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Electronic supplementary information

for

Hetero Diels-Alder reactions of isolable *N*-borylenamines

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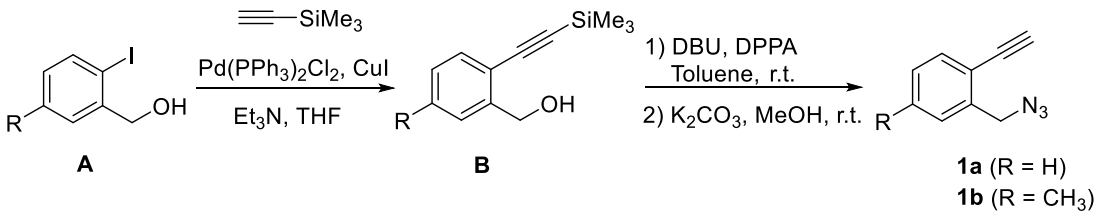
1. General Information

Chemicals and solvents were purchased from commercial suppliers. All manipulations were performed under an atmosphere of dry and oxygen-free N_2 by means of standard Schlenk or glovebox techniques. *n*-Hexane and dichloromethane (CH_2Cl_2) were collected from a (Mikrouna) solvent purification system and stored over activated 3Å molecular sieves. Chloroform-*d* ($CDCl_3$) and benzene-d_6 (C_6D_6) were degassed, dried over calcium hydride and stored over 3 Å molecular sieves in the glovebox for at least 8 h prior to use. The following instruments were used for physical characterization of the compounds: HRMS: Agilent 6224 TOF LC/MS; NMR: Bruker Avance II 400MHz spectrometer (^{1}H: 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 (^{1}H and ^{13}C). Some NMR assignments were supported by additional 2D NMR experiments. 2-Alkynyl benzyl azide derivatives **1a-d** were prepared according to the modified literature procedure,[1] and **1e** was prepared using published procedure.[1] [(1) D. Fischer, H. Tomeba, N. K. Pahadi, N. T. Patil and Y. Yamamoto, *Angew. Chem. Int. Ed*., 2007, **46**, 4764-4766.]

X-Ray diffraction: Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture CMOS-based diffractometer (**2a**, **3a** and **3c**) with graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å) and a dual source Rigaku Oxford Diffraction four-circle diffractometer (**3e**, **3b**, and **3j**),

equipped with a Hybrid Pixel Array detector and Cu_{Ka} radiation (λ = 1.54184 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.) and refined with the ShelXL refinement package (G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.) using Least Squares minimization that implanted in Olex2 (L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **A71**, 59-75.). 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-2346378-2346383 and 2353710-2353711 contains 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/.

2. Synthesis and characterization of 1



Scheme S1

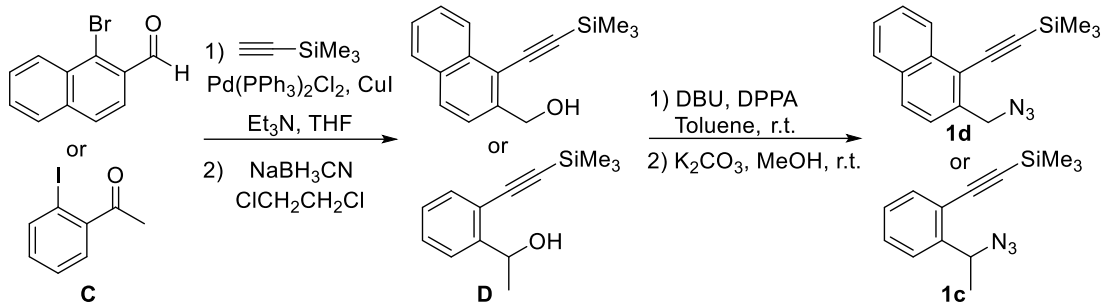
General procedure for 1 (Method A): The mixture of compound **A** (1.0 equiv), ethynyltrimethylsilane (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (1.0 mol%), CuI

(6.0 mol%) and triethylamine (1.5 equiv.) in tetrahydrofuran (THF, 10 mL) was stirred at 35 °C (using an oil bath) for 12 hours. After the reaction was quenched with water and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with saturated NH_4Cl aq. and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **B**.

To the solution of compound **B** (1.2 equiv.) in toluene (10 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.3 equiv.) and diphenylphosphoryl azide (DPPA, 1.2 equiv.) were added. The mixture was stirred at room temperature for 12 h. The reaction was quenched with the saturated aqueous sodium chloride solution, and then extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether (PE) to afford the **1-TMS** product.

Finally, the mixture of **1-TMS** (1.0 equiv.) and K_2CO_3 (2.0 equiv.) in anhydrous MeOH (20 mL) were stirred at room temperature for 8 h. Then brine was added to the reaction mixture. The obtained mixture was extracted with ethyl ether (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue

was purified by flash column chromatography on silica gel to afford the desired product **1**.



Scheme S2

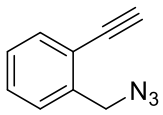
General procedure for 1 (Method B): The mixture of compound **C** (1.0 equiv), ethynyltrimethylsilane (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (1.0 mol%), CuI (6.0 mol%) and triethylamine (1.5 equiv.) in tetrahydrofuran (THF, 10 mL) was stirred at room temperature or 80 °C (using an oil bath) for 12 hours. After the reaction was quenched with water and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with saturated NH_4Cl aq. and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then dissolved in 1,2-dichloroethane (10 mL) and $NaBH_3CN$ (1.1 equiv.) was added as a reducing agent to afford **D**.

To the solution of compound **D** (1.2 equiv.) in toluene (10 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.3 equiv.) and diphenylphosphoryl azide (DPPA, 1.2 equiv.) were added. The mixture was stirred at room temperature for 12 h. The reaction was quenched with the saturated aqueous sodium chloride solution, and then extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over

anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether (PE) to afford the **1-TMS** product.

Finally, the mixture of **1-TMS** (1.0 equiv.) and K_2CO_3 (2.0 equiv.) in anhydrous MeOH (20 mL) were stirred at room temperature for 8 h. Then brine was added to the reaction mixture. The obtained mixture was extracted with ethyl ether (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **1**.

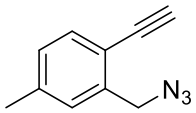
Synthesis and characterization of 1a



1a

According to general procedure for **1** (Method A) from the corresponding **A** (2.4 g, 10.0 mmol, 1.0 equiv.), ethynyltrimethylsilane (1.6 mL, 11.0 mmol, 1.1 equiv.), DBU (2.0 g, 13.0 mmol, 1.3 equiv.), DPPA (3.3 g, 12.0 mmol, 1.2 equiv.), and K_2CO_3 (2.8 g, 20.0 mmol, 2.0 equiv.), the product **1a** was isolated as a yellow liquid (1.4 g, 88% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.56 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.38 (m, 2H), 7.31 (m, 1H), 4.56 (s, 2H), 3.37 (s, 1H). **^{13}C NMR** (101 MHz, 298 K, $CDCl_3$): δ = 137.9, 133.1, 129.2, 128.4, 128.1, 121.6, 82.4, 80.9, 53.0.

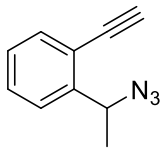
Synthesis and characterization of 1b



1b

According to general procedure for **1** (Method A) from the corresponding **A** (2.0 g, 8.1 mmol, 1.0 equiv.), ethynyltrimethylsilane (1.3 mL, 8.9 mmol, 1.1 equiv.), DBU (1.5 g, 10.5 mmol, 1.3 equiv.), DPPA (2.6 g, 9.7 mmol, 1.2 equiv.), and K_2CO_3 (2.0 g, 16.2 mmol, 2.0 equiv.), the product **1b** was isolated as a yellow liquid (1.2 g, 81% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.44 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.19 (s, 1H), 7.11 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.52 (s, 2H), 3.31 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, 298 K, $CDCl_3$): δ = 139.6, 137.7, 133.0, 129.2, 128.9, 118.6, 81.6, 81.1, 53.0, 21.4.

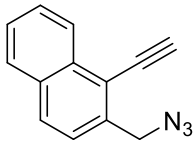
Synthesis and characterization of 1c



1c

According to general procedure for **1** (Method B) from the corresponding **C** (2.5 g, 10.0 mmol, 1.0 equiv.), ethynyltrimethylsilane (1.5 mL, 11.0 mmol, 1.1 equiv.), $NaBH_3CN$ (0.7 g, 11.0 mmol, 1.1 equiv.), DBU (1.9 g, 13.0 mmol, 1.3 equiv.), DPPA (3.2 g, 12.0 mmol, 1.2 equiv.), and K_2CO_3 (2.7 g, 19.4 mmol, 2.0 equiv.), the product **1c** was isolated as a yellow liquid (0.16 g, 10% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.52 (m, 1H), 7.43 (m, 2H), 7.27 (m, 1H), 5.22 (q, $^3J_{HH}$ = 6.8 Hz, 1H), 3.35 (s, 1H), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, 298 K, $CDCl_3$): δ = 143.5, 133.1, 129.5, 127.6, 125.4, 120.4, 82.4, 81.0, 58.6, 21.1.

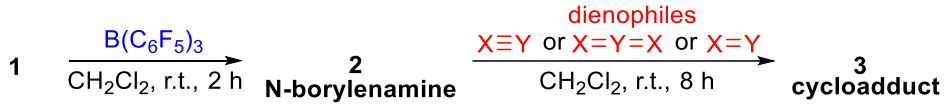
Synthesis and characterization of 1d



1d

According to general procedure for **1** (Method B) from the corresponding **C** (2.0 g, 8.5 mmol, 1.0 equiv.), ethynyltrimethylsilane (1.3 mL, 9.4 mmol, 1.1 equiv.), $NaBH_3CN$ (0.6 g, 9.4 mmol, 1.1 equiv.), DBU (1.2 g, 8.7 mmol, 1.3 equiv.), DPPA (2.2 g, 8.0 mmol, 1.2 equiv.), and K_2CO_3 (1.8 g, 13.3 mmol, 2.0 equiv.), the product **1d** was isolated as a yellow liquid (0.89 g, 50% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 8.41 (m, 1H), 7.88 (m, 2H), 7.62 (m, 1H), 7.55 (m, 1H), 7.51 (m, 1H), 4.78 (s, 2H), 3.79 (s, 1H). **^{13}C NMR** (101 MHz, 298 K, $CDCl_3$): δ = 136.9, 133.6, 132.6, 129.5, 128.2, 127.4, 126.8, 126.3, 125.7, 119.0, 87.7, 79.1, 53.4.

3. Synthesis and characterization of 2 and 3



Scheme S3

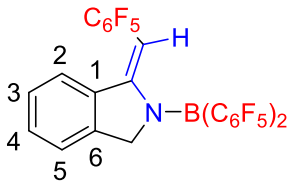
General procedure for 2: A solution of $B(C_6F_5)_3$ (1.0 equiv.) and **1** (1.0 equiv.) in CH_2Cl_2 (5.0 mL) was stirred at room temperature for 2 h. Then the solvent was removed under vacuum to give the product **2**.

General procedure for 3 (Method A): A solution of $B(C_6F_5)_3$ (1.0 equiv.) and **1a** (1.0 equiv.) in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h to obtain compounds **2a**. Then the solution of dienophile (1.0 equiv.) in CH_2Cl_2 (2 mL) was added. The mixture was stirred at room temperature

for another 8 h. After the removal of the solvent under vacuum, the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (V_{PE}:V_{EA} = 30:1) to afford the product **3**.

General procedure for 3 (Method B): A solution of $B(C_6F_5)_3$ (1.0 equiv.) and **1a** (1.0 equiv.) in CH_2Cl_2 (5.0 mL) was stirred at room temperature for 2 h to obtain compounds **2a**. Then the solution of dienophile (1.0 equiv.) in CH_2Cl_2 was added. The mixture was stirred at room temperature for another 8 h. After the removal of the solvent under vacuum, the residue was washed with *n*-hexane (3×3 mL) and dried in vacuo to give the product **3**.

Synthesis and characterization of 2a



2a

According to the General procedure for **2** from compound **1a** (9.8 mg, 0.06 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (32 mg, 0.06 mmol, 1.0 equiv.), the product **2a** was obtained as a white solid (39.5 mg, 99%). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.40 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *H*4), 7.31 (d, $^3J_{HH}$ = 7.6 Hz, 1H, *H*5), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *H*3), 6.93 (d, $^3J_{HH}$ = 7.9 Hz, 1H, *H*2), 5.69 (s, 1H, =C*H*^{C6F5}), 4.87 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 148.6 (*C*=^{CHC6F5}), 139.7 (*C*6), 134.1 (*C*1), 130.4 (*C*4), 128.3 (*C*3), 122.7 (*C*2), 122.6 (*C*5), 95.6 (=*C*HC_6F_5), 56.6 (CH_2). **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^{1}H/δ^{13}C:

5.69/95.6 (=*CH*C_6F_5), 4.87/56.6 (*CH_2*). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: (6.93, 5.69, 4.87)/148.6 (*H*2, =C*H*^{C6F5}, C*H_2*/*C*=^{CHC6F5}). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 36.5 ($v_{1/2}$ ~ 783 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -131.1 (m, 2F), -131.3 (m, 2F), -138.1 (m, 2F) (*o*-C_6F_5), -150.1 (t, $^3J_{FF}$ = 20.0 Hz, 1F), -151.0 (t, $^3J_{FF}$ = 20.9, 1F), -154.5 (t, $^3J_{FF}$ = 20.9 Hz, 1F) (*p*-C_6F_5), -160.2 (m, 2F), -160.5 (m, 2F), -161.4 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{27}H_6BF_{15}N^-$: 640.0359 [M-H]$^-$; found: 640.0363.

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 -25 °C.

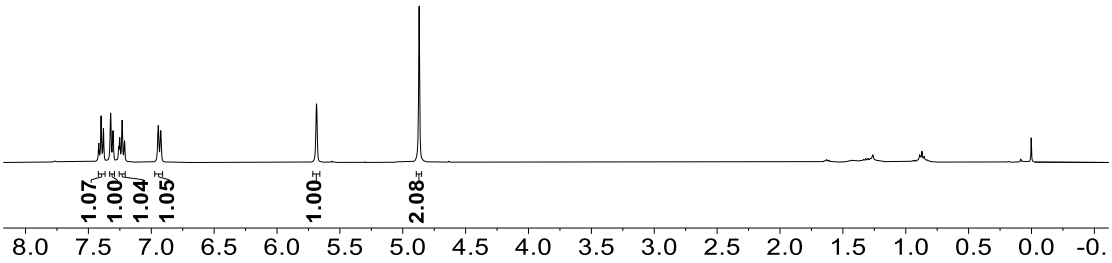


Fig. S1 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **2a**.

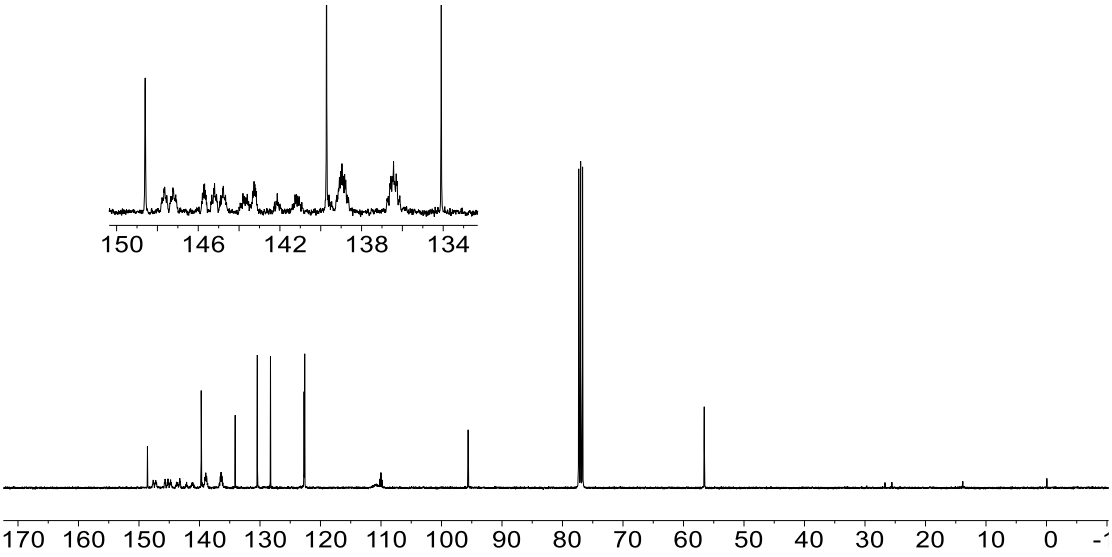


Fig. S2 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **2a**.

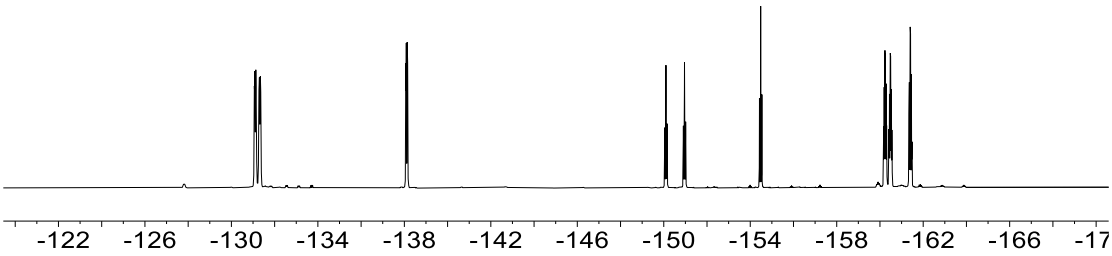


Fig. S3 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **2a**.

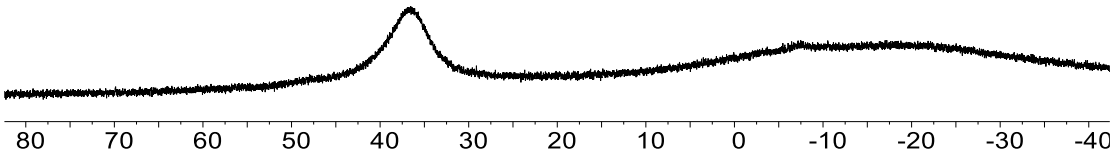


Fig. S4 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **2a**.

