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Electronic Supplementary Information

Anion influences on reactivity and NMR spectroscopic features of NHC precursors

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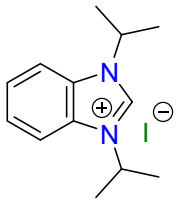
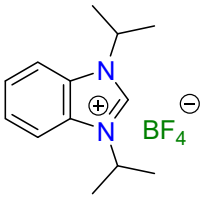
Contents

Experimental Section

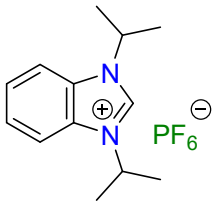
General considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. 1,3-Diisopropylbenzimidazolium Bromide (^{i}Pr$_2$-bimyH$^+$Br$^-$, **A**) was prepared according to the procedure in literature.[S1] ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker ACF 300 spectrometer and the chemical shifts (δ) were internally referenced to the residual protio-solvent signal relative to tetramethylsilane (^{1}H, ^{13}C) or externally to CF_3COOH (^{19}F) and 85% H_3PO_4 (^{31}P). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer with a CH_3OH/H_2O (4:1, v/v) mixture as the mobile phase, a capillary temperature of 200 °C, and a capillary voltage of 21V. Elemental analyses were performed on an Elementar Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore.



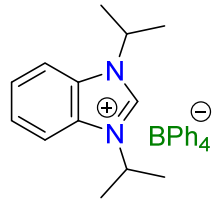
1,3-Diisopropylbenzimidazolium Iodide (B). To the solution of **A** (142 mg, 0.50 mmol) in acetone (1 mL) was added the solution of NaI (150 mg, 1.00 mmol, 2 eq) in acetone and white precipitate came out instantly. The reaction mixture was stirred for 1 hour at room temperature and then filtered over Celite, after which the solvent of the filtrate was removed under vacuum. CH_2Cl_2 (5 mL) was added to partially dissolve the residues. Filtration again over Celite followed by removal of the solvent from the filtrate afforded **B** as an off-white powder (157 mg, 0.48 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.92 (s, 1 H, NCHN), 7.82 (dd, 2 H, Ar–H), 7.65 (dd, 2 H, Ar–H), 5.19 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*$(CH_3)_2$), 1.86 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 140.4 (NCHN), 131.5, 127.7, 114.6 (Ar–C), 53.1 (N*C*H$(CH_3)_2$), 22.9 (CH_3). Anal. Calc. for $C_{13}H_{19}IN_2$: C, 47.29; H, 5.80; N, 8.48. Found: C, 47.37; H, 5.62; N, 8.48. MS (ESI): *m/z* = 203 $[M - I]^+$, 127 $[I]^-$.



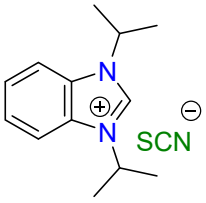
1,3-Diisopropylbenzimidazolium Tetrafluoroborate (C). To the solution of **A** (142 mg, 0.50 mmol) in acetone (1 mL) was added $NaBF_4$ (110 mg, 1.00 mmol, 2 eq) and the reaction mixture was stirred for 1 hour at room temperature. Filtration over Celite followed by removal of the solvent from the filtrate afforded **C** as a white powder (133 mg, 0.46 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (s, 1 H, NCHN), 7.82 (dd, 2 H, Ar–H), 7.64 (dd, 2 H, Ar–H), 5.02 (m, ^3J(H,H) = 6.9 Hz, 2 H, NC*H*$(CH_3)_2$), 1.78 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 139.2 (NCHN), 131.7, 127.7, 114.5 (Ar–C), 53.0 (N*C*H$(CH_3)_2$), 22.3 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ -75.15, -75.20 (s, BF_4). Anal. Calc. for $C_{13}H_{19}BF_4N_2$: C, 53.82; H, 6.60; N, 9.66. Found: C, 53.88; H, 6.49; N, 9.63. MS (ESI): *m/z* = 203 $[M - BF_4]^+$.



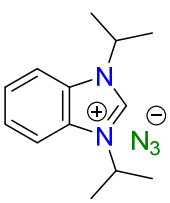
1,3-Diisopropylbenzimidazolium Hexafluorophosphate (D). Salt **D** was prepared in analogy to **B** from KPF_6 (184 mg, 1.00 mmol, 2 eq) in acetone and obtained as a white powder (165 mg, 0.47 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.17 (s, 1 H, NCHN), 7.80 (dd, 2 H, Ar–H), 7.67 (dd, 2 H, Ar–H), 4.98 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*$(CH_3)_2$), 1.79 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 138.5 (NCHN), 131.7, 127.8, 114.6 (Ar–C), 53.2 (N*C*H$(CH_3)_2$), 22.2 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ 3.96 (d, ^1J(P,F) = 711 Hz, PF_6). ^{31}P NMR (202 MHz, $CDCl_3$): δ -143.6 (sept, ^1J(P,F) = 711 Hz, PF_6). Anal. Calc. for $C_{13}H_{19}F_6N_2P$: C, 44.83; H, 5.50; N, 8.04. Found: C, 45.02; H, 5.43; N, 8.12. MS (ESI): *m/z* = 203 $[M - PF_6]^+$, 551 $[2M - PF_6]^+$, 145 $[PF_6]^-$.



1,3-Diisopropylbenzimidazolium Tetraphenylborate (E). Salt **E** was prepared in analogy to **B** from $NaBPh_4$ (342 mg, 1.00 mmol, 2 eq) and obtained as a white powder (242 mg, 0.46 mmol, 93%). Crystals suitable for X-ray diffraction studies was obtained by the slow evaporation of a concentrated solution of **E** in hexane/CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.99 (s, 1 H, NCHN), 6.80 – 8.08 (m, 24 H, Ar–H), 4.59 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*$(CH_3)_2$), 1.58 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 139.6 (NCHN), 136.7, 131.2, 129.4, 128.5, 127.8, 127.6, 126.7, 126.5, 122.6, 114.8 (Ar–C), 53.1 (NCH(CH3)2), 22.4 (CH3). Anal. Calc. for $C_{37}H_{39}BN_2$: C, 85.05; H, 7.52; N, 5.36. Found: C, 82.81; H, 7.04; N, 5.25. MS (ESI): *m/z* = 203 $[M - B(C_6H_5)_4]^+$, 725 $[2M - B(C_6H_5)_4]^+$, 319 $[B(C_6H_5)_4]^-$.

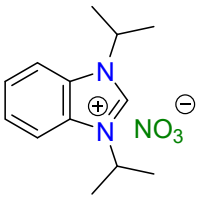


1,3-Diisopropylbenzimidazolium thiocyanate (F). F was prepared in analogy to **B** from KSCN (97 mg, 1.00 mmol, 2 eq). **F** was obtained as an orange powder (128 mg, 0.49 mmol, 98%). Crystals suitable for X-ray diffraction studies was obtained by the slow evaporation of a concentrated solution of **F** in hexane/CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.50 (s, 1 H, NCHN), 7.80 (dd, 2 H, Ar–H), 7.65 (dd, 2 H, Ar–H), 5.10 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*$(CH_3)_2$), 1.85 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 162.5 (SCN), 140.5 (NCHN), 131.7, 127.7, 114.5 (Ar–C), 53.1 (N*C*H$(CH_3)_2$), 22.7 (CH_3). Anal. Calc. for $C_{14}H_{19}N_3S$: C, 64.33; H, 7.33; N, 16.08. Found: C, 64.23; H, 7.03; N, 16.06. MS (ESI): *m/z* = 203 $[M - SCN]^+$.

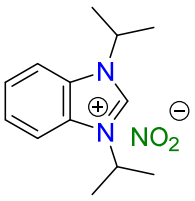


1,3-Diisopropylbenzimidazolium Azide (G). G was prepared in analogy to **B** from NaN_3 (65 mg, 1.00 mmol, 2 eq). **G** was obtained as an off-white powder (115 mg, 0.47 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.89 (s, 1 H,

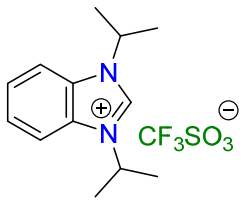
NCHN), 7.78 (dd, 2 H, Ar–H), 7.64 (dd, 2 H, Ar–H), 5.06 (m, ^{3}J(H,H) = 6.6 Hz, 2 H, NC*H*(CH_3)$_2$), 1.83 (d, ^{3}J(H,H) = 6.6 Hz, 12 H, CH_3). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 141.1 (NCHN), 131.6, 127.6, 114.3 (Ar–C), 52.8 (N*C*H(CH_3)$_2$), 22.6 (CH_3). MS (ESI): *m/z* = 203 $[M - N_3]^+$.



1,3-Diisopropylbenzimidazolium Nitrate (H). To the solution of **A** (142 mg, 0.50 mmol) in methanol (1 mL) was added the solution of $AgNO_3$ (170 mg, 1.00 mmol, 2 eq) in methanol and yellow precipitate came out instantly. The reaction mixture was stirred for 1 hour at room temperature and then filtered over Celite, after which the solvent of the filtrate was removed under vacuum. CH_2Cl_2 (5 mL) was added to partially dissolve the residues. Filtration again over Celite followed by removal of the solvent from the filtrate afforded **H** as a white powder (130 mg, 0.49 mmol, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.70 (s, 1 H, NCHN), 7.79 (dd, 2 H, Ar–H), 7.64 (dd, 2 H, Ar–H), 5.04 (hept, ^{3}J(H,H) = 6.8 Hz, 2 H, NC*H*(CH_3)$_2$), 1.79 (d, ^{3}J(H,H) = 6.8 Hz, 12 H, CH_3). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 139.7 (NCHN), 131.2, 127.3, 114.1 (Ar–C), 52.1 (N*C*H(CH_3)$_2$), 22.0 (CH_3). Anal. Calc. for $C_{13}H_{19}N_3O_3$: C, 58.85; H, 7.22; N, 15.84. Found: C, 56.74; H, 6.82; N, 15.46. MS (ESI): *m/z* = 203 $[M - NO_3]^+$.

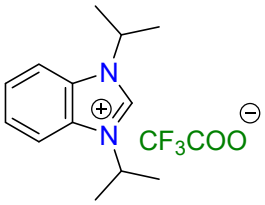


1,3-Diisopropylbenzimidazolium Nitrite (I). To the solution of **A** (142 mg, 0.50 mmol) in methanol (1 mL) was added $AgNO_2$ (154 mg, 1.00 mmol, 2 eq) and yellow precipitate came out instantly. The reaction mixture was stirred for 1 hour at room temperature. Filtration over Celite followed by removal of the solvent from the filtrate afforded **I** as a white powder (122 mg, 0.49 mmol, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.84 (s, 1 H, NCHN), 7.78 (dd, ^{3}J(H,H) = 6.3, 3.2 Hz, 2H, Ar–H), 7.64 (dd, ^{3}J(H,H) = 6.3, 3.2 Hz, 2 H, Ar–H), 5.05 (sept, ^{3}J(H,H) = 6.8 Hz, 2 H, NC*H*(CH_3)$_2$), 1.80 (d, ^{3}J(H,H) = 6.8 Hz, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 140.3 (NCHN), 131.6, 127.7, 114.3 (Ar–C), 52.8 (N*C*H(CH_3)$_2$), 22.5 (CH_3). MS (ESI): *m/z* = 203 $[M - NO_2]^+$.

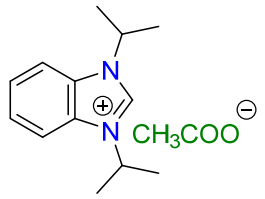


1,3-Diisopropylbenzimidazolium Trifluoromethanesulfonate (J). Salt **J** was prepared in analogy to **I** from AgOTf (257 mg, 1.00 mmol, 2 eq) and obtained as a gray solid (167 mg, 0.47 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.78 (s, 1 H, NCHN), 7.80 (dd, 2 H, Ar–H), 7.65 (dd, 2 H, Ar–H), 5.02 (m, ^{3}J(H,H) = 6.9 Hz, 2 H, NC*H*(CH_3)$_2$), 1.79 (d, ^{3}J(H,H) = 6.9 Hz, 12 H, CH_3). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 138.5 (NCHN), 131.5, 127.6, 114.3 (Ar–C), 121.1 (m, ^{1}J(C,F) = 320 Hz, CF_3), 52.5 (N*C*H(CH_3)$_2$), 22.2 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ -1.81 (s, CF_3). Anal. Calc. for $C_{14}H_{19}F_3N_2O_3S$: C, 47.72; H, 5.44; N,

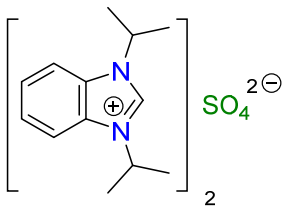
7.95. Found: C, 47.73; H, 5.13; N, 7.95. MS (ESI): *m/z* = 203 [M – CF_3SO_3]$^+$, 555 [2M – CF_3SO_3]$^+$, 149 [CF_3SO_3]$^-$.



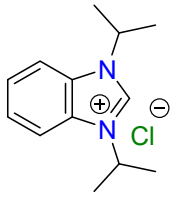
1,3-Diisopropylbenzimidazolium Trifluoroacetate (K). Salt **K** was prepared in analogy to **H** from $AgOCOCF_3$ (221 mg, 1.00 mmol, 2 eq). **K** was obtained as an off-white solid (150 mg, 0.47 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.71 (s, 1 H, NCHN), 7.78 (dd, 2 H, Ar–H), 7.68 (dd, 2 H, Ar–H), 4.94 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*(CH_3)$_2$), 1.73 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 162.8 (q, ^2J(C,F) = 35.7 Hz, COO), 138.7 (NCHN), 131.6, 127.5, 114.3 (Ar–C), 118.0 (q, ^1J(C,F) = 289 Hz, CF_3) 52.7 (N*C*H(CH_3)$_2$), 21.9 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ 2.77 (s, CF_3). MS (ESI): *m/z* = 203 [M – CF_3COO]$^+$.



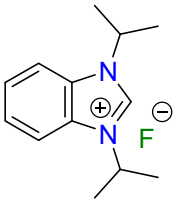
1,3-Diisopropylbenzimidazolium Acetate (L). A suspension of **A** (142 mg, 0.50 mmol) and $Zn(OAc)_2$ (183 mg, 1.00 mmol, 4 eq) in DCM was stirred under reflux at 50˚C for 16 hours. Filtration over Celite followed by removal of the solvent from the filtrate afforded **L** as a sticky solid, which was then washed by ethyl acetate (5 x 5 mL) until **L** became a white powder (124 mg, 0.47 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 1 H, NCHN), 7.81 (dd, 2 H, Ar–H), 7.66 (dd, 2 H, Ar–H), 5.06 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*(CH_3)$_2$), 2.00 (s, 3 H, CH_3COO), 1.80 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 180.4 (COO), 139.8 (NCHN), 131.6, 127.8, 114.6 (Ar–C), 53.1 (N*C*H(CH_3)$_2$), 24.0 (*C*H_3COO), 22.6 (CH(*C*H_3)$_2$). Anal. Calc. for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 62.21; H, 9.82; N, 9.75. MS (ESI): *m/z* = 203 [M – CH_3COO]$^+$.



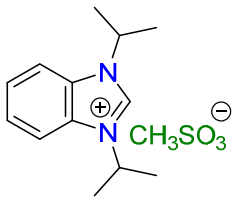
1,3-Diisopropylbenzimidazolium Sulfate (M). To the solution of **A** (283 mg, 1.00 mmol) in methanol (1 mL) was added Ag_2SO_4 (312 mg, 1.00 mmol, 2 eq) and yellow precipitate came out instantly. The reaction mixture was stirred for 1 hour at room temperature. Filtration over Celite followed by removal of the solvent from the filtrate yielded a sticky solid which was then washed by ethyl acetate (5 x 5 mL) until **M** became a white powder (158 mg, 0.31 mmol, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.30 (s, 1 H, NCHN), 7.72 (dd, 2 H, Ar–H), 7.51 (dd, 2 H, Ar–H), 5.30 (m, ^3J(H,H) = 6.0 Hz, 2 H, NC*H*(CH_3)$_2$), 1.79 (d, ^3J(H,H) = 6.0 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 144.5 (NCHN), 131.6, 126.5, 114.7 (Ar–C), 53.1 (N*C*H(CH_3)$_2$), 22.4 (CH_3). Anal. Calc. for $C_{26}H_{38}N_4O_4S$: C, 62.12; H, 7.62; N, 11.15. Found: C, 58.13; H, 7.72; N, 10.22. MS (ESI): *m/z* = 203 [(M – SO_4)/2]$^+$.



