Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic supplementary information

for

Formal [4+1] cycloaddtions of ketiminoboranes and isonitriles

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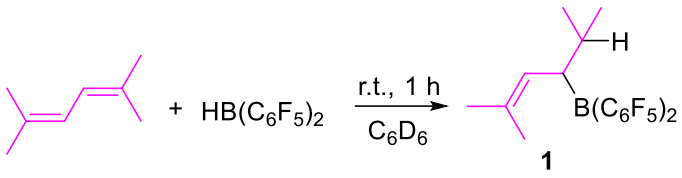
General Information

All manipulations were performed under an atmosphere of dry and oxygen-free N_2 by means of standard Schlenk or glovebox techniques. *n*-hexane and dichloromethane (DCM) were collected from a (Mikrouna) solvent purification system and stored over activated 3 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 3 Å molecular sieves in the glovebox for at least 8 h prior to use. Unless otherwise noted, all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: HRMS: Agilent 6224 TOF LC/MS; NMR: Bruker Avance II 400MHz spectrometer (^{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 (**1-IMes** and **5a**) with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) and a dual source Rigaku Oxford Diffraction four-circle diffractometer (**5j**), equipped with a Hybrid Pixel Array detector and $Cu_{K\alpha}$ 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 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 2256776-2256778 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/.

In-situ generation and characterization of compound 1



Scheme S1

In an NMR tube, a solution of 2,5-dimethylhexa-2,4-diene (16.6 mg, 0.15 mmol) and $HB(C_6F_5)_2$ (51.9 mg, 0.15 mmol) in C_6D_6 (0.6 mL) was kept at room temperature for 1 h, then NMR spectra was conducted.

^{1}H NMR (400 MHz, 299 K, C_6D_6): δ = 4.43 (d, $^3J_{HH}$ = 10.0 Hz, 1H,

=C*H*), 2.76 (t, $^{3}J_{HH}$ = 10.0 Hz, 1H, BC*H*), 1.68 and 0.77 (each s, each 3H, CH_3), 1.56 (m, 1H, C$H^{i\mathrm{Pr}}$), 1.16 (d, $^{3}J_{HH}$ = 4.4 Hz, 3H, C$H_3{}^{i\mathrm{Pr}}$), 0.89 (d, $^{3}J_{HH}$ = 4.8 Hz, 3H, C$H_3{}^{i\mathrm{Pr}}$).

^{13}C {^{1}H} NMR (101 MHz, 299K, C_6D_6): δ = 168.1 (=*C*), 146.9 (dm, $^{1}J_{FC}$ = 247.2 Hz, *C*$_6$F$_5$), 141.7 (dm, $^{1}J_{FC}$ = 254.7 Hz, *C*$_6$F$_5$), 137.7 (dm, $^{1}J_{FC}$ = 254.3 Hz, *C*$_6$F$_5$), 114.0 (brm, *i*-*C*$_6$F$_5$), 106.0 (=*C*H), 53.7 (B*C*H), 31.5 (*C*H$^{i\mathrm{Pr}}$), 27.8, 20.8 (*C*H$_3$), 23.2 (*C*H$_3{}^{i\mathrm{Pr}}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, C_6D_6): δ^{1}H/δ^{13}C: 4.43/106.0 (=*CH*), 2.76/53.7 (B*CH*), 1.68/27.8 (*CH*$_3$), 1.56/31.5 (*CH*$^{i\mathrm{Pr}}$), (1.16, 0.89)/23.2 (*CH*$_3{}^{i\mathrm{Pr}}$), 0.77/20.8 (*CH*$_3$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, C_6D_6): δ^{1}H/δ^{13}C: 4.43/20.8, 27.8, 31.5, 53.7 (=C*H*/*C*H$_3$, *C*H$_3$, *C*H$^{i\mathrm{Pr}}$, B*C*H), 2.76/23.2, 31.5, 106.0, 168.1 (BC*H*/*C*H$_3{}^{i\mathrm{Pr}}$, *C*H$^{i\mathrm{Pr}}$, =*C*H, =*C*), 1.68/106.0, 168.1 (C*H*$_3$/=*C*H, =*C*), 0.89/31.5, 53.7 (C*H*$_3{}^{i\mathrm{Pr}}$/*C*H$^{i\mathrm{Pr}}$, B*C*H).

^{11}B {^{1}H} NMR (128 MHz, 299 K, C_6D_6): δ = 34.3 ($\nu_{1/2}$ ~ 741 Hz).

^{19}F {^{1}H} NMR (377 MHz, 299K, C_6D_6): δ = -130.1 (m, 4F, *o*-C$_6$F$_5$), -152.7 (t, $^{3}J_{FF}$ = 20.7 Hz, 2F, *p*-C$_6$F$_5$), -162.0 (m, 4F, *m*-C$_6$F$_5$) [$\Delta\delta^{19}F_{m,p}$ = 9.3].

HRMS (ESI): m/z calcd for $C_{20}H_{15}BF_{10}$: 473.1140 [M+H_2O-H]$^{-}$; found: 473.1136.

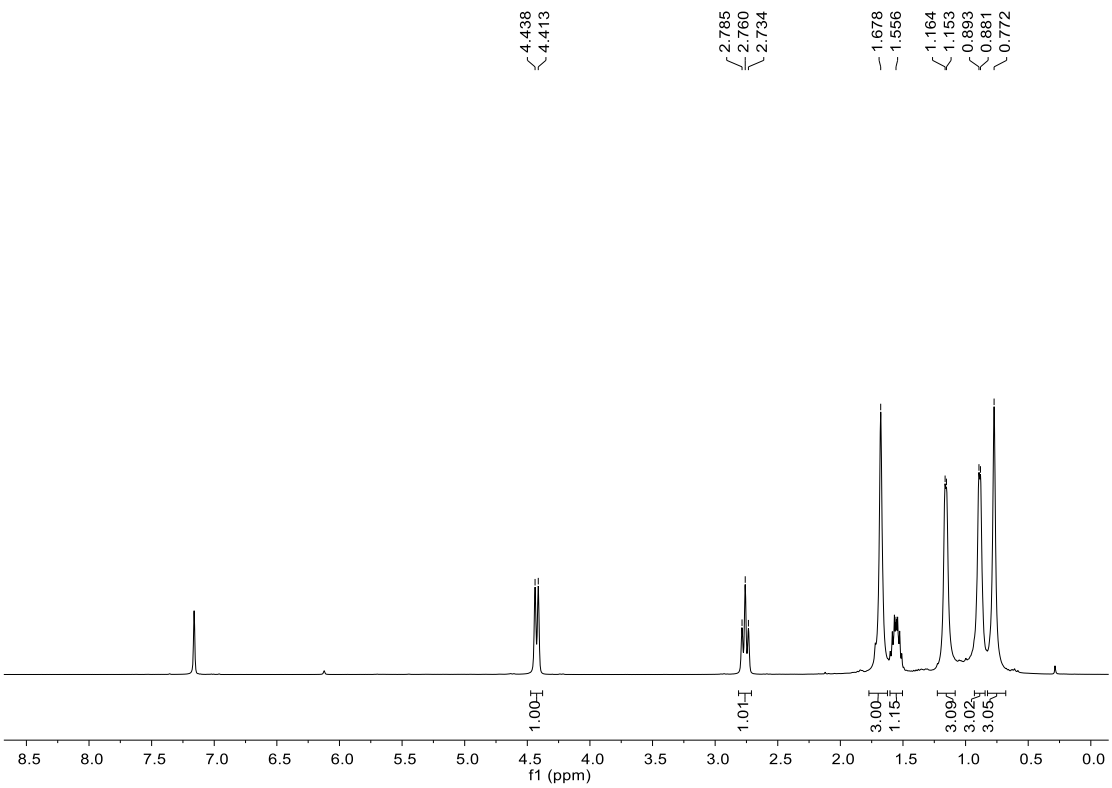


Fig. S1 ^{1}H NMR (400 MHz, 299K, C_6D_6) spectrum of compound **1**.

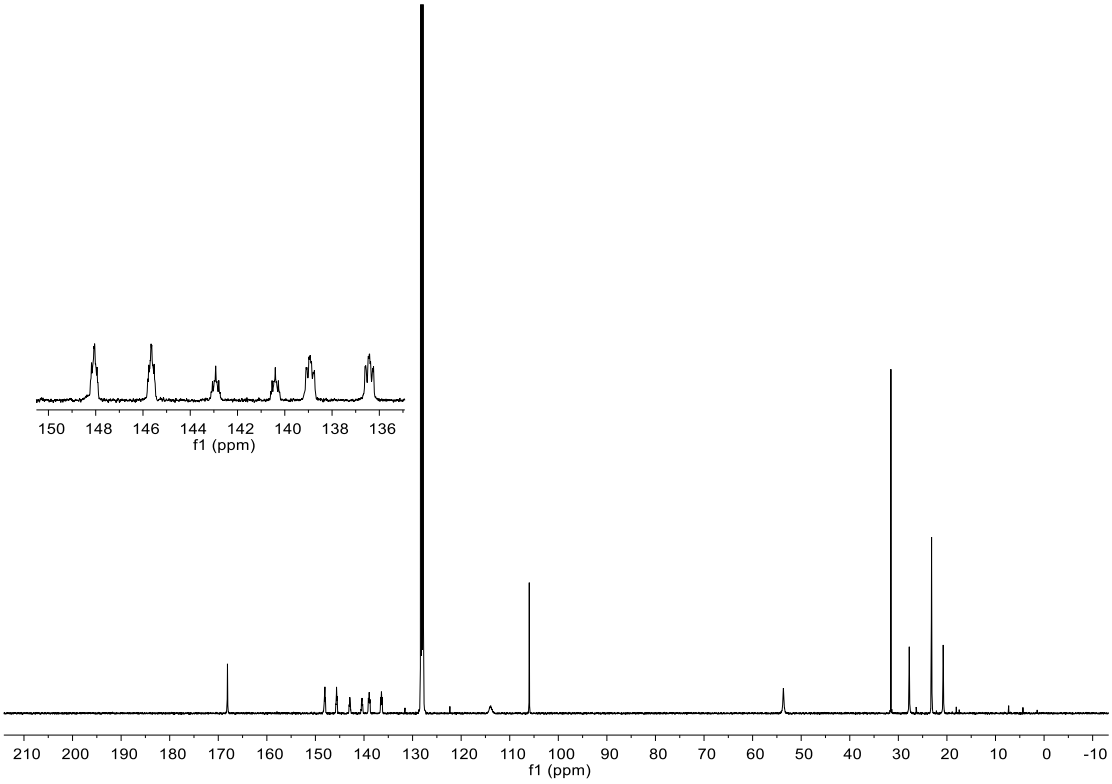


Fig. S2 ^{13}C{^{1}H} NMR (101 MHz, 299K, C_6D_6) spectrum of compound **1**.

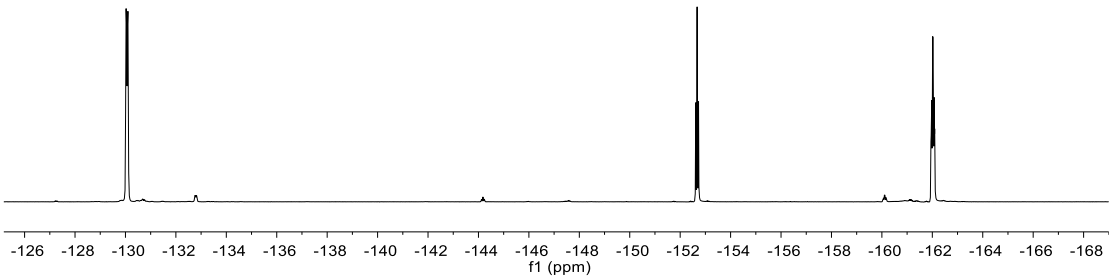


Fig. S3 $^{19}F\{H\}$ NMR (377 MHz, 299K, C_6D_6) spectrum of compound **1**.

