**Electronic supplementary information**

**for**

# Formation of cyclic (boryl)iminomethane derivatives by insertion of isocyanides into the boron-carbon bond

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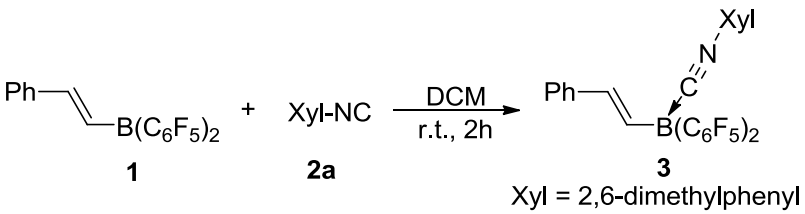
**General information:** All manipulations were performed under an atmosphere of dry and oxygen-free $N_2$ by means of standard Schlenk or glovebox techniques. *n*-hexane, toluene and dichloromethane (DCM) were collected from a (Mikrouna) solvent purification system and stored over activated 4 Å molecular sieves. Dichloromethane-$d_2$ ($CD_2Cl_2$), Chloroform-d ($CDCl_3$) and benzene-$d_6$ ($C_6D_6$) were degassed, dried over calcium hydride and stored over 4 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 ($^1$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.

**X-Ray diffraction:** Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture CMOS-based diffractometer (**3**, **4**, **5a**, **6a**, **6b**, **7**, and **8**) with graphite-monochromated $Mo_{Ka}$ radiation ($\lambda$ = 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 and

refined with the ShelXL refinement package 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 2112836-2112839, 2112841, and 2112842 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/.

**Materials:** Compound **1**[1] and N-propargyldiisopropylamine[2] were prepared according to the literature procedure. Compound **4**[3] was synthesized according to a modified literature procedure. [(1) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503. (2) T. Sugiishi, A. Kimura and H. Nakamura, *J. Am. Chem. Soc*, 2010, **132**, 5332–5333. (3) T. Wang, C. G. Daniliuc, C. Muck-Lichtenfeld, G. Kehr and G. Erker, *J. Am. Chem. Soc*, 2018, **140**, 3635–3643.]

**Synthesis of compound 3**




A solution of compounds **1** (200.1 mg, 0.45 mmol) and **2a** (58.6 mg, 0.45 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the

removal of the solvent under vacuum, *n*-hexane (5 mL) was added to the residue. The obtained suspension was kept at -20 ℃ for 2 h, which was collected by filtration and dried in vacuo to give a white solid. Yield: 203.2 mg, 79%.

[Comments: the solution of compound **3** in toluene is stable for at least 12 h at 100 ℃, and decomposed to several uncharacterized speices at higher temperature.]

**HRMS (ESI)**: m/z calcd for $C_{29}H_{17}BF_{10}N$: 580.1289 $[M+H]^+$; found: 580.1286.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated compound **3** in $CH_2Cl_2$ covered with *n*-hexane at -25 ℃.

**$^1$H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.20-7.43 (m, 8H, Ph), 7.04 (d, 1H, $^3J_{HH}$ = 18.0 Hz, $^B$C*H*=), 6.50 (d, 1H, $^3J_{HH}$ = 18.0 Hz, $^{Ph}$C*H*=), 2.46 (s, 6H, C$H_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 147.9 (dm, $^1J_{FC}$ = 241.2 Hz, *m*-$C_6F_5$), 140.1 (dm, $^1J_{FC}$ = 251.7 Hz, *p*-$C_6F_5$), 137.4 (dm, $^1J_{FC}$ = 252.9 Hz, *o*-$C_6F_5$), 116.5 (br, *i*-$C_6F_5$), 139.3, 137.2, 132.2, 128.9, 128.6, 127.3, 126.3 (Ph), 137.5 ($^{Ph}$C*H*=), 132.4 (br, $^B$*C*H=), 123.1 (br, $^B$*C*≡N), 18.4 (*C*$H_3$).

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): $\delta^1$H/$\delta^{13}$C: 7.04/132.4 ($^B$*CH*=), 6.50/137.5 ($^{Ph}$*CH*=), 2.46/18.4 (*C*$H_3$).

**$^{11}$B NMR** (128 MHz, 298 K, $C_6D_6$): δ = -18.5 ($v_{1/2}$ ~ 176 Hz).

**$^{19}$F{$^{1}$H} NMR** (377 MHz, 298 K, $C_6D_6$): δ = -131.7 (m, 4F, *o*-$C_6F_5$), -156.6 (t, $^{3}J_{FF}$ = 20.8 Hz, 2F, *p*-$C_6F_5$), -162.9 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 6.3].

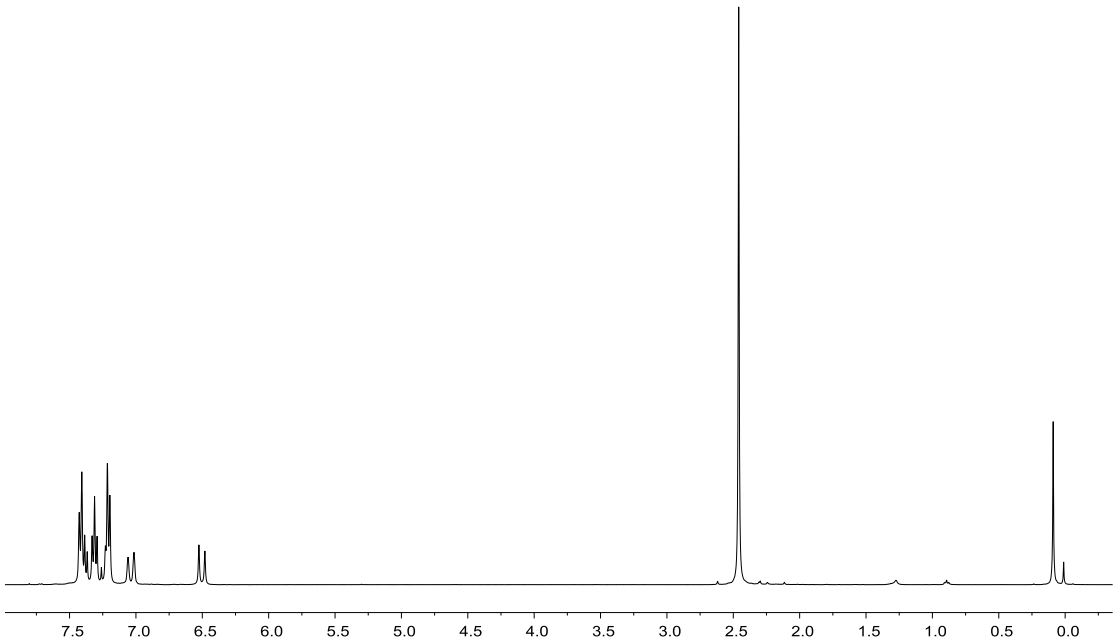



**Fig. S1** $^{1}$H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **3**.

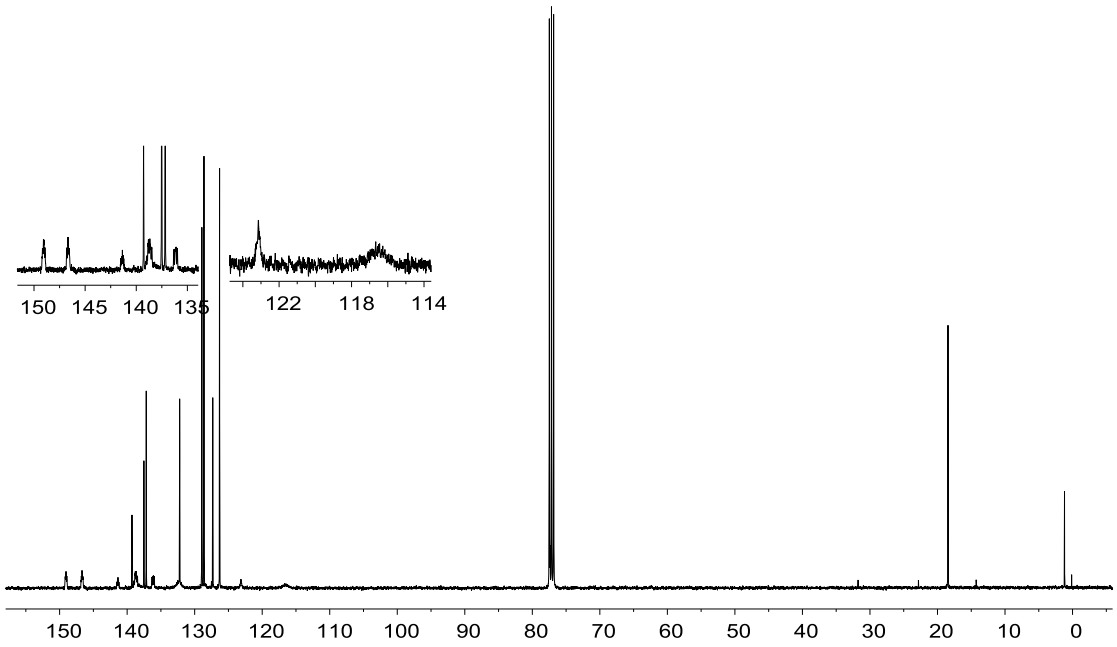



**Fig. S2** $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **3**.

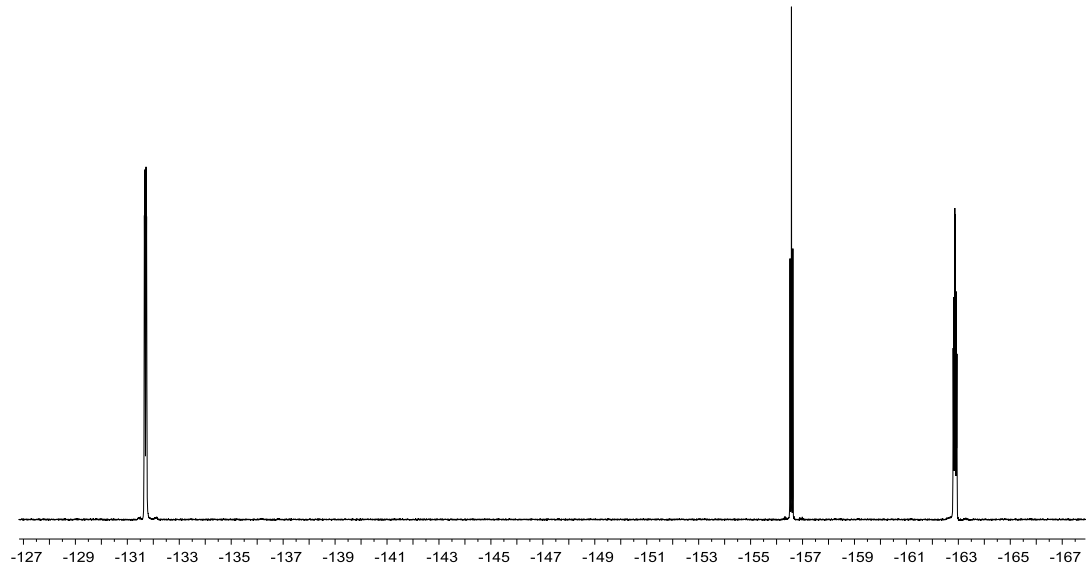



**Fig. S3** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $C_6D_6$) spectrum of compound **3**.

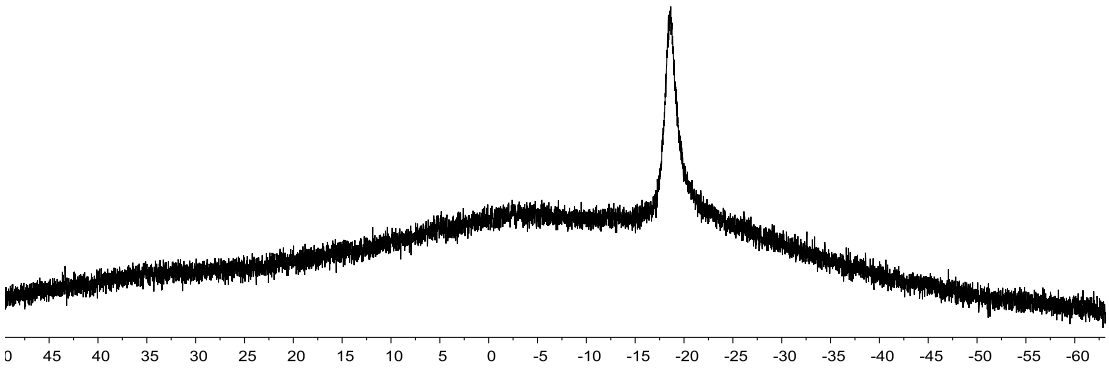



**Fig. S4** $^{11}$B NMR (128 MHz, 298 K, $C_6D_6$) spectrum of compound **3**.

**X-ray crystal structure analysis of compound 3:** formula $C_{29}H_{16}BF_{10}N$, $M$ = 579.24, colourless crystal, 0.46 × 0.43 × 0.24 mm, $a$ = 8.8271(7), $b$ = 11.0748(8), $c$ = 14.0033(9) Å, α = 103.662(2)º, $\beta$ = 107.548(2)º, γ = 100.309(2) º, $V$ = 1221.19(15) Å$^3$, $\rho_{calc}$ = 1.575 gcm$^{-3}$, μ = 0.145 mm$^{-1}$, empirical absorption correction (0.7120 ≤ T ≤ 0.7455), $Z$ = 2, triclinic, space group *P-1*, λ = 0.71073 Å, $T$ = 200.0 K, ω and φ scans, 30127 reflections collected (±*h*, ±*k*, ±*l*), 7121 independent ($R_{int}$ = 0.0567) and 4871 observed reflections [$I$>2σ($I$)], 372 refined parameters, $R$ = 0.0446, $wR^2$ = 0.1037, max. (min.) residual electron density 0.26 (-0.20) e.Å$^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

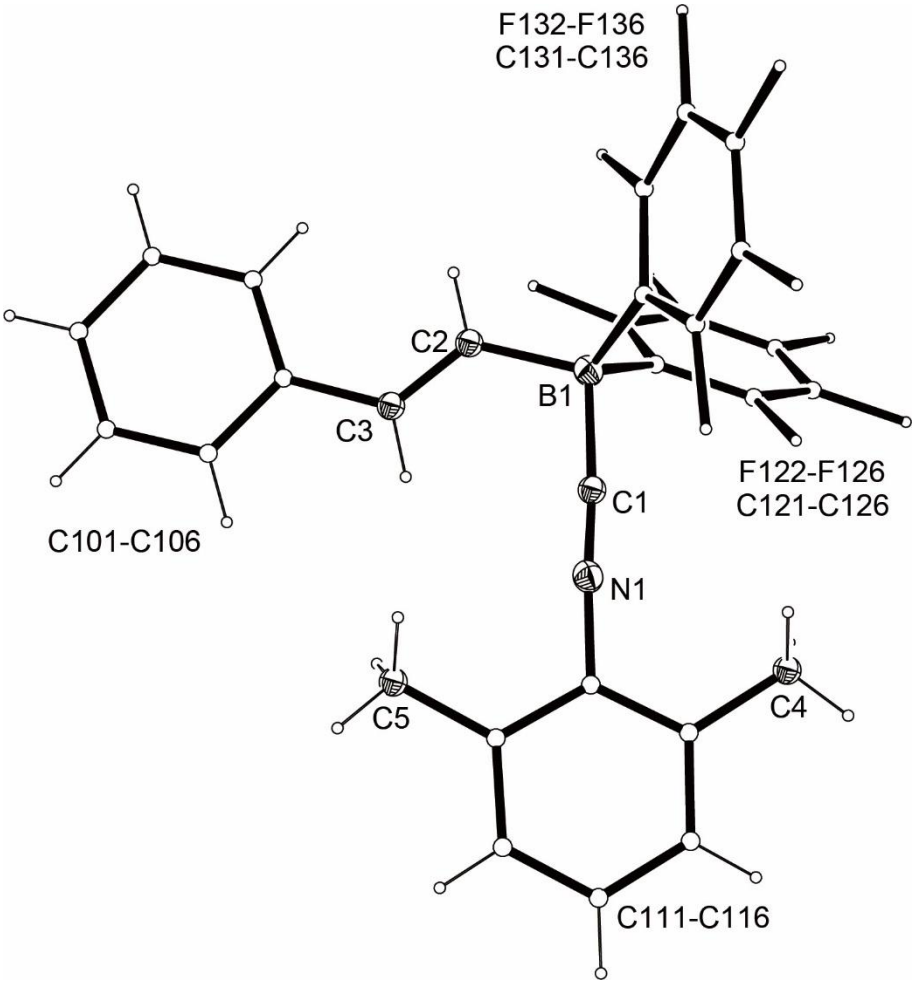
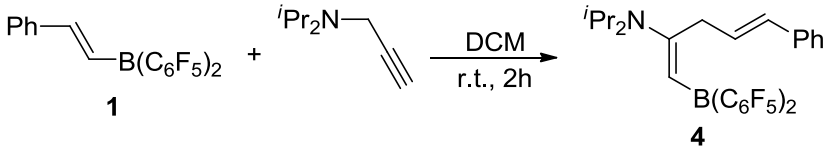



**Fig. S5** A view of the molecular structure of compound **3**.

## Synthesis of compound 4




A solution of N-propargyldiisopropylamine (186.5 mg, 1.34 mmol) and compound **1** (499.3 mg, 1.11 mmol) in $CH_2Cl_2$ (10 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed with *n*-hexane (5 ml) and dried in vacuo to give a yellow solid. Yield: 571.0 mg, 87%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated compound **4** in $CH_2Cl_2$ covered with *n*-hexane at -25 °C.