X-ray crystal structure analysis of 2a: formula $C_{27}H_7BF_{15}N$, M = 641.15, colourless crystal, 0.25 × 0.21 × 0.16 mm, a = 11.505(5), b = 12.536(5), c = 17.074(7) Å, α = 77.759(13)º, β = 87.576(13)º, γ = 77.117(12)º, V = 2345.9(17) $Å^3$, ρ_{calc} = 1.815 gcm^{-3}, μ = 0.190 mm^{-1}, empirical absorption correction (0.6820 ≤ T ≤ 0.7459), Z = 4, triclinic, space group P-1, λ =

0.71073 Å, T = 120.0 K, ω and φ scans, 61778 reflections collected (±h, ±k, ±l), 12880 independent (R_{int} = 0.0594) and 7995 observed reflections [I>2σ(I)], 793 refined parameters, R = 0.0447, wR^2 = 0.1109, max. (min.) residual electron density 0.31 (-0.29) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

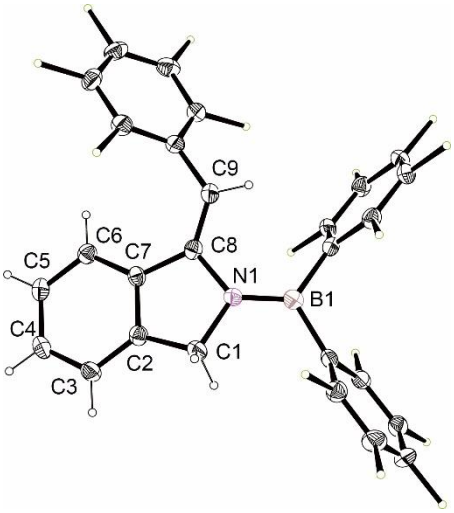
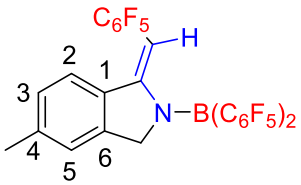


Fig. S5 A view of the molecular structure of compound **2a** (thermal ellipsoids are shown at the 50% probability level).

Synthesis and characterization of 2b



2b

According to the General procedure for **2** from compound **1b** (11.3 mg, 0.06 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (32 mg, 0.06 mmol, 1.0 equiv.), the product **2b** was obtained as a white solid (40.3 mg, 99% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.11 (s, 1H, *H*5), 7.04 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*3), 6.81 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*2), 5.62 (s, 1H, =C*H*^{C6F5}), 4.82 (s, 2H, CH_2), 2.38 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 148.6 (*C*=^{CHC6F5}), 141.1 (*C*4), 140.0 (*C*6), 131.5 (*C*1), 129.3 (*C*3), 123.0 (*C*5), 122.5 (*C*2), 94.6 (=*C*H^{C6F5}), 56.5 (*C*H$_2$), 21.6 (*C*H$_3$). **^{1}H, ^{13}C GHSQC** (400

MHz/101 MHz, 298 K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 5.62/94.6 (=*CH*^{C6F5}), 4.82/56.5 (*CH*$_2$), 2.38/21.6 (*CH*$_3$). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 2.38/(141.1, 129.3, 123.0) (C*H*$_3$/(*C*4, *C*3, *C*5)). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 36.6 ($v_{1/2}$ ~ 816 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -131.2 (m, 2F), -131.3 (m, 2F), -138.2 (m, 2F) (*o*-C_6F_5), -150.2 (t, $^3J_{FF}$ = 20.0 Hz, 1F), -151.1 (t, $^3J_{FF}$ = 20.0 Hz, 1F), -154.8 (t, $^3J_{FF}$ = 20.8 Hz, 1F) (*p*-C_6F_5), -160.3 (m, 2F), -160.6 (m, 2F), -161.6 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{28}H_8BF_{15}N^-$: 654.0516 [M-H]$^-$; found: 654.0521.

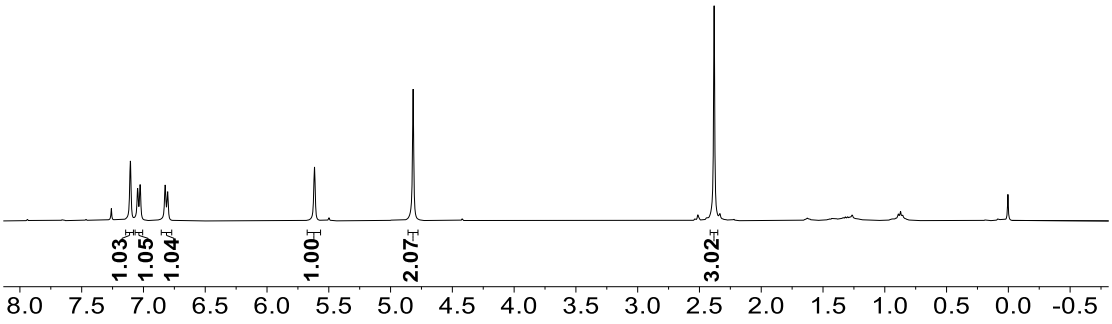


Fig. S6 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **2b**.

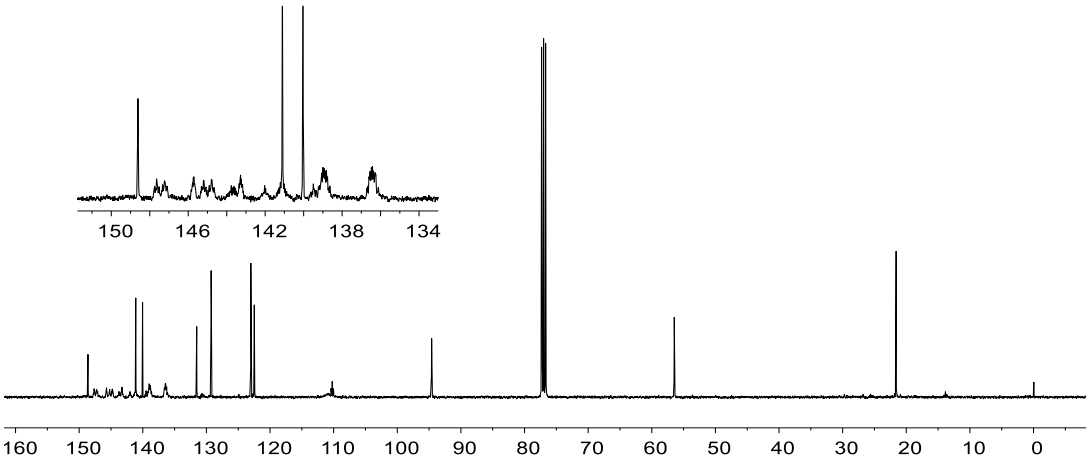


Fig. S7 ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **2b**.

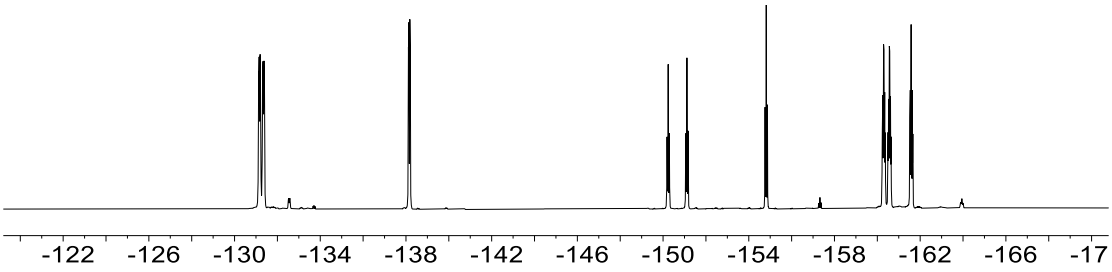


Fig. S8 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **2b**.

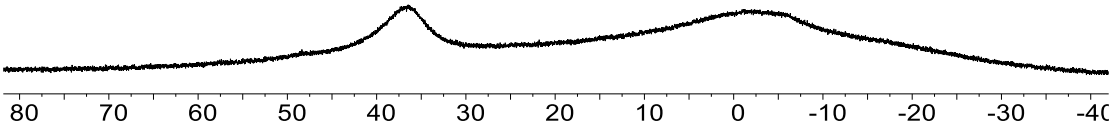
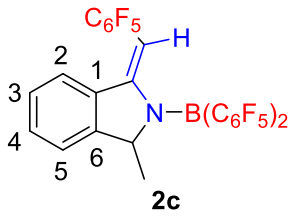


Fig. S9 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **2b**.

Synthesis and characterization of 2c



2c

According to the General procedure for **2** from compound **1c** (11.3 mg, 0.06 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (32 mg, 0.06 mmol, 1.0 equiv.), the product **2c** was obtained as a white solid (40.5 mg, 99% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.41 (m, 1H, *H*4), 7.29 (m, 1H, *H*5), 7.24 (m, 1H, *H*3), 6.93 (m, 1H, *H*2), 5.75 (s, 1H, =C*H*^{C6F5}), 4.93 (q, $^{3}J_{HH}$ = 6.5 Hz, 1H, C*H*^{CH3}), 1.49 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, CH_3^{CH}). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 147.7 (*C*=^{CHC6F5}), 145.9 (*C*6), 132.8 (*C*1), 130.5 (*C*4), 128.2 (*C*3), 122.7 (*C*2), 122.2 (*C*5), 97.4 (=*C*HC_6F_5), 63.5 (*C*H^{CH3}), 23.3 (*C*H_3^{CH}). **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: 6.93/122.7 (CH_2), 5.75/97.4 (=*CH*^{C6F5}), 4.93/63.5 (*CH*^{CH3}), 1.49/23.3 (*CH*$_3^{CH}$). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$:

(7.30 – 7.28 and 1.49)/63.5 (*H*5 and CH_3^{CH}/*C*H^{CH3}), 1.49/145.9 (CH_3^{CH}/*C*6). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 36.7 ($v_{1/2}$ ~ 652 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -128.8 (br, 1F), -129.7 (m, 1F), -132.4 (br, 1F), -132.8 (m, 1F), -138.4 (br, 2F) (*o*-C_6F_5), -151.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F), -151.4 (t, $^3J_{FF}$ = 20.0 Hz, 1F), -154.3 (t, $^3J_{FF}$ = 20.9 Hz, 1F) (*p*-C_6F_5), -160.1 (br, 2F), -160.5 (m, 1F), -160.7 (m, 1F), -161.3 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{28}H_8BF_{15}N^-$: 654.0516 [M-H]$^-$; found: 654.0522.

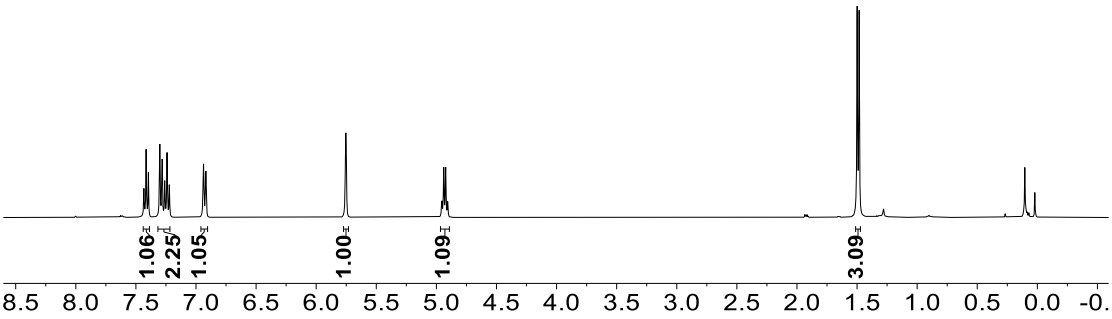


Fig. S10 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **2c**.

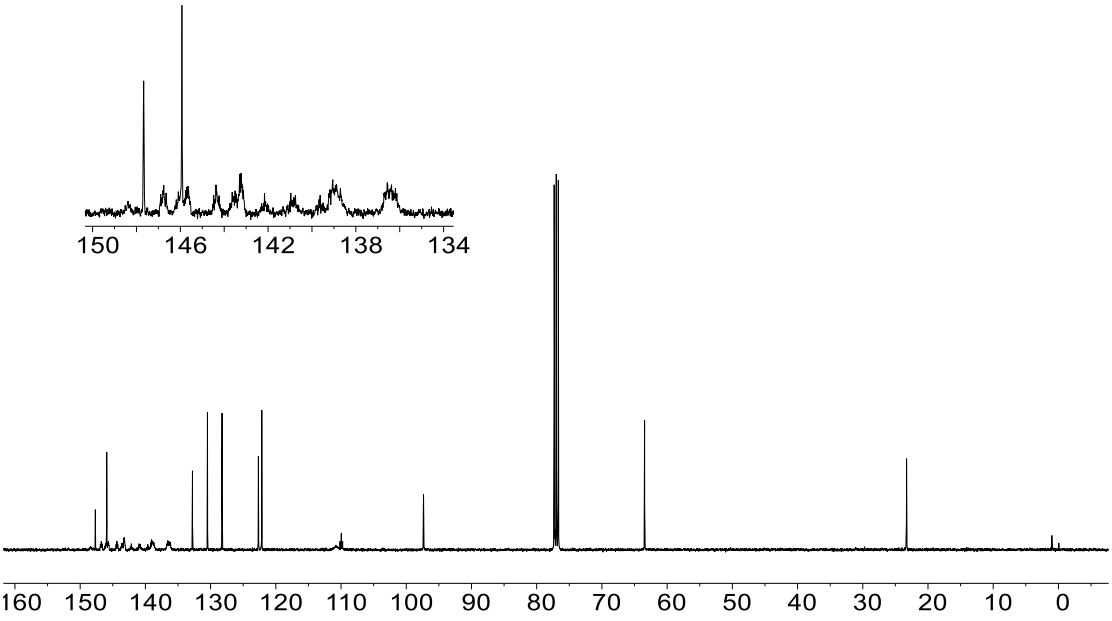


Fig. S11 ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **2c**.

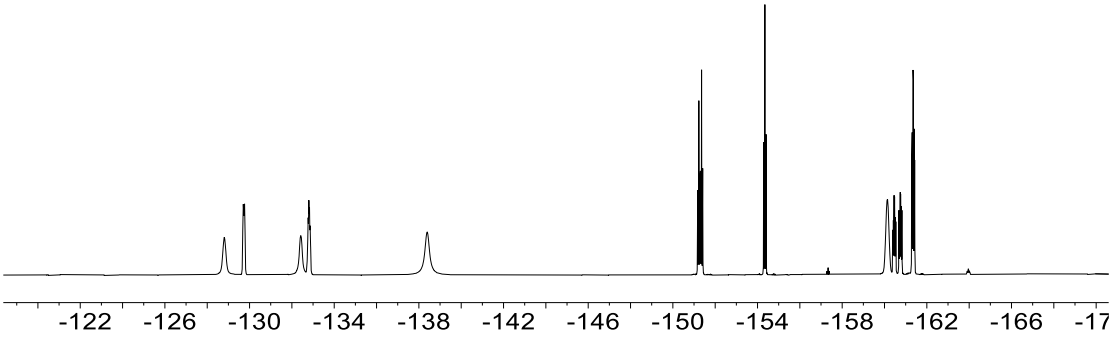


Fig. S12 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **2c**.

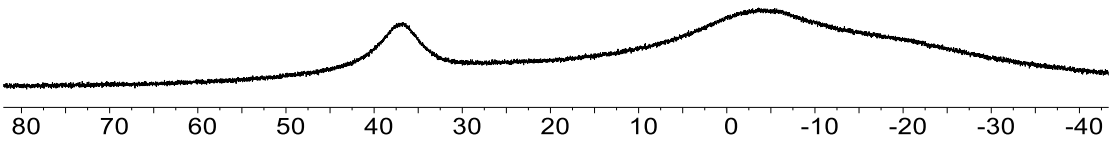
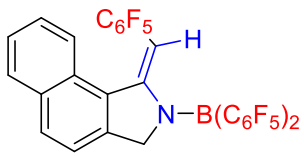


Fig. S13 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **2c**.

Synthesis and characterization of 2d



2d

According to the General procedure for **2** from compound **1d** (12.9 mg, 0.06 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (32 mg, 0.06 mmol, 1.0 equiv.), the product **2d** was obtained as a white solid (42.7 mg, 99% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.96 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, Ph), 7.91 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, Ph), 7.46 (m, 1H, Ph), 7.42 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, Ph), 7.21 (m, 1H, Ph), 6.99 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, Ph), 5.99 (s, 1H, =CH^{C6F5}), 4.95 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 149.3, 140.0, 133.3, 132.4, 131.0, 129.2, 126.8, 126.7, 126.2,

123.8, 119.6, 99.5 (=*C*H^{C6F5}), 56.6 (*C*H$_2$). **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: 5.99/99.5 (=*CH*^{C6F5}), 4.95/56.6 (*CH*$_2$). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 35.2 ($v_{1/2}$ ~ 868 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -130.8 (m, 2F), -131.6 (m, 2F), -138.3 (m, 2F) (*o*-C_6F_5), -150.2 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -151.1 (t, $^3J_{FF}$ = 19.8 Hz, 1F), -154.9 (t, $^3J_{FF}$ = 20.9 Hz, 1F) (*p*-C_6F_5), -160.4 (m, 2F), -160.7 (m, 2F), -162.1 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{31}H_8BF_{15}N^-$: 690.0516 [M-H]$^-$; found: 690.0519.

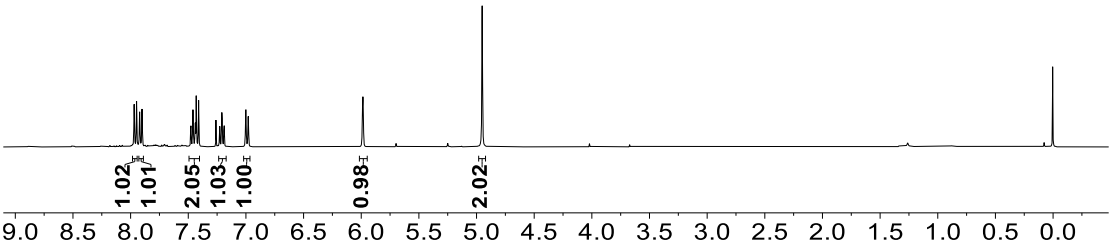


Fig. S14 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **2d**.

