Imidazole-stabilized, electron-deficient boron cations

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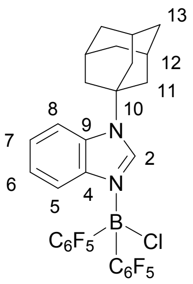
Supporting Information

General information.
All synthetic manipulations were performed under an atmosphere of dry, oxygen-free nitrogen or argon. Solvents were dried by standard procedure prior to use. Commercial reagents were used without further purification. NMR spectra were measured on Bruker AVANCE I 400, Bruker AVANCE III 400 and Agilent DD2 600 MHz spectrometers. Chemical shifts (δ) are reported relative to tetramethylsilane as internal or relative to $(Et_2O)BF_3$ as external standard. CHN analyses were performed in house employing a Perkin-Elmer or an Elementar Vario EL III elemental analyzer. Mass spectra were recorded using a Jeol JMS T100-LC AccuTOF mass spectrometer or an Orbitrap LTQ XL mass spectrometer. Starting materials 1-adamantan-2-yl-1*H*-benzoimidazole and $(C_6F_5)_2BCl$ were prepared according to published procedures.[1, 2] $AlCl_3$ was sublimated and stored in a glove box.



Synthesis of 1a. In a glove box, 1-adamantan-2-yl-1*H*-benzoimidazole (60 mg, 0.238 mmol) was added to $(C_6F_5)_2BCl$ (91 mg, 0.238 mmol) in benzene (1 mL). The mixture was stirred for 10 min at ambient temperature. The solvent was then removed *in vacuo* to yield compound **1a** as a white solid (yield 149 mg, 99%). ^1H NMR (400 MHz, C_6D_6, 300 K): $\delta = 9.05$ (s, 1H, H2), 7.62 (m, 1H, H5), 7.24 (m, 1H, H8), 6.88 (m, 2H, H7 and H6), 1.68 (s, 3H, H12), 1.56 (s, 6H, H11), 1.33 (d, $^2J_{H,H} = 12.6$ Hz, 3H, H13), 1.20 (d, $^2J_{H,H} = 12.4$ Hz, 3H, H13). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 300 K): $\delta = 148.7$ (d, $^1J_{C,F} = 243$ Hz, *o*-C_6F_5), 141.0 (d, $^1J_{C,F} = 252$ Hz, *p*-C_6F_5), 140.8 (C2), 137.8 (d, $^1J_{C,F} = 247$ Hz, *m*-C_6F_5), 136.6 (C4), 131.8 (C9), 125.7 (C6), 125.0 (C7), 118.8 (*ipso*-C_6F_5), 116.5 (C5), 115.6 (C8), 60.6 (C10), 41.1 (C11), 35.3 (C13), 29.4 (C12). ^{19}F NMR (376 MHz, C_6D_6, 300 K): $\delta = -133.8$ (dd, $^3J_{F,F} = 25$ Hz, $^5J_{F,F} = 8$ Hz, 4F, *o*-C_6F_5), –156.3 (t, $^3J_{F,F} = 21$ Hz, 2F, *p*-C_6F_5), –164.0 (m, 4F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_6, 300 K): $\delta = -1.3$ ($B(C_6F_5)_2Cl$). MS (ESI, positive ions): *m/z* (%) = 655.11437 (calcd for [**1a**+Na]$^+$ 655.11457).

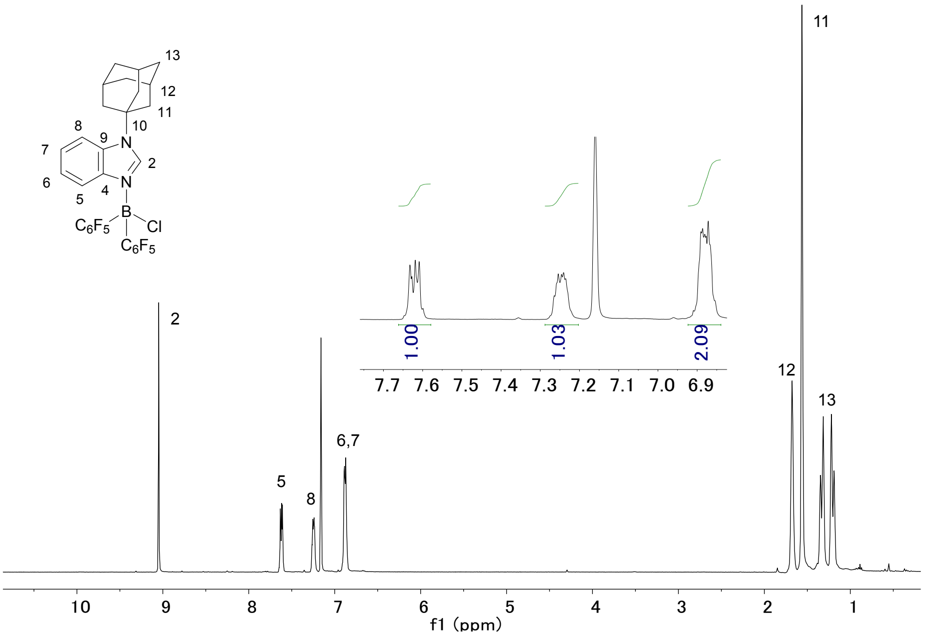


Figure S1. ^1H NMR spectrum of **1a** (in C_6D_6).

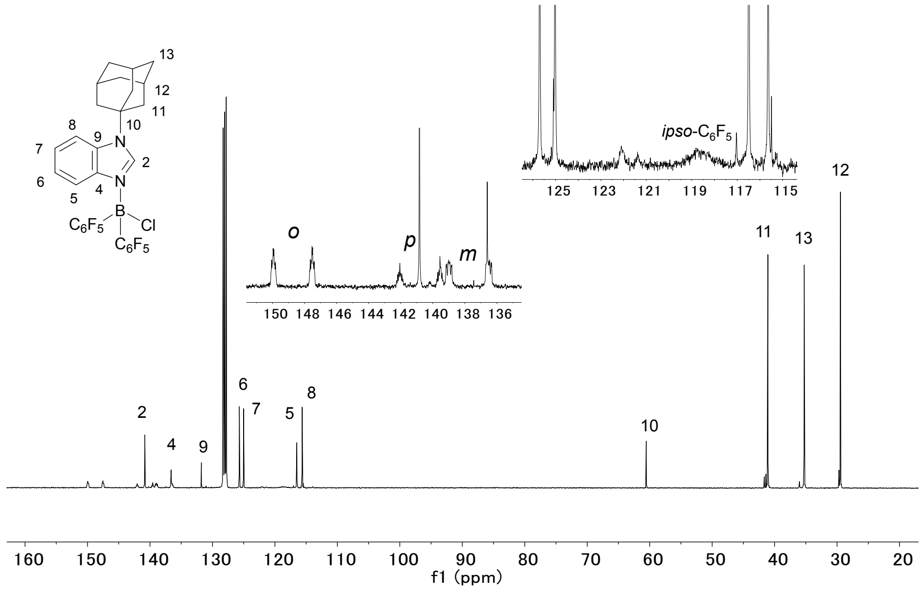


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **1a** (in C_6D_6).

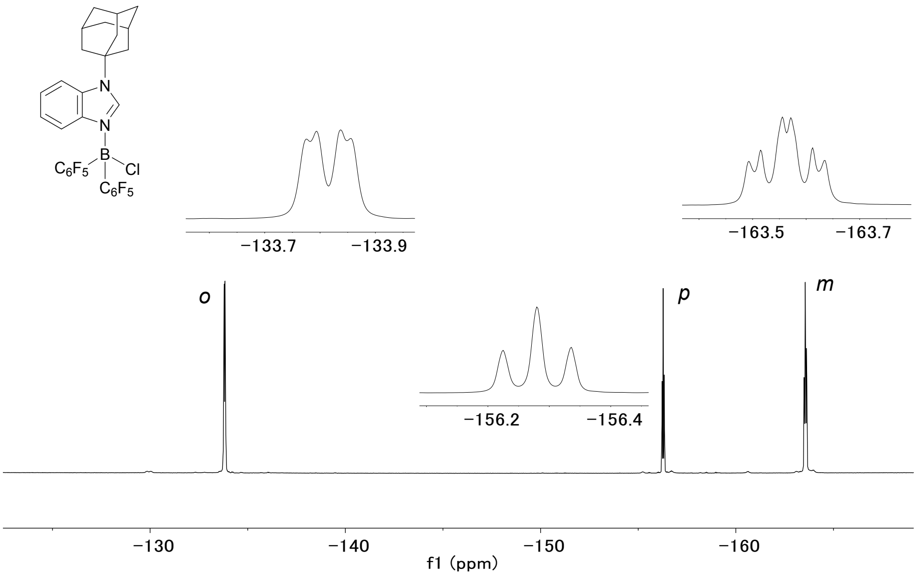


Figure S3. ^{19}F NMR spectrum of **1a** (in C_6D_6).

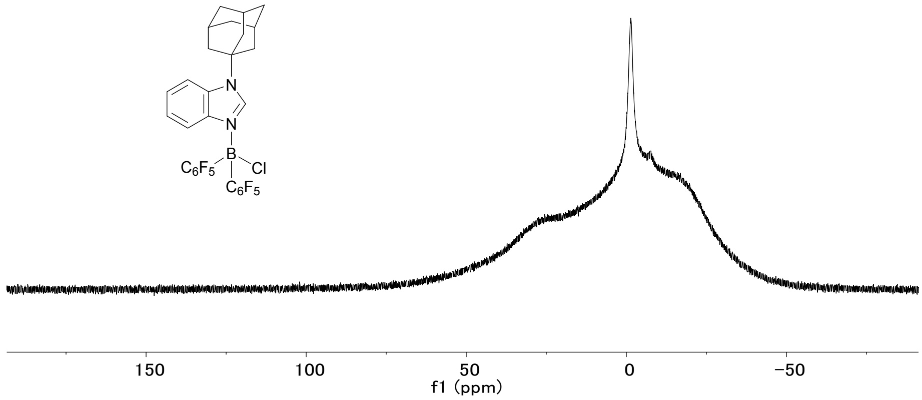
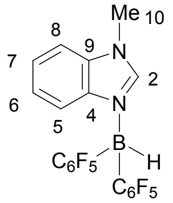


Figure S4. ^{11}B NMR spectrum of **1a** (in C_6D_6).

