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Electronic supplementary information

for

$B(C_6F_5)_3$-mediated direct intramolecular C7-alkenylation of N-propargylindoles

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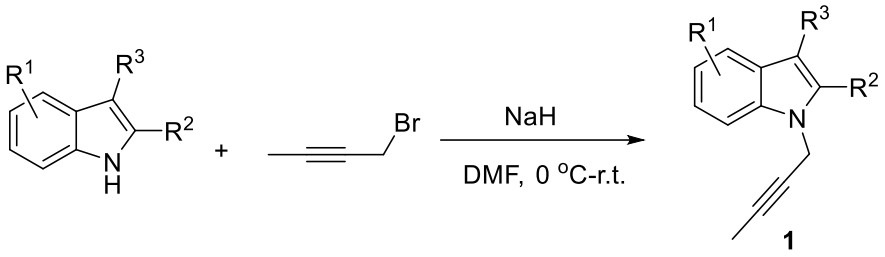
General Information

All manipulations were performed under an atmosphere of dry and oxygen-free N_2 by means of standard Schlenk or glovebox techniques. *n*-hexane, dichloromethane and dichloroethane were collected from a (Mikrouna) solvent purification system and stored over activated 3 Å molecular sieves. Dichloromethane-d_2 (CD_2Cl_2) and benzene-d_6 (C_6D_6) was degassed, dried over calcium hydride and stored over 3 Å molecular sieves in the glovebox for at least 8 h prior to use. Unless otherwise noted, all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: HRMS: Agilent 6224 TOF LC/MS; NMR: Bruker Avance II 400MHz spectrometer (1H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 377 MHz, ^{11}B: 128 MHz). NMR chemical shifts are given relative to $SiMe_4$ and referenced to the respective solvent signals (^1H and ^{13}C). All N-propargyl substituted indoles were prepared according to the modified literature procedure.[1] [(1) X.-Y. Zhu, M. Li, Y.-P. Han, S. Chen, X.-S. Li and Y.-M. Liang, *J. Org. Chem.*, 2017, **82**, 8761.]

X-Ray diffraction: Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture CMOS-based diffractometer (**2a**, **2b**, **3a** and **4a**) with graphite-monochromated MoKa radiation (λ = 0.71073 Å). All of the data were corrected for absorption effects using the multi-scan technique. Final unit cell parameters were based on all observed reflections from integration of all frame data. The structures were solved with the ShelXT structure solution program using Intrinsic Phasing (G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.). The compounds **2a**, **2b** and **4a** were refined with the olex2 platform (L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **A71**, 59-75.). The compound **3a** was refined with the ShelXL refinement package (G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.) using Least Squares minimization that implanted in Olex2. For all compounds, all non-H atoms were refined anisotropically unless otherwise stated, and hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. CCDC-2265176, 2265177, 2265179 and 2265180 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/. For compound **4a**, the solvent mask was used to remove a badly disordered dichloromethane molecule. The final reported sum formula is included the solvent molecule.

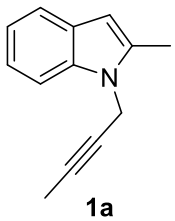
General Procedure I



Scheme S1

To the solution of indole derivatives (1.0 equiv.) in DMF (30 mL), sodium hydride (1.3 equiv.) was slowly added at 0 °C. The resulting mixture was stirred for 30 min at room temperature. Then the mixture was cooled down to 0 °C. Subsequently, 1-bromo-2-butyne (1.3 equiv.) was added and the mixture was stirred at room temperature until disappearance of the starting material (detected by TLC). After that, ethyl acetate was added and the organic layer was extracted three times with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography in silica gel (PE : EA = 30:1) to give the product **1**.

Synthesis and characterization of compound 1a

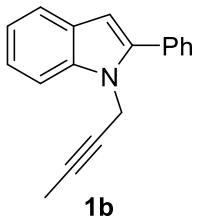


According to General Procedure I from 2-methylindole (1.71 g, 13 mmol),

1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a yellow oil (1.89 g, 79% yield).

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.55 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.38 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.20 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.12 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.29 (s, 1H), 4.78 (q, $^{5}J_{HH}$ = 2.4 Hz, 2H), 2.50 (s, 3H), 1.78 (t, $^{5}J_{HH}$ = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 136.6, 136.2, 128.3, 120.8, 119.8, 119.7, 109.1, 100.6, 79.9, 73.9, 32.8, 12.7, 3.6.

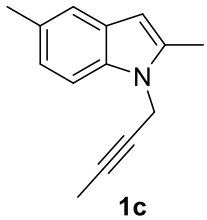


1b

According to General Procedure I from 2-phenylindole (2.52 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol,, 60% dispersion in mineral oil). The product was isolated as a white solid (1.73 g, 54% yield).

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.69-7.66 (m, 3H), 7.58-7.51 (m, 3H), 7.45 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.32 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.21 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 6.61 (s, 1H), 4.81 (q, $^{5}J_{HH}$ = 2.4 Hz, 2H), 1.86 (t, $^{5}J_{HH}$ = 2.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CDCl_3$): δ = 141.0, 137.7, 132.6, 129.4, 128.8, 128.3, 128.1, 122.1, 120.7, 120.4, 110.3, 102.2, 80.7, 74.5, 34.6, 3.8.

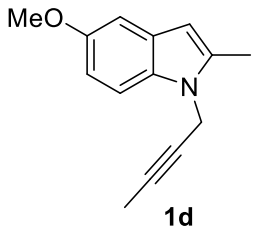


1c

According to General Procedure I from 2,5-dimethylindole (1.89 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a yellow solid (1.34 g, 52% yield).

^1H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.33 (s, 1H), 7.26 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.02 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 6.17 (br, 1H), 4.74 (q, $^5J_{HH}$ = 2.0 Hz, 2H), 2.47 (s, 3H), 2.46 (s, 3H), 1.77 (t, $^5J_{HH}$ = 2.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CDCl_3$): δ = 136.3, 135.0, 128.8, 128.6, 122.3, 119.7, 108.8, 100.1, 79.8, 74.0, 32.8, 21.5, 12.7, 3.6.



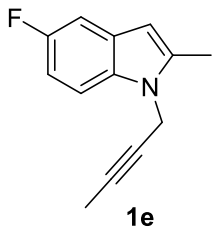
1d

According to General Procedure I from 5-methoxy-2-methylindole (2.10 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a

white solid (1.20 g, 43% yield).

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.24 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H), 7.01 (d, $^{3}J_{HH}$ = 2.4 Hz, 1H), 6.82 (dd, $^{3}J_{HH}$ = 8.8 and 2.4 Hz, 1H), 6.16 (br, 1H), 4.72 (q, $^{5}J_{HH}$ = 2.4 Hz, 2H), 3.84 (s, 3H), 2.45 (s, 3H), 1.75 (t, $^{5}J_{HH}$ = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 154.3, 136.9, 131.9, 128.7, 110.5, 109.8, 102.2, 100.3, 79.9, 73.9, 56.0, 33.0, 12.8, 3.6.

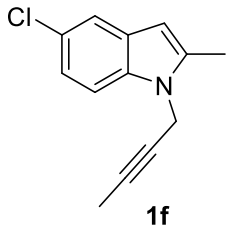


1e

According to General Procedure I from 5-fluoro-2-methylindole (1.94 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a white solid (1.47 g, 56% yield).

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.25 (dd, $^{3}J_{HH}$ = 8.8 and 4.0 Hz, 1H), 7.17 (dd, *J* = 9.6 and 2.4 Hz, 1H), 6.91 (td, $^{3}J_{HH}$ = 9.2 and 2.4 Hz, 1H), 6.22 (br, 1H), 4.73 (q, $^{5}J_{HH}$ = 2.4 Hz, 2H), 2.47 (s, 3H), 2.46 (s, 3H), 1.77 (t, $^{5}J_{HH}$ = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 161.9 (d, $^{1}J_{FC}$ = 234.3 Hz), 138.0, 133.2, 161.9 (d, $^{3}J_{FC}$ = 10.1 Hz), 161.9 (d, $^{3}J_{FC}$ = 9.7 Hz), 161.9 (d, $^{2}J_{FC}$ = 26.2 Hz), 161.9 (d, $^{2}J_{FC}$ = 26.2 Hz), 161.9 (d, $^{4}J_{FC}$ = 4.3 Hz), 80.2, 73.6, 33.1, 12.8, 3.6.

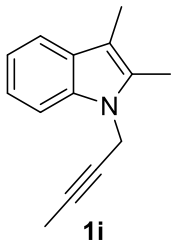


1f

According to General Procedure I from 5-chloro-2-methylindole (2.16 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a white solid (1.73 g, 61% yield).

H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.47 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 7.25 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 7.11 (dd, $^3J_{HH}$ = 8.4 and 2.0 Hz, 1H), 6.20 (s, 1H), 4.72 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 2.46 (s, 3H), 1.76 (t, $^5J_{HH}$ = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 137.8, 135.0, 129.3, 125.4, 121.0, 119.3, 110.1, 100.3, 80.4, 73.5, 33.0, 12.8, 3.6.



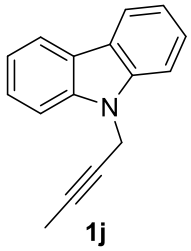
1i

According to General Procedure I from 2,3-dimethylindole (1.89 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a yellow oil (1.67 g, 65% yield).

H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.51 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.34 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.12 (t, $^3J_{HH}$ = 7.2 Hz,

1H), 4.76 (q, $^{5}J_{HH}$ = 2.4 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 1.76 (t, $^{5}J_{HH}$ = 2.4 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, $CDCl_3$): δ = 135.8, 132.0, 128.9, 120.8, 119.0, 118.2, 108.7, 107.2, 79.6, 74.2, 32.9, 10.1, 8.9, 3.6.



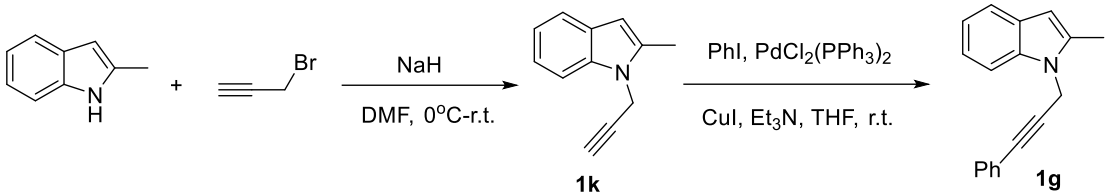
1j

According to General Procedure I from carbazole (2.18 g, 13 mmol), 1-Bromo-2-butyne (1.5 mL, 16.9 mmol) and NaH (0.68 g, 16.9 mmol, 60% dispersion in mineral oil). The product was isolated as a white solid (2.40 g, 84% yield).

H NMR (400 MHz, 299 K, $CDCl_3$): δ = 8.01 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H), 7.41-7.15 (m, 6H), 4.90 (q, $^{5}J_{HH}$ = 2.4 Hz, 2H), 1.66 (t, $^{5}J_{HH}$ = 2.4 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, $CDCl_3$): δ = 140.1, 125.9, 123.3, 120.5, 119.4, 109.0, 80.1, 73.4, 32.8, 3.6.

Synthesis and characterization of compound 1g



1k **1g**

Scheme S2

i) To the solution of 2-methylindole (1.32 g, 10 mmol) in DMF (10 mL), sodium hydride (0.52 g, 13 mmol, 60% dispersion in mineral oil) was slowly added at 0 °C. The resulting mixture was stirred for 30 min at room temperature. Then the mixture was cooled down to 0 °C. Subsequently, 3-bromopropyne (1.55 g, 13 mmol) was added and the mixture was stirred at room temperature until disappearance of the starting material (detected by TLC). After that, ethyl acetate was added and the organic layer was extracted three times with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography to give the product **1k** as a white solid (1.27 g, 75% yield).

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.54 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.36 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.20 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.11 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 6.30 (s, 1H), 4.82 (d, $^4J_{HH}$ = 2.4 Hz, 2H), 2.50 (s, 3H), 2.27 (t, $^4J_{HH}$ = 2.4 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 136.6, 136.1, 128.4, 121.1, 119.99, 119.95, 109.0, 101.1, 78.4, 72.3, 32.5, 12.7.

ii) The compound **1k** (931.0 mg, 5.5 mmol), PhI (0.68 mL, 6.05 mmol), $PdCl_2(PPh_3)_2$ (77.3 mg, 0.11 mmol), CuI (41.9 mg, 0.22 mmol) and Et_3N (2.3 mL, 16.5 mmol) were dissolved in anhydrous THF (10 mL). The mixture was stirred at room temperature for 16 h under N_2. The reaction mixture was filtered and extracted with EtOAc. The combined organic

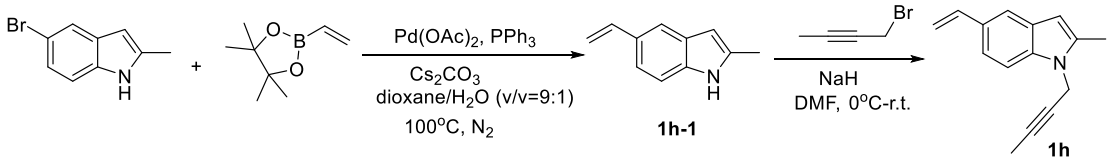
layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography to give the product **1g** as a white solid (1.1 g, 81% yield).

Compound **1k** and **1g** were prepared according to the literature procedure.[2] [(2) J. Zhu, S. Sun, M. Xia, N. Gu and J. Cheng, *Org. Chem. Front.*, 2017, **4**, 2153.]

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.57 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.45 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.39 (dd, $^3J_{HH}$ = 7.2, 1.6 Hz, 2H), 7.31-7.28 (m, 3H), 7.22 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.13 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 6.32 (s, 1H), 5.05 (s, 2H), 2.56 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 136.7, 136.3, 131.9, 128.6, 128.39, 128.37, 122.5, 121.0, 119.9, 119.8, 109.2, 100.9, 84.0, 83.9, 33.4, 12.9.

Synthesis and characterization of compound 1h



Scheme S3

i) A solution of 5-bromo indole (1.26 g, 6 mmol), vinylboronic acid pinacol ester (2.1 mL, 12 mmol), $Pd(OAc)_2$ (27.2 mg, 0.12 mmol), Cs_2CO_3 (7.82 g, 24 mmol), PPh_3 (125.9 mg, 0.48 mmol,) in a mixture of dioxane/water (v/v: 9/1, 10 mL) was heated at 100 °C for 48 h under N_2 in a sealed tube. The reaction mixture was filtered and extracted with

EtOAc. The organic layer was combined, dried over anhydrous Na_2SO_4, evaporated and purified by flash chromatography to give **1h-1** as a white solid (792.4 mg, 84% yield).

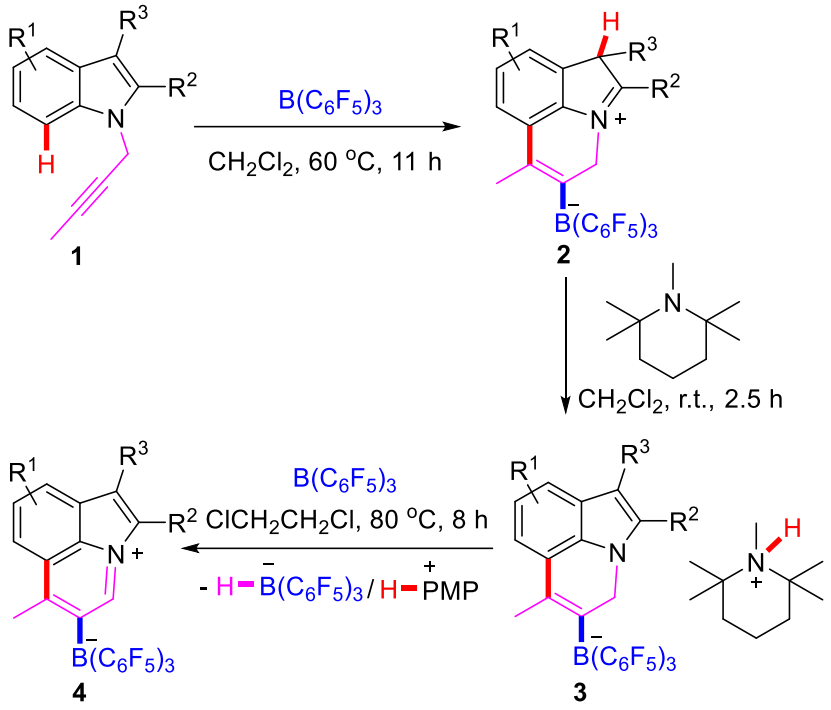
ii) According to General Procedure I from compound **1h-1** (471.7 mg, 3 mmol), 1-bromo-2-butyne (518.7 mg, 3.9 mmol) and NaH (156.0 mg, 3.9 mmol, 60% dispersion in mineral oil). The product **1h** was isolated as a white solid (282.5 mg, 45% yield).

Compound **1h-1** was prepared according to the literature procedure.[3] [(3) Ł. Woźniak, A. A. Rajkiewicz, L. Monsigny, A. Kajetanowicz and K. Grela, *Org. Lett.*, 2020, **22**, 4970.]

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.55 (s, 1H), 7.34-7.26 (m, 2H), 6.84 (dd, $^3J_{HH}$ = 17.2, 10.8 Hz, 1H), 6.25 (s, 1H), 5.70 (d, $^3J_{HH}$ = 17.6 Hz, 1H), 5.14 (d, $^3J_{HH}$ = 10.8 Hz, 1H), 4.74 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 2.47 (s, 3H), 1.77 (t, $^5J_{HH}$ = 2.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 138.2, 136.9, 136.6, 129.7, 128.5, 119.2, 118.3, 110.7, 109.2, 101.0, 80.1, 73.8, 33.0, 12.8, 3.6.

General Procedure II



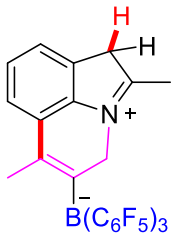
Scheme S4

General Procedure for 2: A solution of the N-propargylindole derivative **1** (1.0 equiv.) and $B(C_6F_5)_3$ (1.0 equiv.) in CH_2Cl_2 (2 mL) was stirred at 60 °C for 11 h to give a suspension. Then the mixture was filtered. The obtained residue was washed with *n*-hexane (3×2 mL) and dried in vacuo to give the product **2**.

General Procedure for 3: A solution of **2** (1.0 equiv.) and 1,2,2,6,6-pentamethylpiperidine (PMP) (1.0 equiv.) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2.5 h. Then all the volatiles were removed in vacuo. The obtained residue was washed with *n*-hexane (3×2 mL) and dried in vacuo to give the product **3**.

General Procedure for 4: A solution of **3** (1.0 equiv.) and $B(C_6F_5)_3$ (1.0 equiv.) in $ClCH_2CH_2Cl$ (2 mL) was stirred at 80 °C for 8 h. Upon completion, the mixture was purified by silica gel column chromatography to give the product **4**.

Synthesis and characterization of compound 2a



2a

According to the General Procedure II (for **2**) from **1a** (55.0 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2a** was isolated as a yellow solid (187.7 mg, 90% yield). [Comment: Compound **2a** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2a** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2a** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **2a** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 7.43-7.40 (m, 1H), 7.35 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.28 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 5.26 (d, $^{2}J_{HH}$ = 21.7 Hz, 1H), 5.08 (d, $^{2}J_{HH}$ = 21.7 Hz, 1H), 4.35 (s, 2H), 2.60 (s, 3H), 1.90 (s, 3H).

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -14.4 ($\nu_{1/2}$ ~ 32 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -129.5 (m, 3F), -132.6 (m, 1F), -134.3 (m, 1F), -135.5 (m, 1F) (*o*-C_6F_5); -162.3 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F), -163.8 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F), -164.7 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F) (*p*-C_6F_5); -165.6 (m, 1F), -166.8 (m, 1F), -167.4 (m, 1F), -168.1 (m, 2F), -168.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{31}H_{13}BF_{15}N$-H^+: 694.0829 $[M-H]^-$; found: 694.0841.

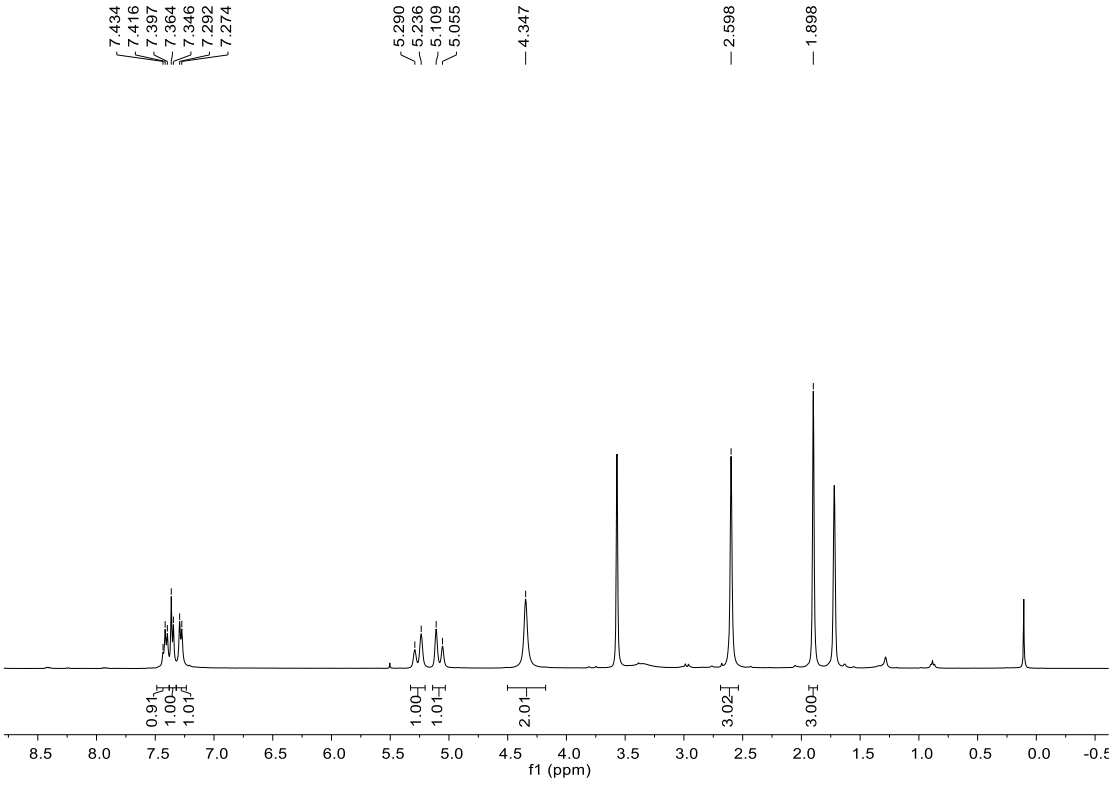


Fig. S1 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **2a**.

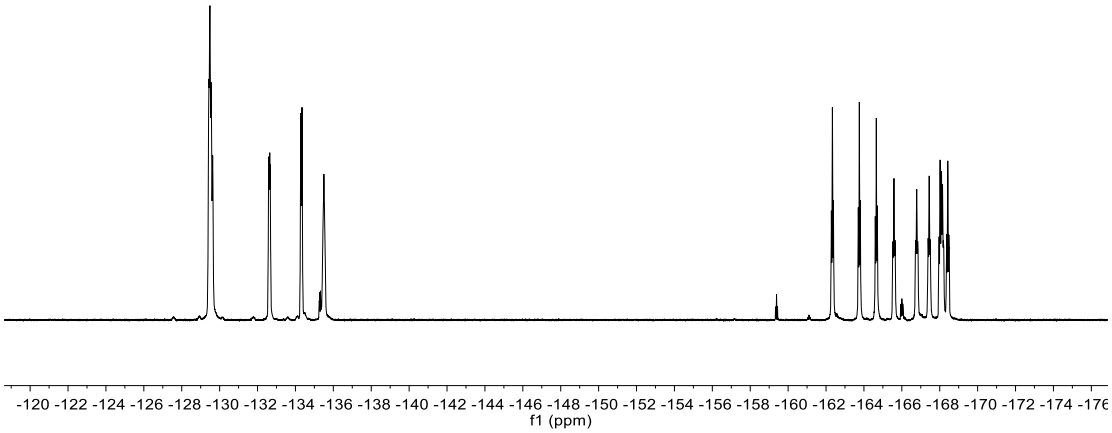


Fig. S2 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **2a**.

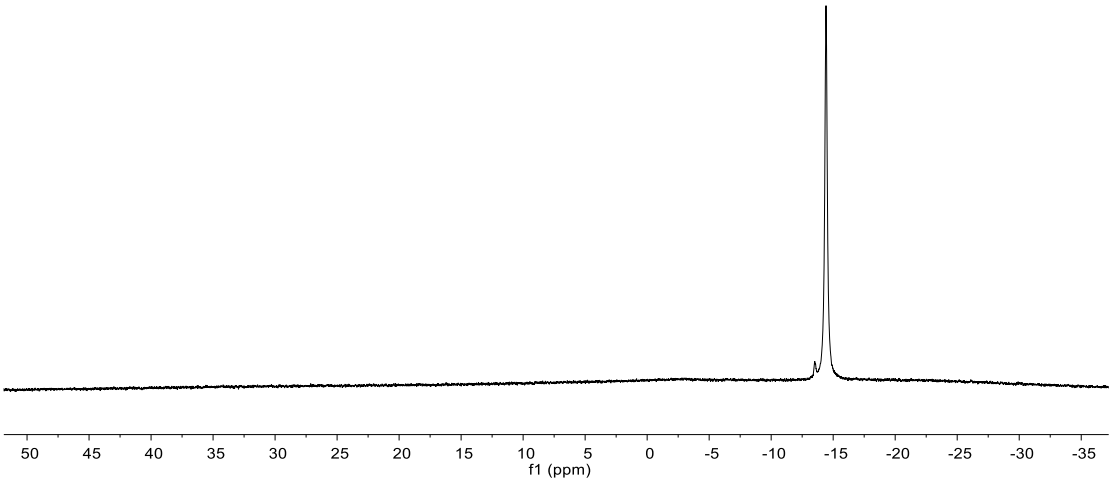


Fig. S3 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **2a**.

X-ray crystal structure analysis of compound 2a·CH_2Cl_2: formula $C_{31.93}H_{14.85}BCl_{1.85}F_{15}N$, M = 774.00, yellow crystal, 0.31 × 0.25 × 0.10 mm, a = 11.3290(19), b = 11.9454(19), c = 12.742(2) Å, α = 63.668(5)º, β = 76.190(5)º, γ = 80.226(5)º, V = 1496.7(4) $Å^3$, ρ_{calc} = 1.717 gcm^{-3}, μ = 0.325 mm^{-1}, empirical absorption correction (0.5180 ≤ T ≤ 0.5624), Z = 2, triclinic, space group *P-1*, λ = 0.71073 Å, T = 120.0 K, ω and φ scans,

26644 reflections collected (±*h*, ±*k*, ±*l*), 6120 independent (R_{int} = 0.0547) and 4294 observed reflections [$I>2\sigma(I)$], 470 refined parameters, R = 0.0486, wR^2 = 0.1375, max. (min.) residual electron density 0.60 (-0.47) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

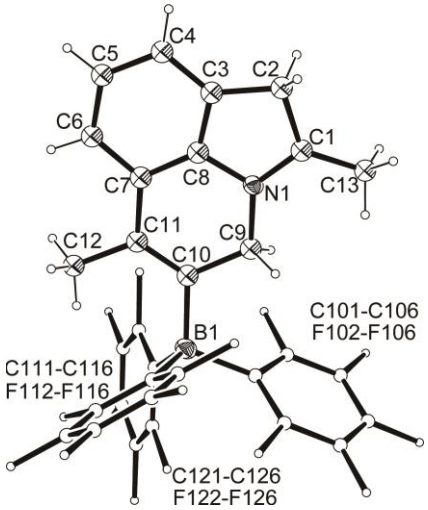
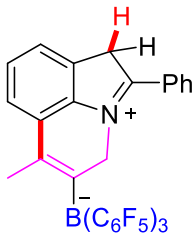


Fig. S4 A view of the molecular structure of compound **2a**.

Synthesis and characterization of compound 2b



2b

According to the General Procedure II (for **2**) from **1b** (73.6 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2b** was isolated as an orange solid (213.6 mg, 94% yield). [Comment: Compound **2b** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2b** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2b** in both of DMSO-D_6 and

THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **2b** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 7.91-7.37 (m, 8H), 5.80 (d, $^2J_{HH}$ = 20.9 Hz, 1H), 5.35 (d, $^2J_{HH}$ = 20.9 Hz, 1H), 5.00 (d, $^2J_{HH}$ = 23.6 Hz, 1H), 4.82 (d, $^2J_{HH}$ = 23.6 Hz, 1H), 1.93 (s, 3H).

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -10.8 ($\nu_{1/2}$ ~ 34 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -125.8 (m, 2F), -126.4 (m, 1F), -128.5 (m, 1F), -131.0 (m, 1F), -132.1 (m, 1F) (*o*-C_6F_5); -158.7 (t, $^3J_{FF}$ = 16.2 Hz, 1F), -160.0 (t, $^3J_{FF}$ = 17.0 Hz, 1F), -160.9 (t, $^3J_{FF}$ = 18.5 Hz, 1F) (*p*-C_6F_5); -161.3 (m, 1F), -163.9 (m, 2F), -164.4 (m, 2F), -164.7 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{36}H_{15}BF_{15}N$-H^+: 756.0985 $[M-H]^-$; found: 756.0999.

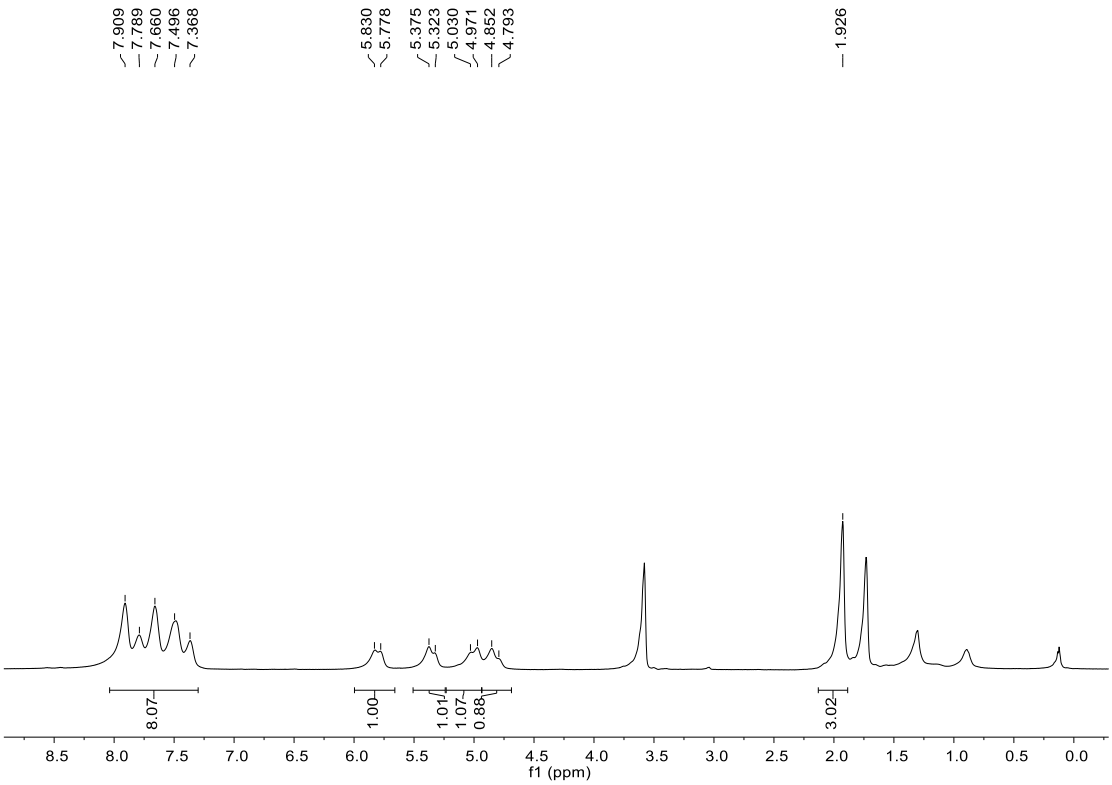


Fig. S5 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **2b**.

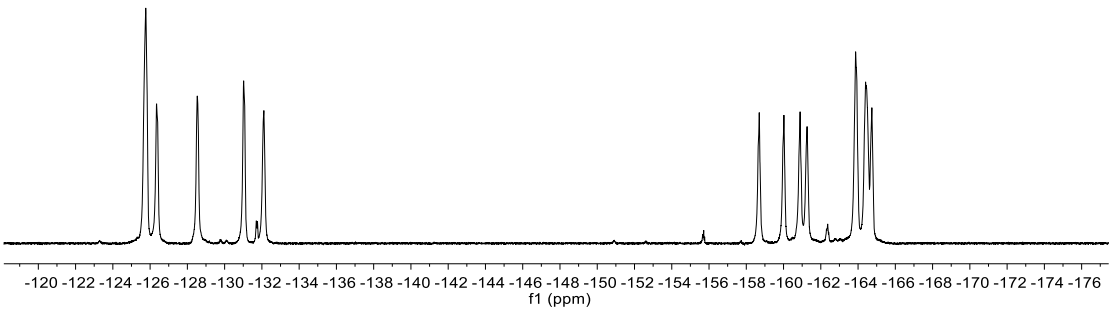


Fig. S6 ^{19}F{^{1}H} NMR (377 MHz, 299K, THF-d_8) spectrum of compound **2b**.

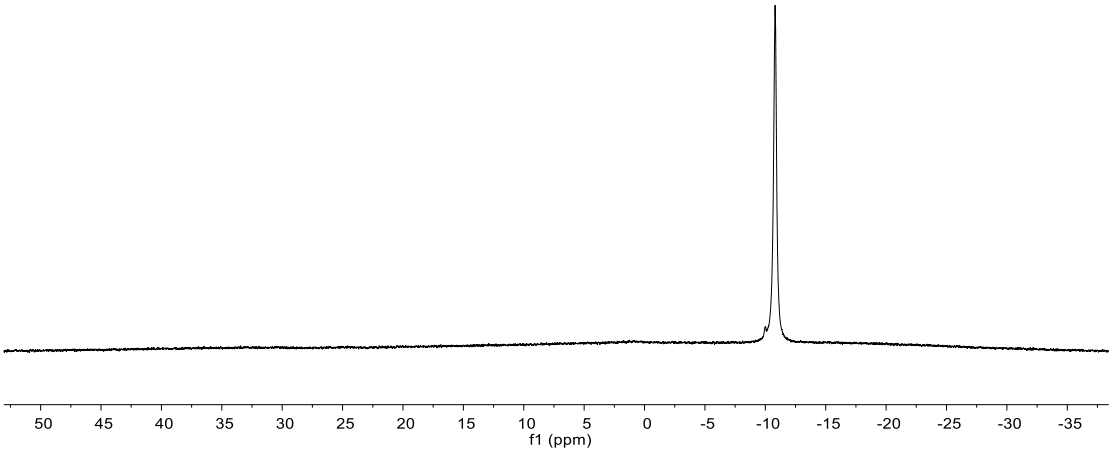


Fig. S7 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **2b**.

X-ray crystal structure analysis of compound 2b·0.5C_6H_{14}: formula $C_{39.96}H_{24.24}BF_{15}N$, M = 814.205, yellow crystal, 0.35 × 0.21 × 0.10 mm, a = 11.025(2), b = 12.418(3), c = 13.411(3) Å, α = 84.392(7)º, β = 82.602(6)º, γ = 67.882(6)º, V = 1684.5(6) Å^3, ρ_{calc} = 1.605 gcm^{-3}, μ = 0.151 mm^{-1}, empirical absorption correction (0.7110 ≤ T ≤ 0.7461), Z = 2, triclinic, space group *P-1*, λ = 0.71073 Å, T = 300.4 K, ω and φ scans, 43304 reflections collected (±h, ±k, ±l), 5800 independent (R_{int} = 0.0730) and 3438 observed reflections [I>2σ(I)], 482 refined parameters, R = 0.0462, wR^2 = 0.1187, max. (min.) residual electron density 0.45 (-0.45) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

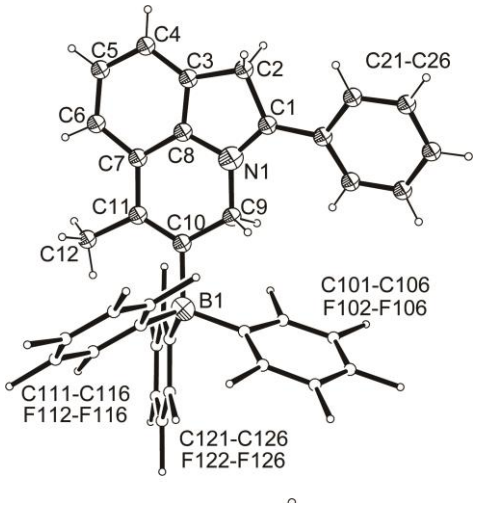
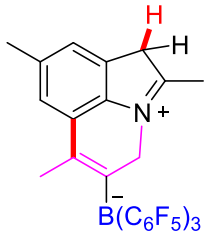


Fig. S8 A view of the molecular structure of compound **2b**.

Synthesis and characterization of compound 2c



2c

According to the General Procedure II (for **2**) from **1c** (59.2 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2c** was isolated as a white solid (191.5 mg, 90% yield). [Comment: Compound **2c** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2c** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2c** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 7.18 (s, 1H), 7.12 (s, 1H), 5.24 (d, $^{2}J_{HH}$ = 21.7 Hz, 1H), 5.05 (d, $^{2}J_{HH}$ = 21.7 Hz, 1H), 4.29 (s, 2H), 2.57 (s, 3H), 2.40 (s, 3H), 1.88 (s, 3H).

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -14.4 ($\nu_{1/2}$ ~ 33 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -129.6 (m, 3F), -132.6 (m, 1F), -134.4 (m, 1F), -135.5 (m, 1F) (*o*-C_6F_5); -162.4 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F), -163.8 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F), -164.7 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F) (*p*-C_6F_5); -165.6 (m, 1F), -166.8 (m, 1F), -167.5 (m, 1F), -168.1 (m, 2F), -168.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{32}H_{15}BF_{15}N$-H^{+}: 708.0985 [M-H]$^{-}$; found: 708.0996.