**HRMS (ESI)**: m/z calcd for $C_{29}H_{23}BF_{10}N$: 586.1769 $[M-H]^-$; found: 586.1764.

**$^1$H NMR** (400 MHz, 298 K, $C_6D_6$): δ = 7.20 (m, 2H, *o*-Ph ), 7.10 (m, 2H, *m*-Ph), 7.02 (m, 1H, *p*-Ph), 6.23 (d, $^3J_{HH}$ = 16.1 Hz, 1H, =C*H*$^{Ph}$), 5.88 (s, 1H, =*H*C$^{B}$), 5.82 (dt, $^3J_{HH}$ = 16.1 and 5.5 Hz, 1H, $^{CH2}$C*H*=), 3.68 and 3.14 (each br, each 1H, C*H*$^{iPr}$), 3.13 (br, 2H, C$H_2$), 1.25 and 0.57 (each d, each 6H, $^3J_{HH}$ = 5.9 Hz, C$H_3^{iPr}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $C_6D_6$): δ = 171.6 ($^{N}$*C*=), 136.9 (*i*-Ph), 133.0 (=*C*H$^{Ph}$), 129.1 (*m*-Ph), 128.3 (*p*-Ph), 126.3 (*o*-Ph), 124.7 ($^{CH2}$*C*H=), 109.9 (br, =H*C*$^{B}$), 51.9 and 47.8 (*C*H$^{iPr}$), 36.0 (*C*$H_2$), 20.1 and 19.9 (*C*$H_3^{iPr}$) [$C_6F_5$ not listed].

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $C_6D_6$): δ$^1$H/δ$^{13}$C: 7.20/126.3 (*o*-Ph), 7.10/129.1 (*m*-Ph), 7.02/128.3 (*p*-Ph), 6.23/133.0 (=*CH*$^{Ph}$), 5.88/109.9 (=*CH*$^{B}$), 5.82/124.7 ($^{CH2}$*CH*=), 3.68/51.9 and 3.14/47.8 (*CH*$^{iPr}$), 3.13/36.0 (*CH*$_2^{CH=}$), 1.25/20.1 and 0.57/19.9 (*CH*$_3^{iPr}$).

**$^1$H-$^{13}$C GHMBC** (400 MHz/101 MHz, 298 K, $C_6D_6$): 7.10/136.9 (*m*-Ph/*i*-Ph), 5.88/171.6 (=*H*C$^{B}$/$^{N}$*C*=).

**$^{11}$B NMR** (128 MHz, 298 K, $C_6D_6$): δ = 45.3 ($v_{1/2}$ ~ 700 Hz).

**$^{19}F\{^1H\}$ NMR** (377 MHz, 298 K, $C_6D_6$): δ = -131.0 (m, 2F, *o*-$C_6F_5$), -154.6, (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-$C_6F_5$), -162.4 (m, 2F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 7.8]; -132.8 (m, 2F, *o*-$C_6F_5'$), -155.3 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-$C_6F_5'$), -162.8 (m, 2F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 7.5].

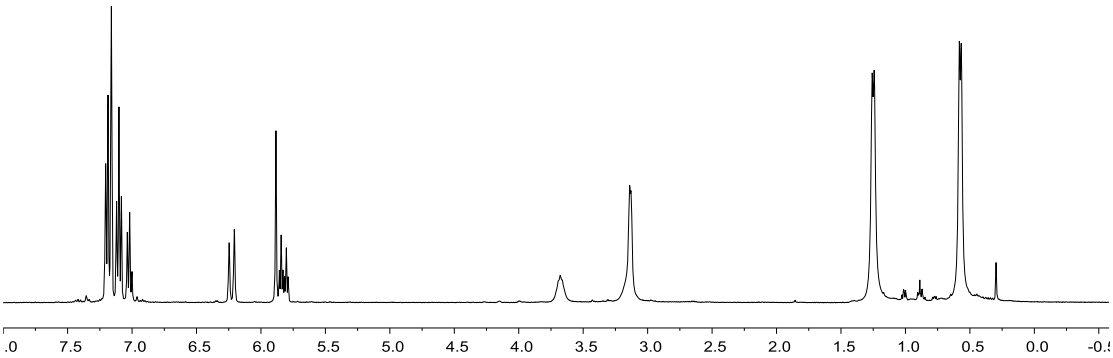



**Fig. S6** $^1H$ NMR (400 MHz, 298 K, $C_6D_6$) spectrum of compound **4**.

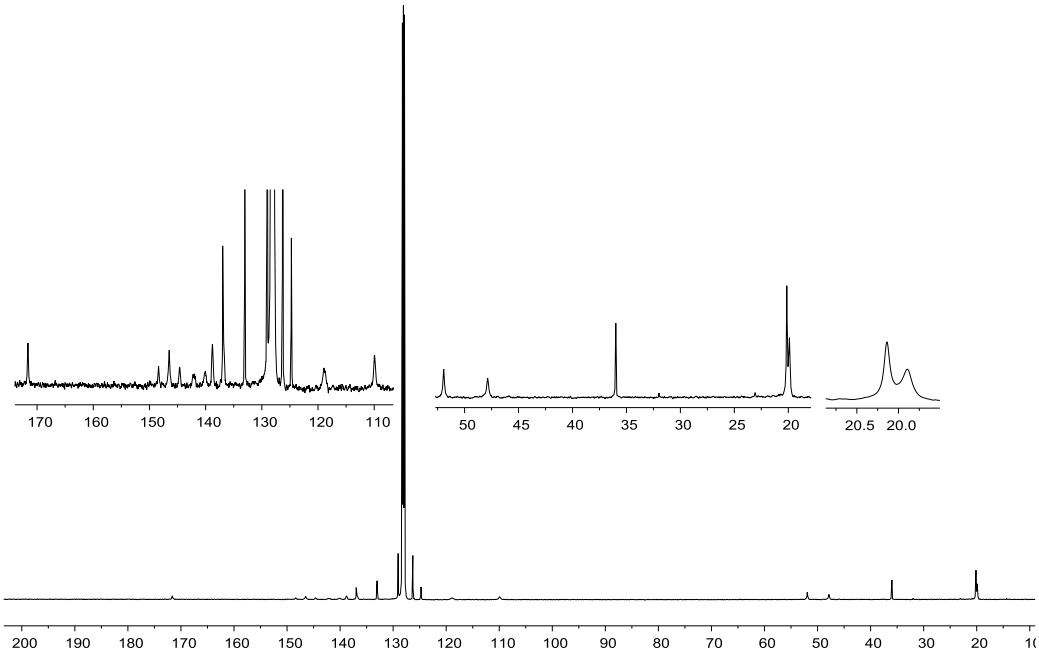



**Fig. S7** $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $C_6D_6$) spectrum of compound **4**.

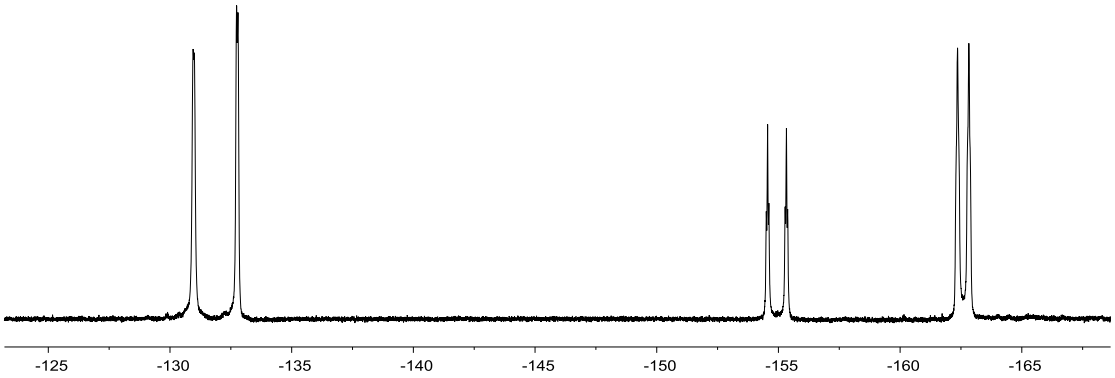



**Fig. S8** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $C_6D_6$) spectrum of compound **4**.

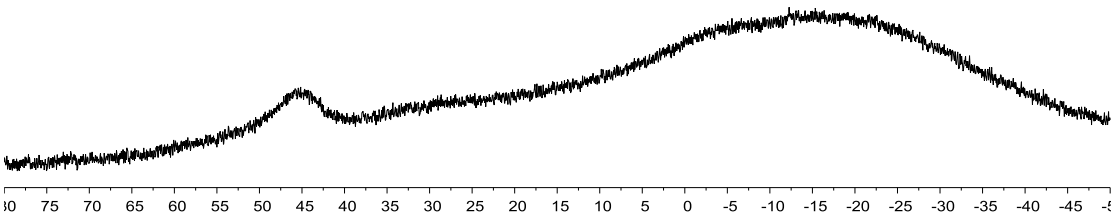



**Fig. S9** $^{11}B$ NMR (128 MHz, 298 K, $C_6D_6$) spectrum of compound **4**.

**X-ray crystal structure analysis of compound 4:** formula $C_{29}H_{24}BF_{10}N$, $M$ = 587.30, yellow crystal, 0.23 × 0.25 × 0.61 mm, $a$ = 28.371(3), $b$ = 8.6644(9), $c$ = 22.055(2) Å, α = $\beta$ = γ = 90.000º, $V$ = 5421.5(9) Å$^3$, $\rho_{calc}$ = 1.439 gcm$^{-3}$, μ = 0.131 mm$^{-1}$, empirical absorption correction (0.6251 ≤ T ≤ 0.7461), $Z$ = 8, monoclinic, space group *Pbcn*, λ = 0.71073 Å, $T$ = 200.0 K, ω and φ scans, 27507 reflections collected (±*h*, ±*k*, ±*l*), 4738 independent ($R_{int}$ = 0.1325) and 2499 observed reflections [$I$>2σ($I$)], 378 refined parameters, $R$ = 0.0682, $wR^2$ = 0.1128, max. (min.) residual electron density 0.18 (-0.23) e.Å$^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

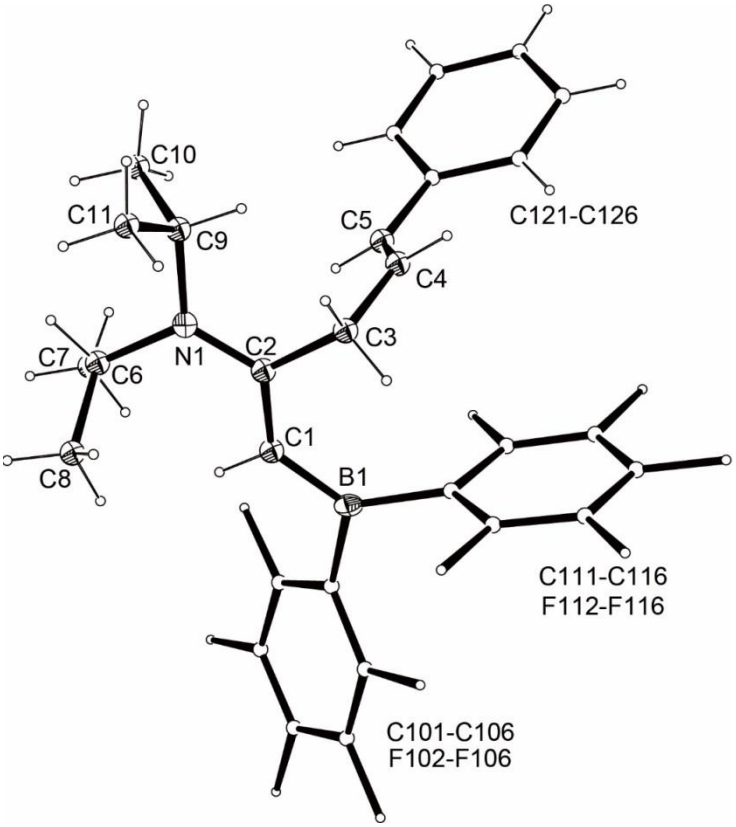
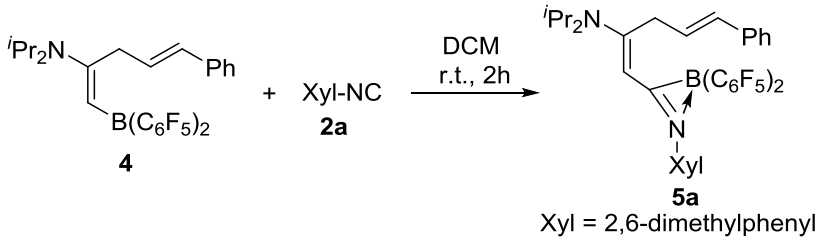



**Fig. S10** A view of the molecular structure of compound **4**.

**Synthesis of compound 5a**




A solution of compounds **4** (176.9 mg, 0.30 mmol) and **2a** (39.5 mg, 0.30 mmol) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed with *n*-hexane (3×2 mL) and dried in vacuo to give compound **5a** as a white solid. Yield: 179.6 mg, 83%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated compound **5a** in $CH_2Cl_2$ covered with *n*-hexane at -25 ℃.

**HRMS (ESI)**: m/z calcd for $C_{40}H_{35}BF_{10}N_3$: 758.2770 $[M\text{-}H+CH_3CN]^-$; found: 758.2769.

**$^1$H NMR** (400 MHz, 298 K, $CD_2Cl_2$): δ = 7.10-7.27 (m, 8H, Ph), 6.20 (s, 2H, C*H*=C*H*$^{Ph}$), 5.46 (s, 1H, C*H*$^{=C}$), 4.26 and 3.87 (each br, each 1H, C*H*$^{iPr}$), 4.11 (br, 2H, C$H_2$), 1.92 (s, 6H, C$H_3^{Ph}$), 1.41 and 1.23 (each br, each 6H, C$H_3^{iPr}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CD_2Cl_2$): δ = 179.7 (brm, B*C*), 165.9 ($^{iPr}$N*C*), 148.3 (dm, $^1J_{FC}$ = 237.0 Hz, *m*-$C_6F_5$), 140.0 (dm, $^1J_{FC}$ = 250.0 Hz, *p*-$C_6F_5$), 137.1 (dm, $^1J_{FC}$ = 250.8 Hz, *o*-$C_6F_5$), 118.6 (brm, *i*-$C_6F_5$), 140.3,

137.2, 132.9, 128.8, 128.7, 127.8, 126.4, 125.9 (Ph), 131.1 and 126.8 (*C*H=*C*H$^{Ph}$), 90.6 (*C*H$^{=C}$), 52.8 and 47.7 (each br, C*H*$^{iPr}$), 33.3 (*C*H$_2$), 20.7 (*C*H$_3^{iPr}$), 19.0 (*C*H$_3^{Ph}$).