1,3-Diisopropylbenzimidazolium Chloride (N). To the solution of **M** (126 mg, 0.25 mmol) in DI water (0.5 mL) was added $BaCl_2 \cdot 2H_2O$ (122 mg, 0.50 mmol, 2eq) in DI water and white precipitate came out instantly. The reaction mixture was stirred for 1 hour at room temperature. The mixture was filtered over Celite and the solvent of the filtrate was removed under reduced pressure. CH_2Cl_2 (10 mL) was added to the residues and filtered again over Celite. Removal of CH_2Cl_2 from the filtrate afforded **N** as a sticky solid, which was then washed by ethyl acetate (3 x 5 mL) until **N** became a white powder (118 mg, 0.50 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.68 (s, 1 H, NCHN), 7.76 (dd, 2 H, Ar–H), 7.61 (dd, 2 H, Ar–H), 5.16 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*(CH_3)$_2$), 1.82 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 142.1 (NCHN), 131.5, 127.4, 114.5 (Ar–C), 52.9 (N*C*H(CH_3)$_2$), 22.9 (CH_3). Anal. Calc. for $C_{13}H_{19}ClN_2$: C, 65.40; H, 8.02; N, 11.73. Found: C, 62.31; H, 8.03; N, 11.26. MS (ESI): *m/z* = 203 $[M - Cl]^+$.

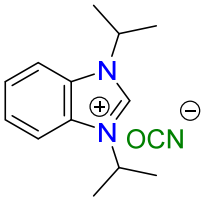


1,3-Diisopropylbenzimidazolium Fluoride (O). To the solution of **H** (133 mg, 0.50 mmol) in methanol (1 mL) was added the solution of KF (58 mg, 1.00 mmol, 2 eq) in methanol white precipitate came out instantly. The reaction mixture was stirred for 2 hours at room temperature. Filtration over Celite followed by removal of the solvent from the filtrate afforded **O** as a sticky solid. CH_2Cl_2 was added dissolve the solid and needle-like crystals formed after overnight. Collection of the crystals and washing by ethyl acetate (5 x 5 mL) afford **O** as a white powder (88 mg, 0.40 mmol, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.10 (s, 1 H, NCHN), 7.78 (dd, 2 H, Ar–H), 7.61 (dd, 2 H, Ar–H), 5.12 (m, ^3J(H,H) = 6.9 Hz, 2 H, NC*H*(CH_3)$_2$), 1.81 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 142.0 (NCHN), 131.6, 127.3, 114.5 (Ar–C), 52.9 (N*C*H(CH_3)$_2$), 22.6 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ -51.42 (s, F). MS (ESI): *m/z* = 203 $[M - F]^+$.



1,3-Diisopropylbenzimidazolium Methanesulfonate (P). To the solution of **H** (133 mg, 0.50 mmol) in methanol (1 mL) was added NaOMs (118 mg, 1.00 mmol, 2 eq) and the reaction mixture was stirred for 2 hours at room temperature. Filtration over Celite followed by removal of the solvent from the filtrate afforded **P** as a white solid. (144 mg, 0.48 mmol, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.67 (s, 1 H, NCHN), 7.77 (dd, 2 H, Ar–H), 7.61 (dd, 2 H, Ar–H), 5.12 (m, ^3J(H,H) = 6.9 Hz, 2 H, NC*H*(CH_3)$_2$), 2.81 (s, 3 H, CH_3SO_3), 1.81 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 141.7 (NCHN), 131.6, 127.3, 114.5 (Ar–C), 53.0 (N*C*H(CH_3)$_2$), 40.2 (CH_3SO_3) , 22.5 (CH(*C*H$_3$)$_2$). Anal. Calc.

for $C_{14}H_{22}N_2SO_3$: C, 56.35; H, 7.43; N, 9.39. Found: C, 56.20; H, 6.94; N, 9.34. MS (ESI): *m/z* = 203 $[M - CH_3SO_3]^+$.



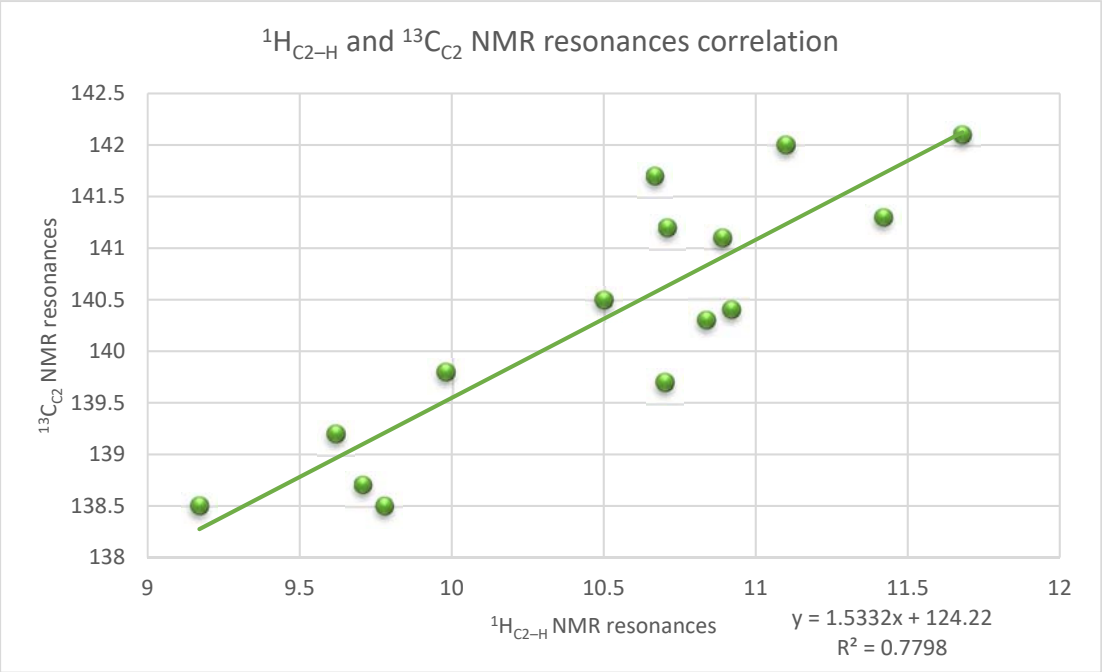
1,3-Diisopropylbenzimidazolium Cyanate (Q). Salt **Q** was prepared in analogy to **P** from KOCN (81 mg, 1.00 mmol, 2 eq). **Q** was obtained as a white powder (113 mg, 0.46 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.71 (s, 1 H, NCHN), 7.79 (dd, 2 H, Ar–H), 7.63 (dd, 2 H, Ar–H), 5.04 (m, ^3J(H,H) = 6.9 Hz, 2 H, NC*H*$(CH_3)_2$), 1.79 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 141.2 (NCHN), 131.6, 127.6 (Ar–C), 124.4 (CN), 114.4 (Ar–C), 124.4 (OCN), 52.8 (N*C*H$(CH_3)_2$), 22.5 (CH_3). MS (ESI): *m/z* = 203 $[M - OCN]^+$.

General procedure for H/D exchange reactions:

An NMR tube was charged with the respective benzimidazolium salt (41.5 µmol, 1 equiv.) and 0.5 mL of a mixed $CD_3OD/CDCl_3$ solution {prepared by mixing 34 µL of CD_3OD (CIL ampoule) and 9.967 mL of freshly distilled $CDCl_3$} were added. The resulting solution was then subjected to ^{1}H NMR spectroscopic measurements (500 Hz) at 20-30 min intervals. The exchange reactions were monitored by comparing the integrals of C2–H proton signal in the ^{1}H NMR spectra recorded over 180 minutes. The results obtained are tabulated below:

Salt A		**Salt B**		**Salt C**	
Time [min]	**Conversion [%]**	**Time [min]**	**Conversion [%]**	**Time [min]**	**Conversion [%]**
3	35	6	2	9	<1
12	36	20	4	30	<1
35	37	40	6	60	<1
65	38	70	8	90	<1
95	40	100	9	120	<1
125	42	130	11	155	<1
160	46	165	11	180	<1
185	48	18 h	11	18 h	<1
18 h	68				

Correlation of $^{1}H_{C2–H}$ and $^{13}C_{C2}$ NMR resonances



Due to the interfering shielding effects of the BPh_4^- anion, salt **E** has been excluded from this correlation.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo-Kα radiation with the SMART suite of Programs.[S2] Data were processed and corrected for Lorentz and polarization effects with SAINT,[S3] and for absorption effect with SADABS.[S4] Structural solution and refinement were carried out with the SHELXTL suite of programs.[S5] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is provided in Table S1.

Table S1. Selected Crystallographic Data

	E	**F**	**N·H$_2$O**
formula	$C_{37}H_{39}BN_2$	$C_{14}H_{19}N_3S$	$C_{13}H_{21}ClON_2$
fw	552.51	261.39	256.77
color, habit	colourless, block	orange, block	colourless, block
cryst size [mm]	0.333×0.287×0.206	0.336×0.305×0.210	0.250×0.209×0.182
mp [K]	100(2)	100(2)	100(2)
crystsyst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a[Å]	9.8653(3)	7.1115(3)	9.765(1)
b [Å]	16.7612(5)	12.4689(7)	14.826(2)
c [Å]	18.1753(5)	15.8457(7)	10.167(1)
α [deg]	90.00	90	90
β [deg]	90.00	93.346(2)°.	108.135(4)
γ [deg]	90.00	90	90
V [Å^3]	3005.36(15)	1402.68(12)	1398.8(3)
Z	4	4	4
D_c [g cm^{-3}]	1.155	1.238	1.219
radiation used	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	0.066	0.218	0.261
θ range [deg]	2.349–28.279	2.575–28.265	2.516–29.651
reflections collected	35919	13226	13329
max., min. transmn	0.7458, 0.7005	0.7455, 0.6846	0.7459, 0.6742
final R indices	R_1 = 0.0445,	R_1 = 0.0479	R_1 = 0.0586
[$I > 2\sigma(I)$]	wR_2 = 0.0805	wR_2 = 0.1037	wR_2 = 0.1047
R indices (all data)	R_1 = 0.0646,	R_1 = 0.0828	R_1 = 0.1186,
	wR_2 = 0.0865	wR_2 = 0.1192	wR_2 = 0.1242
goodness-of-fit	1.032	0.950	1.012
peak/hole [e Å^{-3}]	0.242/-0.202	0.367/-0.313	0.320/-0.372

General procedure for conductivity measurements

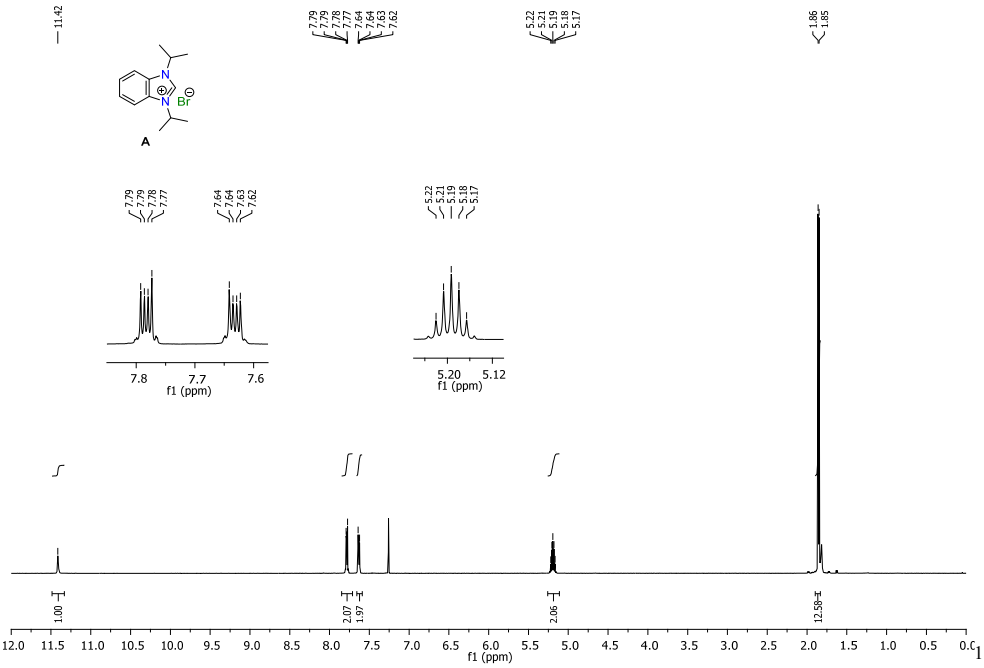
A dried tube was charged with 3 mL solution of the respective benzimidazolium salts (salt **A**, **B**, **C**, **N**) in anhydrous chloroform (concentration: 83 μmol/mL). Then the electrode was dipped into the solution and the conductivity was measured using Philip PW 9526 conductivity meter. The results are shown in table **S2**.

Table S2. Conductivity measurement

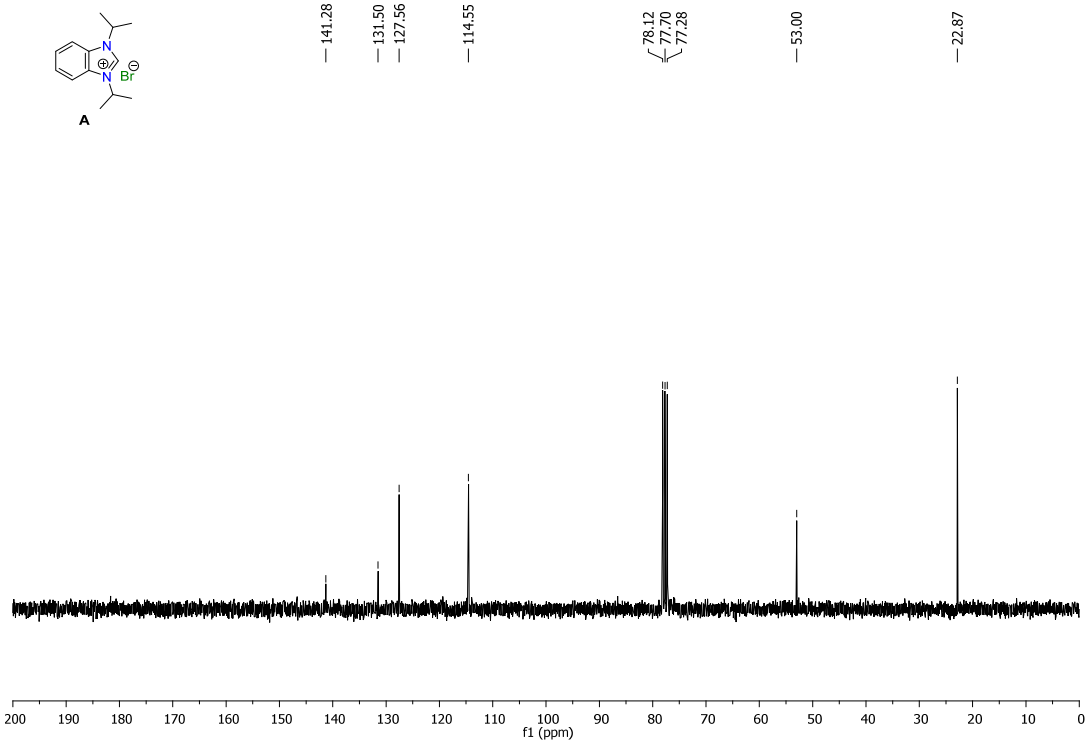
Salt	Conductivity (μS/cm)
A	2.5
B	5.1
C	4.1
N	1.8

Computational Details. Gas-phase structures of N_3^-, NCO^-, SCN^-, NO_2^- and NO_3^- were optimized by the DFT method using B3LYP functional[S6], [S7], [S8] on Gaussian 16 and the aug-cc-pVTZ basis set[S6], [S7], [S8] was used for all atoms. Frequency calculation was performed for all optimized geometries to ensure that the stationary point was minimum. The Mulliken charge of the atoms in the anions were calculated from the optimized geometries.