Synthesis of 1b. In a glove box, 1-methylbenzoimidazole (19 mg, 0.145 mmol) was added to $HB(C_6F_5)_2$ (50 mg, 0.145 mmol) in benzene (1 mL) and the mixture was stirred for 10 min at ambient temperature. The solvent was then removed *in vacuo* and the residue was washed with *n*-pentane (2×2 mL). After removing of the solvent, the resulting solid was dried *in vacuo* to yield compound **1b** as a white solid (yield 58 mg, 83%). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ= 7.75 (d, $^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 1H, H5), 7.29 (s, 1H, H2), 6.97 (m, 2H, H6 and H7), 6.52 (d, $^{3}J_{\mathrm{H,H}}$ = 8.3 Hz, 1H, H8), 5.01 (br m, 1H, BH), 2.24 (s, 3H, H10). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 300 K): δ= 148.7 (d, $^{1}J_{\mathrm{C,F}}$ = 242 Hz, *o*-C_6F_5), 140.1 (d, $^{1}J_{\mathrm{C,F}}$ = 249 Hz, *p*-C_6F_5), 141.8 (C2), 137.6 (d, $^{1}J_{\mathrm{C,F}}$ = 254 Hz, *m*-C_6F_5), 136.3 (C4), 132.7 (C9), 125.8 (C6), 125.6 (C7), 119.1 (*ipso*-C_6F_5), 116.9 (C5), 111.0 (C8), 30.8 (C10). ^{19}F NMR 376 MHz, C_6D_6, 300 K): δ= –133.8 (dd, $^{3}J_{\mathrm{F,F}}$ = 25 Hz, $^{5}J_{\mathrm{F,F}}$ = 9 Hz, 4F, *o*-C_6F_5), –158.3 (t, $^{3}J_{\mathrm{F,F}}$ = 21 Hz, 2F, *p*-C_6F_5), –164.0 (m, 4F, *m*-C_6F_5). ^{11}B NMR (128 MHz, C_6D_6, 300 K): δ= –14.8 ($B(C_6F_5)_2H$). Anal. Calcd. for **1b** ($C_{20}H_9N_2BF_{10}$): C 50.24% , H 1.90%, N 5.86%. Found: C 50.32%, H 1.89%, N 5.79%.



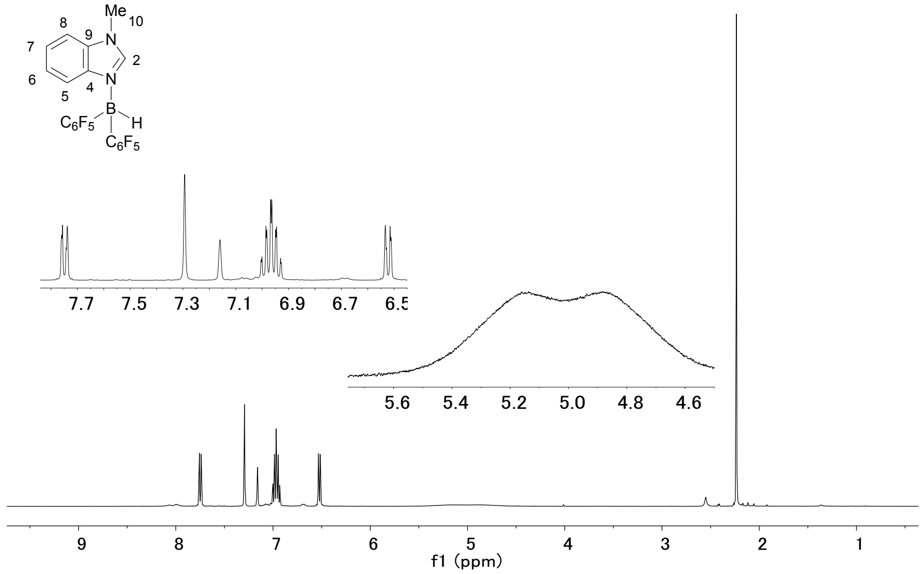


Figure S5. ^{1}H NMR spectrum of **1b** (in C_6D_6).

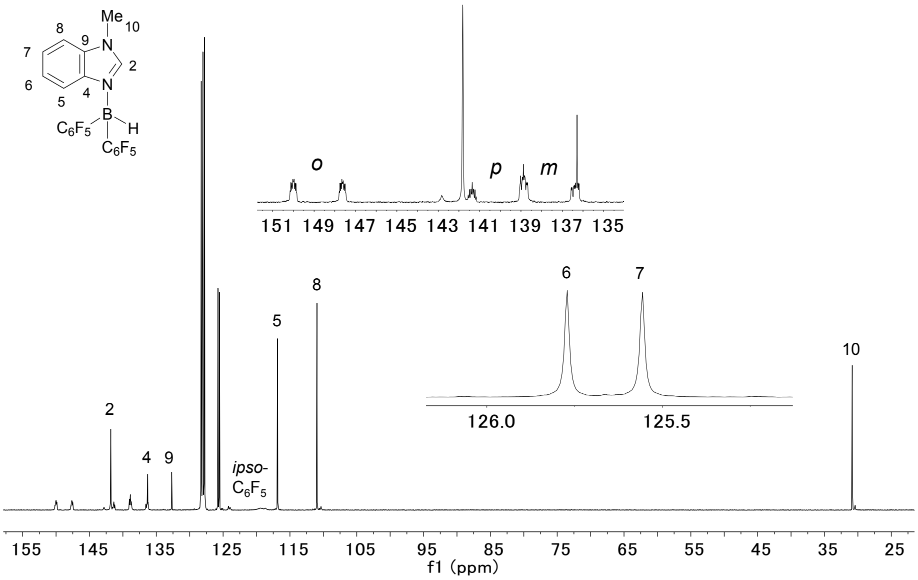


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** (in C_6D_6).

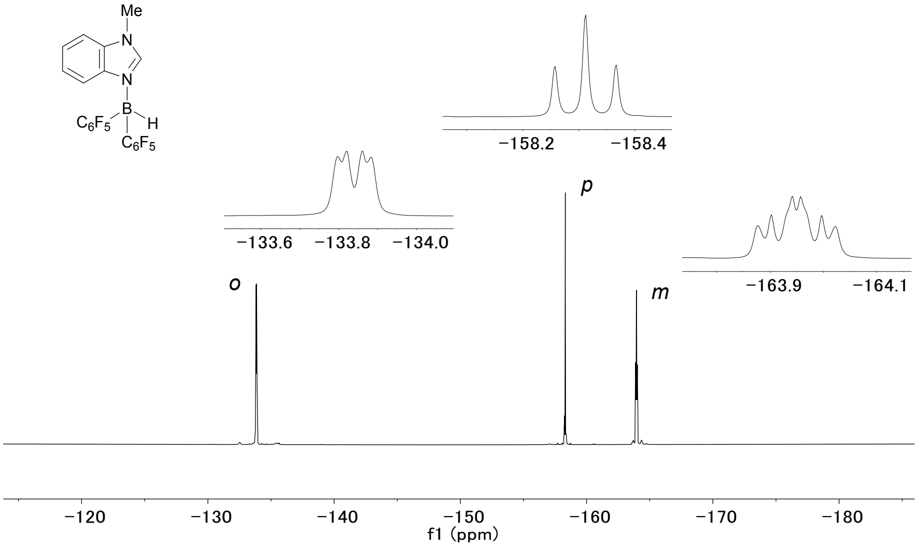


Figure S7. ^{19}F NMR spectrum of **1b** (in C_6D_6).

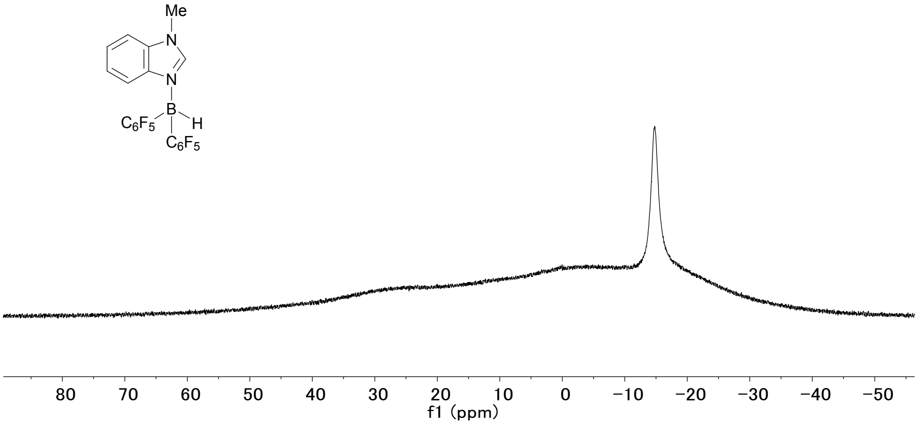
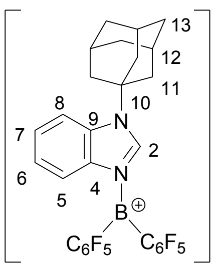


Figure S8. ^{11}B NMR spectrum of **1b** (in C_6D_6).