**$^{1}$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CD_2Cl_2$): $\delta^1H/\delta^{13}C$: 6.20/(131.1, 126.8) (*CH*=*CH*$^{Ph}$), 5.46/90.6 (*CH*$^{=C}$), 4.26/52.8 and 3.87/47.7 (*CH*$^{iPr}$), 4.11/33.3 (*CH*$_2$), 1.92/19.0 (*CH*$_3^{Ph}$), (1.40, 1.23)/20.7 (*CH*$_3^{iPr}$).

**$^{1}$H-$^{13}$C GHMBC** (400 MHz/101 MHz, 298 K, $CD_2Cl_2$): $\delta^1H/\delta^{13}C$: 6.20/165.9 (C*H*=C*H*$^{Ph}$/$^{iPr}$N*C*), 5.46/179.7 (C*H*$^{=C}$/B*C*).

**$^{11}$B NMR** (128 MHz, 298 K, $CD_2Cl_2$): $\delta$ = -16.1 ($\nu_{1/2}$ ~ 100 Hz).

**$^{19}$F{$^{1}$H} NMR** (377 MHz, 298 K, $CD_2Cl_2$): $\delta$ = -133.9 (m, 4F, *o*-$C_6F_5$), -159.1 (t, $^3J_{FF}$ = 20.1 Hz, 2F, *p*-$C_6F_5$), -164.9 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 5.8].

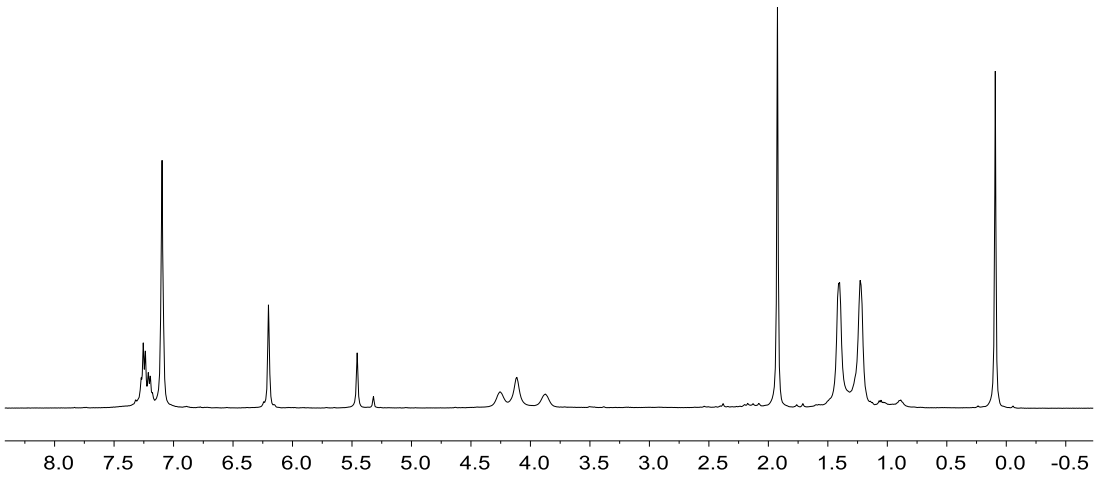



**Fig. S11** $^{1}$H NMR (400 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **5a**.

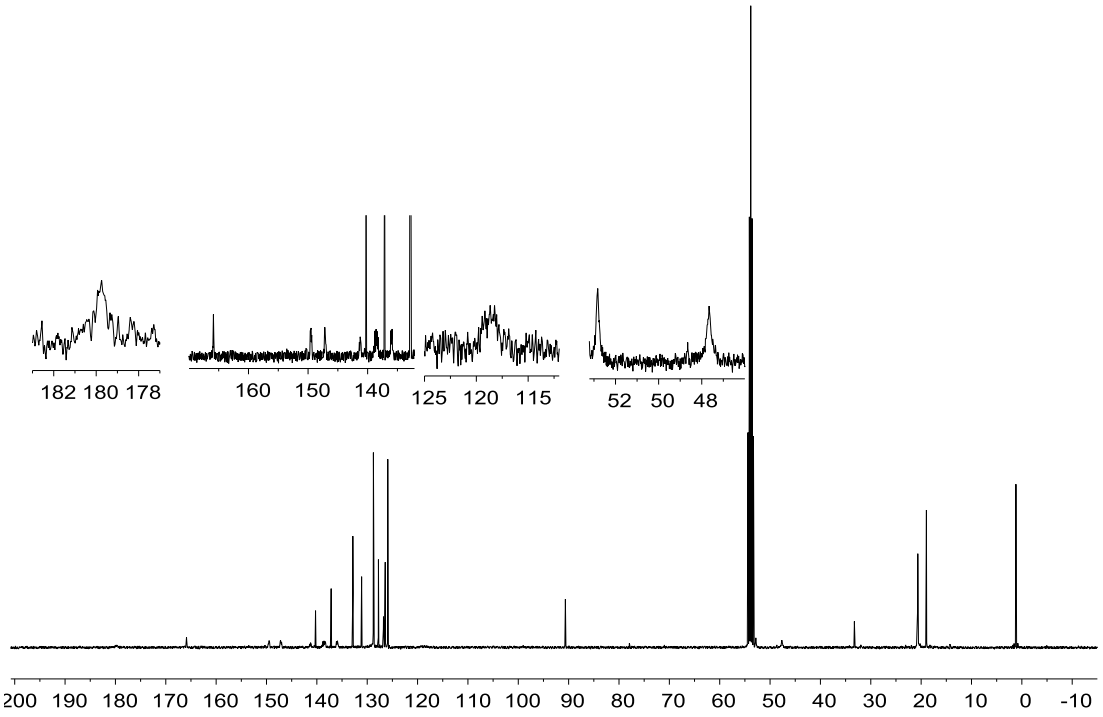



**Fig. S12** $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **5a**.

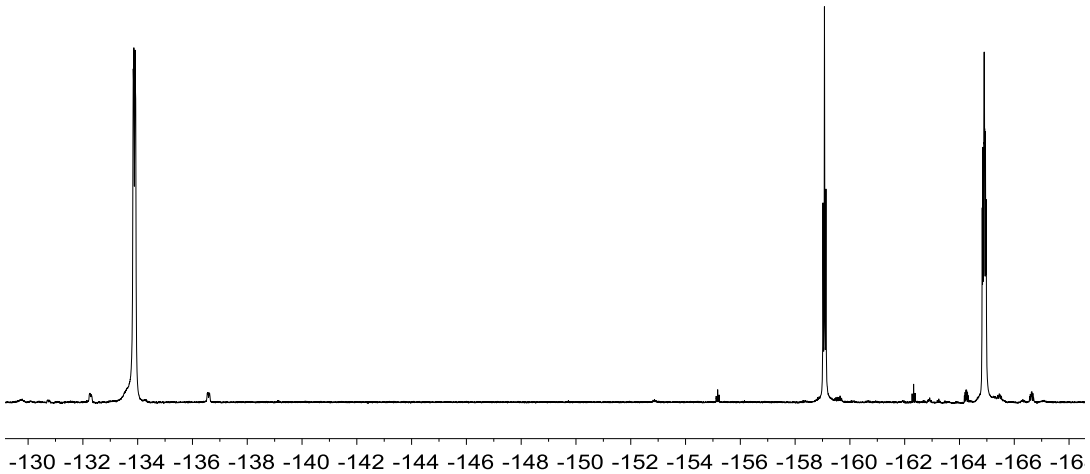



**Fig. S13** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **5a**.

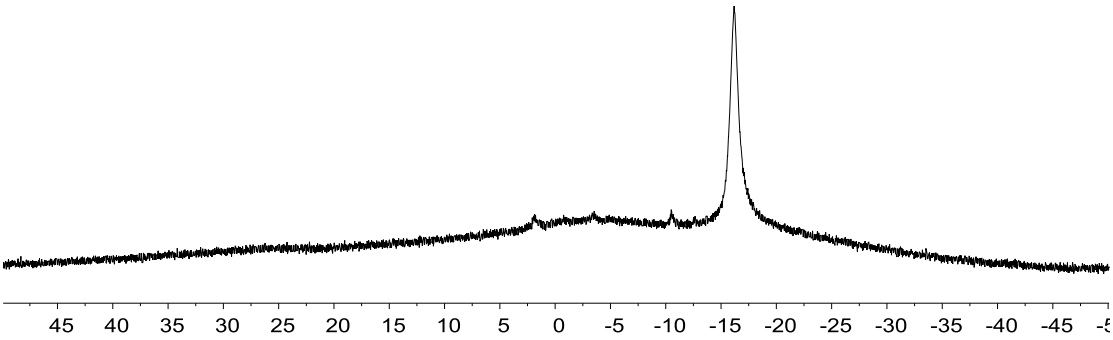



**Fig. S14** $^{11}$B NMR (128 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **5a**.

**X-ray crystal structure analysis of compound 5a:** formula $C_{38}H_{33}BF_{10}N_2$, $M$ = 718.47, colourless crystal, 0.46 × 0.34 × 0.12 mm, $a$ = 14.684(6), $b$ = 12.759(6), $c$ = 19.053(8) Å, α = γ = 90.000 º, $\beta$ = 99.678(9) º, $V$ = 3519(3)Å$^3$, $\rho_{calc}$ = 1.356 gcm$^{-3}$, μ = 0.116 mm$^{-1}$, empirical absorption correction (0.5369 ≤ T ≤ 0.7461), $Z$ = 4, monoclinic, space group *P21/n*, λ = 0.71073 Å, $T$ = 150.2 K, ω and φ scans, 25560 reflections collected (±*h*, ±*k*, ±*l*), 5041 independent ($R_{int}$ = 0.2428) and 2048 observed reflections [$I$>2σ($I$)], 466 refined parameters, $R$ = 0.0846, $wR^2$ = 0.1723, max. (min.) residual electron density 0.30 (-0.37) e.Å$^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

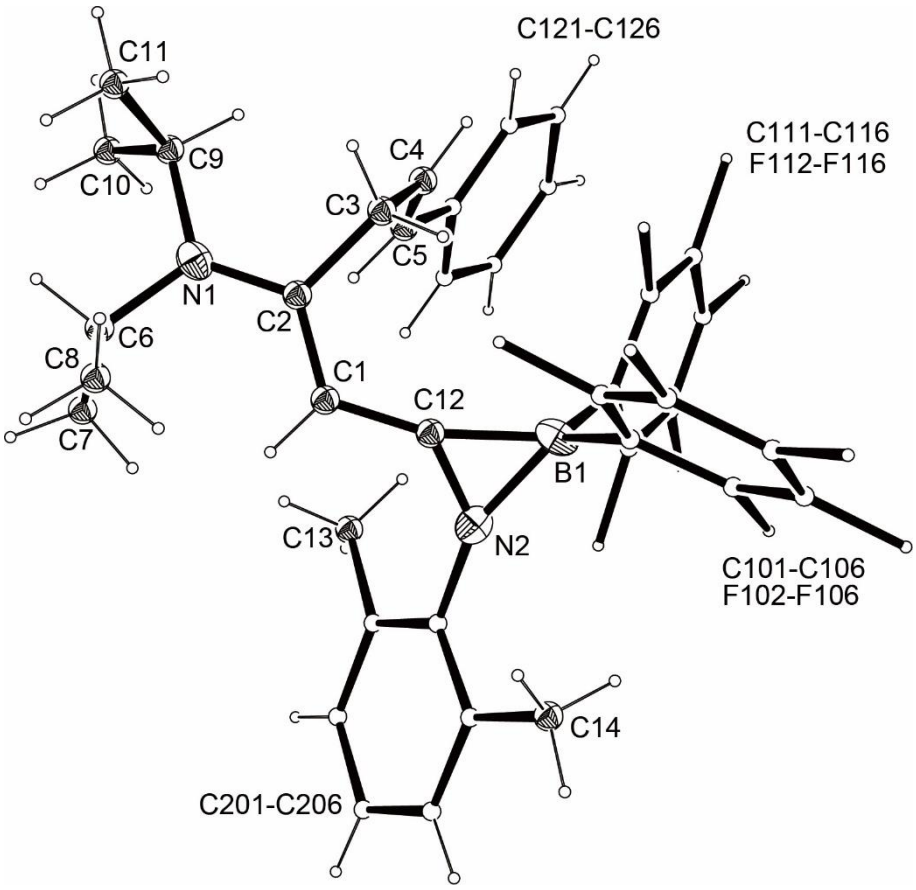
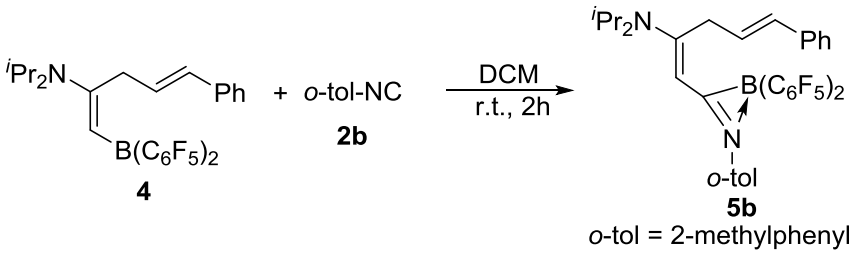



**Fig. S15** A view of the molecular structure of compound **5a**.

## Synthesis of compound 5b




A solution of compounds **4** (117.8 mg, 0.20 mmol) and **2b** (23.5 mg, 0.20 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed with *n*-hexane (2 mL) and dried in vacuo to give a white solid. Yield:

121.2 mg, 86%.

**HRMS (ESI)**: m/z calcd for $C_{37}H_{32}BF_{10}N_2$: 705.2493 $[M+H]^+$; found: 705.2492.

**$^1$H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.08-7.28 (m, 9H, Ph), 6.22 (s, 1H, $^{C=}$C*H*), 6.17 (d, $^3J_{HH}$ = 16.3 Hz, 1H, =C*H*$^{Ph}$), 6.01 (dt, $^3J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 4.3 Hz, 1H, $^{CH2}$C*H*=), 4.29 and 3.97 (each br, each 1H, C*H*$^{iPr}$), 3.98 (br, 2H, C*H*$_2$), 2.14 (s, 3H, C*H*$_3^{Ph}$), 1.58 and 1.25 (each br, each 6H, C*H*$_3^{iPr}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 175.8 (brm, B*C*), 166.9 ($^{iPr}$N*C*), 148.3 (dm, $^1J_{FC}$ = 237.8 Hz, *m*-*C*$_6$F$_5$), 139.7 (dm, $^1J_{FC}$ = 250.2 Hz, *p*-*C*$_6$F$_5$), 136.9 (dm, $^1J_{FC}$ = 251.3 Hz, *o*-*C*$_6$F$_5$), 118.3 (brm, *i*-*C*$_6$F$_5$), 140.5, 136.5, 132.0, 131.7, 128.6, 127.7, 126.4, 125.7, 125.5, 121.0 (Ph), 131.3 (=*C*H$^{Ph}$), 125.3 ($^{CH2}$*C*H=), 89.9 ($^{C=}$*C*H), 52.6 and 47.5 (each br, *C*H$^{iPr}$), 32.6 (*C*H$_2$), 20.9 and 20.7 (*C*H$_3^{iPr}$), 18.5 (*C*H$_3^{Ph}$).