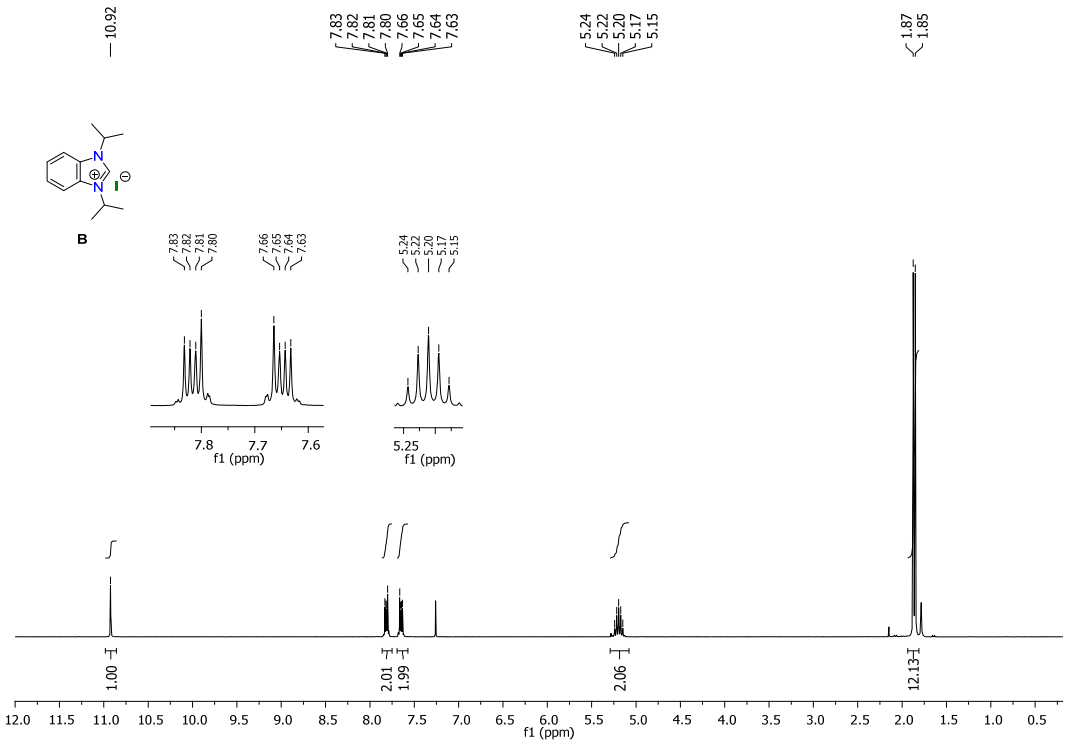
NMR Spectra



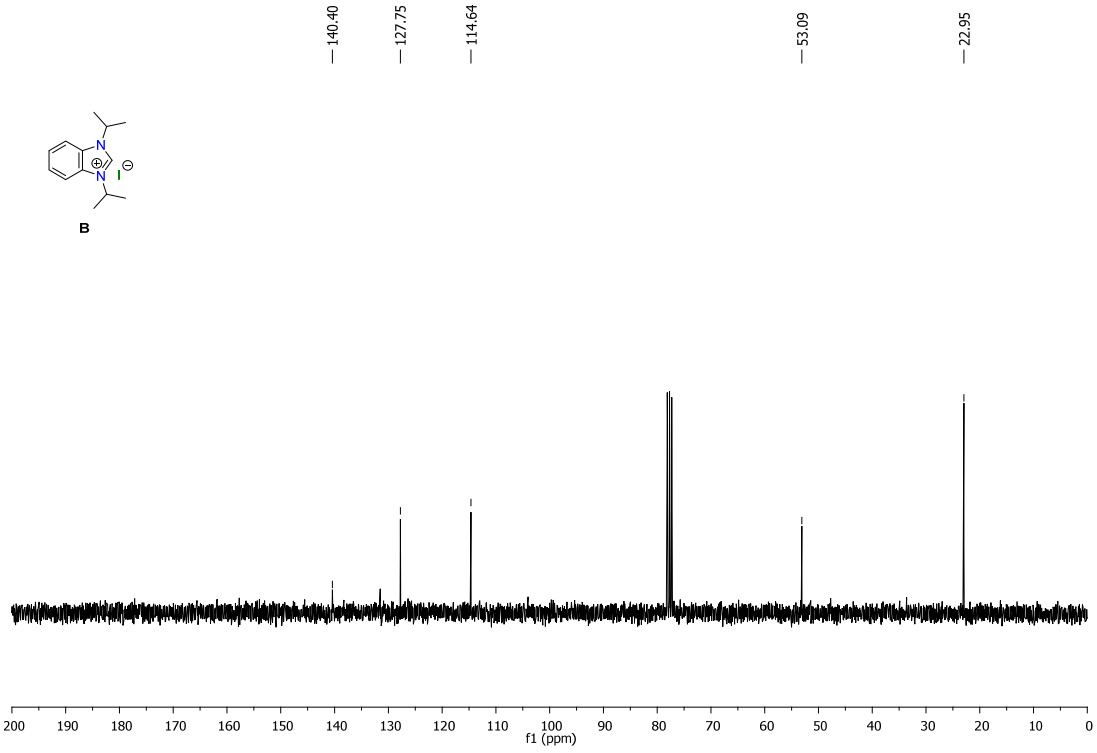
H NMR spectrum of compound **A** (83 µmol/mL, $CDCl_3$, 300 MHz)



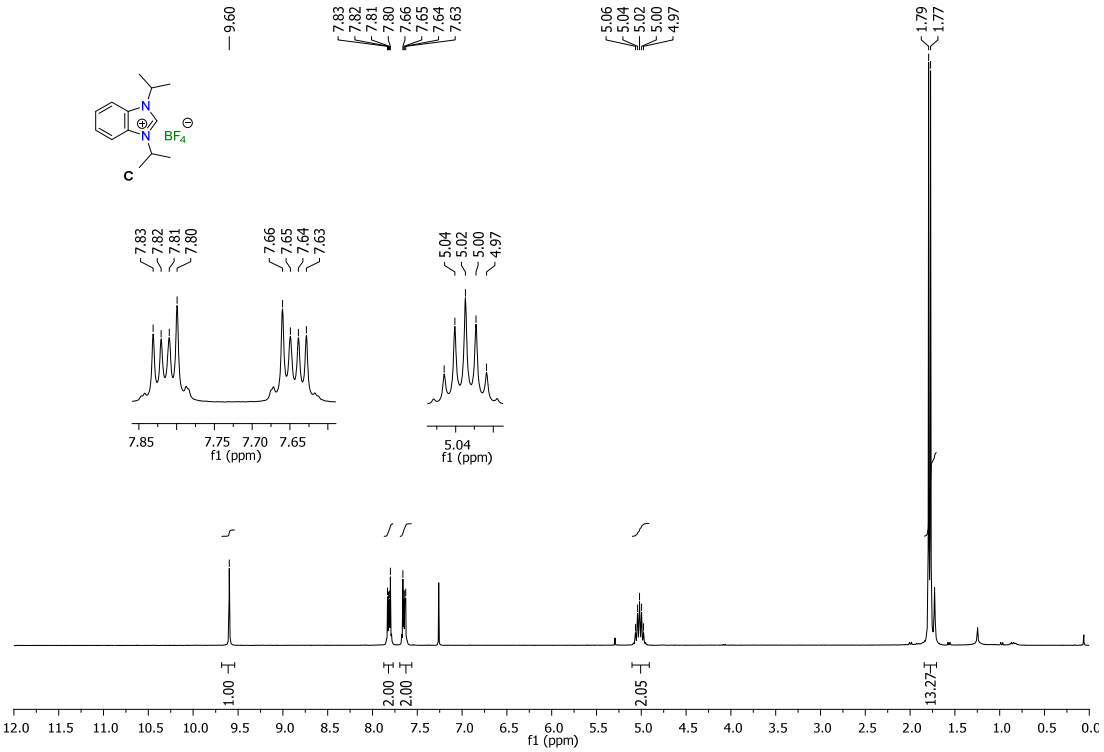
^{13}C NMR spectrum of compound **A** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



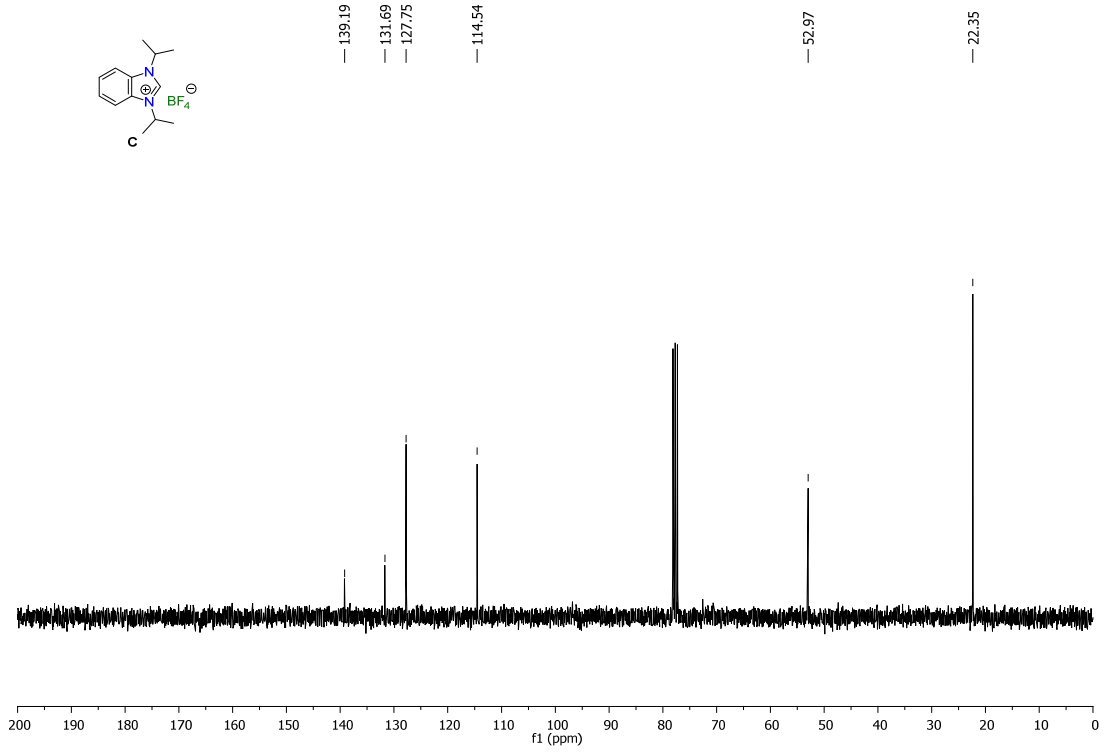
^{1}H NMR spectrum of compound **B** (83 µmol/mL, $CDCl_3$, 300 MHz)



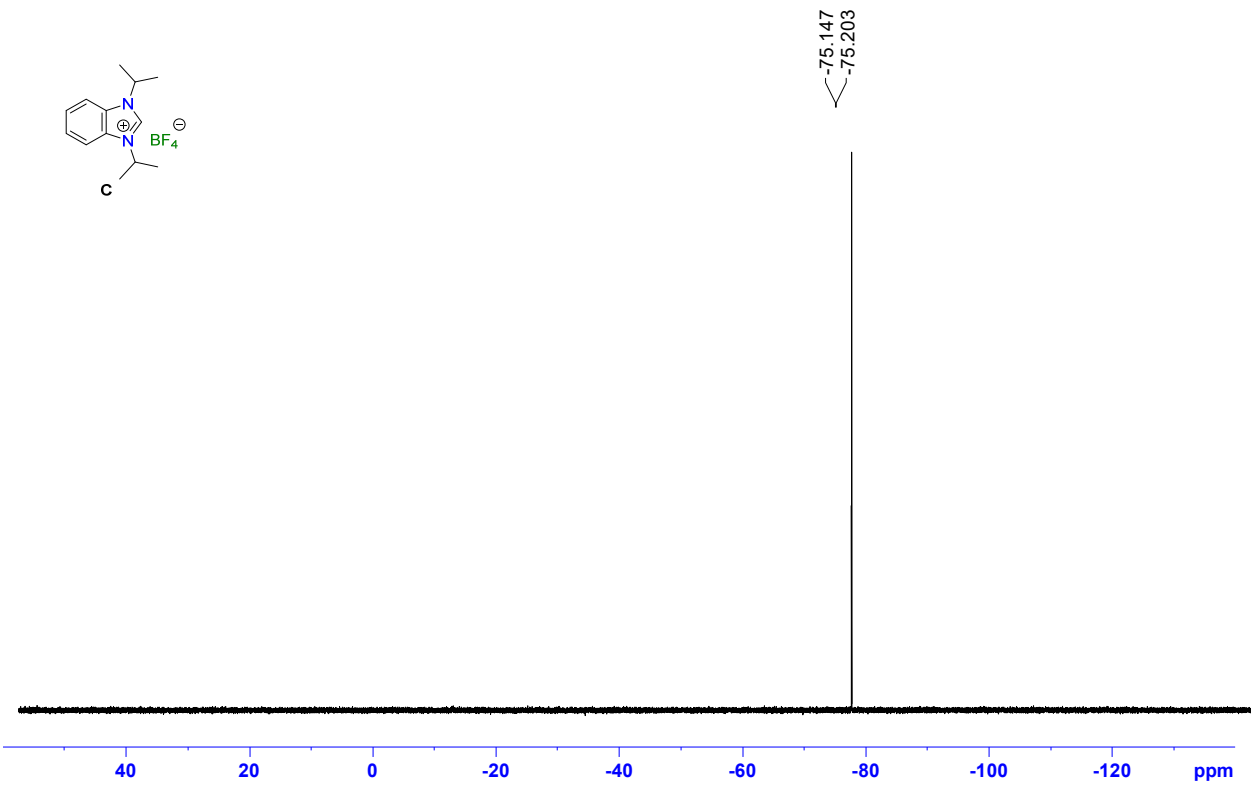
^{13}C NMR spectrum of compound **B** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



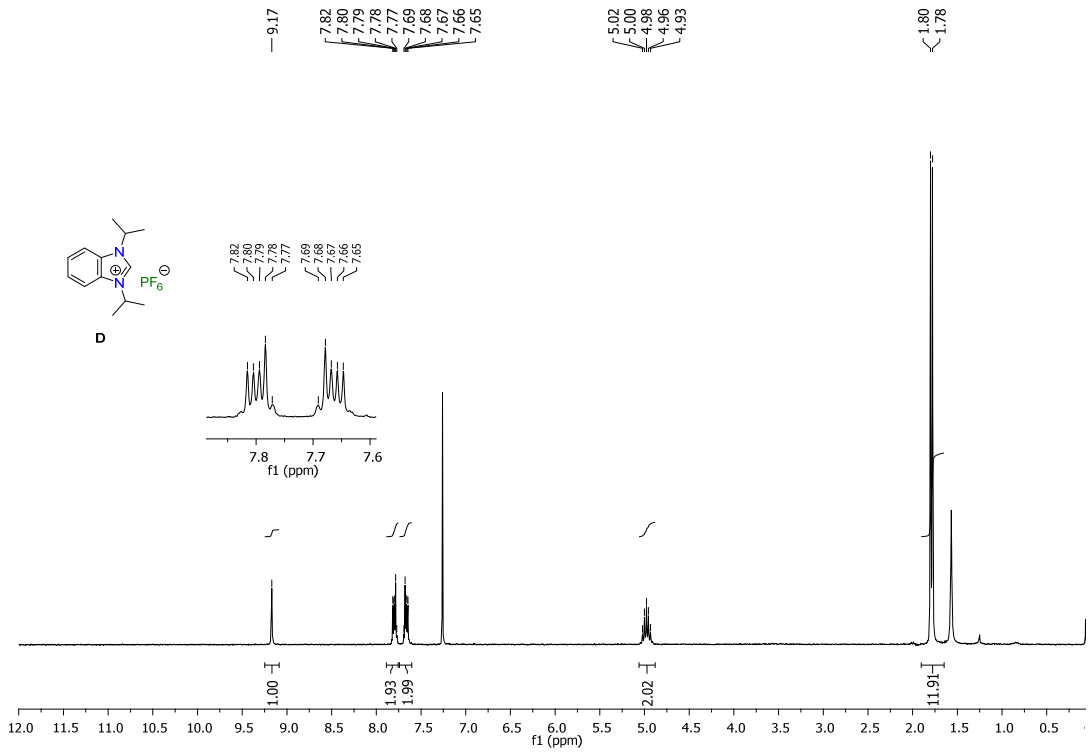
^{1}H NMR spectrum of compound **C** (83 μmol/mL, $CDCl_3$, 300 MHz)



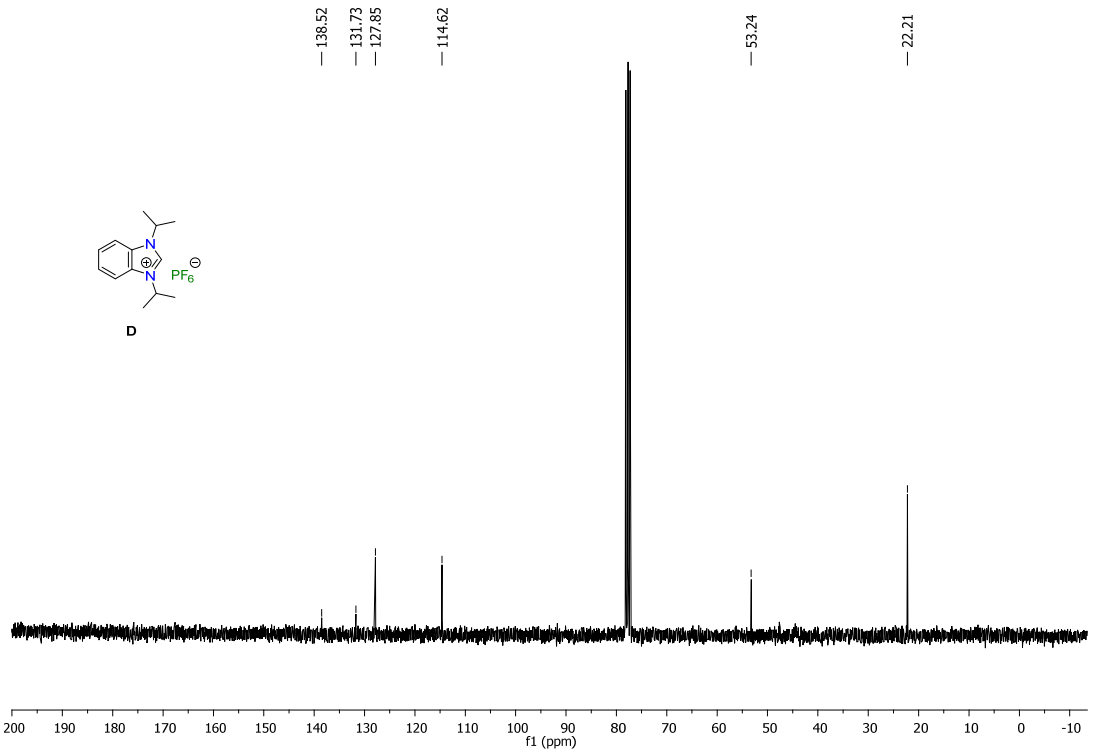
^{13}C NMR spectrum of compound **C** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