Synthesis of 2a' (Al_2Cl_7 salt). In a glove box, $AlCl_3$ (63 mg, 0.470 mmol) was added to **1a** (149 mg, 0.235 mmol) in toluene (2 mL) and the mixture was stirred for 18 h at ambient temperature. A two-layer reaction mixture formed. The top toluene layer was removed and washed with toluene (2×1 mL) to afforded a pale brown oil. The oil was dried *in vacuo* to give **2a** as a pale brown solid (yield 155 mg, 73%). ^1H NMR (400 MHz, CD_2Cl_2, 300 K): $\delta = 8.95$ (s, 1H, H2), 8.27 (d, $^3J_{H,H} = 8.6$ Hz, 1H, H5), 7.83 (t, $^3J_{H,H} = 8.6$ Hz, 1H, H6), 7.72 (t, $^3J_{H,H} = 8.5$ Hz, 1H, H7), 7.48 (d, $^3J_{H,H} = 8.5$ Hz, 1H, H8), 2.49 (s, 9H, H11 and H12), 1.92 (s, 6H, H13). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 300 K): $\delta = 149.3$ (*o*-C_6F_5, $^1J_{C,F} = 255$ Hz), 146.9 (*p*-C_6F_5, $^1J_{C,F} = 265$ Hz), 145.5 (C2), 138.7 (*m*-C_6F_5, $^1J_{C,F} = 256$ Hz), 134.8 (C9), 131.9 (C4), 130.2 (C7), 129.2 (C6), 118.2 (C5), 116.6 (C8), 107.6 (*ipso*-C_6F_5), 66.6 (C10), 41.9 (C11), 35.5 (C13), 30.0 (C12). ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): $\delta = -126.0$ (m, 4F, *o*-C_6F_5), −139.1(m, 2F, *p*-C_6F_5), −157.6 (m, 4F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 300 K): $\delta = 50.1$ (br, $B(C_6F_5)_2$). ^{27}Al NMR (104 MHz, CD_2Cl_2, 300 K): δ 104.5 (br, Al_2Cl_7). Anal. Calcd. for **2a** (Al_2Cl_7 salt) $C_{29}H_{20}N_2Al_2BCl_7F_{10})\cdot 0.5C_7H_8$: C 41.29%, H 2.56%, N 2.96%. Found: C 41.18%, H 2.79%, N 2.93%.

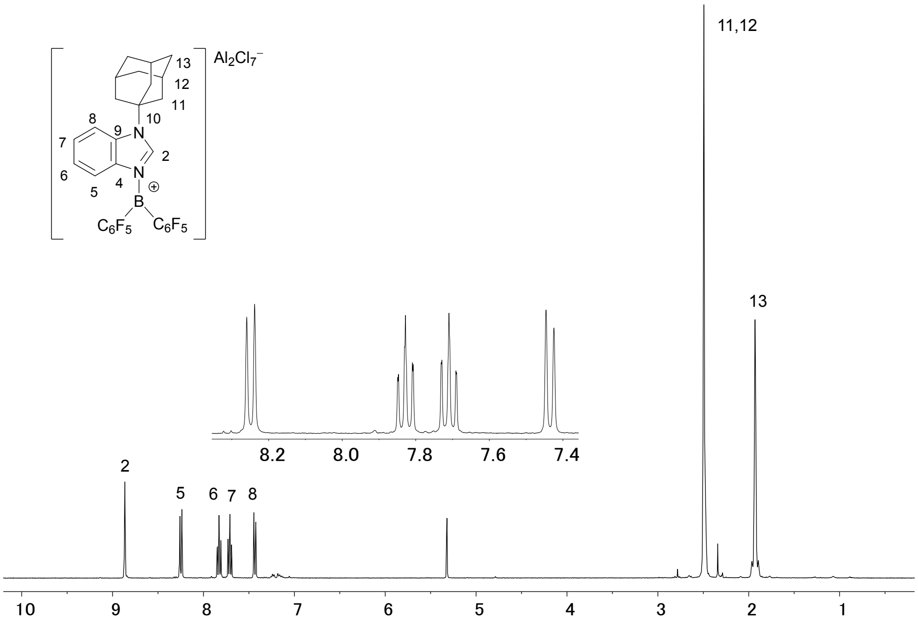


Figure S9. ^1H NMR spectrum of **2a** (Al_2Cl_7 salt in CD_2Cl_2).

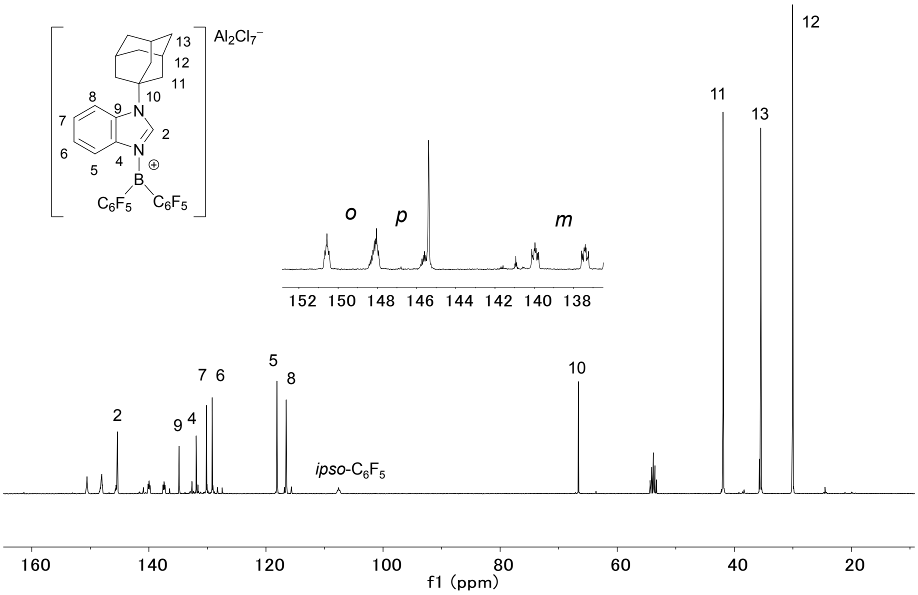


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** (Al_2Cl_7 salt in CD_2Cl_2).

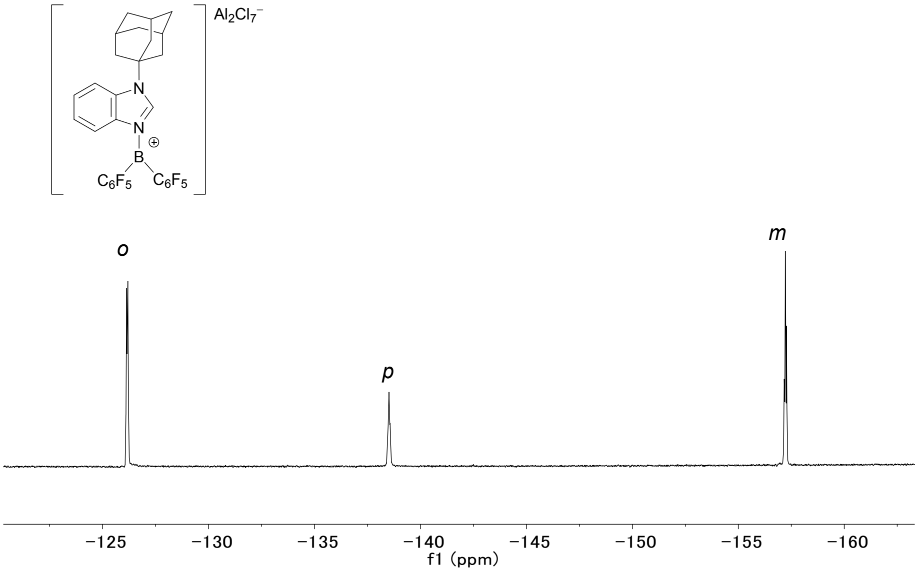


Figure S11. ^{19}F NMR spectrum of **2a** (Al_2Cl_7 salt in CD_2Cl_2).

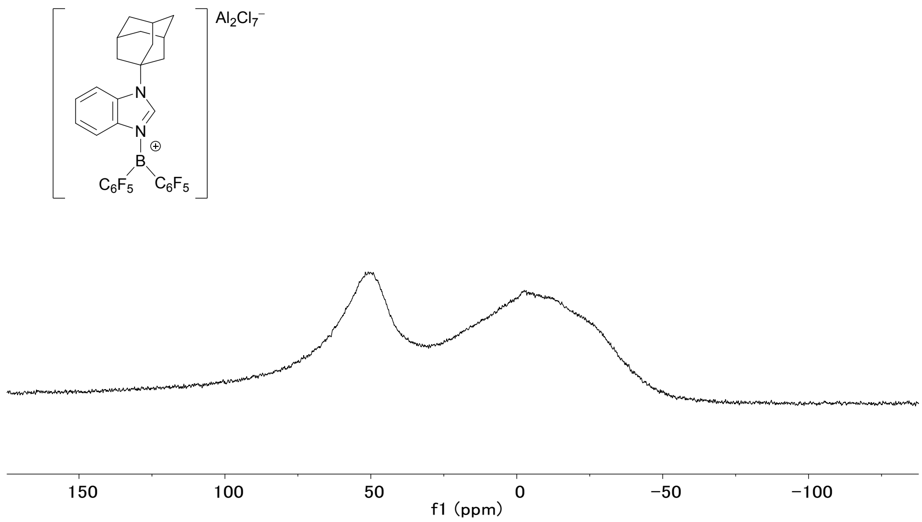


Figure S12. ^{11}B NMR spectrum of **2a** (Al_2Cl_7 salt in CD_2Cl_2).

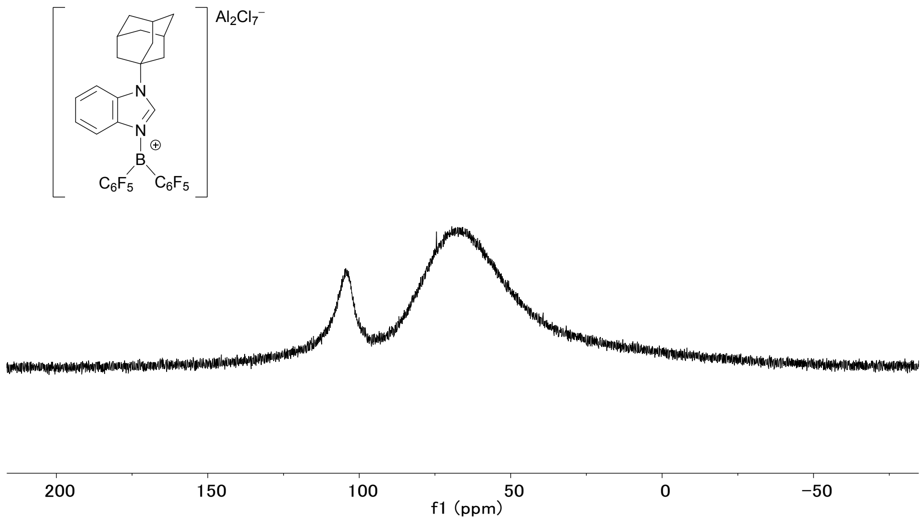
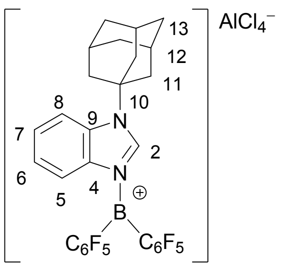


Figure S13. ^{27}Al NMR spectrum of **2a** (Al_2Cl_7 salt in CD_2Cl_2).