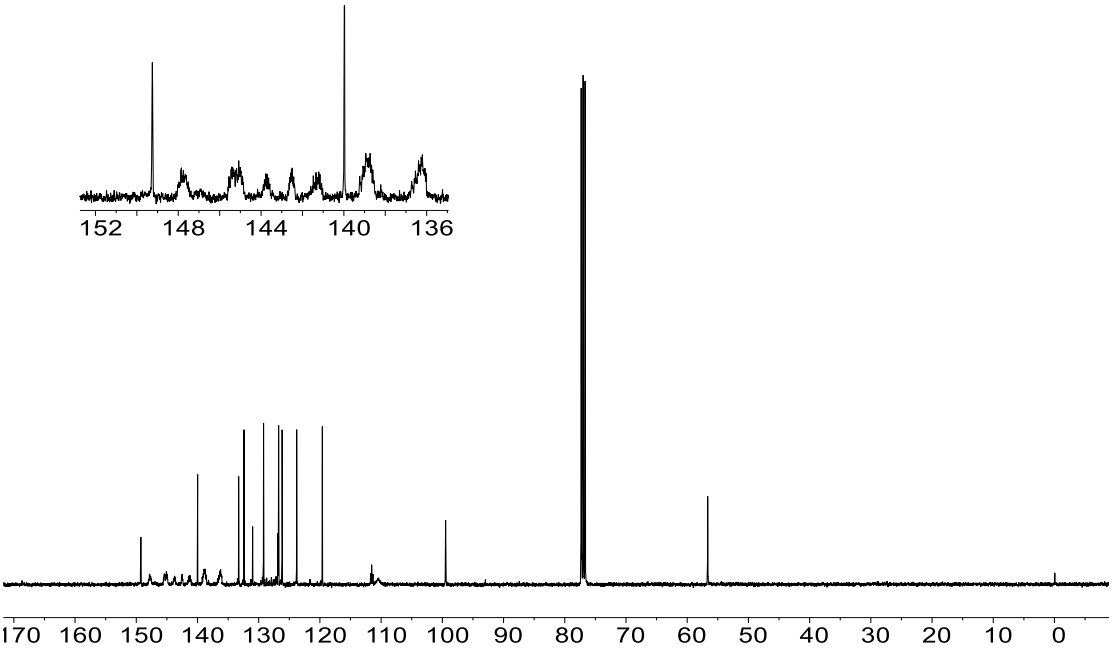


Fig. S15 ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **2d**.

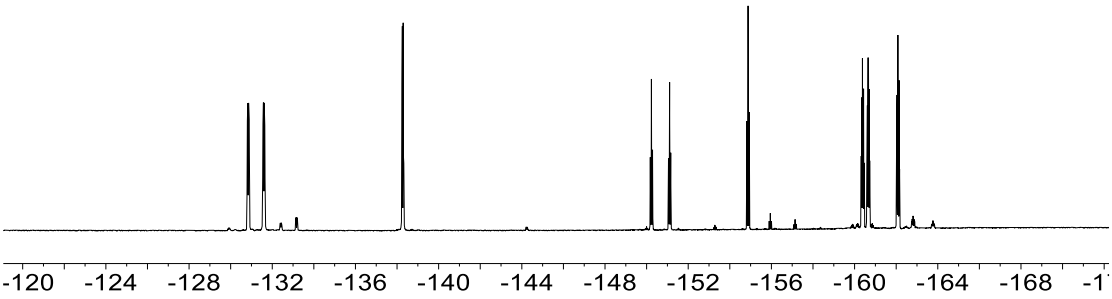


Fig. S16 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **2d**.

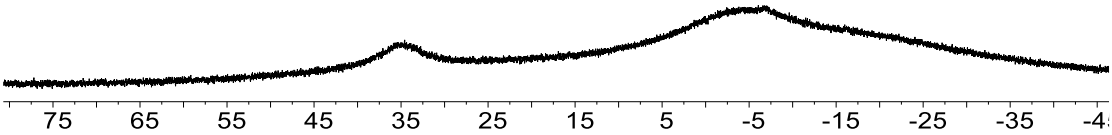
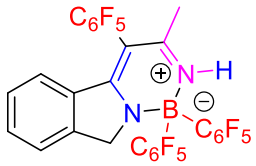


Fig. S17 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **2d**.

Synthesis and characterization of 3a



3a

According to the General procedure for **3** (Method A) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and dry acetonitrile (11.9 mg, 0.29 mmol, 1.0 equiv.), the product **3a** was obtained as a yellow solid (185.3 mg, 93% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.52 (m, 2H, Ph), 7.26 (m, 1H, Ph), 6.46 (m, 1H, Ph), 6.36 (br, 1H, N*H*), 4.62 (s, 2H, CH_2), 2.00 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 163.6 (C^{C6F5}), 163.3 ($C^{=CC6F5}$), 144.9, 134.2, 131.5, 128.3, 123.4, 122.9 (Ph), 82.9 (N=C^{CH3}), 56.5 (CH_2), 22.2 (CH_3) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: 4.62/56.5 (CH_2), 2.00/22.2 (CH_3). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz,

298 K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 6.36/(163.6, 82.9, 22.2) (N*H*/(*C*^{C6F5}, N=*C*^{CH3}, *C*H_3)), 4.62/163.3 (C*H*$_2$/*C*$^{=CC6F5}$), 2.00/(163.6, 82.9) (C*H*$_3$/(*C*^{C6F5}, N=*C*^{CH3})). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -4.2 ($v_{1/2}$ ~ 54 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -137.0 (m, 2F), -137.4 (m, 4F) (*o*-C_6F_5), -152.4 (t, $^3J_{FF}$ = 21.0 Hz, 1F), -156.8 (t, $^3J_{FF}$ = 20.3 Hz, 2F) (*p*-C_6F_5), -160.6 (m, 2F), -162.9 (m, 4F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{29}H_9BF_{15}N_2^-$: 681.0625 [M-H]$^-$; found: 681.0642.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **3a** in $CDCl_3$ covered with *n*-hexane at -25 ℃.

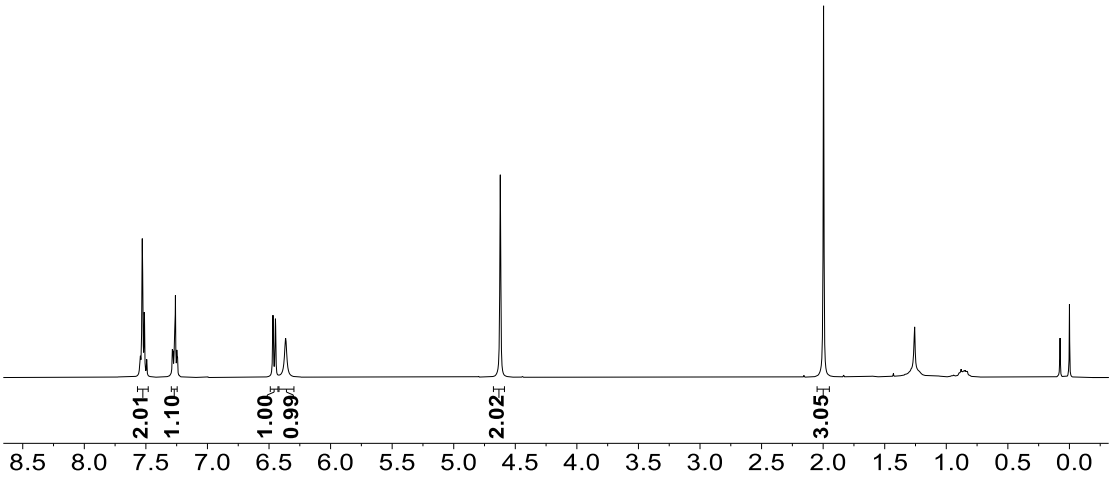


Fig. S18 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3a**.

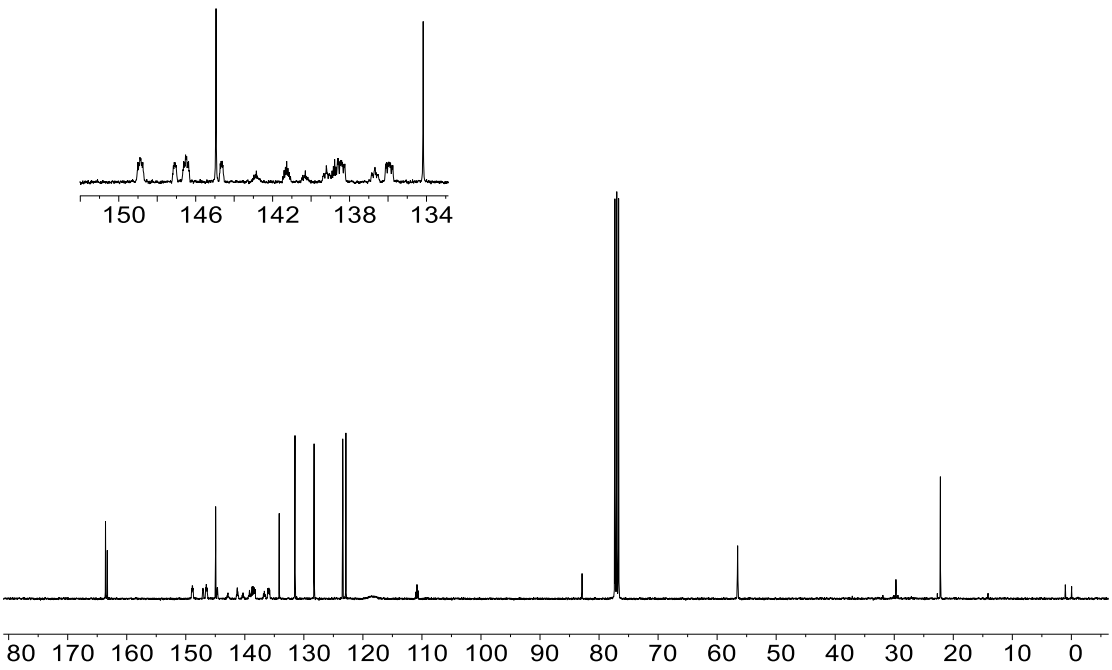


Fig. S19 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3a**.

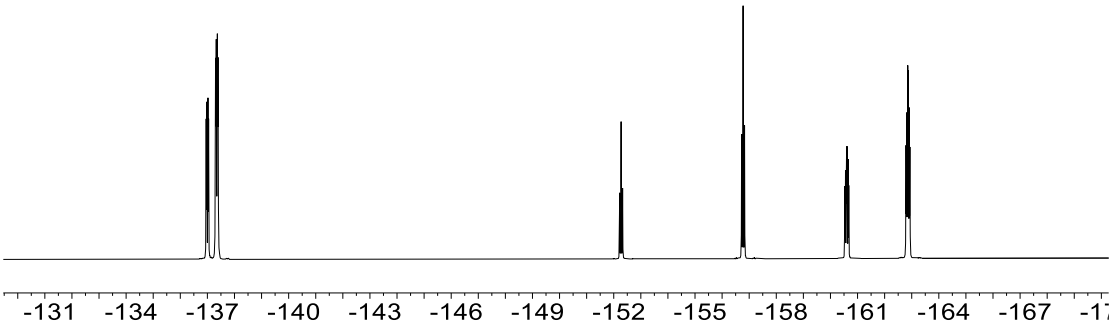


Fig. S20 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3a**.

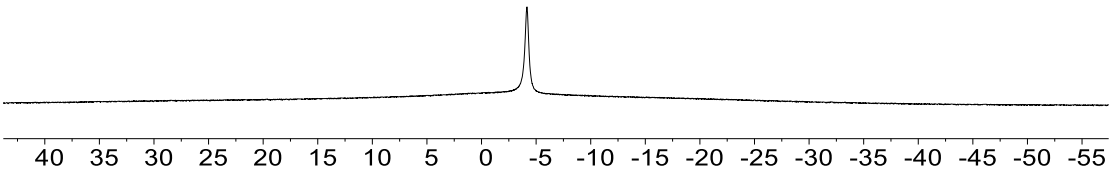


Fig. S21 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3a**.

X-ray crystal structure analysis of compound 3a • $CDCl_3$: formula $C_{30}H_{10}DBCl_3F_{15}N_2$, M = 801.57, yellow crystal, 0.32 × 0.23 × 0.22 mm, a = 34.981(5), b = 9.9268(14), c = 19.229(3) Å, α = γ = 90.000º, β = 109.205(4)º, V = 6305.7(16) $Å^3$, ρ_{calc} = 1.689 gcm^{-3}, μ = 0.407 mm^{-1}, empirical absorption correction (0.5778 ≤ T ≤ 0.7456), Z = 8, monoclinic, space group C2/c, λ = 0.71073 Å, T = 298.6 K, ω and φ scans, 35879 reflections collected (±h, ±k, ±l), 5547 independent (R_{int} = 0.1178) and 2520 observed reflections [I>2σ(I)], 462 refined parameters, R = 0.0770, wR^2 = 0.2212, max. (min.) residual electron density 0.51 (-0.54) e.$Å^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

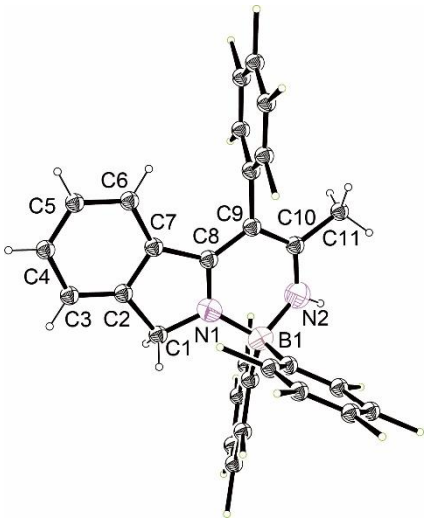
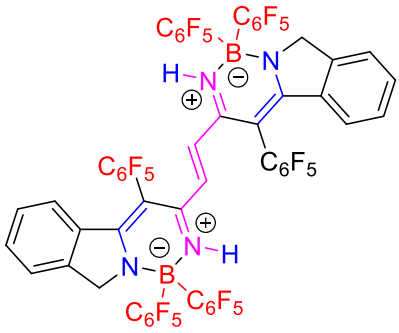


Fig. S22 A view of the molecular structure of compound **3a** (thermal ellipsoids are shown at the 50% probability level).

Synthesis and characterization of 3b



3b

According to the General procedure for **3** (Method B) from compound **1a** (46.0 mg, 0.29 mmol, 2.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 2.0 equiv.) and *trans*-2-butenedinitrile (11.3 mg, 0.15 mmol, 1.0 equiv.), the product **3b** was obtained as an orange solid (156.9 mg, 79% yield). **^{1}H NMR** (400 MHz, 298 K, DMSO-d_6): δ = 8.60 (s, 2H, N*H*), 7.67 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.59 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.34 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ph), 6.86 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ph), 6.59 (s, 2H, C*H*=), 4.67 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, DMSO-d_6): δ = 162.2, 157.9 (=C^{C6F5}), 145.2, 133.1, 131.7, 130.6 (*C*H=), 128.6, 123.9, 123.4, 82.3 (*C*=NH), 56.3 (*C*H_2) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, DMSO-d_6): δ^{1}H/δ^{13}C: 6.59/130.6 (*CH*=), 4.67/56.3 (*CH*$_2$). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, DMSO-d_6): δ^{1}H/δ^{13}C: 8.60/(157.9, 130.6, 82.3) (N*H*/(=C^{C6F5}, *C*H=, *C*=NH)), 6.59/157.9 (C*H*=/=C^{C6F5}). **^{11}B NMR** (128 MHz, 298 K, DMSO-d_6): δ = -4.1 ($\nu_{1/2}$ ~ 301 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, DMSO-d_6): δ = -136.2 (m, 4F), -138.9 (m, 2F) (*o*-C_6F_5), -153.1 (t, $^3J_{FF}$ = 22.1 Hz, 1F), -158.1 (t, $^3J_{FF}$ = 21.3 Hz, 2F) (*p*-C_6F_5), -162.1 (m, 2F), -164.3 (m, 4F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{58}H_{15}B_2F_{30}N_4^-$: 1359.1009 [M-H]$^-$; found: 1359.1000.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **3b** in dichloromethane covered with *n*-hexane at -25 ℃.

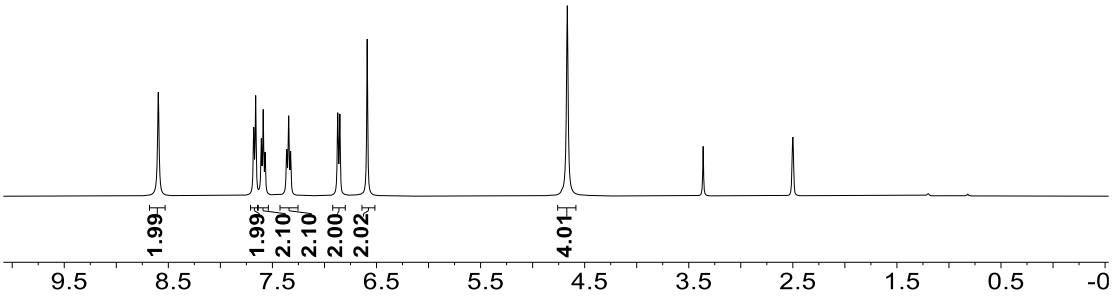


Fig. S23 ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) spectrum of compound **3b**.