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C: 6.22/89.9 ($^{C=}$*CH*), 6.17/131.3 (=*CH*$^{Ph}$), 6.01/125.3 ($^{CH2}$*CH*=), 4.29/52.6 and 3.97/47.5 (*CH*$^{iPr}$), 3.98/32.6 (C*H*$_2$), 2.14/18.5(*C*H$_3^{Ph}$), 1.58/20.9 and 1.25/20.7 (*CH*$_3^{iPr}$).

**$^1$H-$^{13}$C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C : 6.22/175.8 ($^{C=}$C*H*/B*C*), 6.17/166.9 ($^{CH2}$C*H*=/$^{iPr}$N*C*).

**$^{11}$B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -17.5 ($\nu_{1/2}$ ~ 124 Hz).

**$^{19}F\{^1H\}$ NMR** (377 MHz, 298 K, $CDCl_3$): δ = -134.1 (m, 4F, *o*-$C_6F_5$), -158.1 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-$C_6F_5$), -164.1 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 6.0].

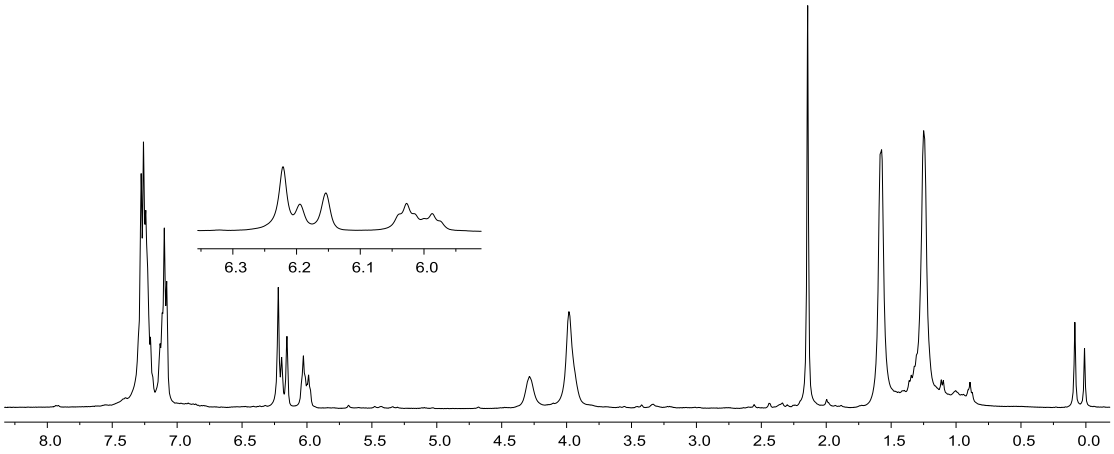



**Fig. S16** $^1H$ NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **5b**.

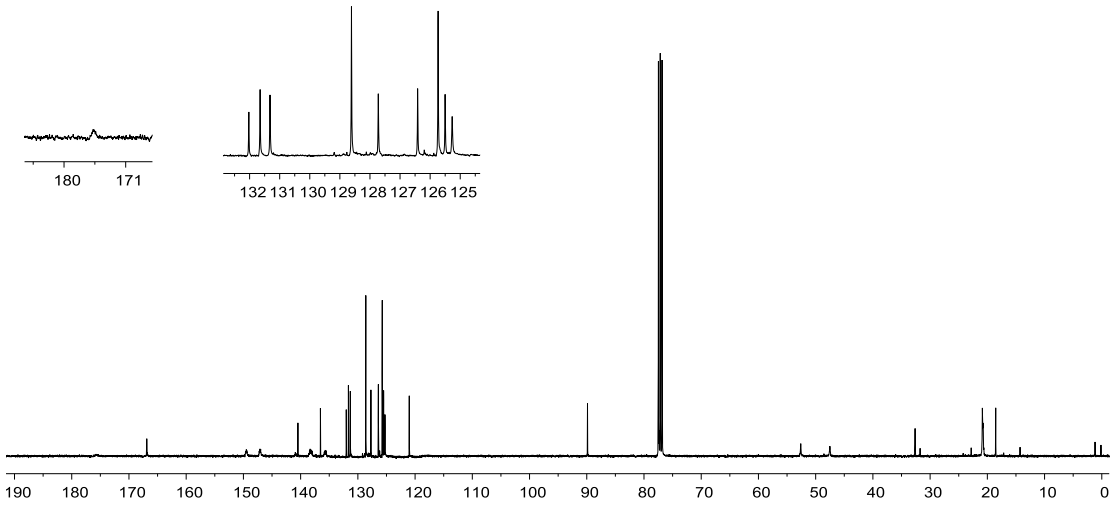



**Fig. S17** $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **5b**.

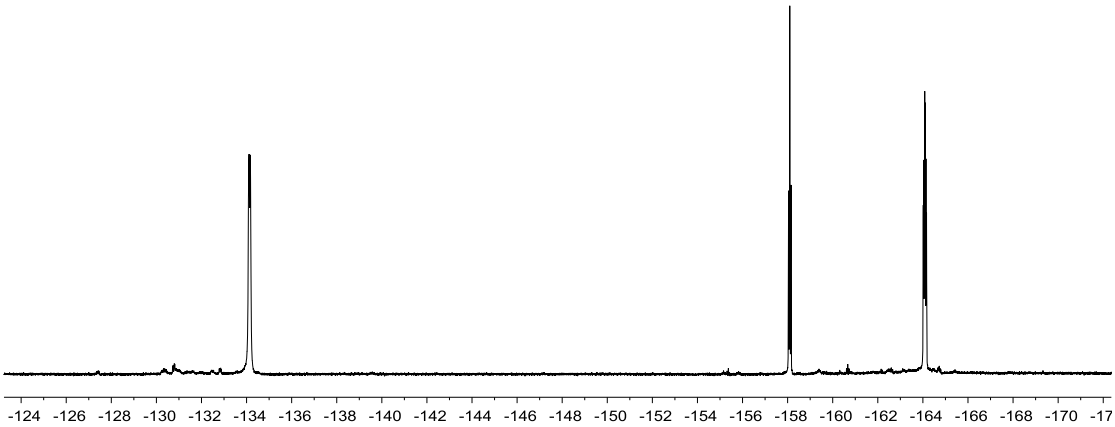



**Fig. S18** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **5b**.

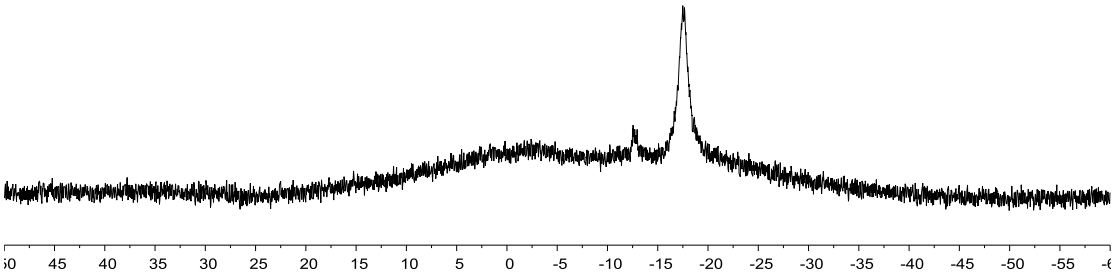
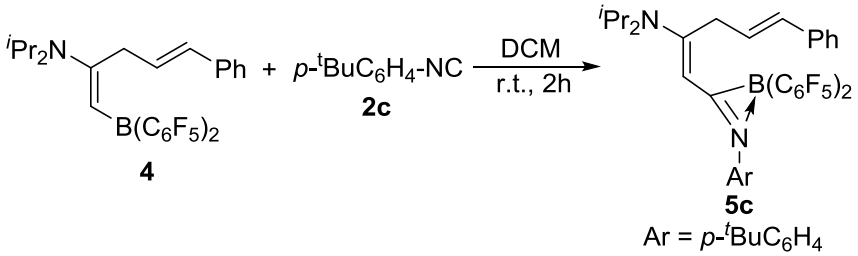



**Fig. S19** $^{11}B$ NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **5b**.

## Synthesis of compound 5c




A solution of compounds **4** (108.1 mg, 0.18 mmol) and **2c** (29.3 mg, 0.18 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed

with *n*-hexane (2 mL) and dried in vacuo to give a white solid. Yield: 116.2 mg, 85%.

**HRMS (ESI)**: m/z calcd for $C_{40}H_{38}BF_{10}N_2$: 747.2963 $[M+H]^+$; found: 747.2970.

**$^1$H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.04-7.48 (m, 9H, Ph), 6.37 (s, 1H, $^{C=}$C*H*), 6.12 (d, $^3J_{HH}$ = 16.2 Hz, 1H, =C*H*$^{Ph}$), 5.99 (dt, $^3J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, $^{CH2}$C*H*=), 4.29 and 3.99 (each br, each 1H, C*H*$^{iPr}$), 4.09 (br, 2H, C$H_2$), 1.64 (d, $^3J_{HH}$ = 5.1 Hz, 3H) and 1.26 (d, $^3J_{HH}$ = 4.0 Hz, 3H) (C$H_3^{iPr}$), 1.34 (s, 9H, C$H_3^{tBu}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 173.5 (brm, B*C*), 167.3 ($^{iPr}$N*C*), 148.1 (dm, $^1J_{FC}$ = 239.1 Hz, *m*-*C*$_6$F$_5$), 139.6 (dm, $^1J_{FC}$ = 250.6 Hz, *p*-*C*$_6$F$_5$), 136.9 (dm, $^1J_{FC}$ = 247.2 Hz, *o*-*C*$_6$F$_5$), 117.2 (brm, *i*-*C*$_6$F$_5$), 148.2, 138.3, 136.5, 128.6, 127.7, 126.4, 125.7, 121.0 (Ph), 131.2 (=*C*H$^{Ph}$), 125.3 ($^{CH2}$*C*H=), 90.7 ($^{C=}$*C*H), 52.7 and 47.6 (each br, *C*H$^{iPr}$), 34.7 (*C*$^{tBu}$), 32.4 (*C*$H_2$), 31.5(*C*$H_3^{tBu}$), 20.8 (*C*$H_3^{iPr}$).

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C: 6.37/90.7 ($^{C=}$*CH*), 6.12/131.2 (=*CH*$^{Ph}$), 5.99/125.3 ($^{CH2}$*CH*=), 4.29/52.7 and 3.99/47.6 (*CH*$^{iPr}$), 4.09/32.4 (*CH*$_2$), (1.64, 1.26)/20.8 (*CH*$_3^{iPr}$), 1.34/31.5 (*C*H$_3^{tBu}$).

**$^1$H-$^{13}$C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C : 6.37/173.5 ($^{C=}$C*H*/B*C*), 5.99/167.3 ($^{CH2}$C*H*=/$^{iPr}$N*C*), 1.34/34.7 (C$H_3^{tBu}$/*C*$^{tBu}$).

**$^{11}$B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -19.6 ($\nu_{1/2}$ ~ 125 Hz).

**$^{19}$F{$^1$H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -134.0 (m, 4F, *o*-$C_6F_5$), -158.6 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*-$C_6F_5$), -164.2 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 5.6].

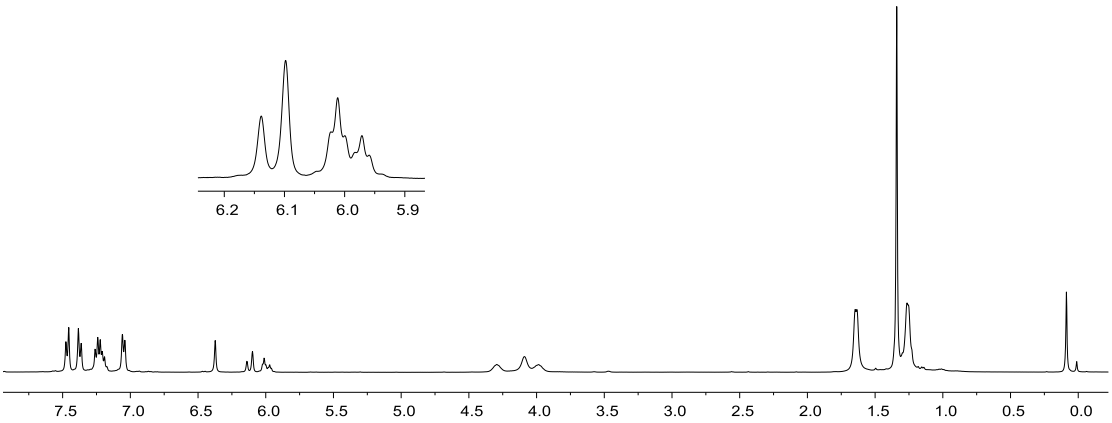



**Fig. S20** $^1$H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **5c**.

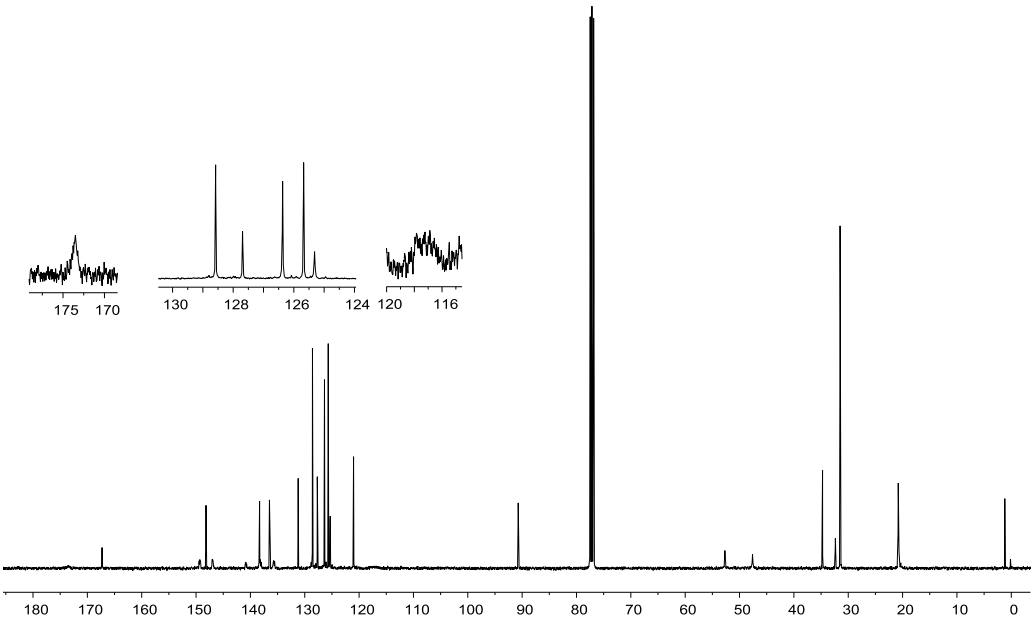



**Fig. S21** $^{13}$C{$^1$H} NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **5c**.

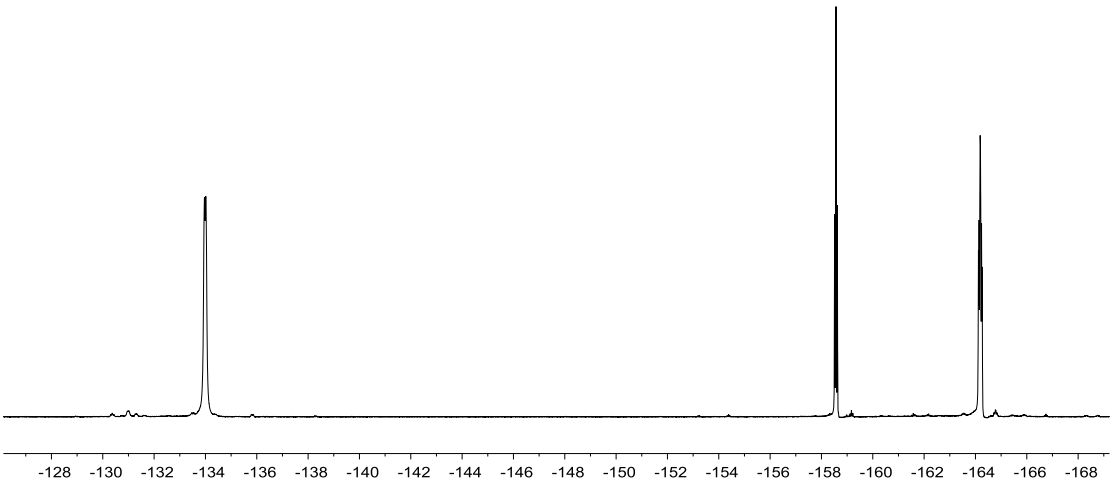



**Fig. S22** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **5c**.

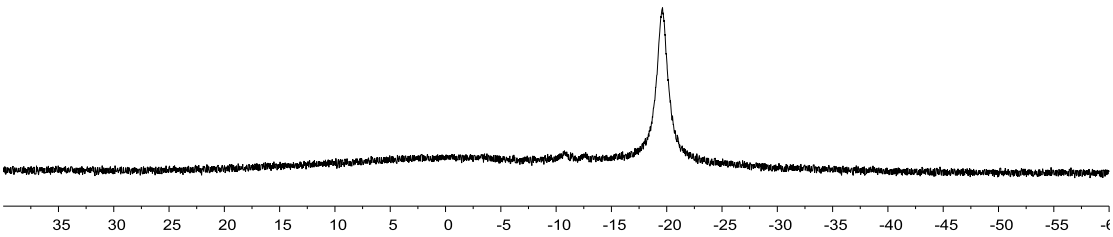
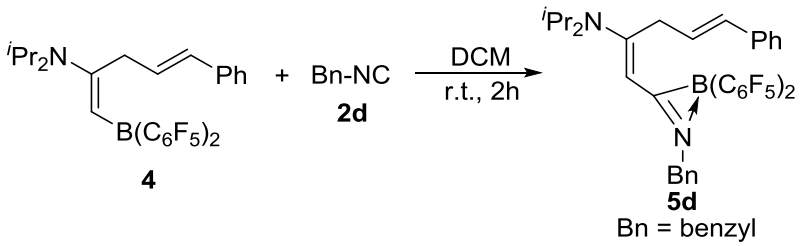