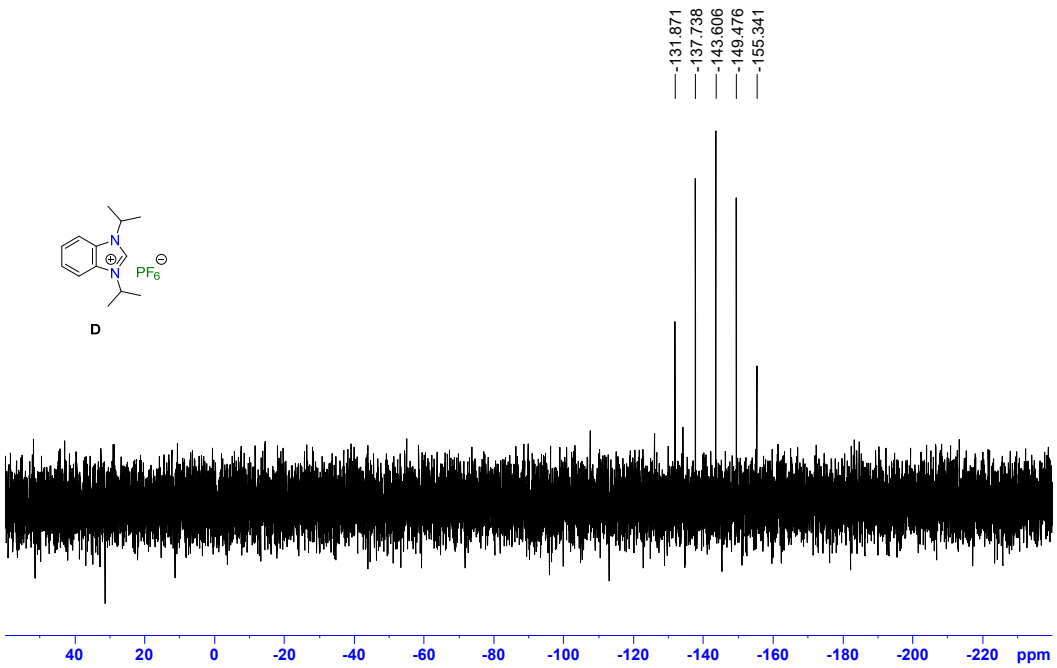
^{19}F NMR spectrum of compound **C** (83 μmol/mL, $CDCl_3$, 282.4 MHz)



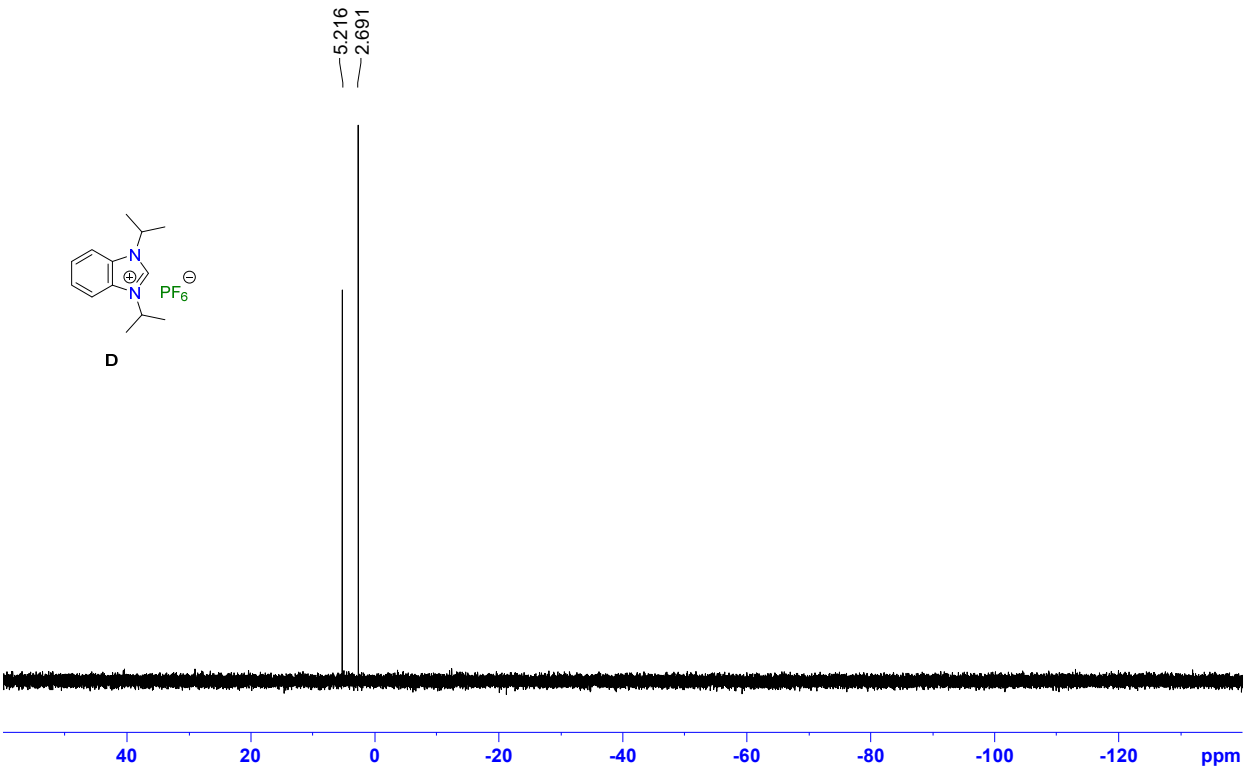
^{1}H NMR spectrum of compound **D** (83 µmol/mL, $CDCl_3$, 300 MHz)



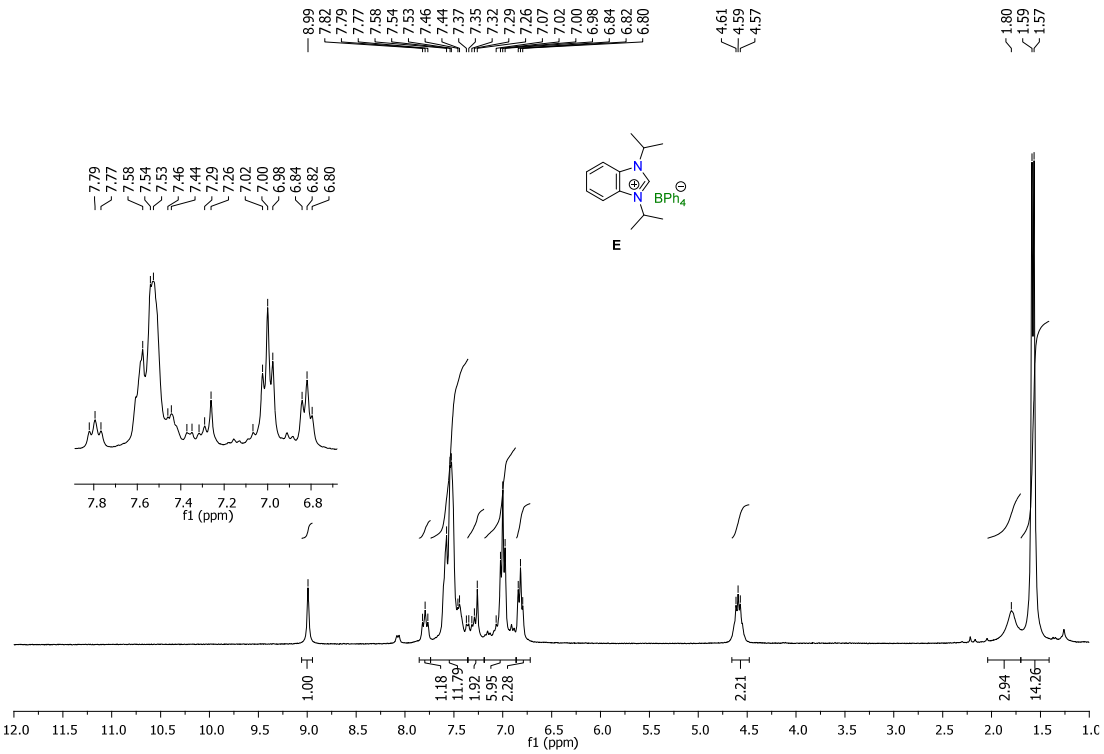
^{13}C NMR spectrum of compound **D** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



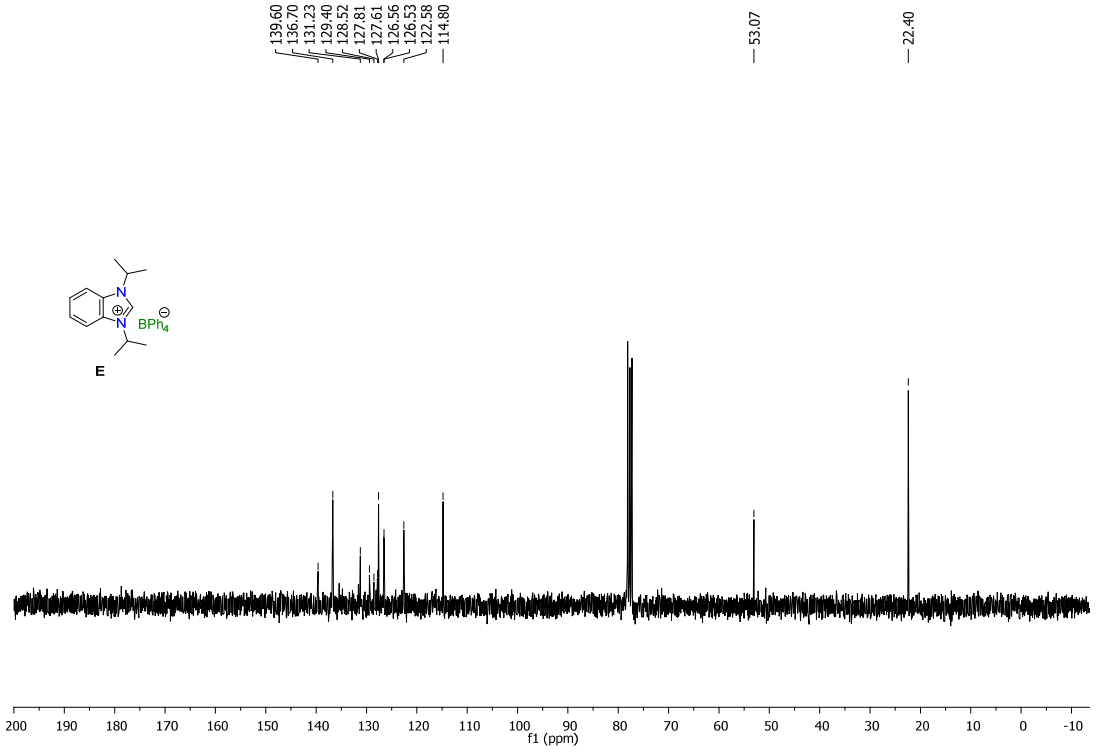
^{31}P NMR spectrum of compound **D** (83 µmol/mL, $CDCl_3$, 202 MHz)



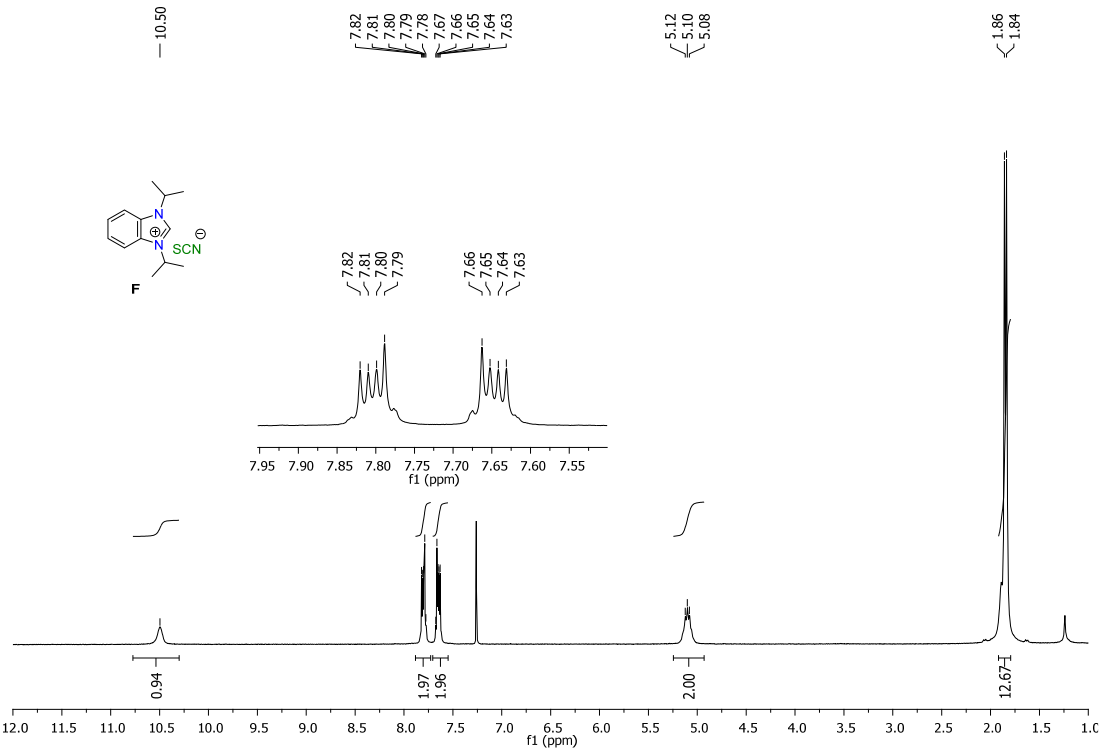
^{19}F NMR spectrum of compound **D** (83 µmol/mL, $CDCl_3$, 282 MHz)



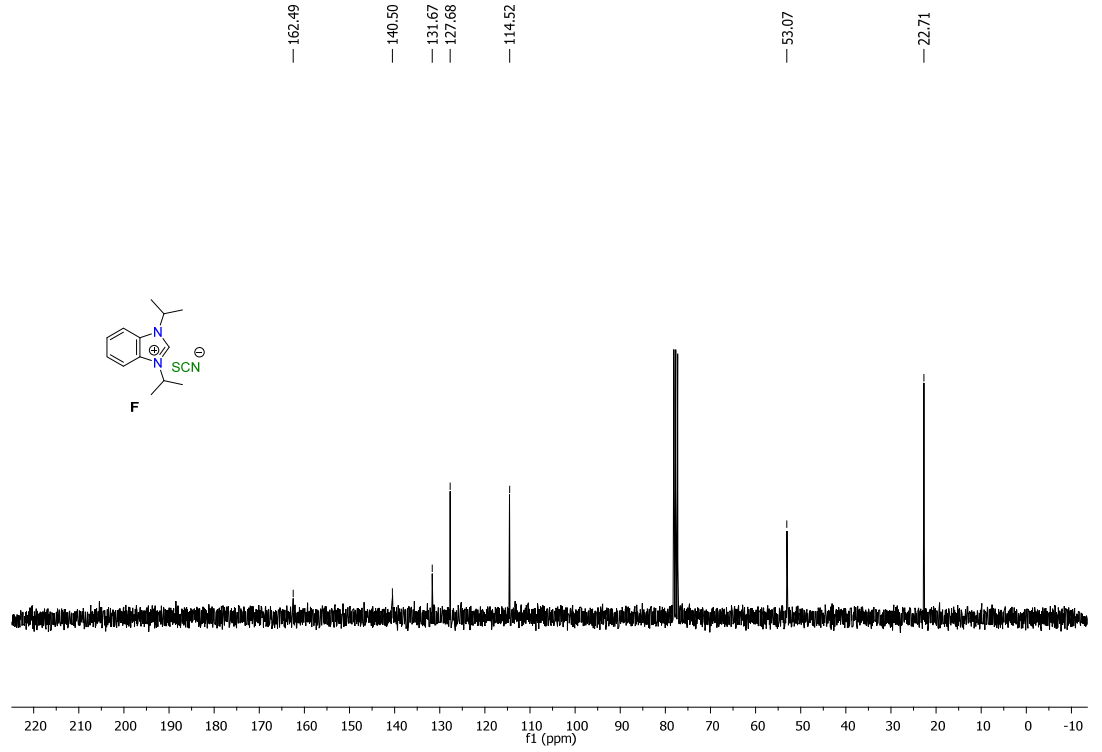
^{1}H NMR spectrum of compound **E** (83 µmol/mL, $CDCl_3$, 300 MHz)