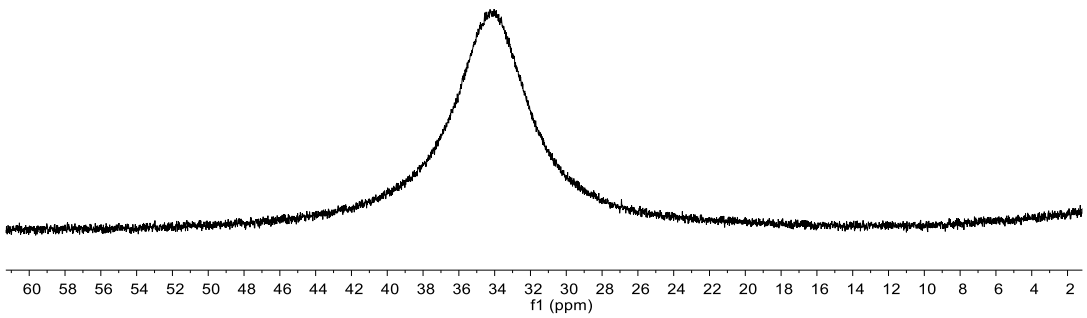
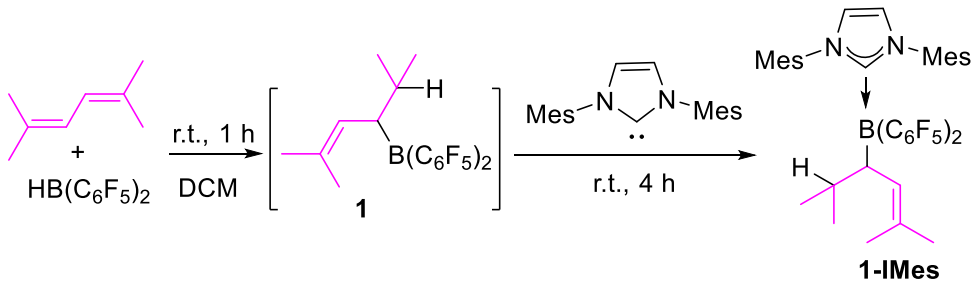


Fig. S4 ^{11}B NMR (128 MHz, 299K, C_6D_6) spectrum of compound **1**.

Synthesis and characterization of compound 1-IMes



Scheme S2

The compound **1** (0.3 mmol) was *in-situ* prepared according to the above procedure. Then IMes (91.4 mg, 0.3 mmol) was added to give an orange

solution. The reaction mixture was stirred at room temperature for 4 h. After completion, all the volatiles were removed in vacuo. The obtained residue was washed with *n*-hexane (3×2 mL) and dried in vacuo to give a yellow solid **1-IMes**. Yield: 146.4 mg, 64%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **1-Imes** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.07 and 6.97 (each m, each 2H, Mes), 6.78 and 6.40 (each s, each 1H, C*H*=C*H*), 4.91 (d, $^{3}J_{HH}$ = 11.2 Hz, 1H, =C*H*), 2.40, 2.34, 2.26, 2.20, 1.92 and 1.51 (each s, each 3H, CH_3^{Mes}), 2.40 (m, 1H, BC*H*), 2.18 (m, 1H, CH^{iPr}), 1.41 and 1.39 (each s, each 3H, CH_3), -0.16 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, CH_3^{iPr}), -0.38 (d, $^{3}J_{HH}$ = 6.0 Hz, 3H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, CD_2Cl_2): δ = 140.6, 139.8, 137.43, 137.40, 135.9, 135.6, 135.3, 135.22, 135.20, 131.6, 130.0, 129.9, 129.0, 128.9, 128.6, 128.2, 126.5, 125.6, 32.8, 26.1, 25.6, 21.0, 20.7, 19.7, 19.5, 18.92, 18.85, 18.5, 18.3, 17.7, 17.6, 17.5, 17.4, 17.2, 17.14, 17.11, 17.1.

^{11}B {^{1}H} NMR (128 MHz, 299 K, CD_2Cl_2): δ = -12.1 ($\nu_{1/2}$ ~ 89 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, CD_2Cl_2): δ = -119.4, -121.0, -122.6, 127.5 (each m, each 1F, *o*-C_6F_5), -161.9 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -162.8 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), -166.7 (m, 2F, *m*-C_6F_5), -167.7 (m, 1F, *m*-C_6F_5), -169.2 (m, 1F, *m*-C_6F_5).

HRMS (ESI): m/z calcd for $C_{41}H_{39}BF_{10}N_2$: 795.2741 $[M+Cl]^-$; found: 795.2736.

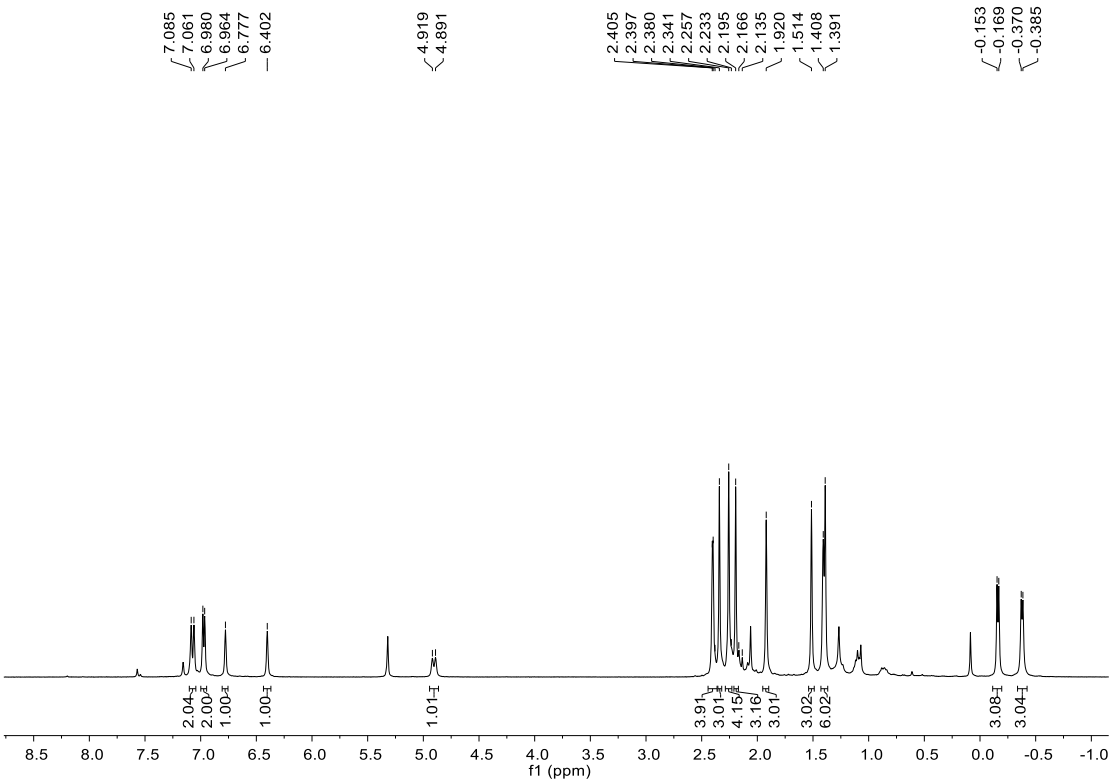


Fig. S5 ^1H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **1-IMes**.

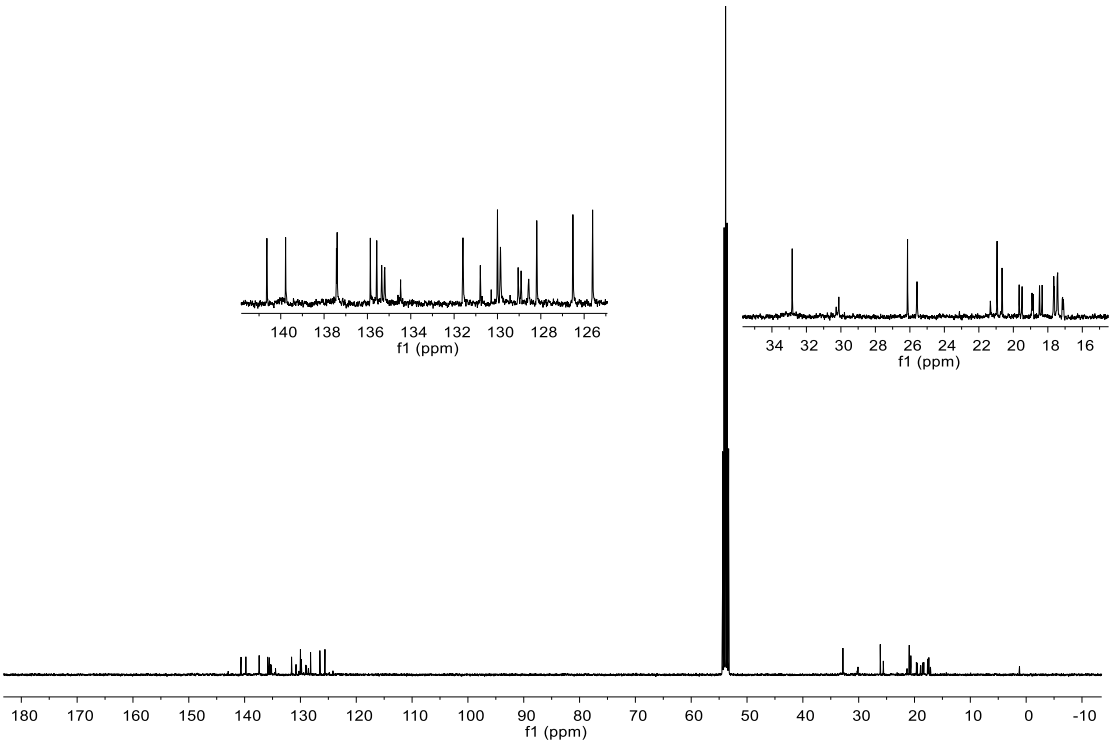


Fig. S6 ^{13}C {H} NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **1-IMes**.

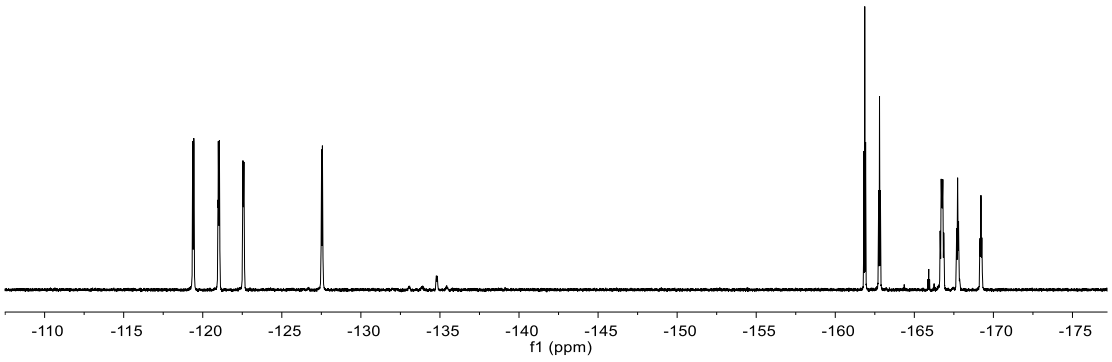


Fig. S7 ^{19}F{H} NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **1-IMes**.

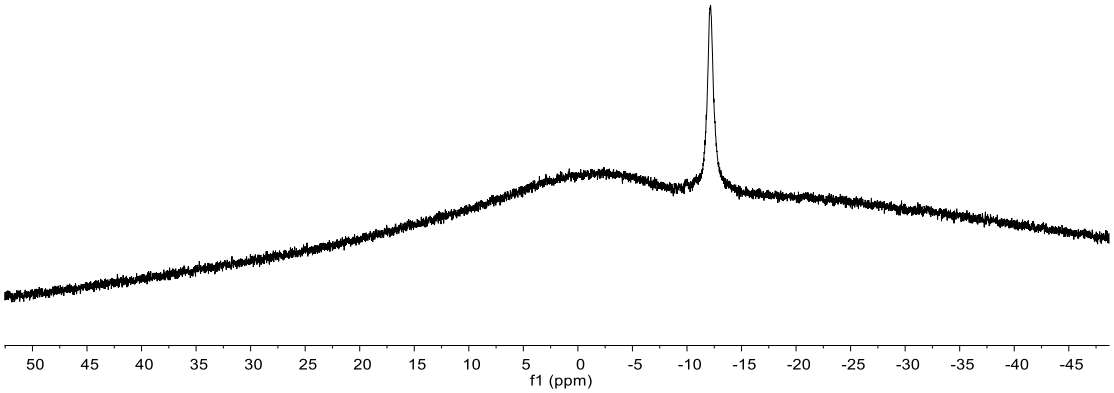


Fig. S8 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **1-IMes**.