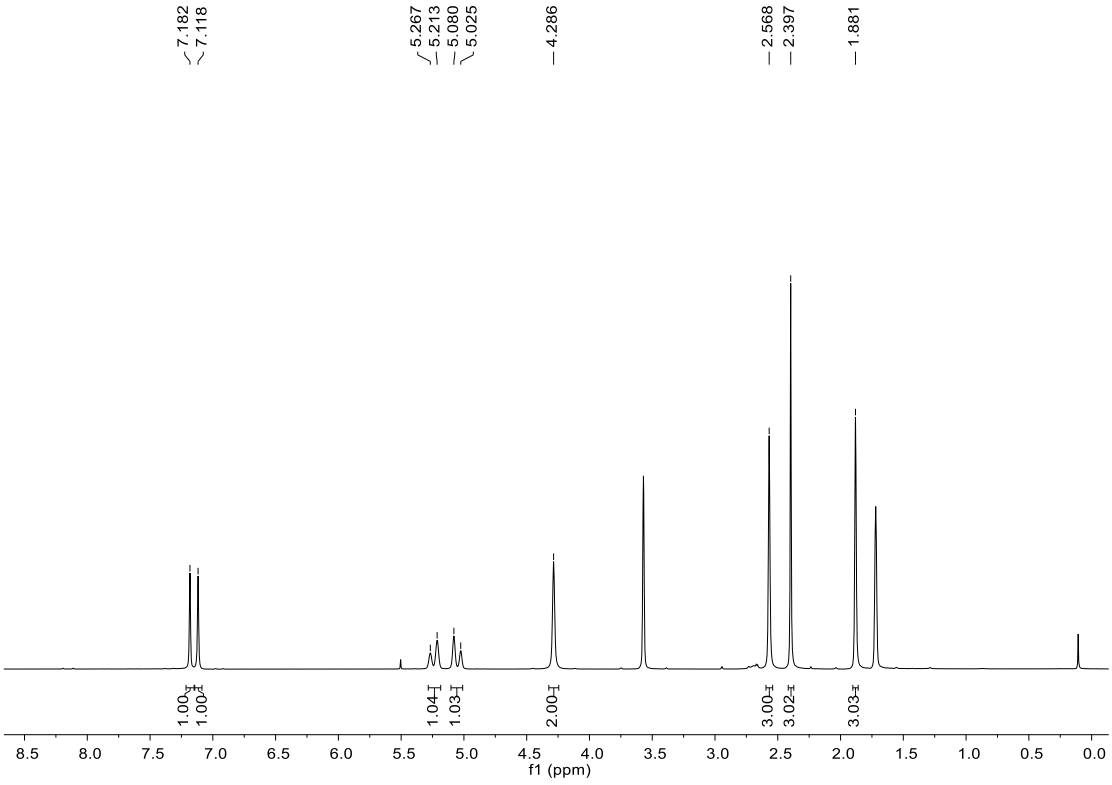


Fig. S9 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **2c**.

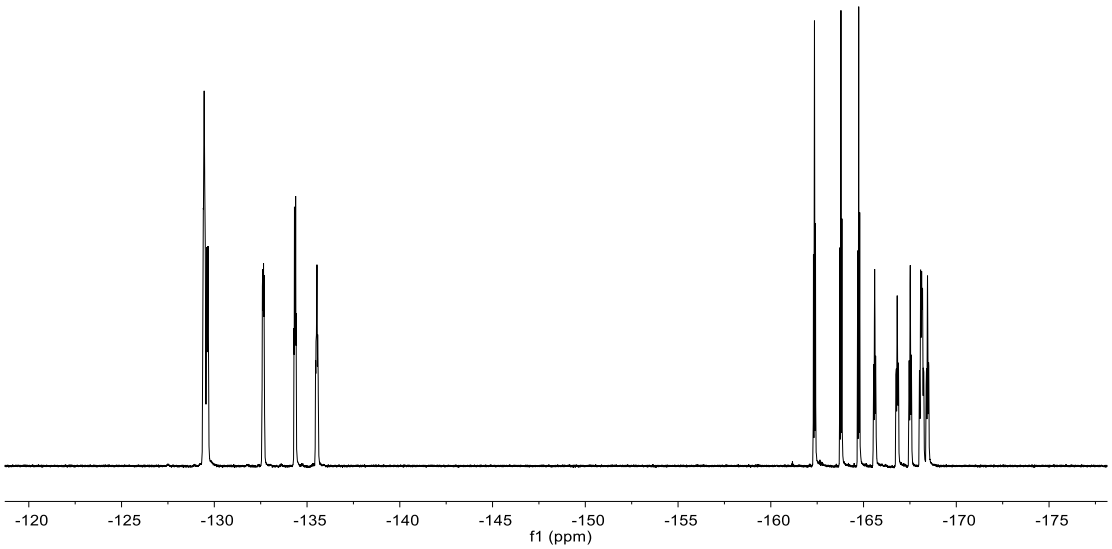


Fig. S10 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **2c**.

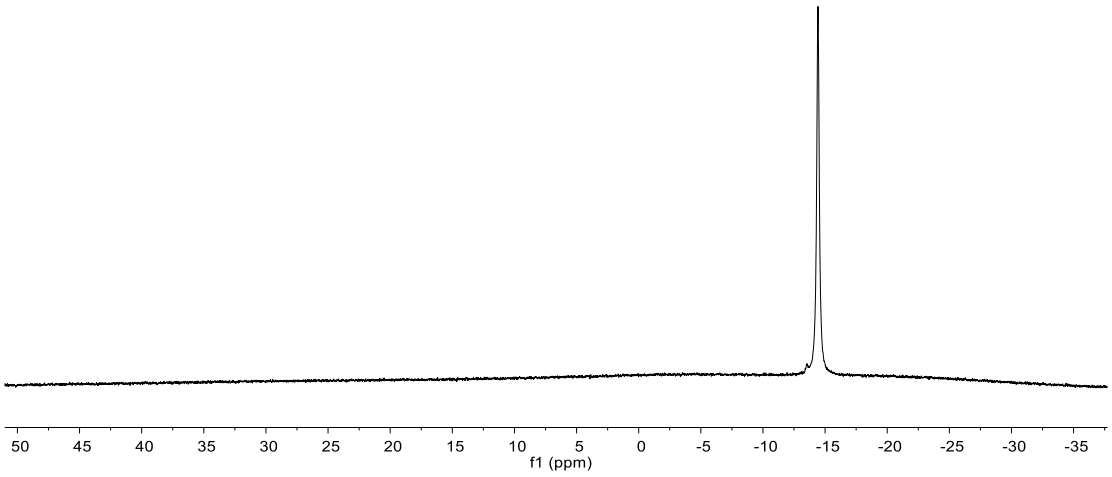
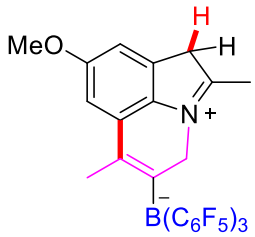


Fig. S11 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **2c**.

Synthesis and characterization of compound 2d



2d

According to the General Procedure II (for **2**) from **1d** (64.0 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2d** was isolated as a yellow solid (193.6 mg, 89% yield). [Comment: Compound **2d** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2d** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2d** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 6.94 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 6.83 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 5.24 (d, $^2J_{HH}$ = 21.8 Hz, 1H), 5.05 (d, $^2J_{HH}$ = 21.8 Hz, 1H), 4.27 (s, 2H), 3.83 (s, 3H), 2.55 (s, 3H), 1.88 (s, 3H).

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -14.4 ($\nu_{1/2}$ ~ 33 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -129.4 (m, 2F), -129.7 (m, 1F), -132.6 (m, 1F), -134.3 (m, 1F), -135.5 (m, 1F) (*o*-C_6F_5); -162.3 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -163.7 (t, $^3J_{FF}$ = 20.2 Hz, 1F), -164.7 (t, $^3J_{FF}$ = 19.9 Hz, 1F) (*p*-C_6F_5); -165.6 (m, 1F), -166.8 (m, 1F), -167.5 (m, 1F), -168.1 (m, 2F), -168.5 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{32}H_{15}BF_{15}NO\text{-}H^+$: 724.0934 $[M\text{-}H]^-$; found: 724.0948.

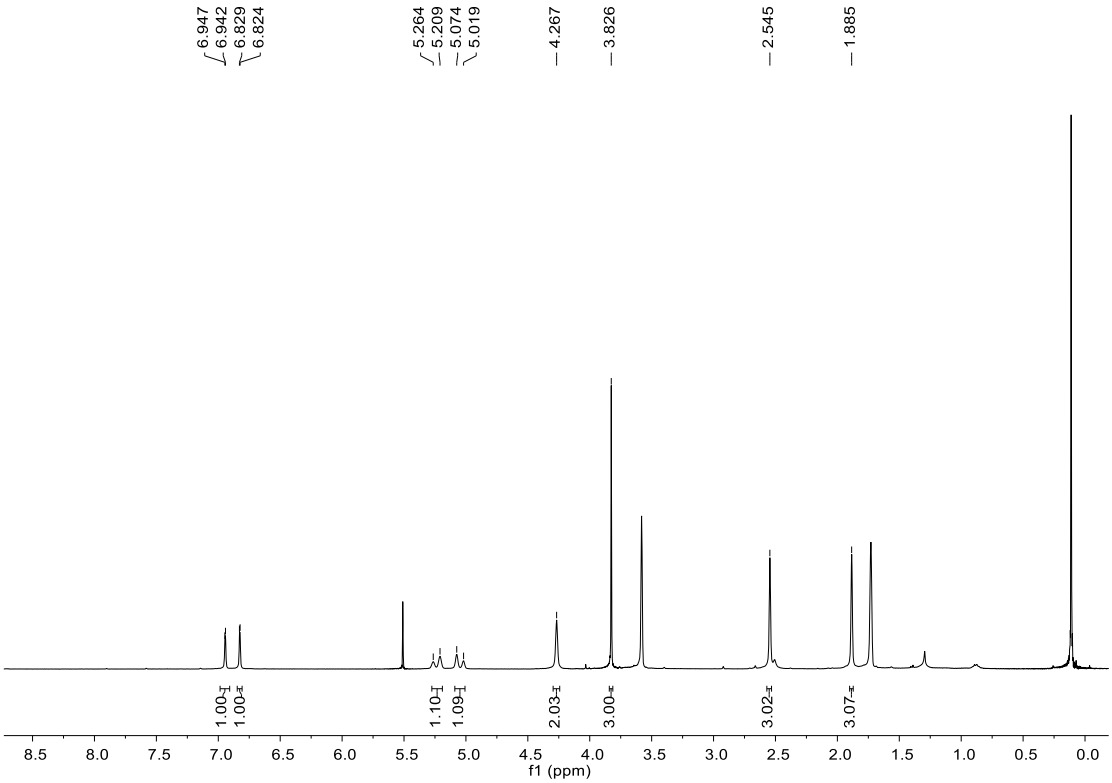


Fig. S12 ^1H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **2d**.

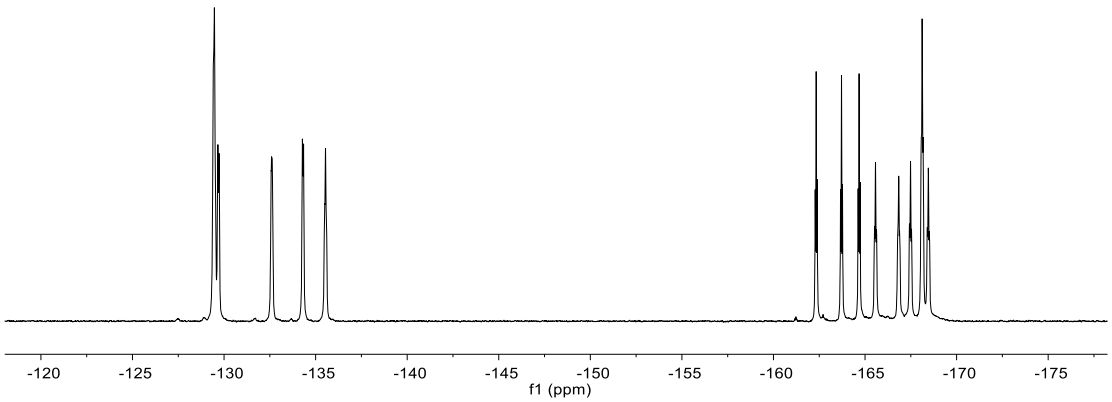


Fig. S13 $^{19}F\{^1H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **2d**.

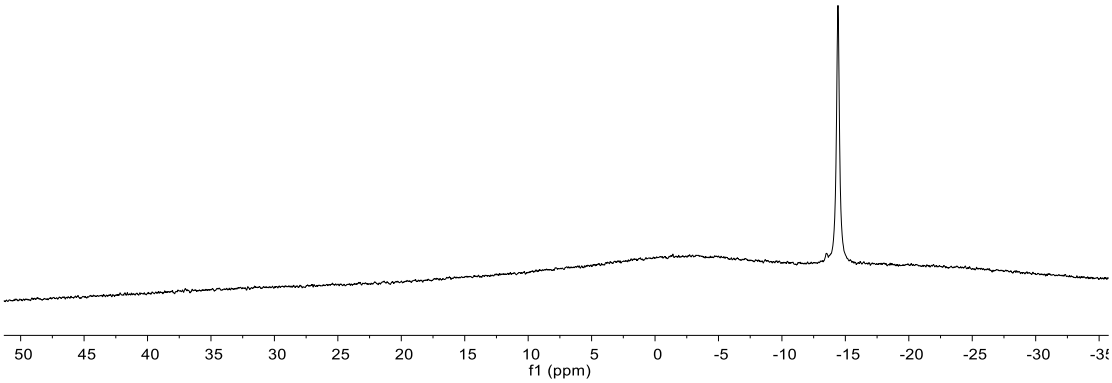
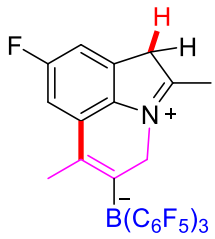


Fig. S14 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **2d**.

Synthesis and characterization of compound 2e



2e

According to the General Procedure II (for **2**) from **1e** (60.4 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2e** was isolated as a yellow solid (194.7 mg, 91% yield). [Comment: Compound **2e** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2e** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2e** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 7.15 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H), 7.08 (d, $^{3}J_{HH}$ = 9.9 Hz, 1H), 5.29 (d, $^{2}J_{HH}$ = 22.0 Hz, 1H), 5.10 (d, $^{2}J_{HH}$ = 22.0 Hz, 1H), 4.37 (s, 2H), 2.60 (s, 3H), 1.88 (s, 3H).

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -14.4 ($\nu_{1/2}$ ~ 30 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -111.3 (s, 1F), -129.6 (m, 3F), -132.6 (m, 1F), -134.2 (m, 1F), -135.6 (m, 1F) (*o*-C_6F_5); -162.2 (t, $^{3}J_{FF}$ = 19.5 Hz, 1F), -163.6 (t, $^{3}J_{FF}$ = 19.8 Hz, 1F), -164.4 (t, $^{3}J_{FF}$ = 19.5 Hz, 1F) (*p*-C_6F_5); -165.5 (m, 1F), -166.7 (m, 1F), -167.3 (m, 1F), -168.0 (m, 2F), -168.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{31}H_{12}BF_{16}N$-H^+: 712.0734 $[M-H]^-$; found: 712.0743.

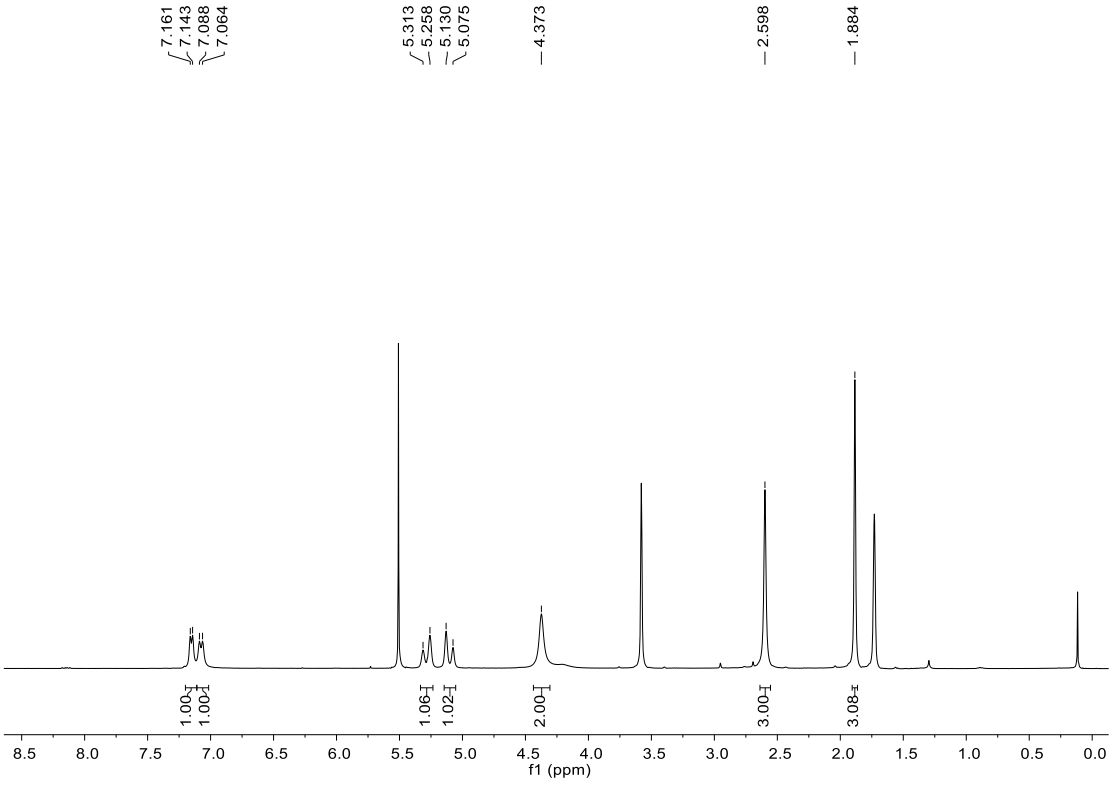


Fig. S15 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **2e**.

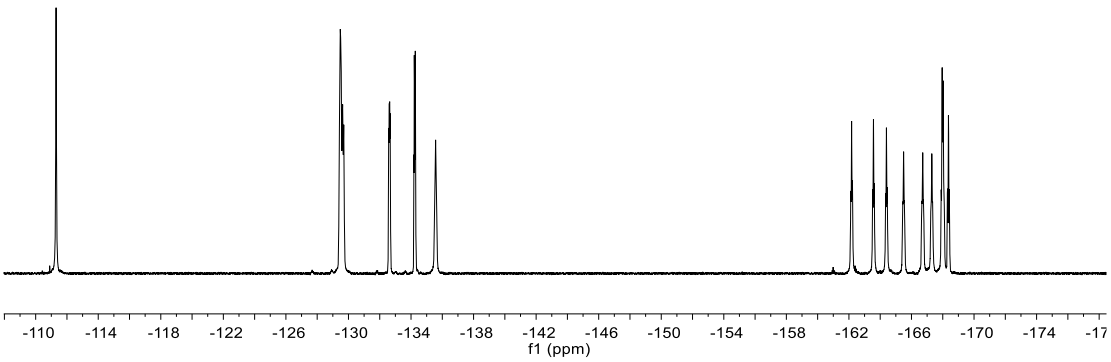


Fig. S16 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **2e**.

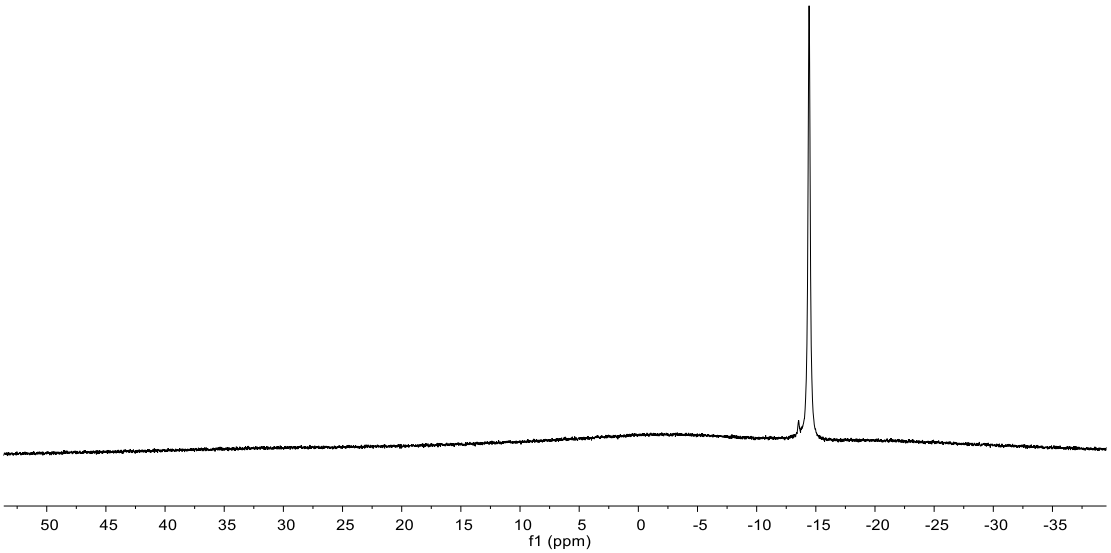
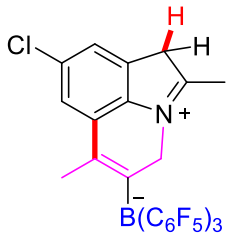


Fig. S17 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **2e**.

Synthesis and characterization of compound 2f



2f

According to the General Procedure II (for **2**) from **1f** (65.3 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2f** was isolated as a yellow solid (19.2 mg, 91% yield). [Comment: Compound **2f** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2f** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2f** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 7.40 (s, 1H), 7.31 (s, 1H), 5.28 (d, $^2J_{HH}$ = 21.7 Hz, 1H), 5.10 (d, $^2J_{HH}$ = 21.7 Hz, 1H), 4.39 (s, 2H), 2.60 (s, 3H), 1.88 (s, 3H).

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -14.4 ($\nu_{1/2}$ ~ 35 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -129.6 (m, 3F), -132.6 (m, 1F), -134.3 (m, 1F), -135.6 (m, 1F) (*o*-C_6F_5); -162.2 (t, $^3J_{FF}$ = 19.1 Hz, 1F,), -163.5 (t, $^3J_{FF}$ = 19.0 Hz, 1F), -164.4 (t, $^3J_{FF}$ = 18.4 Hz, 1F) (*p*-C_6F_5); -165.5 (m, 1F), -166.7 (m, 1F), -167.3 (m, 1F), -168.0 (m, 2F), -168.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{31}H_{12}BClF_{15}N$-H^+: 728.0439 [M-H]$^-$; found: 728.0449.

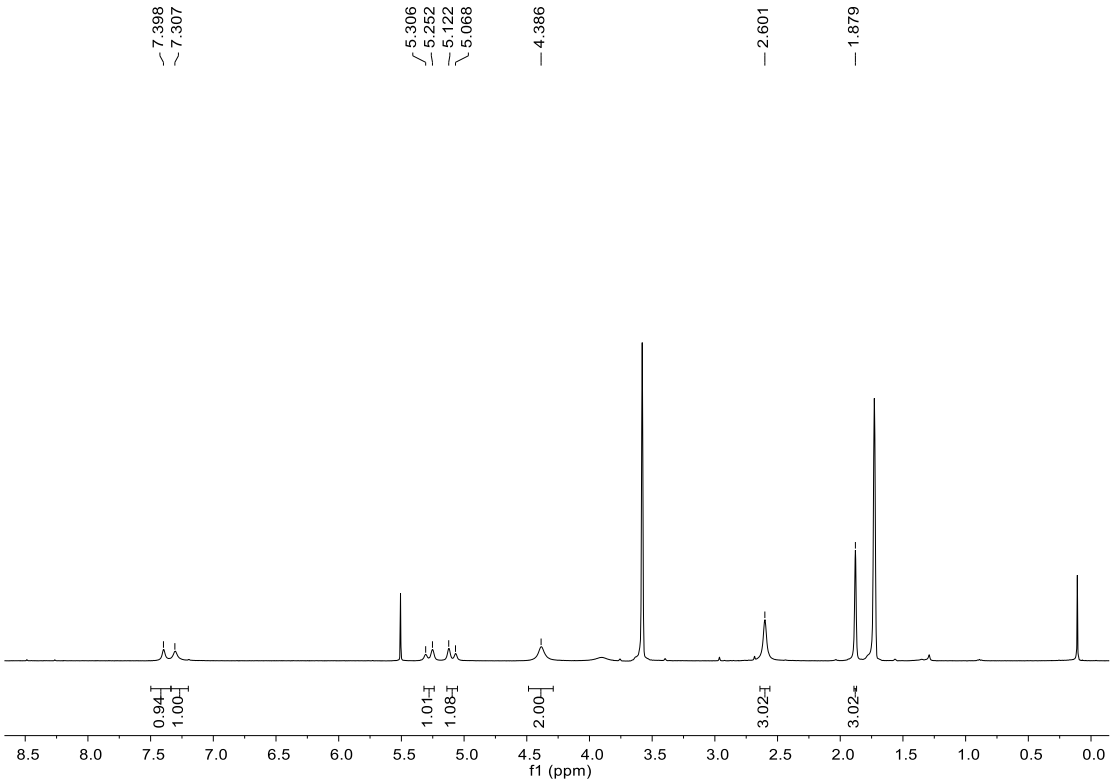


Fig. S18 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **2f**.

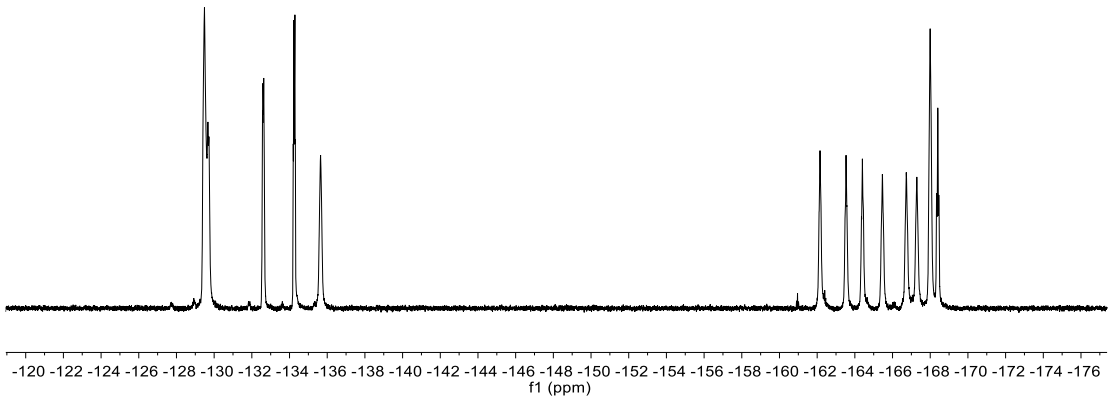


Fig. S19 ^{19}F{^{1}H} NMR (377 MHz, 299K, THF-d_8) spectrum of compound **2f**.

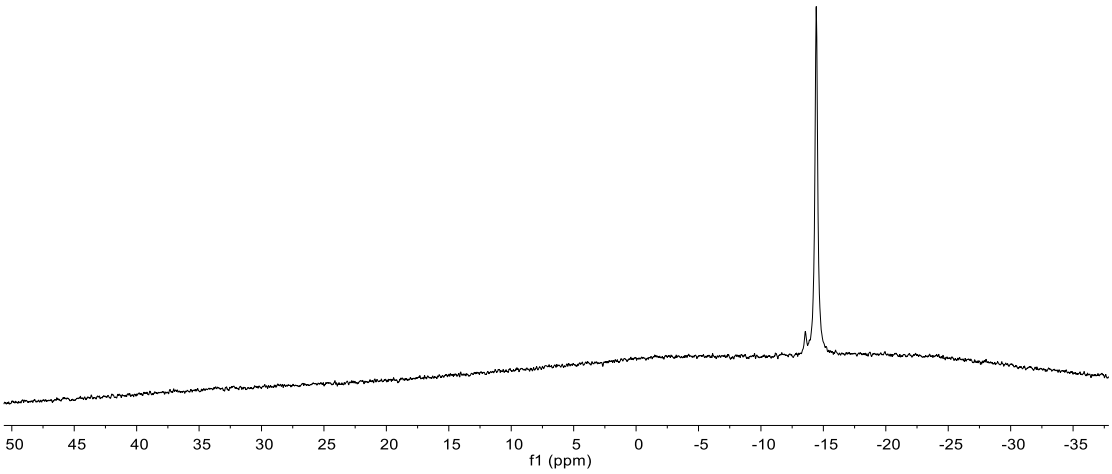
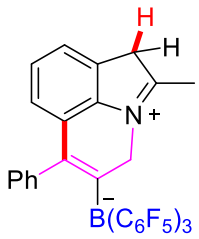


Fig. S20 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **2f**.

Synthesis and characterization of compound 2g



2g

According to the General Procedure II (for **2**) from **1g** (73.6 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2g** was isolated as a pale yellow solid (193.1 mg, 85% yield). [Comment: Compound **2g** is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2g** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2g** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.35 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.32 (s, 1H), 7.28 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.17-7.08 (m, 4H), 6.42 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 5.50 (br, 1H), 5.19 (br, 1H), 4.29 (s, 2H), 2.68 (s, 3H).

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.5 ($\nu_{1/2}$ ~ 22 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, CD_2Cl_2): δ = -127.8 (br, 1F), -130.1 (m, 1F), -131.0 (br, 1F), -131.4 (br, 1F), -131.5 (m, 2F) (*o*-C_6F_5); -161.0 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F), -162.9 (m, 2F) (*p*-C_6F_5); -164.9 (m, 1F), -166.0 (m, 1F), -167.2 (m, 2F), -167.6 (br, 1F), -168.3 (br, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{36}H_{15}BF_{15}N$-H^+: 756.0985 [M-H]$^-$; found: 756.0981.

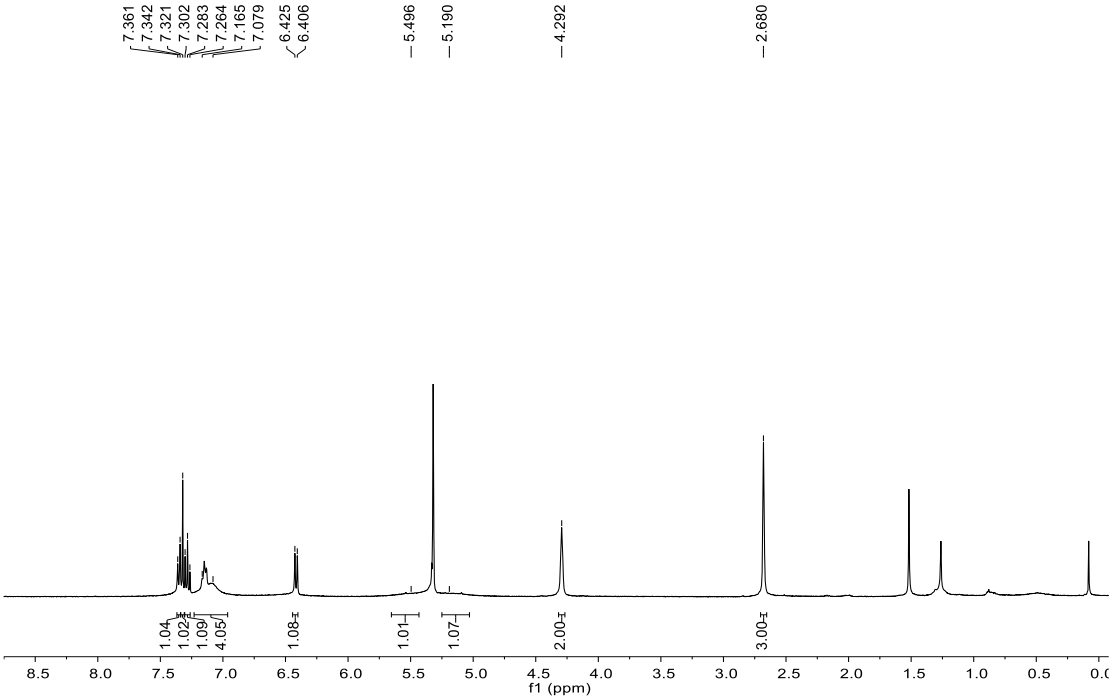


Fig. S21 ^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **2g**.

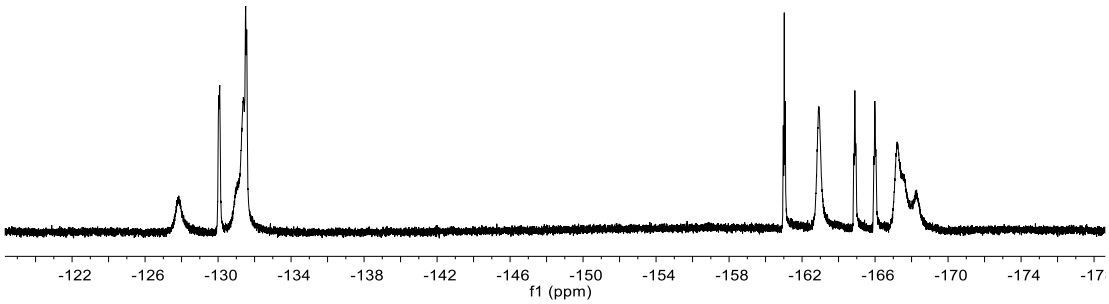


Fig. S22 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **2g**.

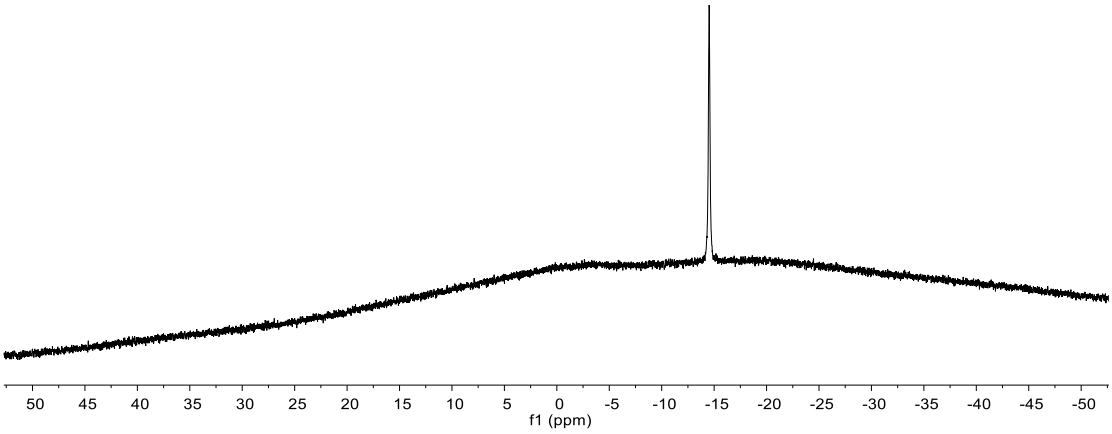
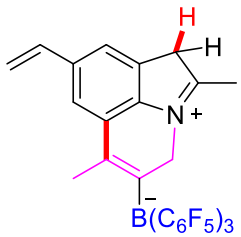


Fig. S23 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **2g**.

Synthesis and characterization of compound 2h



2h

According to the General Procedure II (for **2**) from **1h** (62.8 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol). The product **2h** was isolated as a pale yellow solid (194.8 mg, 90% yield). [Comment: Compound **2h**

is insoluble in $CDCl_3$, C_6D_6, toluene-d_8, and CD_2Cl_2. **2h** is well soluble in DMSO-D_6 and THF-d_8, but the solution of **2h** in both of DMSO-D_6 and THF-d_8 are unstable. Therefore, the above-mentioned reasons prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.42 (s, 1H), 7.33 (s, 1H), 5.83 (d, $^3J_{HH}$ = 17.6 Hz, 1H), 5.38 (d, $^3J_{HH}$ = 17.6 Hz, 1H), 5.28 (d, $^2J_{HH}$ = 20.0 Hz, 1H), 5.11 (d, $^2J_{HH}$ = 20.0 Hz, 1H), 4.22 (s, 2H), 2.61 (s, 3H), 1.92 (s, 3H).

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.5 ($\nu_{1/2}$ ~ 29 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, CD_2Cl_2): δ = -129.8, -130.0, -130.2, -132.6, -134.3, -135.8 (each m, each 1F, *o*-C_6F_5); -160.9 (t, $^3J_{FF}$ = 19.6 Hz, 1F), -162.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -163.1 (t, $^3J_{FF}$ = 21.2 Hz, 1F) (*p*-C_6F_5); -164.4 (m, 1F), -165,5 (m, 1F), -166.3 (m, 1F), -167.3 (m, 3F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{33}H_{15}BF_{15}N$-H^+: 754.0829 $[M-H]^-$; found: 754.0828.