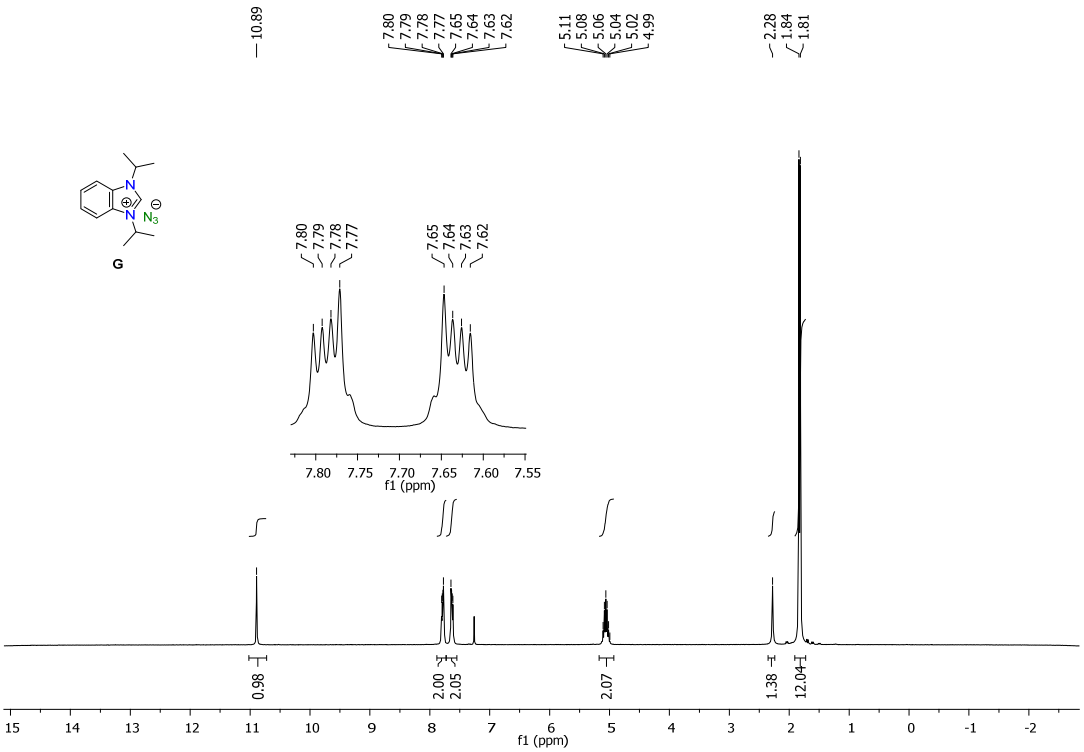
^{13}C NMR spectrum of compound **E** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



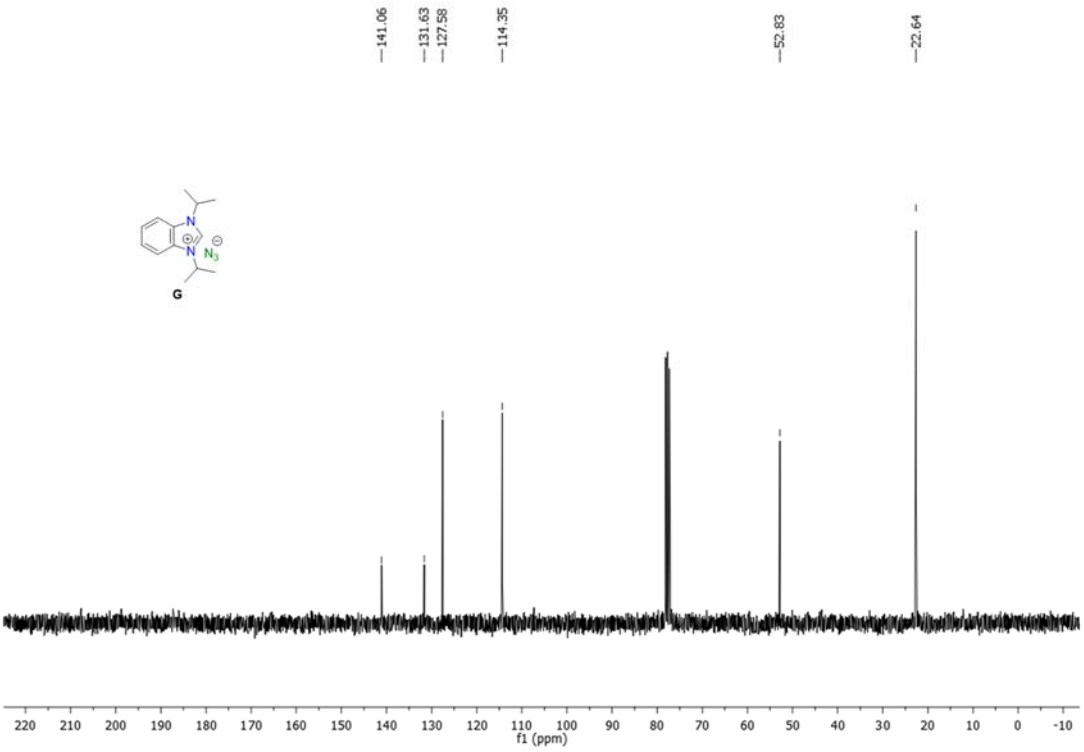
^{1}H NMR spectrum of compound **F** (83 μmol/mL, $CDCl_3$, 300 MHz)



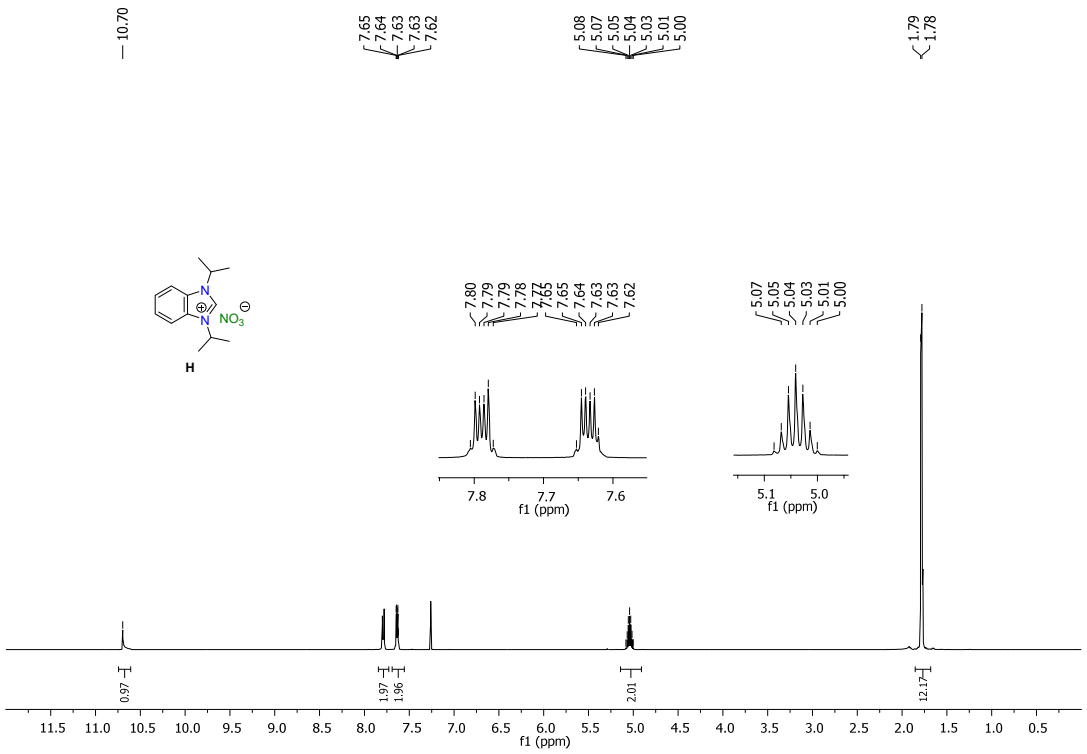
^{13}C NMR spectrum of compound **F** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



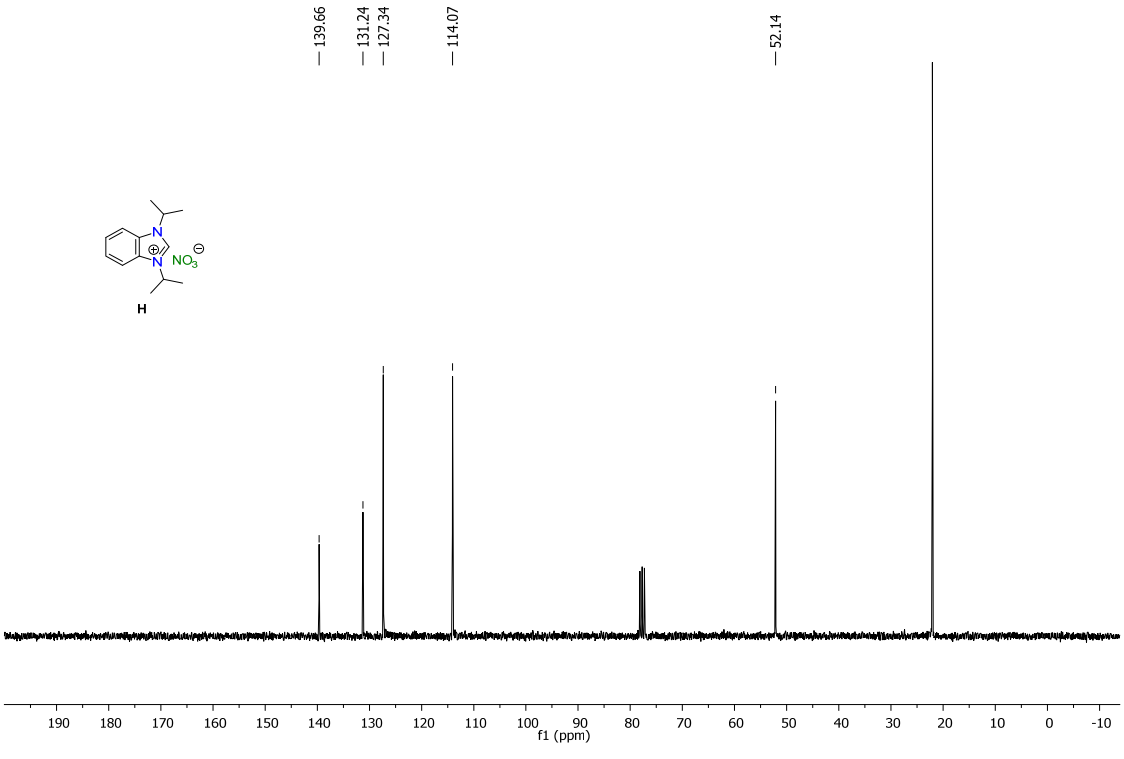
^{1}H NMR spectrum of compound **G** (83 µmol/mL, $CDCl_3$, 300 MHz)



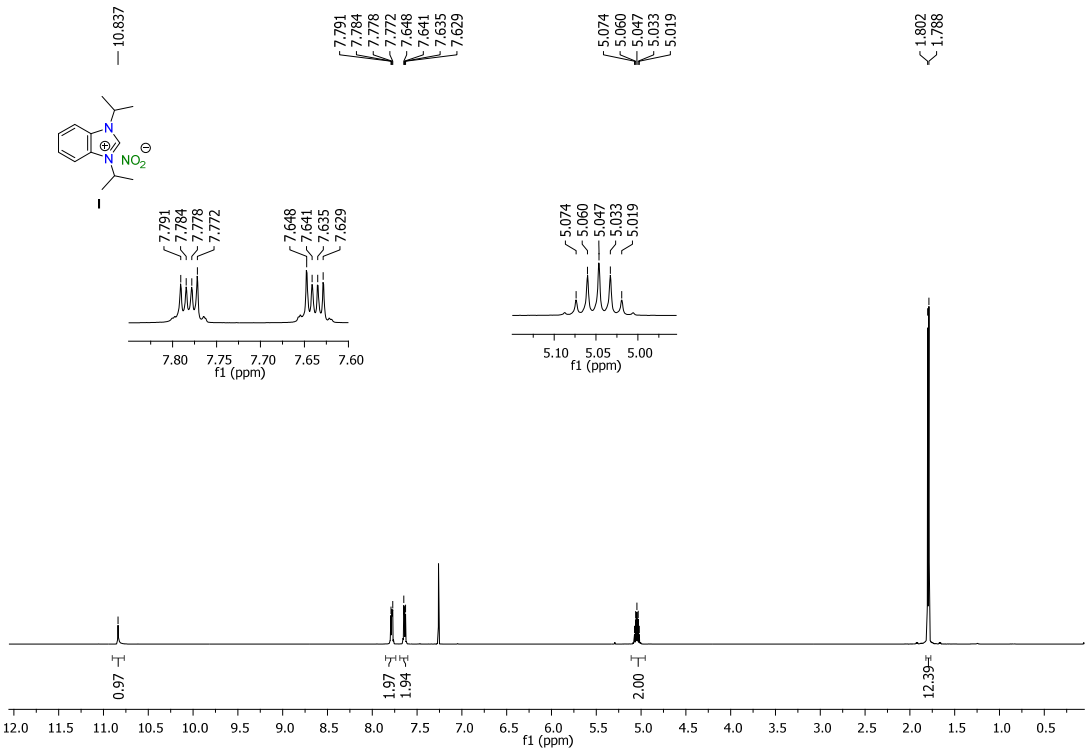
^{13}C NMR spectrum of compound **G** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



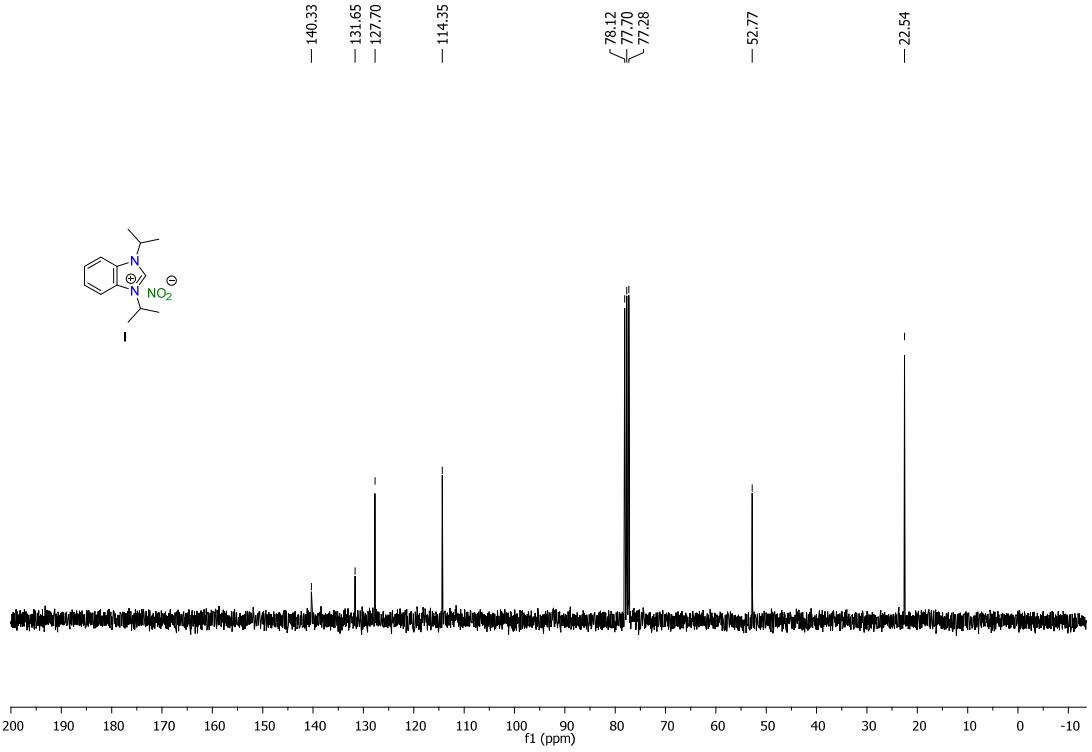
^{1}H NMR spectrum of compound **H** (83 μmol/mL, $CDCl_3$, 500 MHz)