Synthesis of 2a (AlCl$_4$ salt). In a glove box, AlCl$_3$ (4.2 mg, 0.0316 mmol) was added to **1a** (20 mg, 0.0316 mmol) in dichloromethane (1 mL) and the mixture was stirred for 1 h at ambient temperature. The solvent from the reaction mixture was removed *in vacuo* to give **2a** (AlCl$_4$ salt) as a pale brown solid (yield 19 mg, 78%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 300 K): δ = 9.10 (s, 1H, H2), 8.21 (d, $^3J_{\mathrm{H,H}}$ = 8.5 Hz, 1H, H5), 7.77 (t, $^3J_{\mathrm{H,H}}$ = 8.2 Hz, 1H, H6), 7.66 (t, $^3J_{\mathrm{H,H}}$ = 8.1 Hz, 1H, H7), 7.41 (d, $^3J_{\mathrm{H,H}}$ = 8.5 Hz, 1H, H8), 2.51 (s, 6H, H11), 2.45 (s, 3H, H12),1.91 (s, 6H, H13). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 300 K): δ= 149.3 (*o*-C$_6$F$_5$, $^1J_{\mathrm{C,F}}$ = 253 Hz), 146.5 (*p*-C$_6$F$_5$, $^1J_{\mathrm{C,F}}$ = 264 Hz), 145.8 (C2), 138.7 (*m*-C$_6$F$_5$, $^1J_{\mathrm{C,F}}$ = 256 Hz), 135.0 (C9), 132.0 (C4), 129.6 (C7), 128.7 (C6), 118.0 (C5), 116.5 (C8), 108.5 (*ipso*-C$_6$F$_5$), 66.3 (C10), 42.0 (C11), 35.6 (C13), 30.1 (C12). ^{19}F NMR (376 MHz, CD$_2$Cl$_2$, 300 K): δ= –126.8 (br, 4F, *o*-C$_6$F$_5$), –140.9 (br, 2F, *p*-C$_6$F$_5$), –158.5 (br, 4F, *m*-C$_6$F$_5$). ^{11}B NMR (128 MHz, CD$_2$Cl$_2$, 300 K): δ= 54.9 (br, B(C$_6$F$_5$)$_2$). ^{27}Al NMR (104 MHz, CD$_2$Cl$_2$, 300 K): δ = 103.8 (br, AlCl$_4$). Anal. Calcd. for **2a** (AlCl$_4$ salt) (C$_{29}$H$_{20}$N$_2$AlBCl$_4$F$_{10}$): C 45.47% , H 2.63%, N 3.66%. Found: C 45.18%, H 2.84%, N 3.45%.

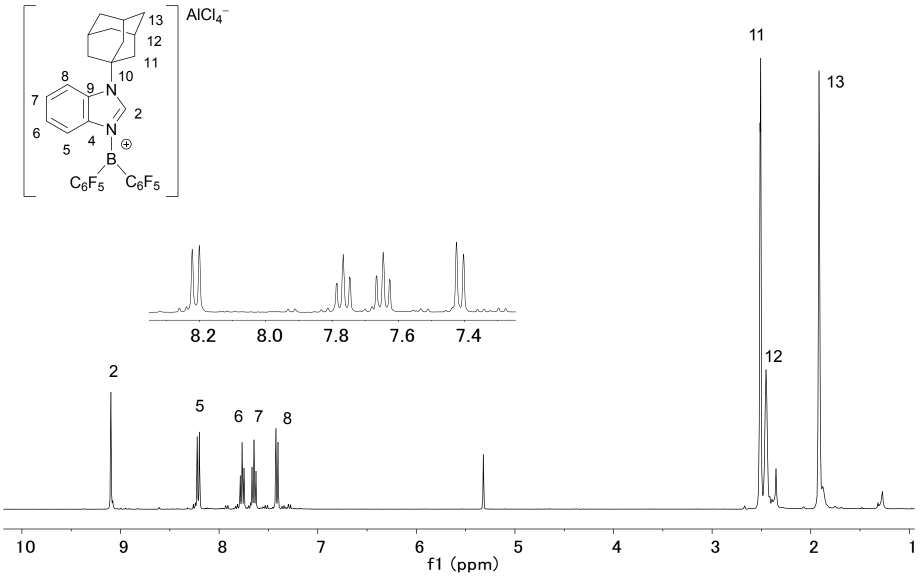


Figure S14. ^{1}H NMR spectrum of **2a** (AlCl$_4$ salt in CD$_2$Cl$_2$).

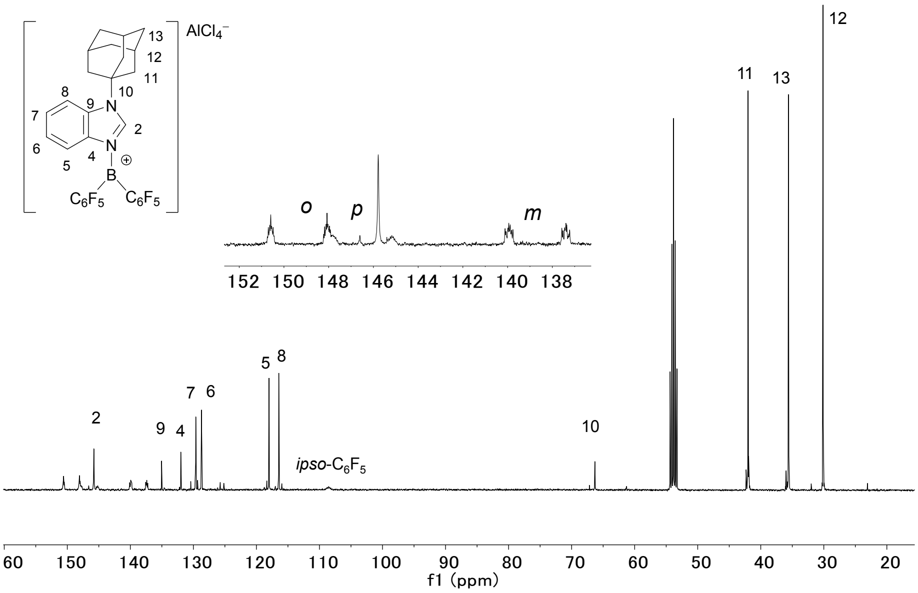


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** ($AlCl_4$ salt in CD_2Cl_2).

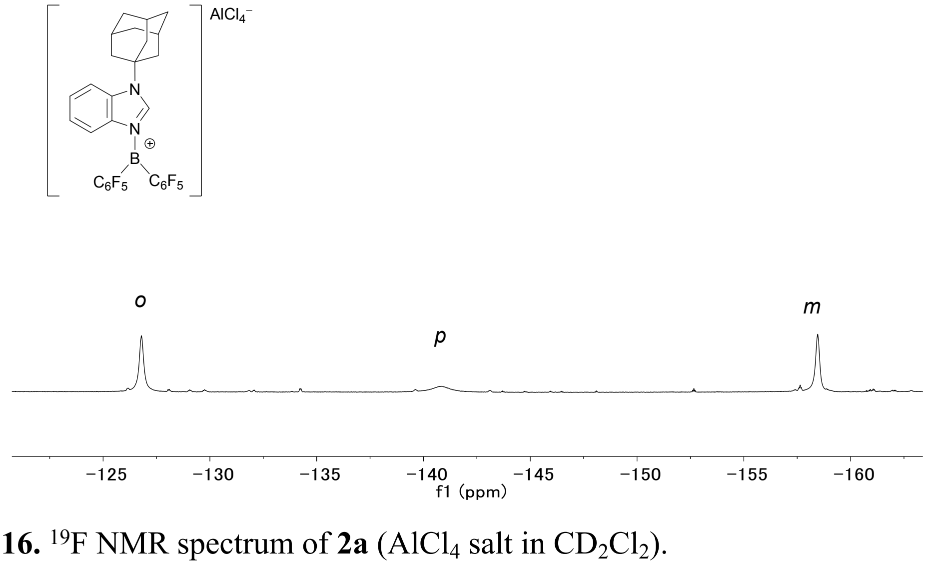


Figure S16. ^{19}F NMR spectrum of **2a** ($AlCl_4$ salt in CD_2Cl_2).

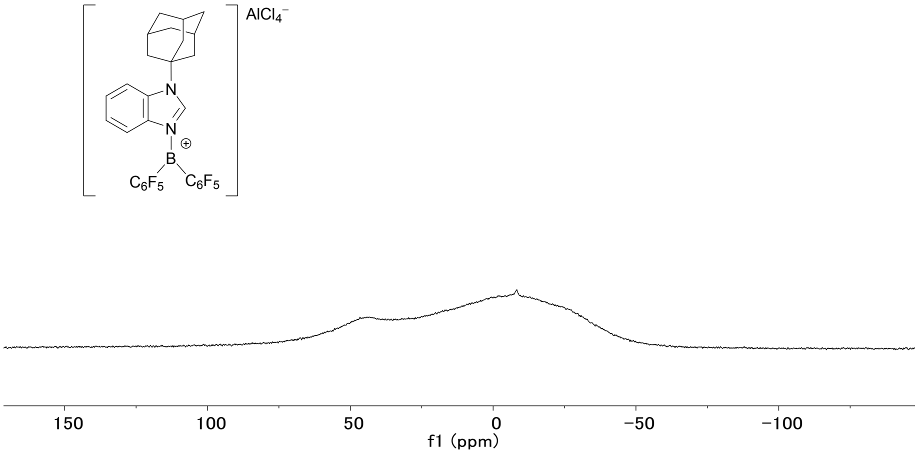


Figure S17. ^{11}B NMR spectrum of **2a** ($AlCl_4$ salt in CD_2Cl_2).