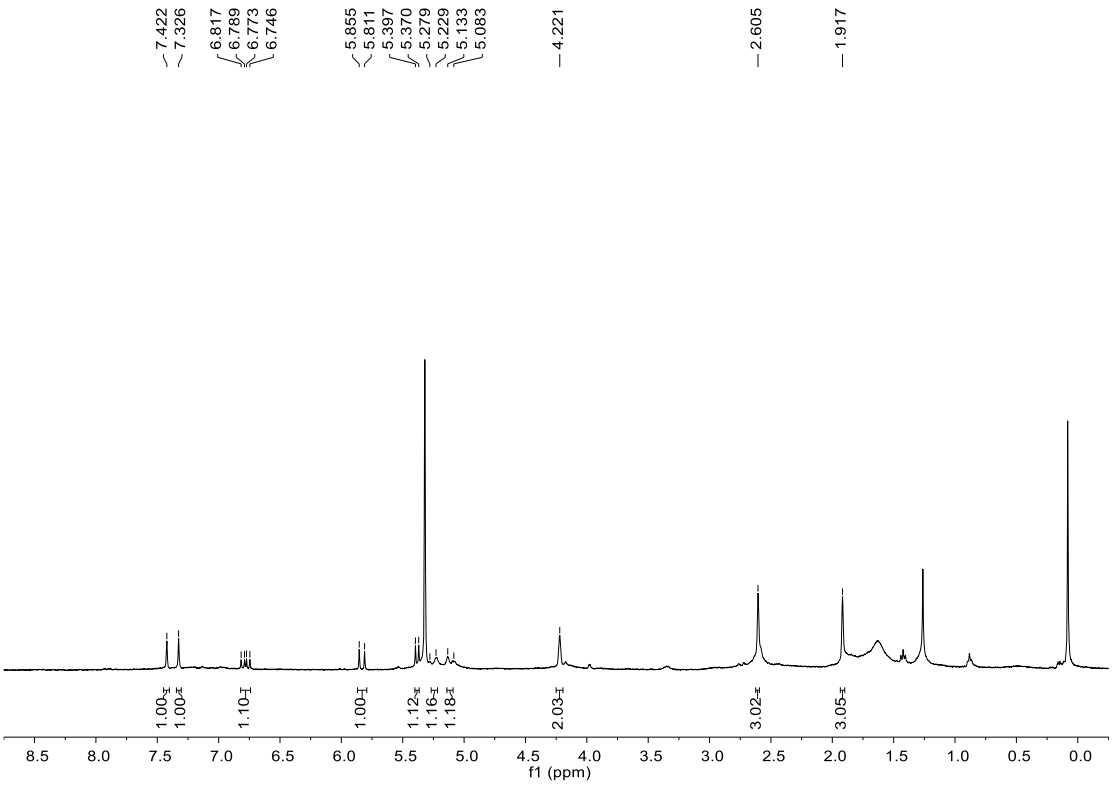


Fig. S24 ^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **2h**.

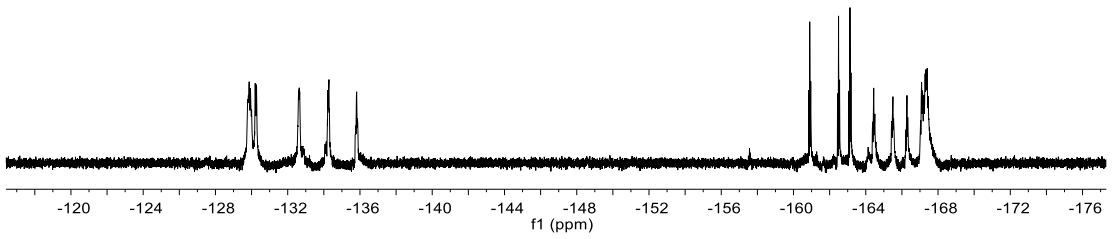


Fig. S25 ^{19}F{^{1}H} NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **2h**.

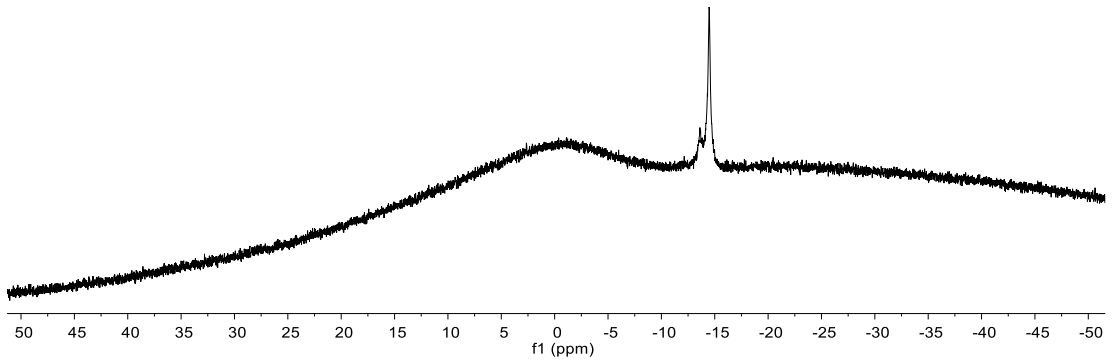
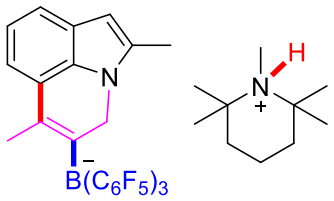


Fig. S26 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **2h**.

Synthesis and characterization of compound 3a



3a

According to the General Procedure II (for **3**) from **2a** (139.1 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3a** was isolated as a green solid (158.4 mg, 93% yield).

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **3a** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.10 (d, $^{3}J_{HH}$ = 6.5 Hz, 1H), 6.80 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 6.66 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.05 (s, 1H), 5.02 (d, $^{2}J_{HH}$ = 16.4 Hz, 1H), 4.85 (d, $^{2}J_{HH}$ = 16.4 Hz, 1H), 3.75 (br, 1H), 2.34 (s, 3H), 2.20 (s, 3H), 1.81 (s, 3H), 1.53-1.49 (m, 6H), 1.11 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, 299K, CD_2Cl_2): δ = 136.5, 134.0, 127.6, 127.5, 125.0, 124.1, 120.1, 117.3, 111.6, 98.3, 66.7, 48.9, 38.6, 30.1, 25.1, 16.2, 15.8, 11.9. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.2 ($\nu_{1/2}$ ~ 55 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, CD_2Cl_2): δ = -128.7, -129.8, -130.0, -133.3, -133.8, -134.8 (each m, each 1F, *o*-C_6F_5); -162.6 (t, $^{3}J_{FF}$ = 20.4 Hz,

1F), -163.6 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -164.6 (t, $^{3}J_{FF}$ = 20.6 Hz, 1F) (*p*-C_6F_5); -165.8 (m, 1F), -166.6 (m, 1F), -167.3 (m, 1F), -167.6 (m, 3F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{41}H_{34}BF_{15}N_2$: 694.0829 $[M]^-$, found: 694.0832; 156.1747 $[M]^+$, found: 156.1745.

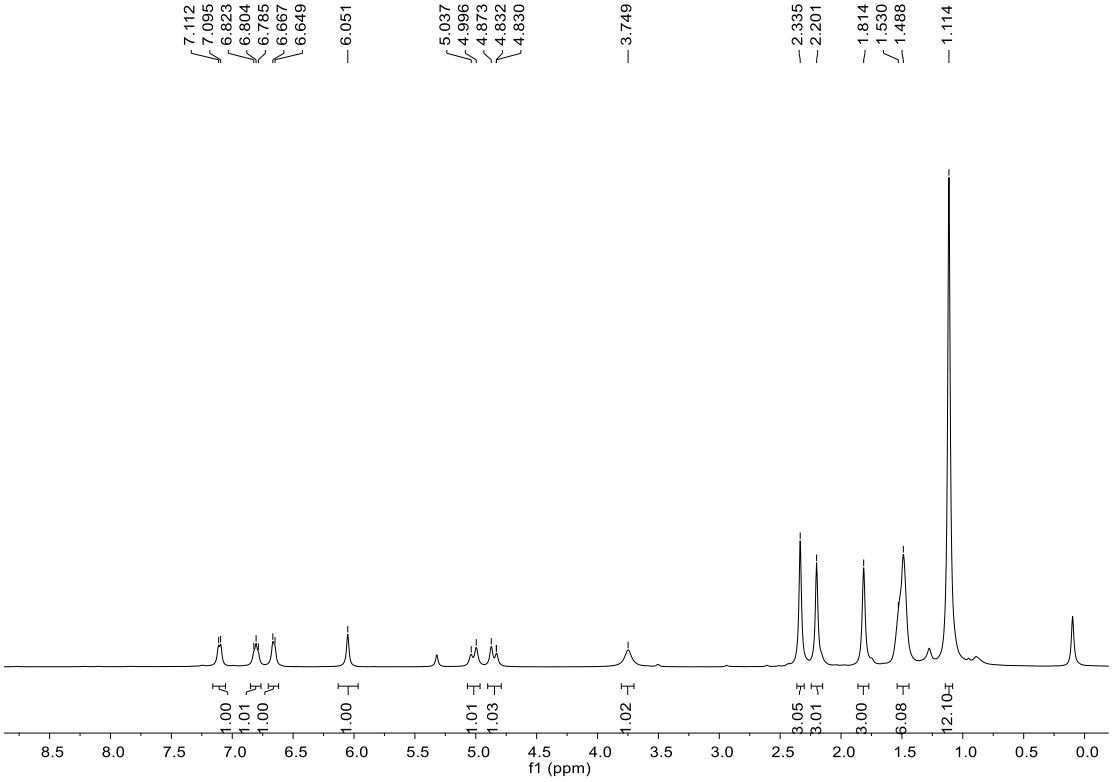


Fig. S27 ^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3a**.

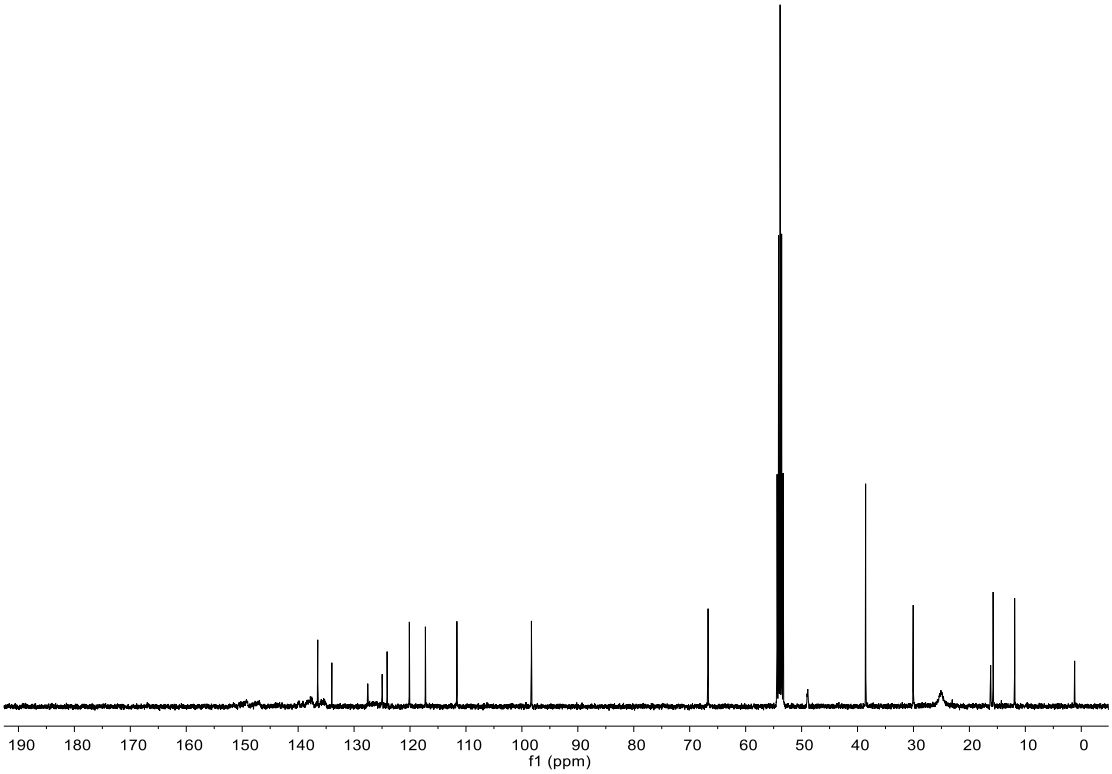


Fig. S28 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3a**.

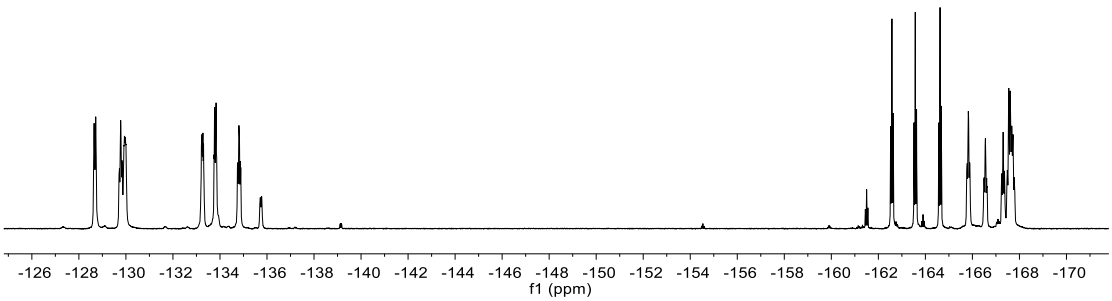


Fig. S29 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3a**.

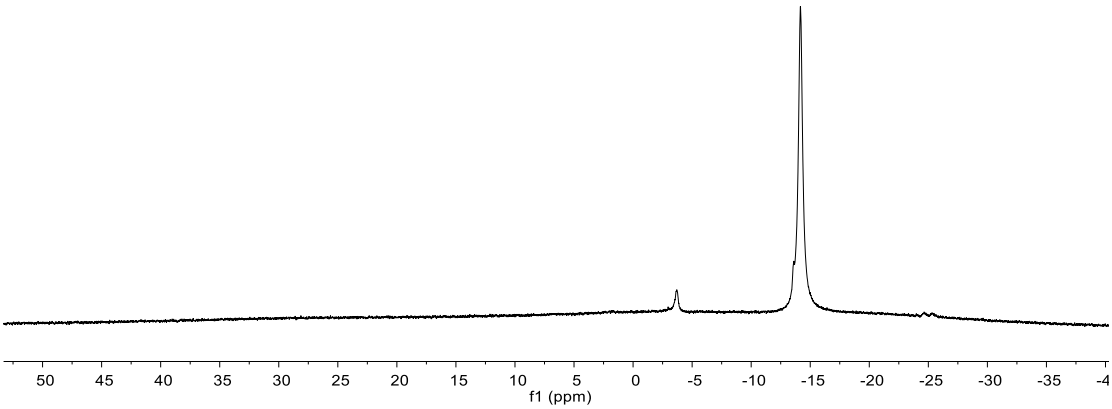


Fig. S30 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **3a**.

X-ray crystal structure analysis of compound 3a: formula $C_{41}H_{34}BF_{15}N_2$, M = 850.51, colourless crystal, 0.23 × 0.41 × 0.40 mm, a = 17.8727(12), b = 12.5536(8), c = 18.2517(11) Å, α = γ = 90º, β = 110.948(3) º, V = 3824.4(4) Å^3, ρ_{calc} = 1.477 gcm^{-3}, μ = 0.137 mm^{-1}, empirical absorption correction (0.4865 ≤ T ≤ 0.5624), Z = 4, monoclinic, space group *P2(1)/c*, λ = 0.71073 Å, T = 190.0 K, ω and φ scans, 29815 reflections collected (±h, ±k, ±l), 7723 independent (R_{int} = 0.1434) and 3328 observed reflections [I>2σ(I)], 539 refined parameters, R = 0.0619, wR^2 = 0.1564, max. (min.) residual electron density 0.22 (-0.25) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

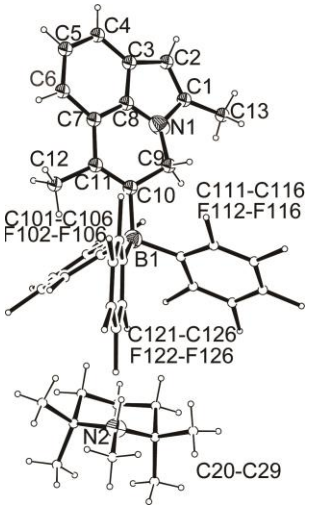
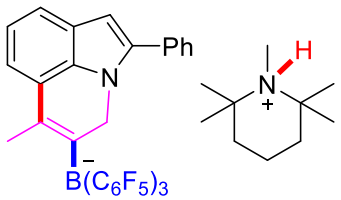


Fig. S31 A view of the molecular structure of compound **3a**.

Synthesis and characterization of compound 3b



According to the General Procedure II from **2b** (for **3**) (151.5 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3b** was isolated as a white solid (166.1 mg, 91% yield).

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.48 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 7.36 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.30 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.22 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 6.89 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 6.75 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 6.47 (s, 1H), 5.27 (d, $^2J_{HH}$ = 17.4 Hz, 1H), 4.87 (d, $^2J_{HH}$ = 17.4 Hz, 1H), 3.35 (br, 1H), 2.45 (s, 3H), 1.84 (s, 3H), 1.55 (s, 6H), 1.18 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, CD_2Cl_2): δ = 140.7, 135.9, 133.2, 128.9, 127.9, 127.8, 127.6, 127.5, 126.2, 124.7, 120.9, 118.0, 113.0, 101.1, 67.1, 50.8, 38.6, 30.5, 30.2, 19.7, 16.1, 15.7. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.2 ($\nu_{1/2}$ ~ 48 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2): δ = -129.0 (m, 1F), -129.7 (m, 2F), -132.9 (m, 1F), -133.9 (m, 1F), -134.9 (m, 1F) (*o*-C_6F_5); -162.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -163.6 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -164.6 (t, $^3J_{FF}$ = 20.5 Hz, 1F) (*p*-C_6F_5); -165.5 (m, 1F), -167.3 (m, 2F), -167.6 (m, 3F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{46}H_{36}BF_{15}N_2$: 756.0985 $[M]^-$; found: 756.0988.

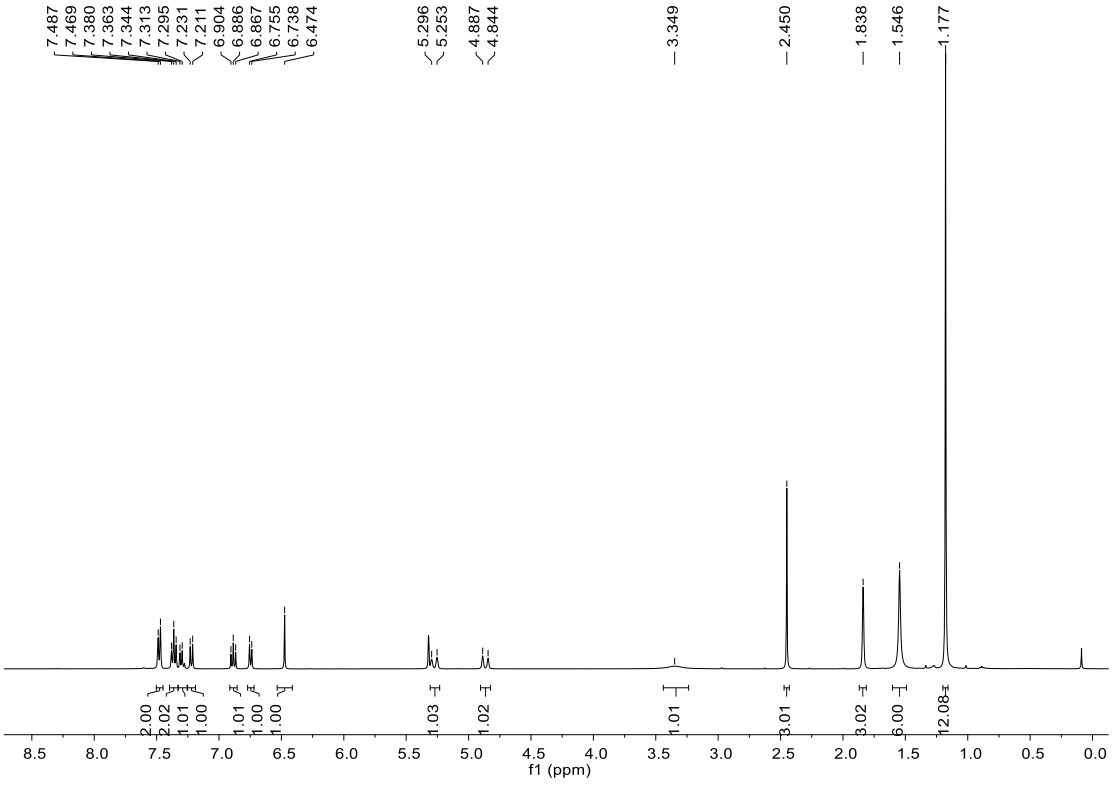


Fig. S32 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3b**.

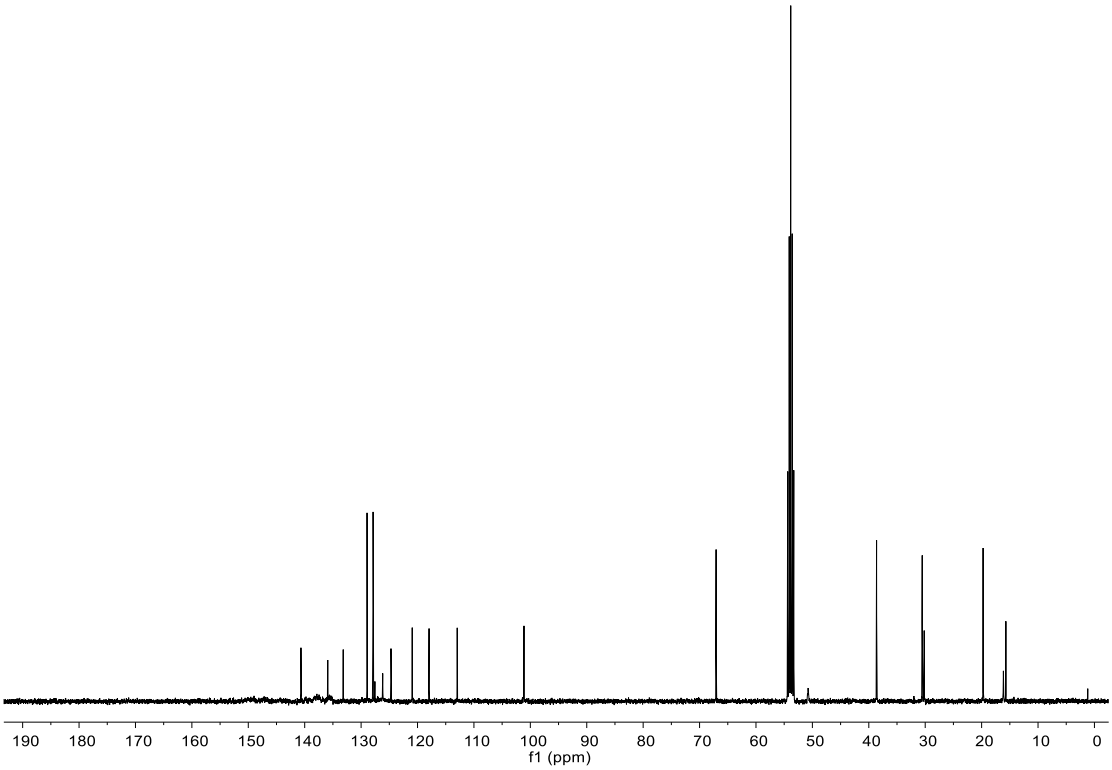


Fig. S33 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3b**.

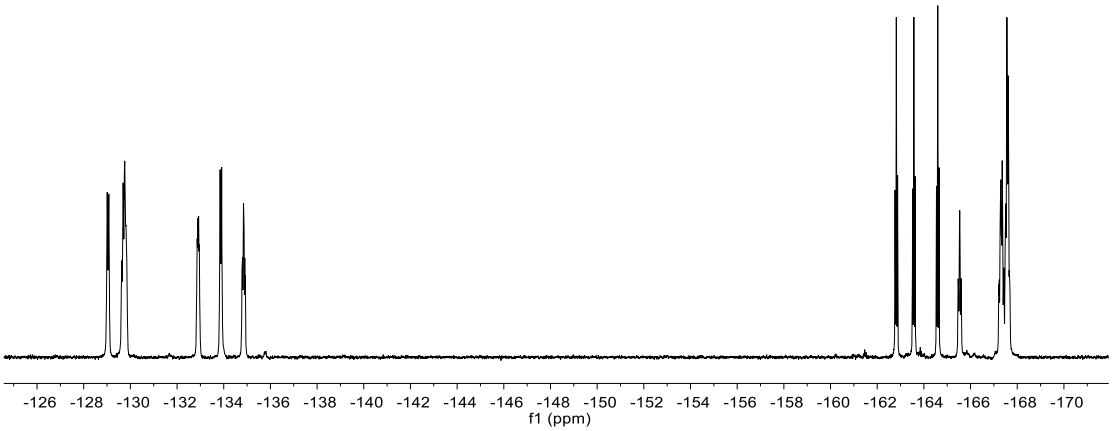


Fig. S34 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3b**.

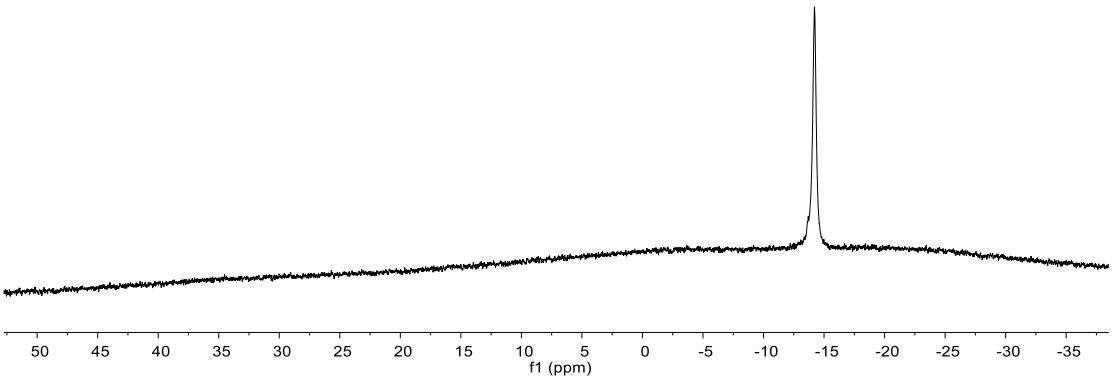
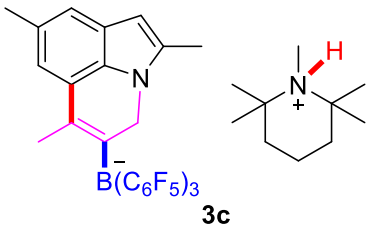


Fig. S35 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **3b**.

Synthesis and characterization of compound 3c



According to the General Procedure II (for **3**) from **2c** (141.9 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3c** was isolated as a white solid (152.2 mg, 88% yield).

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 6.89 (s, 1H), 6.52 (s, 1H), 5.96 (s, 1H), 4.99 (d, $^2J_{HH}$ = 17.8 Hz, 1H), 4.82 (d, $^2J_{HH}$ = 17.8 Hz, 1H), 3.36 (br, 1H), 2.30 (s, 6H), 2.18 (s, 3H), 1.80 (s, 3H), 1.52-1.44 (m, 6H), 1.10 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, CD_2Cl_2): δ = 136.3, 132.4, 129.2, 127.6, 127.5, 124.7, 124.0, 116.7, 113.7, 97.8, 66.8, 48.9, 38.5, 30.0, 25.1, 22.1, 16.2, 15.8, 11.9. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.2 ($\nu_{1/2}$ ~ 53 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2): δ = -128.8 (m, 1F), -129.9 (m, 2F), -133.2 (m, 1F), -133.9 (m, 1F), -135.0 (m, 1F) (*o*-C_6F_5); -162.7 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -163.7 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -164.7 (t, $^3J_{FF}$ = 20.5 Hz, 1F) (*p*-C_6F_5); -165.8 (m, 1F), -166.7 (m, 1F), -167.4 (m, 1F), -167.7 (m, 3F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{42}H_{36}BF_{15}N_2$: 708.0985 $[M]^-$; found: 708.0994.

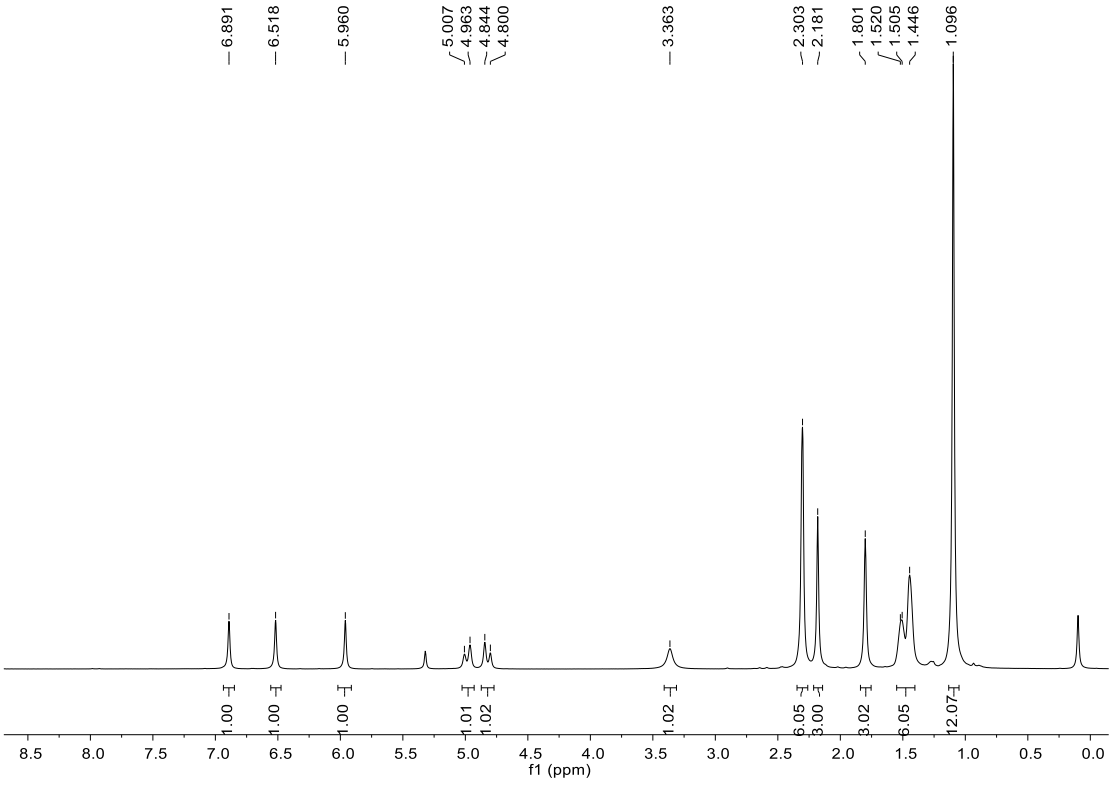


Fig. S36 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3c**.

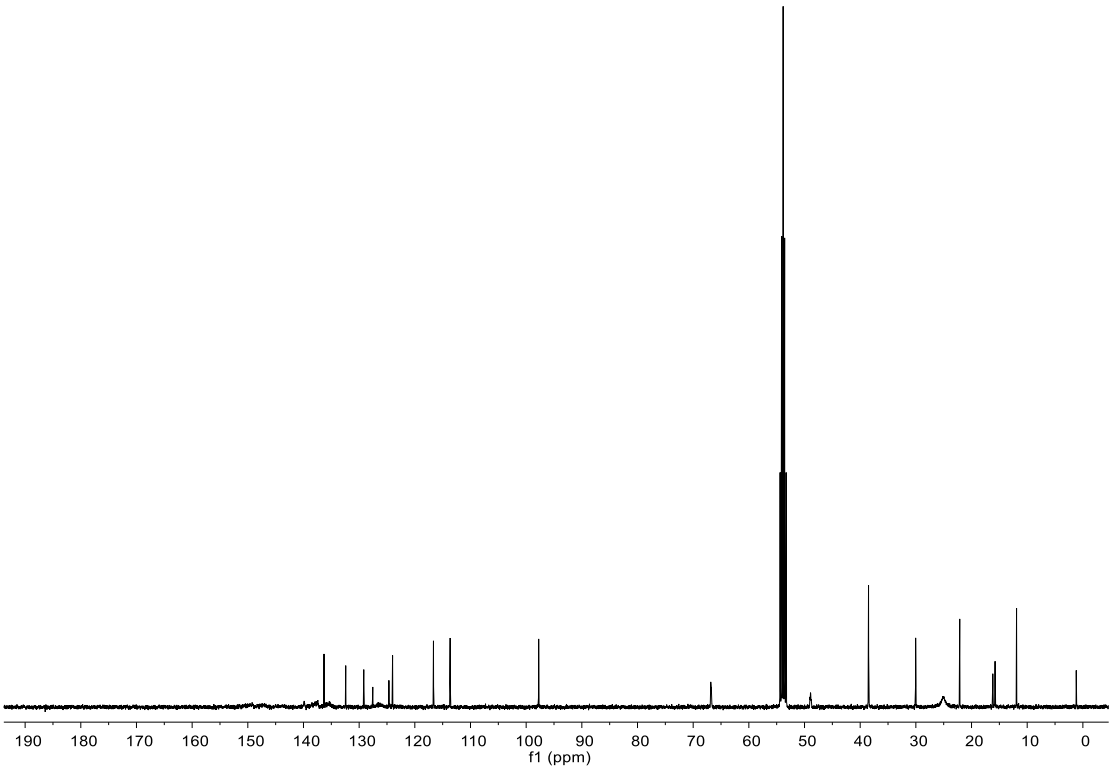


Fig. S37 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3c**.

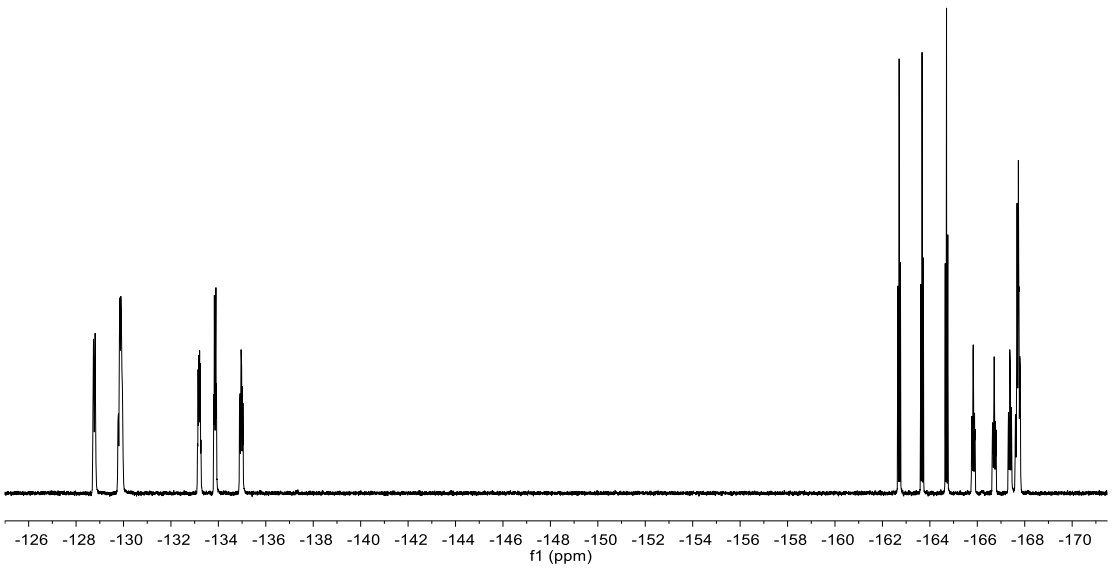


Fig. S38 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3c**.

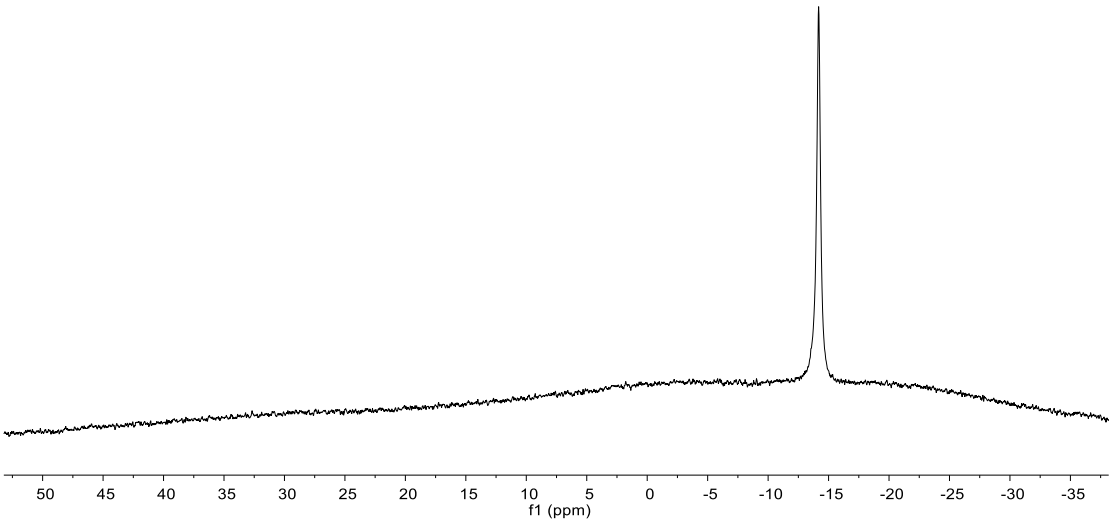
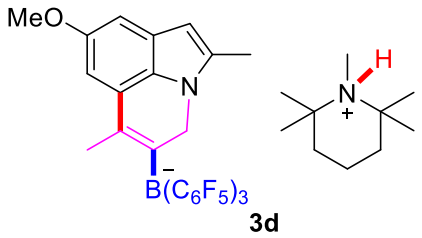


Fig. S39 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **3c**.

Synthesis and characterization of compound 3d



3d

According to the General Procedure II (for **3**) from **2d** (145.1 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3d** was isolated as a yellow solid (160.3 mg, 91% yield).