**Fig. S23** $^{11}B$ NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **5c**.

## Synthesis of compound 5d




A solution of compounds **4** (120.0 mg, 0.20 mmol) and **2d** (23.9 mg, 0.20 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed

with *n*-hexane (2 mL) and dried in vacuo to give a white solid. Yield: 102.3 mg, 71%.

**HRMS (ESI)**: m/z calcd for $C_{37}H_{32}BF_{10}N_2$: 705.2493 $[M+H]^+$; found: 705.2495.

**$^1$H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.06-7.31 (m, 10H, Ph), 6.08 (d, $^3J_{HH}$ = 16.2 Hz, 1H, =C*H*$^{Ph}$), 5.99 (dt, $^3J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, $^{CH2}$C*H*=), 5.18 (s, 1H, $^{C=}$C*H*), 4.87 (s, 2H, C$H_2^{Ph}$), 4.14 and 3.72 (br, each 1H, C*H*$^{iPr}$), 3.97 (br, 2H, C$H_2$), 1.16 (br, 12H, C$H_3^{iPr}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 179.6 (brm, B*C*), 164.3 ($^{iPr}$N*C*), 148.0 (dm, $^1J_{FC}$ = 239.1 Hz, *m*-$C_6F_5$), 139.5 (dm, $^1J_{FC}$ = 250.1 Hz, *p*-$C_6F_5$), 136.9 (dm, $^1J_{FC}$ = 251.4 Hz, *o*-$C_6F_5$), 117.6 (brm, *i*-$C_6F_5$), 136.8, 136.4, 128.8, 128.7, 128.6, 127.7, 127.5, 125.7 (Ph), 130.9 (=*C*H$^{Ph}$), 126.2 ($^{CH2}$*C*H=), 88.3 ($^{C=}$*C*H), 52.3 (*C*$H_2^{Ph}$), 51.9 and 46.9 (each br, $^{iPrN}$*C*H), 32.4 (*C*$H_2$), 20.6 and 20.3 (*C*$H_3^{iPr}$).

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C: 6.08/130.9 (=*CH*$^{Ph}$), 5.99/126.2 ($^{CH2}$*CH*=), 5.18/88.3 ($^{C=}$*CH*), 4.87/52.3 (C$H_2^{Ph}$), 4.14/51.9 and 3.71/46.9 (*CH*$^{iPr}$), 3.97/32.4 (*CH*$_2$), 1.16/(20.6, 20.3) (*CH*$_3^{iPr}$).

**$^{11}$B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -18.7 ($\nu_{1/2}$ ~ 70 Hz).

**$^{19}$F{$^1$H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -134.6 (m, 4F, *o*-$C_6F_5$), -158.9 (t, $^3J_{FF}$ = 20.2 Hz, 2F, *p*-$C_6F_5$), -164.3 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 5.4].

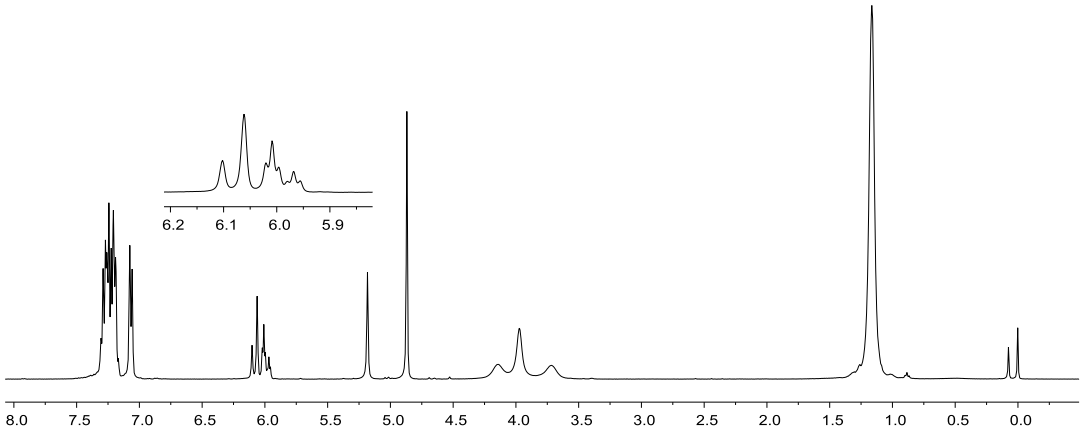



**Fig. S24** $^{1}$H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **5d**.

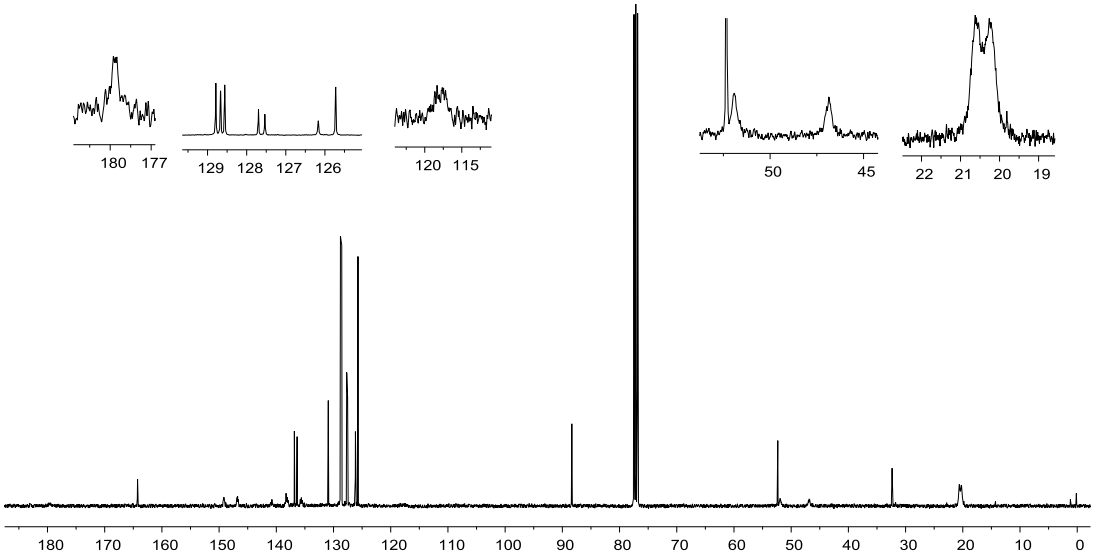



**Fig. S25** $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **5d**.

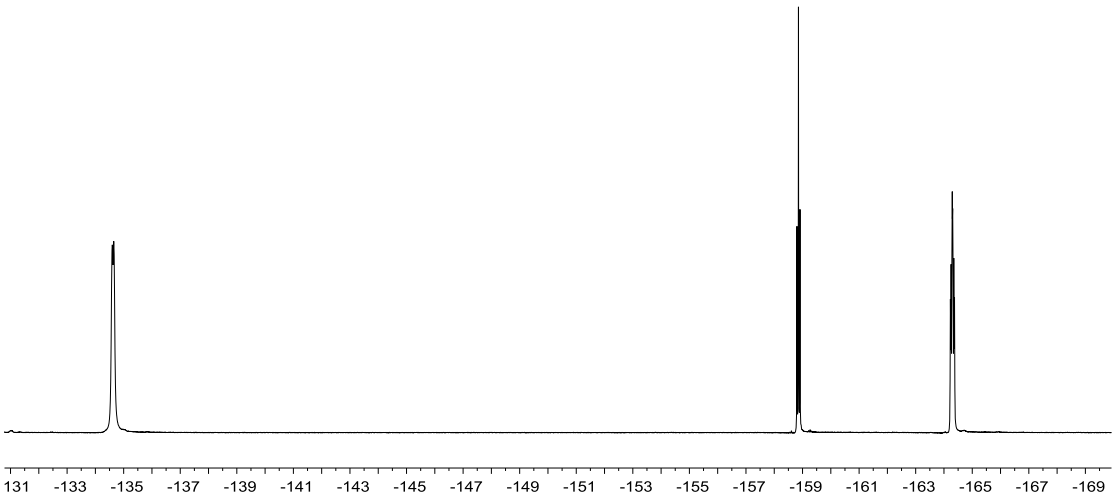



**Fig. S26** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **5d**.

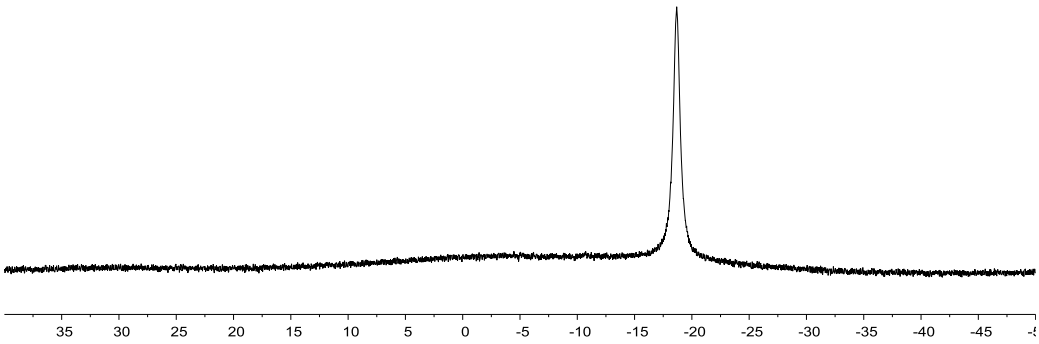
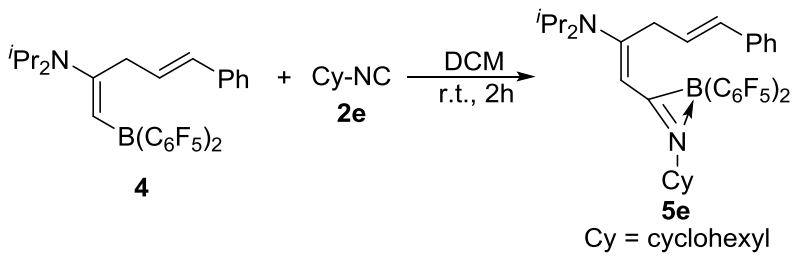



**Fig. S27** $^{11}B$ NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **5d**.

## Synthesis of compound 5e




A solution of compounds **4** (120.0 mg, 0.20 mmol) and **2e** (22.3 mg, 0.20

mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed with *n*-hexane (2 mL) and dried in vacuo to give a white solid. Yield: 110.3 mg, 78%.

**HRMS (ESI)**: m/z calcd for $C_{36}H_{36}BF_{10}N_2$: 697.2806 $[M+H]^+$; found: 697.2812.

**$^1$H NMR** (400 MHz, 298 K, $CDCl_3$): δ = 7.06-7.26 (m, 5H, Ph), 6.12 (d, $^3J_{HH}$ = 16.1 Hz, 1H, =C*H*$^{Ph}$), 5.96 (dt, $^3J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, $^{CH2}$C*H*=), 5.72 (s, 1H, $^{C=}$C*H*), 4.14 (br, 1H, C*H*$^{iPr}$), 3.96 (br, 3H, C*H*$^{iPr}$ and C$H_2$), 3.79 (m, 1H, C*H*$^{Cy}$), 1.16-2.00 (m, 22H, C$H_2^{Cy}$ and C$H_3^{iPr}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CDCl_3$): δ = 178.5 (brm, B*C*), 163.9 ($^{iPr}$N*C*), 148.0 (dm, $^1J_{FC}$ = 239.1 Hz, *m*-$C_6F_5$), 139.5 (dm, $^1J_{FC}$ = 240.4 Hz, *p*-$C_6F_5$), 136.9 (dm, $^1J_{FC}$ = 250.7 Hz, *o*-$C_6F_5$), 119.1 (brm, *i*-$C_6F_5$), 136.9, 128.5, 127.5, 125.7 (Ph), 130.9 (=*C*H$^{Ph}$), 126.2 ($^{CH2}$*C*H=), 88.3 ($^{C=}$*C*H), 58.5 (*C*H$^{Cy}$), 51.8 and 47.1 (br, $^{iPrN}$*C*H), 32.3 (*C*$H_2$), 31.7, 25.8, 25.0, 20.7 ($^{Cy}$*C*$H_2$ and *C*$H_3^{iPr}$).

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C: 6.12/130.9 (=*CH*$^{Ph}$), 5.96/126.2 ($^{CH2}$*CH*=), 5.72/88.3 ($^{C=}$*CH*), 4.14/51.8 and 3.96/47.1 (*CH*$^{iPr}$), 3.96/32.3 (C*H*$_2$), 3.79/58.5(*CH*$^{Cy}$).

**$^1$H-$^{13}$C GHMBC** (400 MHz/101 MHz, 298 K, $CDCl_3$): δ$^1$H/δ$^{13}$C: 5.72/178.5 ($^{C=}$C*H*/B*C*), 5.96/163.9 ($^{CH2}$C*H*=/$^{iPr}$N*C*).

**$^{11}$B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -19.8 ($\nu_{1/2}$ ~ 75 Hz).

**$^{19}F\{^1H\}$ NMR** (377 MHz, 298 K, $CDCl_3$): δ = -134.6 (m, 4F, *o*-$C_6F_5$), -159.1 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*-$C_6F_5$), -164.5 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 5.4].