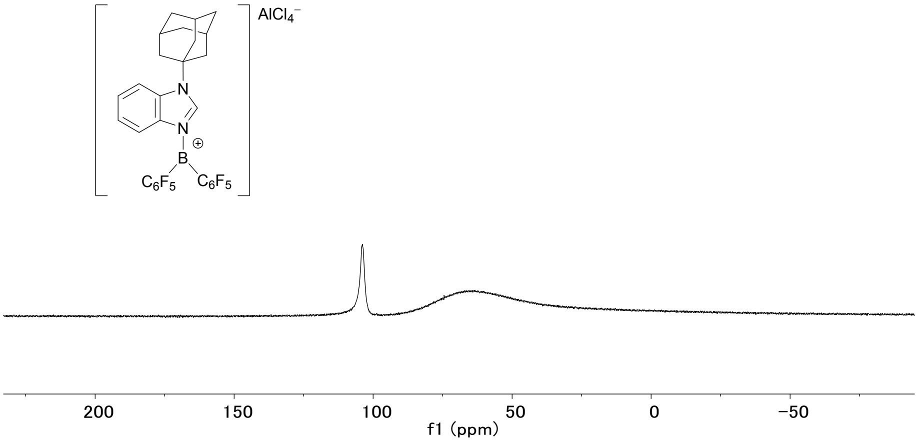
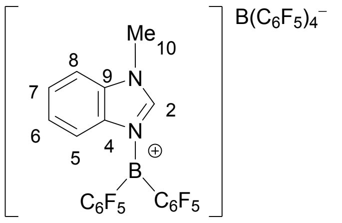


Figure S18. ^{27}Al NMR spectrum of **2a** ($AlCl_4$ salt in CD_2Cl_2).



Synthesis of 2b. In a glove box, CPh$_3$[B(C$_6$F$_5$)$_4$] (178 mg, 0.193 mmol) in benzene (2 mL) was added dropwise to a solution of **1b** (116 mg, 0.243 mmol) in benzene (3 mL). The mixture was stirred for 1 h at ambient temperature. The reaction separated into two layers. The top benzene layer was separated the solvent was removed. Washing with benzene (3×3 mL) afforded a pale brown oil. The oil was dried *in vacuo* to give **2b** as a pale brown solid (yield 206 mg, 89%). ^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ = 8.70 (s, 1H, H2), 7.85 (m, 2H, H7 and H8), 7.75 (t, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 1H, H6), 7.40 (d, $^3J_{\mathrm{H,H}}$ = 8.5 Hz, 1H, H5), 4.17 (s, 3H, H10). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 300 K): δ = 149.2 (*o*-C$_6$F$_5$, $^1J_{\mathrm{C,F}}$ = 255 Hz), 148.5 (*o*-C$_6$F$_5$-BAr$^\mathrm{F}$, $^1J_{\mathrm{C,F}}$ = 242 Hz), 147.3 (*p*-C$_6$F$_5$, $^1J_{\mathrm{C,F}}$ = 265 Hz), 138.8 (*m*-C$_6$F$_5$ and *p*-C$_6$F$_5$-BAr$^\mathrm{F}$), 136.8 (*m*-C$_6$F$_5$-BAr$^\mathrm{F}$, $^1J_{\mathrm{C,F}}$ = 247 Hz), 146.2 (C2), 133.7 (C9), 133.5 (C4), 131.3 (C7), 130.6 (C6), 124.4 (*ipso*-C$_6$F$_5$-BAr$^\mathrm{F}$), 116.1 (C5), 114.5 (C8), 107.0 (*ipso*-C$_6$F$_5$), 35.6 (C10). ^{19}F NMR (376 MHz, CD$_2$Cl$_2$, 300 K): δ = –127.6 (m, 4F, *o*-C$_6$F$_5$), –133.2 (m, 8F, *o*-C$_6$F$_5$-BAr$^\mathrm{F}$), –138.0 (m, 2F, *p*-C$_6$F$_5$), –157.1 (m, 4F, *m*-C$_6$F$_5$), –163.5 (m, 4F, *p*-C$_6$F$_5$-BAr$^\mathrm{F}$), –167.6 (m, 8F, *m*-C$_6$F$_5$-BAr$^\mathrm{F}$). ^{11}B NMR (128 MHz, CDCl$_3$, 300 K): δ = 47.5 (br, B(C$_6$F$_5$)$_2$), –16.7 (Bar$^\mathrm{F}$). Anal. Calcd. for **2b**·C$_6$H$_6$ (C$_{44}$H$_8$N$_2$B$_2$F$_{30}$)·C$_6$H$_6$: C 48.66% , H 1.14%, N 2.27%. Found: C 48.86%, H 1.20%, N 2.36%.

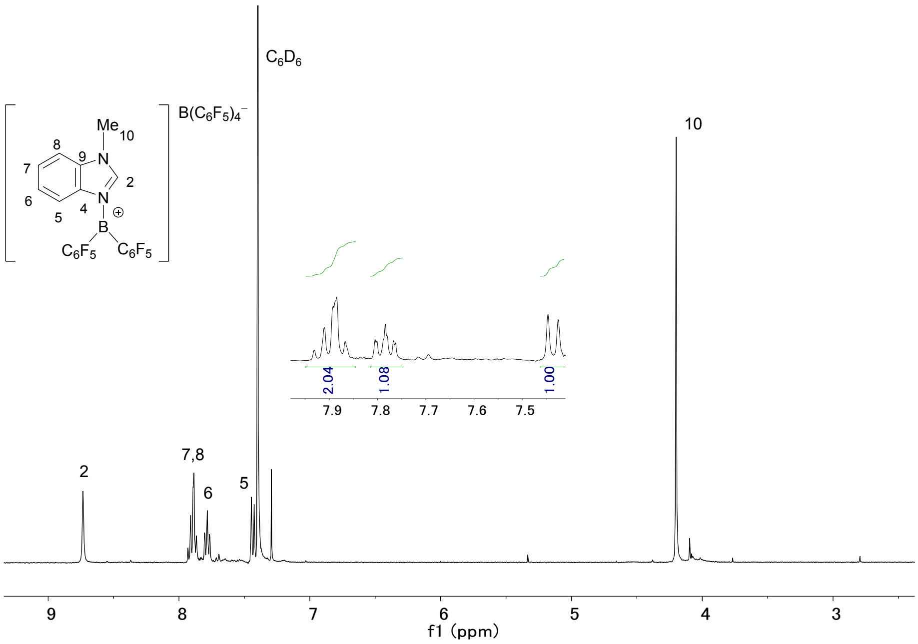


Figure S19. ^{1}H NMR spectrum of **2b** (in CDCl$_3$).

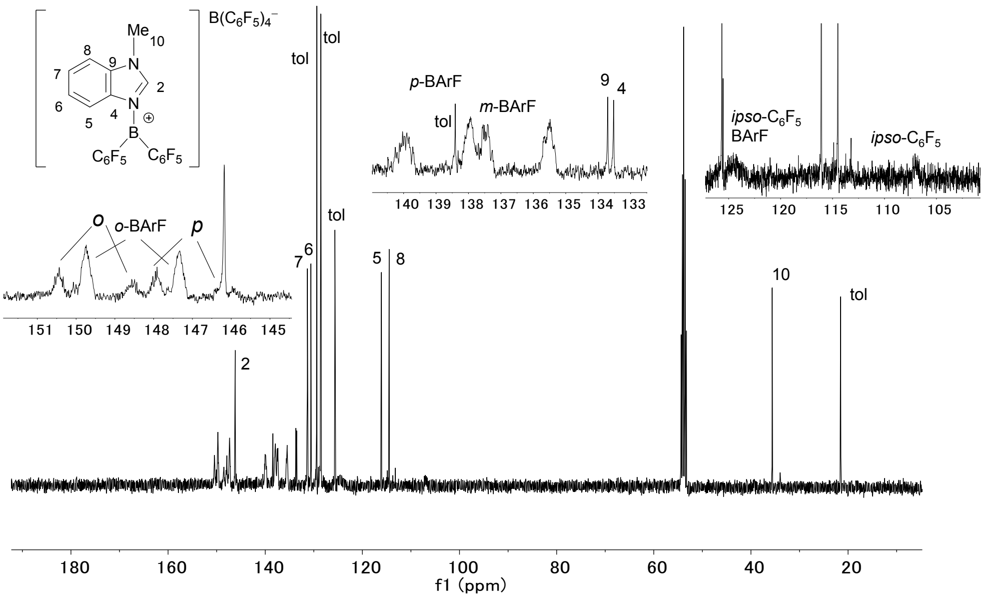


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** (in CD_2Cl_2).

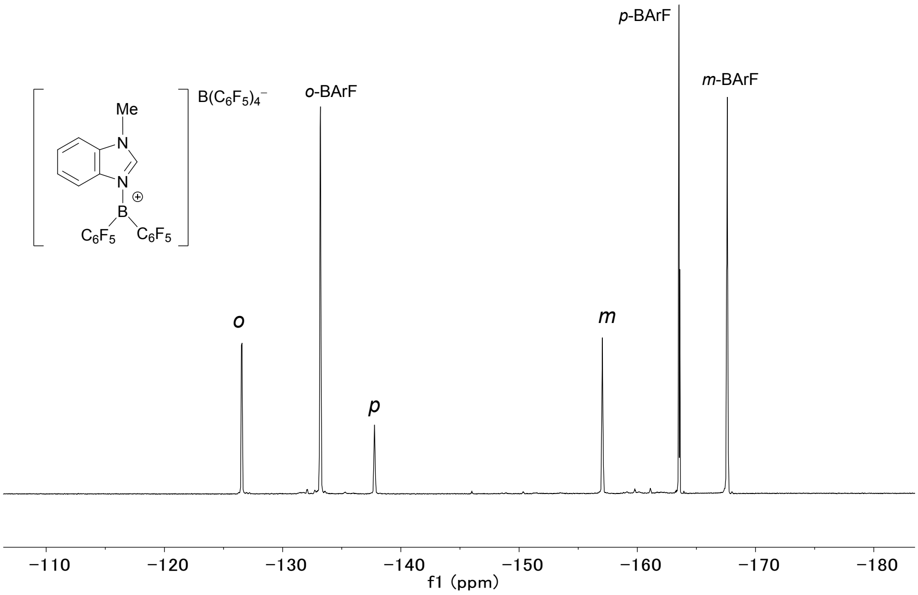


Figure S21. ^{19}F NMR spectrum of **2b** (in CD_2Cl_2).