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 6.62 (s, 1H), 6.35 (s, 1H), 5.99 (s, 1H), 5.00 (d, $^2J_{HH}$ = 17.9 Hz, 1H), 4.83 (d, $^2J_{HH}$ = 17.9 Hz, 1H), 3.99 (br, 1H), 3.75 (s, 3H), 2.40 (s, 3H), 2.18 (s, 3H), 1.80 (s, 3H), 1.56-1.51 (m, 6H), 1.15 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, CD_2Cl_2): δ = 155.4, 136.7, 129.7, 127.3, 127.2, 126.3, 125.7, 123.8, 102.8, 99.7, 98.3, 66.5, 57.0, 49.0, 38.7, 30.1, 25.2, 16.2, 15.9, 11.9. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.1 ($\nu_{1/2}$ ~ 57 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2): δ = -128.6, -129.6, -130.0, -133.3, -133.8, -134.7 (each m, each 1F, *o*-C_6F_5); -162.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -163.5 (t, $^3J_{FF}$ = 20.2 Hz, 1F), -164.6 (t, $^3J_{FF}$ = 20.4 Hz, 1F) (*p*-C_6F_5); -166.5 (m, 1F), -167.3 (m, 1F), -167.5 (m, 2F), -167.8 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{42}H_{36}BF_{15}N_2O$: 724.0934 $[M]^-$; found: 724.0937.

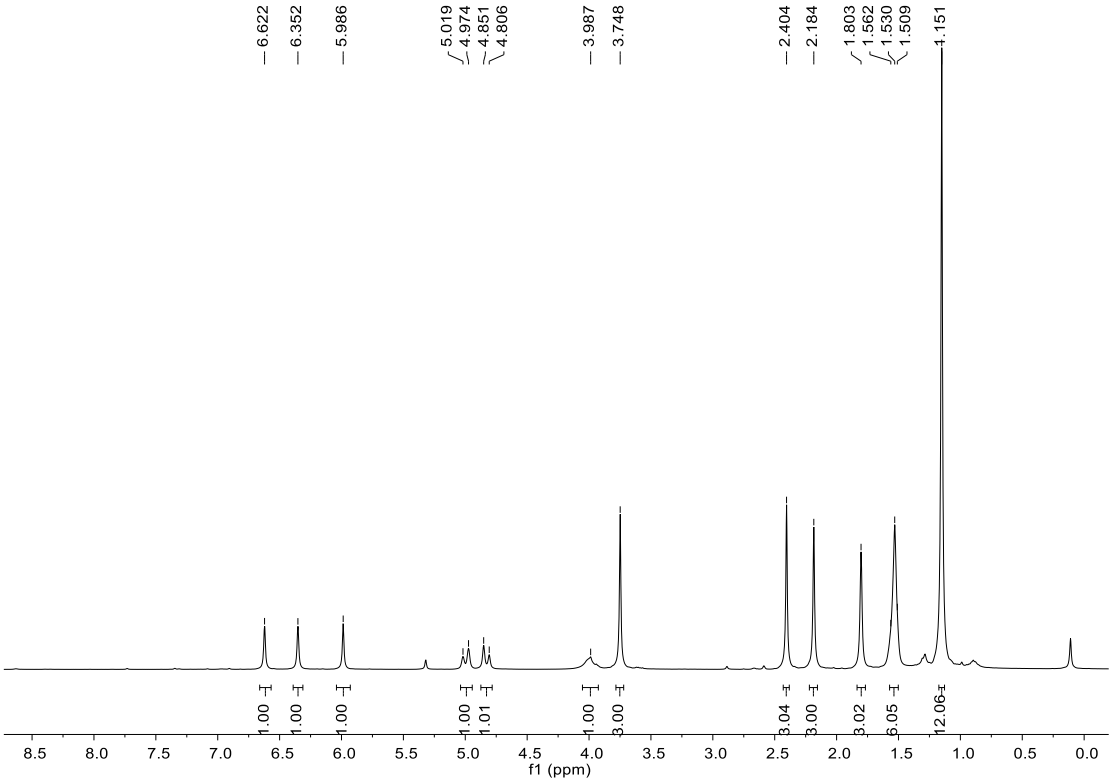


Fig. S40 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3d**.

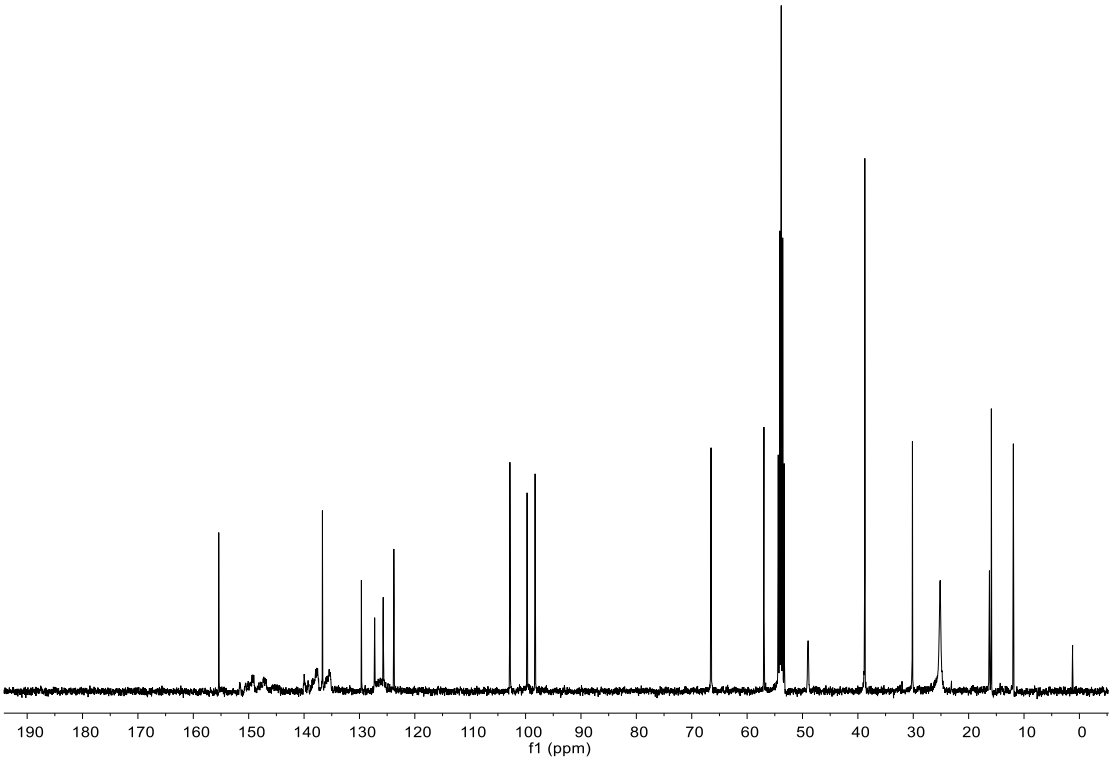


Fig. S41 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3d**.

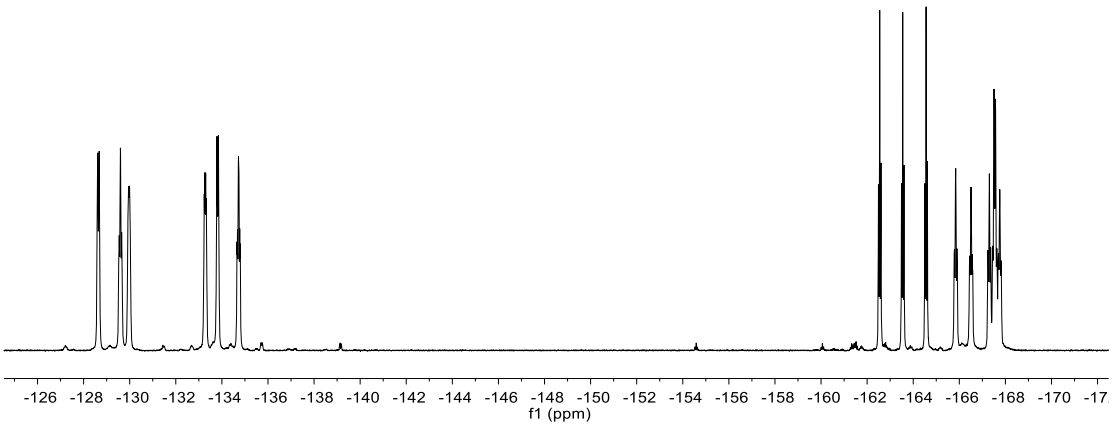


Fig. S42 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3d**.

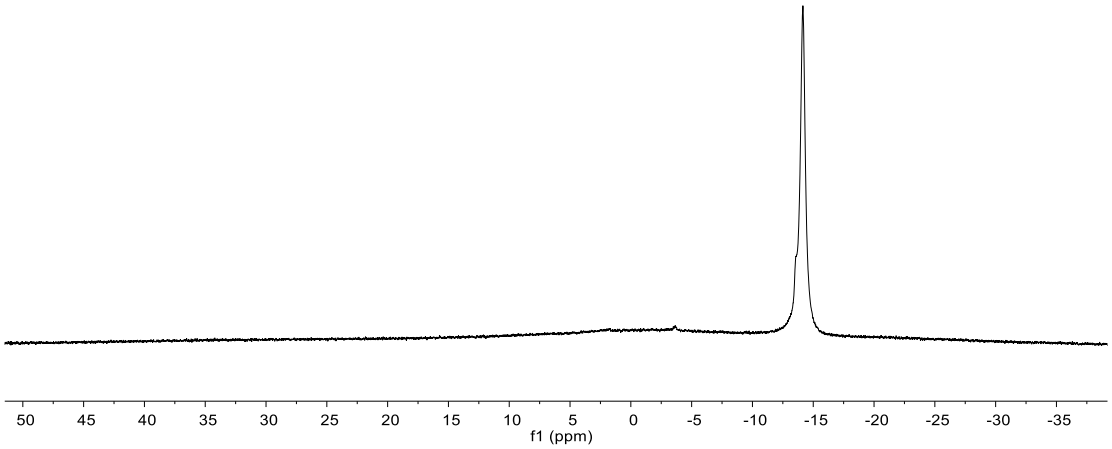
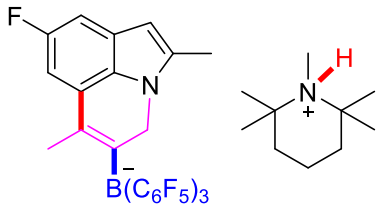


Fig. S43 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **3d**.

Synthesis and characterization of compound 3e



3e

According to the General Procedure II (for **3**) from **2e** (142.7 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3e** was isolated as a yellow solid (147.7 mg, 85% yield).

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 6.76 (d, $^3J_{HH}$ = 10.0 Hz, 1H), 6.43 (d, $^3J_{HH}$ = 10.7 Hz, 1H), 6.03 (s, 1H), 5.02 (d, $^2J_{HH}$ = 18.0 Hz, 1H), 4.85 (d, $^2J_{HH}$ = 18.0 Hz, 1H), 3.89 (br, 1H), 2.49 (s, 3H), 2.19 (s, 3H), 1.80 (s, 3H), 1.57 (s, 6H), 1.19 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, CD_2Cl_2): δ = 160.6, 158.3, 137.7, 130.4, 127.0, 125.7 (d, $^3J_{FC}$ = 9.3 Hz), 123.4 (d, $^3J_{FC}$ = 11.0 Hz), 101.2 (d, $^2J_{FC}$ = 24.6 Hz), 100.3 (d, $^2J_{FC}$ = 27.8 Hz), 98.5 (d, $^4J_{FC}$ = 4.6 Hz), 66.9, 38.8, 30.2, 25.3, 16.2, 15.8, 12.0. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.2 ($\nu_{1/2}$ ~ 43 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2): δ = -125.6 (s, 1F), -128.7, -129.7, -130.0, -133.2, -133.8, -134.8 (each m, each 1F, *o*-C_6F_5); -162.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -163.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -164.4 (t, $^3J_{FF}$ = 20.5 Hz, 1F,) (*p*-C_6F_5); -165.7 (m, 1F), -166.4 (m, 1F), -167.4 (m, 4F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{41}H_{33}BF_{16}N_2$: 712.0735 $[M]^-$; found: 712.0742.

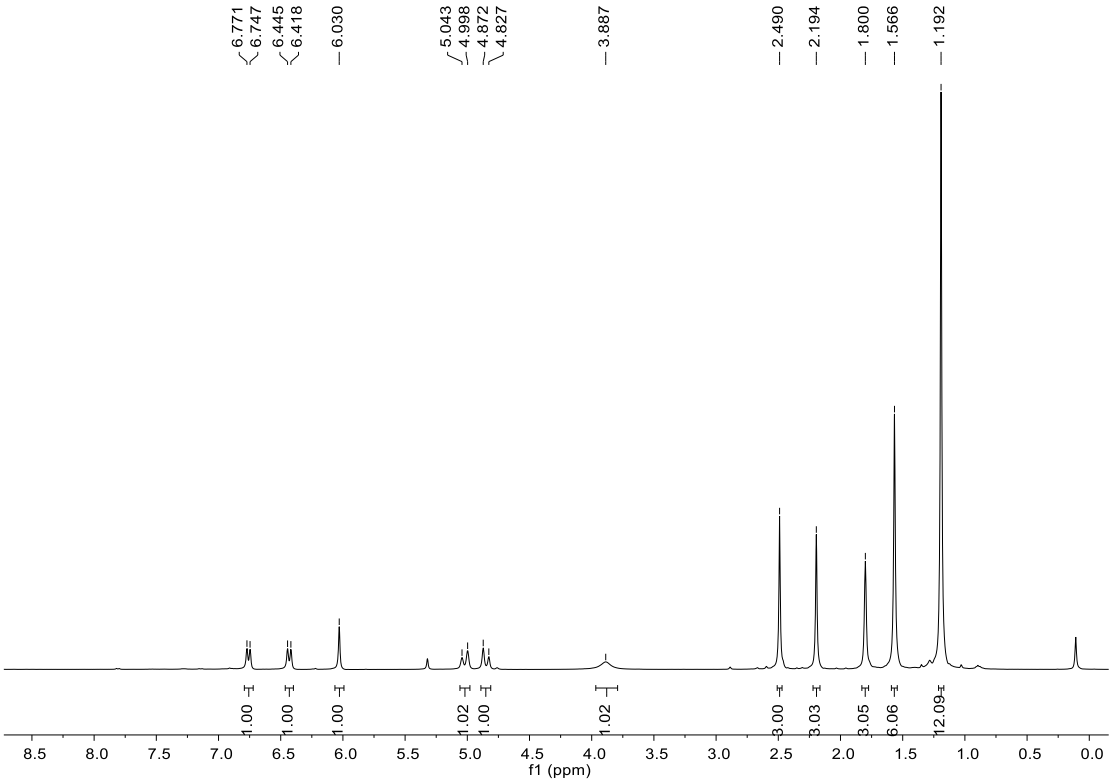


Fig. S44 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3e**.

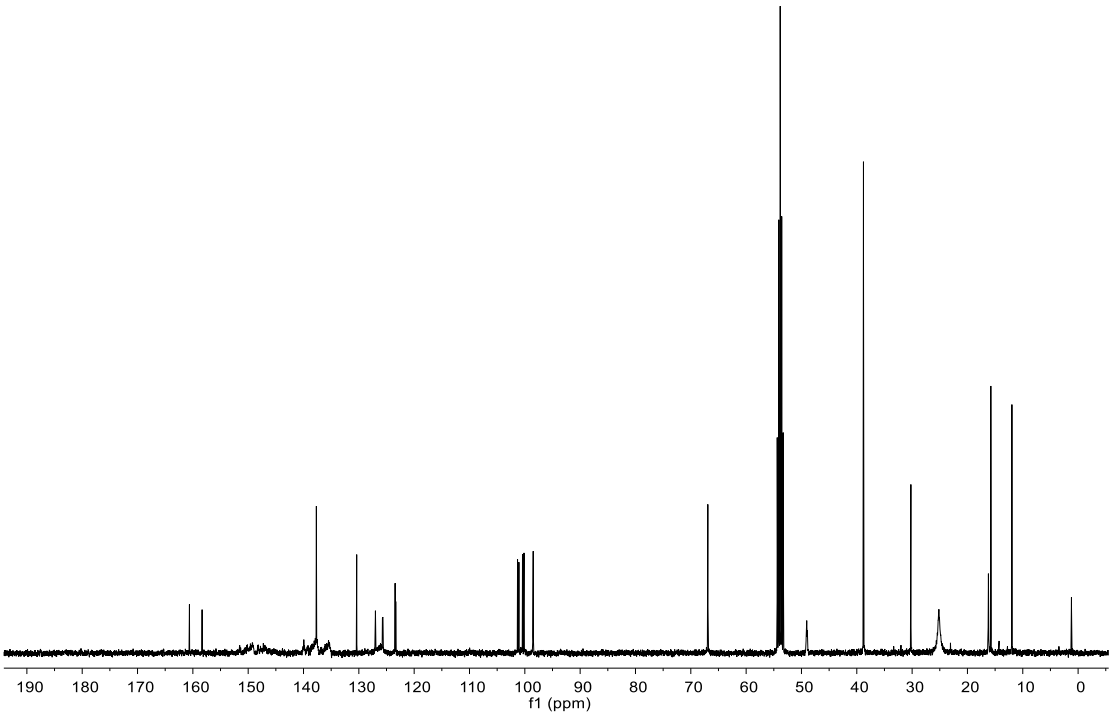


Fig. S45 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3e**.

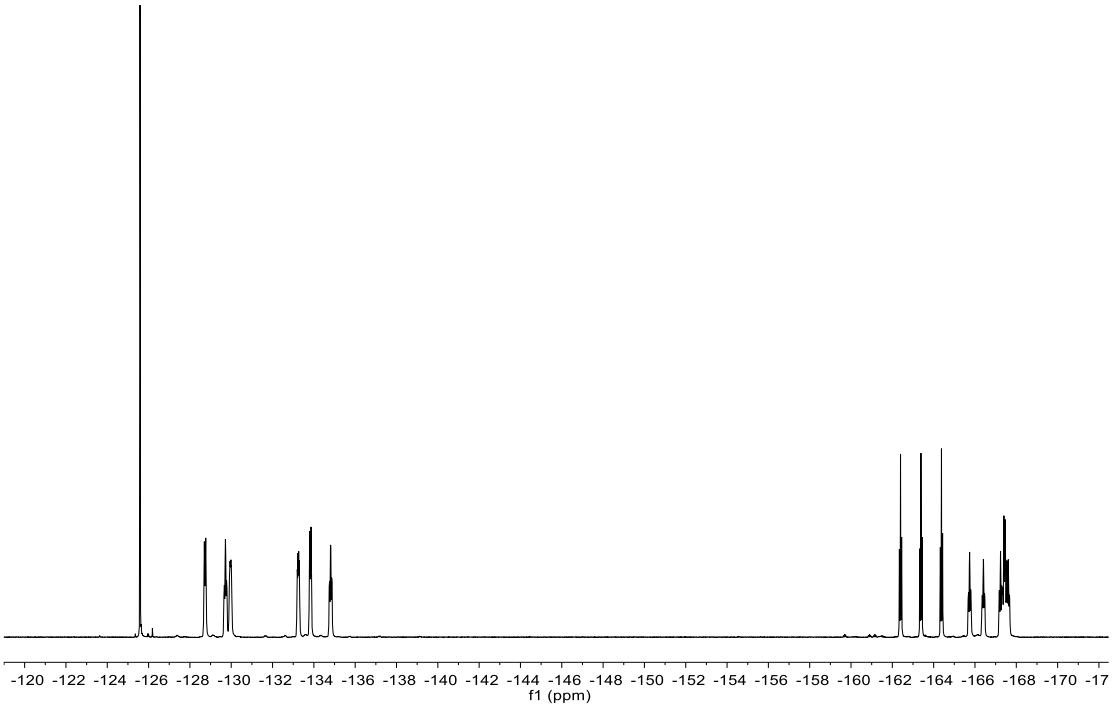


Fig. S46 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3e**.

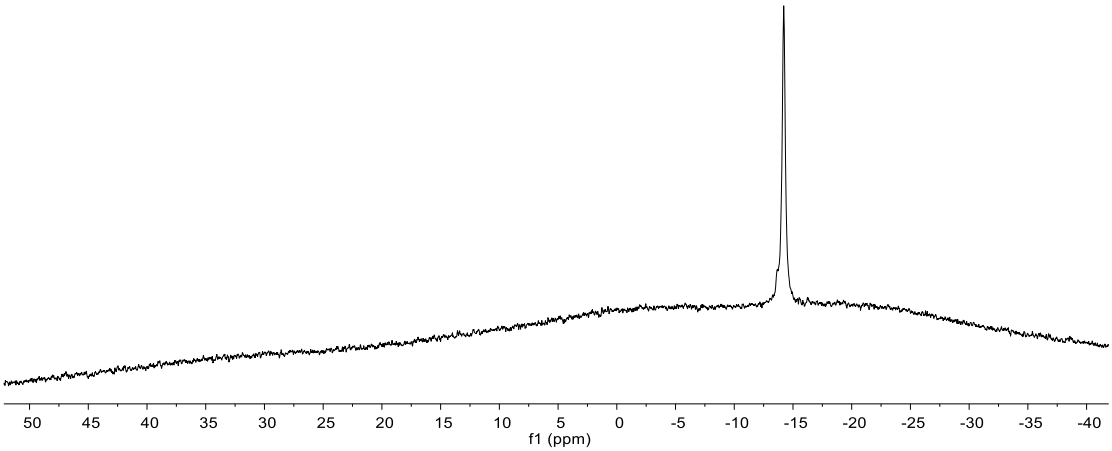
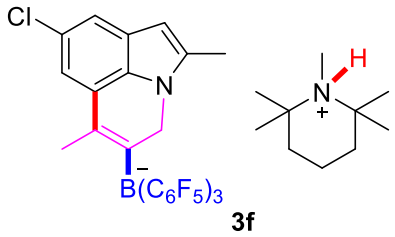


Fig. S47 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum ofcompound **3e**.

Synthesis and characterization of compound 3f



3f

According to the General Procedure II (for **3**) from **2f** (146.0 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3f** was isolated as a white solid (146.9 mg, 83% yield).

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.08 (s, 1H), 6.61 (s, 1H), 6.02 (s, 1H), 5.01 (d, $^2J_{HH}$ = 18.0 Hz, 1H), 4.84 (d, $^2J_{HH}$ = 18.0 Hz, 1H), 3.76 (br, 1H), 2.50 (s, 3H), 2.19 (s, 3H), 1.79 (s, 3H), 1.57 (s, 6H), 1.20 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, CD_2Cl_2): δ = 137.7, 132.2, 126.8, 126.8, 126.2, 125.9, 125.5, 124.8, 116.2, 112.0, 98.1, 67.2, 49.0, 38.8, 30.3, 25.2, 16.2, 15.7, 11.9. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.2 ($\nu_{1/2}$ ~ 49 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2): δ = -128.8, -129.8, -130.0, -133.2, -133.9, -134.9 (each m, each 1F, *o*-C_6F_5); =162.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -163.4 (t, $^3J_{FF}$ = 20.5 Hz, 1F), -164.4 (t, $^3J_{FF}$ = 20.5 Hz, 1F) (*p*-C_6F_5); -165.7 (m, 1F), -166.4 (m, 1F), -167.2 (m, 1F), -167.5 (m, 3F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{41}H_{33}BClF_{15}N_2$: 728.0439 $[M]^-$; found: 728.0439.

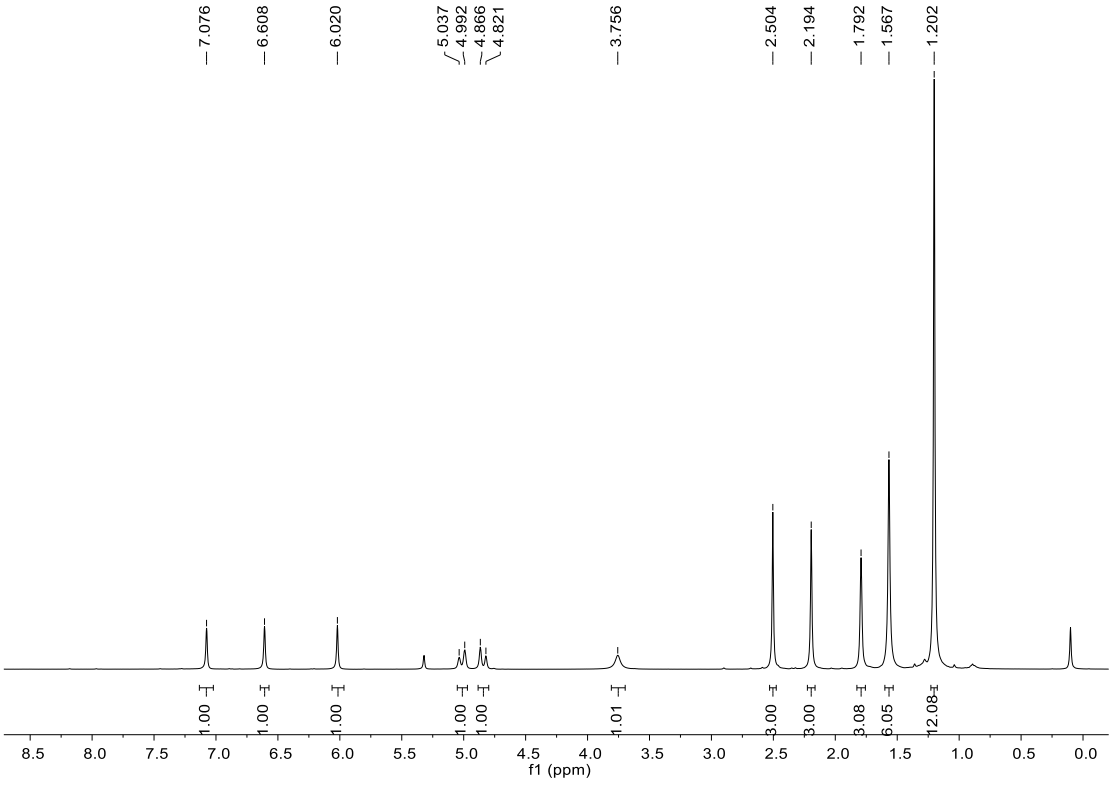


Fig. S48 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3f**.

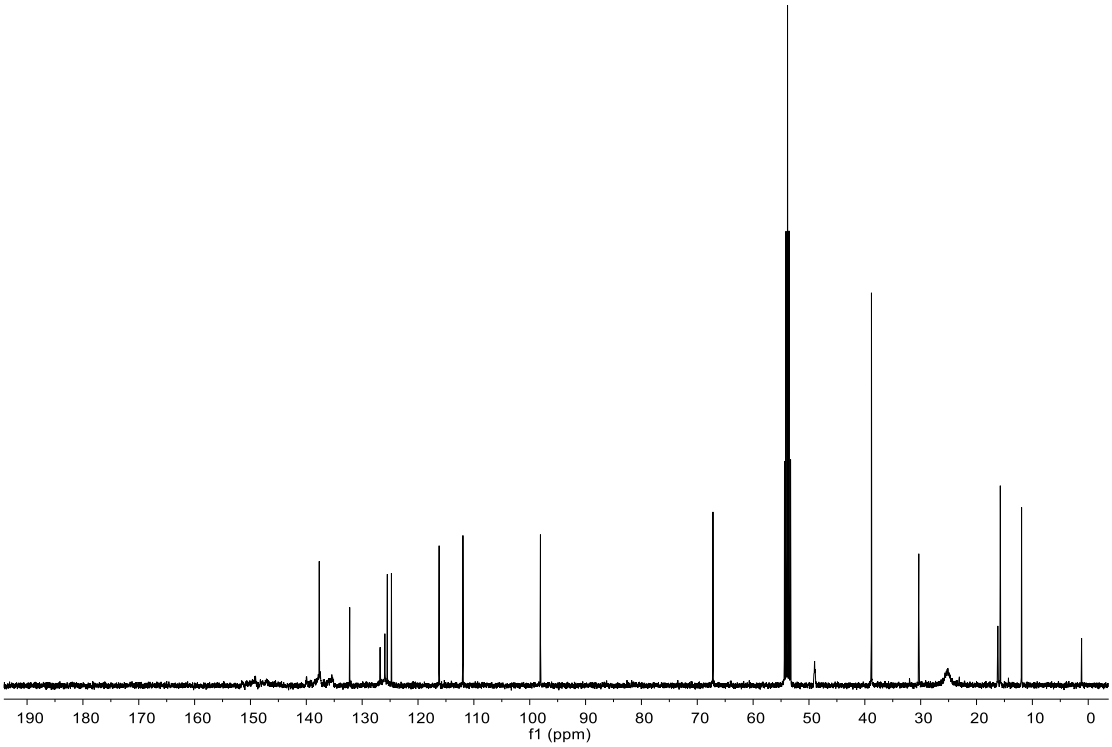


Fig. S49 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3f**.

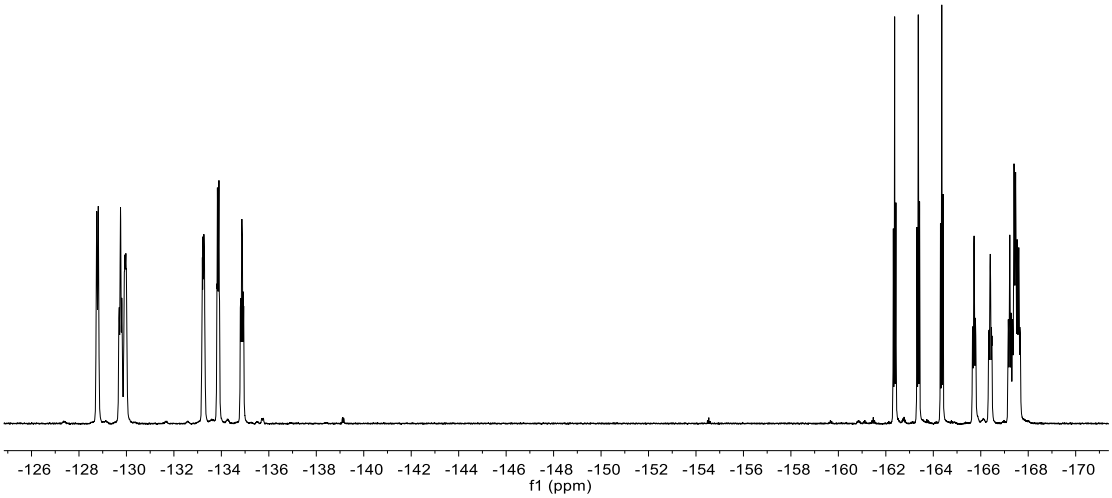


Fig. S50 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3f**.

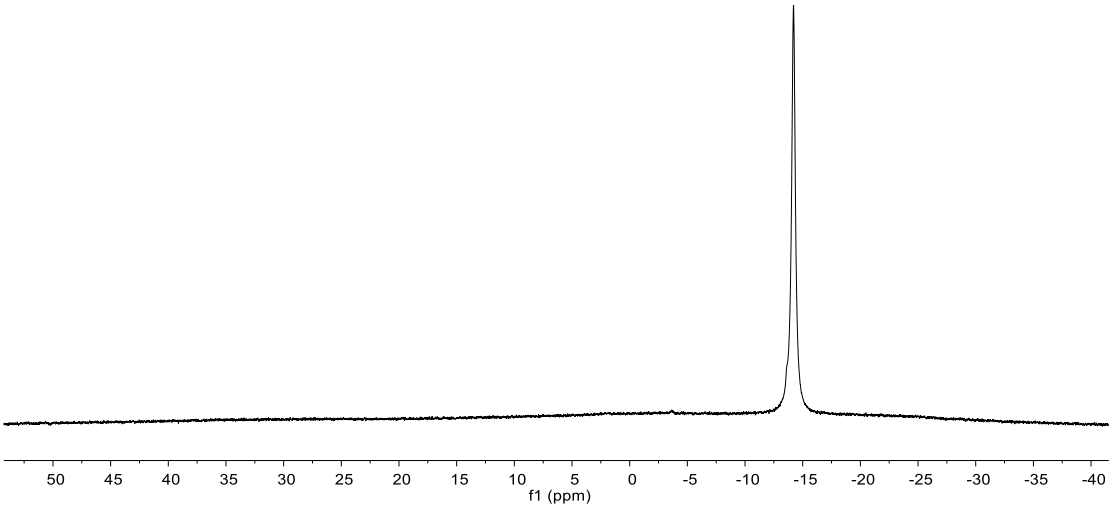
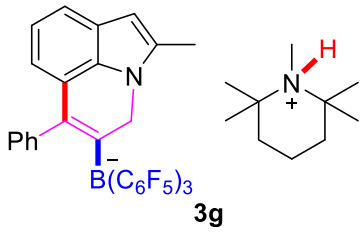


Fig. S51 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **3f**.

Synthesis and characterization of compound 3g



3g

According to the General Procedure II (for **3**) from **2g** (151.5 mg, 0.2 mmol) and PMP (31.1 mg, 0.2 mmol). The product **3g** was isolated as a white solid (153.3 mg, 84% yield).

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.19-6.95 (m, 6H), 6.60 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 6.52 (br, 1H), 6.08 (s, 1H), 5.71 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 4.77 (br, 1H), 3.65 (br, 1H), 2.42 (s, 3H), 2.25 (s, 3H), 1.70-1.35 (m, 6H), 1.16 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, CD_2Cl_2): δ = 140.8, 136.7, 134.0, 133.5, 130.3, 127.1, 126.5, 125.7, 124.2, 120.0, 117.2, 114.9, 98.5, 67.2, 49.5, 38.7, 30.7, 30.4, 19.9, 15.8, 11.9. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -14.2 ($\nu_{1/2}$ ~ 42 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2): δ = -126.0 (br, 1F), -129.6 (m, 1F), -130.2 (br, 1F), -130.6 (br, 1F), -132.2 (m, 2F) (*o*-C_6F_5); -162.8 (t, $^3J_{FF}$ = 19.6 Hz, 1F), -164.2 (m, 2F) (*p*-C_6F_5); -166.5 (m, 1F), -167.0 (m, 1F), -167.2 (br, 1F), -168.4 (m, 3F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{46}H_{36}BF_{15}N_2$: 756.0985 $[M]^-$; found: 756.0982.

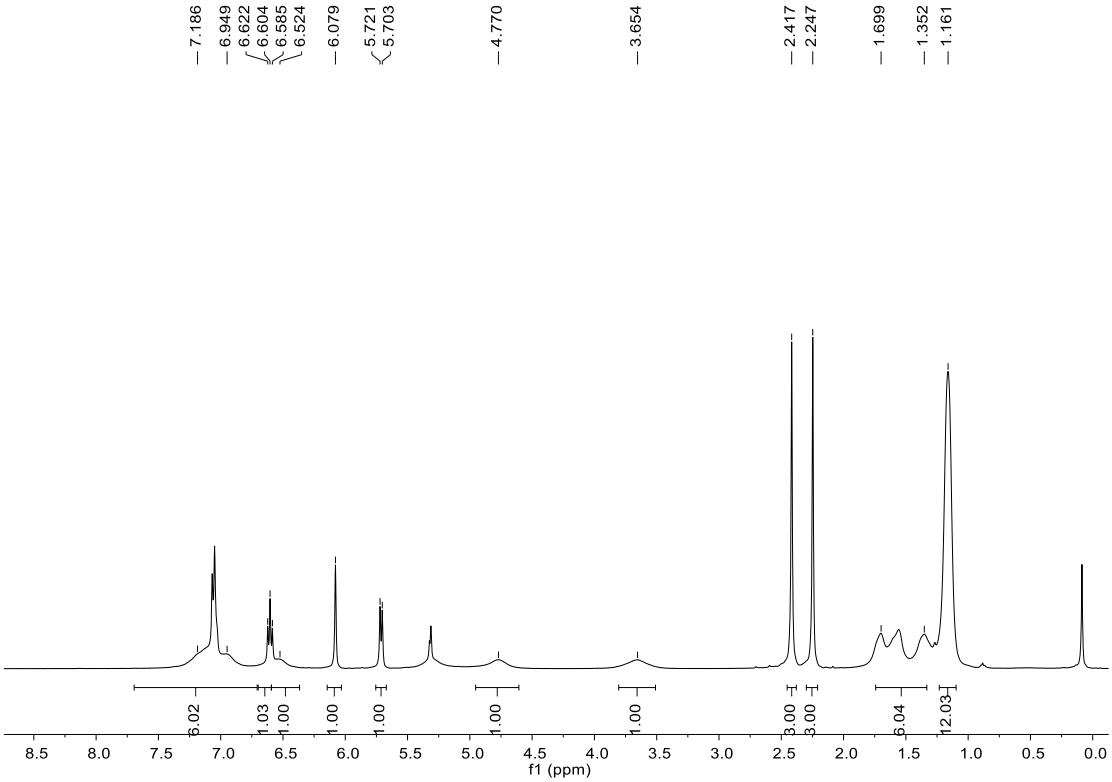


Fig. S52 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **3g**.

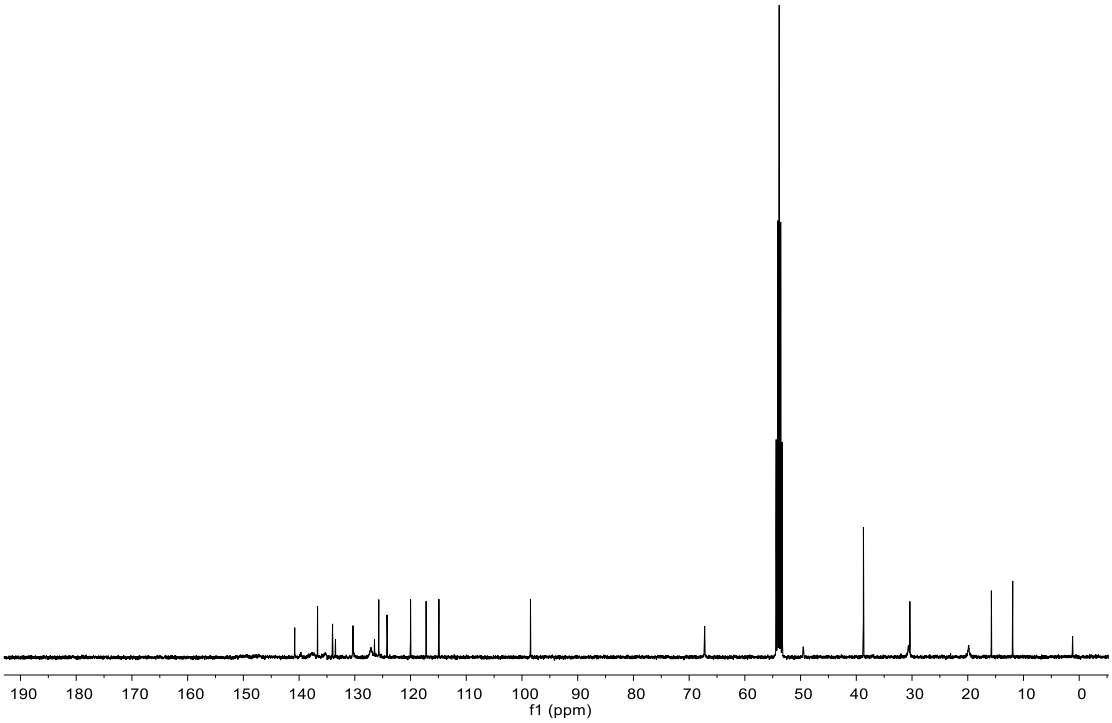


Fig. S53 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **3g**.