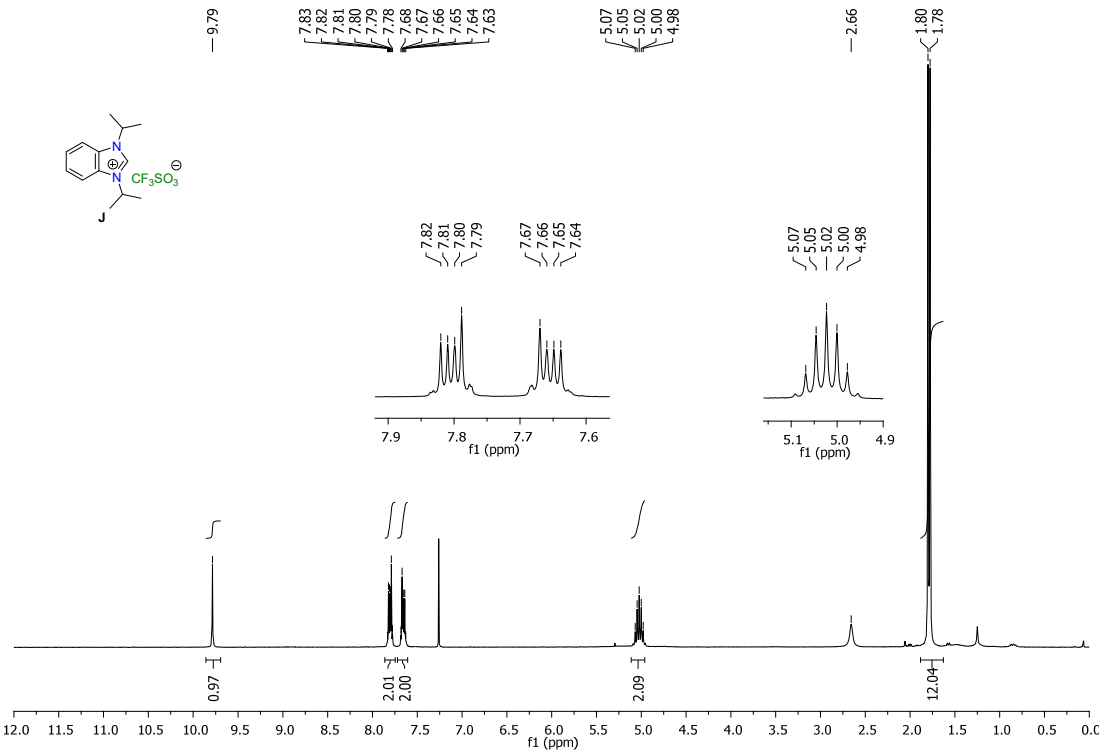
^{13}C NMR spectrum of compound **H** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



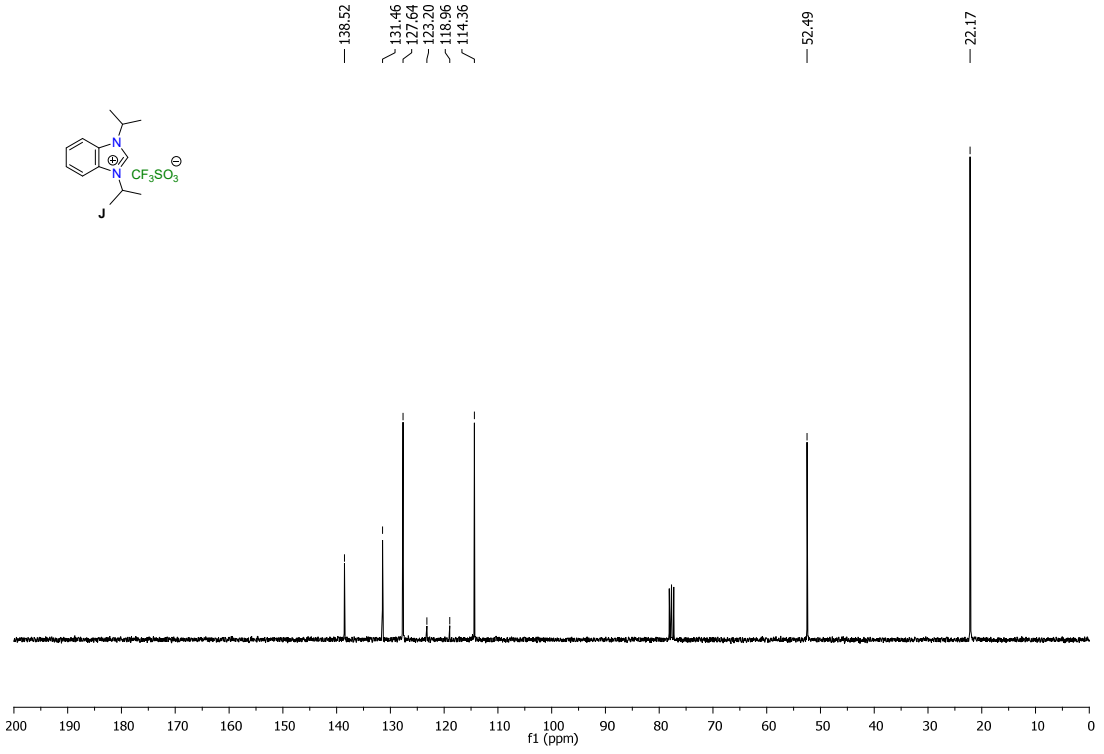
^{1}H NMR spectrum of compound **I** (83 µmol/mL, $CDCl_3$, 500 MHz)



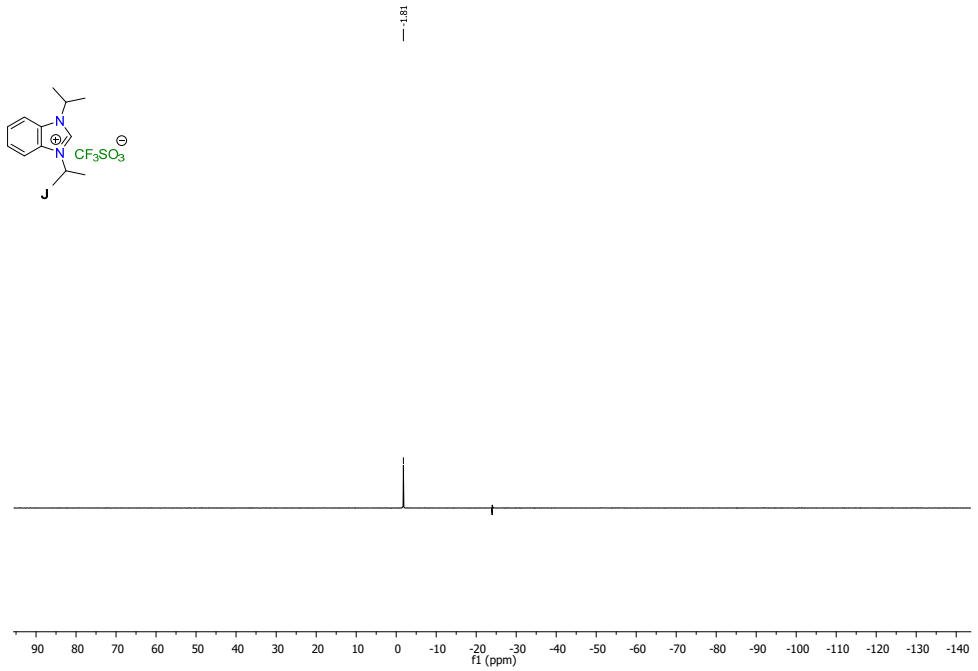
^{13}C NMR spectrum of compound **I** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



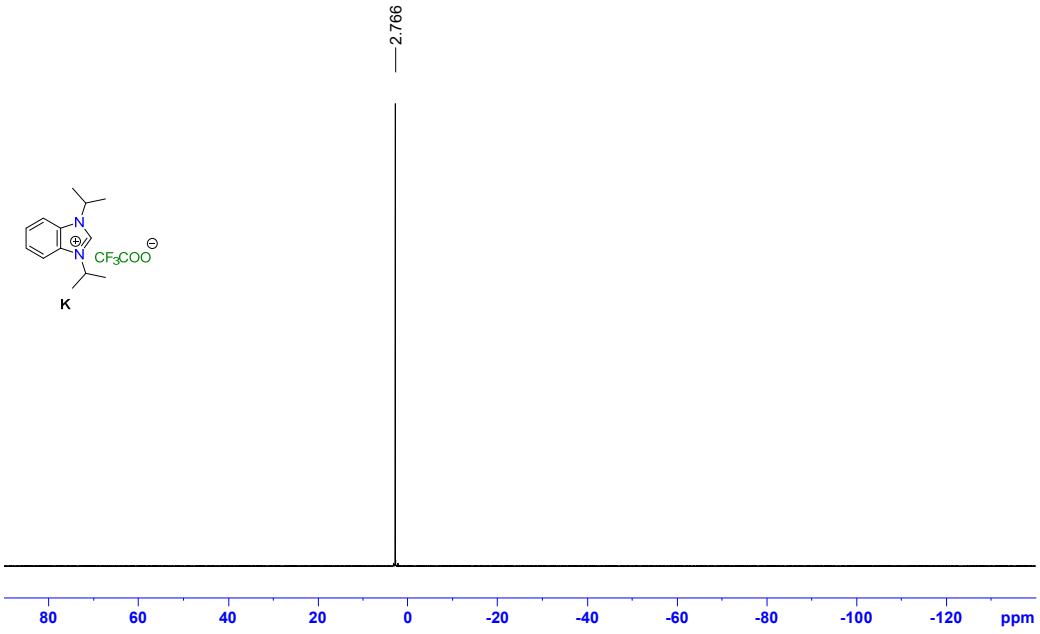
^{1}H NMR spectrum of compound **J** (83 μmol/mL, $CDCl_3$, 300 MHz)



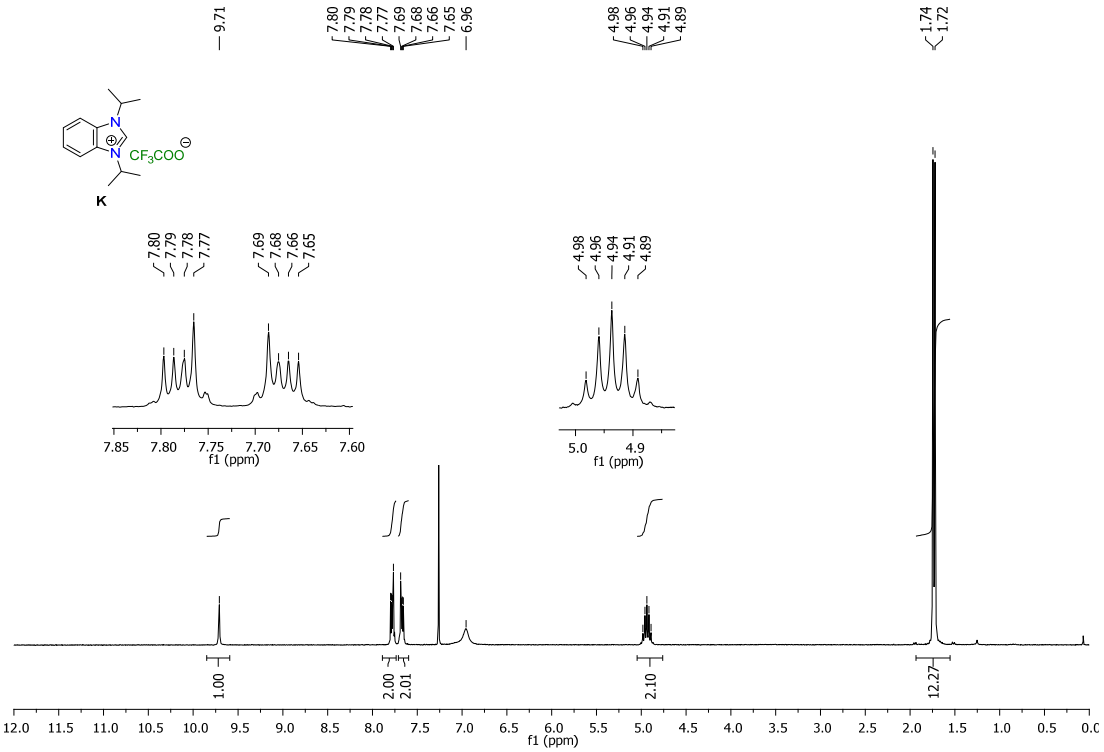
^{13}C NMR spectrum of compound **J** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



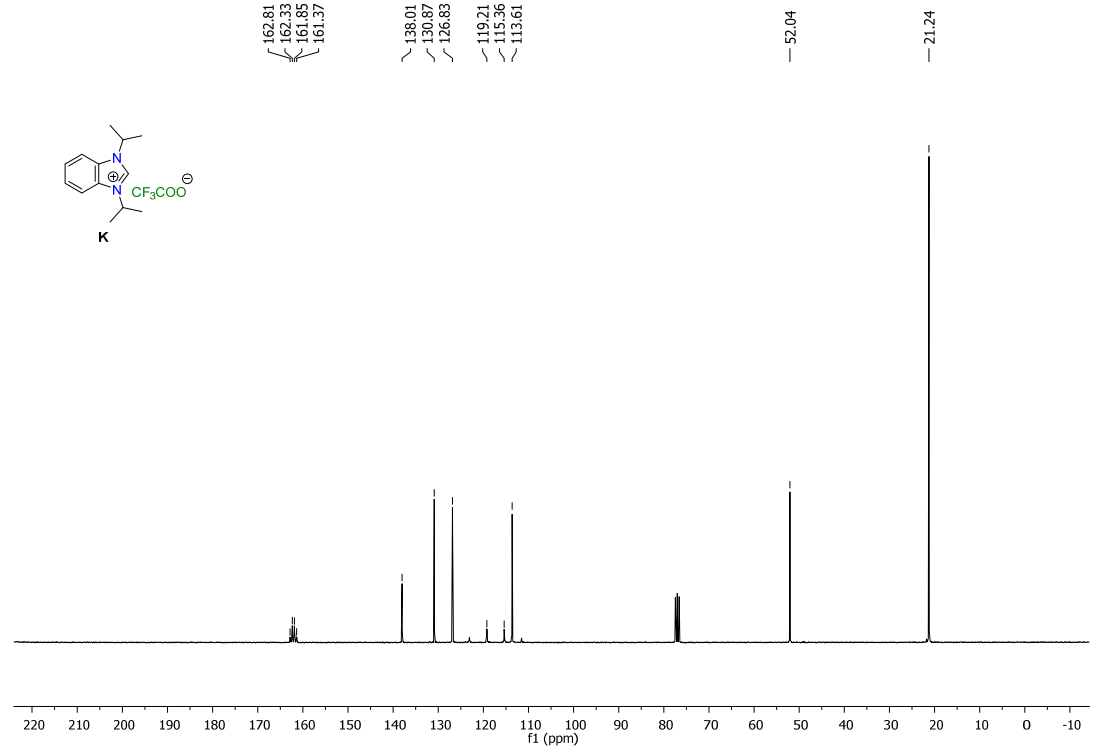
^{19}F NMR spectrum of compound **J** (83 μmol/mL, $CDCl_3$, 282 MHz)



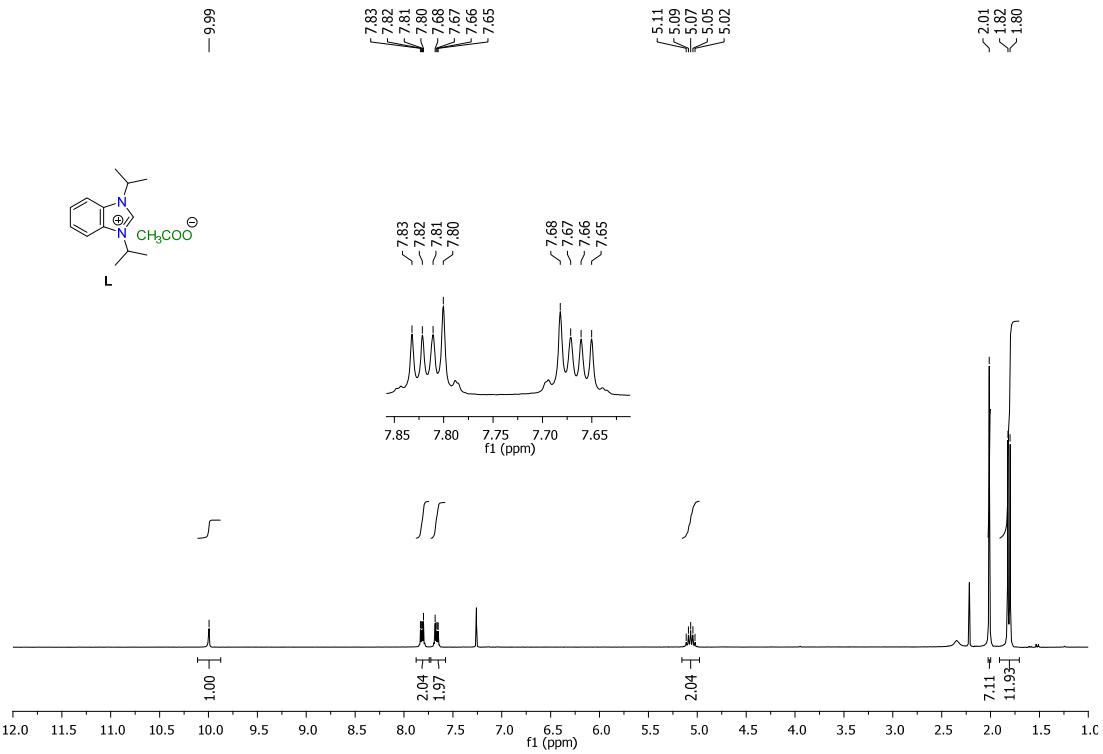
^{19}F NMR spectrum of compound **K** (83 μmol/mL, $CDCl_3$, 282 MHz)