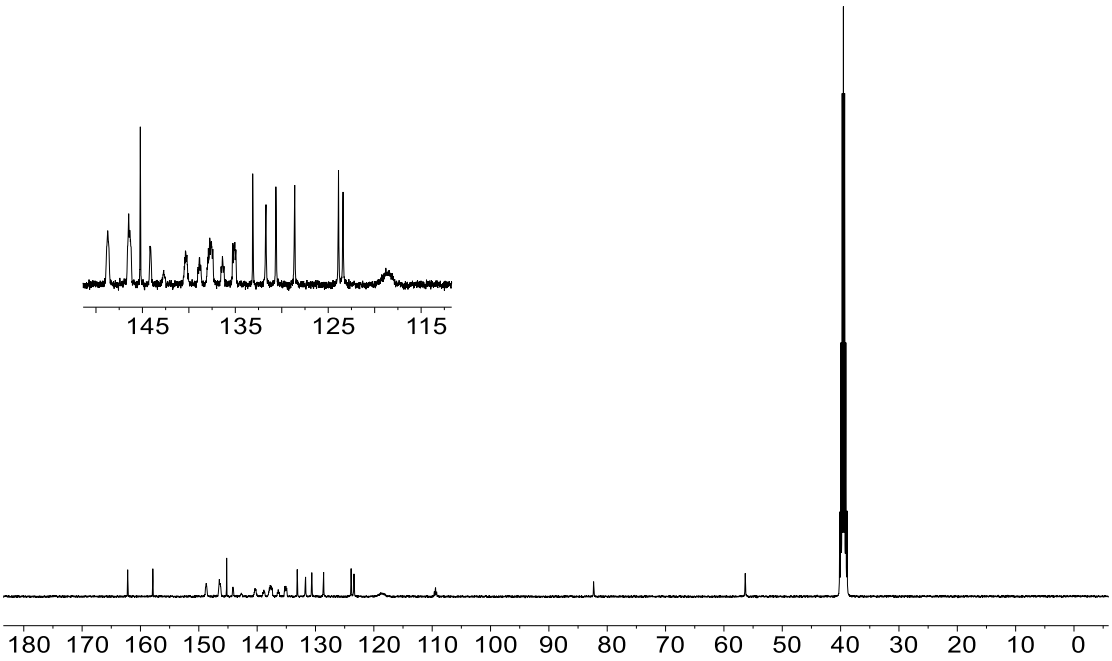


Fig. S24 ^{13}C{^{1}H} NMR (101 MHz, 298 K, DMSO-d_6) spectrum of compound **3b**.

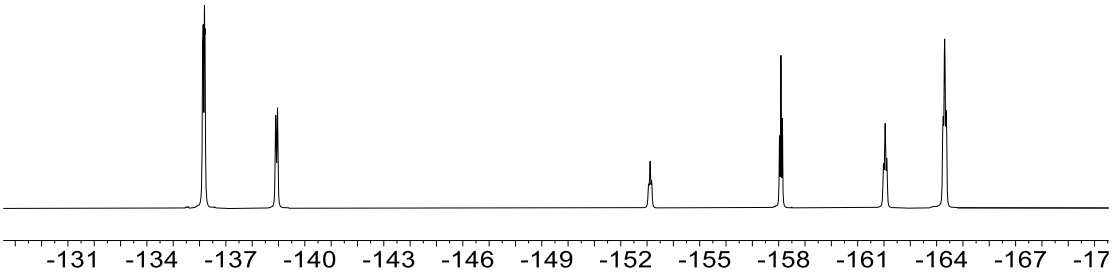


Fig. S25 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, DMSO-d_6) spectrum of compound **3b**.

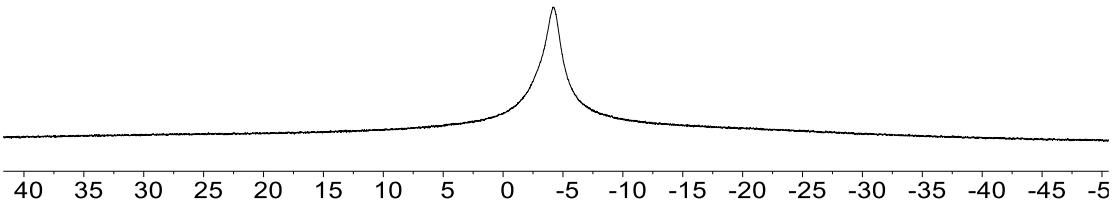


Fig. S26 ^{11}B NMR (128 MHz, 298 K, DMSO-d_6) spectrum of compound **3b**.

X-ray crystal structure analysis of 3b: formula $C_{58}H_{16}B_2F_{30}N_4$, M = 1360.36, yellow crystal, 0.12 × 0.10 × 0.08 mm, a = 13.6313(3), b = 19.4305(6), c = 24.1940(8) Å, α = γ = 90.000º, β = 99.003(3)º, V = 6329.1(3) Å^3, ρ_{calc} = 1.428 gcm^{-3}, μ = 1.323 mm^{-1}, empirical absorption correction (0.47492 ≤ T ≤ 1.00000), Z = 8, monoclinic, space group I2/a, λ = 1.54184 Å, T = 292.5(8) K, ω and φ scans, 31061 reflections collected (±h, ±k, ±l), 5772 independent (R_{int} = 0.0470) and 4186 observed reflections [I>2σ(I)], 424 refined parameters, R = 0.0714, wR^2 = 0.2472, max. (min.) residual electron density 0.68 (-0.37) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

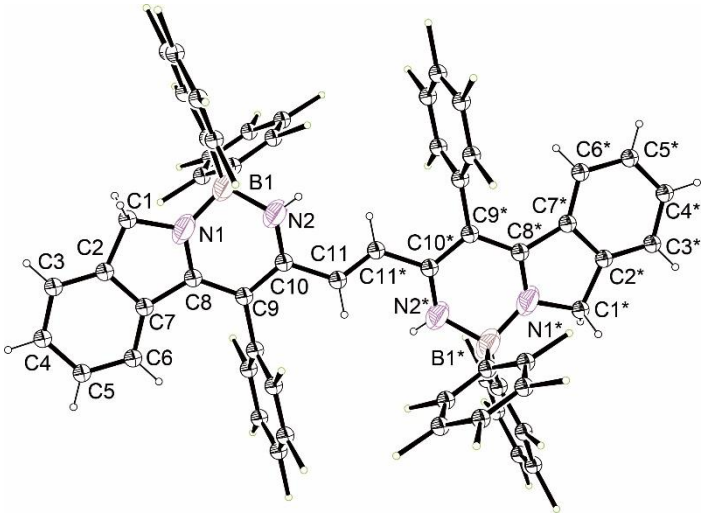
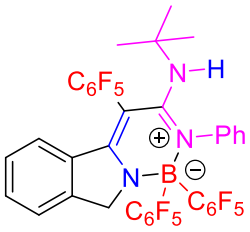


Fig. S27 A view of the molecular structure of compound **3b** (thermal ellipsoids are shown at the 50% probability level).

Synthesis and characterization of 3c



3c

According to the General procedure for **3** (Method A) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and *N*-*tert*-butyl-*N*'-phenylmethanediimine (50.5 mg, 0.29 mmol, 1.0 equiv.), the product **3c** was obtained as a yellow solid (157.9 mg, 66% yield, yellow solid). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ =7.48 (m, 2H, Ph), 7.27 (m, 1H, Ph), 7.13 (m, 3H, Ph), 7.06 (m, 2H, Ph), 6.61 (m, 1H, Ph), 4.51 (s, 2H, CH_2), 3.66 (s, 1H, N*H*), 0.68 (s, 9H, C(CH_3)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 162.6 ($C^{=CC6F5}$), 162.4, 145.2, 144.9, 134.7, 130.9, 128.5, 128.4, 128.0, 126.5, 123.2, 122.8, 79.5 (=C^{C6F5}), 56.3 (CH_2), 56.2 ($C^{(CH3)3}$), 29.8 (C(CH_3)$_3$) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^{1}H/δ^{13}C: 4.51/56.3 (CH_2), 0.68/29.8

(*CH*$_3$). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: 3.66/(79.5, 29.8) (N*H*/(*C*^{C6F5}, C(*C*H_3)$_3$)), 0.68/56.2 (C(C*H*$_3$)$_3$/*C*$^{(CH3)3}$). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -2.5 ($v_{1/2}$ ~ 89 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -132.7 (m, 4F), -135.0 (m, 2F) (*o*-C_6F_5), -152.01 (t, $^3J_{FF}$ = 21.0 Hz, 1F), -156.9 (t, $^3J_{FF}$ = 20.4 Hz, 2F) (*p*-C_6F_5), -160.4 (m, 2F), -164.0 (m, 4F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{38}H_{20}BF_{15}N_3^-$: 814.1516 [M-H]$^-$; found: 814.1506.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **3c** in dichloromethane covered with *n*-hexane at -25 °C.

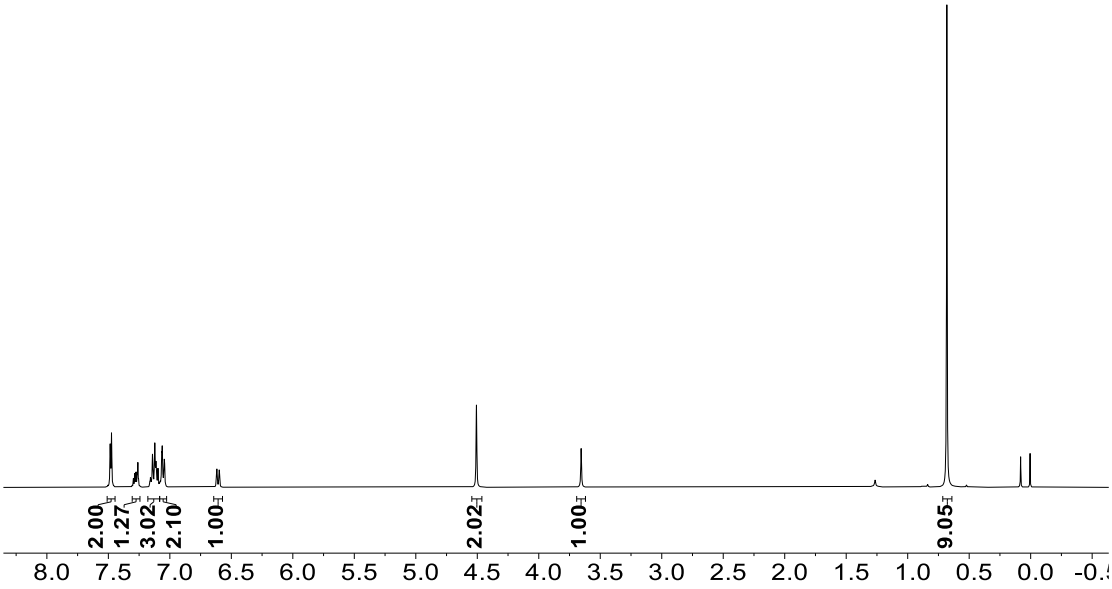


Fig. S28 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3c**.

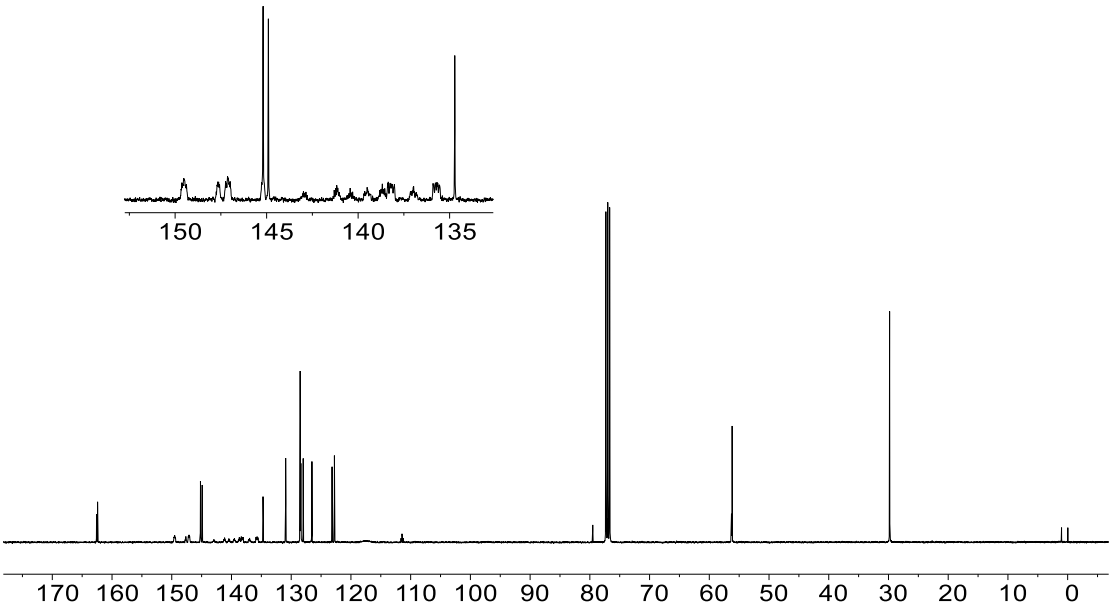


Fig. S29 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3c**.

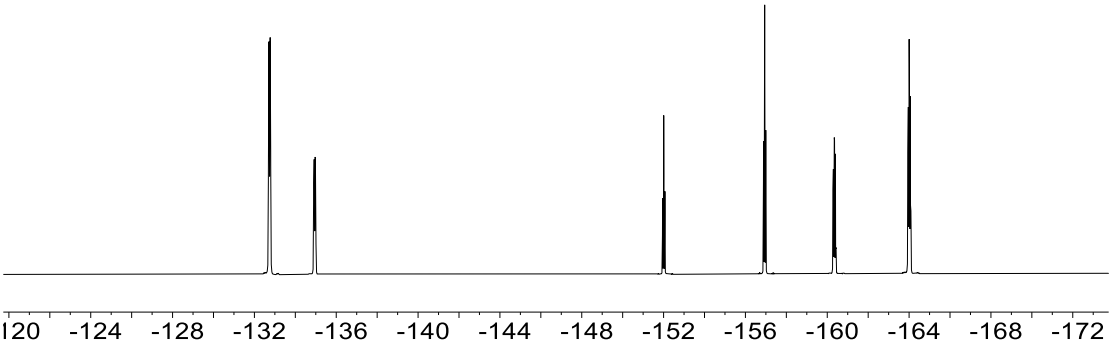


Fig. S30 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3c**.

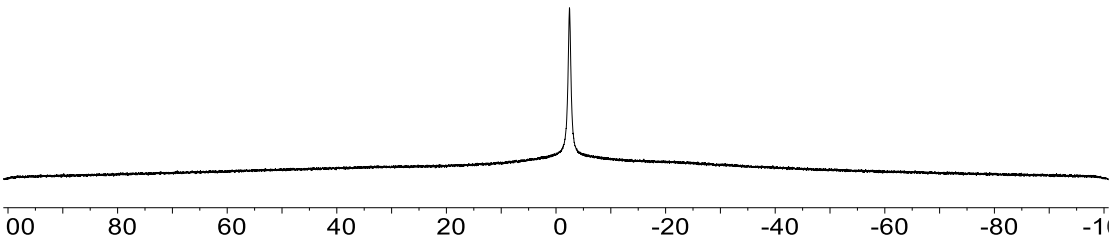


Fig. S31 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3c**.

X-ray crystal structure analysis of 3c: formula $C_{38}H_{21}BF_{15}N_3$, M = 815.39, yellow crystal, 0.19 × 0.16 × 0.12 mm, a = 12.1553(9), b = 18.4902(16), c = 15.9842(14) Å, α = γ = 90.000º, β = 111.521(2)º, V = 3342.1(5) $Å^3$, ρ_{calc} = 1.621 gcm^{-3}, μ = 0.154 mm^{-1}, empirical absorption correction (0.6956 ≤ T ≤ 0.7461), Z = 4, monoclinic, space group $P2_1/c$, λ = 0.71073 Å, T = 120.0 K, ω and φ scans, 44713 reflections collected (±h, ±k, ±l), 9881 independent (R_{int} = 0.0725) and 6630 observed reflections [I>2σ(I)], 517 refined parameters, R = 0.0508, wR^2 = 0.1291, max. (min.) residual electron density 0.63 (-0.69) e.$Å^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

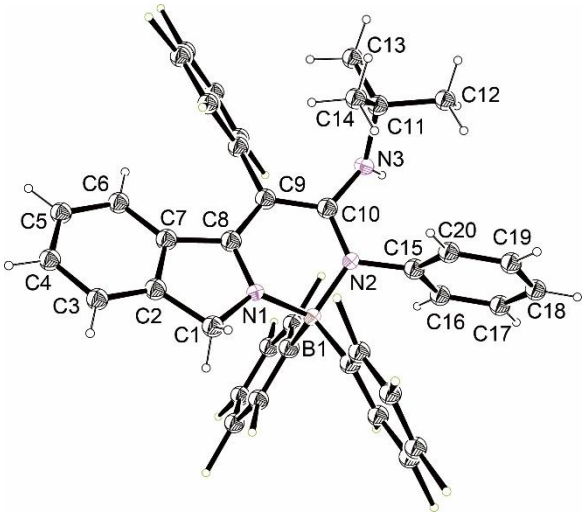
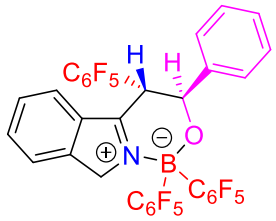


Fig. S32 A view of the molecular structure of compound **3c** (thermal ellipsoids are shown at the 50% probability level).

Synthesis and characterization of 3d



3d

According to the General procedure for **3** (Method B) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and benzaldehyde (30.8 mg, 0.29 mmol, 1.0 equiv.), the product **3d** was obtained as a white solid (171.0 mg, 78% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.71 (m, 2H, Ph), 7.43 (m, 1H, Ph), 7.28 (m, 3H, Ph), 7.18 (m, 2H, Ph), 6.91 (m, 1H, Ph), 5.44 and 4.70 (each d, each 1H, $^2J_{HH}$ = 23.2 Hz, CH_2), 4.86 (s, 2H, CH^{C6F5} and C*H*-O). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 177.7, 146.5, 139.8, 134.4, 133.9, 129.1, 128.6, 128.4, 126.3, 123.7, 123.3, 74.0 (*C*H-O), 60.6 (*C*H_2), 43.3 (*C*H^{C6F5}) [C_6F_5 not listed]. **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 0.9 ($\nu_{1/2}$ ~ 309 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -133.0 (m, 2F), -134.8 (m, 2F), -139.3 (m, 1F), -140.7 (m, 1F) (*o*-C_6F_5), -150.9 (t, $^3J_{FF}$ = 20.9 Hz, 1F), -156.1 (t, $^3J_{FF}$ = 20.2 Hz, 1F), -157.0 (t, $^3J_{FF}$ = 20.3 Hz, 1F) (*p*-C_6F_5), -159.4 (m, 2F), -162.9 (m, 2F), -163.4 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{34}H_{12}BF_{15}NO^-$: 746.0778 [M-H]$^-$; found: 746.0776.