X-ray crystal structure analysis of compound 1-IMes: formula $C_{41}H_{39}BF_{10}N_2$, M = 760.55, colourless crystal, 0.1 × 0.1 × 0.1 mm, a = 41.95(7), b = 11.256(17), c = 16.35(2) Å, α = γ = 90º, β = 110.28(4)º, V = 7242(19) Å^3, ρ_{calc} = 1.395 gcm^{-3}, μ = 0.117 mm^{-1}, empirical absorption correction (0.6568 ≤ T ≤ 0.7458), Z = 8, monoclinic, space group *C2/c*, λ = 0.71073 Å, T = 120.0 K, ω and φ scans, 33864 reflections collected (±h, ±k, ±l), 6166 independent (R_{int} = 0.3375) and 2532 observed reflections [I>2σ(I)], 498 refined parameters, R = 0.0713, wR^2 = 0.1249, max. (min.) residual electron density 0.32 (-0.27) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

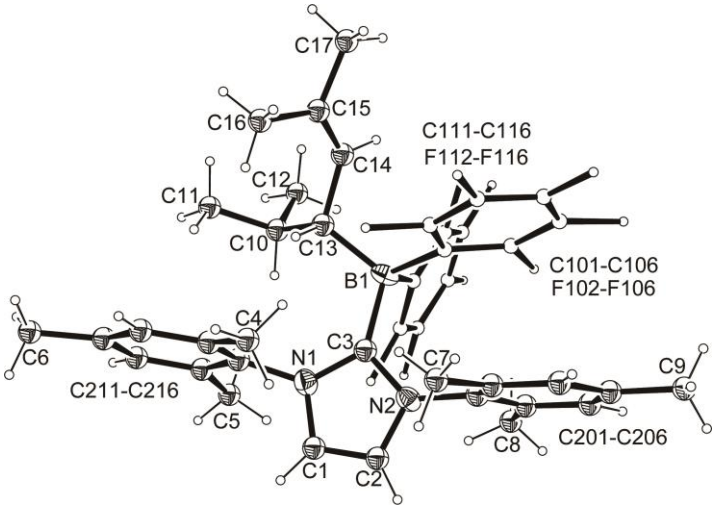
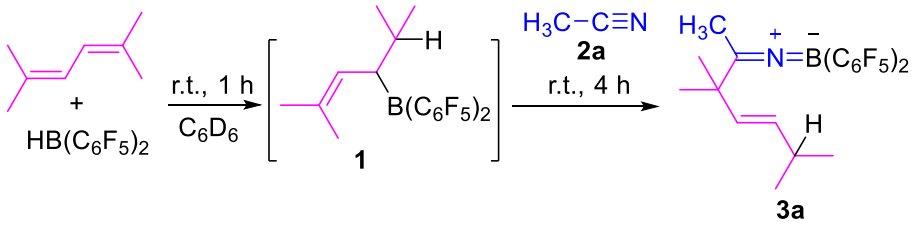


Fig. S9 A view of the molecular structure of compound **1-IMes**.

***In-situ* generation and characterization of compound 3a**



Scheme S3

In an NMR tube, compound **2a** (6.2 mg, 0.15 mmol) was added to a solution of *in-situ* generated compound **1** (0.15 mmol) in C_6D_6 (0.6 mL). The mixture was kept at room temperature for 6 h, then NMR spectra was conducted.

^{1}H NMR (400 MHz, 299 K, C_6D_6): δ = 5.34 (dd, $^3J_{HH}$ = 16.0 and 5.6 Hz, 1H, =C*H*^{iPr}), 5.29 (d, $^3J_{HH}$ = 16.0 Hz, 1H, =C*H*$^{-CMe_2}$), 2.11 (m, 1H, C*H*^{iPr}), 1.81 (s, 3H, C$H_3^{C=N}$), 1.06 (s, 6H, CH_3^{C}), 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {H} NMR (101 MHz, 299K, C_6D_6): δ = 166.0 ($C^{=N}$), 148.3 (dm, $^1J_{FC}$ = 245.3 Hz, C_6F_5), 142.1 (dm, $^1J_{FC}$ = 255.0 Hz, C_6F_5), 137.7 (dm, $^1J_{FC}$ = 250.9 Hz, C_6F_5), 138.0 (=CH^{iPr}), 131.5 (=CH$^{-CMe_2}$), 109.8 (brm, *i*-C_6F_5), 45.1 ($C^{CH=}$), 31.6 (CH^{iPr}), 24.7 (CH$_3^C$), 22.9 (CH$_3^{C=N}$), 22.4 (CH$_3^{iPr}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, C_6D_6): δ^{1}H/δ^{13}C: 5.34/138.0 (=CH^{iPr}), 5.29/131.5 (=CH^{-CMe_2}), 2.11/31.6 (CH^{iPr}), 1.81/22.9 ($CH_3^{C=N}$), 1.06/24.7 (CH_3^C), 0.87/22.4 (CH_3^{iPr}).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, C_6D_6): δ^{1}H/δ^{13}C: 5.34/45.1, 31.6 (=CH^{iPr}/$C^{CH=}$, CH^{iPr}), 5.29/24.7, 138.0 (=CH^{-CMe_2}/CH$_3^C$, =CH^{iPr}), 1.81/45.1, 166.0 (C$H_3^{C=N}$/$C^{CH=}$, $C^{=N}$), 1.06/45.1, 131.5, 166.0 (CH_3^C/$C^{CH=}$, =CH$^{-CMe_2}$, $C^{=N}$), 0.87/31.6, 138.0 (CH_3^{iPr}/CH^{iPr}, =CH^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, C_6D_6): δ = 20.9 ($\nu_{1/2}$ ~ 318 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, C_6D_6): δ = -132.8 (m, 4F, *o*-C_6F_5), -152.5 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -162.3 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 9.8].

HRMS (ESI): m/z calcd for $C_{22}H_{18}BF_{10}N$: 498.1446 $[M+H]^+$; found: 498.1437.

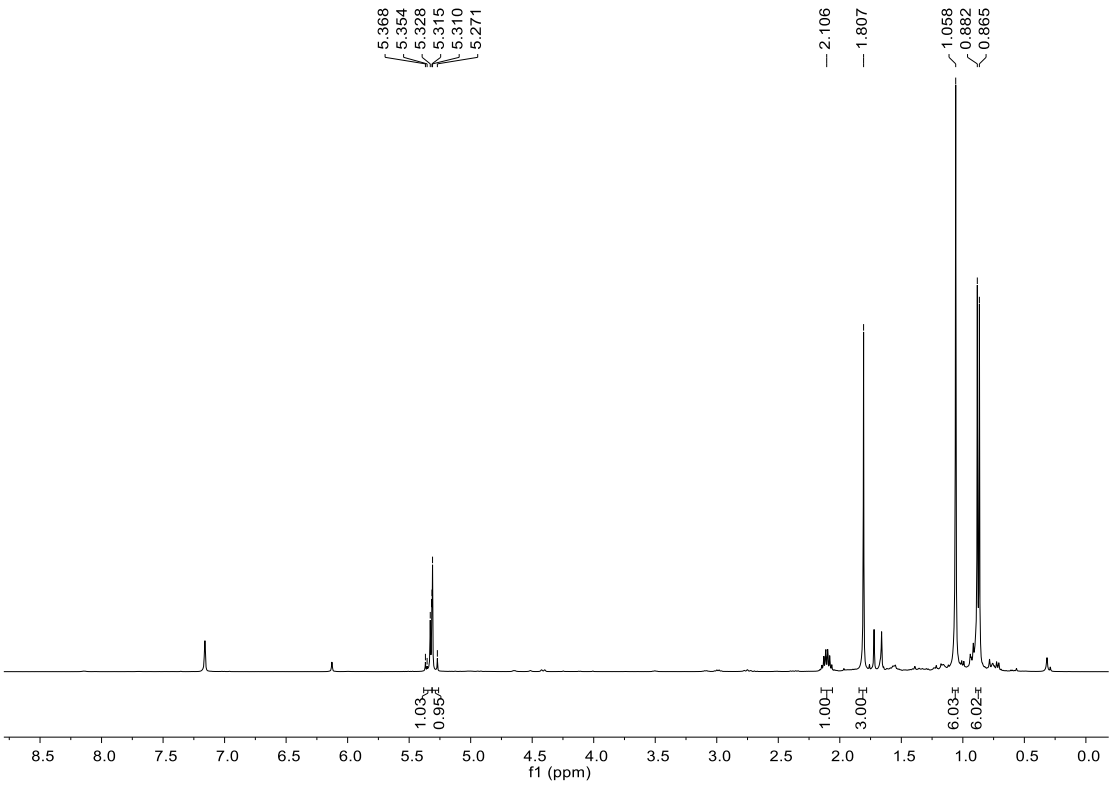


Fig. S10 ^{1}H NMR (400 MHz, 299K, C_6D_6) spectrum of compound **3a**.

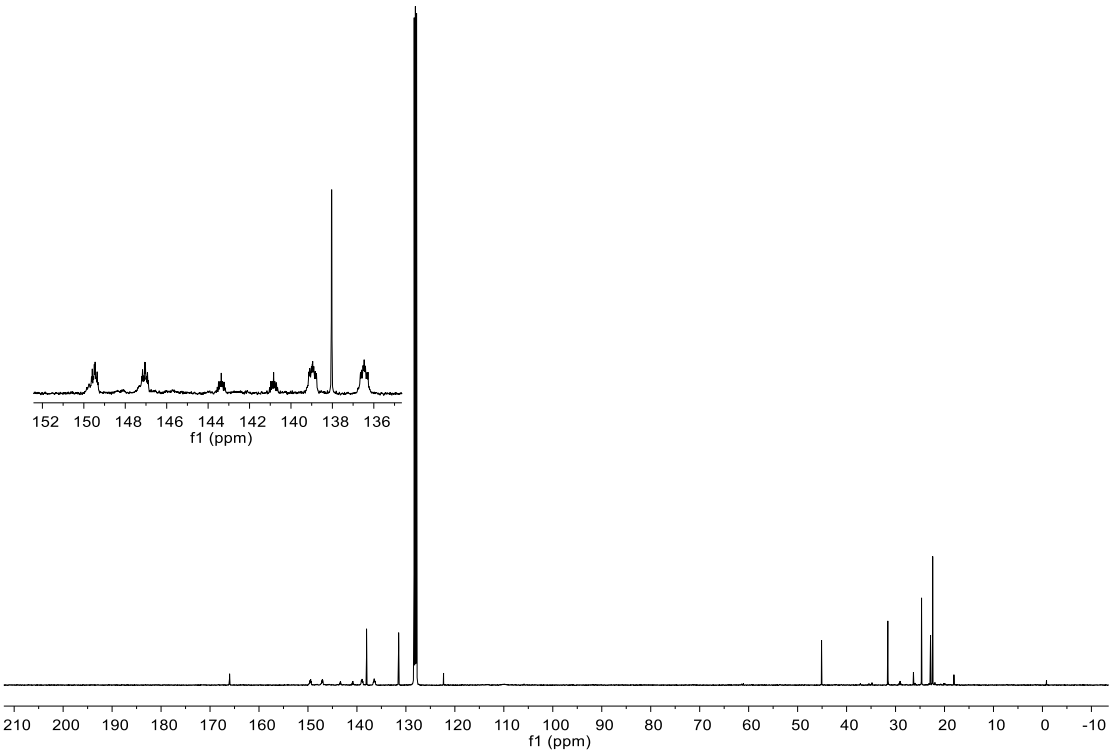


Fig. S11 ^{13}C {^{1}H} NMR (101 MHz, 299K, C_6D_6) spectrum of compound **3a**.

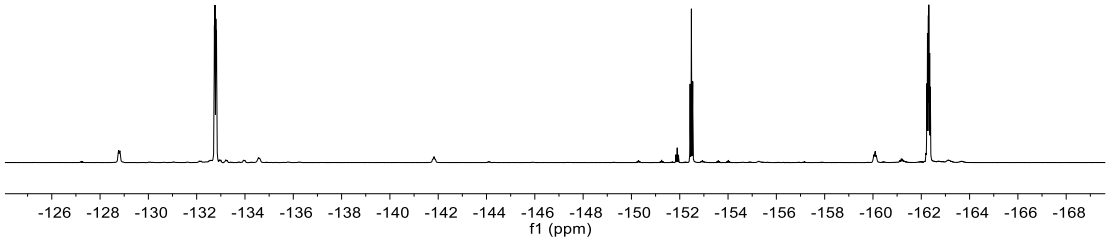


Fig. S12 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, C_6D_6) spectrum of compound **3a**.