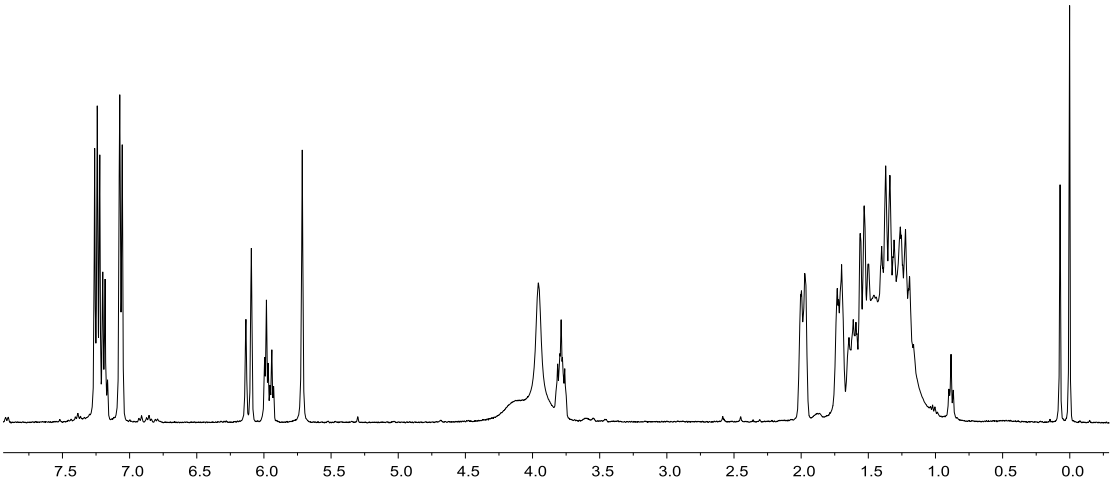



**Fig. S28** $^1H$ NMR (400 MHz, 298 K, $CDCl_3$) spectrum of compound **5e**.

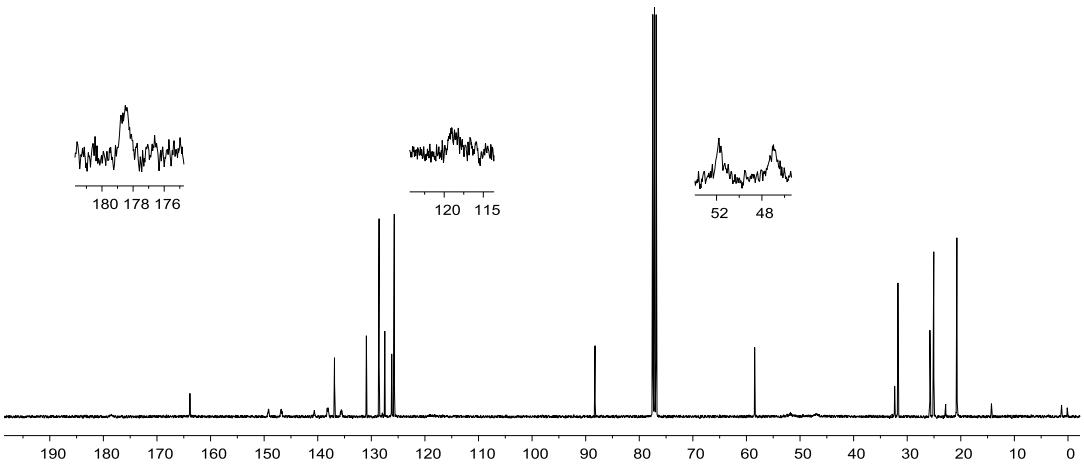



**Fig. S29** $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of compound **5e**.

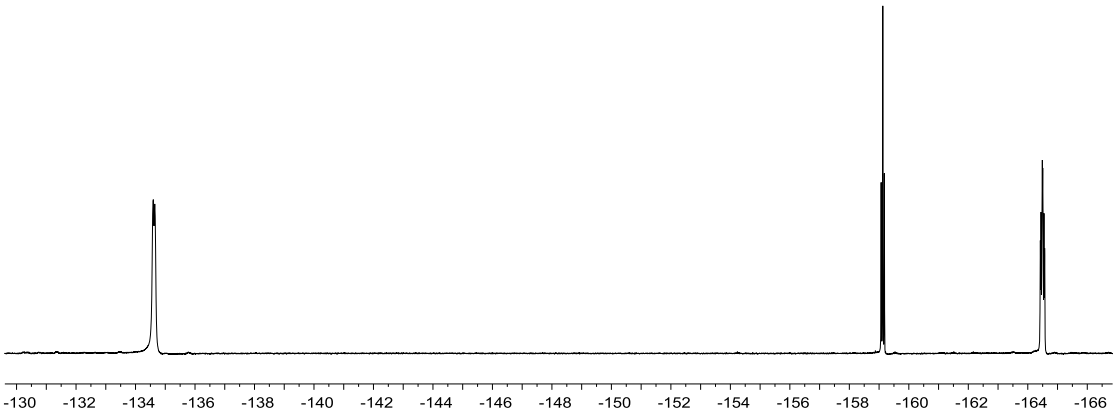



**Fig. S30** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$) spectrum of compound **5e**.

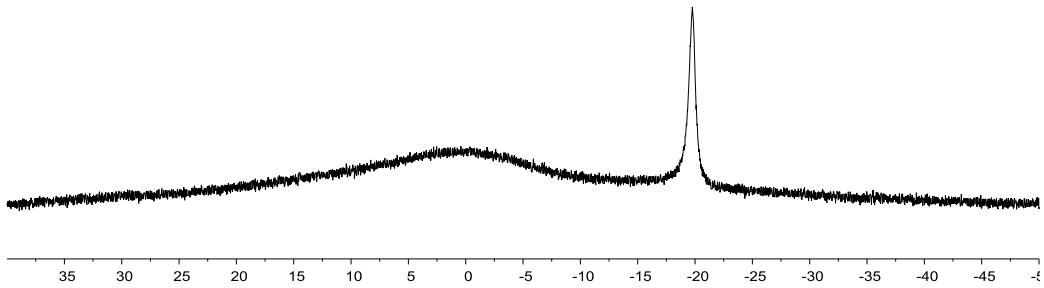
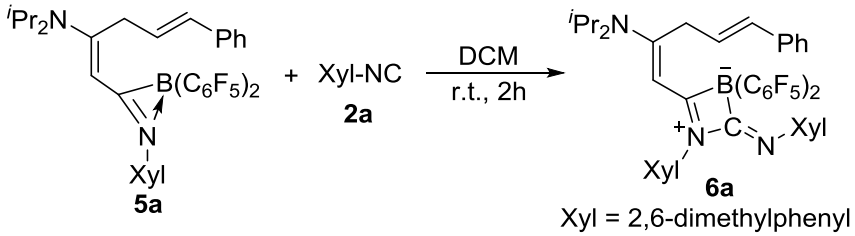



**Fig. S31** $^{11}B$ NMR (128 MHz, 298 K, $CDCl_3$) spectrum of compound **5e**.

## Synthesis of compound 6a

### *Method A*




A solution of compounds **5a** (200.0 mg, 0.28 mmol) and **2a** (40.2 mg, 0.31 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was

washed with *n*-hexane (3×3 ml) and dried in vacuo to give a white solid. Yield: 200.0 mg, 85%.

***Method B***


Xyl = 2,6-dimethylphenyl

A solution of compounds **4** (100.0 mg, 0.17 mmol) and **2a** (44.6 mg, 0.34 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 4 h. After the removal of the solvent under vacuum, the obtained residue was washed with *n*-hexane (3×3 ml) and dried in vacuo to give a white solid. Yield: 117.3 mg, 81%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated compound **6a** in $CH_2Cl_2$ covered with *n*-hexane at -25 ℃.

**HRMS (ESI)**: m/z calcd for $C_{47}H_{43}BF_{10}N_3$: 850.3385 $[M+H]^+$; found: 850.3383.

**$^1$H NMR** (400 MHz, 298 K, $CD_2Cl_2$): δ = 6.69-7.32 (m, 11H, Ph), 6.00 (d, 1H, $^3J_{HH}$ = 16.1 Hz, $^{Ph}CH$=), 5.71 (s, 1H, $^{C=}CH$), 5.50 (dt, 1H, $^3J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 4.8 Hz, $^{CH2}CH$=), 4.18 and 3.81 (each m, each 1H, $CH^{iPr}$), 3.49 (m, 2H, $CH_2$), 2.38 and 1.71 (s, each 6H, $CH_3^{Ph}$), 1.13 ($^3J_{HH}$ = 6.6 Hz), 1.19 ($^3J_{HH}$ = 7.1 Hz) (each d, each 3H, $CH_3^{iPr}$).

**$^{13}C\{^1H\}$ NMR** (101 MHz, 298 K, $CD_2Cl_2$): δ = 199.3 (br, NCN) ,174.5 (br, B$C^{CH}$), 169.4 ($^{iPrN}C$), 148.4 (dm, $^1J_{FC}$ = 238.6 Hz, *m*-$C_6F_5$), 139.7 (dm, $^1J_{FC}$ = 242.7 Hz, *p*-$C_6F_5$), 137.1 (dm, $^1J_{FC}$ = 240.5 Hz, *o*-$C_6F_5$), 116.7 (brm, *i*-$C_6F_5$), 147.1, 137.2, 136.1, 134.1, 129.5, 129.00, 128.95, 128.3, 127.5, 127.1, 125.9, 122.1 (Ph), 131.9 ($^{Ph}C$H=), 122.7 ($^{CH2}C$H=), 99.0 ($^{C=}C$H), 54.0 and 48.7 (each br, $CH^{iPr}$), 33.1 ($CH_2$), 20.7 and 20.2 ($CH_3^{iPr}$), 18.2 ($CH_3^{Ph}$).

**$^1H$-$^{13}C$ GHSQC** (400 MHz/101 MHz, 298 K, $CD_2Cl_2$): $\delta^1H/\delta^{13}C$: 6.00/131.9 ($^{Ph}CH$=), 5.71/99.0 ($^{C=}CH$), 5.50/122.7 ($^{CH2}CH$=), 4.18/54.0 and 3.81/48.7 ($CH^{iPr}$), 3.49/33.1 ($CH_2$), (2.38, 1.71)/18.2 ($CH_3^{Ph}$), 1.19/20.7 and 1.13/20.2 ($CH_3^{iPr}$).

**$^1H$-$^{13}C$ GHMBC** (400 MHz/101 MHz, 298 K, $CD_2Cl_2$): $\delta^1H/\delta^{13}C$: 5.71/199.3 ($^{C=}CH$, $CH_3^{Ph}$/NCN), 3.81/169.4 ($CH^{iPr}$/$^{iPrN}C$).

**$^{11}B$ NMR** (128 MHz, 298 K, $CD_2Cl_2$): δ = -10.6 ($\nu_{1/2}$ ~ 44 Hz).

**$^{19}F\{^1H\}$ NMR** (377 MHz, 298 K, $CD_2Cl_2$): δ = -129.8 (m, 4F, *o*-$C_6F_5$), -159.6 (t, $^3J_{FF}$ = 20.2 Hz, 2F, *p*-$C_6F_5$), -165.4 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 5.8].