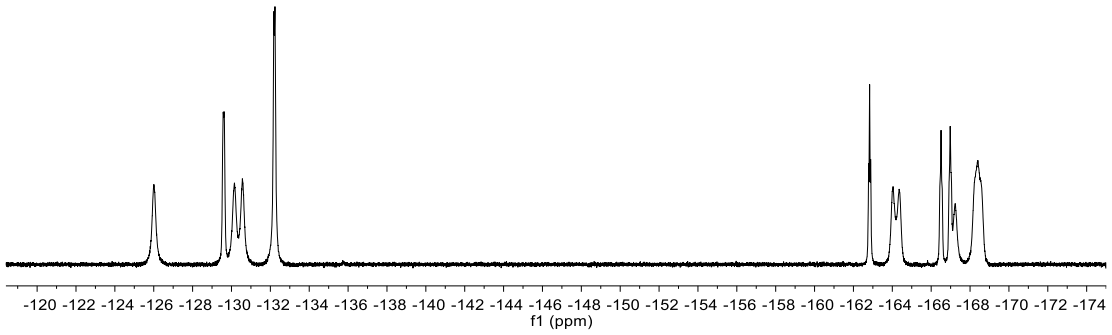


Fig. S54 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **3g**.

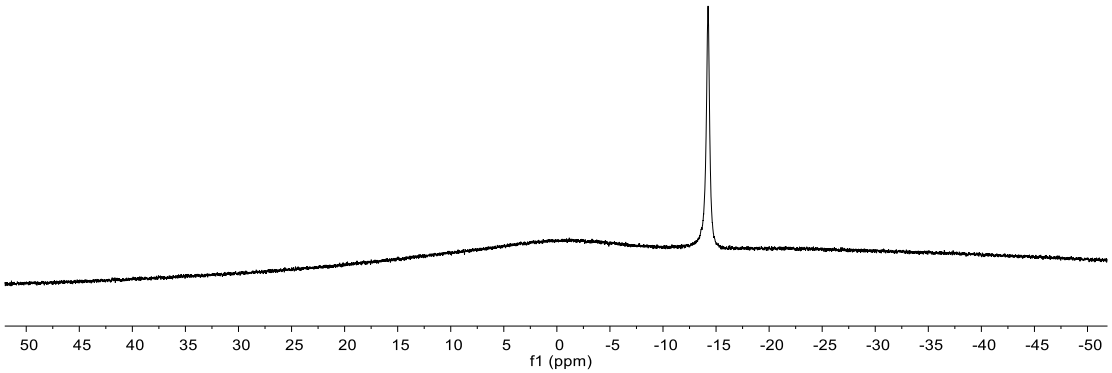
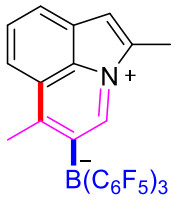


Fig. S55 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **3g**.

Synthesis and characterization of compound 4a



4a

According to the General Procedure II (for **4**) from **3a** (170.4 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4a** was isolated as a yellow solid (116.5mg, 84% yield).

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **4a** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 8.91 (s, 1H), 8.45 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 8.27 (d, $^3J_{HH}$ = 5.8 Hz, 1H), 7.95 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.23 (s, 1H), 3.04 (s, 3H), 2.72 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, 299K, THF-d_8): δ = 168.5, 142.7, 141.6, 132.4, 131.6, 131.3, 131.1, 126.6, 126.3, 123.9, 116.7, 19.1, 10.6. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 24 Hz).

$^{19}F\{^1H\}$ NMR (377 MHz, 299 K, THF-d_8): δ = -127.5, -128.9, -131.7, -132.6, -133.4, -134.5 (each m, each 1F, *o*-C_6F_5); -161.0 (t, $^3J_{FF}$ = 20.1 Hz, 1F), -162.3 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -162.5 (t, $^3J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5); -164.7 (m, 1F), -166.0 (m, 1F), -166.6 (m, 1F), -166.9 (m, 2F), -167.3 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{31}H_{11}BF_{15}N$-H^+: 692.0672 $[M-H]^-$; found: 692.0681.

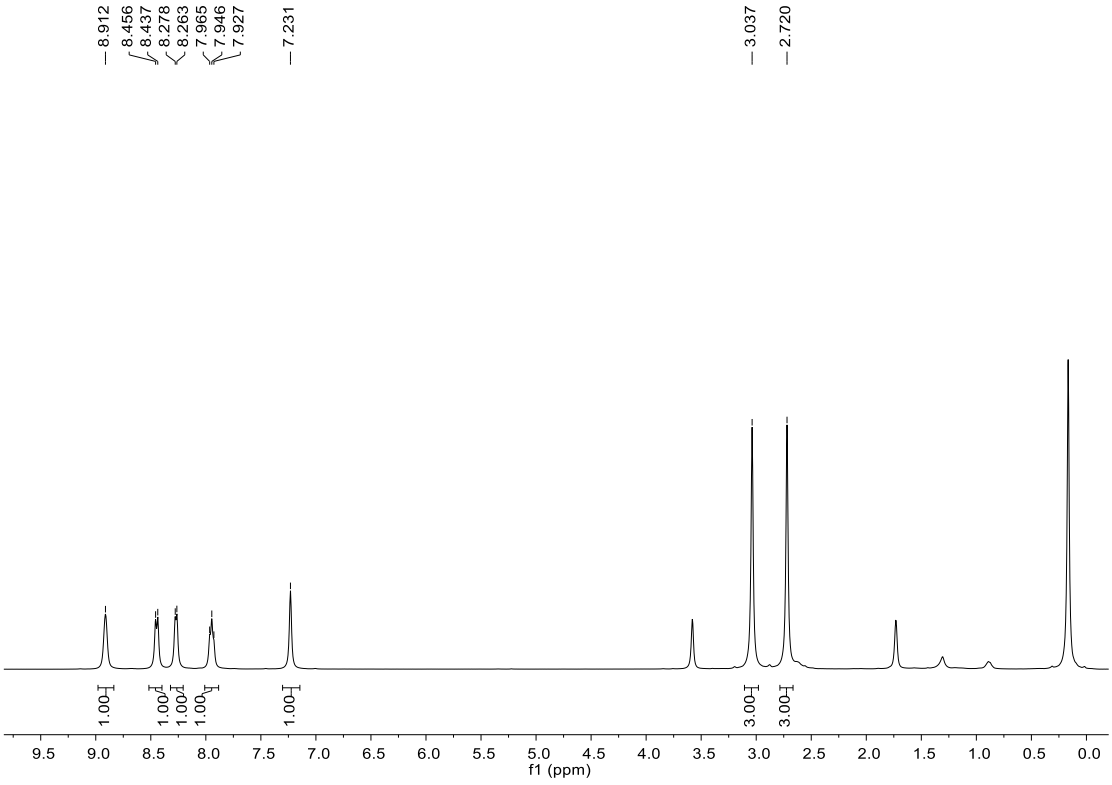


Fig. S56 ^1H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4a**.

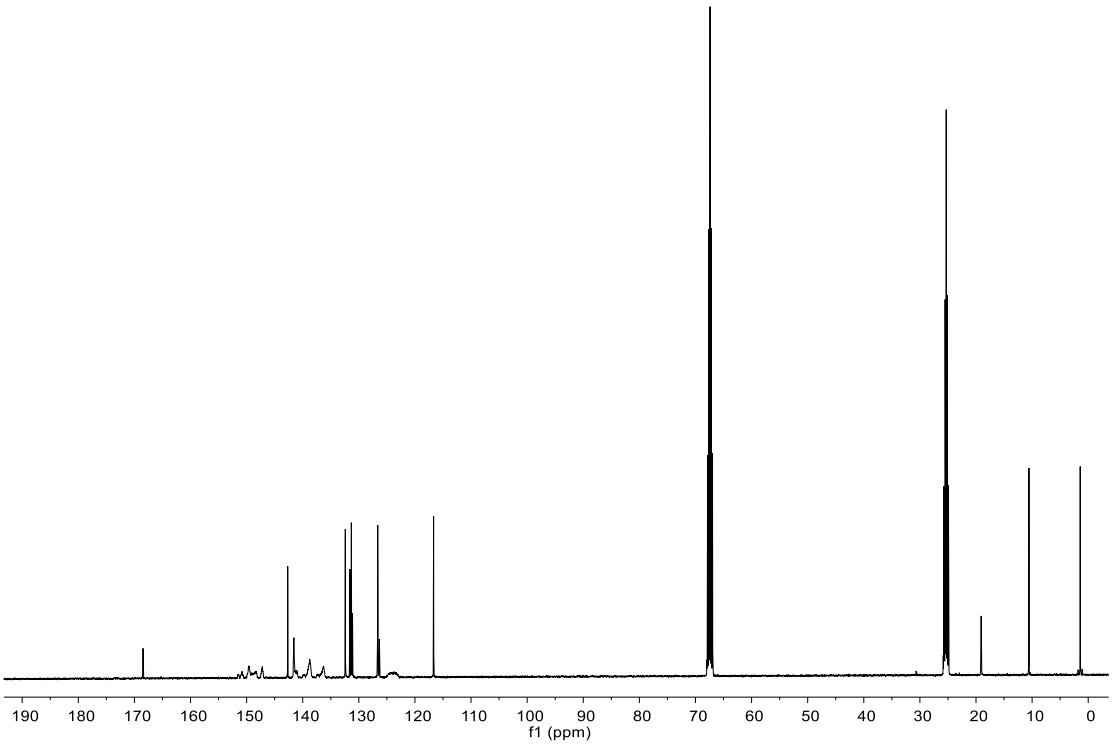


Fig. S57 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4a**.

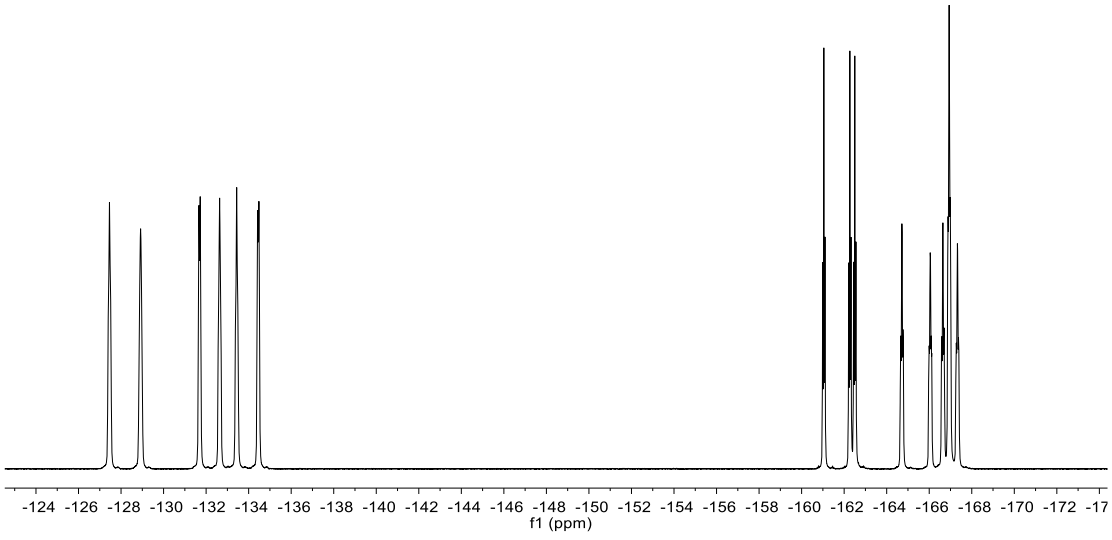


Fig. S58 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4a**.

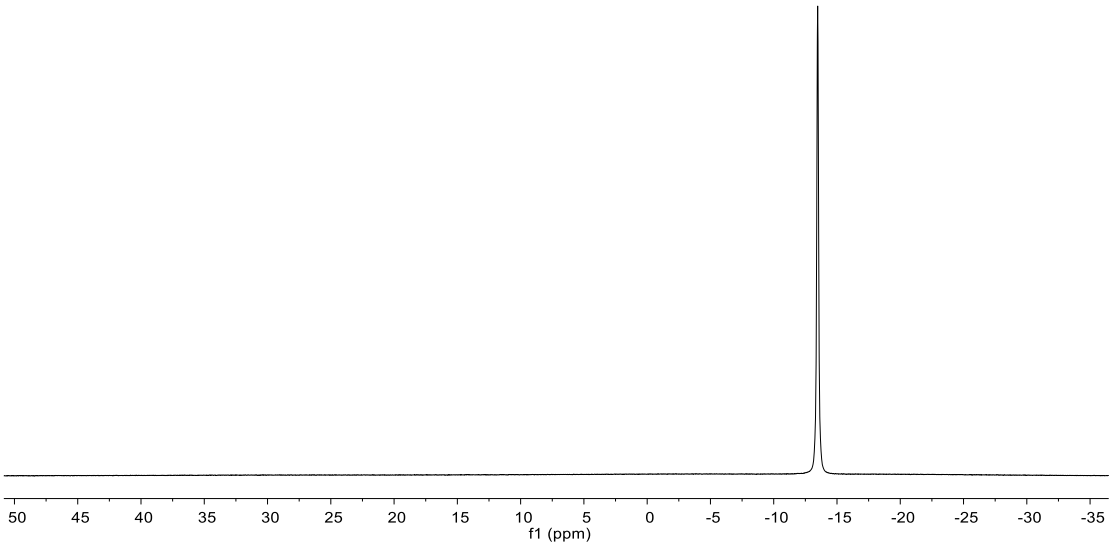


Fig. S59 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4a**.

X-ray crystal structure analysis of compound 4a·0.5CH_2Cl_2: formula $C_{31.5}H_{12}BClF_{15}N$, M = 735.706, yellow crystal, 0.53 × 0.65 × 0.43 mm, a = 20.3655(6), b = 13.5543(6), c = 20.8012(8) Å, α = γ = 90º, β = 93.360(2)º, V = 5732.1(4) Å^3, ρ_{calc} = 1.705 gcm^{-3}, μ = 0.258 mm^{-1}, empirical absorption correction (0.4857 ≤ T ≤ 0.5629), Z = 8, monoclinic, space group *C2/c*, λ = 0.71073 Å, T = 190.0 K, ω and φ scans, 39948 reflections collected (±h, ±k, ±l), 5324 independent (R_{int} = 0.0876) and 3818 observed reflections [I>2σ(I)], 436 refined parameters, R = 0.0396, wR^2 = 0.1020, max. (min.) residual electron density 0.36 (-0.29) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

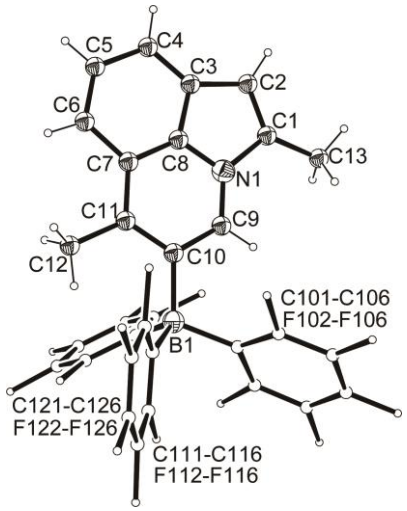
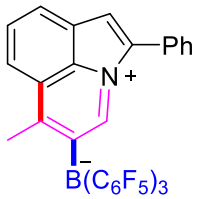


Fig. S60 A view of the molecular structure of compound **4a**.

Synthesis and characterization of compound 4b



4b

According to the General Procedure II (for **4**) from **3b** (182.8 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4b** was isolated as a yellow oil (134.4mg, 89% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 9.03 (s, 1H), 8.56 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 8.45 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 8.05 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.72-7.62 (m, 6H), 3.06 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 169.1, 145.3, 143.4, 133.3, 131.8, 131.5, 131.4, 131.2, 130.3, 130.2, 127.8, 127.5, 126.7, 123.9, 117.4, 19.1. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.6 ($\nu_{1/2}$ ~ 24 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -126.8, -128.8, -131.9, -132.2, -133.6, -134.6 (each m, each 1F, *o*-C_6F_5); -161.2 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F), -162.1 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -162.3 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5); -163.9 (m, 1F), -166.3 (m, 1F), -166.5 (m, 1F), -166.9 (m, 2F), -167.2 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{36}H_{13}BF_{15}N$-H^+: 754.0829 $[M-H]^-$; found: 754.0843.

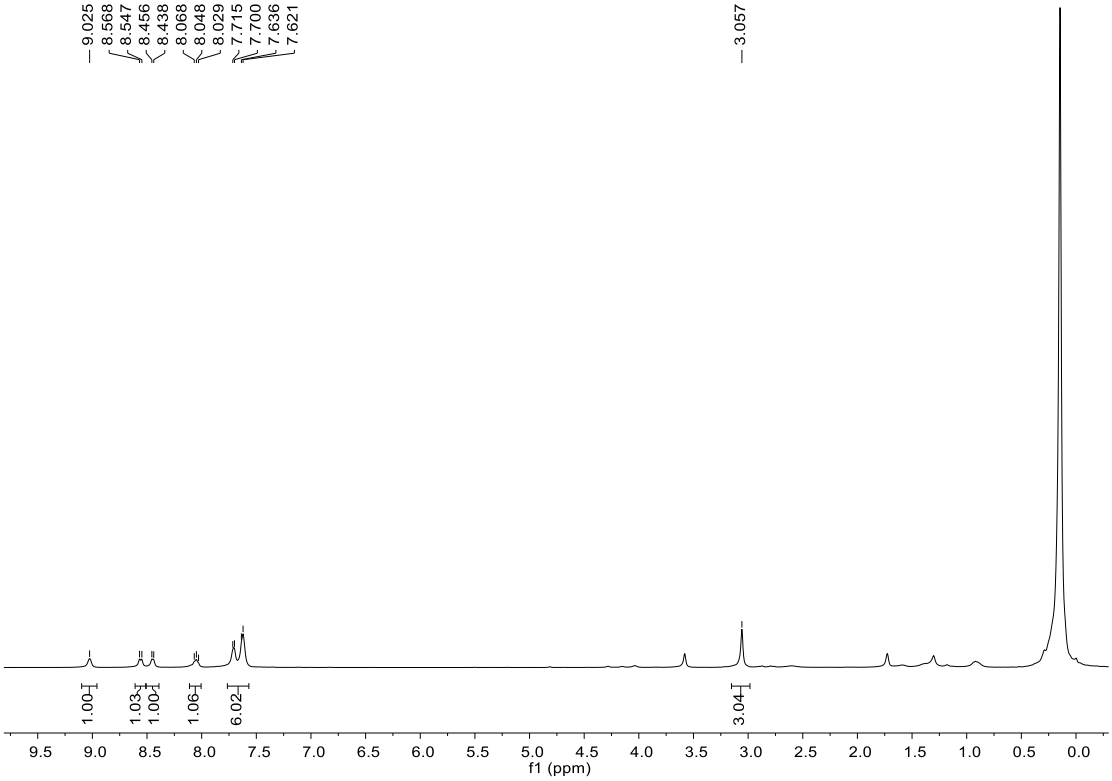


Fig. S61 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4b**.

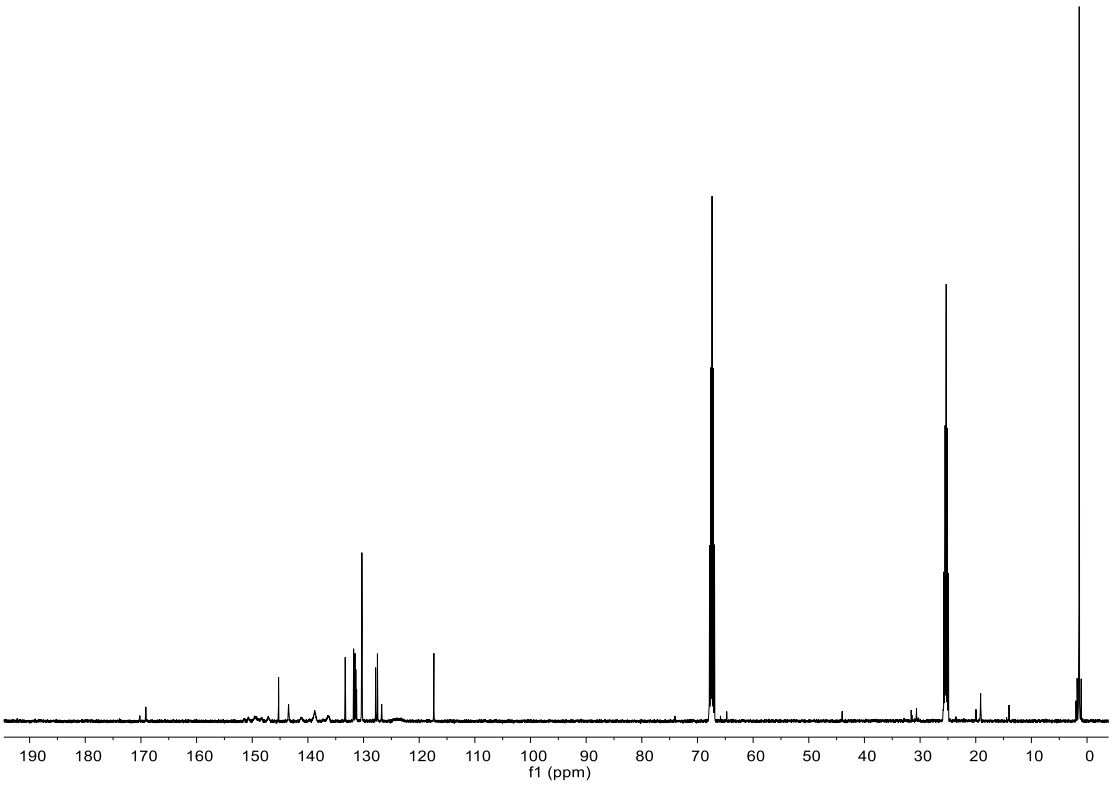


Fig. S62 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4b**.

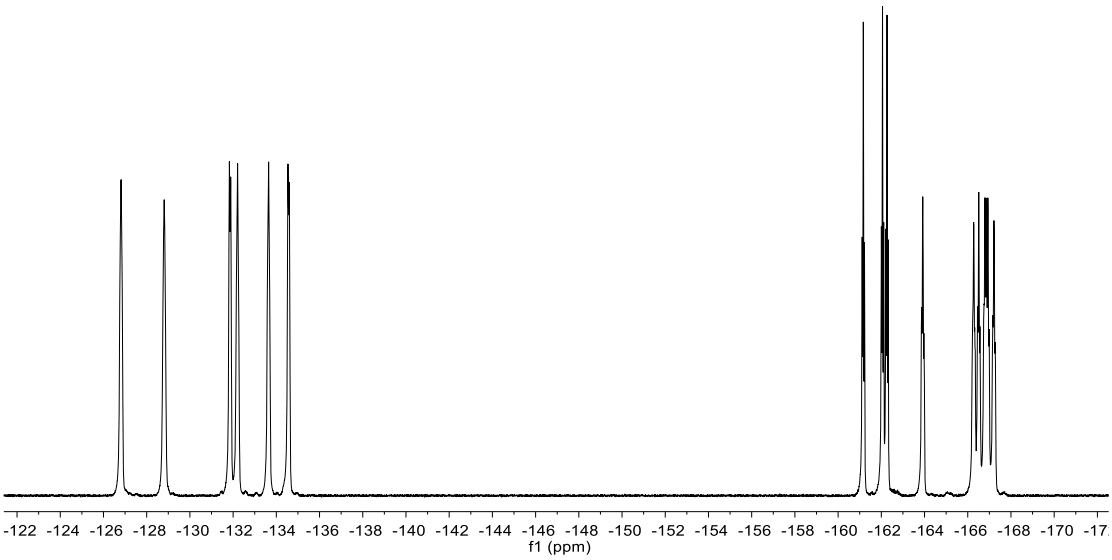


Fig. S63 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4b**.

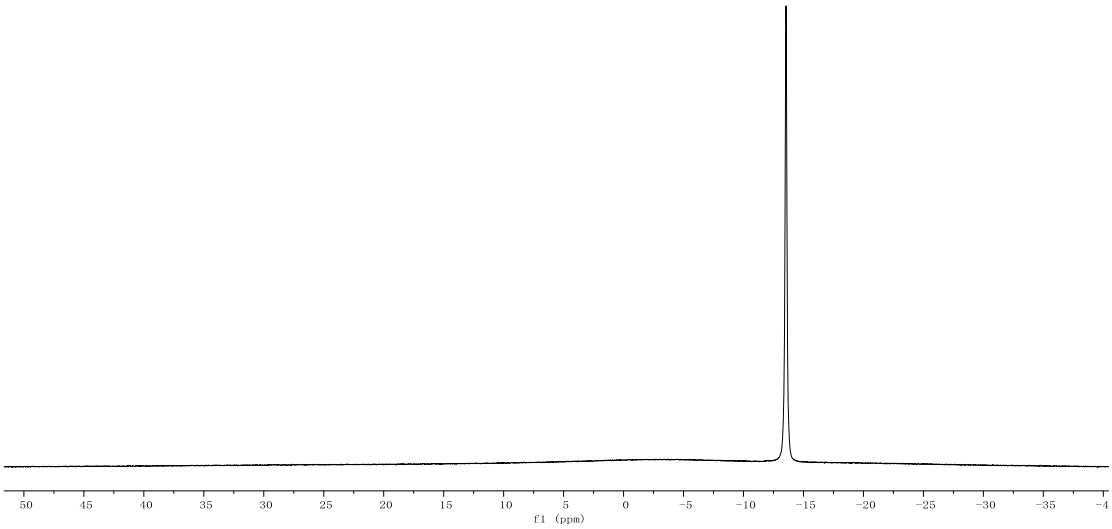
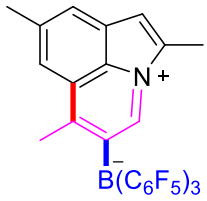


Fig. S64 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4b**.

Synthesis and characterization of compound 4c



4c

According to the General Procedure II (for **4**) from **3c** (173.2 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4c** was isolated as a yellow solid (130.1 mg, 92% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 8.83 (s, 1H), 8.22 (s, 1H), 8.13 (s, 1H), 7.18 (s, 1H), 2.99 (s, 3H), 2.70 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 167.4, 142.9, 142.4, 140.6, 134.4, 131.5, 129.9, 126.2, 125.3, 124.0, 116.5, 22.2, 19.0, 10.6. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 22 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -127.4, -128.9, -131.7, -132.7, -133.5, -134.5 (each m, each 1F, *o*-C_6F_5); -161.1 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -162.3 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F), -162.6 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5); -164.8 (m, 1F), -166.1 (m, 1F), -166.7 (m, 1F), -167.0 (m, 2F), -167.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{32}H_{13}BF_{15}N$-H^+: 706.0829 [M-H]$^-$; found: 706.0836.

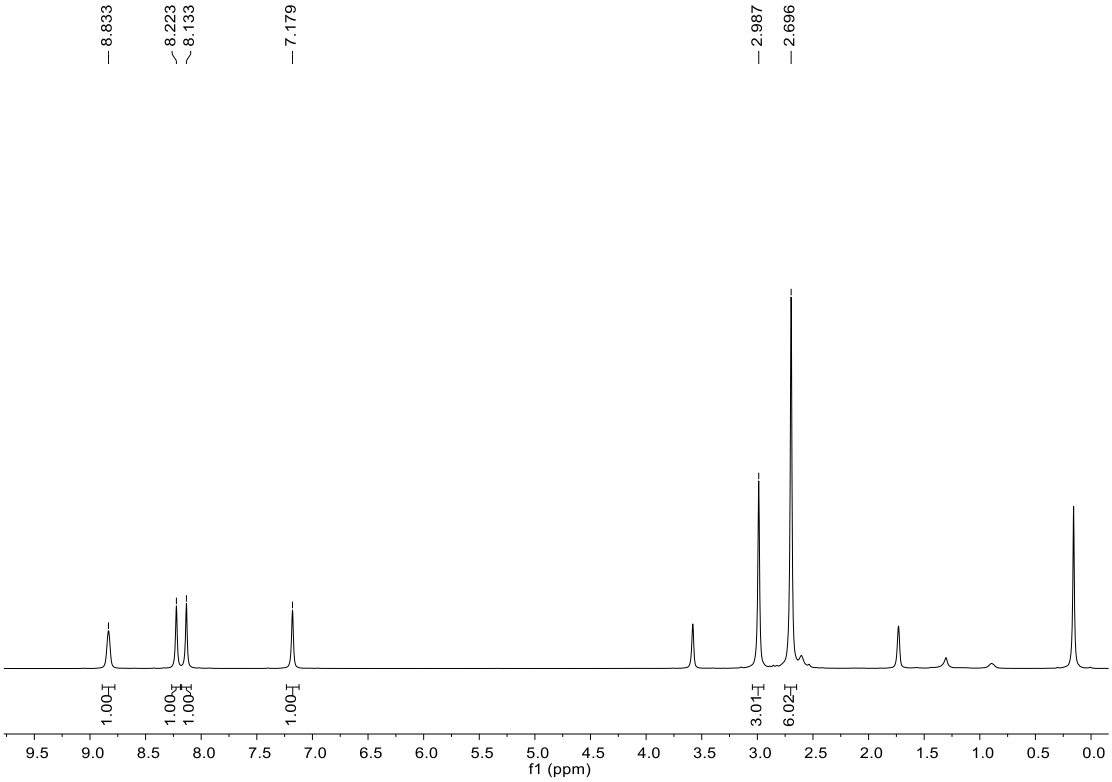


Fig. S65 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4c**.

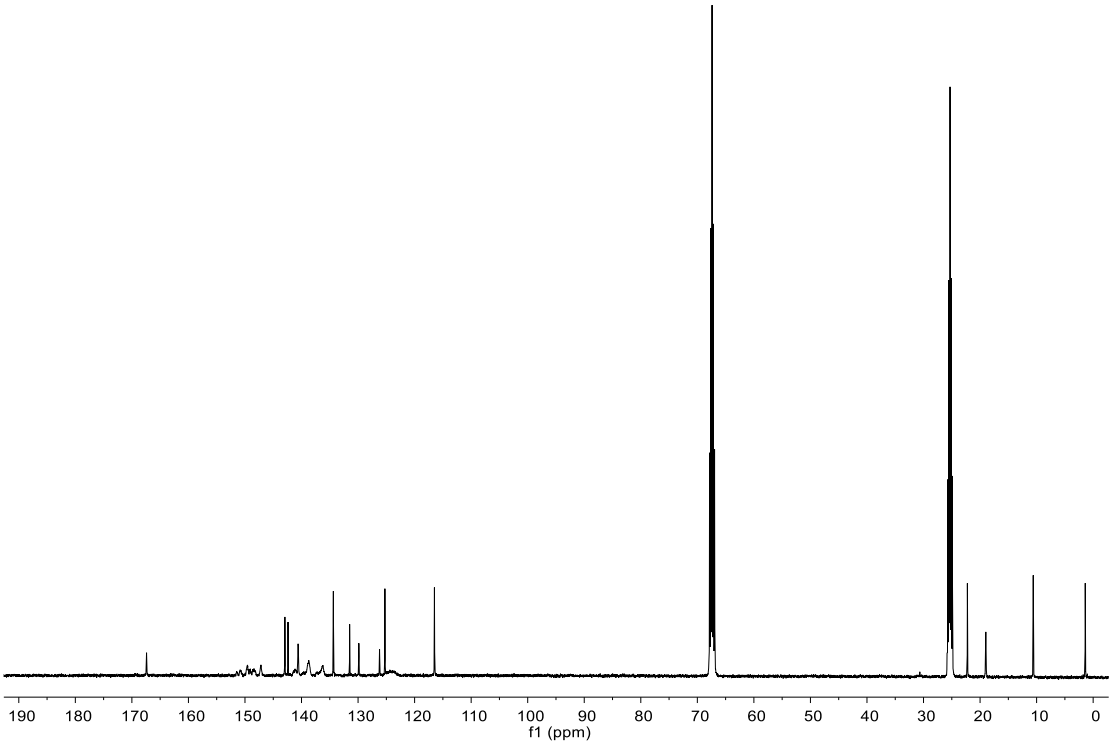


Fig. S66 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4c**.

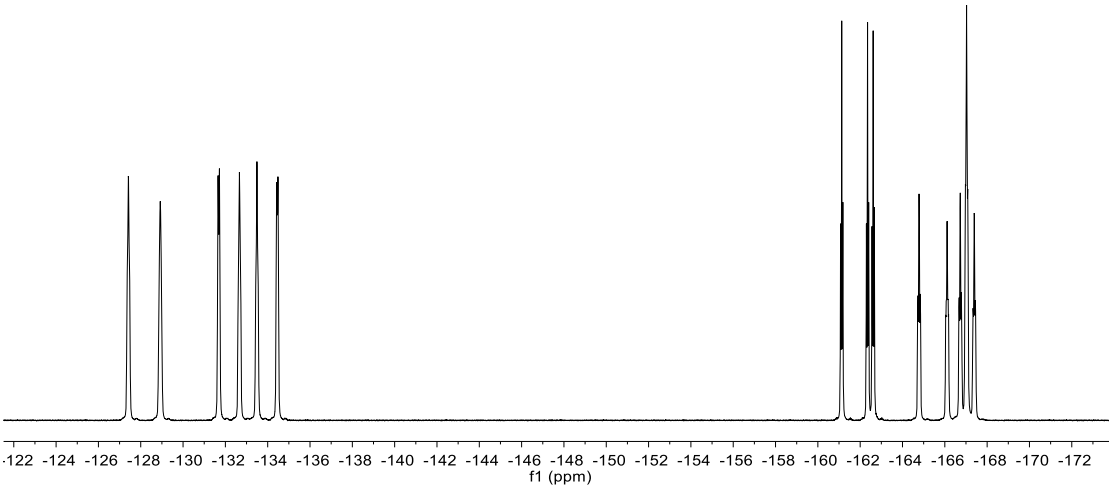


Fig. S67 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4c**.

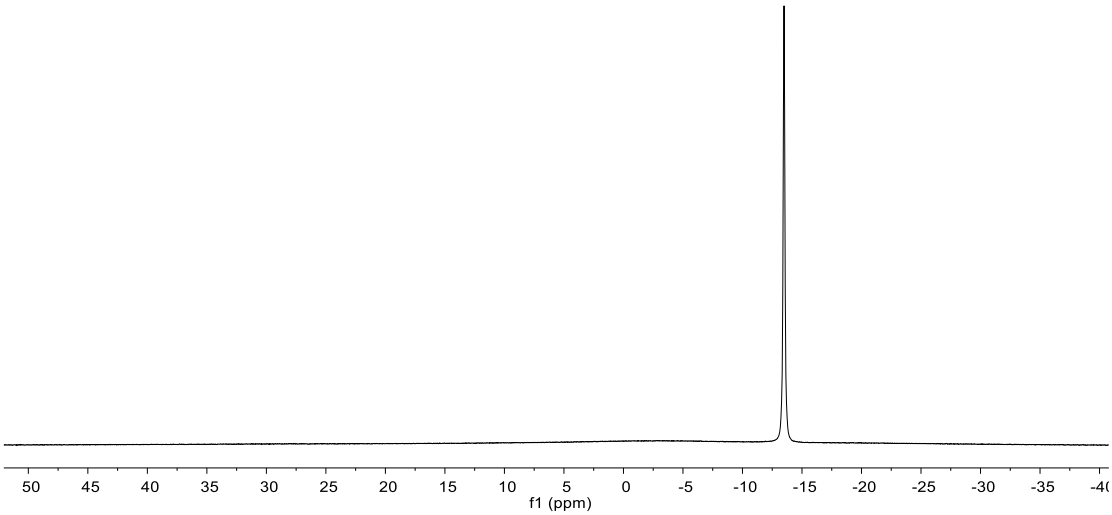
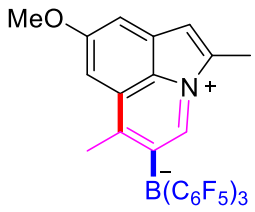


Fig. S68 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4c**.

Synthesis and characterization of compound 4d



4d

According to the General Procedure II (for **4**) from **3d** (176.4 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4d** was isolated as a yellow solid (123.0 mg, 85% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 8.75 (s, 1H), 7.91 (s, 1H), 7.61 (s, 1H), 7.15 (s, 1H), 4.05 (s, 3H), 2.96 (s, 3H), 2.69 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 165.9, 162.9, 144.2, 139.0, 132.7, 127.4, 127.1, 125.4, 124.1, 116.2, 103.4, 56.9, 19.0, 10.7. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 22 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -127.4, -128.9, -131.6, -132.7, -133.5, -134.4 (each m, each 1F, *o*-C_6F_5); -161.2 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F,), -162.3 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F), -162.7 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F) (*p*-C_6F_5); -164.8 (m, 1F), -166.2 (m, 1F), -166.8 (m, 1F), -167.1 (m, 2F), -167.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{32}H_{13}BF_{15}NO$-H^+: 722.0778 [M-H]$^-$; found: 722.0791.