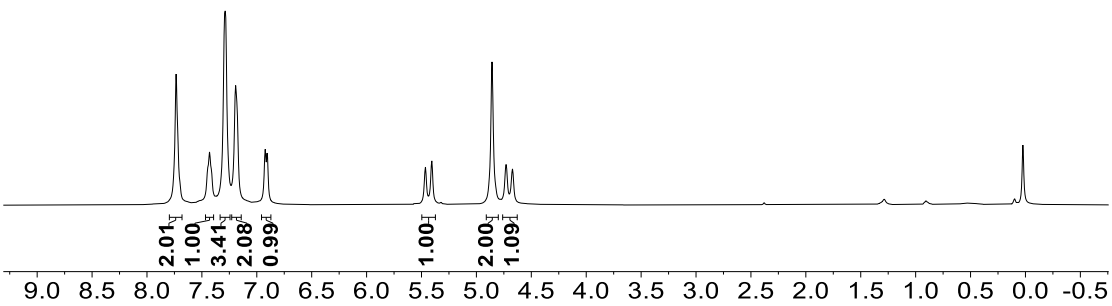


Fig. S33 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3d**.

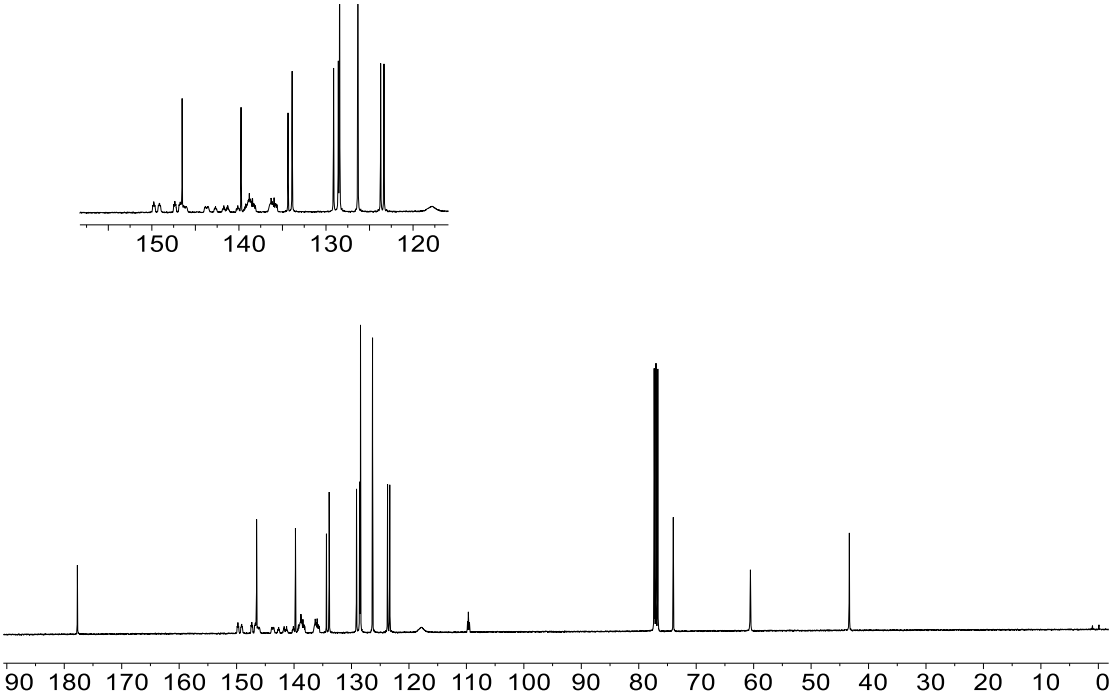


Fig. S34 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3d**.

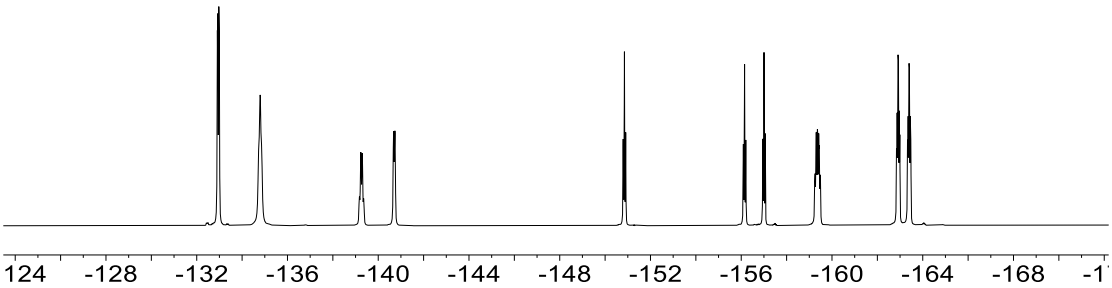


Fig. S35 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3d**.

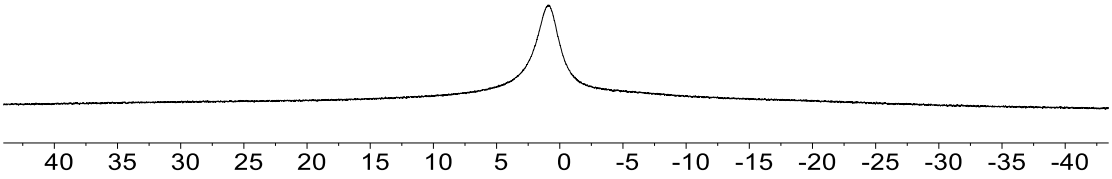
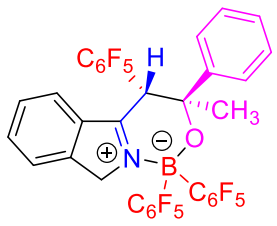


Fig. S36 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3d**.

Synthesis and characterization of 3e



3e

According to the General procedure for **3** (Method B) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and acetophenone (34.8 mg, 0.29 mmol, 1.0 equiv.), the product **3e** was obtained as a white solid (149.1 mg, 67% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.70 (m, 2H, Ph), 7.42 (m, 3H, Ph), 7.23 (m, 3H, Ph), 6.96 (m, 1H, Ph), 5.39 and 4.83 (each d, each $^2J_{HH}$ = 23.2 Hz, each 1H, CH_2), 5.17 (s, 1H, CH^{C6F5}), 1.46 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 177.4, 146.3, 144.7, 134.7, 133.9, 129.1, 128.0, 127.8, 125.5, 123.3, 123.3, 75.9 (*C*-O), 60.8 (*C*H_2), 45.1 (*C*H^{C6F5}), 23.6 (*C*H_3) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^{1}H/δ^{13}C: (5.39, 4.83)/60.8 (*C*H_2), 5.17/45.1 (*C*H^{C6F5}), 1.46/23.6 (*C*H_3). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.17/(75.9, 23.6) (CH^{C6F5}/(*C*-O, *C*H_3)). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -0.3 ($v_{1/2}$ ~ 203 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -133.6 (br, 4F), -135.6 (m, 1F), -138.6 (m, 1F) (*o*-C_6F_5), -150.8 (t, $^3J_{FF}$ = 21.1 Hz, 1F), -157.0 (t, $^3J_{FF}$ = 20.5 Hz, 1F), -157.6 (t, $^3J_{FF}$ = 20.3 Hz, 1F) (*p*-C_6F_5), -159.4 (m, 1F), -159.7 (m, 1F), -163.2 (m, 2F), -163.5 (br, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{35}H_{14}BF_{15}NO^-$: 760.0934 [M-H]$^-$; found: 760.0932.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **3e** in dichloromethane covered with *n*-hexane at -25 ℃.

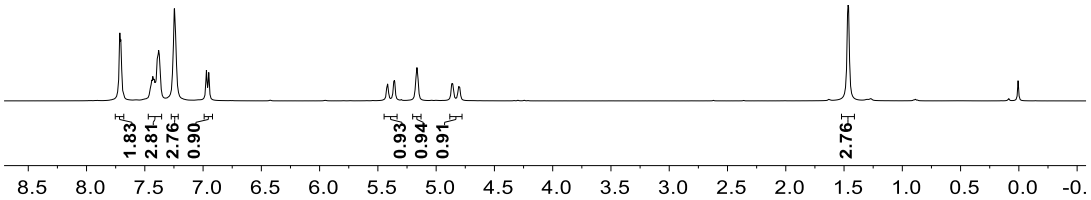


Fig. S37 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3e**.

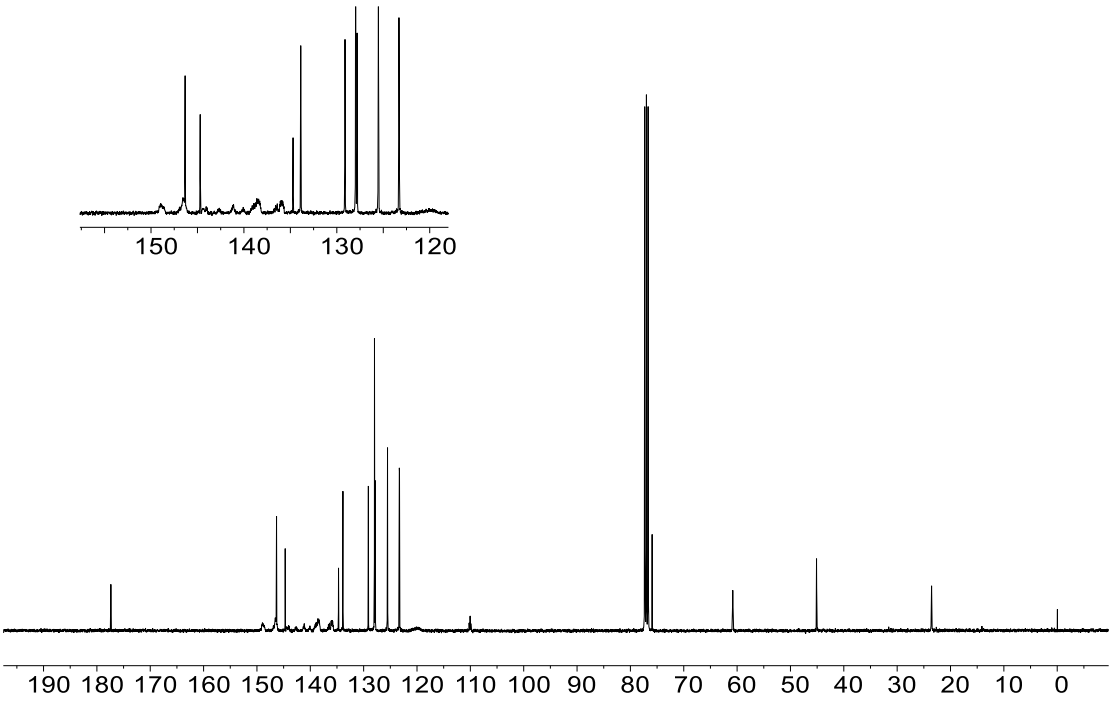


Fig. S38 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3e**.

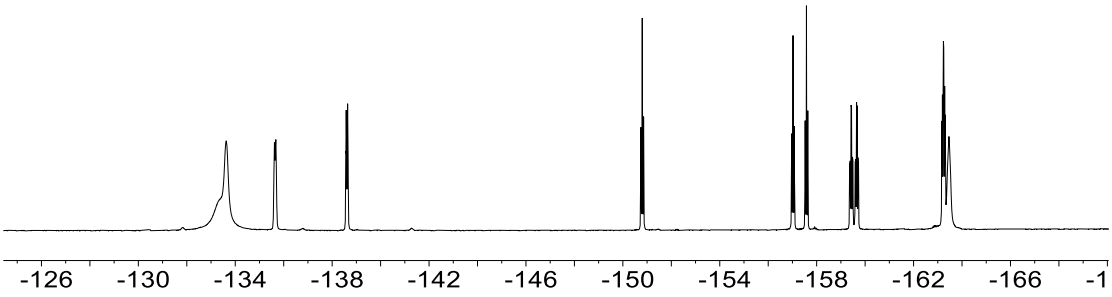


Fig. S39 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3e**.

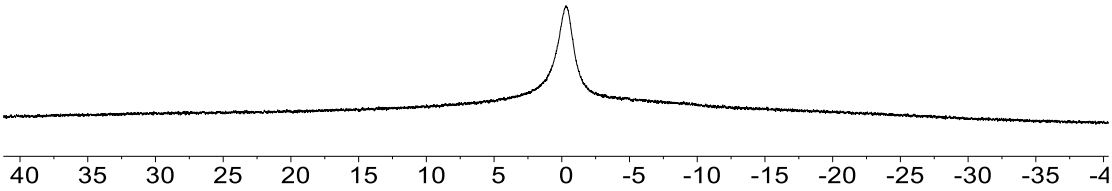


Fig. S40 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3e**.

X-ray crystal structure analysis of 3e: formula $C_{35}H_{15}BF_{15}NO$, M = 761.29, yellow crystal, 0.2 × 0.17 × 0.1 mm, a = 10.78652(15), b = 21.7974(3), c = 17.9089(2) Å, α = γ = 90.000º, β = 105.2648(14)º, V = 4062.16(9) $Å^3$, ρ_{calc} = 1.245 gcm^{-3}, μ = 1.097 mm^{-1}, empirical absorption correction (0.43896 ≤ T ≤ 1.00000), Z = 4, monoclinic, space group $P2_1/n$, λ = 1.54184 Å, T = 300.15 K, ω and φ scans, 21384 reflections collected (±h, ±k, ±l), 7334 independent (R_{int} = 0.0191) and 6030 observed reflections [I>2σ(I)], 579 refined parameters, R = 0.0494, wR^2 = 0.1578, max. (min.) residual electron density 0.18 (-0.20) e.$Å^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

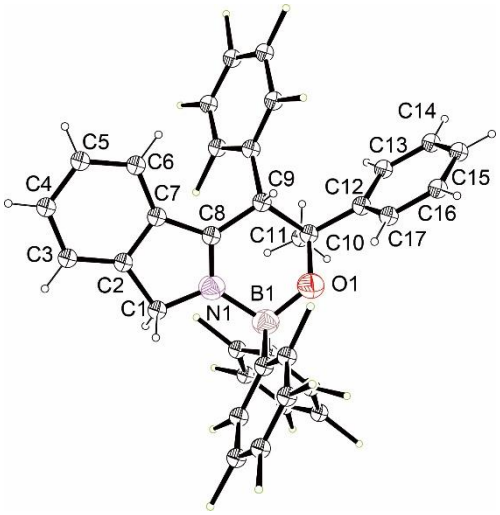
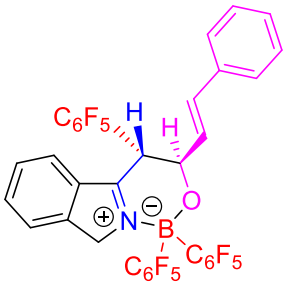


Fig. S41 A view of the molecular structure of compound **3e** (thermal ellipsoids are shown at the 50% probability level).

Synthesis and characterization of 3f



3f

According to the General procedure for **3** (Method A) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and trans-cinnamaldehyde (38.3 mg, 0.29 mmol, 1.0 equiv.), the product **3f** was obtained as a white solid (136.7 mg, 60% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.71 (m, 2H, Ph), 7.44 (m, 1H, Ph), 7.23 (m, 6H, Ph), 6.97 (m, 1H, Ph), 6.41 (d, $^3J_{HH}$ = 15.7 Hz, 1H, =C*H*Ph), 6.23 (dd, $^3J_{HH}$ = 15.7 and 6.9 Hz, 1H, C*H*$^{=CHPh}$), 5.40 and 4.66 (each d, each $^2J_{HH}$ = 23.2 Hz and $^5J_{HH}$ = 3.3 Hz, each 1H, CH_2), 4.82 (dt, $^3J_{HH}$ = 7.1 Hz and $^5J_{HH}$ = 3.3 Hz 1H, C*H*^{C6F5}), 4.51 (t, $^3J_{HH}$ = 7.1 Hz, 1H, C*H*-O). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 177.7, 146.4, 135.8, 134.4, 133.9, 133.8 (=*C*HPh), 129.2, 128.5, 128.1, 126.7, 126.7 (*C*H$^{=CHPh}$), 123.6, 123.3, 72.6 (*C*H-O), 60.7 (*C*H_2), 41.2 (*C*H^{C6F5}) [C_6F_5 not

listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: 6.41/133.8 (=*CH*Ph), 6.23/126.7 (*CH*$^{=CHPh}$), (5.40, 4.66)/60.7 (*CH*$_2$), 4.82/41.2 (*CH*^{C6F5}), 4.51/72.6 (*CH*-O). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: 4.51/133.8 (C*H*-O/=*C*HPh). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 0.7 ($v_{1/2}$ ~ 288 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -133.2 (m, 2F), -134.8 (m, 2F), -139.0 (br, 1F), -140.2 (br, 1F) (*o*-C_6F_5), -150.5 (t, $^3J_{FF}$ = 21.0 Hz, 1F), -155.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -156.7 (t, $^3J_{FF}$ = 20.3 Hz, 1F) (*p*-C_6F_5), -158.6 (br, 1F), -158.9 (br, 1F), -162.7 (m, 2F), -163.3 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{36}H_{14}BF_{15}NO^-$: 772.0934 $[M-H]^-$; found: 772.0933.

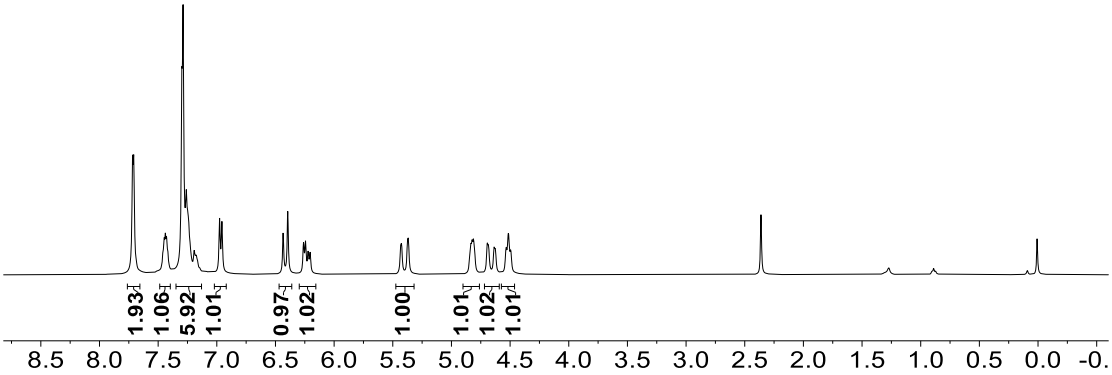


Fig. S42 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3f**.