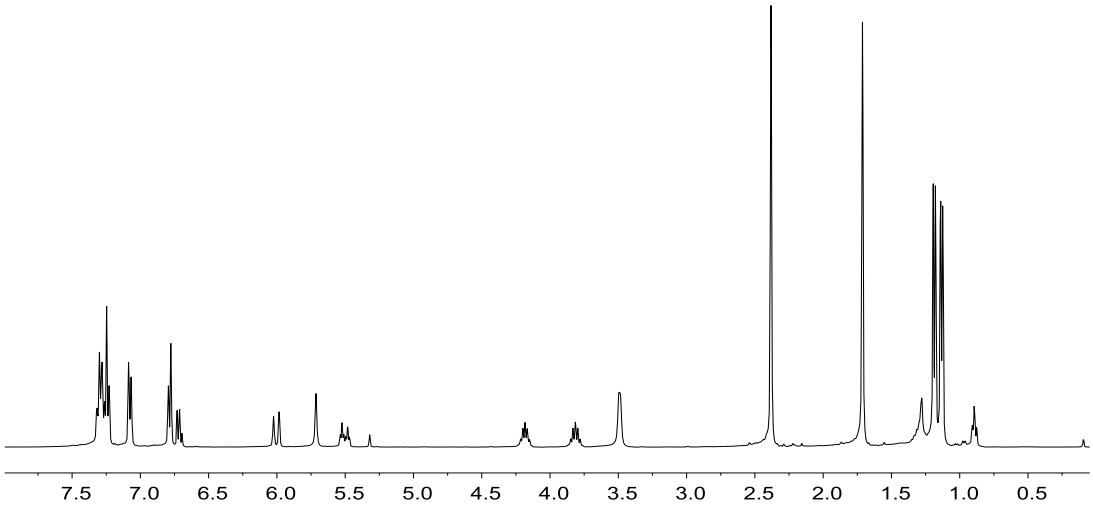



**Fig. S32** $^{1}$H NMR (400 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **6a**.

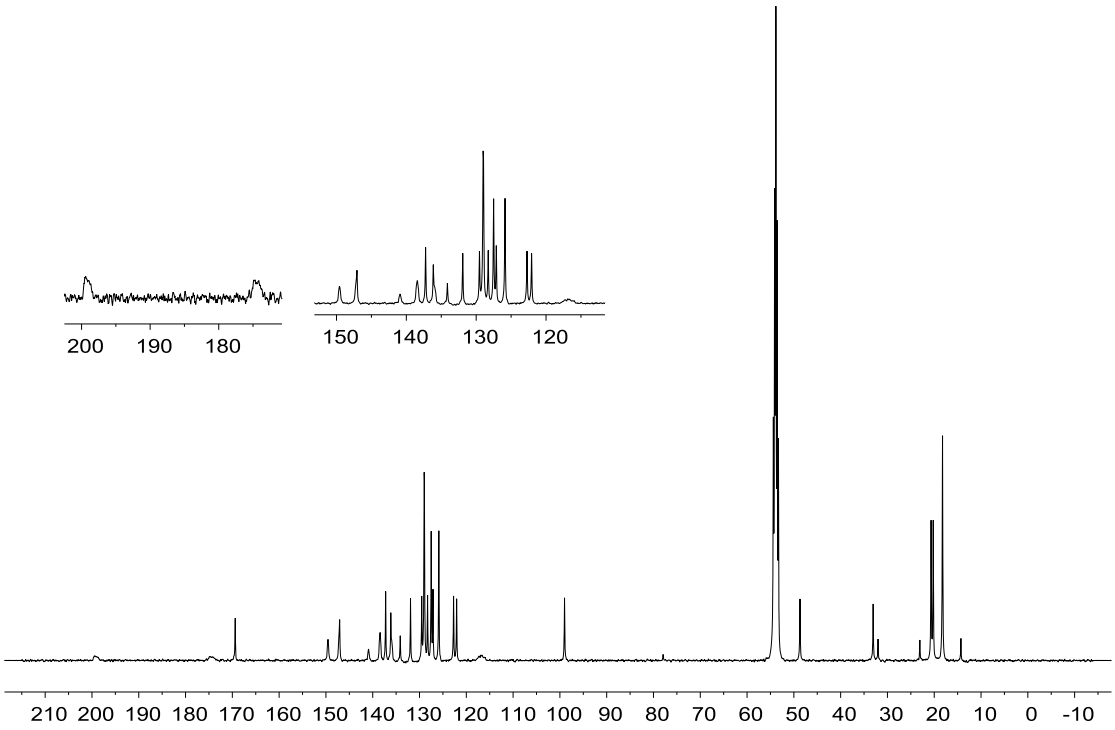



**Fig. S33** $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **6a**.

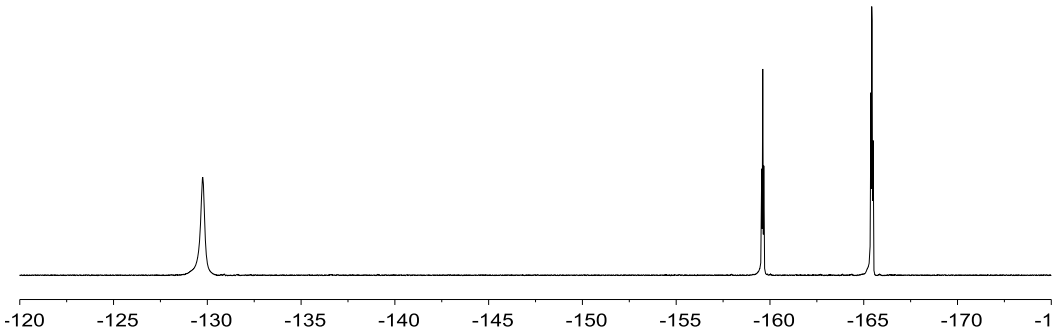



**Fig. S34** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **6a**.

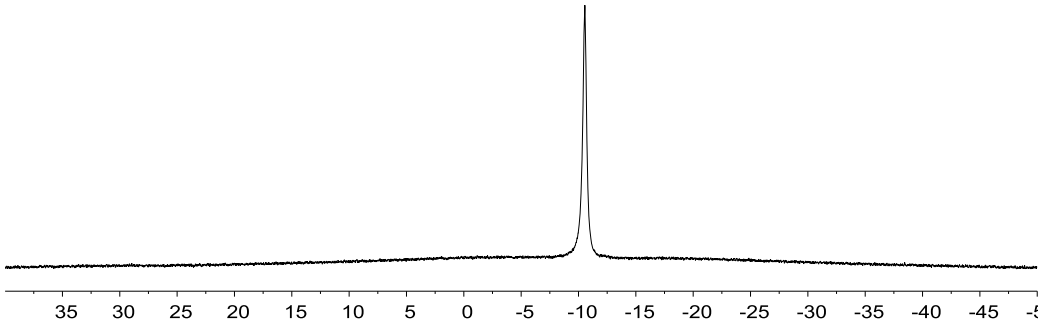



**Fig. S35** $^{11}B$ NMR (128 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **6a**.

**X-ray crystal structure analysis of compound 6a:** formula $C_{48}H_{44}BCl_2F_{10}N_3$, $M$ = 934.57, colourless crystal, 0.47 × 0.45 × 0.24 mm, $a$ = 12.158(3), $b$ = 24.328(5), $c$ = 15.731(4) Å, α = γ = 90.000 º, $\beta$ = 99.003(6) º, $V$ = 4595.6(19) Å$^3$, $\rho_{calc}$ = 1.351 gcm$^{-3}$, μ = 0.219 mm$^{-1}$, empirical absorption correction ($0.6706 \leq T \leq 0.7461$), $Z$ = 4, monoclinic, space group $P2_1/n$, λ = 0.71073 Å, $T$ = 150.2 K, ω and φ scans, 55725 reflections collected (±$h$, ±$k$, ±$l$), 8079 independent ($R_{int}$ = 0.0741) and 6265 observed reflections [$I$>2σ($I$)], 585 refined parameters, $R$ = 0.0615, $wR^2$ = 0.1762, max. (min.) residual electron density 1.12 (-0.90) e.Å$^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

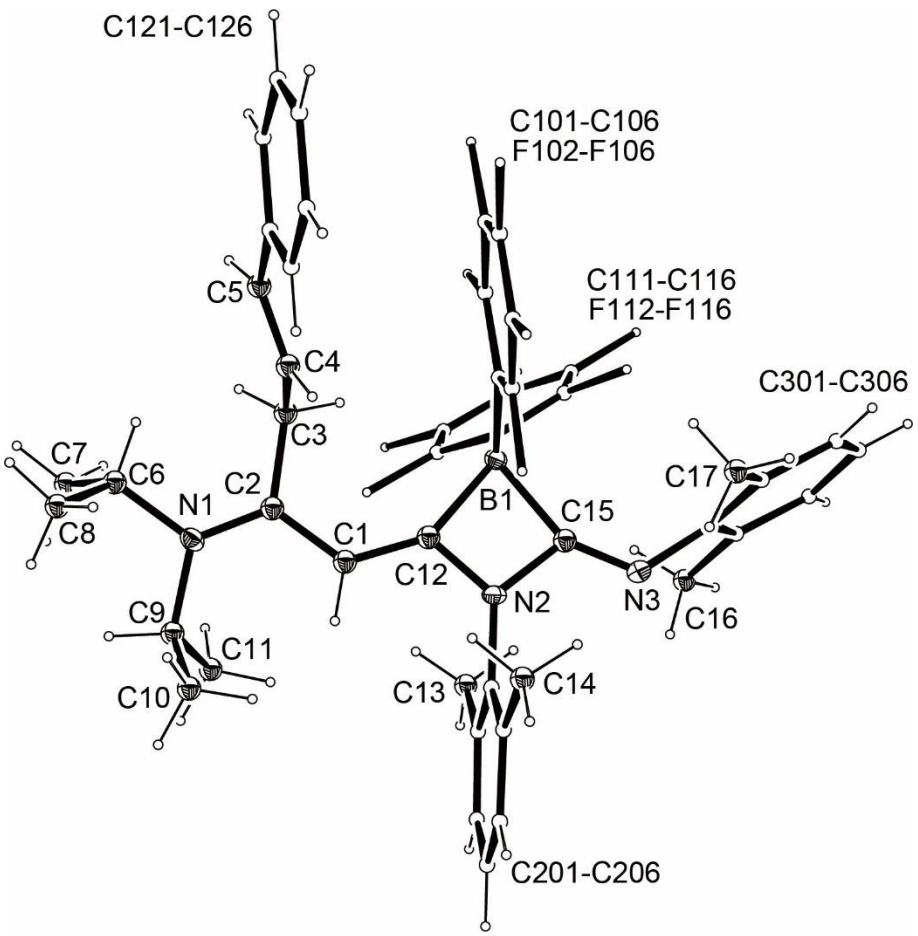
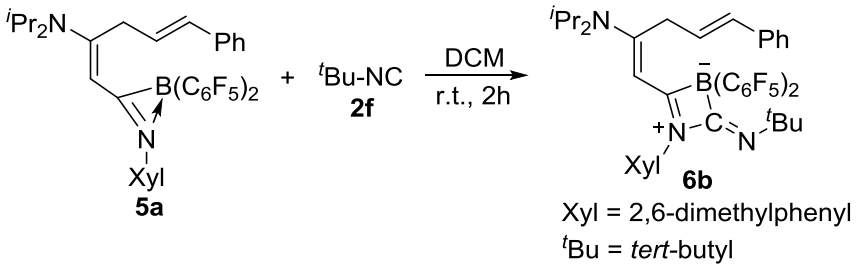



**Fig. 36** A view of the molecular structure of compound **6a** (thermal ellipsoids are shown at the 30% probability level). Selected bond lengths (Å) and angles (deg): N1-C2 1.331(3), C2-C1 1.412(4), C1-C12 1.372(4), C12-N2 1.367(3), N2-C201 1.444(3), N2-C15 1.427(3), N3-C15 1.263(3), B1-C15 1.689(4), B1-C12 1.668(4), B1-C101 1.628(4), B1-C111 1.632(4); N1-C2-C1 121.9(2), C2-C1-C12 126.3(2), B1-C12-N2 91.4(2), C12-N2-C15 100.5(2), N2-C15-B1 88.51(18), C15-B1-C12 79.55(18); $\sum N1^{CCC}$ 359.9, $\sum N2^{CCC}$ 359.3.

**Synthesis of compound 6b**




A solution of compounds **5a** (150.1 mg, 0.21 mmol) and **2f** (17.8 mg, 0.21 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 2 h. After the removal of the solvent under vacuum, the obtained residue was washed with *n*-hexane (3×3 ml) and dried in vacuo to give a white solid. Yield: 130.5 mg, 78%.

[Comments: Compound **6b** is not stable in solution. The obvious conversion of compound **6a** to **7** can be observed after 1 hour in solution at room temperure by the in-situ NMR, which prevents the $^{13}C\{^1H\}$ NMR and related 2D NMR spectroscopic studies.]

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated compound **6b** in $CH_2Cl_2$ covered with *n*-hexane at -25 ℃.

**HRMS (ESI)**: m/z calcd for $C_{43}H_{43}BF_{10}N_3$: 802.3385 $[M+H]^+$; found: 802.3391.

**$^1$H NMR** (400 MHz, 298 K, $C_6D_6$): δ = 6.92-7.14 (m, 8H, Ph), 5.94 (d, H, $^3J_{HH}$ = 16.3 Hz, $^{Ph}CH$=), 5.59 (dt, 1H, $^3J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 5.1 Hz,

$^{CH2}$C*H*=), 5.57 (s, 1H, $^{C=}$C*H*), 3.53 and 2.85 (each, m, each 1H, C*H*$^{iPr}$), 3.30 (d, 2H, C$H_2$), 2.42 (s, 6H, C$H_3^{Ph}$), 1.32 (s, 9H, C$H_3^{tBu}$), 0.74, 0.38 (each m, each 6H, C$H_3^{iPr}$).

**$^{11}$B NMR** (128 MHz, 298 K, $C_6D_6$): δ = -9.2 ($\nu_{1/2}$ ~ 45 Hz).

**$^{19}$F{$^1$H} NMR** (377 MHz, 298 K, $C_6D_6$): δ = -127.3 (m, 4F, *o*-$C_6F_5$), -157.9 (t, $^3J_{FF}$ = 21.0 Hz, 2F, *p*-$C_6F_5$), -164.2 (m, 4F, *m*-$C_6F_5$) [$\Delta\delta^{19}F_{m,p}$ = 6.3].

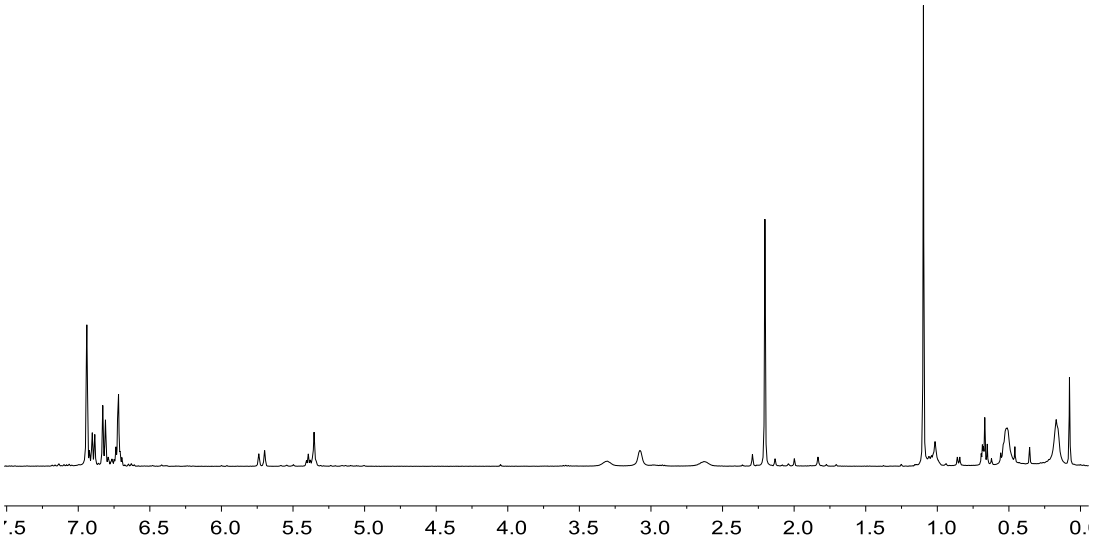



**Fig. S37** $^1$H NMR (400 MHz, 298 K, $C_6D_6$) spectrum of compound **6b**.

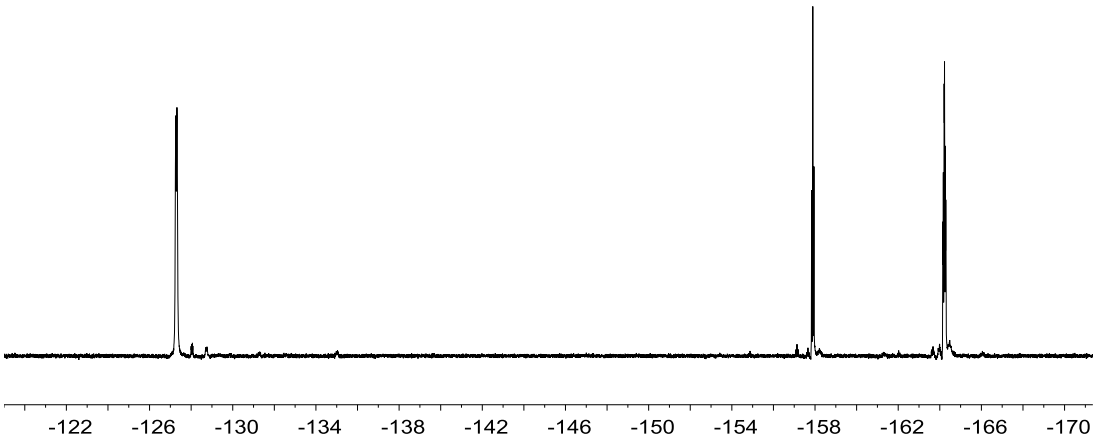



**Fig. S38** $^{19}$F{$^1$H} NMR (377 MHz, 298 K, $C_6D_6$) spectrum of compound **6b**.

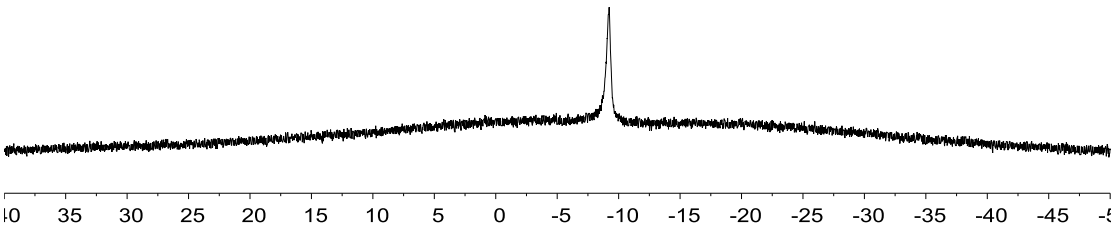



**Fig. S39** $^{11}$B NMR (128 MHz, 298 K $C_6D_6$) spectrum of compound **6b**.

**X-ray crystal structure analysis of compound 6b:** formula $C_{46}H_{49}BF_{10}N_3$, $M$ = 844.69, colorless crystal, 0.45 × 0.44 × 0.2 mm, $a$ = 16.808(3), $b$ = 16.731(3), $c$ = 31.076(6) Å, α = γ = 90.000 º, $\beta$ = 90.186(4) º, $V$ = 8739(3) Å$^3$, $\rho_{calc}$ = 1.284 gcm$^{-3}$, μ = 0.104 mm$^{-1}$, empirical absorption correction (0.6528 ≤ T ≤ 0.7461), $Z$ = 8, monoclinic, space group *C2/c*, λ = 0.71073 Å, $T$ = 150.0 K, ω and φ scans, 42794 reflections collected (±*h*, ±*k*, ±*l*), 6870 independent ($R_{int}$ = 0.2369) and 2639 observed reflections [$I$>2σ($I$)], 523 refined parameters, $R$ = 0.0850, $wR^2$ = 0.1748, max. (min.) residual electron density 0.32 (-0.22) e.Å$^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

