | 1.387 | 1.383(2) - 1.391(2) | 1.41179 | 1.3962(15) | / | 1.4194 | / | / | / |
| | *d*(B-H) | / | / | / | / | / | / | / | / | / | / | / | / | / | / | / |
| | *d*(C≡N) | / | / | / | 1.141 | 1.137(2) - 1.145(2) | 1.15795 | 1.144 | 1.143(2) - 1.145(2) | 1.15722 | 1.144 | 1.1426(18) - 1.1459(18) | 1.15646 | 1.146 | 1.1456(18) - 1.1466(18) | 1.15554 |
| ° | ∢(B-C-N) | / | / | / | 178.99 | 178.59(15) - 179.39(17) | 179.9984 | 178.093 | 176.95(18) - 179.45(19) | 179.74986 | 178.6 | 178.07 - 179.62 | 179.2416 | 178.2 | 176.98(14) - 178.69(14) | 180.00 |
| | ∢(NC-B-CN) | / | / | / | / | / | / | 107.78 | 107.43(14) - 108.13(14) | 109.514 | 108.6 | 107.33(10) - 109.25(10) | 108.8852 | 109.5 | 108.13(10) - 110.95(10) | 109.471 |
| | ∢(NC-B-F) | / | / | / | 108.77 | 107.99(11) - 109.26(13) | 108.90703 | 109.52 | 108.21(15) - 110.75(14) | 109.1795 | 331.10 | 110.09(11) - 110.69(10) | 110.0511 | / | / | / |
| | ∢(NC-B-H) | / | / | / | / | / | / | / | / | / | / | / | / | / | / | / |
| | ∢(F-B-F) | 109.5 | 107.56(11) - 110.72(12) | 109.47122 | 110.17 | 109.23(12) - 110.73(13) | 110.02946 | 110.88 | 110.73(15) - 111.04(15) | 110.59308 | / | / | / | / | / | / |
| | ∢(H-B-H) | / | / | / | / | / | / | / | / | / | / | / | / | / | / | / |
| | ∢(F-B-H) | / | / | / | / | / | / | / | / | / | / | / | / | / | / | / |

**Table S11: Experimental and calculated bonding parameters of [BFH(CN)$_2$]$^-$, [BH$_3$(CN)]$^-$, [BH$_2$(CN)$_2$]$^-$ and [BH(CN)$_3$]$^-$.**

| Anion | | [BFH(CN)$_2$]$^-$  | | | [BH$_3$(CN)]$^-$  | | | [BH$_2$(CN)$_2$]$^-$  | | | [BH(CN)$_3$]$^-$  | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mean value | range | calc. | mean value | range | calc. | mean value | range | calc. | mean value | range | calculated |
| [Å] | *d*(B-C) | 1.615 | 1.605(5) - 1.625(5) | 1.60957 | 1.587 | 1.587(2) - 1.586(2) | 1.58968 | 1.589 | 1.588(2) - 1.590(2) | 1.58889 | 1.589 | 1.5884(19) - 1.589(2) | 1.5908 |
| | *d*(B-F) | 1.406 | 1.386(4) - 1.421(4) | 1.43586 | / | / | / | / | / | / | / | / | / |
| | *d*(B-H) | 1.15 | 1.09(4) - 1.23(3) | 1.21624 | 1.130 | 1.10(2) - 1.15(2) | 1.22354 | 1.12 | 1.08(2) - 1.15(2) | 1.21455 | 1.110(17) | / | 1.20998 |
| | *d*(C≡N) | 1.141 | 1.138(4) - 1.146(4) | 1.1586 | 1.151 | 1.148(2) - 1.153(2) | 1.16376 | 1.147 | 1.146(2) - 1.148(2) | 1.16007 | 1.147 | 1.1456(18) - 1.1482(18) | 1.15741 |
| ° | ∢(B-C-N) | 178.7 | 178.0(3) - 179.3(4) | 177.33701 | 179.52 | 179.34(18) - 179.69(19) | 180 | 178.39 | 177.97(16) - 178.80(16) | 177.4882 | 178.51 | 178.03(14) - 179.30(15) | 177.81037 |
| | ∢(NC-B-CN) | 107.1 | 105.3(3) - 107.9(3) | 109.56447 | / | / | / | 110.03(13) | / | 111.8709 | 109.94 | 109.25(11) - 110.53(11) | 110.95751 |
| | ∢(NC-B-F) | 109.6 | 108.0(3) - 110.7(3) | 110.09776 | / | / | / | / | / | / | / | / | / |
| | ∢(NC-B-H) | 109.7 | 106.1(16) - 114.3(15) | 107.74600 | 109.07 | 107.4(12) - 111.0(11) | 108.9381 | 108.88 | 107.8(11) - 110.8(10) | 108.8356 | 108.9 | 108.7(9) - 109.4(9) | 107.94056 |
| | ∢(F-B-F) | / | / | / | / | / | / | / | / | / | / | / | / |
| | ∢(H-B-H) | / | / | / | 109.85 | 106.3(17) - 113.9(16) | 109.9990 | 111.3(15) | / | 109.6052 | / | / | / |
| | ∢(F-B-H) | 111.0 | 109.9(16) - 113.(2) | 111.51972 | / | / | / | / | / | / | / | / | / |

# 16 Literature

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