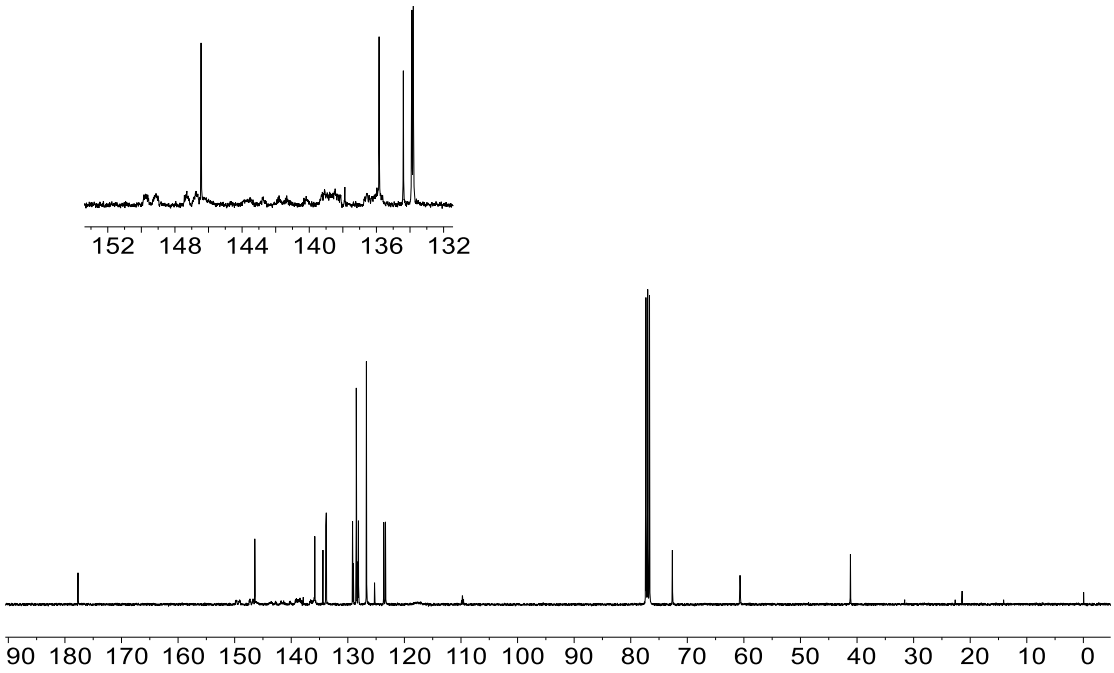


Fig. S43 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3f**.

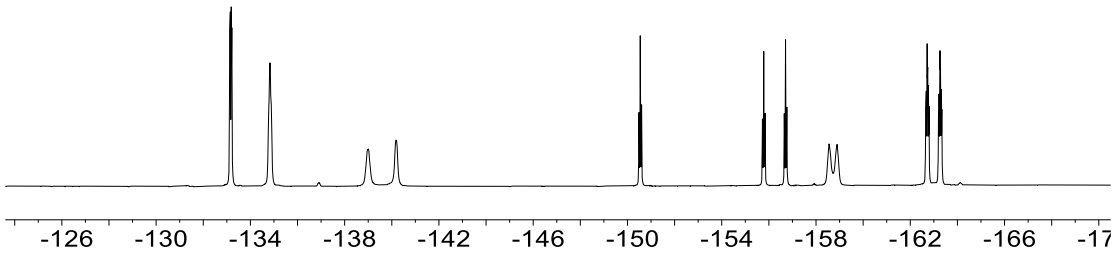


Fig. S44 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3f**.

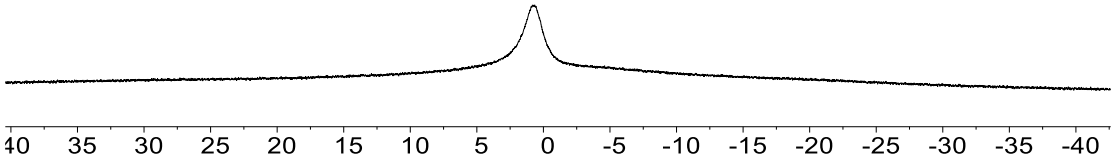
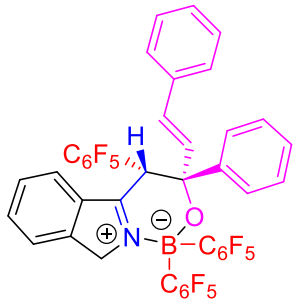


Fig. S45 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3f**.

Synthesis and characterization of 3g



3g

According to the General procedure for **3** (Method B) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and trans-chalcone (60.4 mg, 0.29 mmol, 1.0 equiv.), the product **3g** was obtained as a white solid (157.1 mg, 63% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.78 (m, 2H, Ph), 7.59 (m, 2H, Ph), 7.29 – 6.97 (m, 11H, Ph and =C*H*), 6.21 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =C*H*), 5.70 (s, 1H, C*H*^{C6F5}), 5.40 and 4.95 (each d, each 1H, $^2J_{HH}$ = 23.0 Hz, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 176.3, 146.7, 141.4, 136.5, 134.4, 134.3, 131.5 (=*C*H), 130.5, 129.3, 128.5, 127.9, 127.7, 127.3, 127.2, 126.4, 123.4, 123.0, 77.8 (*C*-O), 61.6 (*C*H_2), 39.2 (*C*H^{C6F5}) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^{1}H/δ^{13}C: 6.21/131.5 (=*CH*), 5.70/39.2 (*CH*^{C6F5}), 5.40 and 4.95/61.6 (*CH*$_2$). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^{1}H/δ^{13}C: (6.21, 5.70)/77.8 ((=C*H*, C*H*^{C6F5})/*C*-O). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 0.4 ($\nu_{1/2}$ ~ 304 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -131.7 (br, 2F), -134.0 (br, 2F), -138.3 (m, 1F), -140.8 (br, 1F) (*o*-C_6F_5), -151.3 (t, $^3J_{FF}$ = 21.2 Hz, 1F), -157.2 (t, $^3J_{FF}$ = 20.5 Hz, 1F), -159.1 (t, $^3J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5), -159.9 (m, 1F), -161.1 (m, 1F), -163.5 (br, 2F), -164.9 (br, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{42}H_{18}BF_{15}NO^-$: 848.1247 [M-H]$^-$; found: 848.1249.

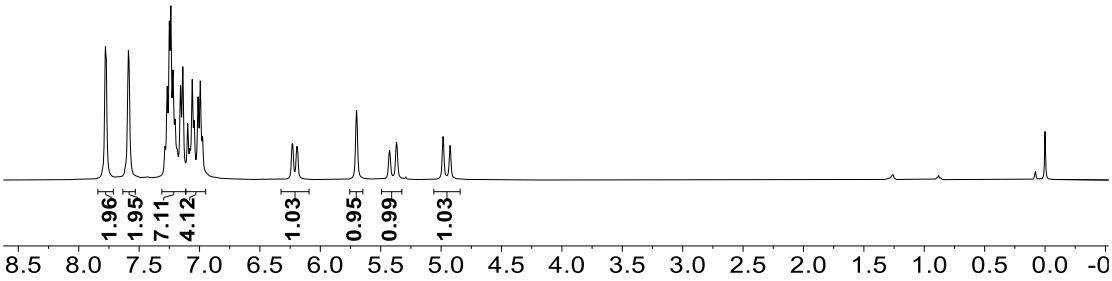


Fig. S46 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3g**.

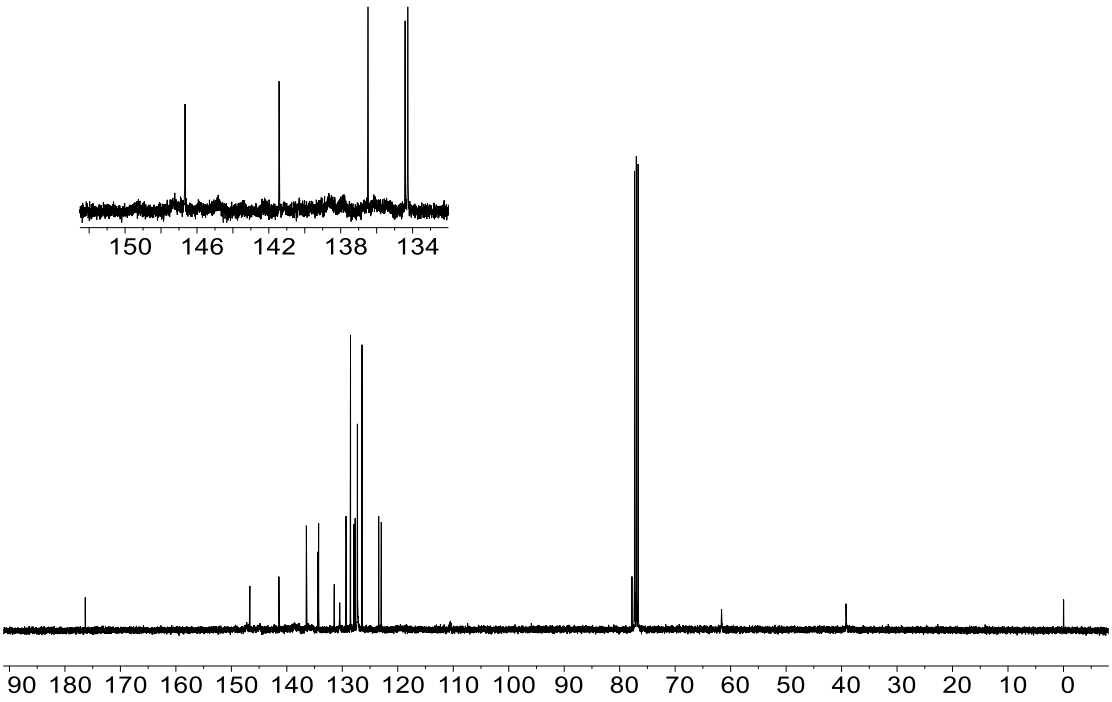


Fig. S47 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3g**.

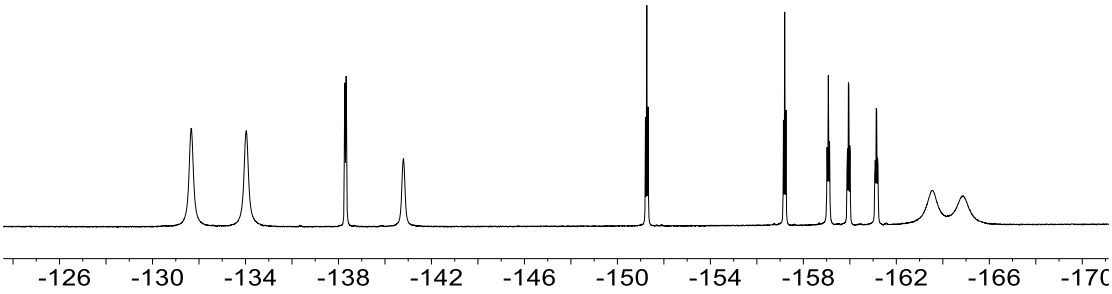


Fig. S48 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3g**.

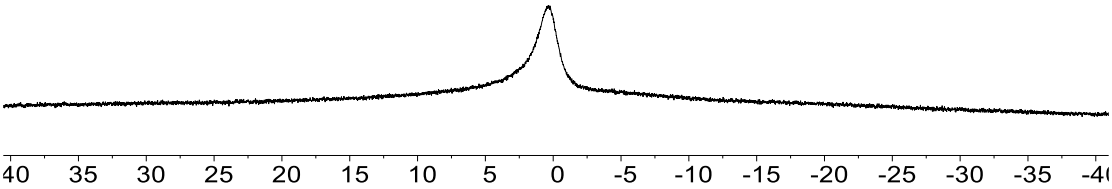
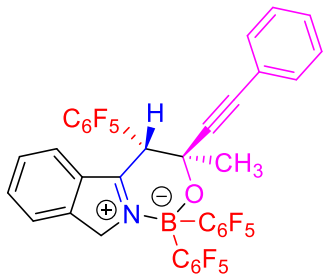


Fig. S49 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3g**.

Synthesis and characterization of 3h



3h

According to the General procedure for **3** (Method B) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and 4-phenyl-3-butyn-2-one (41.8 mg, 0.29 mmol, 1.0 equiv.), the product **3h** was obtained as a pink solid (129.0 mg, 56% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.71 (m, 2H, Ph), 7.44 (m, 1H, Ph), 7.23 (m, 3H, Ph), 6.97 (m, 3H, Ph), 5.51and 4.60 (each dd, each $^2J_{HH}$ = 23.2 Hz and $^5J_{HH}$ = 3.3 Hz, each 1H, CH_2), 4.95 (t, $^5J_{HH}$ = 3.3 Hz, 1H, CH^{C6F5}), 1.81 (d, $^4J_{HH}$ = 3.0 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 176.5, 146.0, 134.8, 133.8, 130.8, 129.1, 128.7, 128.2, 123.4, 123.2, 121.3, 87.7 ($C{\equiv}^{CPh}$), 86.7 ($^{C}{\equiv}C$Ph), 69.2, 60.9 (CH_2), 46.0 (CH^{C6F5}), 31.8 (CH_3) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: (5.51, 4.60)/69.2 (CH_2), 4.95/46.0 (CH^{C6F5}) 1.81/31.8 (CH_3). **^{1}H, ^{13}C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ^1H/δ^{13}C: (4.95, 1.81)/87.7 ((CH^{C6F5},

CH_3)/$C\equiv^{CPh}$). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -0.3 ($\nu_{1/2}$ ~ 214 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -130.0 (m, 1F), -133.7 (m, 2F), -134.8 (br, 2F), -139.3 (m, 1F) (*o*-C_6F_5), -150.3 (t, $^3J_{FF}$ = 21.1 Hz, 1F), -156.1 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -158.4 (t, $^3J_{FF}$ = 20.1 Hz, 1F) (*p*-C_6F_5), -159.2 (m, 1F), -160.1 (m, 1F), -162.8 (m, 2F), -165.2 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{37}H_{14}BF_{15}NO^-$: 784.0934 [M-H]$^-$; found: 784.0930.

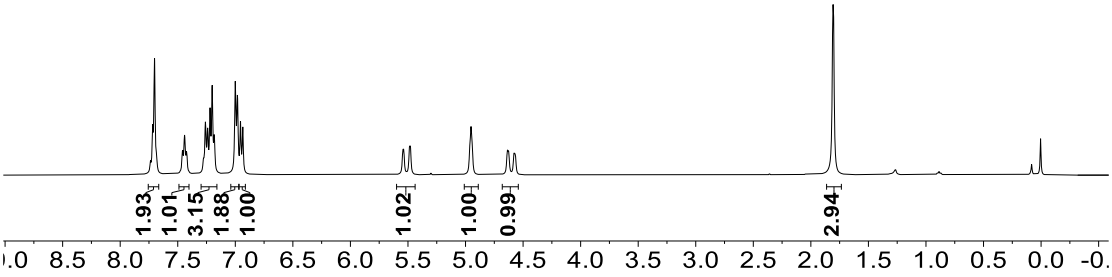


Fig. S50 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3h**.

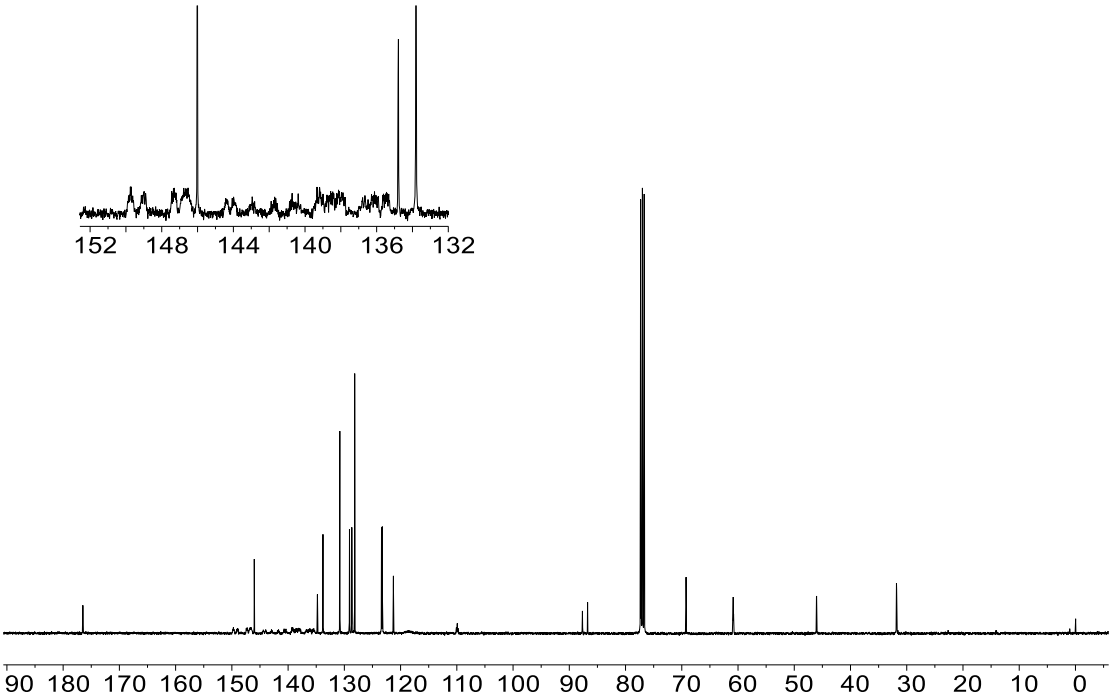


Fig. S51 ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3h**.

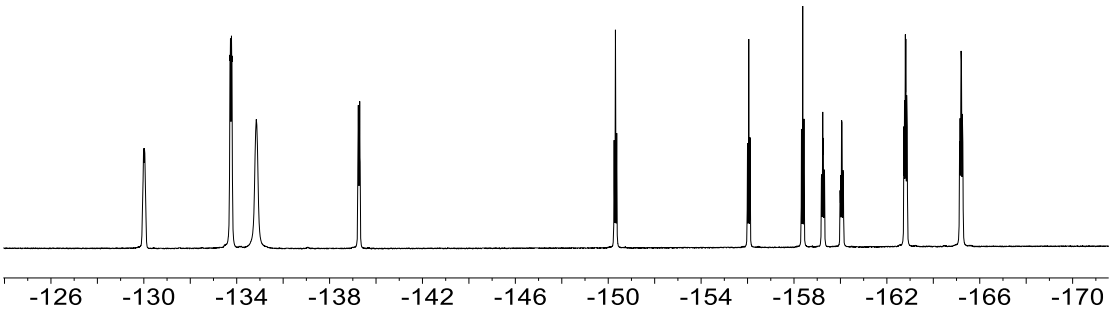


Fig. S52 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3h**.