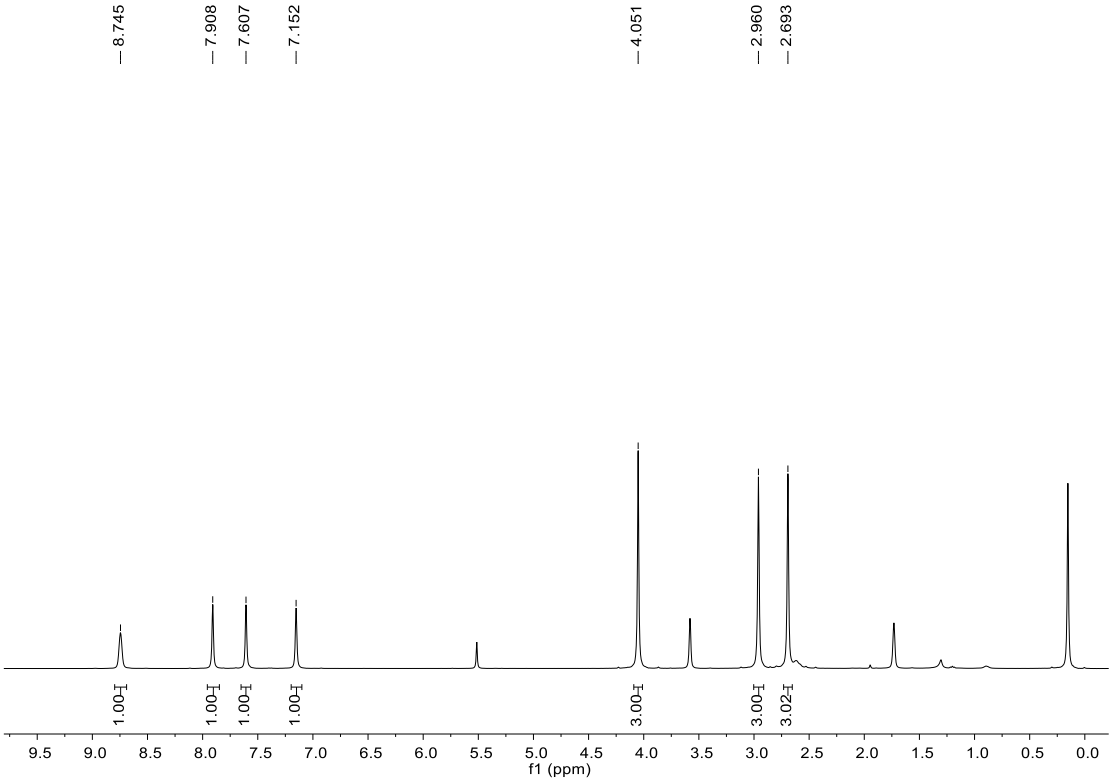


Fig. S69 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4d**.

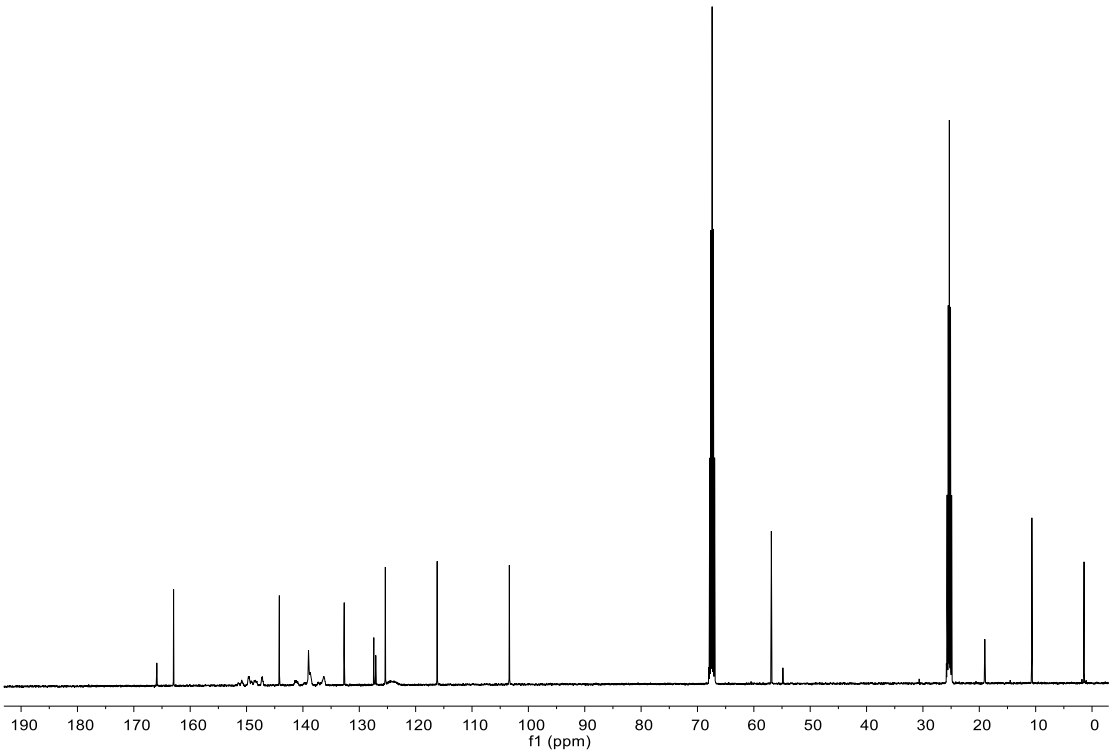


Fig. S70 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4d**.

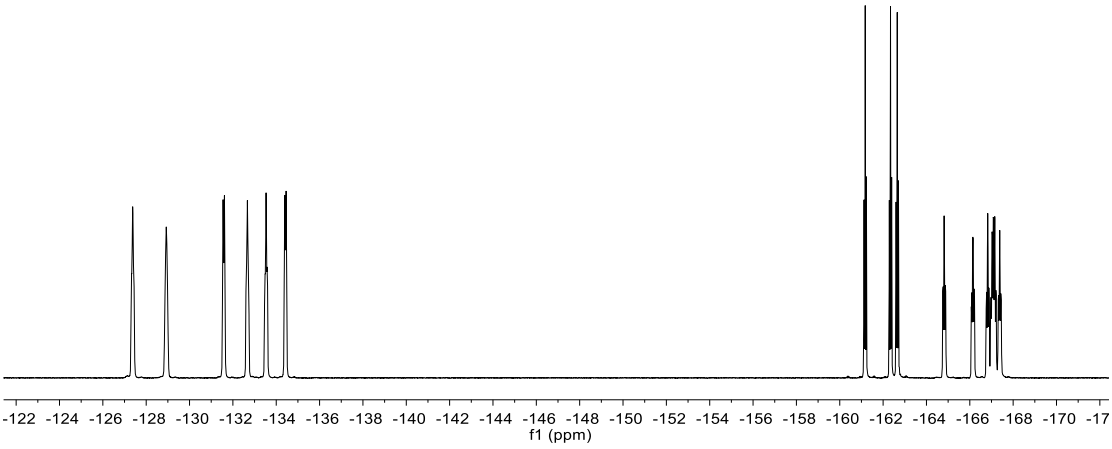


Fig. S71 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4d**.

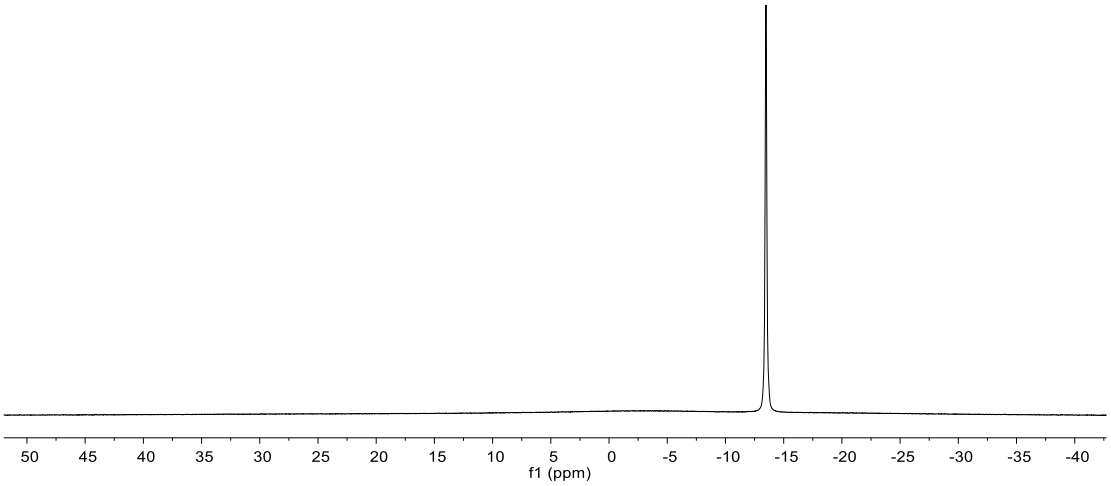
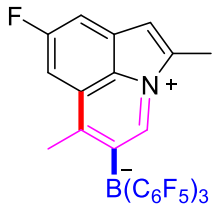


Fig. S72 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4d**.

Synthesis and characterization of compound 4e



4e

According to the General Procedure II (for **4**) from **3e** (173.9 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4e** was isolated as a yellow solid (125.2 mg, 88% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 8.91 (s, 1H), 8.21-8.15 (m, 2H), 7.25 (s, 1H), 4.05 (s, 3H), 3.01 (s, 3H), 2.75 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 168.5, 165.8, 163.3, 145.0, 141.8, 133.8 (d, $^3J_{FC}$ = 10.7 Hz), 128.3, 126.6 (d, $^3J_{FC}$ = 10.3 Hz), 123.9,

122.3 (d, $^{2}J_{FC}$ = 30.1 Hz), 116.3 (d, $^{4}J_{FC}$ = 2.8 Hz), 110.3 (d, $^{2}J_{FC}$ = 25.9 Hz), 19.3, 10.7. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 24 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -107.8 (s, 1F), -127.6, -128.9, -131.7, -132.7, -133.5, -134.4 (each m, each 1F, *o*-C_6F_5); -161.0 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -162.2 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -162.4 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5); -164.7 (m, 1F), -166.0 (m, 1F), -166.5 (m, 1F), -166.9 (m, 2F), -167.3 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{31}H_{10}BF_{16}N$-H^{+}: 710.0578 [M-H]$^{-}$; found: 710.0589.

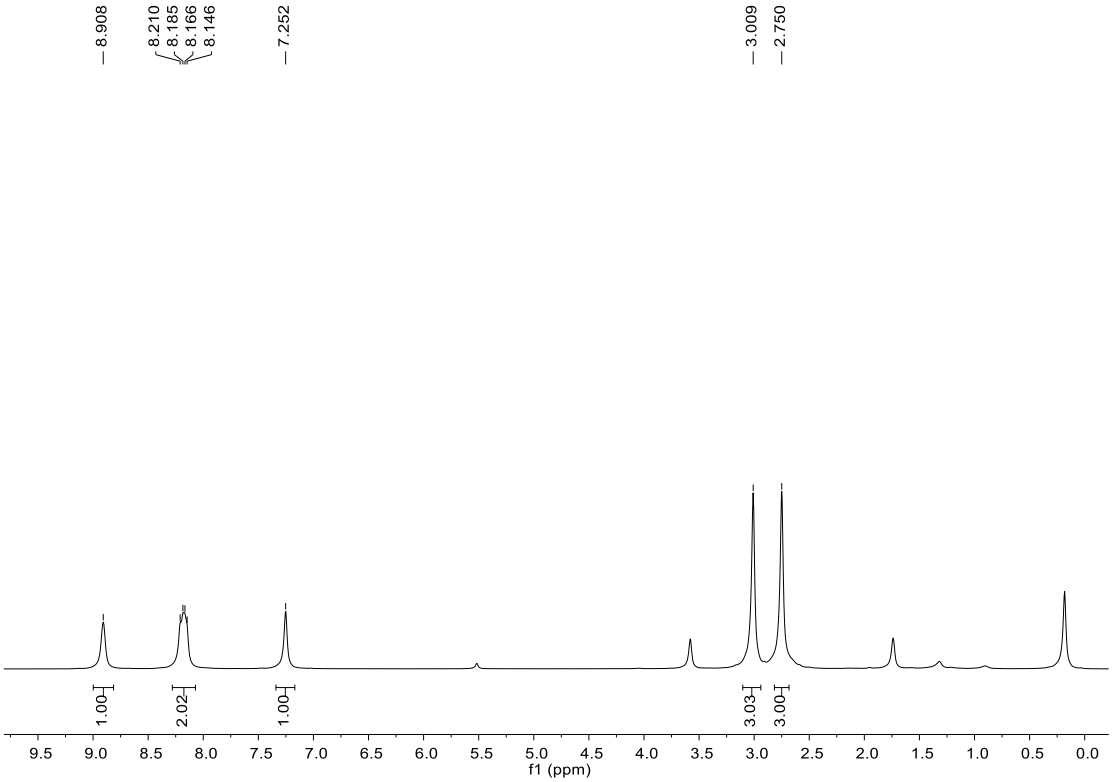


Fig. S73 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4e**.

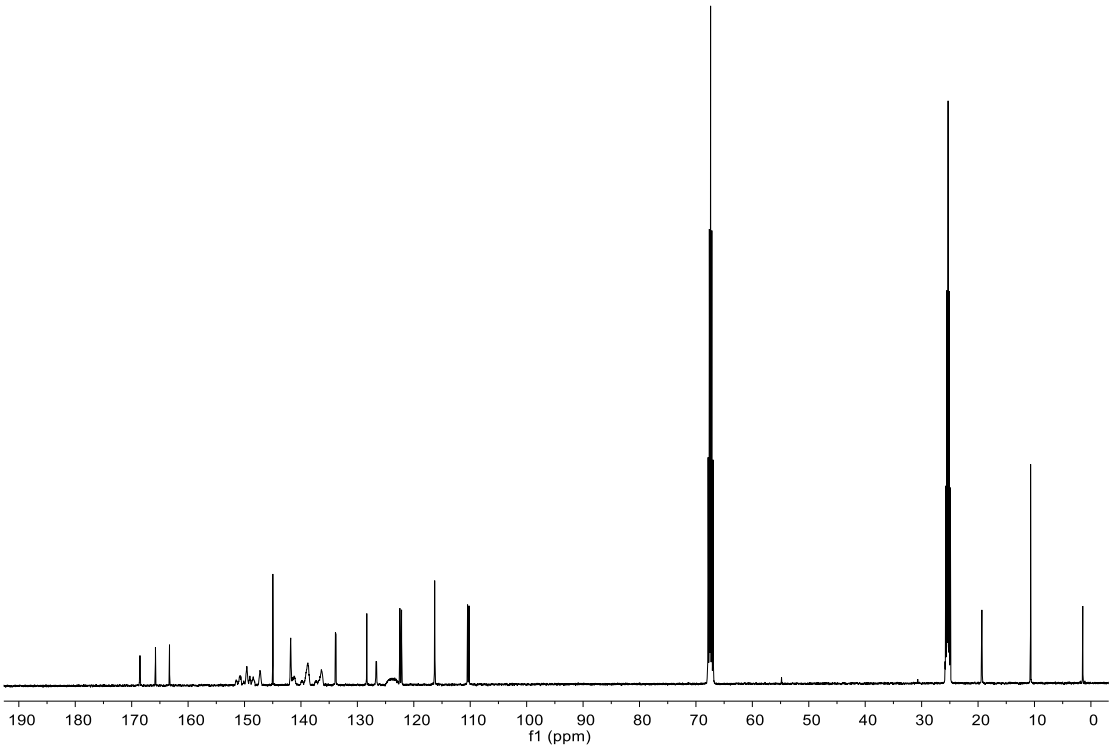


Fig. S74 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4e**.

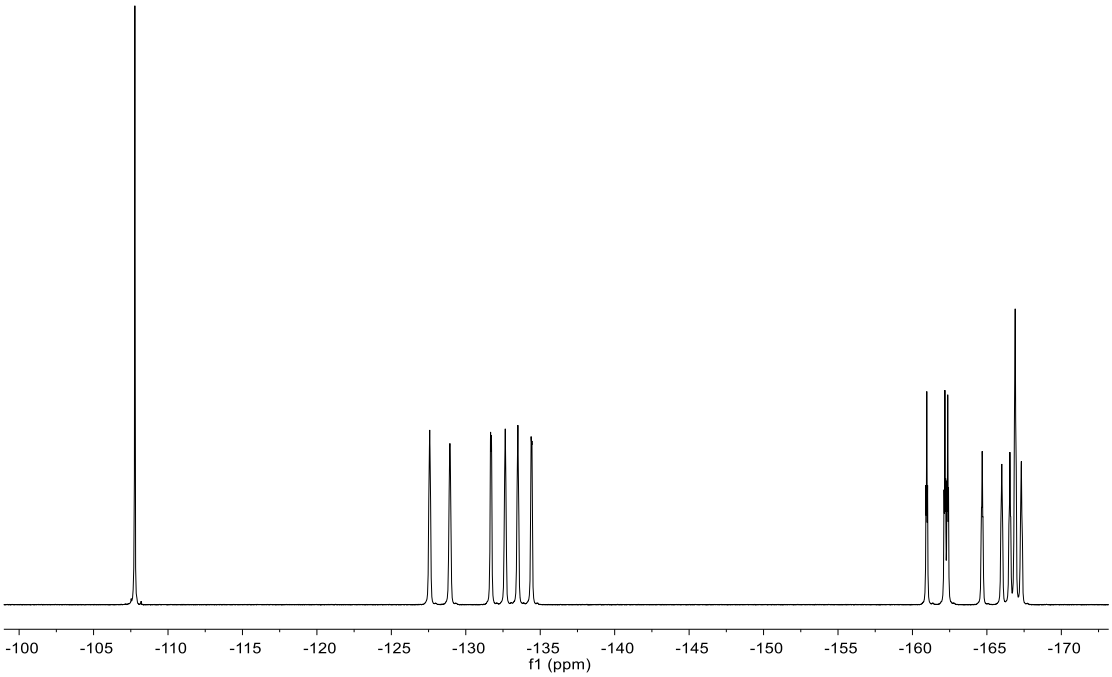


Fig. S75 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4e**.

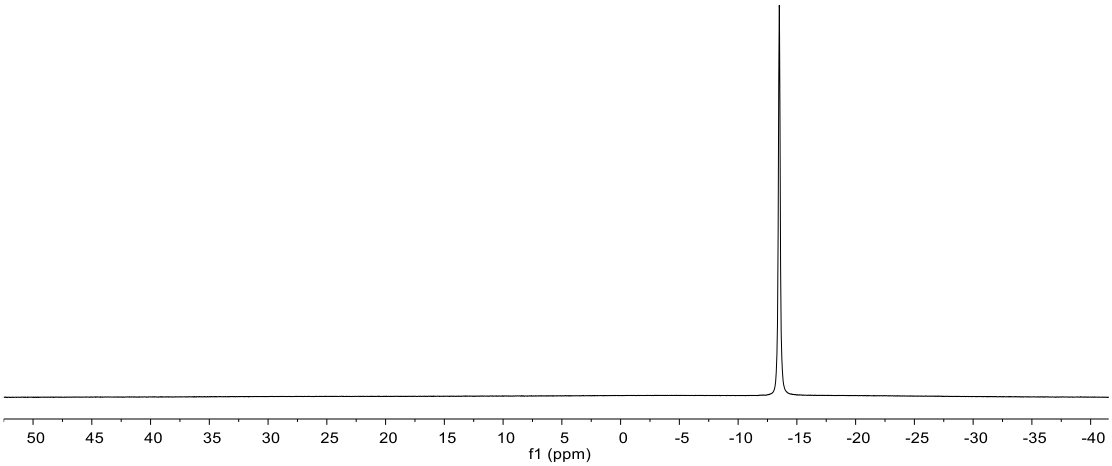
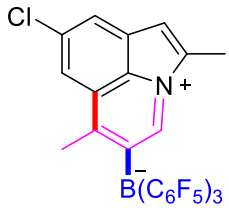


Fig. S76 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4e**.

Synthesis and characterization of compound 4f



4f

According to the General Procedure II (for **4**) from **3f** (177.2 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4f** was isolated as a yellow solid (133.9 mg, 92% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 8.85 (s, 1H), 8.50 (s, 1H), 8.27 (s, 1H), 7.21 (s, 1H), 2.97 (s, 3H), 2.69 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 168.3, 144.7, 142.1, 137.2, 133.3, 132.6, 129.9, 126.5, 125.4, 123.8, 116.1, 19.2, 10.6. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 22 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -127.6, -128.9, -131.8, -132.6, -133.5, -134.4 (each m, each 1F, *o*-C_6F_5); -160.9 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F), -162.1 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -162.3 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5); -164.6 (m, 1F), -166.0 (m, 1F), -166.5 (m, 1F), -166.9 (m, 2F), -167.3 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{31}H_{10}BClF_{15}N$-H^+: 726.0282 $[M-H]^-$; found: 726.0291.

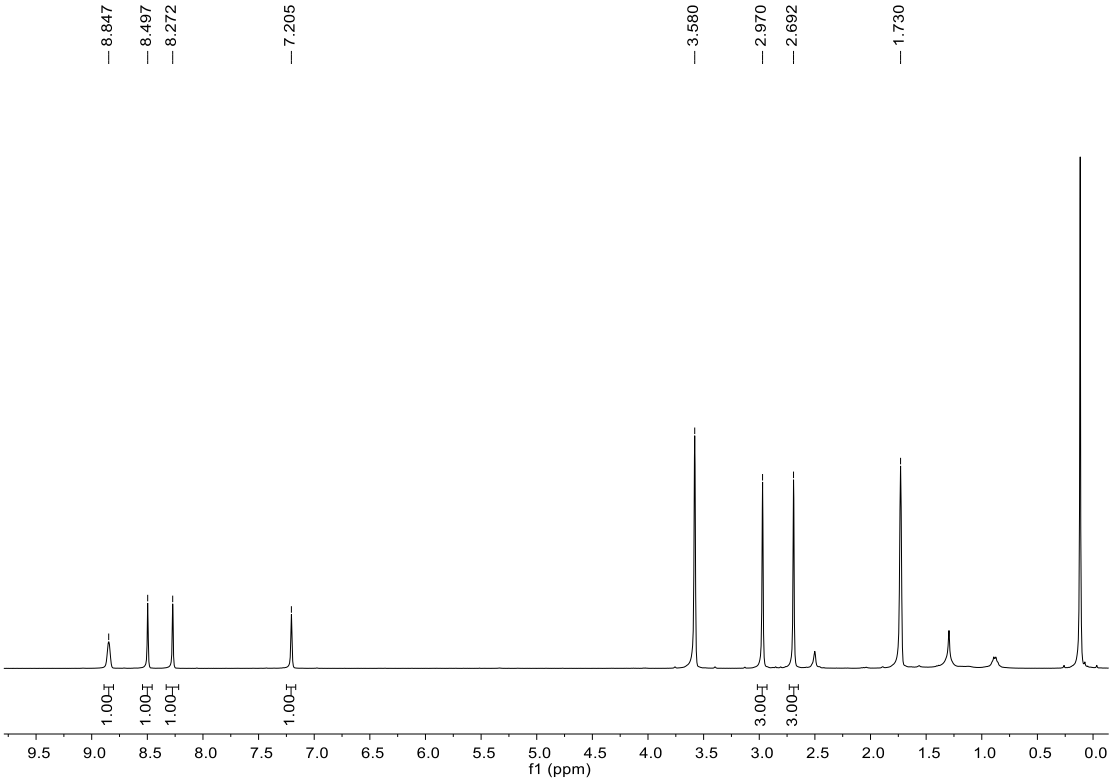


Fig. S77 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4f**.

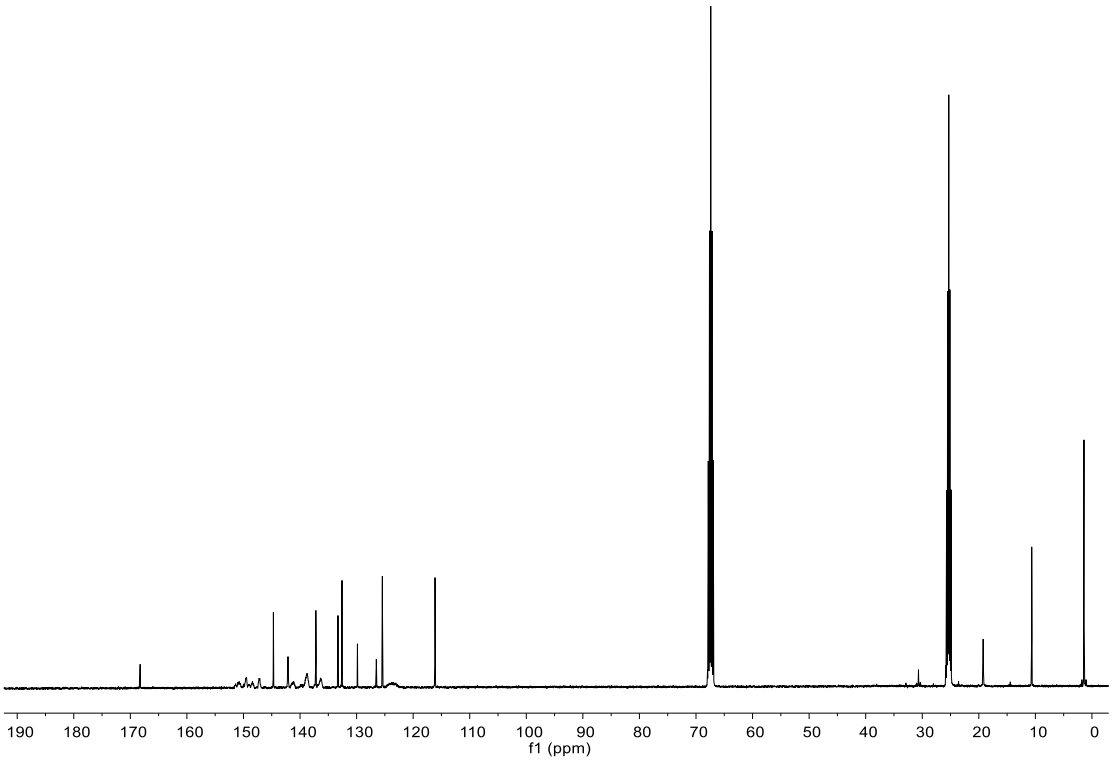


Fig. S78 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4f**.

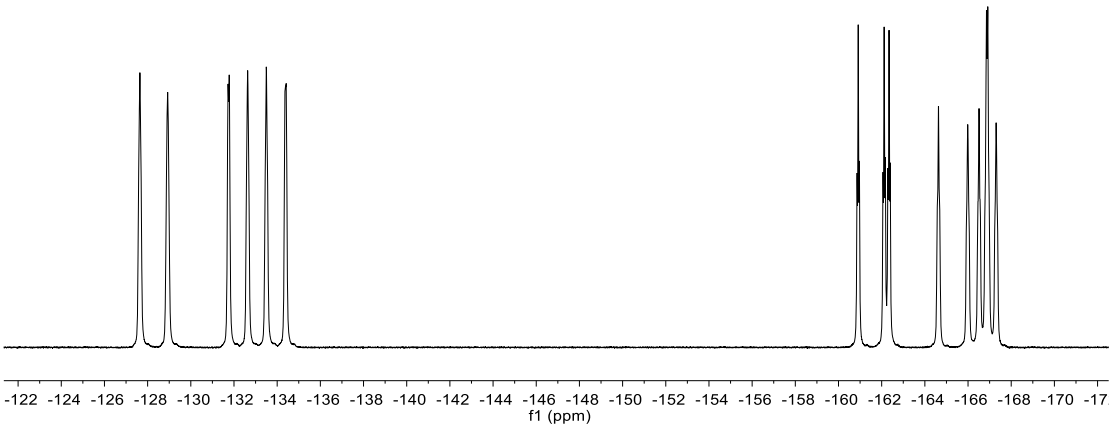


Fig. S79 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4f**.

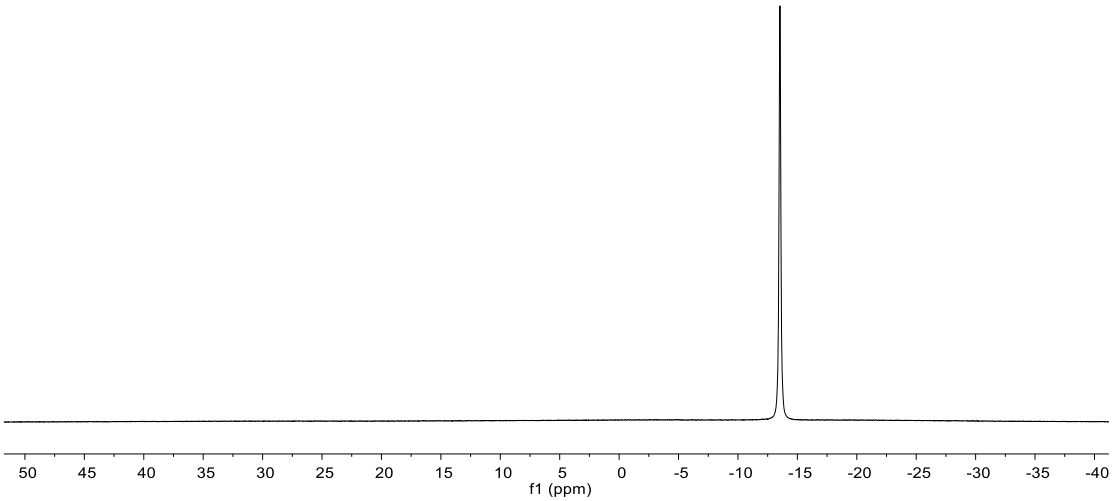
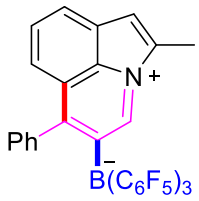


Fig. S80 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4f**.

Synthesis and characterization of compound 4g



4g

According to the General Procedure II (for **4**) from **3g** (182.5 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol). The product **4g** was isolated as a yellow solid (110.3 mg, 73% yield). [Comment: The poor solubility of compound **4g** prevented its $^{13}C\{^1H\}$ NMR characterization.]

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 9.05 (s, 1H), 8.16 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.72 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.38 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.32 (s, 1H), 7.28 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.21 (br, 1H), 7.18 (d, $^3J_{HH}$ = 1.2 Hz, 2H), 6.66 (br, 1H), 2.73 (s, 3H).

^{11}B NMR (128 MHz, 299 K, CD_2Cl_2): δ = -13.6 ($\nu_{1/2}$ ~ 18 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, CD_2Cl_2): δ = -126.2 (m, 1F), -127.6 (br, 1F), -129.2 (br, 1F), -131.8 (br, 2F), -132.4 (m, 1F) (*o*-C_6F_5); -159.8 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -161.8 (m, 2F) (*p*-C_6F_5); -163.6 (m, 1F), -165.3 (m, 1F), -166.8 (br, 4F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{36}H_{13}BF_{15}N$-H^+: 754.0829 [M-H]$^-$; found: 754.0828.

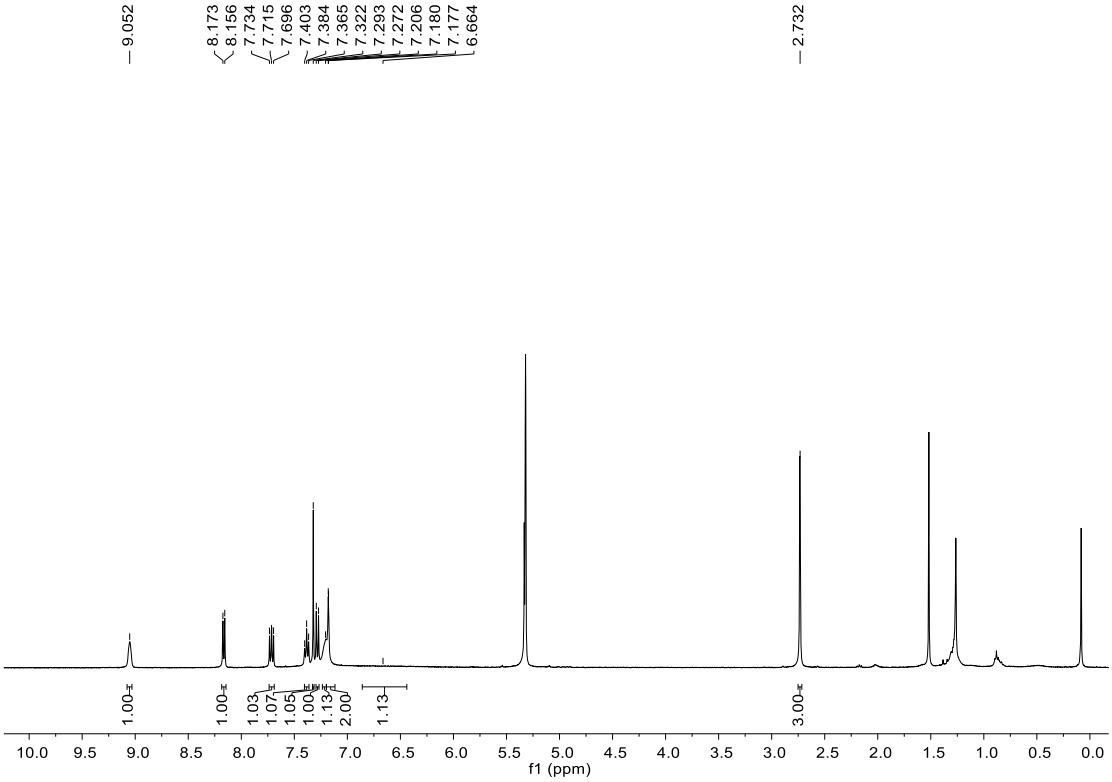


Fig. S81 ^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **4g**.

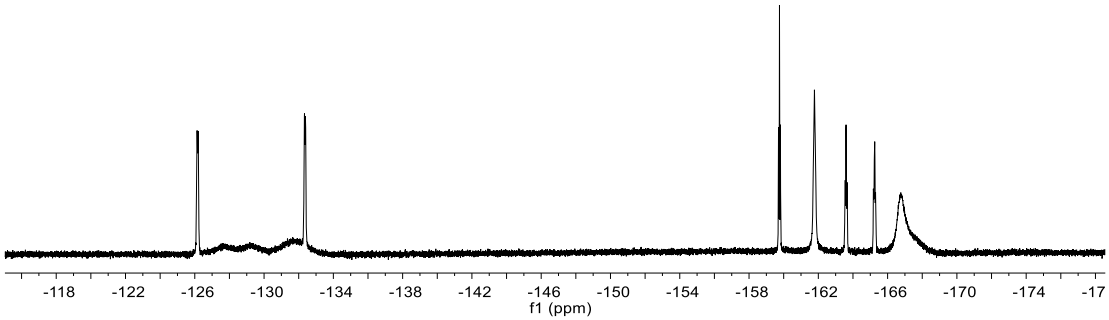


Fig. S82 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **4g**.

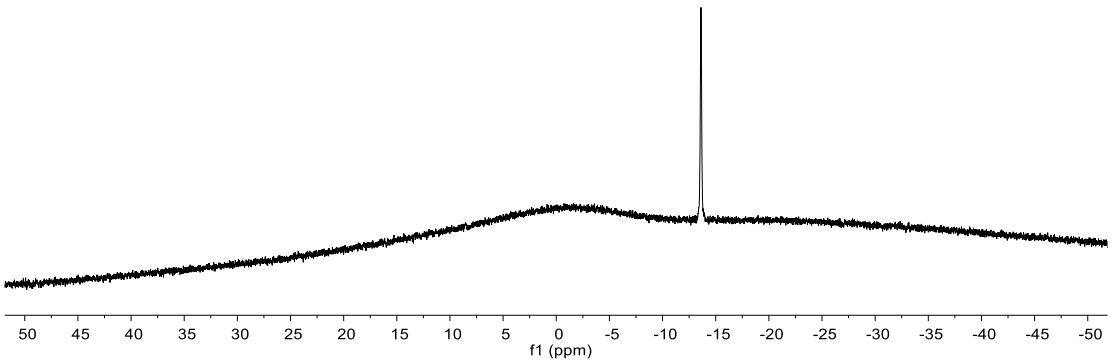
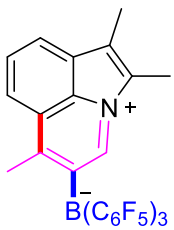


Fig. S83 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **4g**.

Synthesis and characterization of compound 4i



4i

A solution of 2,3-dimethyl substituted N-propargylindole **1i** (79.0 mg, 0.4 mmol) and $B(C_6F_5)_3$ (204.8 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was stirred

at 60 °C for 11 h to *in-situ* generate C7-alkenylation compound **2i** as a major product. After that, 1,2,2,6,6-pentamethylpiperidine (62.2 mg, 0.4 mmol) was added and the mixture was stirred at room temperature for another 4 h. Then all the volatiles were removed in vacuo. The crude product was purified by silica gel column chromatography to give product **4i** as an orange solid (132.9 mg, 47% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 8.78 (s, 1H), 8.40 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 8.26 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H), 7.93 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 2.95 (s, 3H), 2.58 (s, 3H), 2.46 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 166.6, 141.2, 137.1, 133.4, 131.2, 130.4, 130.3, 126.7, 126.3, 126.0, 124.2, 18.9, 8.9, 8.3. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 24 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -127.6, -128.9, -131.9, -132.7, -133.7, -134.5 (each m, each 1F, *o*-C_6F_5); -161.1 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F), -162.4 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F), -162.6 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F) (*p*-C_6F_5); -164.7 (m, 1F), -166.1 (m, 1F), -166.7 (m, 1F), -167.0 (m, 2F), -167.5 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{32}H_{13}BF_{15}N$-H^+: 706.0829 $[M-H]^-$; found: 706.0835.