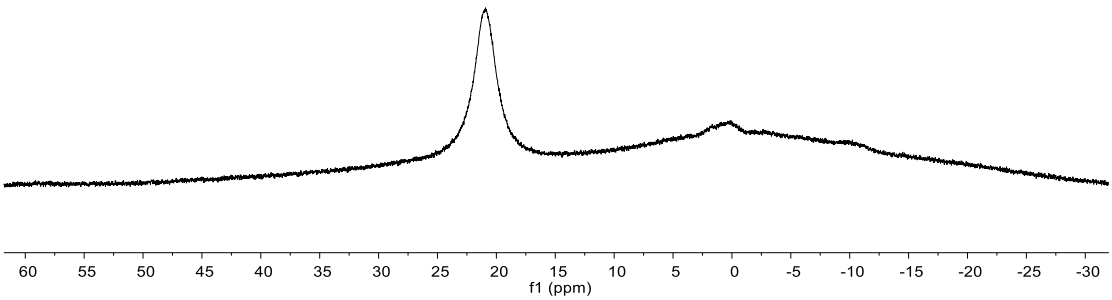
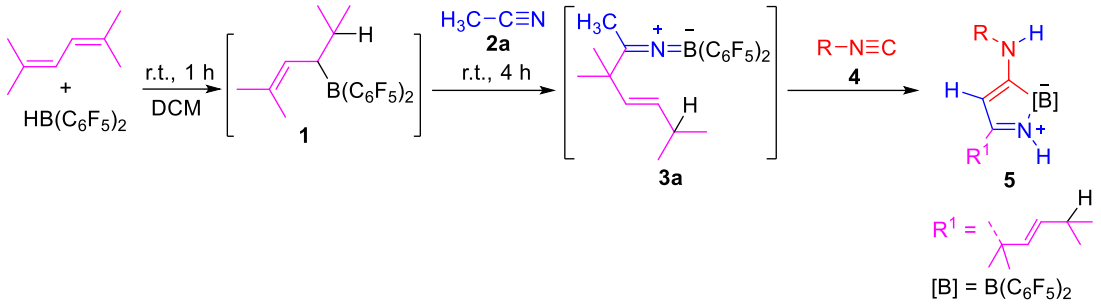


Fig. S13 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, C_6D_6) spectrum of compound **3a**.

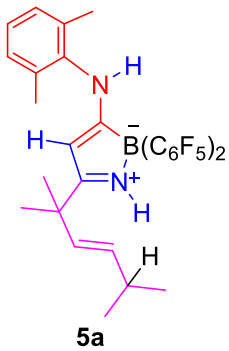
General Procedure I



Scheme S4

A solution of 2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 1 h to *in-situ* generate compound **1**. After that, acetonitrile (20.5 mg, 0.5 mmol) was added to give a colourless solution. The reaction mixture was stirred at room temperature for another 4 h to *in-situ* generate compound **3a**. Finally, isonitriles **4** (0.5 mmol) were added to the mixture to give products **5**. Specific purification methods were described for each compound.

Synthesis and characterization of compound 5a



5a

The compound **3a** was *in-situ* prepared according to the General Procedure I. Then 2,6-dimethylphenylisonitrile (Xyl-N≡C **4a**, 65.6 mg, 0.5 mmol) was added to give a pale yellow solution immediately. The solution was stirred at room temperature for 6 h. Then all the volatiles were removed in vacuo. The obtained residue was washed with *n*-hexane (3×2 mL) and dried in vacuo to give a white solid **5a**. Yield: 223.0 mg, 71%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **5a** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.41 and 6.88 (each br, each 1H, N*H*), 7.12 (m, 3H, Xyl), 5.57 (dd, $^{3}J_{HH}$ = 16.0 and 7.2 Hz, 1H, =C*H*^{iPr}), 5.43 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H, =C*H*$^{-CMe_2}$), 4.85 (s, 1H, C*H*$^{C=N}$), 2.34 (m, 1H, C*H*^{iPr}), 2.06 (s, 6H, CH_3^{Xyl}), 1.27 (s, 6H, CH_3^{C}), 1.00 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 191.8 (brm, B*C*), 191.1 (*C*$^{=N}$), 147.9 (dm, $^{1}J_{FC}$ = 238.1 Hz, *C*$_6F_5$), 139.7 (dm, $^{1}J_{FC}$ = 231.7 Hz, *C*$_6F_5$), 137.2 (dm, $^{1}J_{FC}$ = 232.7 Hz, *C*$_6F_5$), 139.0 (=*C*H^{iPr}), 137.1, 135.4, 128.8, 127.7 (Xyl), 130.8 (=*C*H$^{-CMe_2}$), 118.2 (brm, *i*-*C*$_6F_5$), 95.4 (*C*H$^{C=N}$), 40.6 (*C*^{CH_3}), 31.4 (*C*H^{iPr}), 26.1 (*C*H$_3^{C}$), 22.6 (*C*H$_3^{iPr}$), 17.8 (*C*H$_3^{Xyl}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 5.57/139.0 (=*CH*^{iPr}), 5.43/130.8 (=*CH*$^{-CMe_2}$), 4.85/95.4 (*CH*$^{C=N}$), 2.34/31.4 (*CH*^{iPr}), 2.06/17.8 (*CH*$_3^{Xyl}$), 1.27/26.1 (*CH*$_3^{C}$), 1.00/22.6 (*CH*$_3^{i Pr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 7.41/95.4 (N*H*/*C*H$^{C=N}$), 5.57/130.8 (=C*H*^{iPr}/=*C*H$^{-CMe_2}$), 5.43/139.0 (=C*H*$^{-CMe_2}$/=*C*H^{iPr}), 4.85/191.1 (C*H*$^{C=N}$/*C*$^{=N}$), 1.27/(40.6, 130.8) (C*H*$_3^{C}$/ *C*^{CH_3}, =*C*H$^{-CMe_2}$), 1.00/(31.4, 139.0) (C*H*$_3^{i Pr}$/*C*H$^{i Pr}$, =*C*H$^{i Pr}$).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -7.7 ($\nu_{1/2}$ ~ 62 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -133.8 (m, 4F, *o*-C_6F_5), -158.0 (t, $^{3}J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -163.2 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.2].

HRMS (ESI): m/z calcd for $C_{31}H_{27}BF_{10}N_2$: 627.2035 $[M-H]^-$; found: 627.2052.

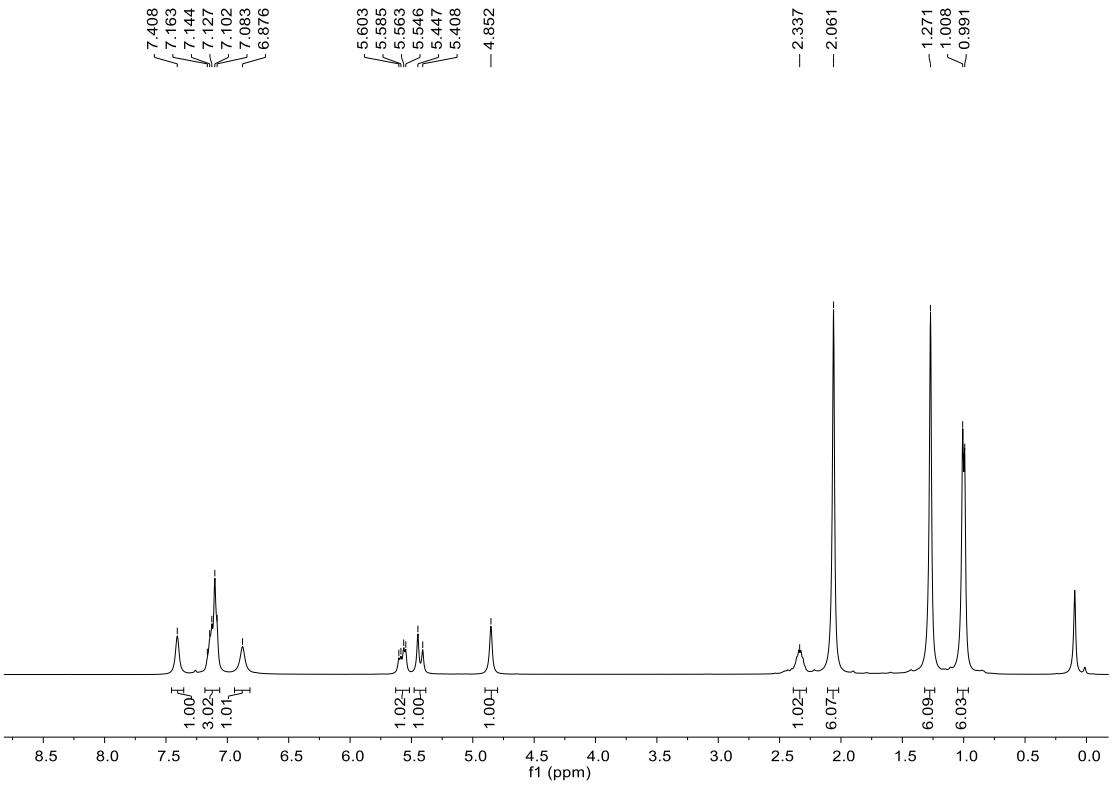


Fig. S14 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5a**.

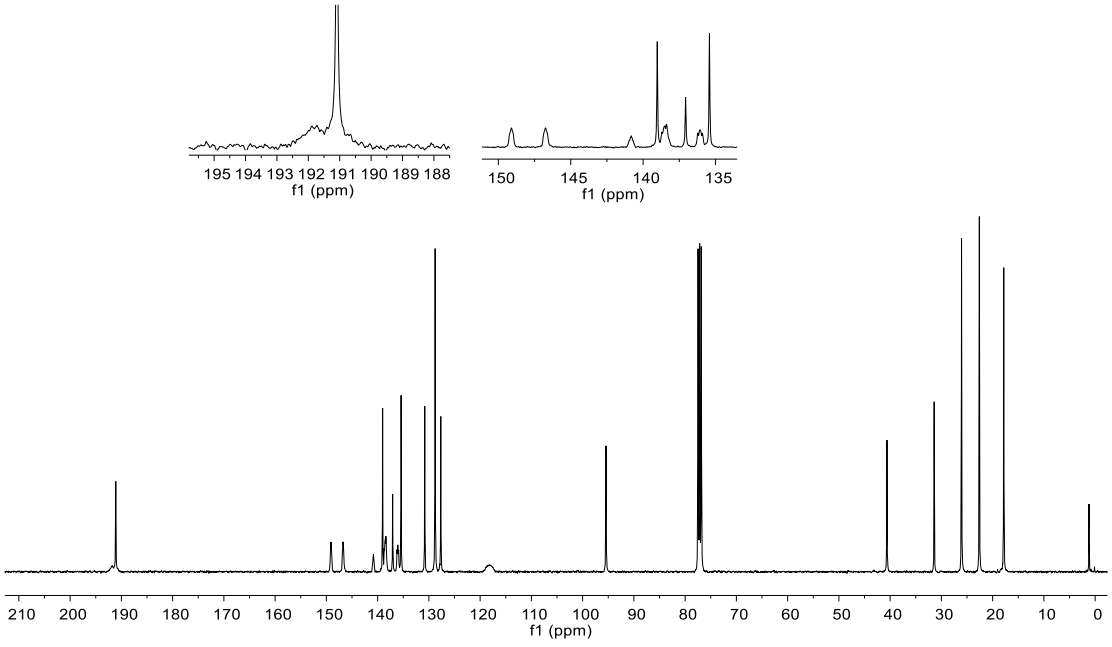


Fig. S15 ^{13}C {H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5a**.