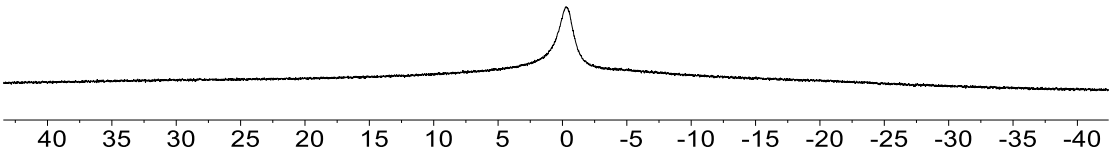
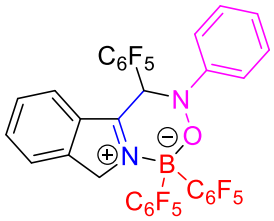


Fig. S53 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3h**.

Synthesis and characterization of 3i



3i

According to the General procedure for **3** (Method A) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and nitrosobenzene (31.0 mg, 0.29 mmol, 1.0 equiv.), the product **3i** was obtained as a yellow solid (141.6 mg, 65% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.79 (m, 2H, Ph), 7.54 (m, 1H, Ph), 7.46 (br, 1H, Ph), 7.26 (m, 4H, Ph), 7.06 (br, 1H, Ph), 6.52 (br, 1H, C*H*^{C6F5}), 5.54 and 5.08 (each br, each 1H, C*H*$_2$). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 175.7, 147.2, 134.2, 132.9, 129.3, 128.6, 123.5, 122.9, 60.8 (*C*H$_2$), 57.5 (*C*H^{C6F5}) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: (5.54, 5.08)/60.8 (*CH*$_2$), 6.52/57.5

(*CH*^{C6F5}). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 2.4 ($v_{1/2}$ ~ 333 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -130.3 (br, 2F), -135.5 (br, 2F), -137.2 (br, 2F) (*o*-C_6F_5), -149.7 (br, 1F), -156.3 (br, 1F), -158.2 (br, 1F) (*p*-C_6F_5), -159.9 (br, 2F), -163.0 (br, 2F), -164.2 (br, 2F) (*m*-C_6F_5). [**Comment**: The ^{1}H and ^{19}F NMR signals are broad rendering an unambiguous assignment difficult.] **HRMS (ESI)**: m/z calcd. for $C_{33}H_{11}BF_{15}N_2O^-$: 747.0730 [M-H]$^-$; found: 747.0740.

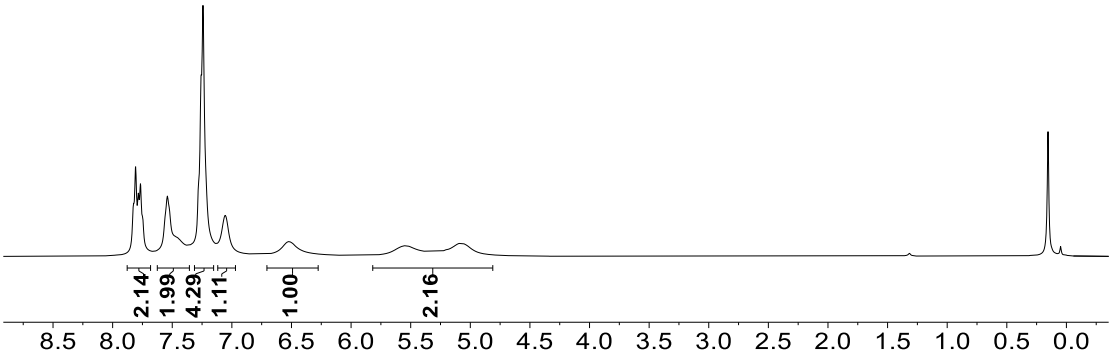


Fig. S54 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3i**.

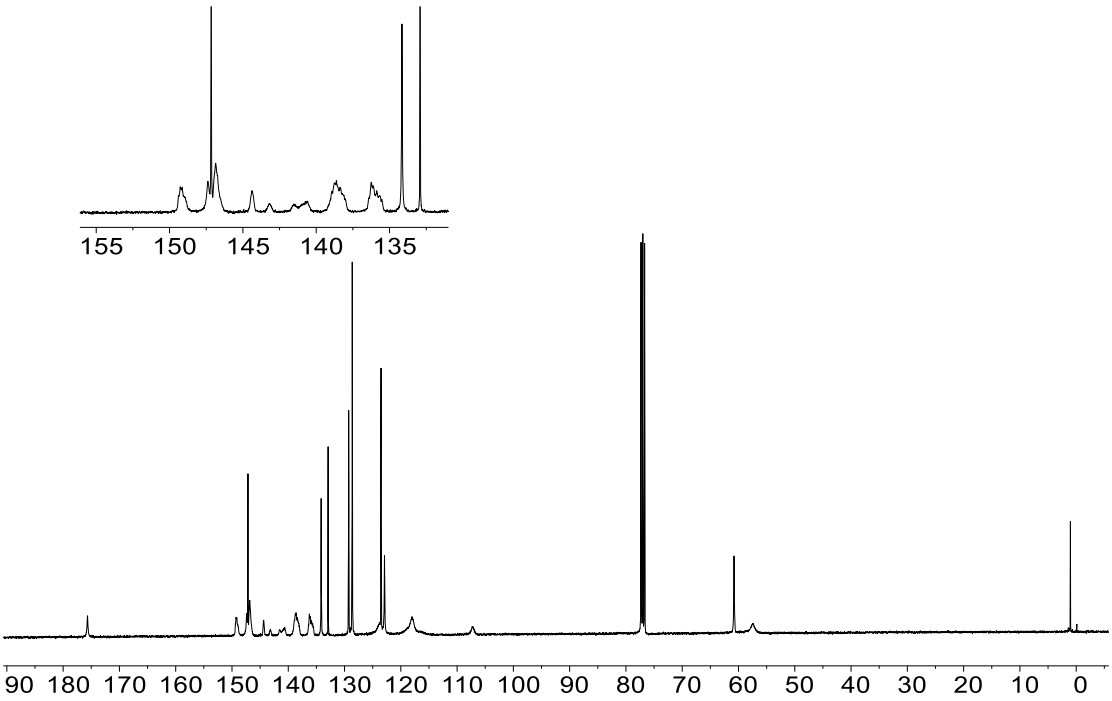


Fig. S55 ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3i**.

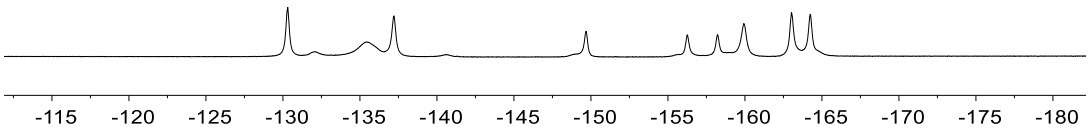


Fig. S56 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3i**.

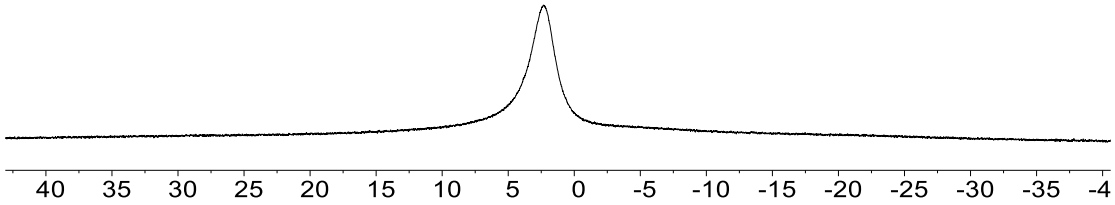
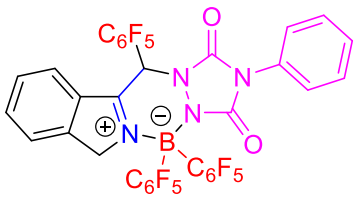


Fig. S57 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3i**.

Synthesis and characterization of 3j



3j

According to the General procedure for **3** (Method B) from compound **1a** (46.0 mg, 0.29 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 1.0 equiv.) and 4-phenyl-1,2,4-triazoline-3,5-dione (50.8 mg, 0.29 mmol, 1.0 equiv.), the product **3j** was obtained as a yellow solid (142.1 mg, 59% yield). **^{1}H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.82 (m, 2H), 7.57 (m, 1H), 7.42 (m, 4H), 7.33 (m, 2H), 6.76 (s, 1H, CH^{C6F5}), 5.34 and 5.23 (each d, each $^{2}J_{HH}$ = 23.3 Hz, each 1H, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 173.3, 154.8, 151.9, 146.7, 135.3, 131.7, 130.8, 130.0, 129.1, 128.4, 125.8, 123.7, 123.7, 62.0 (*C*H_2), 50.5

(*C*H^{C6F5}) [C_6F_5 not listed]. **^{1}H, ^{13}C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: 6.76/50.5 (*CH*^{C6F5}), (5.34, 5.23)/62.0 (*CH_2*). **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -4.5 ($v_{1/2}$ ~ 302 Hz). **^{19}F{^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -134.9 (m, 2F), -135.5 (m, 2F), -139.0 (m, 2F) (*o*-C_6F_5), -147.7 (t, $^{3}J_{FF}$ = 21.0 Hz, 1F), -154.37 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -154.43 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F) (*p*-C_6F_5), -158.5 (m, 2F), -161.9 (m, 2F), -162.4 (m, 2F) (*m*-C_6F_5). **HRMS (ESI)**: m/z calcd. for $C_{35}H_{11}BF_{15}N_4O_2^-$: 815.0741 [M-H]$^-$; found: 815.0742.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **3j** in dichloromethane covered with *n*-hexane at -25 °C.

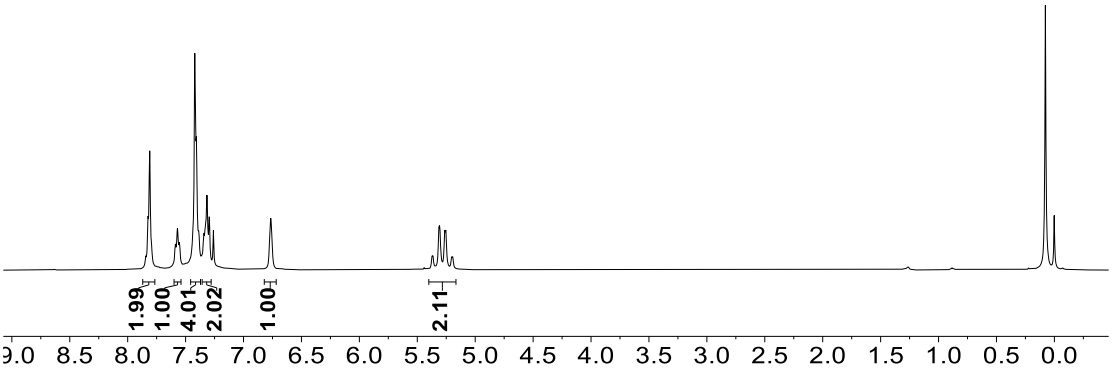


Fig. S58 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3j**.

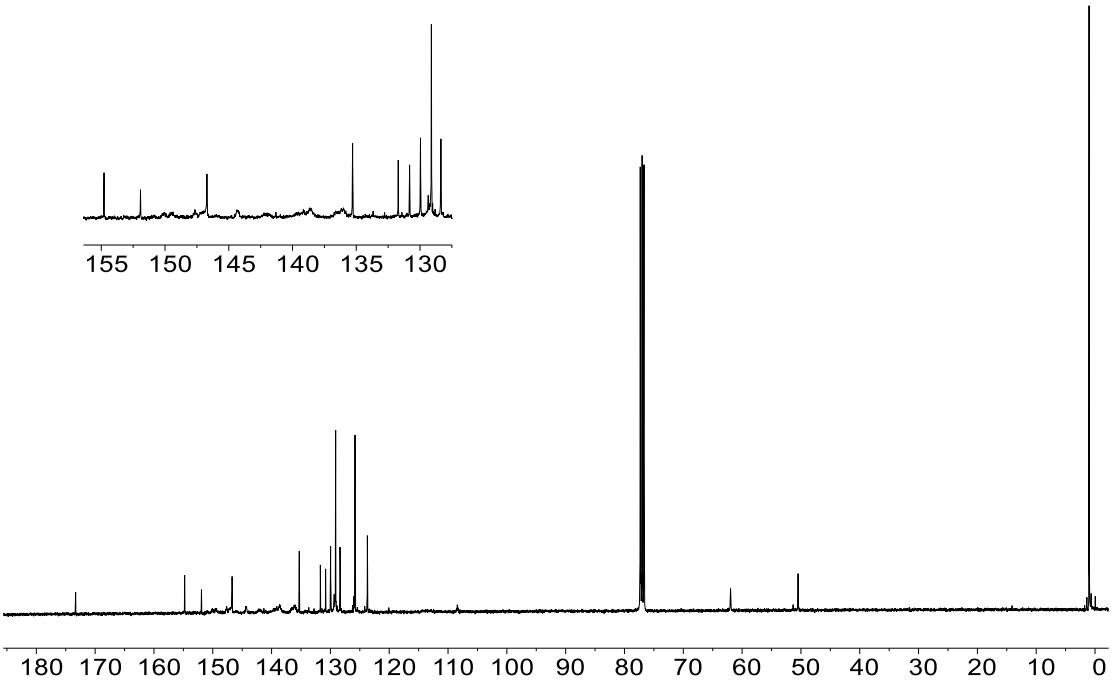


Fig. S59 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3j**.

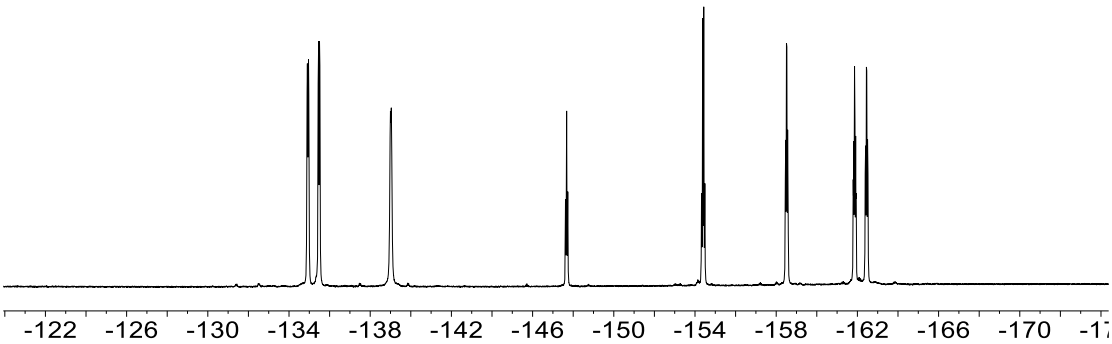


Fig. S60 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **3j**.

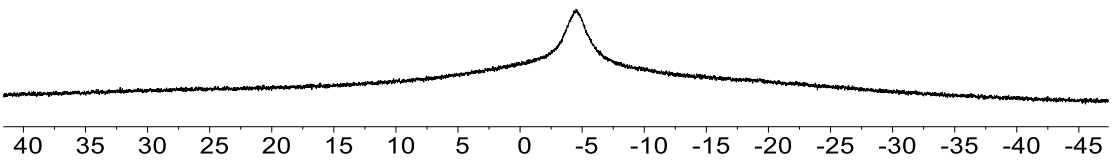


Fig. S61 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **3j**.

X-ray crystal structure analysis of 3j: formula $C_{35}H_{12}BF_{15}N_4O_2$, M = 816.30, red crystal, 0.22 × 0.13 × 0.09 mm, a = 12.0468(2), b = 16.3233(3), c = 15.7150(3) Å, α = γ = 90.000º, β = 95.2169(16)º, V = 3077.45(9) Å^3, ρ_{calc} = 1.762 gcm^{-3}, μ = 1.555 mm^{-1}, empirical absorption correction (0.41390 ≤ T ≤ 1.00000), Z = 4, monoclinic, space group $P2_1/c$, λ = 1.54184 Å, T = 300.15 K, ω and φ scans, 16044 reflections collected (±h, ±k, ±l), 5559 independent (R_{int} = 0.0360) and 4527 observed reflections [I>2σ(I)], 515 refined parameters, R = 0.0502, wR^2 = 0.1490, max. (min.) residual electron density 0.34 (-0.36) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

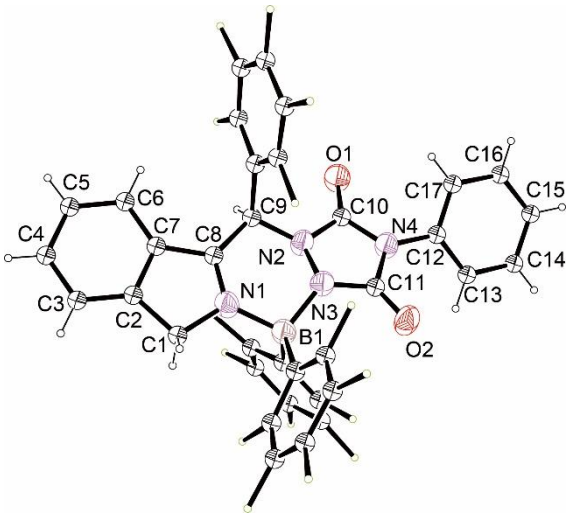
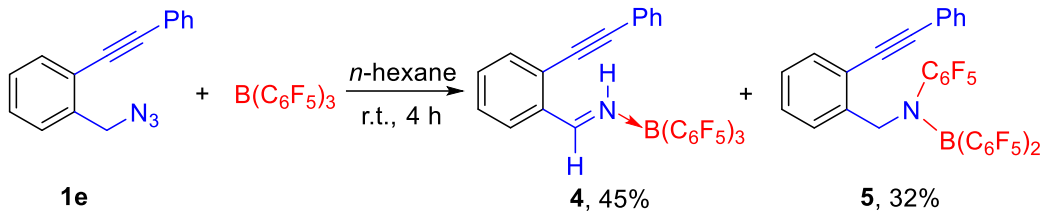


Fig. S62 A view of the molecular structure of compound **3j** (thermal ellipsoids are shown at the 50% probability level).