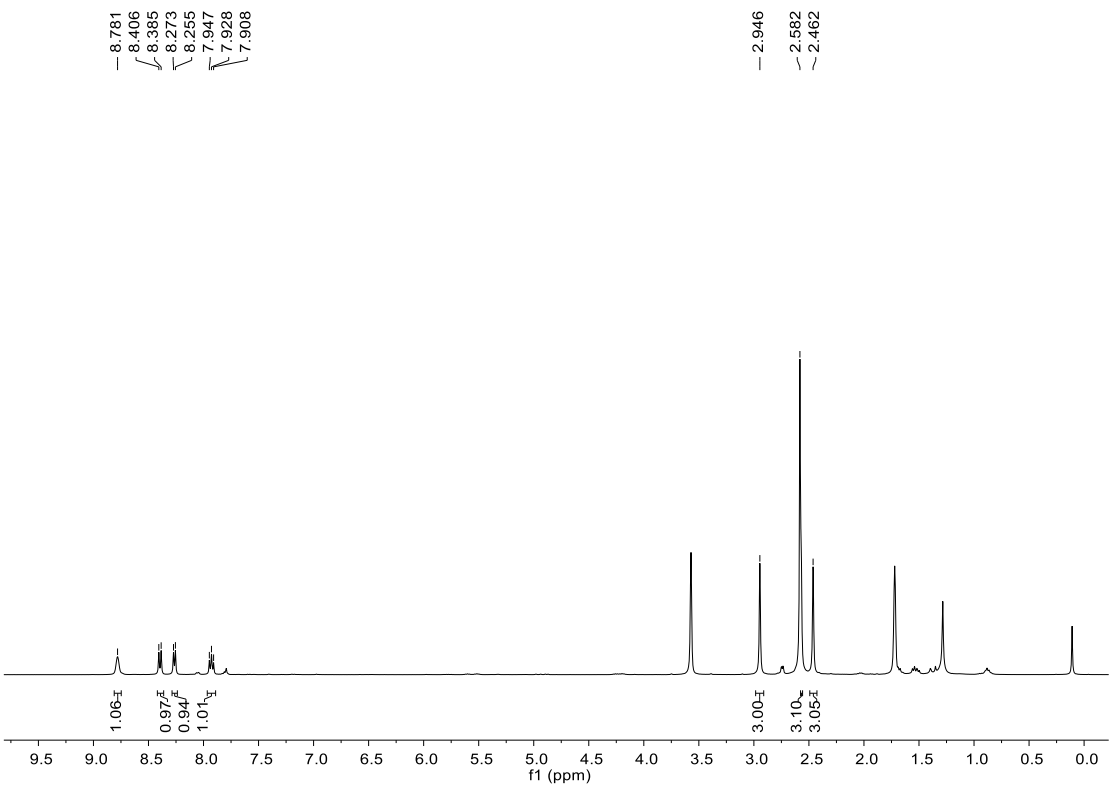


Fig. S84 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4i**.

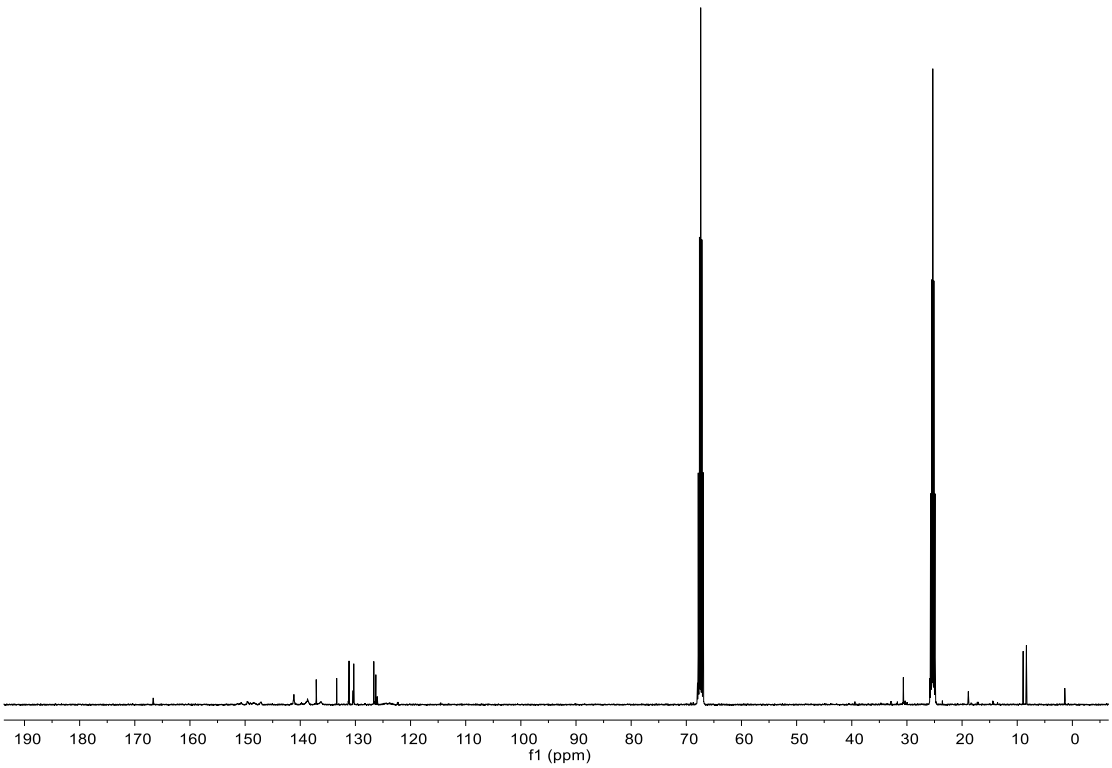


Fig. S85 ^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4i**.

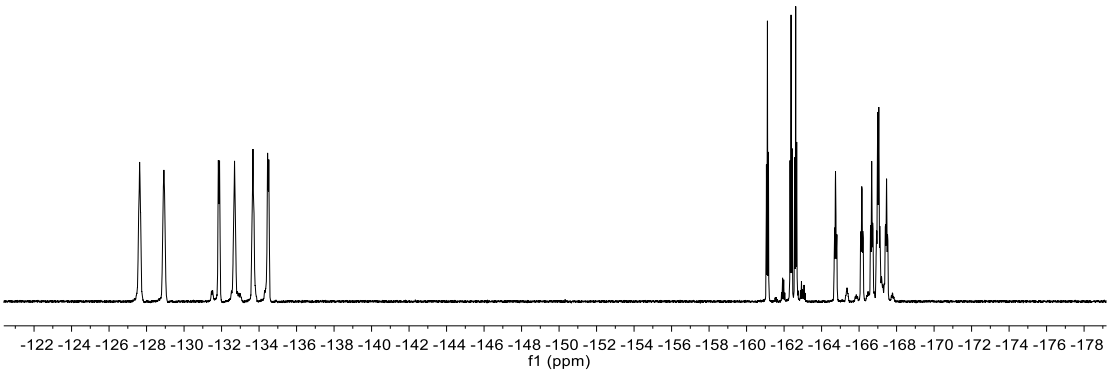


Fig. S86 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4i**.

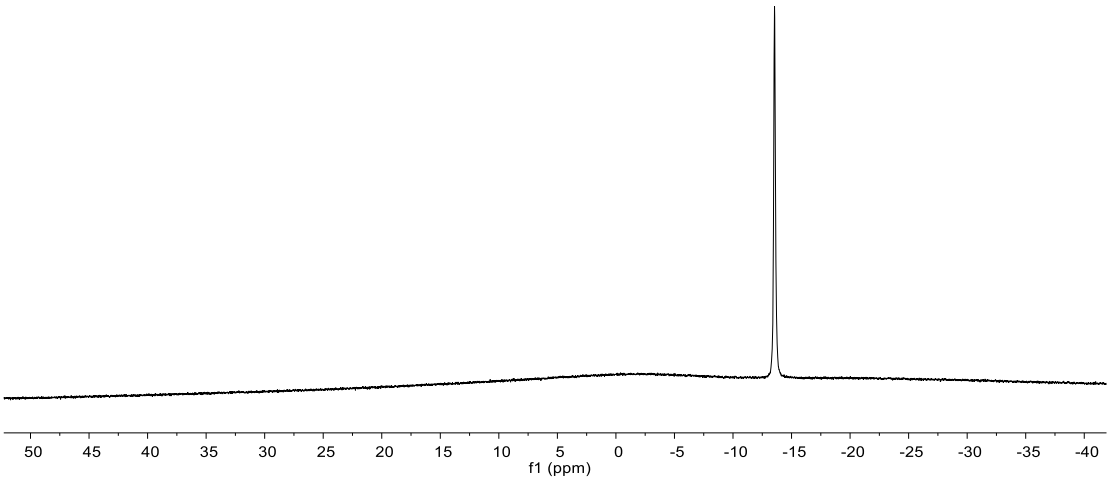
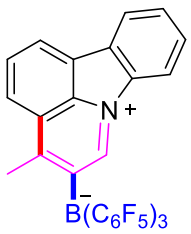


Fig. S87 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4i**.

Synthesis and characterization of compound 4j



4j

A solution of carbazole derivatived N-propargylindole **1j** (87.8 mg, 0.4 mmol) and $B(C_6F_5)_3$ (204.8 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was stirred at 60 °C for 10 h to *in-situ* generate C7-alkenylation compound **2j** as a major product. After that, 1,2,2,6,6-pentamethylpiperidine (62.2 mg, 0.4 mmol) was added and the mixture was stirred at room temperature for another 4 h. Then all the volatiles were removed in vacuo. The crude product was purified by silica gel column chromatography to give product **4j** as a yellow green solid (157.5 mg, 54% yield).

^{1}H NMR (400 MHz, 299 K, THF-d_8): δ = 9.38 (s, 1H), 8.64 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 8.52 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 8.34 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 8.29 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 8.08 (t, $^3J_{HH}$ = 6.8 Hz, 1H), 7.71 (m, 2H), 3.05 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8): δ = 167.6, 141.0, 140.8, 133.8, 131.5, 130.9, 130.6, 129.2, 127.5, 126.8, 124.0, 123.8, 115.1, 19.3. [C_6F_5 and BC not listed]

^{11}B NMR (128 MHz, 299 K, THF-d_8): δ = -13.5 ($\nu_{1/2}$ ~ 28 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299 K, THF-d_8): δ = -127.6, -128.9, -131.6, -133.0, -133.4, -134.4 (each m, each 1F, *o*-C_6F_5); -161.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -162.3 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -162.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F) (*p*-C_6F_5); -165.2 (m, 1F), -165.7 (m, 1F), -166.6 (m, 1F), -166.9 (m, 2F), -167.4 (m, 1F) (*m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{34}H_{11}BF_{15}N$-H^+: 728.0672 $[M-H]^-$; found:

728.0677.

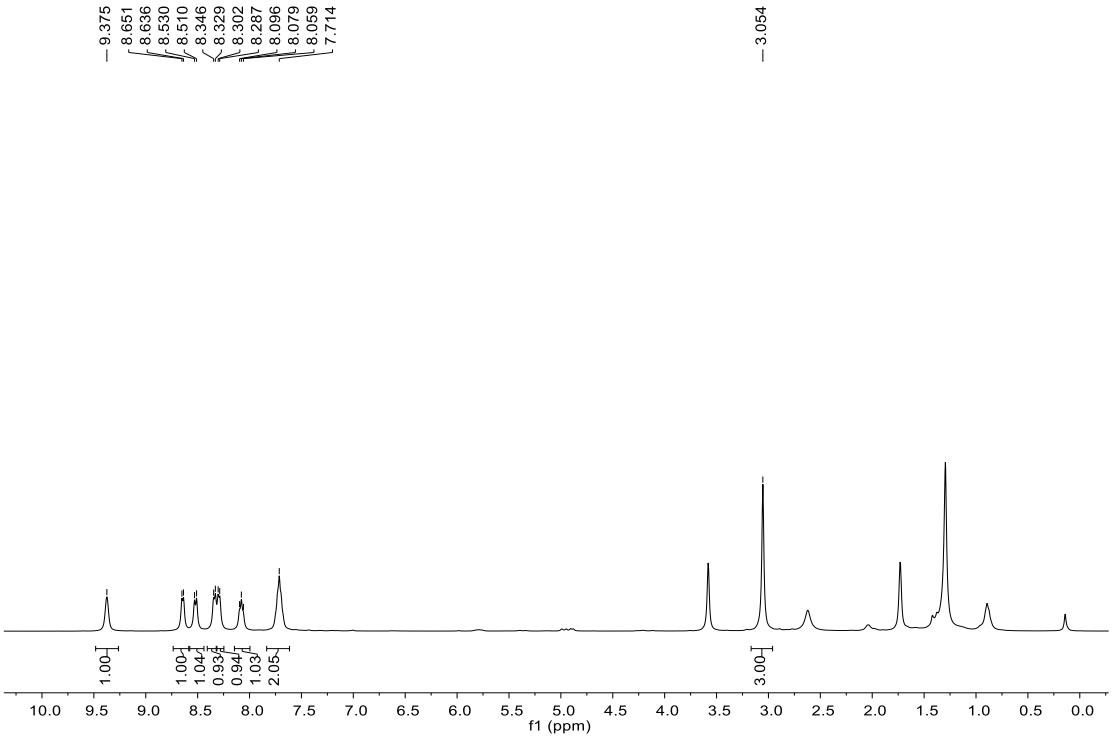


Fig. S88 ^{1}H NMR (400 MHz, 299K, THF-d_8) spectrum of compound **4j**.

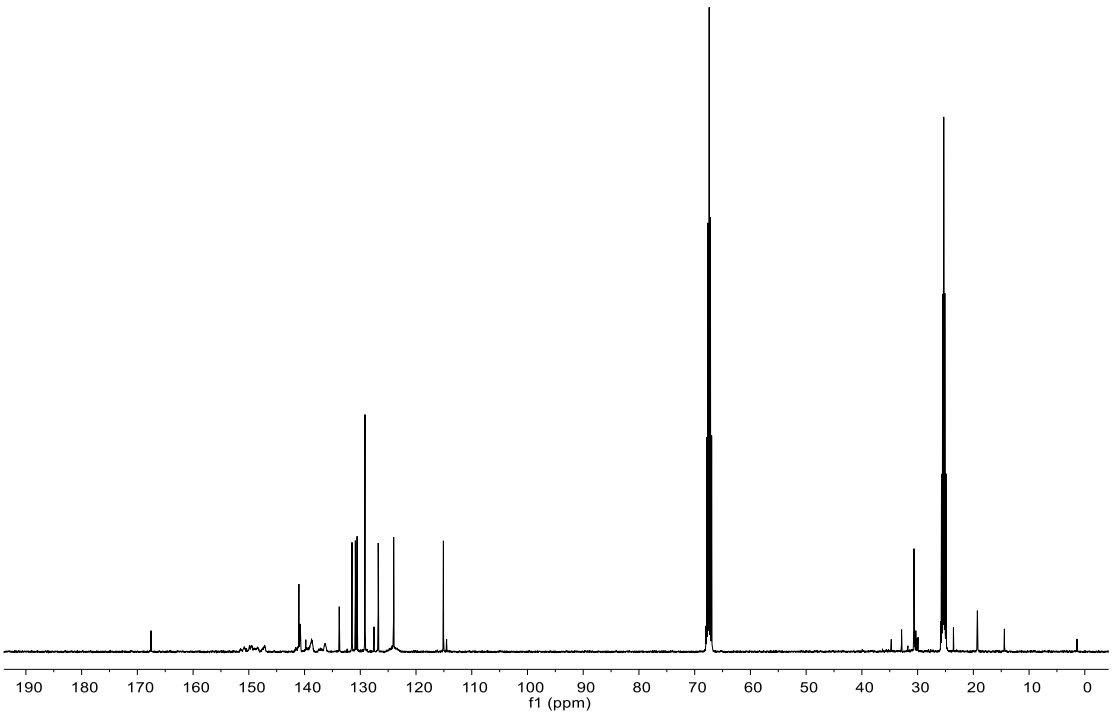


Fig. S89 ^{13}C{^{1}H} NMR (101 MHz, 299K, THF-d_8) spectrum of compound **4j**.

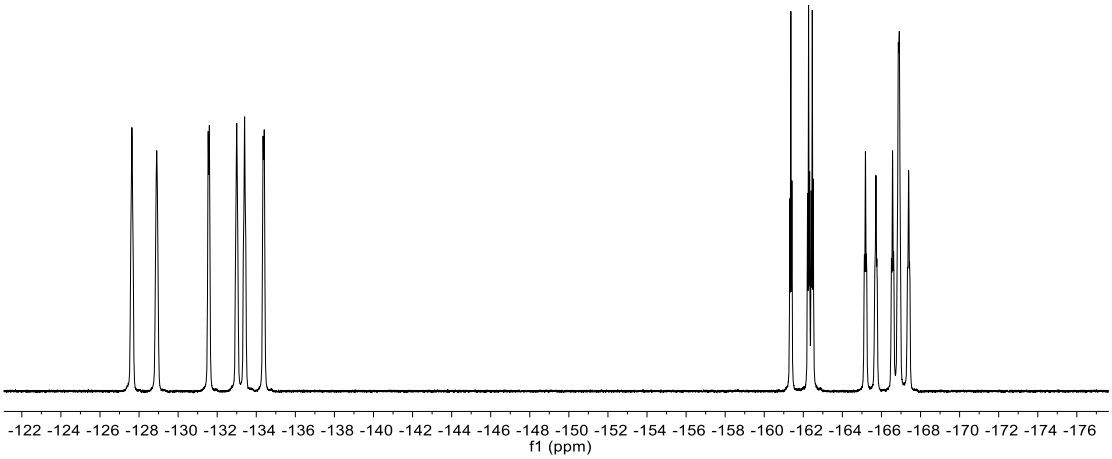


Fig. S90 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF-d_8) spectrum of compound **4j**.

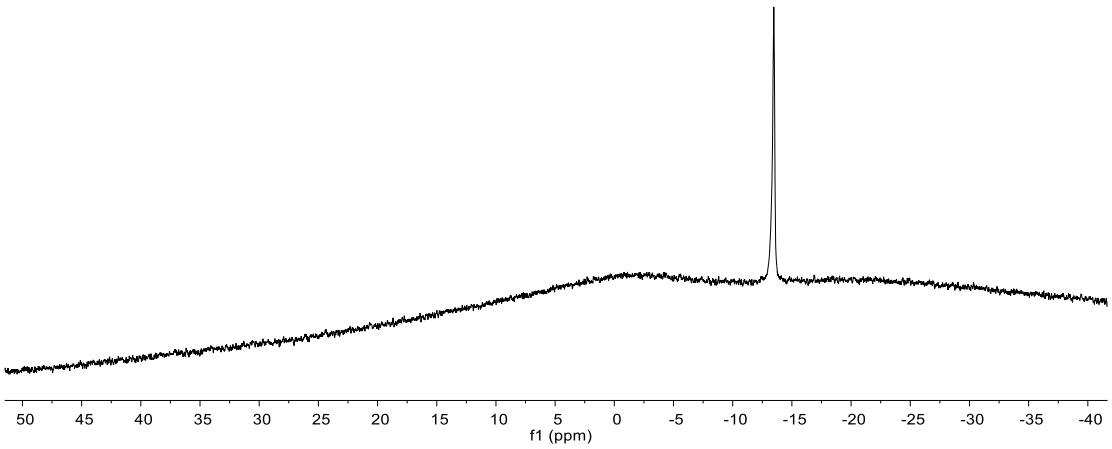
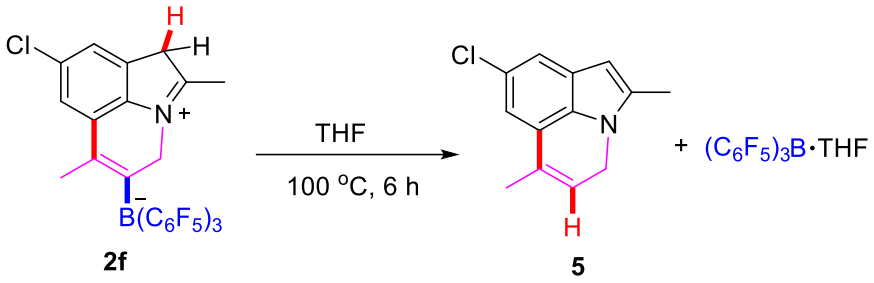


Fig. S91 ^{11}B NMR (128 MHz, 299K, THF-d_8) spectrum of compound **4j**.

Synthesis and characterization of compound 5



Scheme S5

A solution of compound **2f** (291.9 mg, 0.4 mmol) in THF (2 mL) was stirred at 100 °C for 6 h. Then all the volatiles were removed in vacuo. The crude product was purified by column chromatography in silica gel (PE:EA = 30:1) to give the product **5.** Yield: 74.9 mg, 86%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.15 (s, 1H), 6.66 (s, 1H), 5.99 (s, 1H), 5.53 (s, 1H), 4.75 (s, 2H), 2.19 (s, 3H), 1.96 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 136.6, 132.1, 129.6, 125.4, 125.3, 121.0, 119.8, 118.8, 114.0, 99.1, 44.6, 17.6, 12.0.

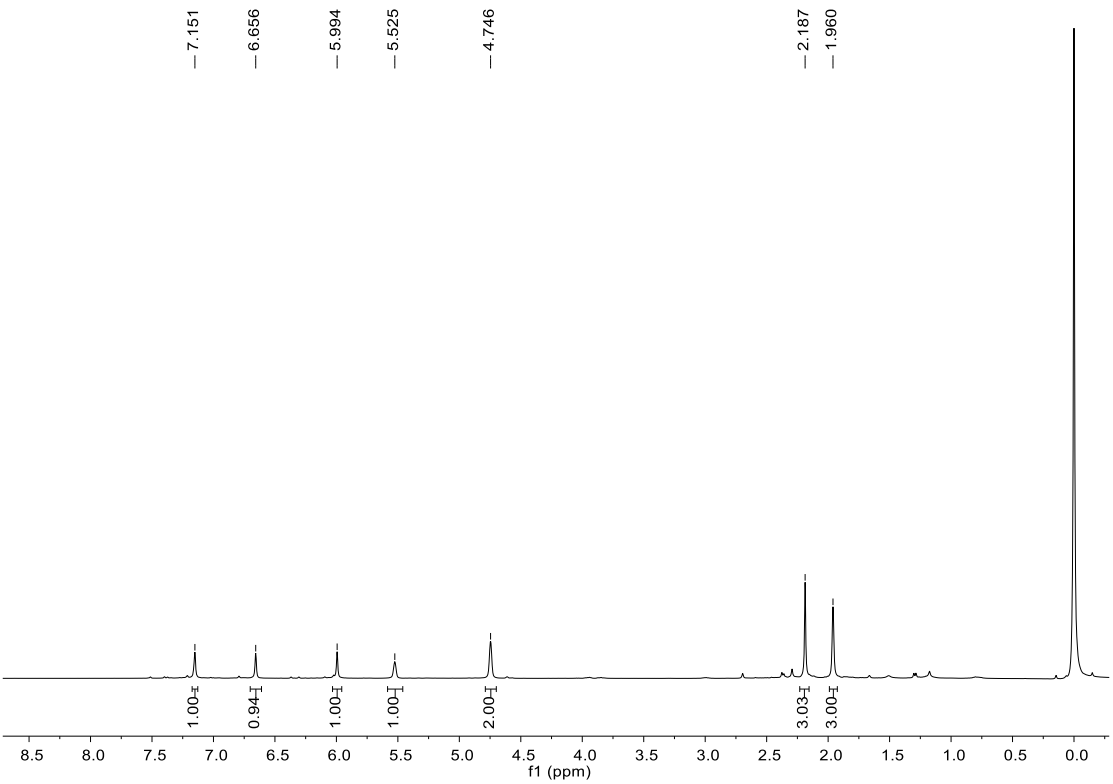


Fig. S92 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5**.

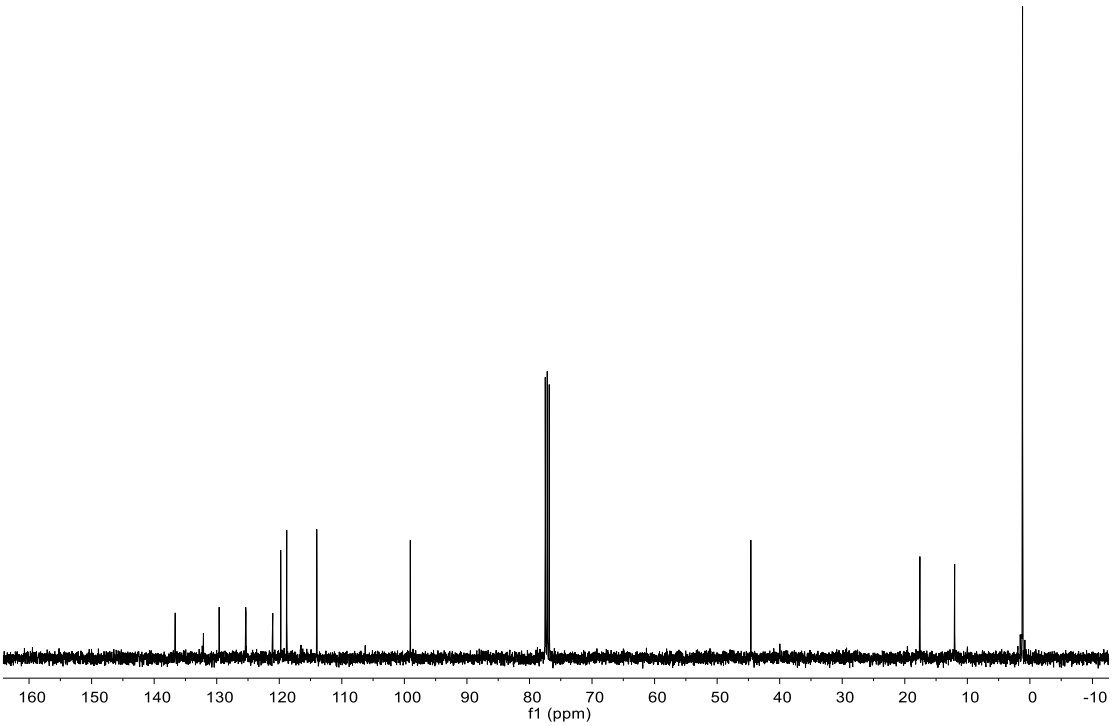
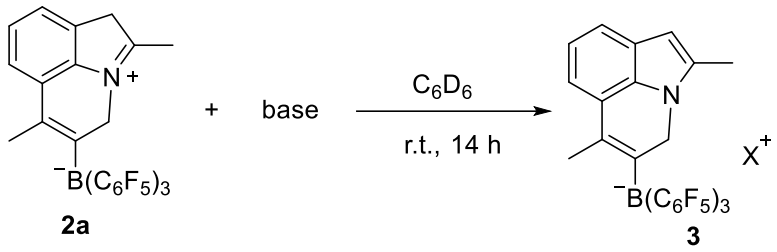


Fig. S93 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5**.

The reaction of 2a with different bases



entry	base	yield of **3** (detected by NMR)
1	PMP	quantitatively (X = H-PMP)
2	Cs_2CO_3	quantitatively (X = Cs)
3	K_2CO_3	No reaction
4	PPh_3	No reaction

Scheme S6

In an NMR tube, a solution of compound **2a** (10.5 mg, 0.015 mmol) and base (0.015 mmol) in C_6D_6 (0.6 mL) was kept at room temperature for 14 h. The *in-situ* NMR spectroscopy showed deprotonation could occur in the presence of PMP and Cs_2CO_3, while the less basic bases (i.e. K_2CO_3 and PPh_3) could not react with **2a** to generate the desired deprotonation product. For preparing deprotonation products, we chose PMP as the reagent.

The *in-situ* NMR spectra of reaction of **2a** with Cs_2CO_3 is listing as follows:

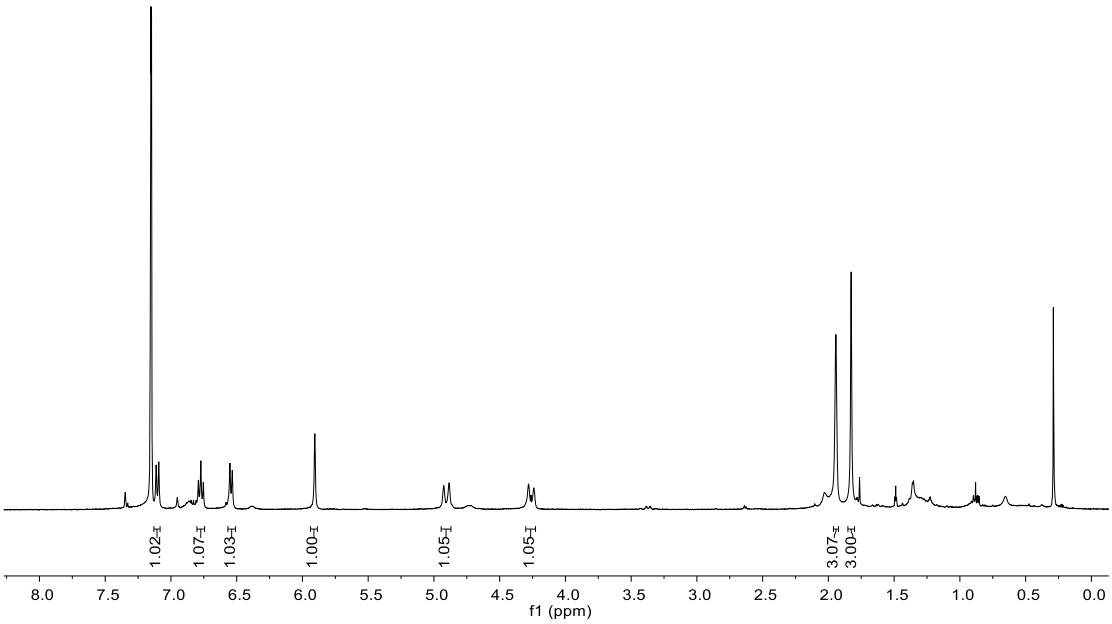


Fig. S94 The *in-situ* ^{1}H NMR (400 MHz, 299K, C_6D_6) spectrum of reaction of **2a** and Cs_2CO_3.

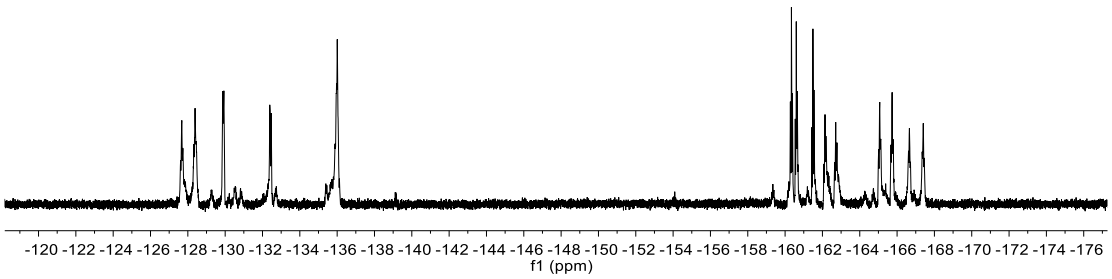


Fig. S95 The *in-situ* $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, C_6D_6) spectrum of reaction of **2a** and Cs_2CO_3.

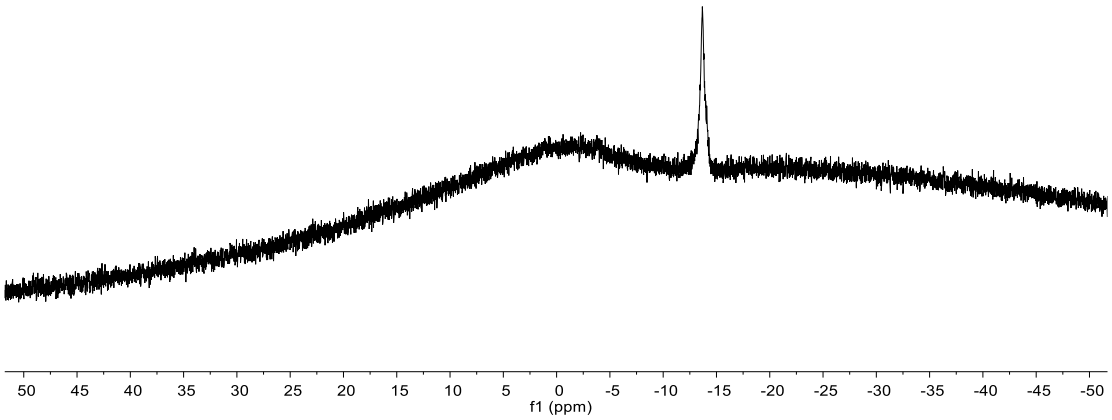
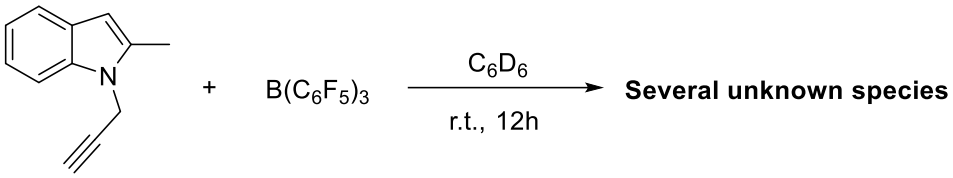


Fig. S96 The *in-situ* ^{11}B NMR (128 MHz, 299K, C_6D_6) spectrum of reaction of **2a** and Cs_2CO_3.

The reaction of 1k with $B(C_6F_5)_3$



1k

Scheme S7

In an NMR tube, a solution of N-propargylindole **1k** (8.5 mg, 0.05 mmol) and $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) in C_6D_6 (0.6 mL) was kept at room temperature for 12 h. A messy result was observed by *in-situ* NMR spectroscopy (see below).

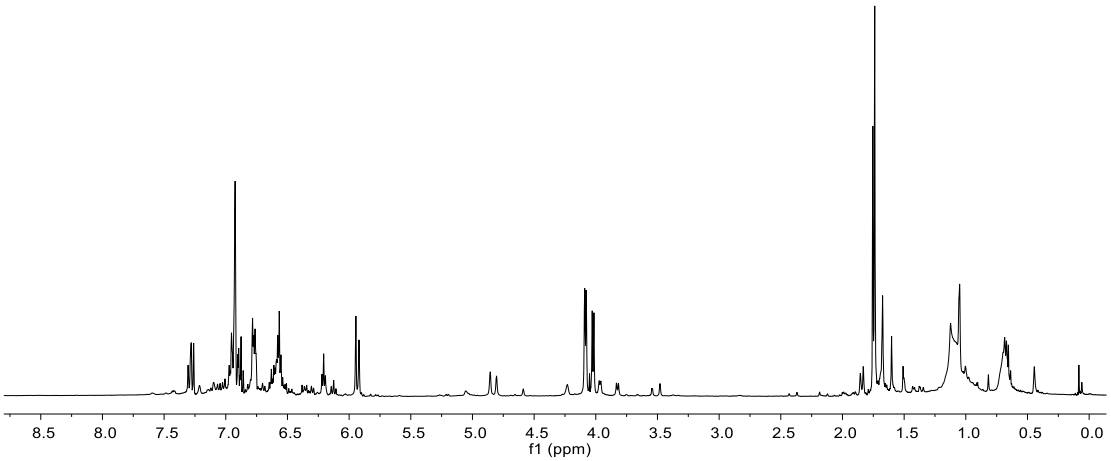


Fig. S97 The *in-situ* ^{1}H NMR (400 MHz, 299K, C_6D_6) spectrum of reaction of **1k** with $B(C_6F_5)_3$.

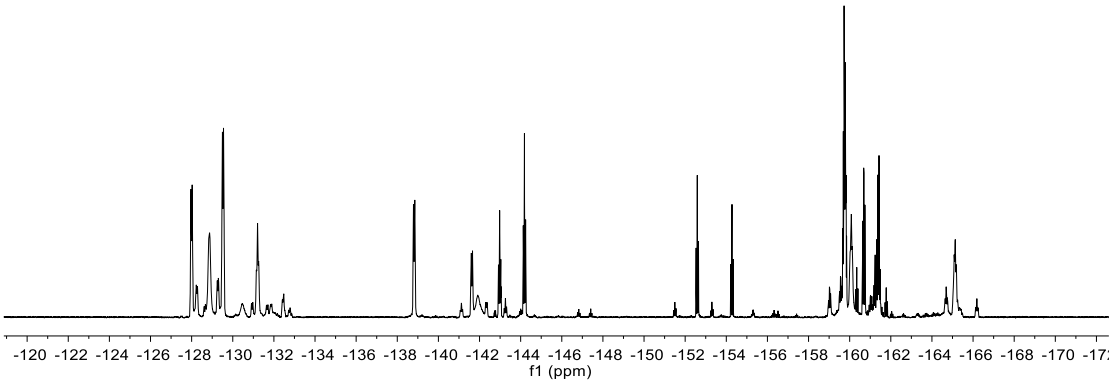


Fig. S98 The *in-situ* $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, C_6D_6) spectrum of reaction of **1k** with $B(C_6F_5)_3$.