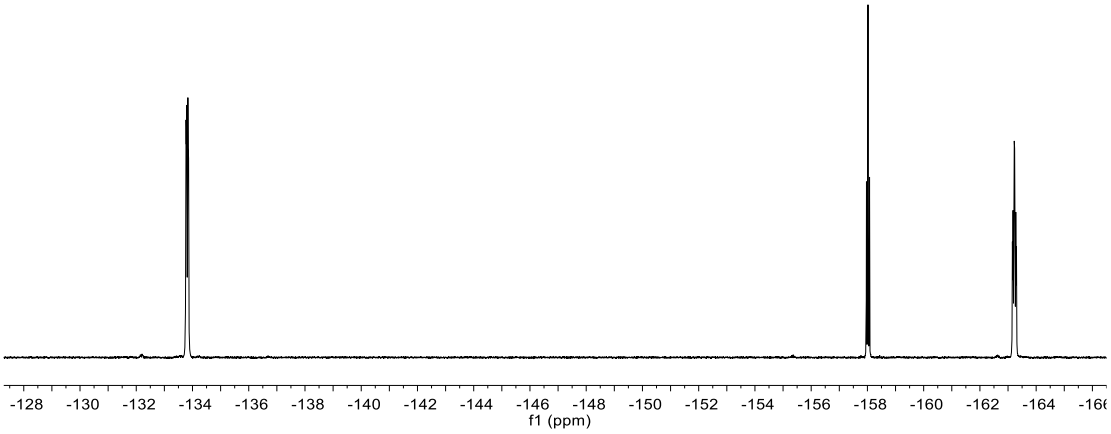


Fig. S16 $^{19}F\{H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5a**.

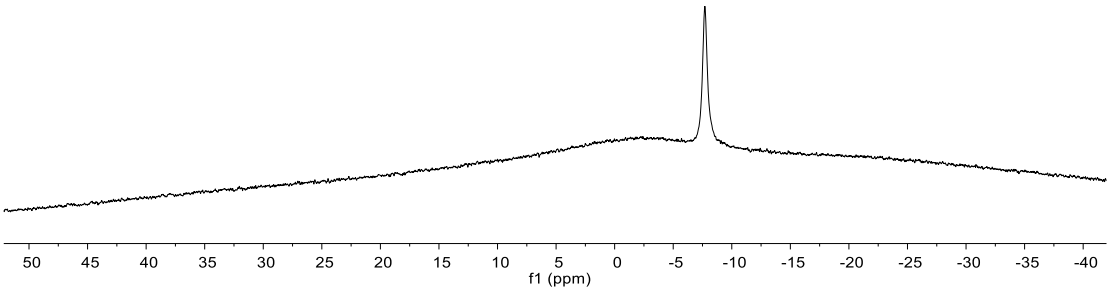


Fig. S17 ^{11}B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5a**.

X-ray crystal structure analysis of compound 5a: formula $C_{31}H_{27}BF_{10}N_2$, M = 628.35, colourless crystal, 0.41 × 0.35 × 0.21 mm, a = 9.8832(10), b = 12.8668(13), c = 13.2576(15) Å, α = 118.991(3)º, β = 94.734(3)º, γ = 91.945(3)º, V = 1464.3(3) $Å^3$, ρ_{calc} = 1.425 gcm^{-3}, μ = 0.128 mm^{-1}, empirical absorption correction (0.6749 ≤ T ≤ 0.7456), Z = 2, triclinic, space group *P-1*, λ = 0.71073 Å, T = 200.0 K, ω and φ scans, 23798 reflections collected (±h, ±k, ±l), 6630 independent (R_{int} = 0.0917) and 3332 observed reflections [I>2σ(I)], 403 refined parameters, R =

0.0614, wR^2 = 0.1528, max. (min.) residual electron density 0.33 (-0.31) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

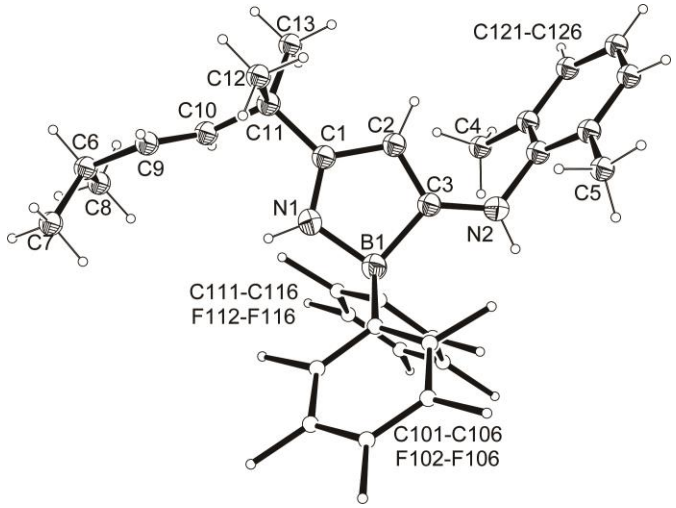
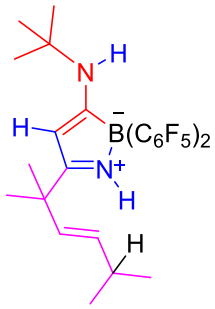


Fig. S18 A view of the molecular structure of compound **5a**.

Synthesis and characterization of compound 5b



5b

The compound **3a** was *in-situ* prepared according to the General Procedure I. Then ^{t}BuN≡C **4b** (41.6 mg, 0.5 mmol) was added to give a pale yellow solution immediately. The solution was stirred at room temperature for 6 h. Then all the volatiles were removed in vacuo. The *n*-hexane (1 mL) was added and then stored at -25 ^{o}C for 1 h. After filtration, the obtained residue was dried in vacuo to give white solid **5b**.

Yield: 217.6 mg, 75%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 6.49 and 6.33 (each br, each 1H, N*H*), 5.57 (dd, $^{3}J_{HH}$ = 16.0 and 6.8 Hz, 1H, =C*H*^{iPr}), 5.45 (d, $^{3}J_{HH}$ = 16.0 Hz, 1H, =C*H*$^{-CMe_2}$), 5.36 (s, 1H, C*H*$^{C=N}$), 2.34 (m, 1H, C*H*^{iPr}), 1.35 (s, 9H, CH_3^{tBu}), 1.34 (s, 6H, CH_3^{C}), 1.00 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 190.8 (brm, B*C*), 189.7 (*C*$^{=N}$), 147.9 (dm, $^{1}J_{FC}$ = 238.6 Hz, *C*$_6F_5$), 139.4 (dm, $^{1}J_{FC}$ = 250.0 Hz, *C*$_6F_5$), 137.2 (dm, $^{1}J_{FC}$ = 253.1 Hz, *C*$_6F_5$), 138.4 (=*C*H^{iPr}), 131.3 (=*C*H$^{-CMe_2}$), 118.5 (brm, *i*-*C*$_6F_5$), 93.7 (*C*H$^{C=N}$), 53.6 (*C*^{tBu}), 40.5 (*C*^{CH_3}), 31.4 (*C*H^{iPr}), 28.5 (*C*H_3^{tBu}), 26.3 (*C*H_3^{C}), 22.7 (*C*H_3^{iPr}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.57/138.4 (=*CH*^{iPr}), 5.45/131.3 (=*CH*$^{-CMe_2}$), 5.36/93.7 (*CH*$^{C=N}$), 2.34/31.4 (*CH*^{iPr}), 1.35/28.5 (*CH*$_3^{tBu}$), 1.34/26.3 (*CH*$_3^{C}$), 1.00/22.7 (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.57/(22.7, 40.5, 131.3) (=C*H*^{iPr}/*C*H_3^{iPr}, *C*^{CH_3}, =*C*H$^{-CMe_2}$), 5.45/(26.3, 31.4, 40.5, 138.4, 189.7) (C*H*$^{-CMe_2}$/*C*H_3^{C}, *C*H^{iPr}, *C*^{CH_3}, =*C*H^{iPr}, *C*$^{=N}$), 5.36/189.7 (C*H*$^{C=N}$/*C*$^{=N}$), 1.34/(40.5, 131.3, 189.7) (C*H*$_3^{C}$/*C*^{CH_3}, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 1.35/53.6 (C*H*$_3^{tBu}$/*C*^{tBu}), 1.00/(31.4, 138.4) (C*H*$_3^{iPr}$/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -7.2 ($\nu_{1/2}$ ~ 47 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -133.9 (m, 4F, *o*-C_6F_5), -158.6 (t, $^{3}J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -163.6 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.0].

HRMS (ESI): m/z calcd for $C_{27}H_{27}BF_{10}N_2$: 579.2035 $[M-H]^-$; found: 579.2051.

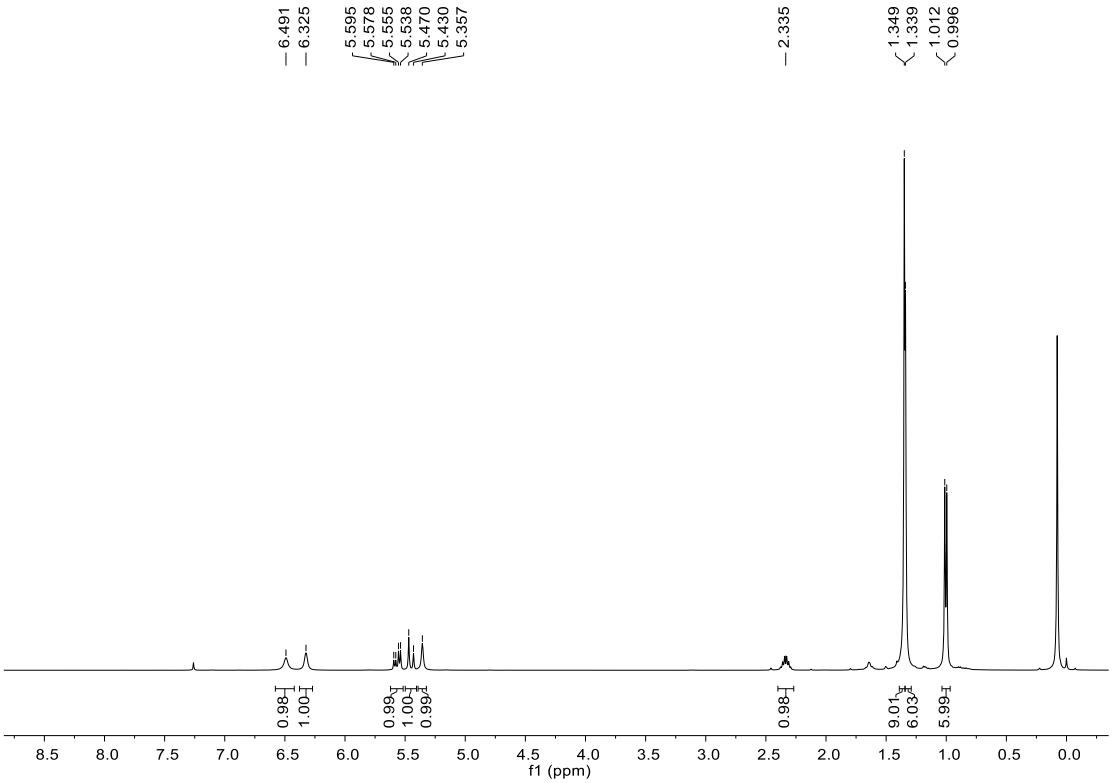


Fig. S19 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5b**.