4. Synthesis and characterization of 4 and 5



Scheme S4

A solution of $B(C_6F_5)_3$ (200.0 mg, 0.39 mmol, 1.0 equiv.) and **1e** (91.0 mg, 0.39 mmol, 1.0 equiv.) in *n*-hexane (10 mL) was stirred at room temperature for 4 h to give a white suspension. The white solid was collected by filtration and dried in vacuo. It was identified as compound **4** (Yield: 127.2 mg, 45% yield). Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **4** in CH_2Cl_2 covered with *n*-hexane at -25 ℃. **HRMS (ESI)**: m/z calcd. for $C_{33}H_{10}BF_{15}N^-$: 716.0672; $[M-H]^-$ found: 716.0666. The *n*-hexane solution was collected, concentrated to ca. 1 mL, and then stored at -25 ℃ for 2 h to give a colorless crystalline solid, which was collected by filtration and dried in vacuo to give a white solid (compound **5**, 90.1 mg, 32% yield). Crystals suitable for the X-ray crystal structure analysis were obtained from using a solution of compound **5** in *n*-hexane at -25 ℃. **HRMS (ESI)**: m/z calcd. for $C_{33}H_{10}BF_{15}N^-$: 716.0672; $[M-H]^-$ found: 716.0666.

NMR data for 4

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 11.48 (d, $^{3}J_{HH}$ = 19.9 Hz, 1H, N*H*$^{=CH}$), 8.49 (d, $^{3}J_{HH}$ = 20.1 Hz, 1H, C*H*$^{=NH}$), 7.80 – 7.69 (m, 3H), 7.62 (m, 1H), 7.44 (m, 1H), 7.36 (m, 2H), 7.29 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 168.8 (*C*H$^{=NH}$), 135.7, 134.9, 132.1, 131.4, 130.2, 129.6, 128.6, 128.2, 124.8, 120.2, 99.7, 83.8. [C_6F_5 not listed]. **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -7.3 ($v_{1/2}$ ~ 176 Hz). **^{19}F {^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -133.2 (m, 6F) (*o*-C_6F_5), -156.0 (t, $^{3}J_{FF}$ = 20.4 Hz, 3F) (*p*-C_6F_5), -162.9 (m, 6F) (*m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.9].

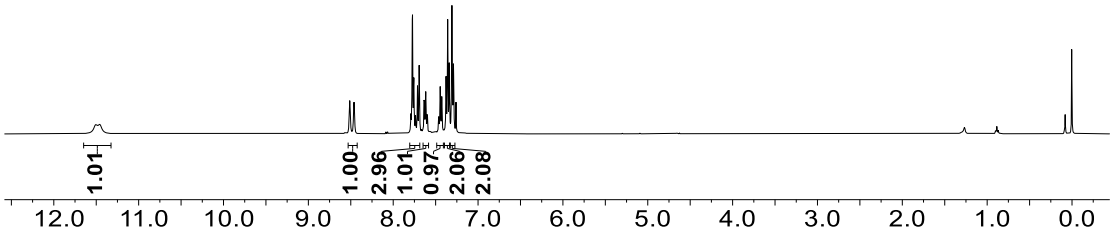


Fig. S63 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **4**.

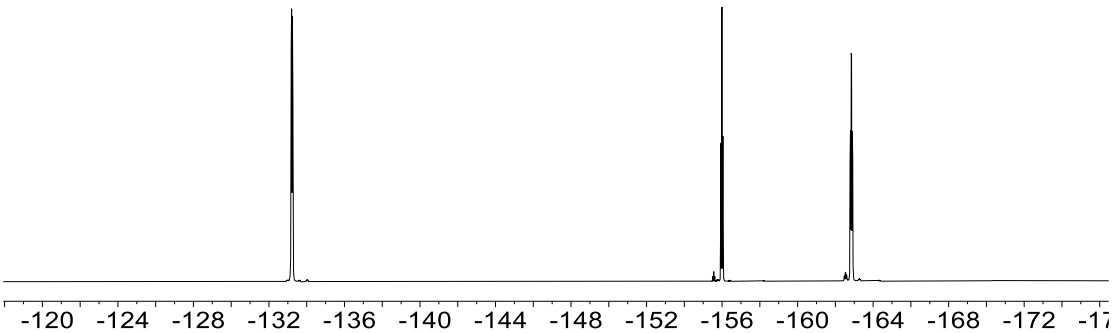


Fig. S64 ^{19}F{^{1}H} NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **4**.

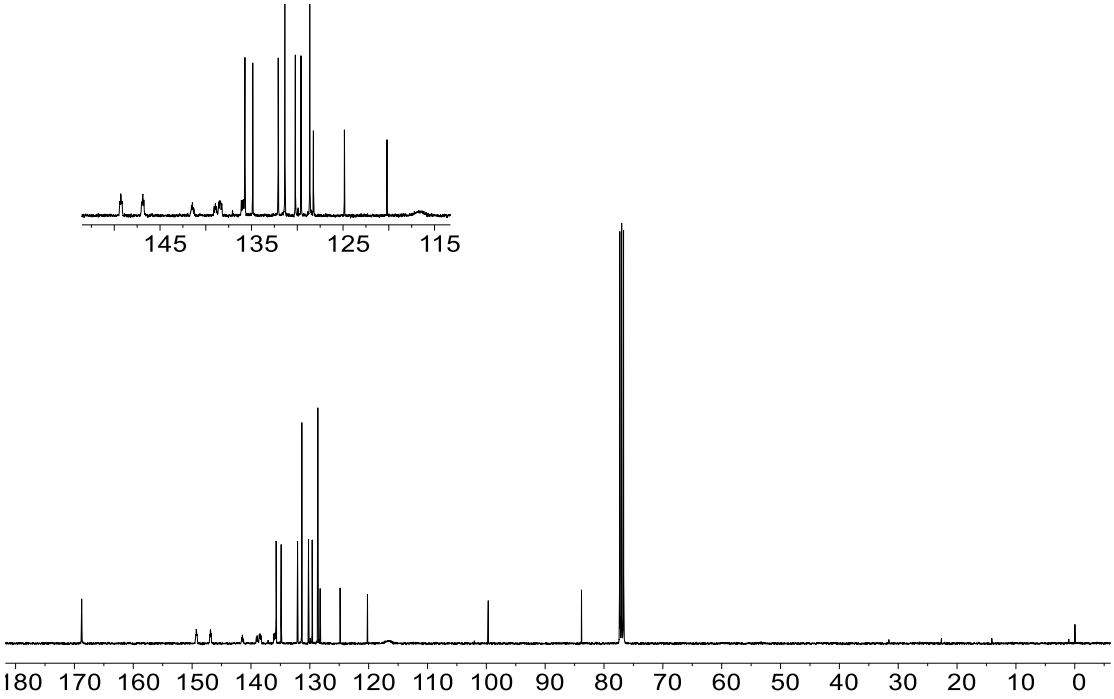


Fig. S65 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **4**.

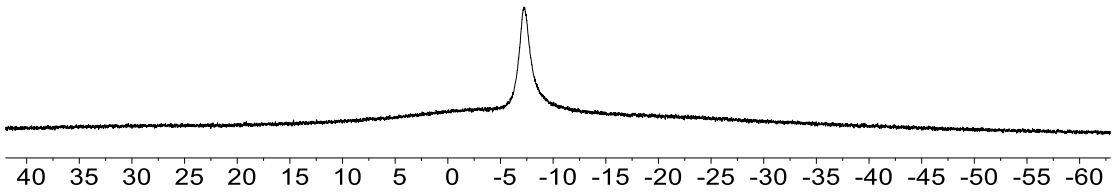


Fig. S66 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **4**.

X-ray crystal structure analysis of compound 4: formula $C_{33}H_{11}BF_{15}N$, M = 717.24, colourless crystal, 0.3 × 0.22 × 0.17 mm, a = 9.3635(15), b = 12.334(2), c = 13.652(2) Å, α = 108.894(5)º, β = 103.287(5)º, γ = 96.811(5)º, V = 1419.5(4) Å^3, ρ_{calc} = 1.678 gcm^{-3}, μ = 0.167 mm^{-1}, empirical absorption correction (0.7010 ≤ T ≤ 0.7399), Z = 2, triclinic, space group P-1, λ = 0.71073 Å, T = 120.0 K, ω and φ scans, 46301 reflections collected

(±*h*, ±*k*, ±*l*), 8683 independent (R_{int} = 0.0618) and 6280 observed reflections [$I>2\sigma(I)$], 451 refined parameters, R = 0.0445, wR^2 = 0.1199, max. (min.) residual electron density 0.86 (-0.24) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

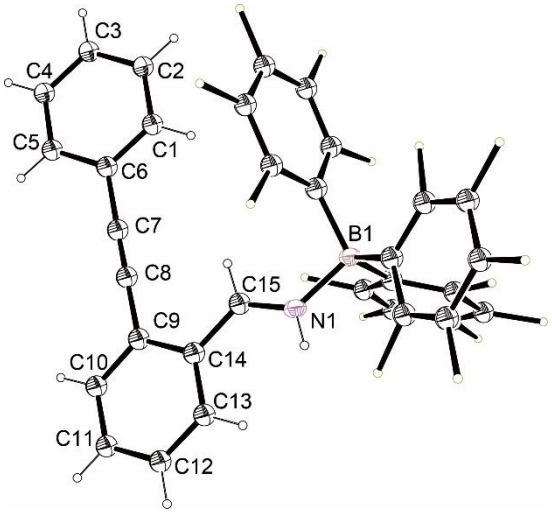


Fig. S67 A view of the molecular structure of compound **4** (thermal ellipsoids are shown at the 50% probability level).

NMR data for 5

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 7.55 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.510 (m, 2H), 7.41 – 7.34 (m, 5H), 7.26 (m, 1H), 5.08 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 135.7, 132.4, 131.5, 129.0, 128.8, 128.8, 128.6, 128.5, 123.4, 122.3, 94.1, 85.6, 55.5 (*C*H_2). [C_6F_5 not listed]. **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ = 40 ($\nu_{1/2}$ ~ 890 Hz). **^{19}F {^{1}H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -130.0 (m, 2F), -131.6 (m, 2F), -144.4 (m, 2F) (*o*-C_6F_5), -150.1 (t, $^3J_{FF}$ = 20.1 Hz, 1F), -150.4 (t, $^3J_{FF}$ = 20.0 Hz, 1F), -153.4 (t, $^3J_{FF}$ = 21.6 Hz, 1F) (*p*-C_6F_5), -159.9 (m, 2F), -160.3 (m, 2F), -160.8 (m, 2F) (*m*-C_6F_5).

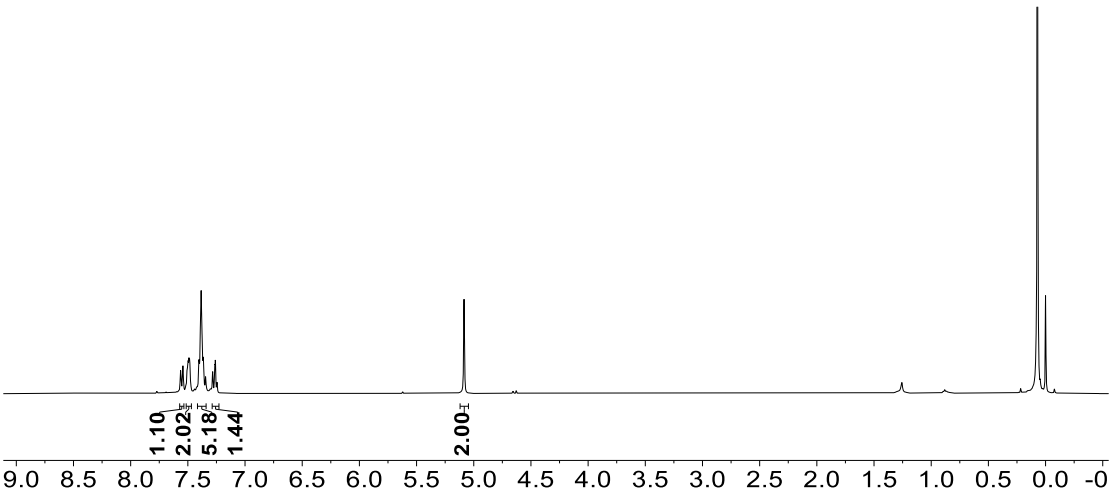


Fig. S68 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **5**.

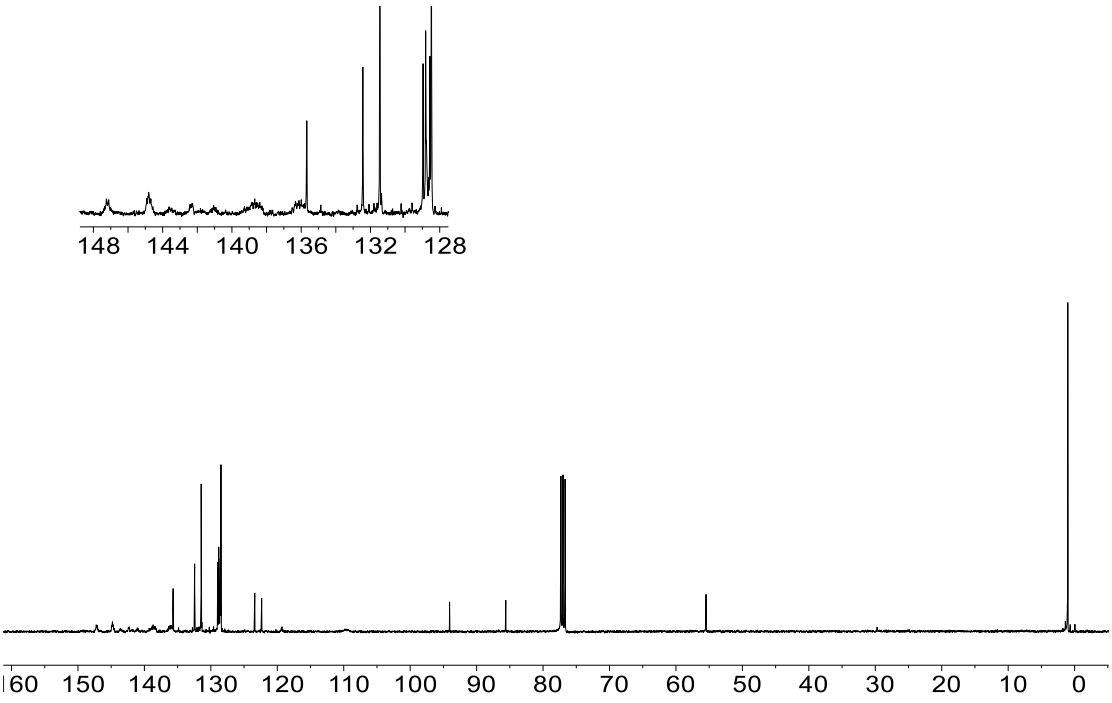


Fig. S69 $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **5**.

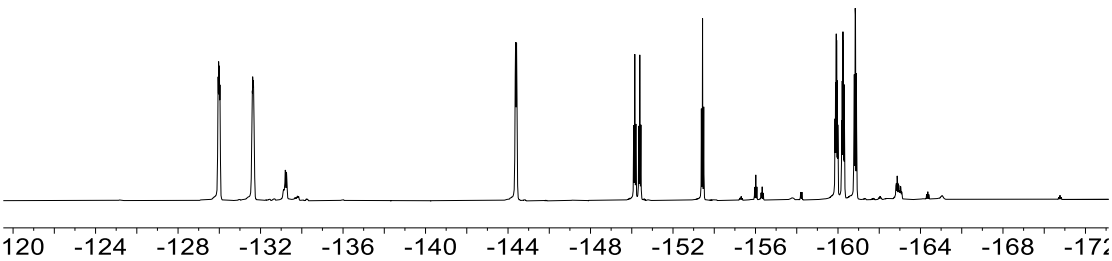


Fig. S70 $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **5**.

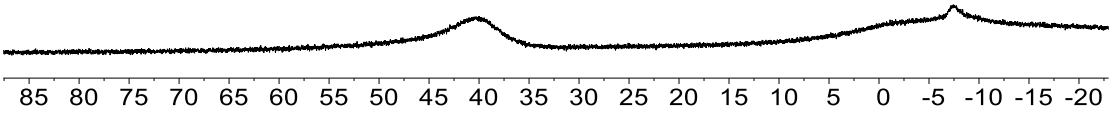


Fig. S71 ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **5**.

X-ray crystal structure analysis of compound 5: formula $C_{33}H_{11}BF_{15}N$, M = 717.24, colourless crystal, 0.21 × 0.2 × 0.11 mm, a = 10.152(3), b = 10.204(3), c = 14.905(4) Å, α = 100.952(9)º, β = 99.276(8)º, γ = 103.819(8)º, V = 1437.0(7) Å^3, ρ_{calc} = 1.658 gcm^{-3}, μ = 0.165 mm^{-1}, empirical absorption correction (0.6736 ≤ T ≤ 0.7458), Z = 2, triclinic, space group P-1, λ = 0.71073 Å, T = 120.0 K, ω and φ scans, 29331 reflections collected (±h, ±k, ±l), 7436 independent (R_{int} = 0.0671) and 4753 observed reflections [I>2σ(I)], 451 refined parameters, R = 0.0492, wR^2 = 0.1244, max. (min.) residual electron density 0.31 (-0.31) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

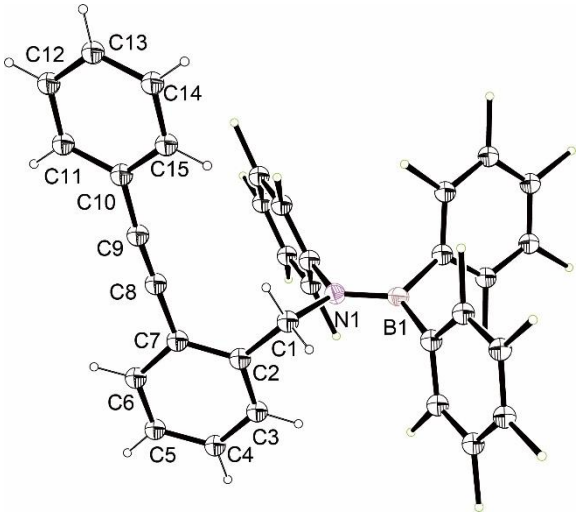


Fig. S72 A view of the molecular structure of compound **5** (thermal ellipsoids are shown at the 50% probability level).