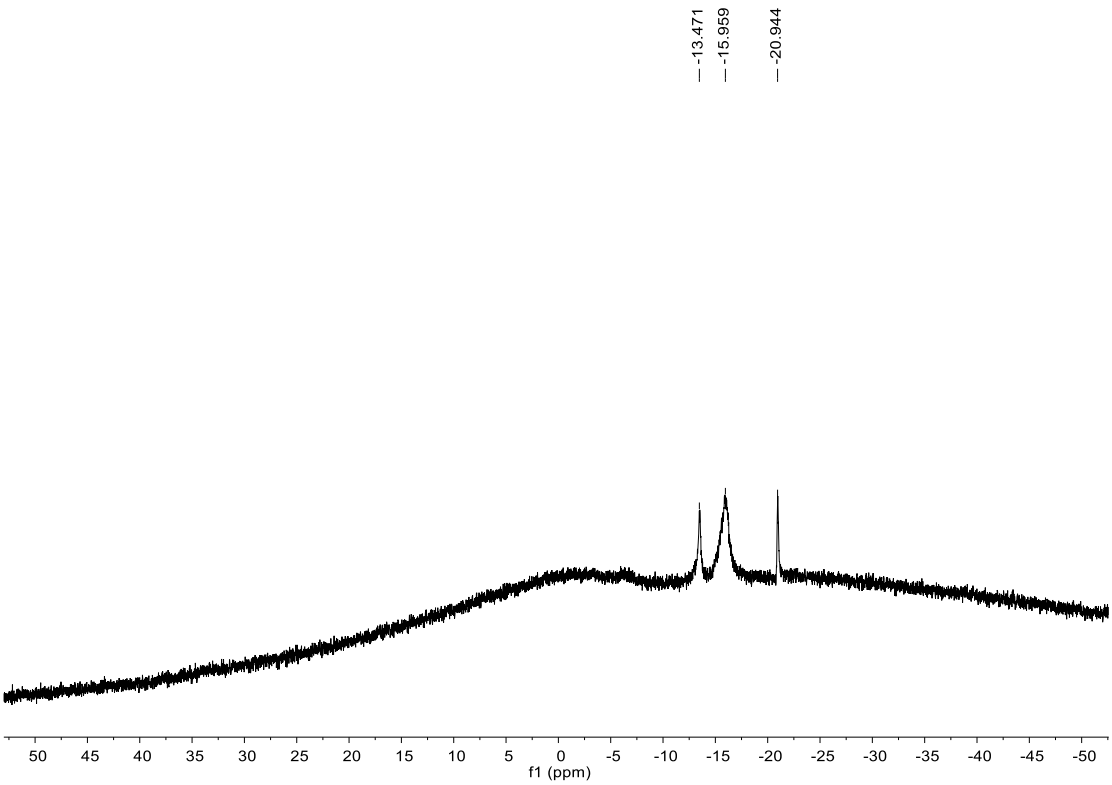
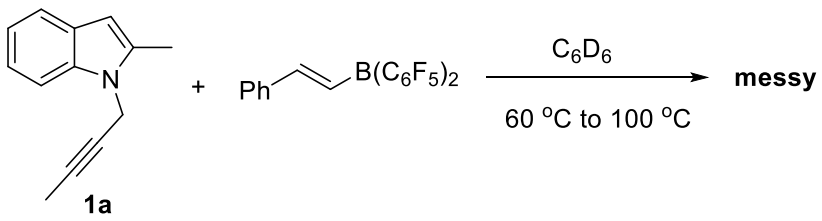


Fig. S99 The *in-situ* ^{11}B NMR (128 MHz, 299K, C_6D_6) spectrum of reaction of **1k** with $B(C_6F_5)_3$.

The reaction of 1a with different boranes



Scheme S8

1st Experiment: In an NMR tube, a solution of N-propargylindole **1a** (7.4 mg, 0.04 mmol) and $PhCH{=}CHB(C_6F_5)_2$ (20.5 mg, 0.04 mmol) in C_6D_6 (0.6 mL) was heated from 60 °C to 100 °C. A messy result was observed by *in-situ* NMR spectroscopy (see below).

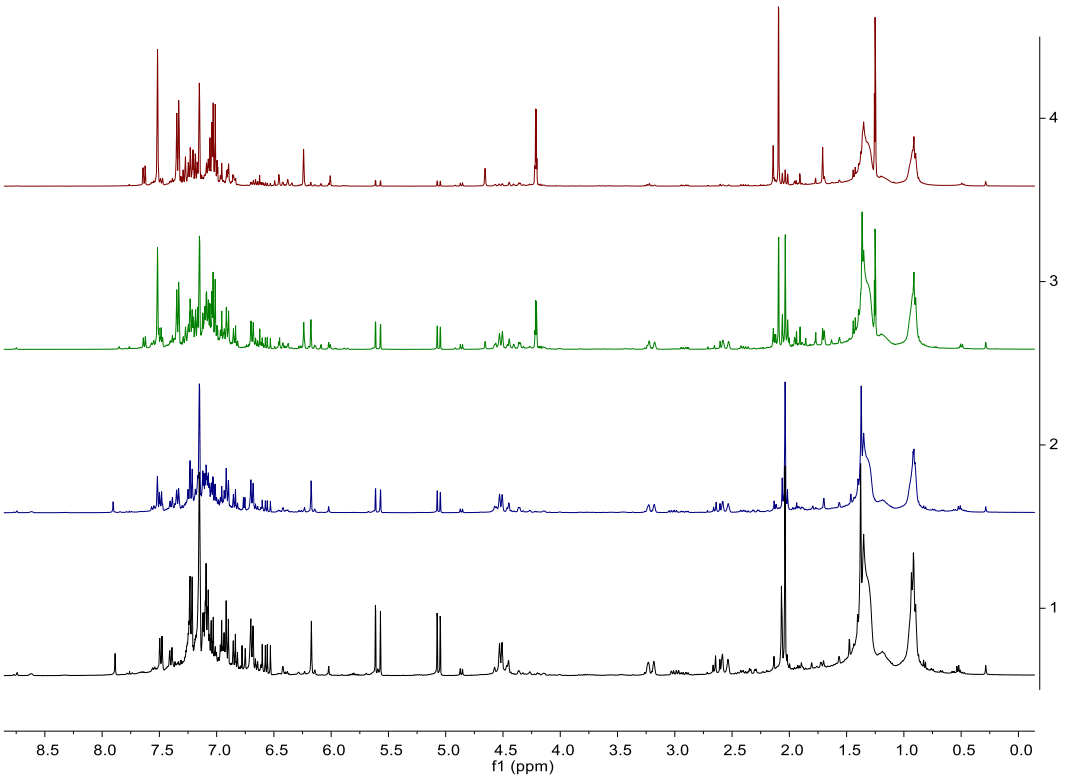


Fig. S100 The *in-situ* ^{1}H NMR (400 MHz, 299K, C_6D_6) spectra of reaction of **1a** with PhCH=CHB(C_6F_5)$_2$. (1) The mixture was heated at 100 ℃ for 32 h. (2) The mixture was heated at 100 ℃ for 10 h. (3) The mixture was heated at 80 ℃ for 10 h. (4) The mixture was heated at 60 ℃ for 10 h.

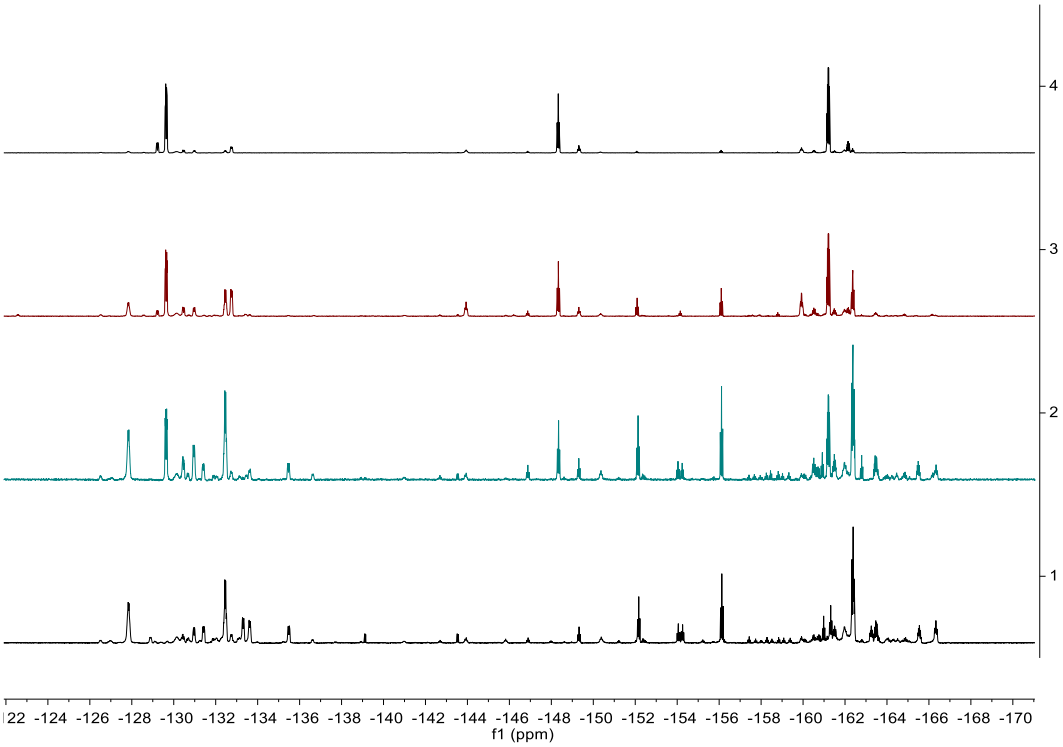


Fig. S101 The *in-situ* $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, C_6D_6) spectra of reaction of **1a** with $PhCH=CHB(C_6F_5)_2$. (1) The mixture was heated at 100 ℃ for 32 h. (2) The mixture was heated at 100 ℃ for 10 h. (3) The mixture was heated at 80 ℃ for 10 h. (4) The mixture was heated at 60 ℃ for 10 h.

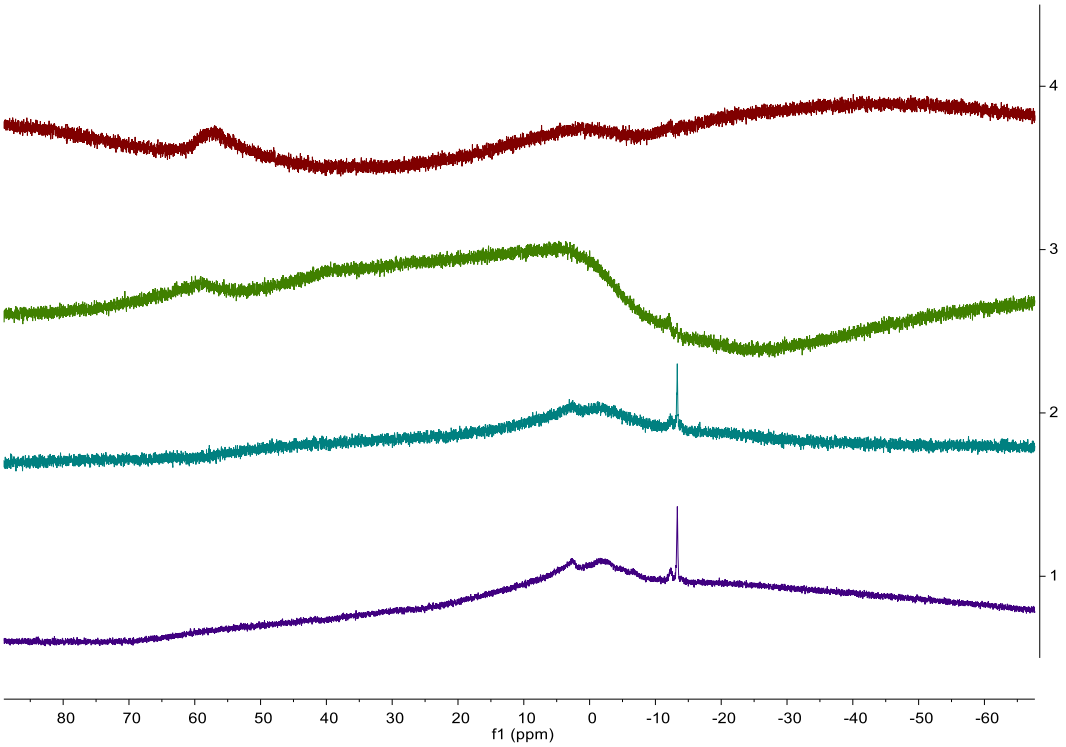
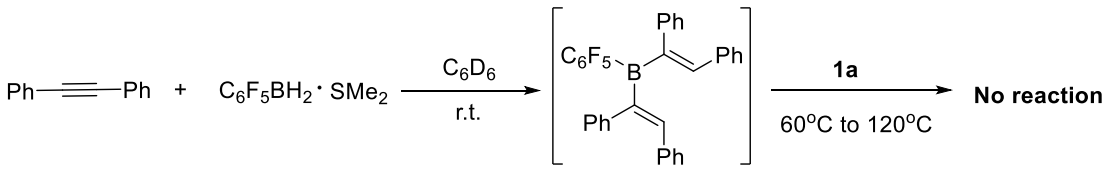


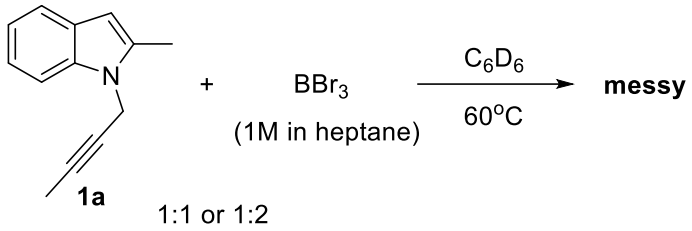
Fig. S102 The *in-situ* ^{11}B NMR (128 MHz, 299K, C_6D_6) spectra of reaction of **1a** with $PhCH{=}CHB(C_6F_5)_2$. (1) The mixture was heated at 100 ℃ for 32 h. (2) The mixture was heated at 100 ℃ for 10 h. (3) The mixture was heated at 80 ℃ for 10 h. (4) The mixture was heated at 60 ℃ for 10 h.



Scheme S9

2nd Experiment: In an NMR tube, a solution of $(PhCH{=}CPh)_2BC_6F_5$ was *in-situ* generated by the reaction of $C_6F_5BH_2{\cdot}SMe_2$ (9.7 mg, 0.04 mmol) and 1,2-diphenylethyne (14.3 mg, 0.08 mmol) at room temperature in C_6D_6 (0.6 mL), then **1a** (7.4 mg, 0.04 mmol) was added. The mixture was

heated from 60 °C to 120 °C. NMR studies showed that compound **1a** kept unchanged.



Scheme S10

3rd Experiment: In an NMR tube, a solution of N-propargylindole **1a** (18.4 mg, 0.1 mmol) and BBr_3 (0.1 mL, 0.1 mmol; 0.2 mL, 0.2 mmol, 1M in heptane) in a 1:1 or 1:2 molar ratio in C_6D_6 (0.6 mL) was heated at 60 °C for 10 h. The *in-situ* NMR studies showed that a messy result was obtained eventhough the starting materials was consumed completely.

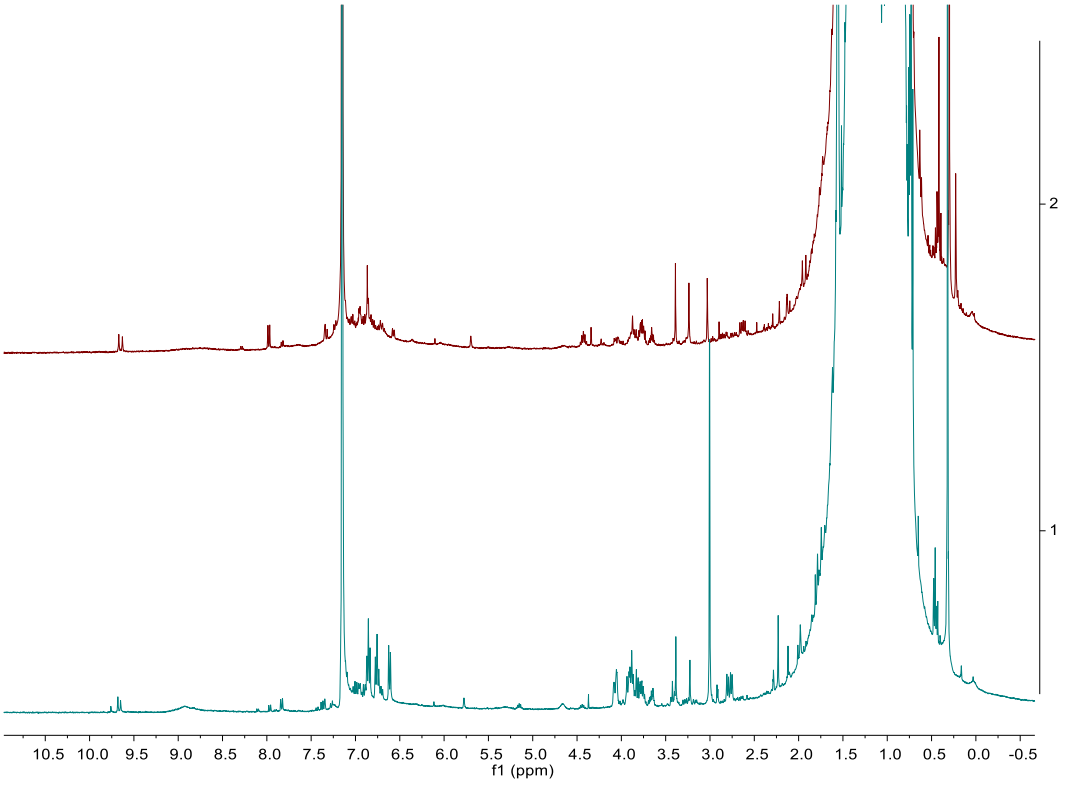


Fig. S103 The *in-situ* ^{1}H NMR (400 MHz, 299K, C_6D_6) spectra of reaction of **1a** with BBr_3. (1) The reaction of **1a** with BBr_3 in a 1:2 molar ratio. (2) The reaction of **1a** with BBr_3 in a 1:1 molar ratio.

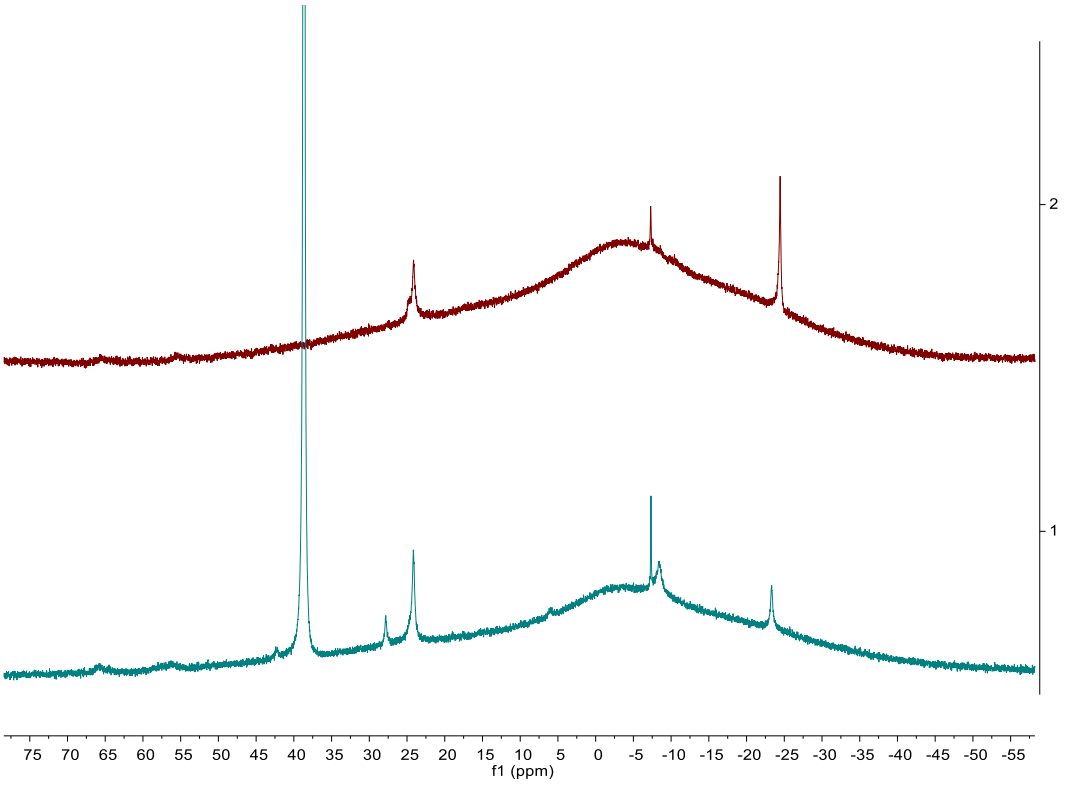
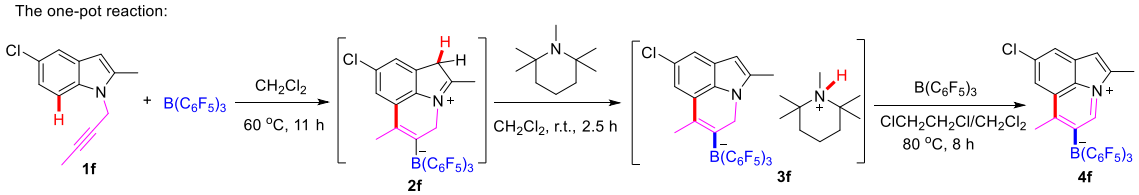


Fig. S104 The *in-situ* ^{11}B NMR (128 MHz, 299K, C_6D_6) spectra of reaction of **1a** with BBr_3. (1) The reaction of **1a** with BBr_3 in a 1:2 molar ratio.

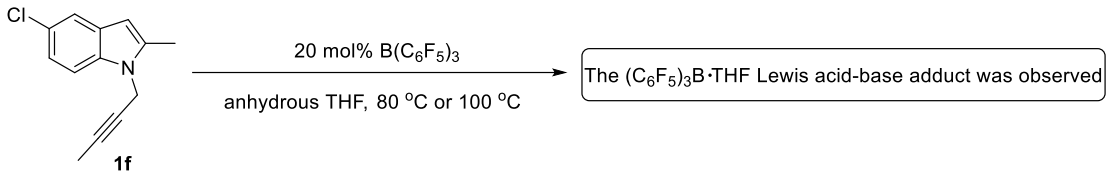
The one-pot reaction of 1f with $B(C_6F_5)_3$



Scheme S11

The one-pot reaction: A solution of compound **2f** was *in-situ* generated by the reaction of N-propargylindole **1f** (65.4 mg, 0.3 mmol) and $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) at 60 °C for 11 h, then 1,2,2,6,6-pentamethylpiperidine (46.6 mg, 0.3 mmol) was added. The mixture was stirred at room temperature for 2.5 h to *in-situ* generate compound **3f**. Finally, $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol) was added to the mixture. A solution of *in-situ* generated compound **3f** and $B(C_6F_5)_3$ in $ClCH_2CH_2Cl/CH_2Cl_2$ (4 mL) was stirred at 80 °C for another 8 h. Upon completion, the mixture was purified by silica gel column chromatography to give the product **4f** (187.8 mg, 86% yield). The NMR spectroscopy of compound **4f** was consistent with those of the step-by-step obtained product.

The reaction of 1f with catalytic $B(C_6F_5)_3$



Scheme 12

In an NMR tube, a solution of N-propargylindole **1f** (9.8 mg, 0.045 mmol) and $B(C_6F_5)_3$ (4.6 mg, 0.009 mmol) in anhydrous THF (0.6 mL) was stirred at 80 °C or 100 °C for 11 h. The $(C_6F_5)_3B{\cdot}$THF Lewis acid-base

adduct as observed by *in-situ* NMR spectroscopy (see below), which was so stable that no dissociation occurred at 100 °C.

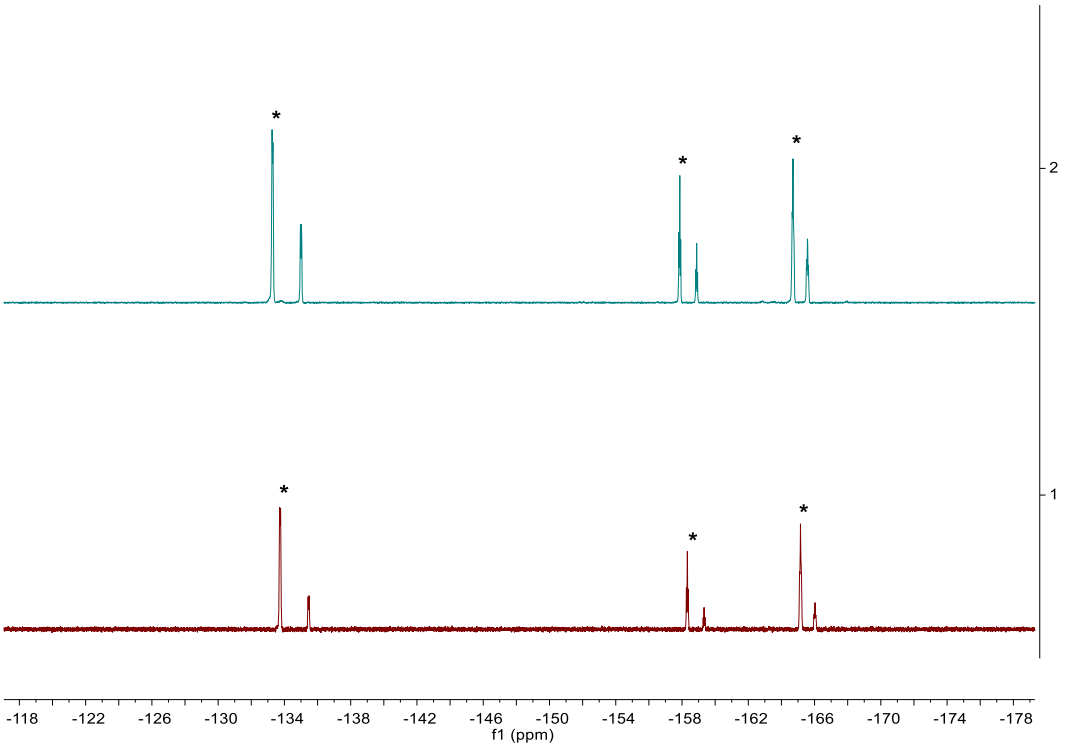


Fig. S105 The *in-situ* $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, THF) spectra of reaction of **1f** with 20 mol% $B(C_6F_5)_3$. (1) The mixture was heated at 100 °C for 11 h. (2) The mixture was heated at 80 °C for 11 h. [* $(C_6F_5)_3B{\cdot}THF$ Lewis acid-base adduct]

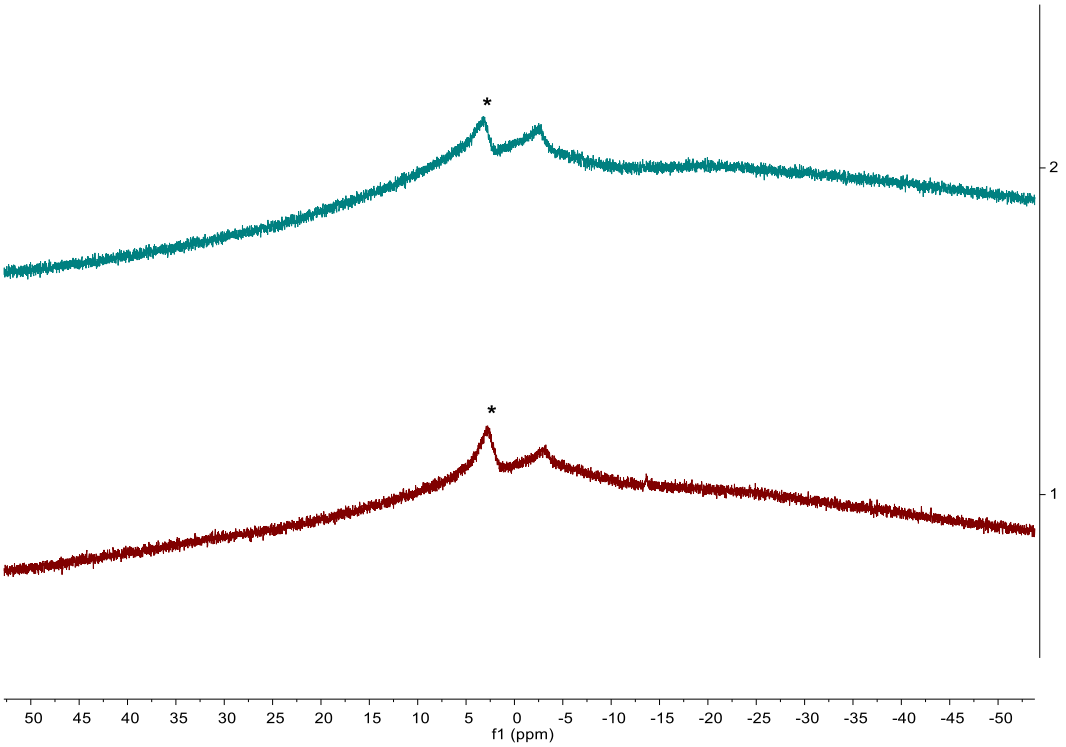
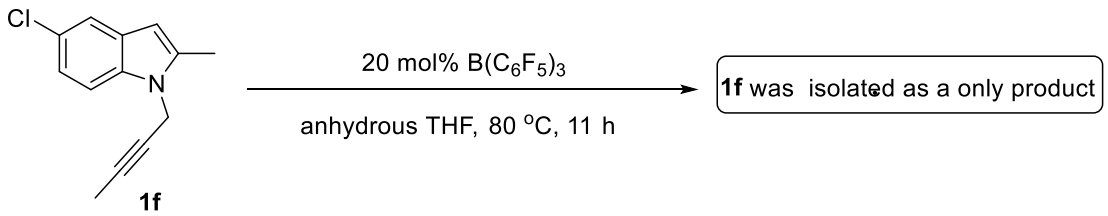


Fig. S106 The *in-situ* ^{11}B NMR (128 MHz, 299K, THF) spectra of reaction of **1f** with 20 mol% $B(C_6F_5)_3$. (1) The mixture was heated at 100 ℃ for 11 h. (2) The mixture was heated at 80 ℃ for 11 h. [* $(C_6F_5)_3B{\cdot}THF$ Lewis acid-base adduct]



Scheme 13

A solution of N-propargylindole **1f** (87.1 mg, 0.4 mmol) and $B(C_6F_5)_3$ (204.8 mg, 0.4 mmol) in anhydrous THF (2 mL) was stirred at 80 °C for 11 h. Then all the volatiles were removed in vacuo. The crude product was purified by column chromatography in silica gel. Compound **1f** was

isolated as a sole product (67.1 mg, 77% yield). Its structure was confirmed by NMR spectroscopy (see below).

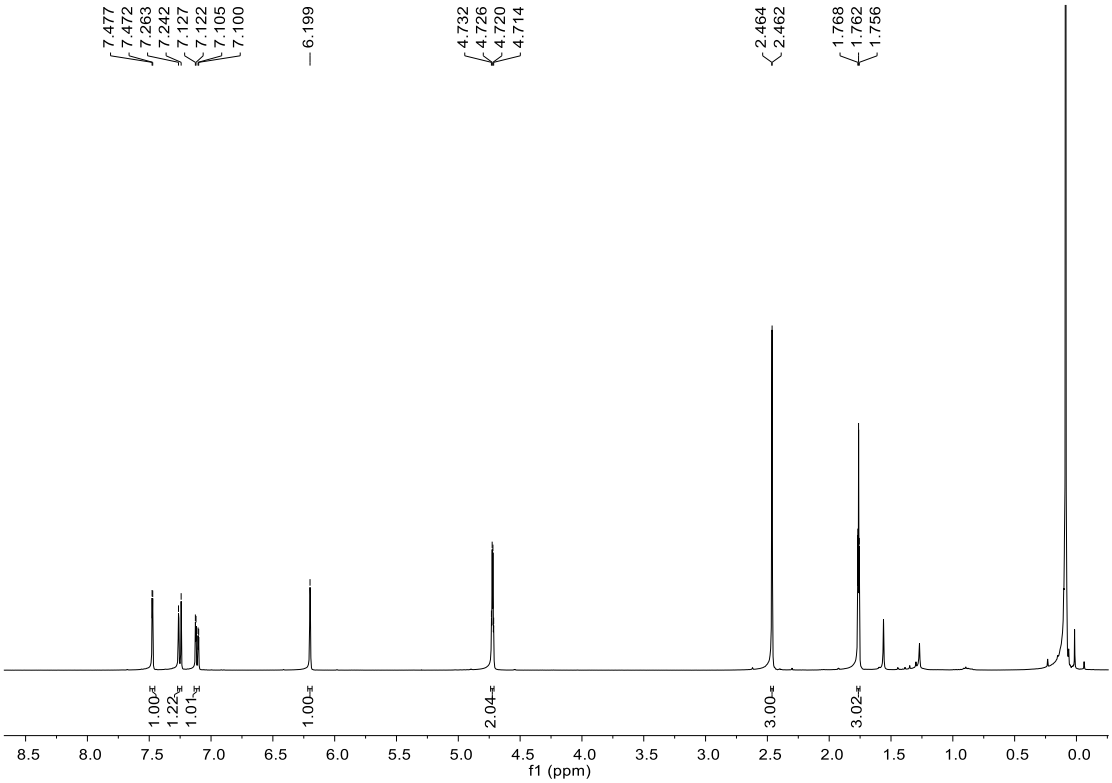


Fig. S107 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **1f**.

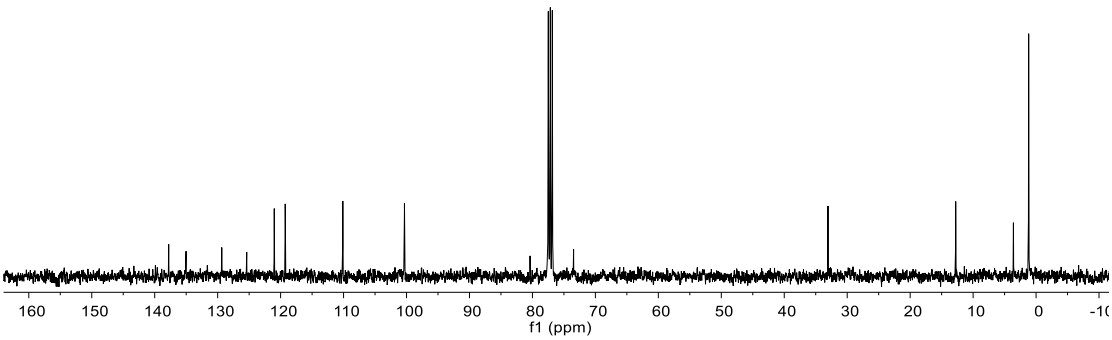


Fig. S108 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **1f**.

FT-IR spectra

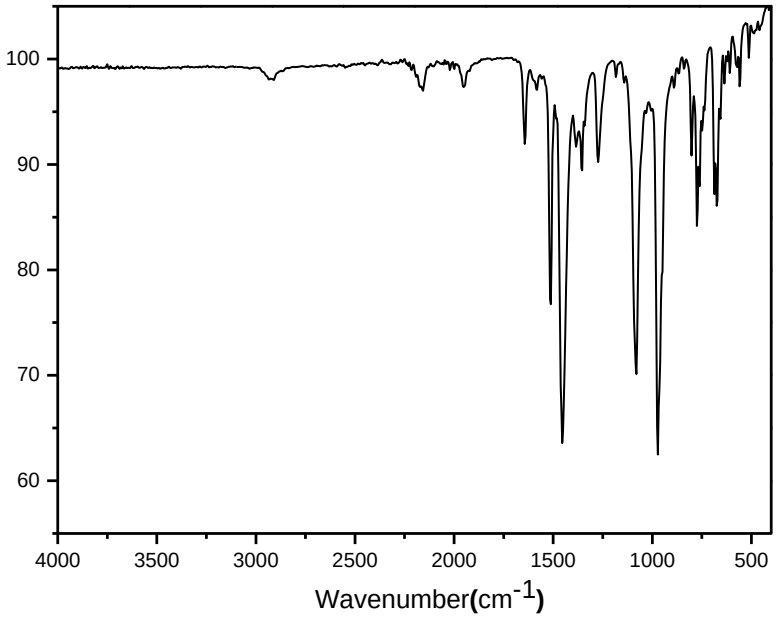


Fig. S109 FT-IR spectrum of compound **2a**.

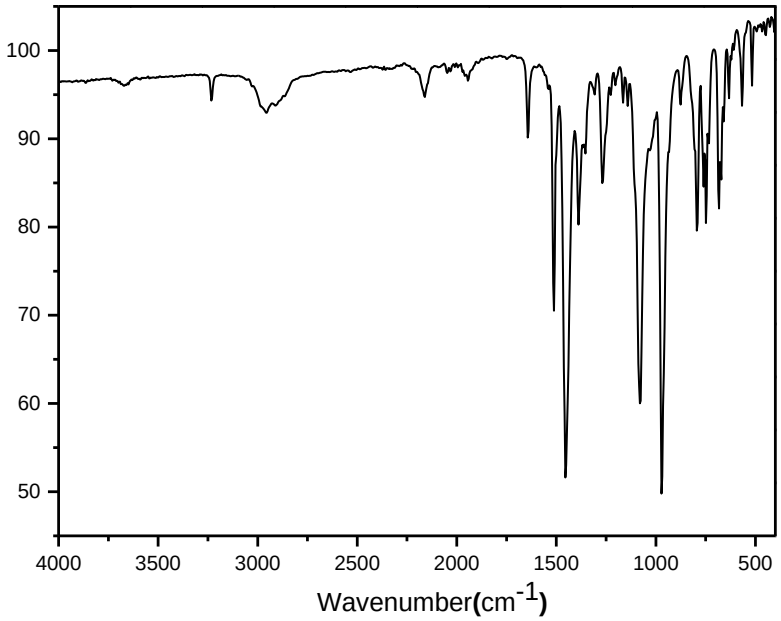


Fig. S110 FT-IR spectrum of compound **3a**.

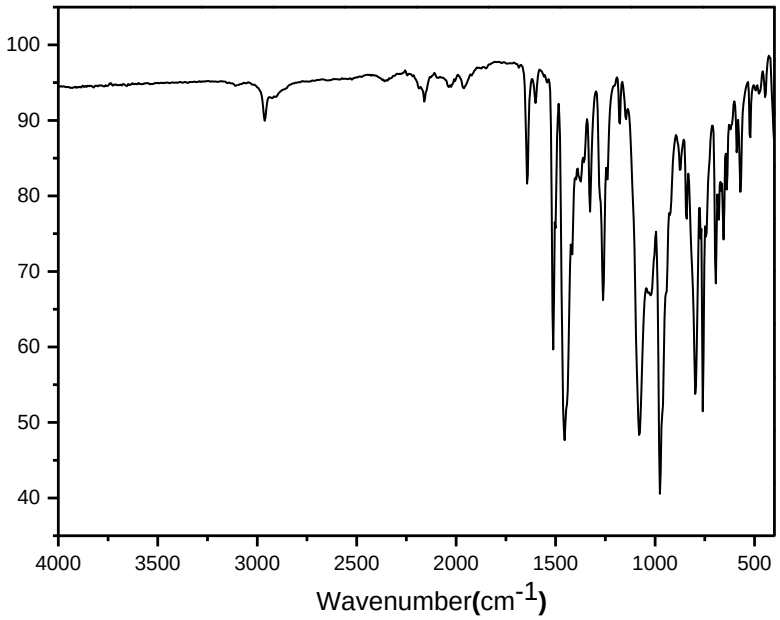


Fig. S111 FT-IR spectrum of compound **4a**.