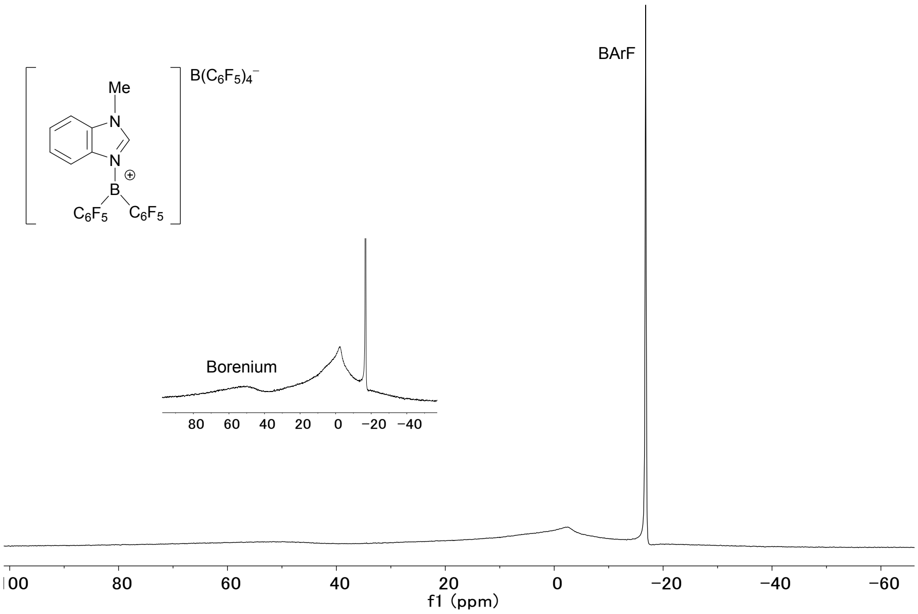
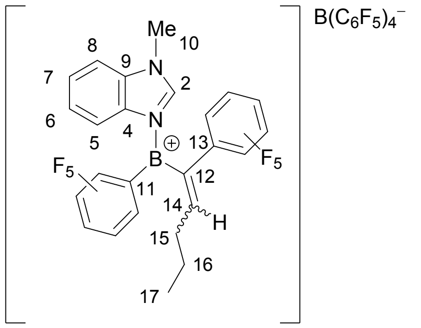


Figure S22. ^{11}B NMR spectrum of **2b** (in CDCl$_3$).

Synthesis of 3. In a glove box, 1-pentyne (2.3 mg, 0.033 mmol) in dichloromethane 0.5 mL) was added dropwise to **2b**·C_6H_6 (41 mg, 0.033 mmol) in dichloromethane (2 mL) and the mixture was stirred for 10 min at ambient temperature. Subsequently, the solvent was removed *in vacuo* the brown oil obtained was washed with benzene (2×2 mL). The oils was then dried *in vacuo* to give **3** as a brown solid (yield 42 mg, 98%). ^{1}H NMR 400 MHz, $CDCl_3$, 300 K): ***E*-isomer**: δ = 8.75 (s, 1H, H2), 7.78 (m, 2H, H7 and H8), 7.74 (m, 2H, H5 and H6), 7.24 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, H14), 4.12 (s, 3H, H10), 2.00 (m, 2H, H15), 1.44 (sext, $^3J_{H,H}$ = 7.3 Hz, 2H, H16), 0.77 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, H17); ***Z*-isomer**: δ = 8.66 (s, 1H, H2), 7.77 (m, 2H, H7 and H8), 7.66 (t, $^3J_{H,H}$ = 8.5 Hz, 1H, H6), 7.42 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H5), 7.09 (t, $^3J_{H,H}$ = 7.7 Hz, 1H, H14), 4.12 (s, 3H, H10), 2.32 (m, $^3J_{H,H}$ = 7.6 Hz, 2H, H15), 1.44 (sext, $^3J_{H,H}$ = 7.3 Hz, 2H, H16), 0.89 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, H17). ^{13}C NMR (101 MHz, CD_2Cl_2, 300 K): ***E*-isomer**: δ = 161.0 (C14), 145.2 (C2), 148.5 (*o*-C_6F_5), 148.0 (*o*-C_6F_5-BAr^F), 146.1 (*p*-C_6F_5), 144.1 (*o*-C_6F_5), 140.8 (*p*-C_6F_5), 138.1 (*m*-C_6F_5), 138.0 (*m*-C_6F_5, *p*-C_6F_5-BAr^F), 136.2 (*m*-C_6F_5-BAr^F), 133.7 (C9), 132.7 (C4), 130.6 (C6), 129.9 (C7), 124.0 (C12), 123.8 (*ipso*-C_6F_5-BAr^F), 115.9 (C5), 114.2 (C13), 113.7 (C8), 106.3 (C11), 35.9 (C15), 34.5 (C10), 22.0 (C16), 13.2 (C17); ***Z*-isomer**: δ = 170.0 (C14), 148.3 (*o*-C_6F_5), 148.0 (*o*-C_6F_5-BAr^F), 145.8 (*p*-C_6F_5), 144.3 (C2), 142.3 (*o*-C_6F_5), 141.4 (*p*-C_6F_5), 138.0 (*p*-C_6F_5-BAr^F), 137.9 (*m*-C_6F_5), 137.7 (*m*-C_6F_5), 136.2 (*m*-C_6F_5-BAr^F), 133.2 (C4 and C9), 130.0 (C6), 129.7 (C7), 127.1 (C12), 123.8 (*ipso*-BAr^F), 115.6 (C5), 113.6 (C8), 111.5 (C13), 106.3 (C11), 35.6 (C15), 34.4 (C10), 21.0 (C16), 13.8 (C17). ^{19}F NMR (376 MHz, $CDCl_3$, 300 K): ***E*-isomer**: δ = –126.7 (m, 2F, *o*-C_6F_5), –132.9 (m, 8F, *o*-C_6F_5-BAr^F), –138.1 (m, 1F, *p*-C_6F_5), –142.2 (m, 2F, *o*-C_6F_5), –151.8 (t, $^3J_{F,F}$ = 21 Hz, 1F, *p*-C_6F_5), –156.3 (m, 2F, *m*-C_6F_5), –159.4 (m, 2F, *m*-C_6F_5), –162.6 (t, $^3J_{FF}$ = 20 Hz, 4F, *p*-C_6F_5-BAr^F), –166.9 (m, 8F, *m*-C_6F_5-BAr^F); ***Z*-isomer**: δ = –127.2 (m, 2F, *o*-C_6F_5), –132.9 (m, 8F, *o*-C_6F_5-BAr^F), –138.9 (m, 2F, *o*-C_6F_5), –139.0 (m, 1F, *p*-C_6F_5), –150.6 (t, $^3J_{F,F}$ = 21 Hz, 1F, *p*-C_6F_5), –156.5 (m, 2F, *m*-C_6F_5), –159.0 (m, 2F, *m*-C_6F_5), –162.6 (t, $^3J_{F,F}$ = 20 Hz, 4F, *p*-C_6F_5-BAr^F), –166.9 (m, 8F, *m*-C_6F_5-BAr^F). ^{11}B NMR (128 MHz, CD_2Cl_2, 300 K): δ = 16.7 (only one signal was detected). Anal. calcd. for **3**·C_6H_6 ($C_{49}H_{16}N_2B_2F_{30}$)·C_6H_6: C 50.72% , H 1.70%, N 2.15%. Found: C 50.34%, H 1.76%, N 2.19%.



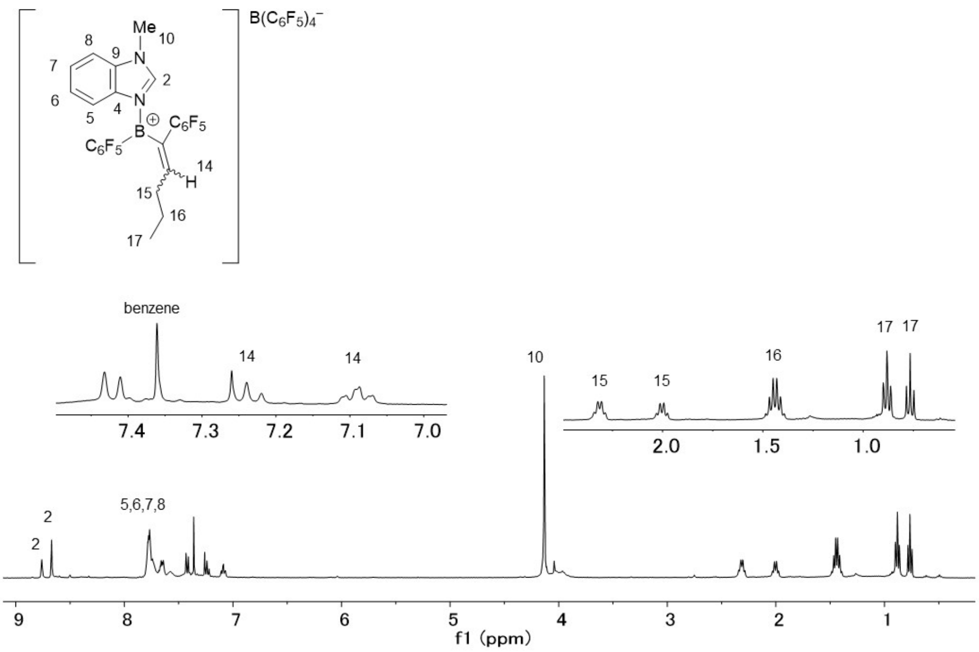


Figure S23. ^{1}H NMR spectrum of **3** (in $CDCl_3$).