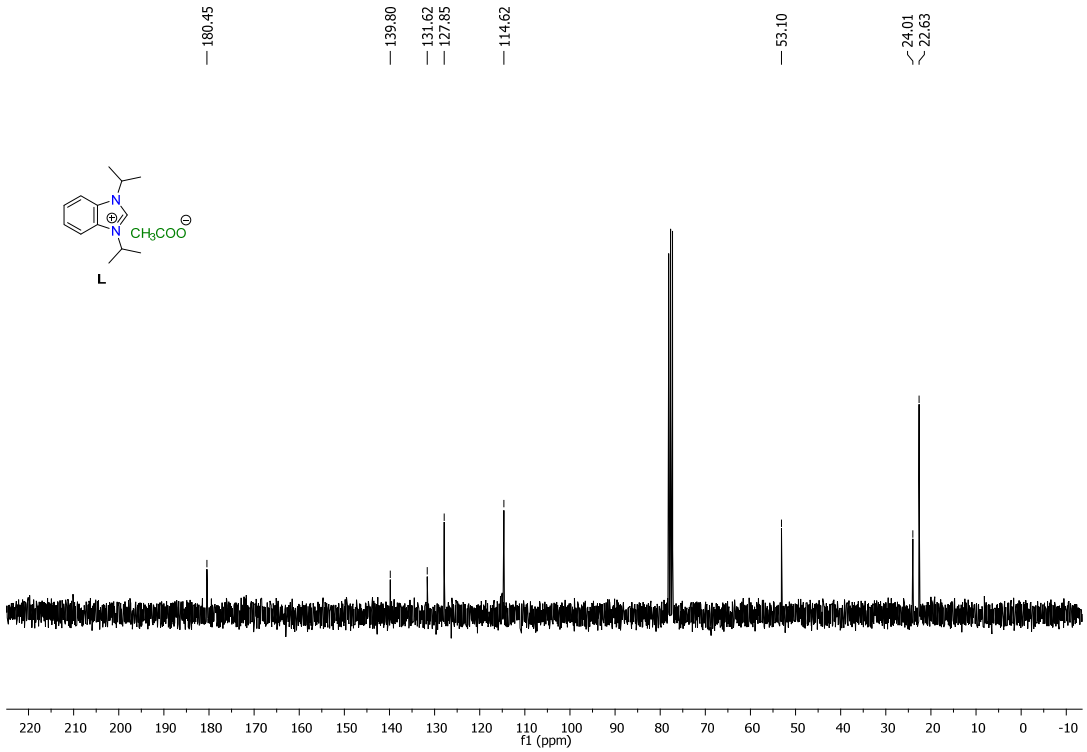
^{1}H NMR spectrum of compound **K** (83 μmol/mL, $CDCl_3$, 300 MHz)



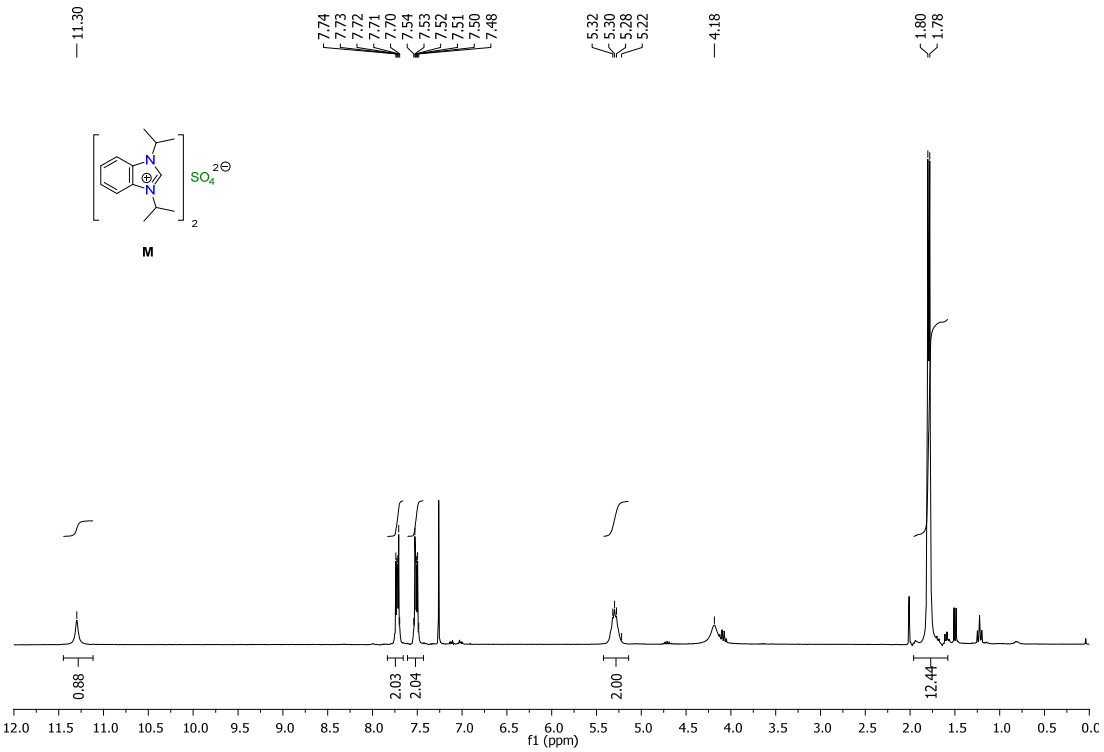
^{13}C NMR spectrum of compound **K** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



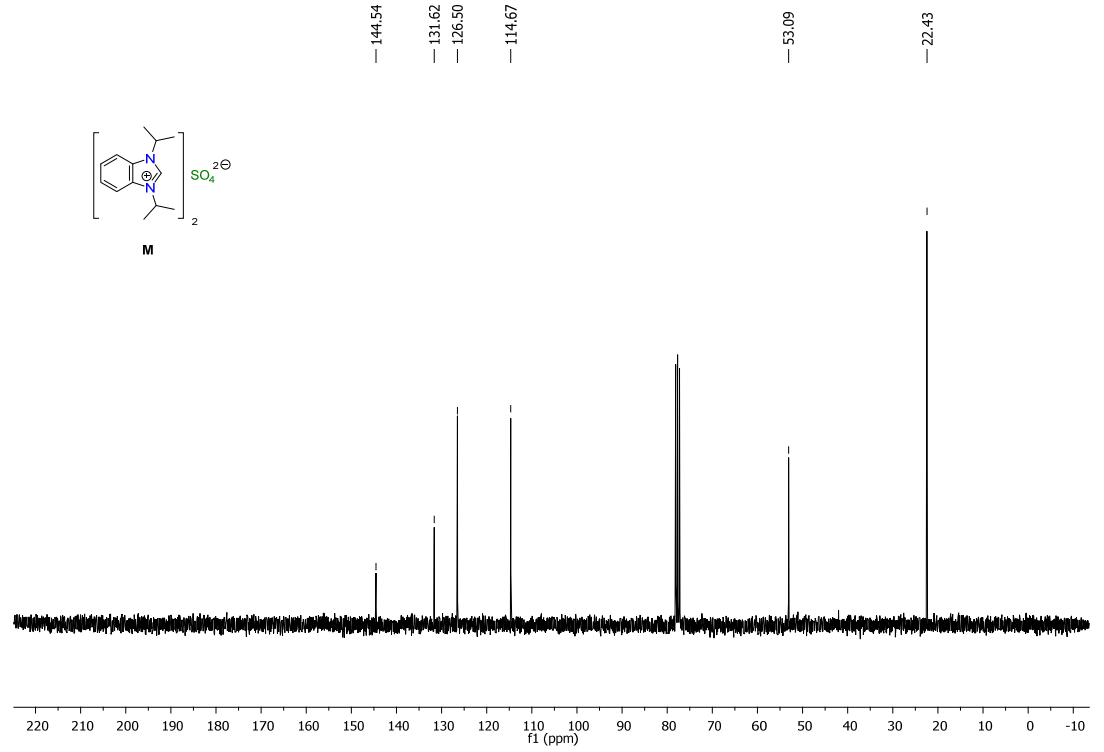
^{1}H NMR spectrum of compound **L** (83 μmol/mL, $CDCl_3$, 300 MHz)



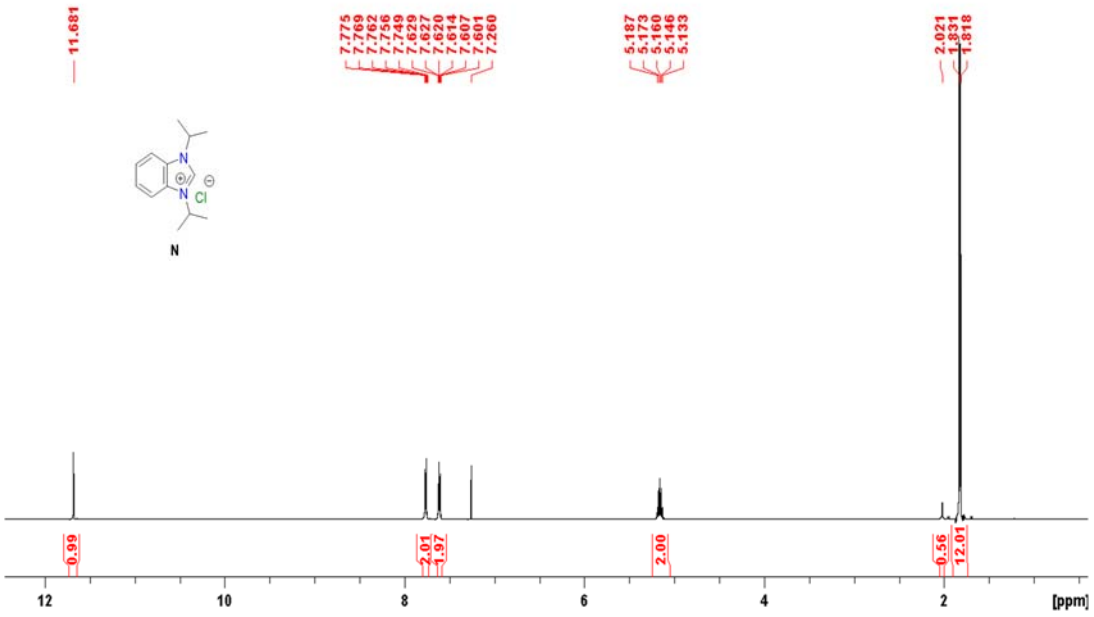
^{13}C NMR spectrum of compound **L** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



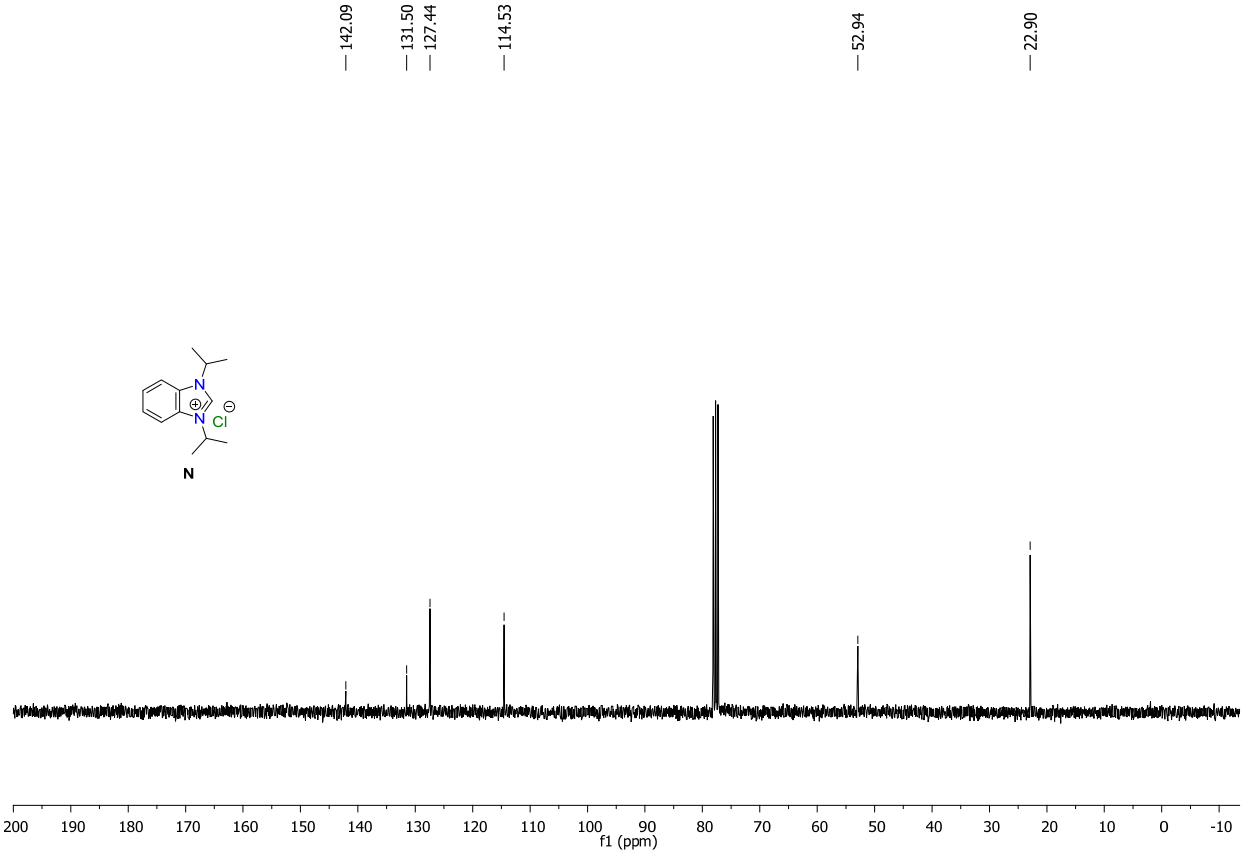
^{1}H NMR spectrum of compound **M** (83 μmol/mL, $CDCl_3$, 300 MHz)



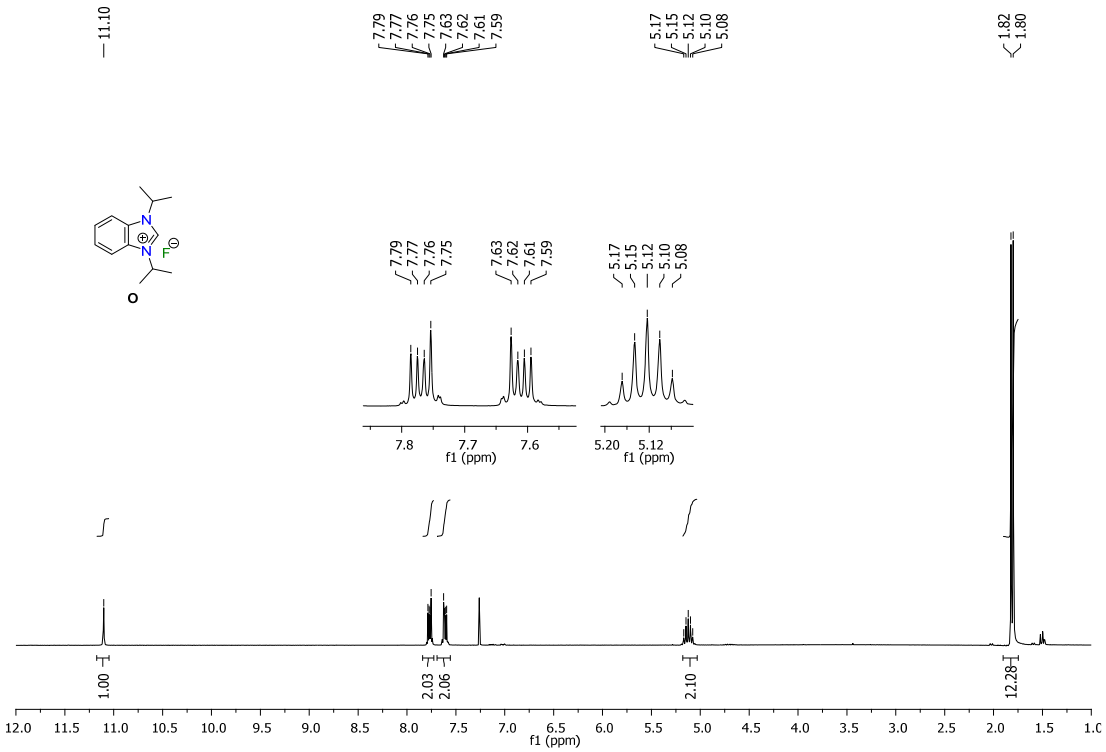
^{13}C NMR spectrum of compound **M** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