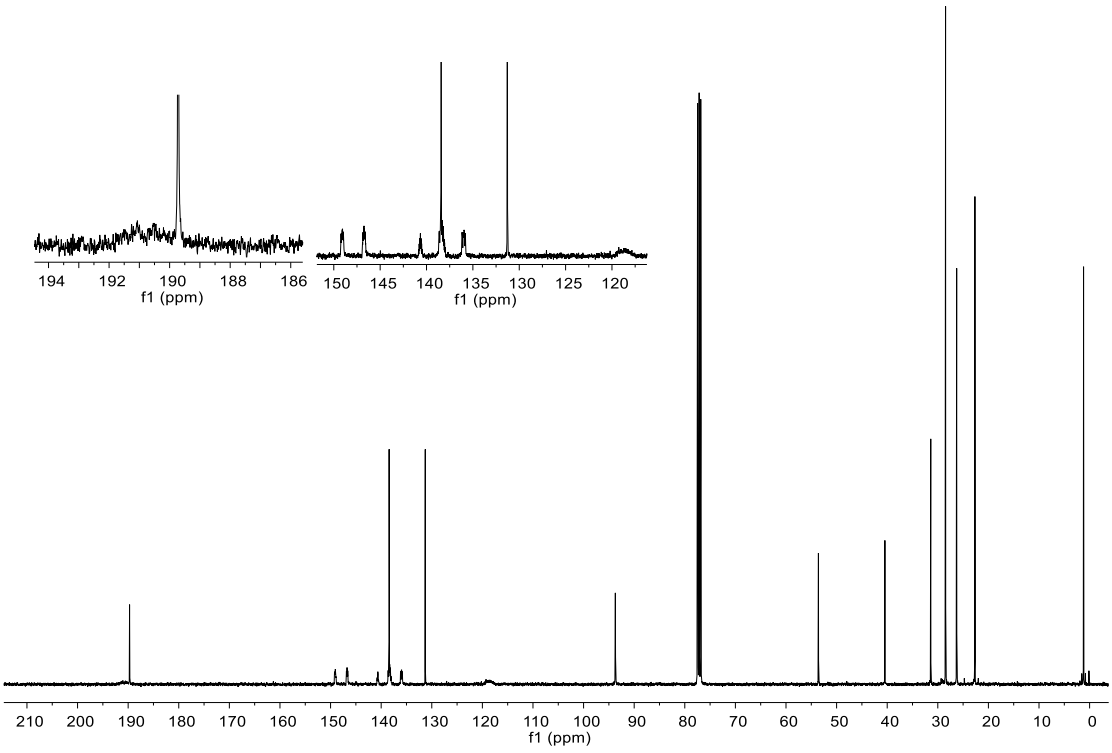


Fig. S20 ^{13}C {H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5b**.

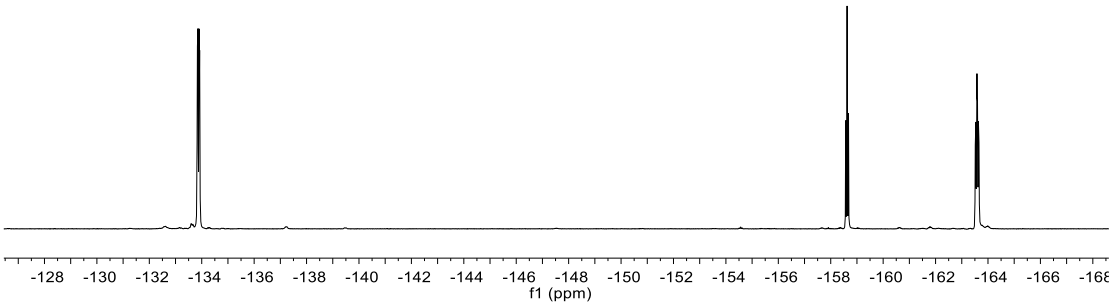


Fig. S21 $^{19}F\{H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5b**.

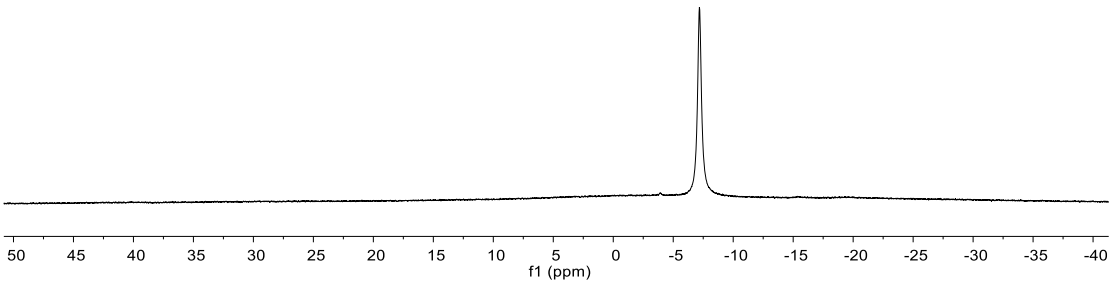
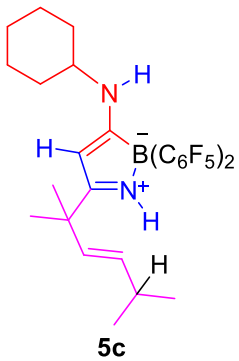


Fig. S22 ^{11}B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5b**.

Synthesis and characterization of compound 5c



5c

The compound **3a** was prepared in-situ according to the General Procedure I. Then Cy-N≡C (54.6 mg, 0.5 mmol) was added to give a pale yellow solution immediately. The solution was stirred at 60 °C for 24 h. Then all the volatiles were removed in vacuo. The *n*-hexane (1 mL) was added and then stored at -25 °C for 1 h. After filtration, the obtained residue was dried in vacuo to give white solid **5c**. Yield: 218.3 mg, 72%.

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 6.49 (br, 1H, N*H*), 6.18 (br, 1H, N*H*^{Cy}), 5.58 (dd, $^{3}J_{HH}$ = 15.8 and 6.7 Hz, 1H, =C*H*^{iPr}), 5.47 (d, $^{3}J_{HH}$ = 15.9 Hz, 1H, =C*H*$^{-CMe_2}$), 5.28 (s, 1H, C*H*$^{C=N}$), 3.30 (m, 1H, C*H*^{Cy}), 2.33 (m, 1H, C*H*^{iPr}), 1.96-1.24 (m, 10H, CH_2^{Cy}), 1.33 (s, 6H, CH_3^{C}), 1.00 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, CD_2Cl_2): δ = 192.3 (brm, B*C*), 190.5 (*C*$^{=N}$), 148.2 (dm, $^{1}J_{FC}$ = 241.9 Hz, *C*$_6$F$_5$), 139.9 (dm, $^{1}J_{FC}$ = 217.7 Hz, *C*$_6$F$_5$), 137.3 (dm, $^{1}J_{FC}$ = 216.5 Hz, *C*$_6$F$_5$), 138.6 (=*C*H^{iPr}), 131.6 (=*C*H$^{-CMe_2}$), 119.5 (brm, *i*-*C*$_6$F$_5$), 92.6 (*C*H$^{C=N}$), 54.3 (*C*H^{Cy}), 40.8 (*C*^{CH_3}), 32.2, 25.9, 24.9 (*C*H_2^{Cy}), 31.7 (*C*H^{iPr}), 26.4 (*C*H_3^{C}), 22.7 (*C*H_3^{iPr}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, CD_2Cl_2): δ^{1}H/δ^{13}C: 5.58/138.6 (=*CH*^{iPr}), 5.47/131.6 (=*CH*$^{-CMe_2}$), 5.28/92.6 (*CH*$^{C=N}$), 3.30/54.3 (*CH*^{Cy}), 2.33/31.7 (*CH*^{iPr}), 1.94/32.2 (*CH*$_2^{Cy}$), 1.76/25.1 (*CH*$_2^{Cy}$), 1.33/26.4 (*CH*$_3^{C}$), 1.00/22.7 (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, CD_2Cl_2): δ^{1}H/δ^{13}C: 5.28/190.5 (C*H*$^{C=N}$/*C*$^{=N}$), 5.58/(40.8, 131.6) (=C*H*^{iPr}/*C*^{CH_3}, =*C*H$^{-CMe_2}$),

5.47/138.6 (=C*H*$^{-CMe_2}$/=*C*H^{iPr}), 1.33/40.8 (CH_3^C/C^{CH_3}), 1.00/31.7 (CH_3^{iPr}/*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, CD_2Cl_2): δ = -7.8 ($\nu_{1/2}$ ~ 50 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, CD_2Cl_2): δ = -134.1 (m, 4F, *o*-C_6F_5), -159.7 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -164.6 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.9].

HRMS (ESI): m/z calcd for $C_{29}H_{29}BF_{10}N_2$: 605.2191 [M-H]$^-$; found: 605.2199.

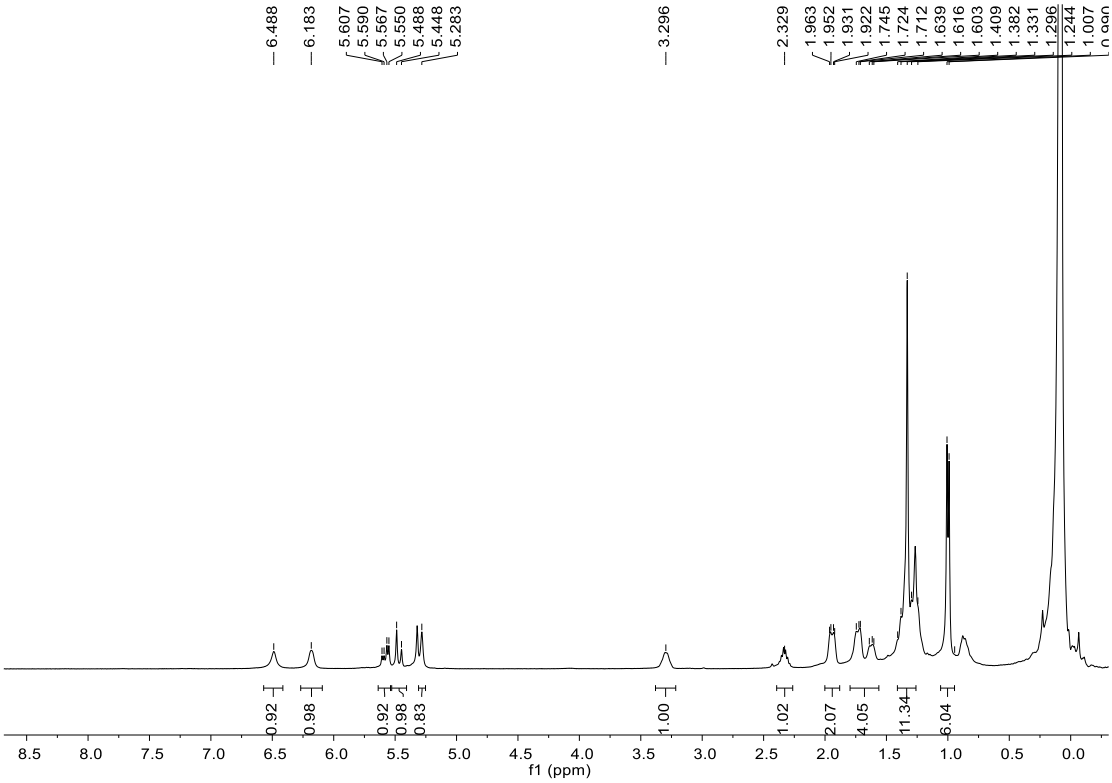


Fig. S23 ^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **5c**.

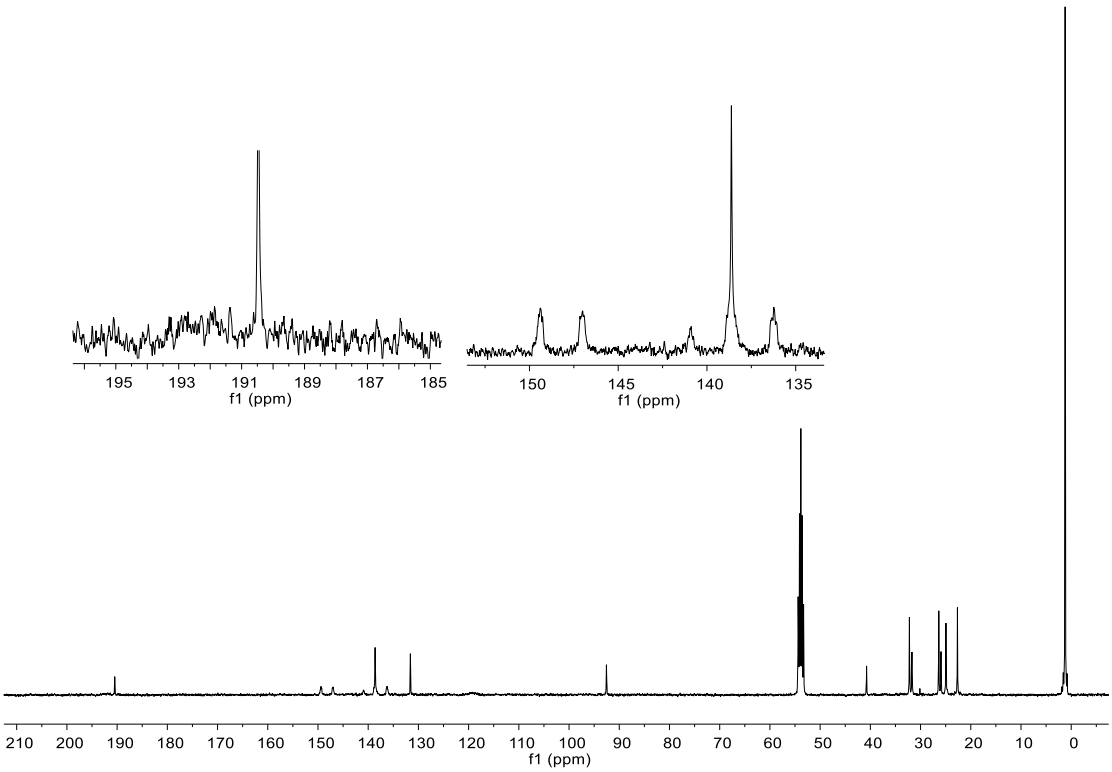


Fig. S24 ^{13}C {^{1}H} NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **5c**.