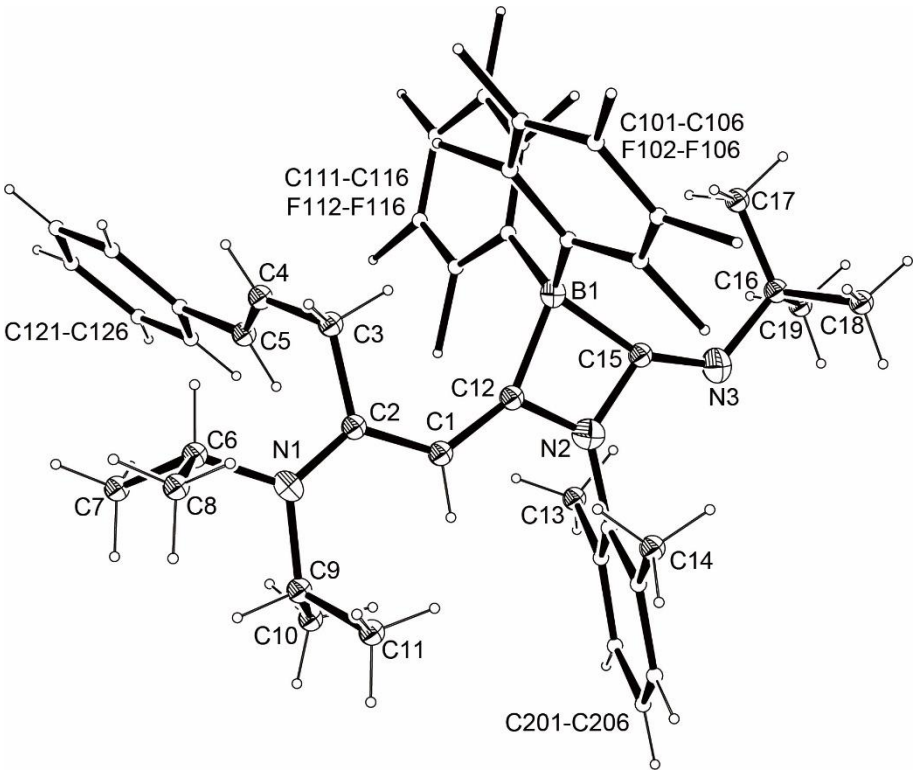
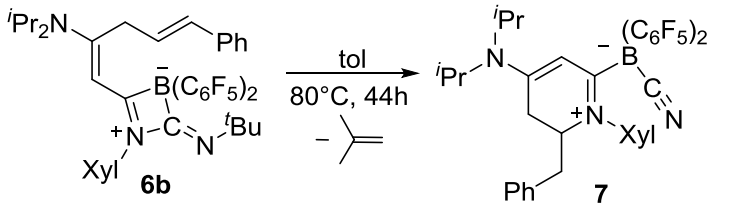



**Fig. S40** A view of the molecular structure of compound **6b** (thermal ellipsoids are shown at the 30% probability level). Selected bond lengths (Å) and angles (deg): N1-C2 1.327(6), C2-C1 1.396(7), C1-C12 1.382(7), C12-N2 1.344(6), N2-C201 1.441(6), N2-C15 1.422(7), N3-C15 1.286(6), B1-C15 1.674(8), B1-C12 1.660(8), B1-C101 1.641(8), B1-C111 1.631(8); N1-C2-C1 124.2(5), C2-C1-C12 127.9(5), B1-C12-N2 92.1(4), C12-N2-C15 100.1(5), N2-C15-B1 88.8(4), C15-B1-C12 79.0(4); $\sum N1^{CCC}$ 360.0, $\sum N2^{CCC}$ 360.0.

**Synthesis of compound 7**




A solution of compound **6a** (267.3 mg, 0.33 mmol) in toluene (10 mL) was heated at 80 ℃ for 44 h. After the removal of the solvent under vacuum, the obtained residue was dissolved in dichloromethane (2 mL) and added dropwise to *n*-hexane (40 mL). The filtrate was collected and concentrated to ca. 10 mL, then kept at -25 ℃ for 12 h to give a orange crystalline solid, which was collected by filtration and dried in vacuo. Yield: 167.3 mg, 67%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated compound **7** in $CH_2Cl_2$ covered with *n*-hexane at -25 ℃.

**HRMS (ESI)**: m/z calcd for $C_{39}H_{34}BF_{10}N_3Na$: 768.2578 $[M+Na]^+$; found: 768.2574.

**$^1$H NMR** (400 MHz, 298 K, $CD_2Cl_2$): δ = 6.84-7.33 (m, 8H, Ph), 6.11 (s, 1H, C*H*=), 3.98 (m, 1H, C$H^{CH2Ph}$), 3.94 and 3.80 (m, 2H, C$H^{iPr}$), 2.91 (m, 2H, $^{Ph}CH_2$), 2.82 (dd, 1H, $^2J_{HH}$ =16.5 Hz, $^3J_{HH}$ = 6.0 Hz) and 2.52 (dd, 1H, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 6.4 Hz, $^{iPrNC}CH_2$), 2.38 and 2.36 (each s, each 3H,

C$H_3^{Ph}$), 1.44 (m, 3H), 1.26 (m, 3H) and 1.10 (m, 6H) (C$H_3^{iPr}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, $CD_2Cl_2$): δ =186.0 (br, B*C*), 157.1 (br, $^{iPr2}$N*C*), not observed (B-*C*≡N), 148.2 (dm, $^1J_{FC}$ = 232.2 Hz, *m*-$C_6F_5$), 139.6 (dm, $^1J_{FC}$ = 232.3 Hz, *p*-$C_6F_5$), 137.2 (dm, $^1J_{FC}$ = 242.4 Hz, *o*-$C_6F_5$), 119.4 (brm, *i*-$C_6F_5$), 140.6, 136.8, 136.64, 136.57, 129.5, 129.4, 129.1 129.0, 128.7, 127.7 (Ph), 101.6 (*C*H=), 62.3 (*C*H$^{CH2Ph}$), 50.8 and 49.2 (each br, *C*H$^{iPr}$), 34.7 ($^{Ph}$*C*H$_2$), 29.0 ($^{iPrNC}$C*H*$_2$), 21.2, 20.7 and 20.6 (*C*H$_3^{iPr}$), 19.0 and 19.6 (*C*H$_3^{Ph}$).

**$^1$H-$^{13}$C GHSQC** (400 MHz/101 MHz, 298 K, $CD_2Cl_2$): δ$^1$H/δ$^{13}$C: 6.11/101.6 (*CH*=), 3.98/62.3 (*CH*$^{CH2Ph}$), 3.94/49.2 and 3.80/50.8 (*CH*$^{iPr}$), 2.91/34.7 ($^{Ph}$*CH*$_2$), (2.82, 2.52)/29.0 ($^{iPrNC}$*CH*$_2$), (2.38, 2.36)/(19.0, 19.6) (*CH*$_3^{Ph}$), (1.44, 1.26, 1.10)/(21.2, 20.7, 20.6) (*CH*$_3^{iPr}$).

**$^{11}$B NMR** (128 MHz, 298 K, $CDCl_3$): δ = -20.3 ($\nu_{1/2}$ ~ 34 Hz).

**$^{19}$F{$^1$H} NMR** (377 MHz, 298 K, $CDCl_3$): δ = -127.0 (m, 4F, *o*-$C_6F_5$), -158.8 (m, 2F, *p*-$C_6F_5$), -164.6 (m, 4F, *m*-$C_6F_5$), [$\Delta\delta^{19}F_{m,p}$ = 5.8].

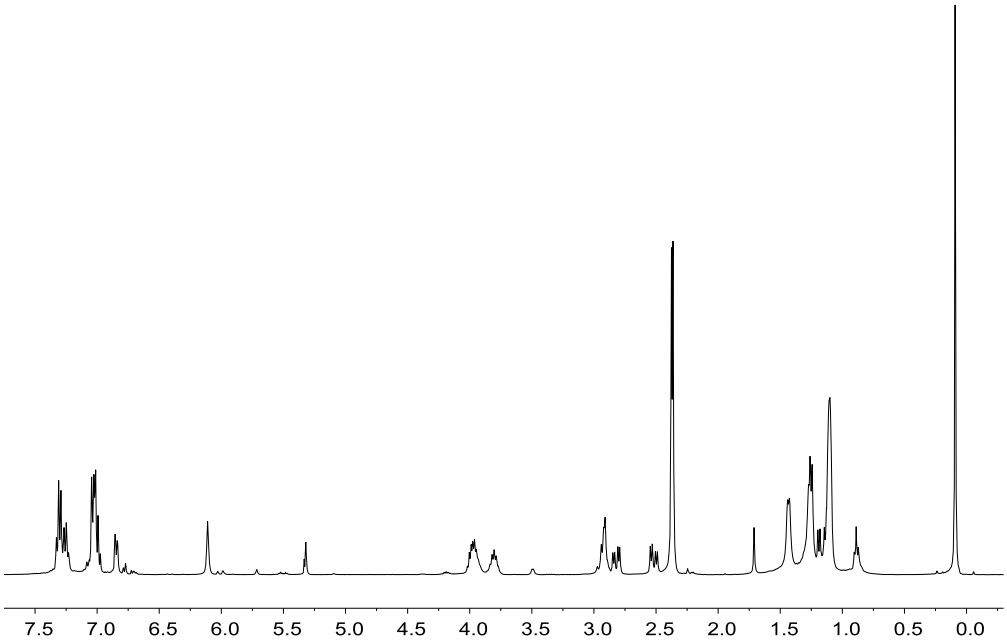



**Fig. S41** $^{1}$H NMR (400 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **7**.

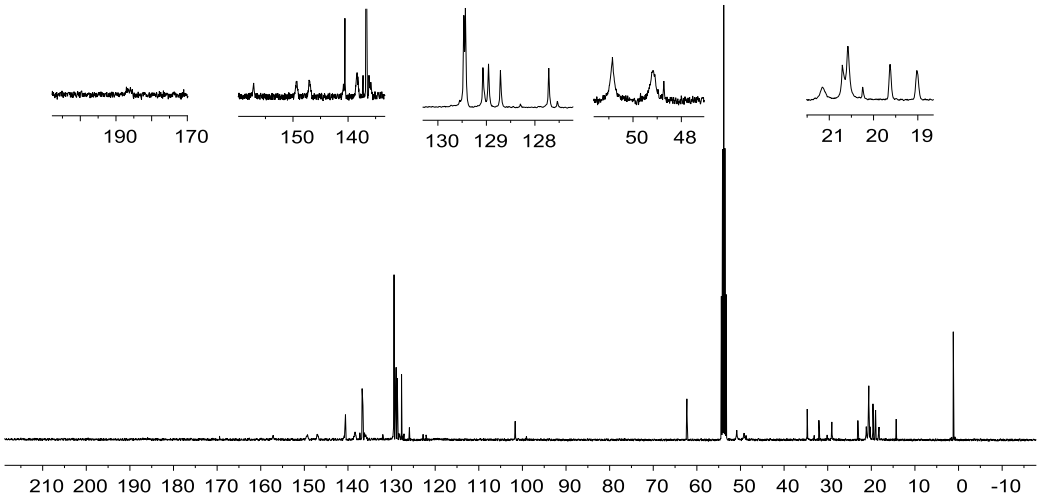



**Fig. S42** $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **7**.

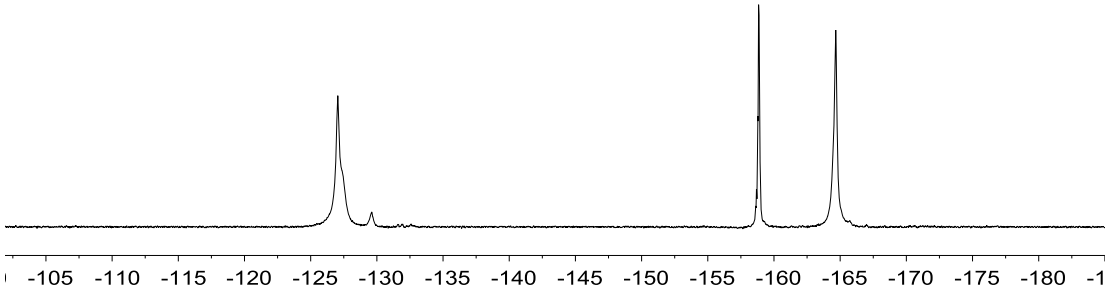



**Fig. S43** $^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **7**.

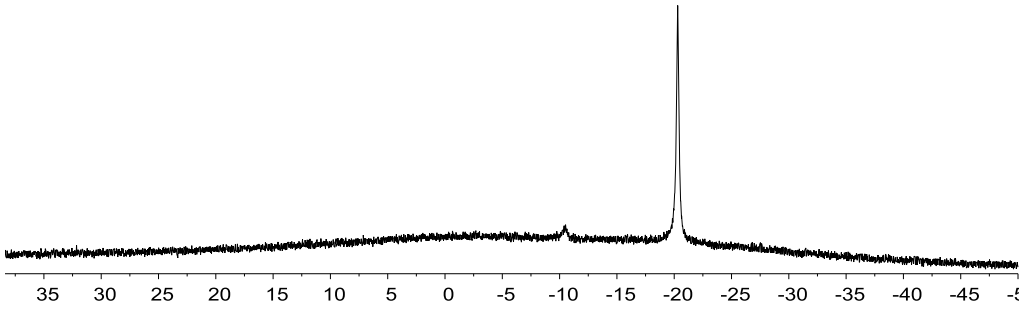



**Fig. S44** $^{11}B$ NMR (128 MHz, 298 K, $CD_2Cl_2$) spectrum of compound **7**.

**X-ray crystal structure analysis of compound 7:** formula $C_{39}H_{34}BF_{10}N_3$, $M$ = 745.50, orange crystal, 0.46 × 0.45 × 0.21 mm, $a$ = 9.2344(8), $b$ = 18.7674(16), $c$ = 20.7528(19) Å, α = γ = 90.000 º, $\beta$ = 100.808(3) º, $V$ = 3532.8(5) $Å^3$, $\rho_{calc}$ = 1.402 $gcm^{-3}$, μ = 0.119 $mm^{-1}$, empirical absorption correction (0.6442 ≤ T ≤ 0.7461), $Z$ = 4, monoclinic, space group $P2_1/c$, λ = 0.71073 Å, $T$ = 150.0 K, ω and φ scans, 43451 reflections collected (±$h$, ±$k$, ±$l$), 10578 independent ($R_{int}$ = 0.0948) and 4573 observed reflections [$I$>2σ($I$)], 484 refined parameters, $R$ = 0.0656, $wR^2$ = 0.1146, max. (min.) residual electron density 0.35 (-0.33) e.$Å^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

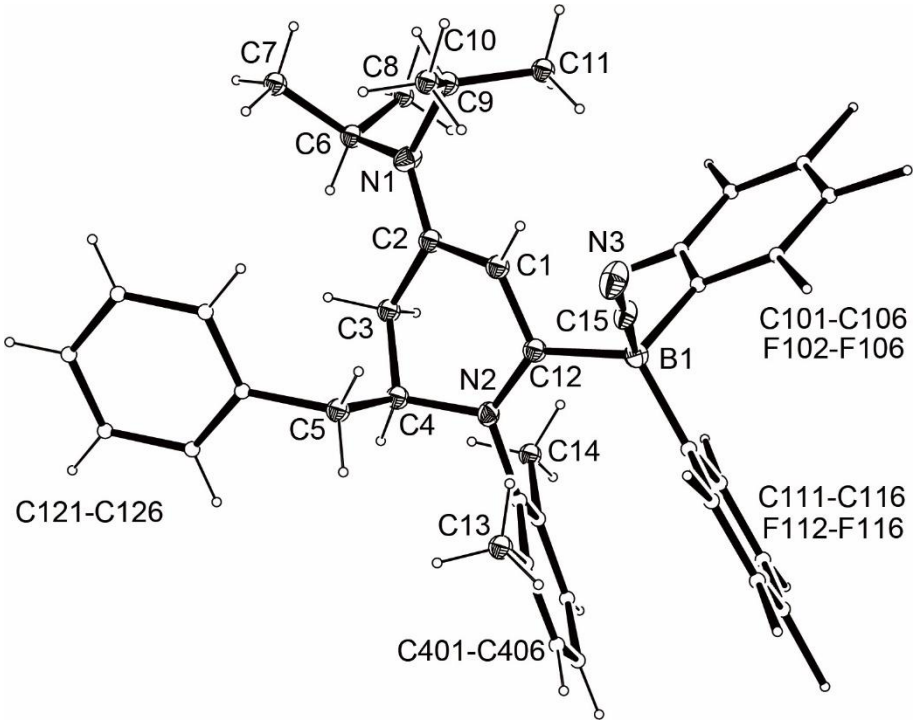



**Fig. S45** A view of the molecular structure of compound **7**.