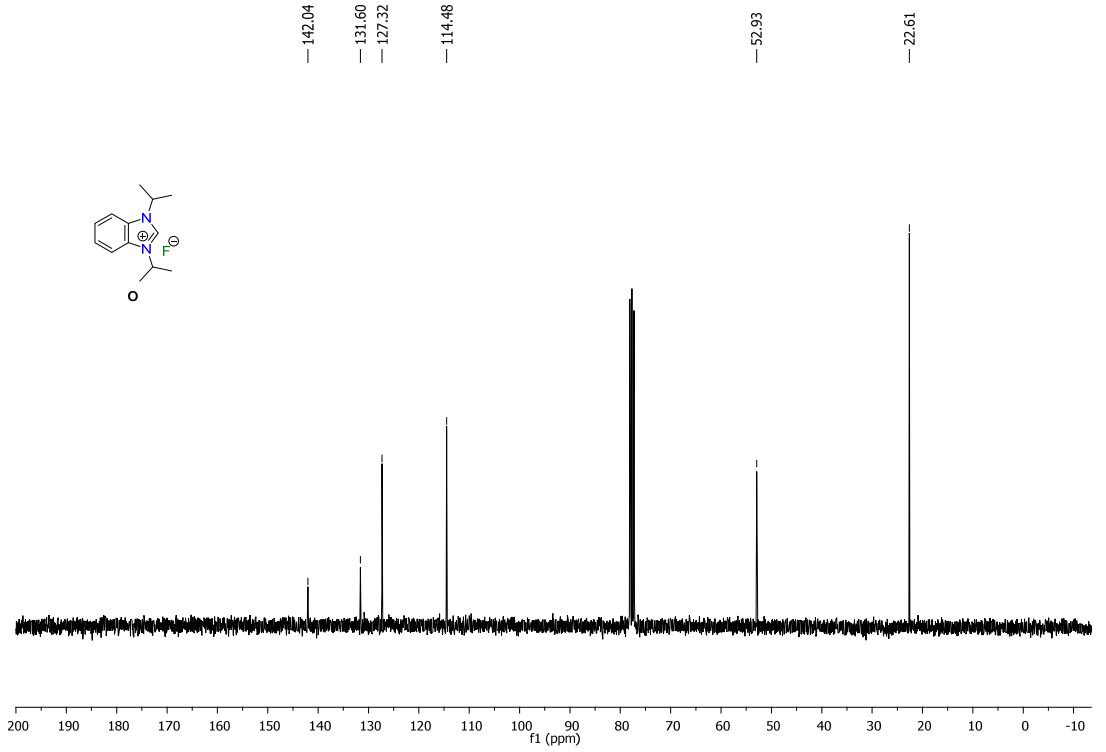
^{1}H NMR spectrum of compound **N** (83 µmol/mL, $CDCl_3$, 500 MHz)



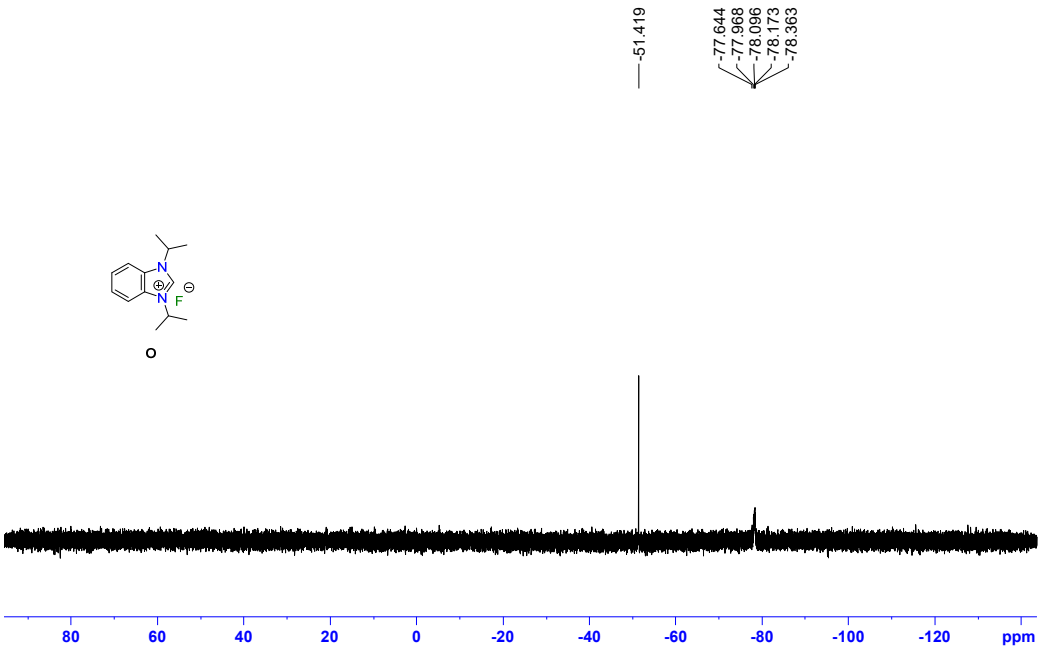
^{13}C NMR spectrum of compound **N** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



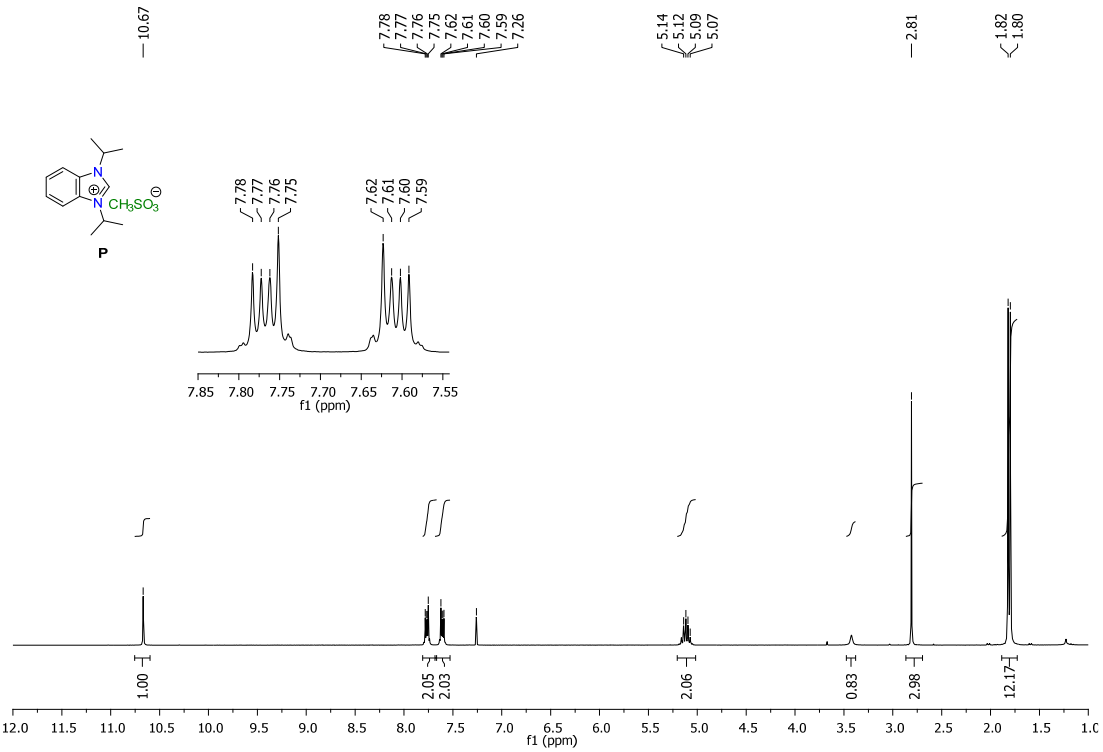
^{1}H NMR spectrum of compound **O** (83 μmol/mL, $CDCl_3$, 300 MHz)



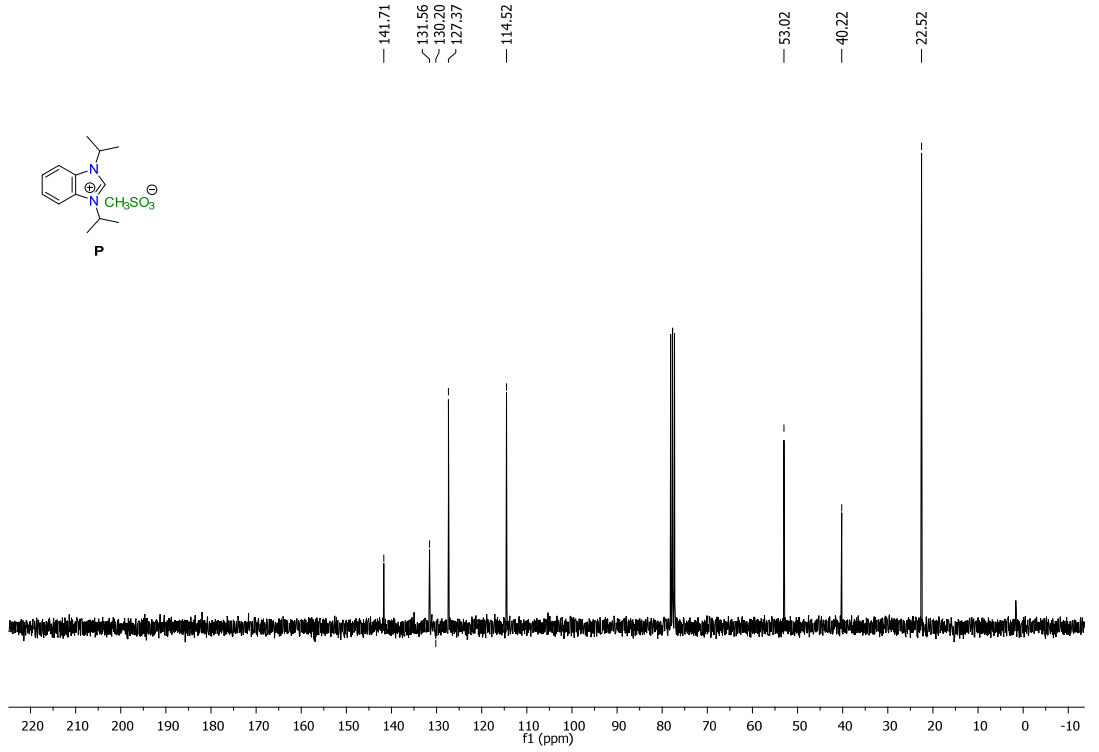
^{13}C NMR spectrum of compound **O** (83 μmol/mL, $CDCl_3$, 75.5 MHz)



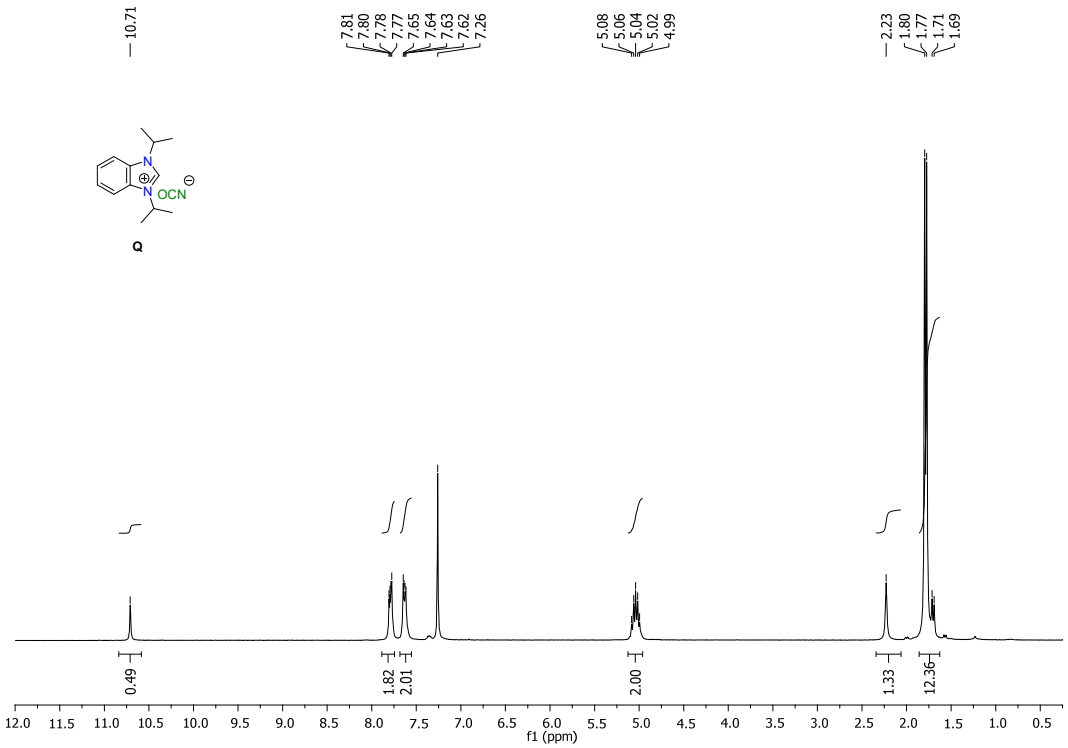
^{19}F NMR spectrum of compound **O** (83 μmol/mL, $CDCl_3$, 282 MHz)



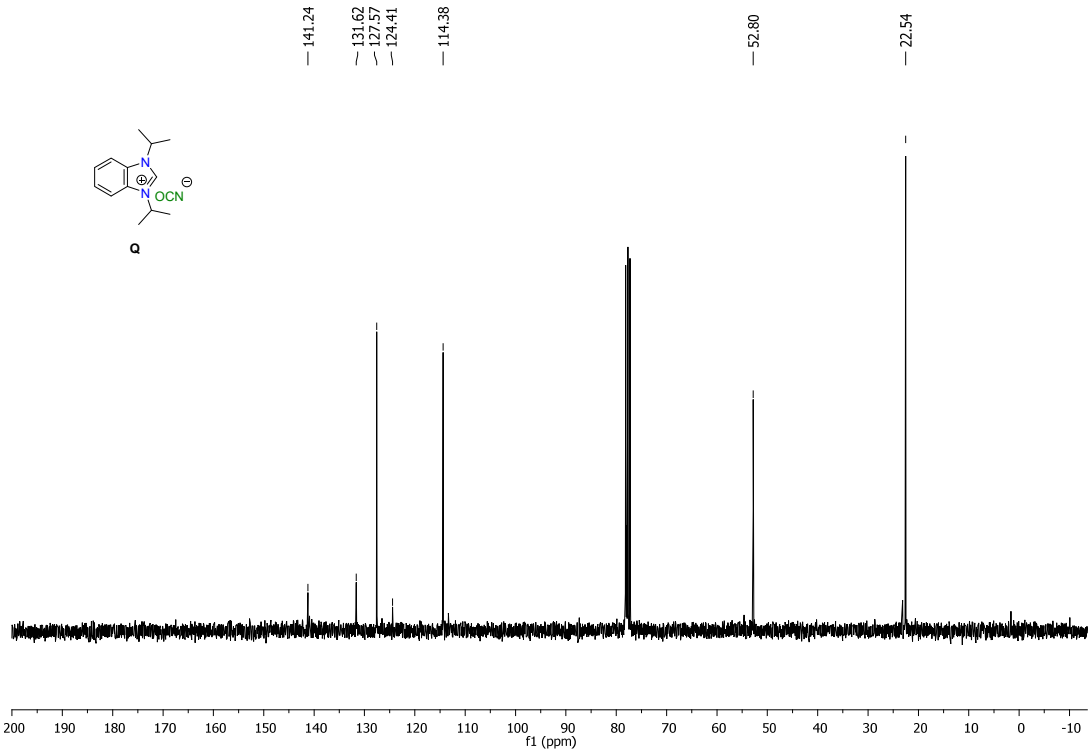
^{1}H NMR spectrum of compound **P** (83 µmol/mL, $CDCl_3$, 300 MHz)



^{13}C NMR spectrum of compound **P** (83 µmol/mL, $CDCl_3$, 75.5 MHz)



^{1}H NMR spectrum of compound **Q** (83 μmol/mL, $CDCl_3$, 300 MHz)



^{13}C NMR spectrum of compound **Q** (83 μmol/mL, $CDCl_3$, 75.5 MHz)

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