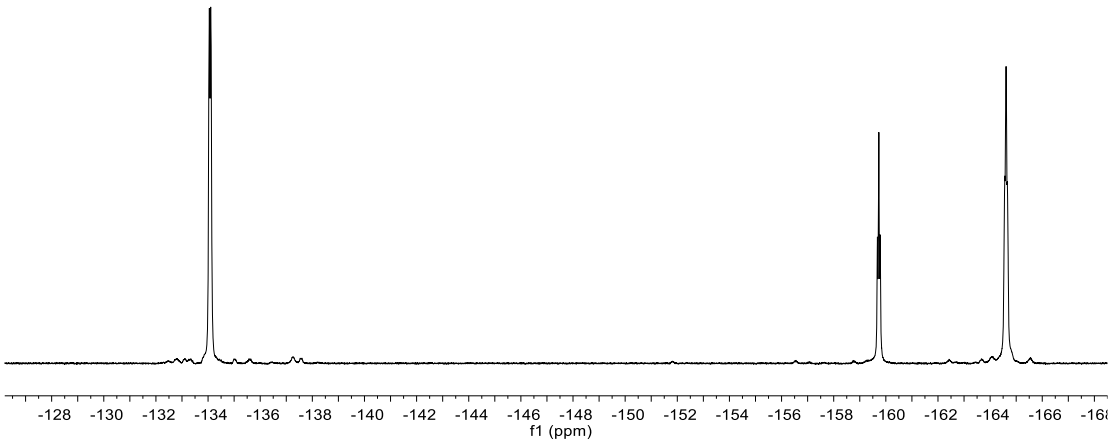


Fig. S25 ^{19}F{^{1}H} NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **5c**.

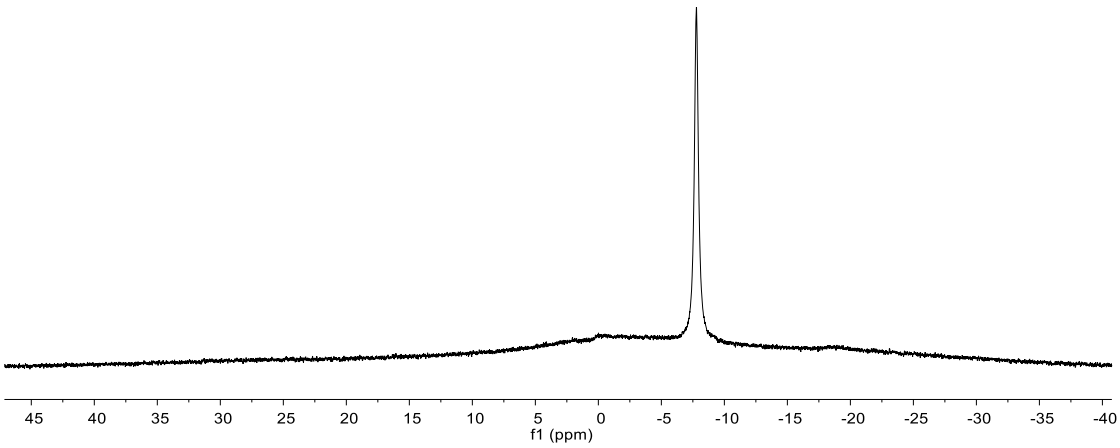
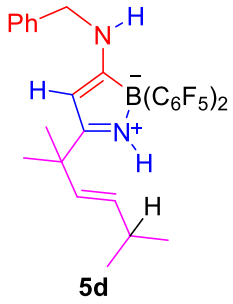


Fig. S26 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **5c**.

Synthesis and characterization of compound 5d



5d

The compound **3a** was prepared in-situ according to the General Procedure I. Then BnN≡C **4d** (58.6 mg, 0.5 mmol) was added to give a black solution. The solution was stirred at 60 °C for 24 h. Then all the volatiles were removed in vacuo. The *n*-hexane (1 mL) was added and then stored at -25 °C for 1 h. After filtration, the obtained residue was dried in vacuo to give a black solid **5d**. Yield: 205.8 mg, 67%.

^{1}H NMR (400 MHz, 299 K, CD_2Cl_2): δ = 7.38-7.27 (m, 5H, Ph), 6.74 (br, 1H, N*H*), 6.49 (br, 1H, NH^{Bn}), 5.61 (dd, $^3J_{HH}$ = 15.6 and 6.8 Hz, 1H,

=C*H*^{iPr}), 5.48 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H, =C*H*$^{-CMe_2}$), 5.39 (s, 1H, C*H*$^{C=N}$), 4.38 (d, $^{3}J_{HH}$ = 5.2 Hz, 2H, CH_2^{Ph}), 2.34 (m, 1H, C*H*^{iPr}), 1.34 (s, 6H, CH_3^{C}), 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, CD_2Cl_2): δ = 193.2 (brm, B*C*), 191.1 (*C*$^{=N}$), 148.2 (dm, $^{1}J_{FC}$ = 238.5 Hz, *C*$_6F_5$), 139.8 (dm, $^{1}J_{FC}$ = 233.4 Hz, *C*$_6F_5$), 137.5 (dm, $^{1}J_{FC}$ = 230.6 Hz, *C*$_6F_5$), 137.5, 129.2, 128.2, 128.0 (Ph), 138.9 (=*C*H^{iPr}), 131.3 (=*C*H$^{-CMe_2}$), 118.6 (brm, *i*-*C*$_6F_5$), 93.8 (*C*H$^{C=N}$), 50.2 (*C*H_2^{Ph}), 40.9 (*C*^{CH_3}), 31.7 (*C*H^{iPr}), 26.3 (*C*H_3^{C}), 22.6 (*C*H_3^{iPr}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, CD_2Cl_2): δ^{1}H/δ^{13}C: 5.61/138.9 (=*CH*^{iPr}), 5.48/131.3 (=*CH*$^{-CMe_2}$), 5.39/93.8 (*CH*$^{C=N}$), 4.38/50.2 (*CH*$_2^{Ph}$), 2.34/31.7 (*CH*^{iPr}), 1.34/26.3 (*CH*$_3^{C}$), 1.01/22.6 (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, CD_2Cl_2): δ^{1}H/δ^{13}C: 5.39, /191.1 (C*H*$^{C=N}$/*C*$^{=N}$), 5.61/(22.6, 40.9, 131.3) (=C*H*^{iPr}/*C*H$_3^{iPr}$, *C*^{CH_3}, =*C*H$^{-CMe_2}$), 5.48/(26.3, 31.7, 40.9) (=C*H*$^{-CMe_2}$/*C*H_3^{C}, *C*H^{iPr}, *C*^{CH_3}), 1.34/(40.9, 131.3) (C*H*$_3^{C}$/*C*^{CH_3}, =*C*H$^{-CMe_2}$), 1.01/(31.7, 138.9) (C*H*$_3^{iPr}$/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, CD_2Cl_2): δ = -7.7 ($\nu_{1/2}$ ~ 49 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, CD_2Cl_2): δ = -134.1 (m, 4F, *o*-C_6F_5), -159.5 (t, $^{3}J_{FF}$ = 20.2 Hz, 2F, *p*-C_6F_5), -164.4 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.0].

HRMS (ESI): m/z calcd for $C_{30}H_{25}BF_{10}N_2$: 613.1878 [M-H]$^{-}$; found: 613.1870.

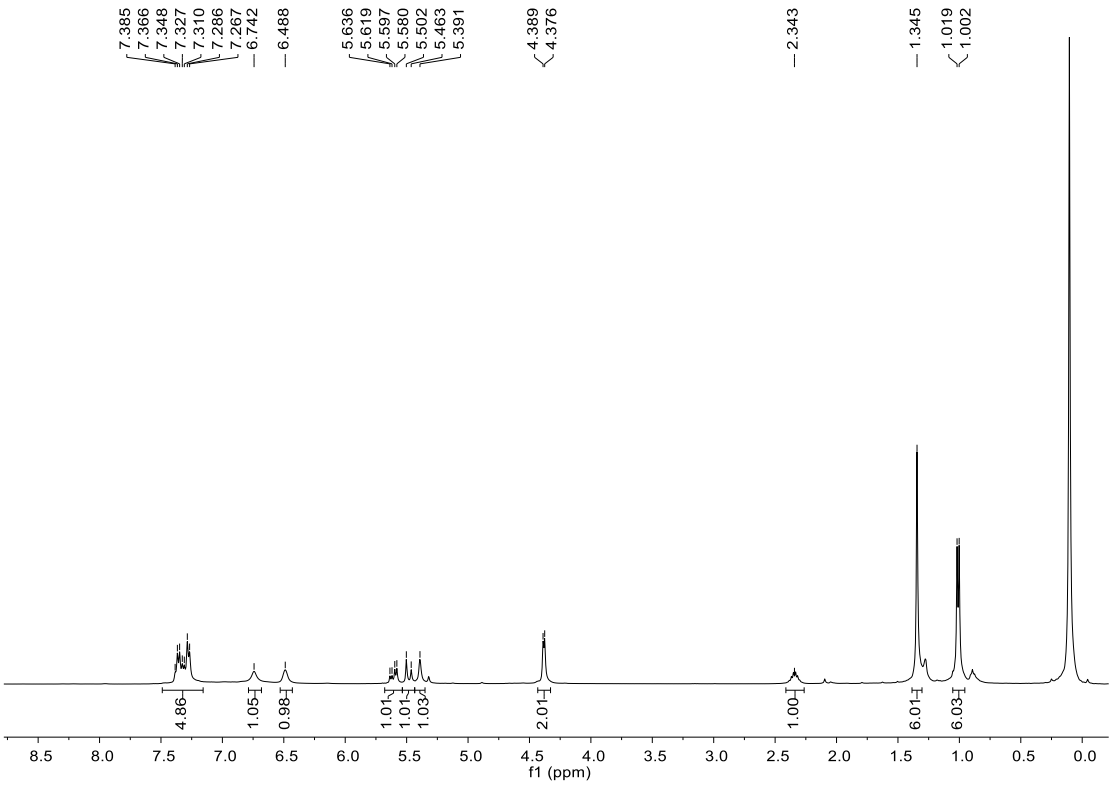


Fig. S27^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of compound **5d**.