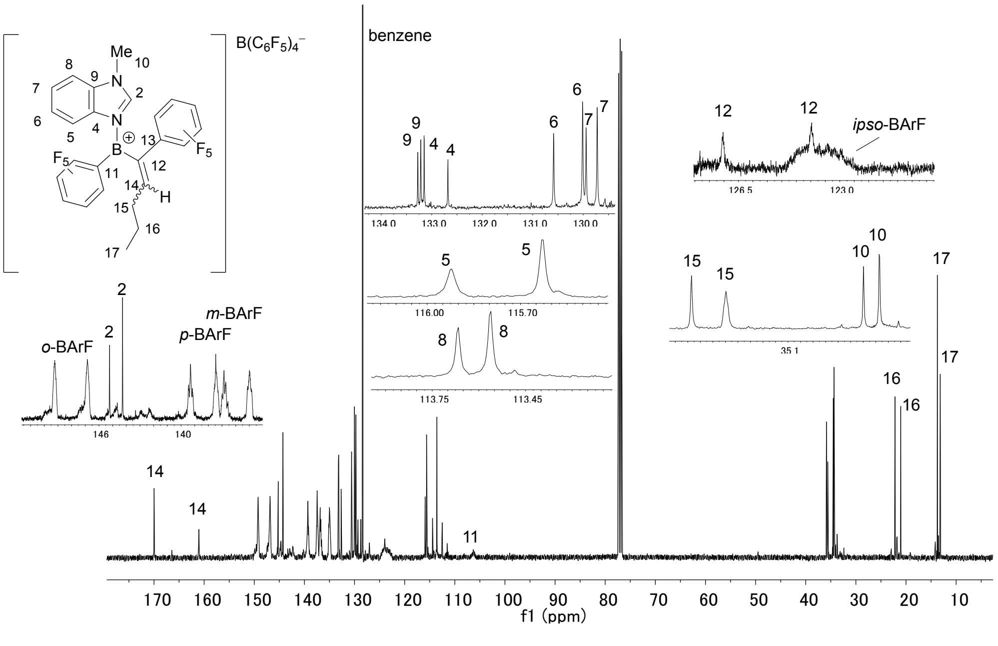


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **3** (in CD_2Cl_2).

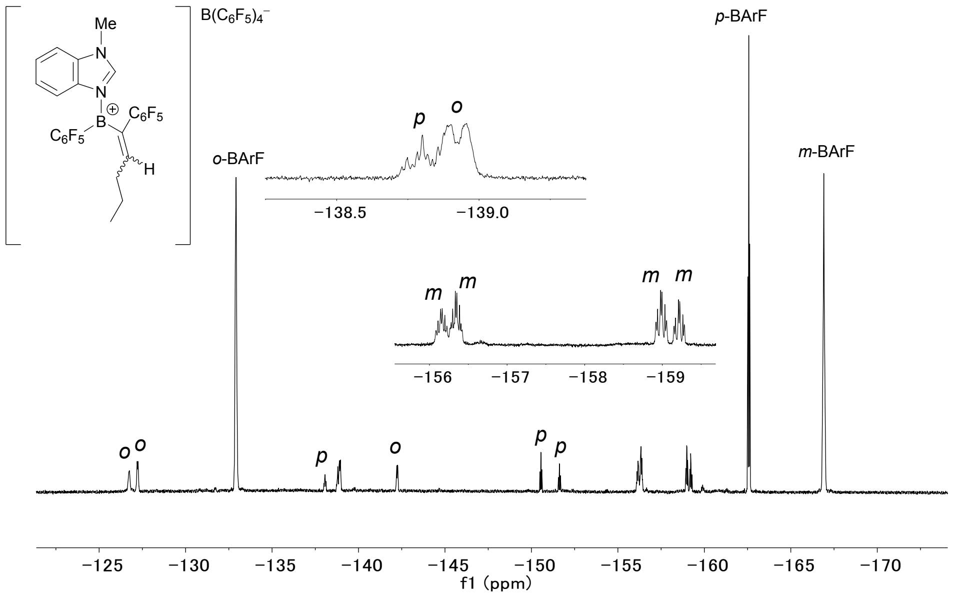


Figure S25. ^{19}F NMR spectrum of **3** (in CDCl$_3$).

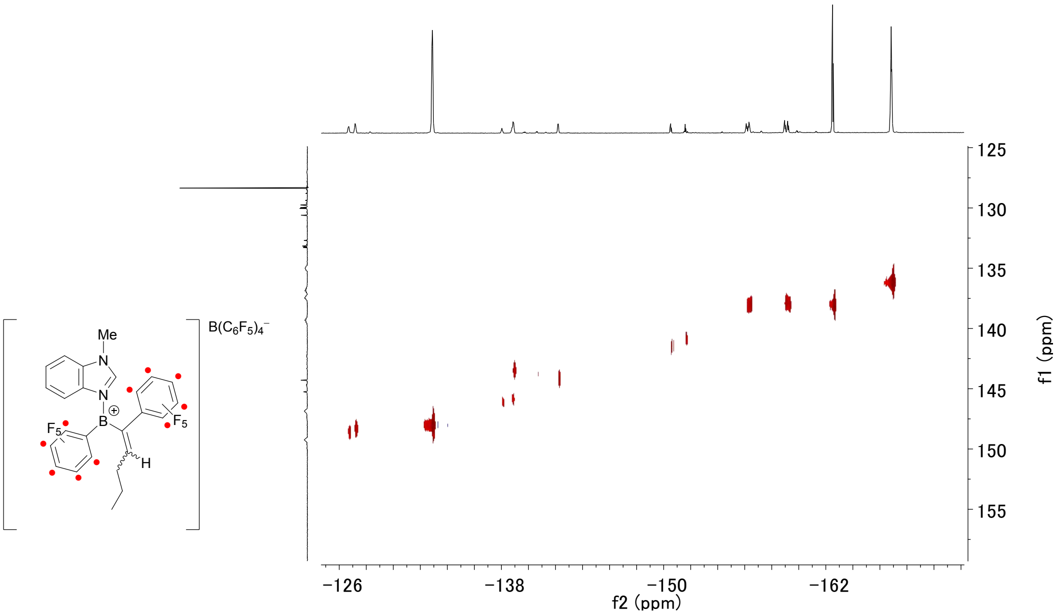


Figure S26. HSQC spectrum of **3**.

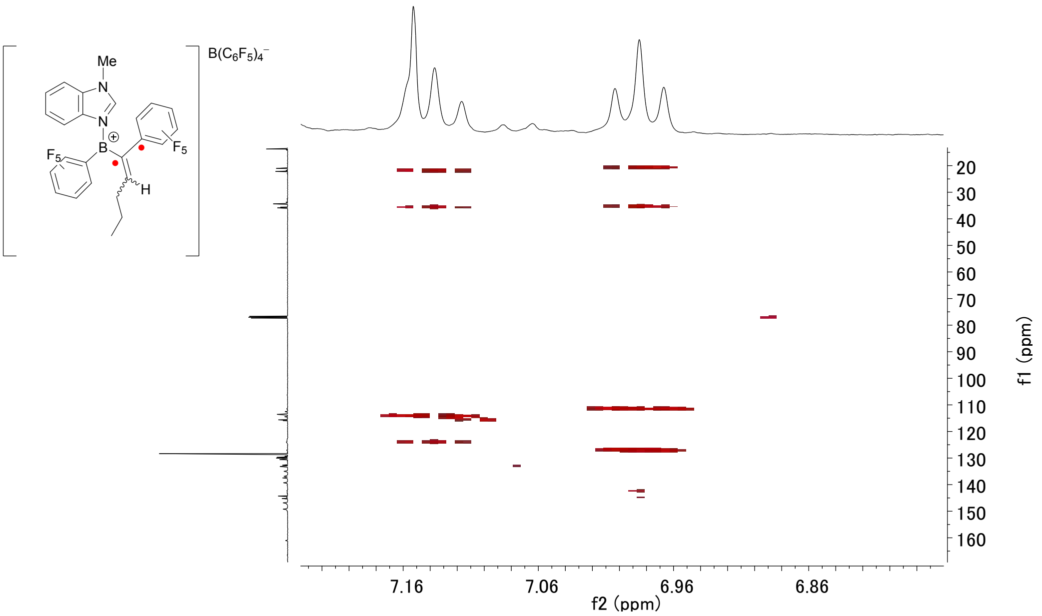
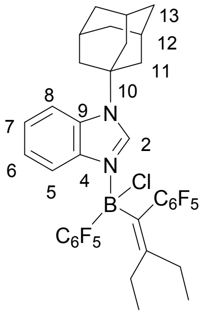


Figure S27. HMBC spectrum of **3**.



Synthesis of 5. In a glove box, 3-hexyne (6.5 mg, 0.0790 mmol) in dichloromethane (0.2 mL) was added dropwise to **2a** (Al_2Cl_7 salt) (35 mg, 0.0395 mmol) in dichloromethane (1 mL). The mixture was stirred for 3 h at ambient temperature. Then tetraethylammonium chloride (6.5 mg, 0.0395 mmol) in dichloromethane (0.2 mL) or THF (0.5 mL) was added to the resulting brown solution. Immediately the reaction solution turned colorless. The volatiles were removed *in vacuo*, and the residue was washed with *n*-pentane and extracted with toluene. The resulting solution was left for several days in a glove box to afford colorless crystals **5** (yield 17 mg, 60%). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ = 8.76 (s, 1H, H2), 7.93 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H5 and H8), 7.47 (t, $^3J_{H,H}$ = 7.8 Hz, 1H), 7.37 (t, $^3J_{H,H}$ = 7.7 Hz, 1H), 2.40 (s, 9H, H11 and H12), 2.13 (br, 2H, CH_2CH_3), 2.00 (quin, $^3J_{H,H}$ = 7.2 Hz, 2H, CH_2CH_3), 1.90 (s, 6H, H13), 0.94 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_2CH_3), 0.71 (br, 3H, CH_2CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, 300 K): δ = –124.75 (br), –138.49 (br), –139.30 (br), –157.85 (br), –159.86 (br), –163.08 (br), –163.63 (br), –165.15 (br). ^{11}B NMR (128 MHz, CD_2Cl_2, 300 K): δ = –0.5.

The broad signals in the spectra are presumably due to the intramolecular or intermolecular interactions. Due to the limited solubility of **5** no ^{13} C NMR spectrum was not obtained.

HRMS (ESI, positive ions): *m/z* (%) = 737.19239 (calcd for [**5**+Na]$^+$: 737.19348).

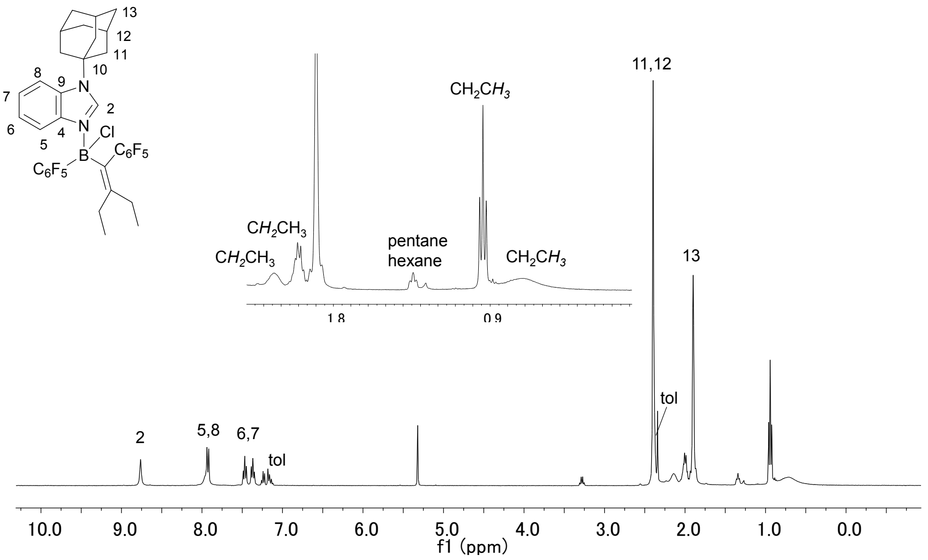


Figure S28. ^{1}H NMR spectrum of **5** (in CD_2Cl_2).

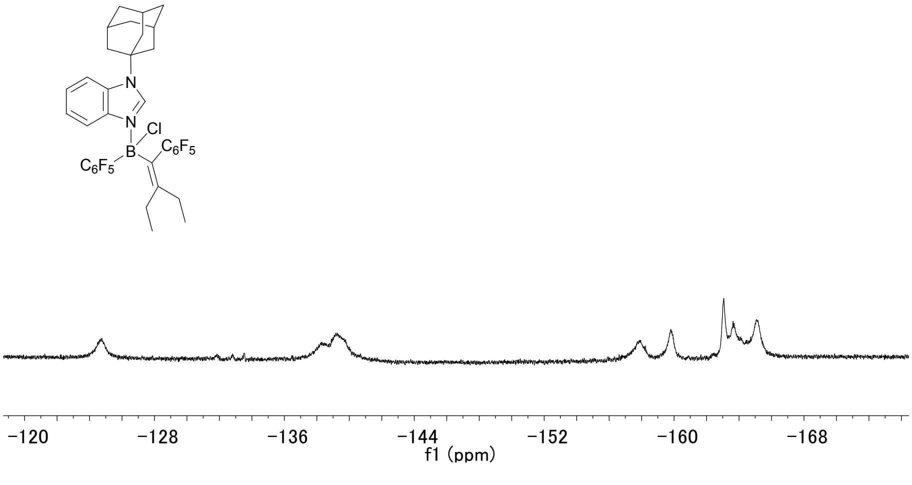
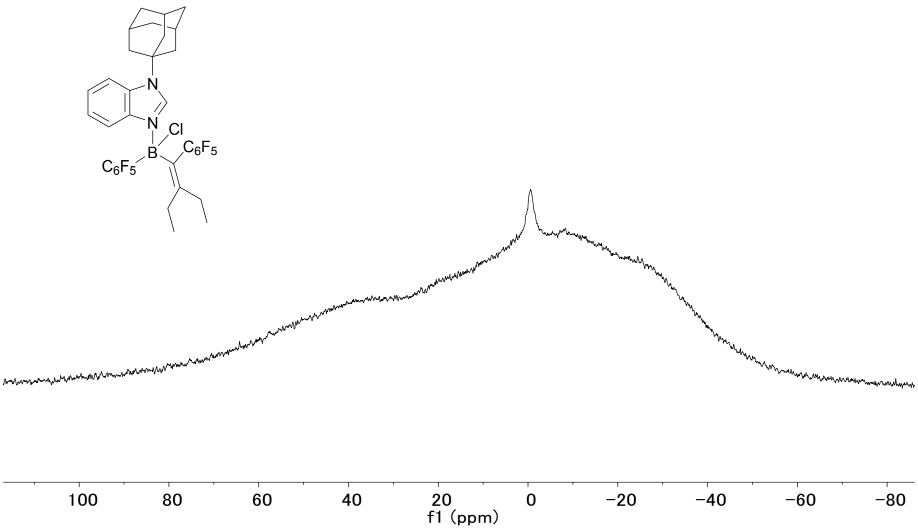


Figure S29. ^{19}F NMR spectrum of **3** (in $CDCl_3$).



Lewis acidity test.

The Lewis-acidity determination was performed via the Gutmann-Beckett method using the described procedure[3]. In a NMR tube, 3:1 mixture of ratio of **2b** and Et_3PO was dissolvd in CD_2Cl_2. ^{31}P NMR spectrum showed a signal at 85.95 ppm.

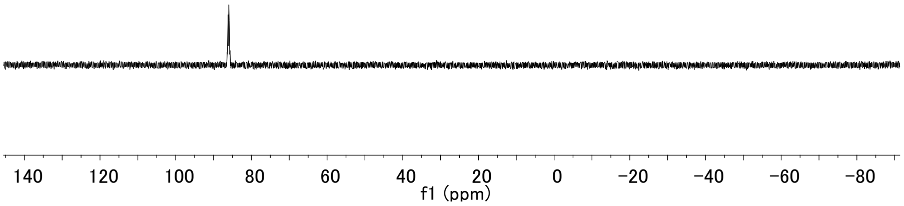


Figure S30. ^{31}P NMR spectrum of **2b** used for the determination of the Gutmann acceptor number (in CD_2Cl_3).

Reaction of 2b/PMes$_2$ with elemental hydrogen.

$$\mathbf{2b} \xrightarrow{\text{PMes}_{3,}\ \text{H}_2\ \text{(4 atm)}} \mathbf{1b}$$

In a glove box, trimesitylphosphine (6.3 mg, 0.0162 mmol) in $CDCl_3$ (0.4 mL) was added to **2b**·C_6H_6 (20 mg, 0.0162 mmol) in $CDCl_3$ (0.4 mL). The reaction solution was put under hydrogen pressure (4 atm). After 16 h, the solvent was removed *in vacuo*. The residue was washed with hexane and the following extraction with benzene gave **1b** (7 mg, 88% yield).

X-ray Crystallography.

X-ray diffraction data were collected at $T = 153(2)$ K (for [**2a**]($AlCl_4$)·1.5C_7H_8) or $T = 100(2)$ K (for [**5**]·0.5C_7H_8) using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and were corrected for absorption. Structure solutions were found with the *SHELXS-97* package using direct methods and were refined with *SHELXL-2016* against $|F^2|$ of all data using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystal data and structure refinement details for compound [2a]($AlCl_4$)·1.5C_7H_8.

Single crystals of [**2a**]($AlCl_4$)·1.5C_7H_8 were grown by slow vapor diffusion of *n*-hexane into a saturated toluene solution of [**2a**]($AlCl_4$) at ambient temperature. $C_{39.5}H_{26}N_2AlBCl_4F_{10}$, $M = 898.211$ g·mol^{-1}, colorless needles, 0.41 × 0.18 × 0.14 mm^3, triclinic, space group $P{-1}$, $Z = 2$, $a = 8.9781(5)$, $b = 13.5353(7)$, $c = 17.3740(9)$ Å, $\alpha = 88.344(3)$, $\beta = 83.681(3)$, $\gamma = 74.068(3)$°, $V = 2017.9(2)$ Å^3, $\rho_{calc} = 1.478$ g·cm^{-3}, $\mu = 0.394$ mm^{-1}, ω- and φ-scans, 31412 measured intensities ($5.52° \leq 2\theta \leq 57.05°$), 10165 unique intensities ($R_{int} = 4.01\%$), 7352 intensities with $I > 2\sigma(I)$, refinement of 488 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. $R = 0.0492$, $wR = 0.1295$, $R_{all} = 0.075$, $wR_{all} = 0.1408$. The asymmetric unit contains 1 formula unit of compound [**2a**]($AlCl_4$), half a molecule of toluene disordered about the inversion center and 1 toluene molecule disordered over 3 positions (occupancies 28:31:41). The positional parameters of disordered atoms were refined with isotropic displacement parameters, and no hydrogen positions were calculated for disordered carbon atoms.

Crystal data and structure refinement details for compound [5]·0.5C_7H_8.

Single crystals of [**5**]·0.5C_7H_8 were grown by slow vapor diffusion of *n*-hexane into a saturated THF/toluene solution of [**5**] at ambient temperature. $C_{38.5}H_{34}N_2BClF_{10}$, $M = 760.93$ g·mol^{-1}, colorless needles, 0.43 × 0.02 × 0.01 mm^3, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 7.8738(4)$, $b = 17.6595(9)$, $c = 24.5898(12)$ Å, $\beta = 97.103(2)$°, $V = 3392.9(3)$ Å^3, $\rho_{calc} = 1.490$ g/·cm^{-3}, $\mu = 0.201$ mm^{-1}, ω- and φ-scans, 12731 measured intensities ($4.06° \leq 2\theta \leq 51.40°$), 6350 unique intensities ($R_{int} = 7.1\%$), 3801 reflections with $I > 2\sigma(I)$, refinement of 471 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. $R = 0.0907$, $wR = 0.1846$, $R_{all} = 0.1852$, $wR_{all} = 0.2408$. The asymmetric unit contains 1 formula unit of compound **5** and half a molecule of toluene disordered about the inversion center. The positional parameters of disordered atoms were refined with isotropic displacement parameters, and no hydrogen positions were calculated for disordered carbon atoms. The structure was refined as a two-component twin with a twin scale factor of 0.396.

1. K. Hirano, A. T. Biju and F. Glorius, *J. Org. Chem*, 2009, **74**, 9570.
2. D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.
3. G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2007, 3407.