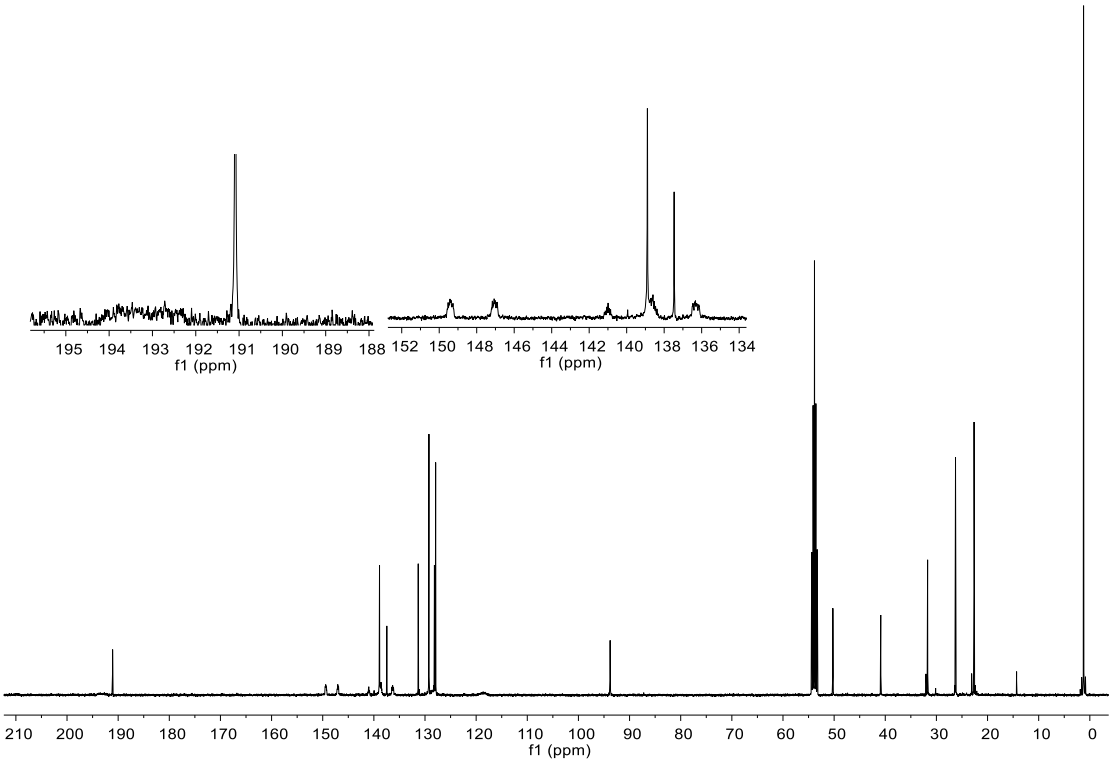


Fig. S28 ^{13}C {H} NMR (101 MHz, 299K, CD_2Cl_2) spectrum of compound **5d**.

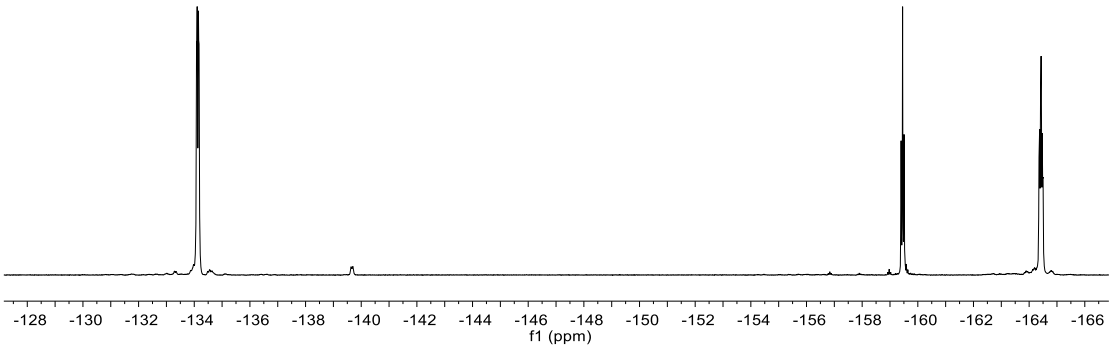


Fig. S29 $^{19}F\{H\}$ NMR (377 MHz, 299K, CD_2Cl_2) spectrum of compound **5d**.

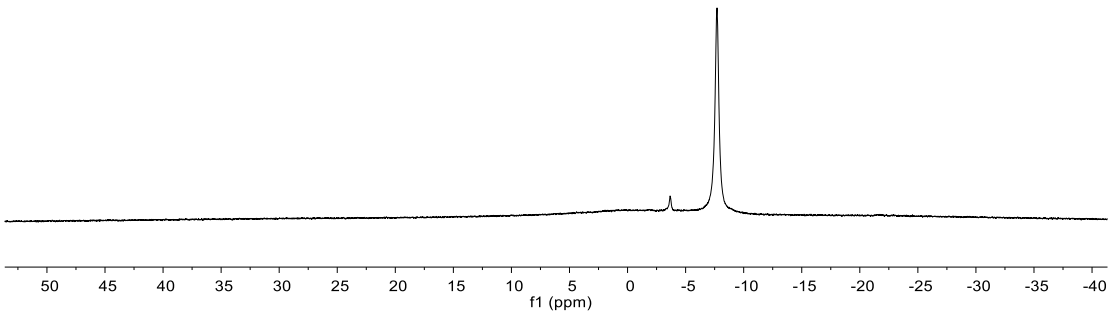
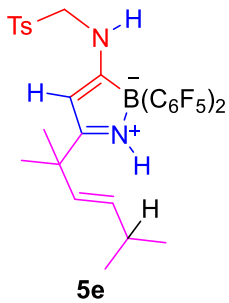


Fig. S30 ^{11}B NMR (128 MHz, 299K, CD_2Cl_2) spectrum of compound **5d**.

Synthesis and characterization of compound 5e



5e

The compound **3a** was prepared in-situ according to the General Procedure I. Then $TsCH_2N{\equiv}C$ **4e** (97.6 mg, 0.5 mmol) was added to give a pale yellow solution immediately. The solution was stirred at room temperature for 18 h. After that, the reaction mixture was concentrated to 1 mL, which was added to *n*-hexane (20 mL) to give a yellow precipitate. After filtration, the obtained residue was dried in vacuo to give yellow solid **5e**. Yield: 218.1 mg, 63%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.53 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, Ph), 7.19 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, Ph), 7.08 (br, 1H, N*H*), 6.36 (br, 1H, N*H*^{CH_2Ts}), 5.57 (dd, $^{3}J_{HH}$ = 15.8 and 6.9 Hz, 1H, =C*H*$^{i\mathrm{Pr}}$), 5.35 (d, $^{3}J_{HH}$ = 15.9 Hz, 1H, =C*H*$^{\text{-}CMe_2}$), 5.18 (s, 1H, C*H*$^{C=N}$), 4.58 (d, $^{3}J_{HH}$ = 6.6 Hz, 2H, CH_2^{Ts}), 2.41 (s, 3H, CH_3^{Ts}), 2.34 (m, 1H, C*H*$^{i\mathrm{Pr}}$), 1.22 (s, 6H, CH_3^{C}), 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C$H_3^{i\mathrm{Pr}}$).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 191.5 (*C*$^{=N}$), 190.4 (brm, B*C*), 147.7 (dm, $^{1}J_{FC}$ = 239.8 Hz, C_6F_5), 139.8 (dm, $^{1}J_{FC}$ = 234.4 Hz, C_6F_5), 137.2 (dm, $^{1}J_{FC}$ = 245.9 Hz, C_6F_5), 145.8, 134.2, 129.9, 128.9 (Ph), 139.8 (=*C*H$^{i\mathrm{Pr}}$), 130.0 (=*C*H$^{\text{-}CMe_2}$), 116.9 (brm, *i*-C_6F_5), 95.6 (*C*H$^{C=N}$), 66.6 (*C*H_2^{Ts}), 40.8 (*C*^{CH_3}), 31.4 (*C*H$^{i\mathrm{Pr}}$), 25.9 (*C*H_3^{C}), 22.6 (*C*$H_3^{i\mathrm{Pr}}$), 21.7 (*C*H_3^{Ts}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: 7.53/128.9 and 7.19/129.9 (Ph), 5.57/139.8 (=*CH*$^{i\mathrm{Pr}}$), 5.35/130.0

(=*CH*$^{\text{-CMe}_2}$), 5.18/95.6 (*CH*$^{\text{C=N}}$), 4.58/66.6 (*CH*$_2^{\text{Ts}}$), 2.41/21.7 (*CH*$_3^{\text{Ts}}$), 2.34/31.4 (*CH*$^{i\text{Pr}}$), 1.22/25.9 (*CH*$_3^{\text{C}}$), 1.00/22.6 (*CH*$_3^{i\text{Pr}}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.18/191.5 (C*H*$^{\text{C=N}}$/*C*$^{\text{=N}}$), 7.08/95.6 (N*H*/*C*H$^{\text{C=N}}$), 6.36/(66.6, 95.6) (N*H*$^{\text{CH}_2\text{Ts}}$/*C*H$_2^{\text{Ts}}$, *C*H$^{\text{C=N}}$), 5.57/(22.6, 40.8, 130.0) (=C*H*$^{i\text{Pr}}$/*C*H$_3^{i\text{Pr}}$, *C*$^{\text{CH}_3}$, =*C*H$^{\text{-CMe}_2}$), 5.35/(25.9, 31.4, 40.8, 139.8) (=C*H*$^{\text{-CMe}_2}$/*C*H$_3^{\text{C}}$, *C*H$^{i\text{Pr}}$, *C*$^{\text{CH}_3}$, =*C*H$^{i\text{Pr}}$), 1.22/(25.9, 40.8, 130.0) (C*H*$_3^{\text{C}}$/*C*H$_3^{\text{C}}$, *C*H$^{i\text{Pr}}$, *C*$^{\text{CH}_3}$, =*C*H$^{\text{-CMe}_2}$), 1.00/(31.4, 139.8) (C*H*$_3^{i\text{Pr}}$/*C*H$^{i\text{Pr}}$, =*C*H$^{i\text{Pr}}$).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -7.6 ($\nu_{1/2}$ ~ 69 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -133.7 (m, 4F, *o*-C_6F_5), -157.3 (t, $^{3}J_{FF}$ = 20.7 Hz, 2F, *p*-C_6F_5), -162.7 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.4].

HRMS (ESI): m/z calcd for $C_{31}H_{27}BF_{10}N_2O_2S$: 691.1654 $[M-H]^-$; found: 691.1662.

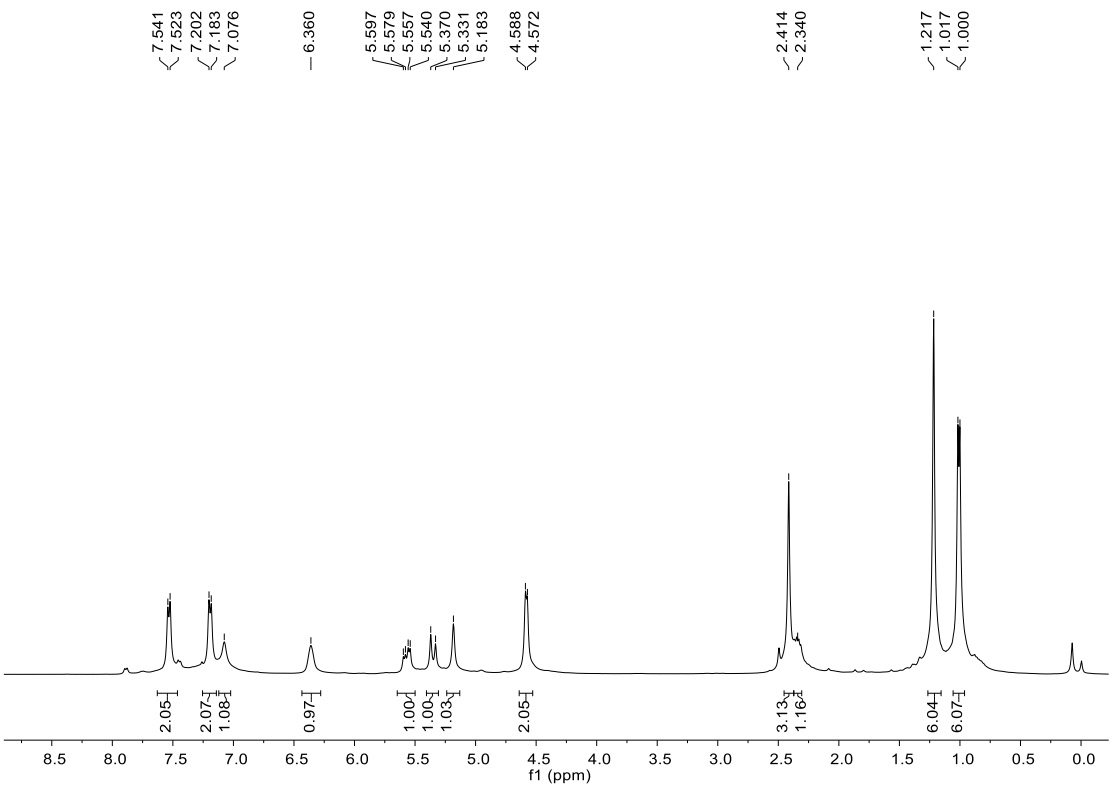


Fig. S31 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5e**.

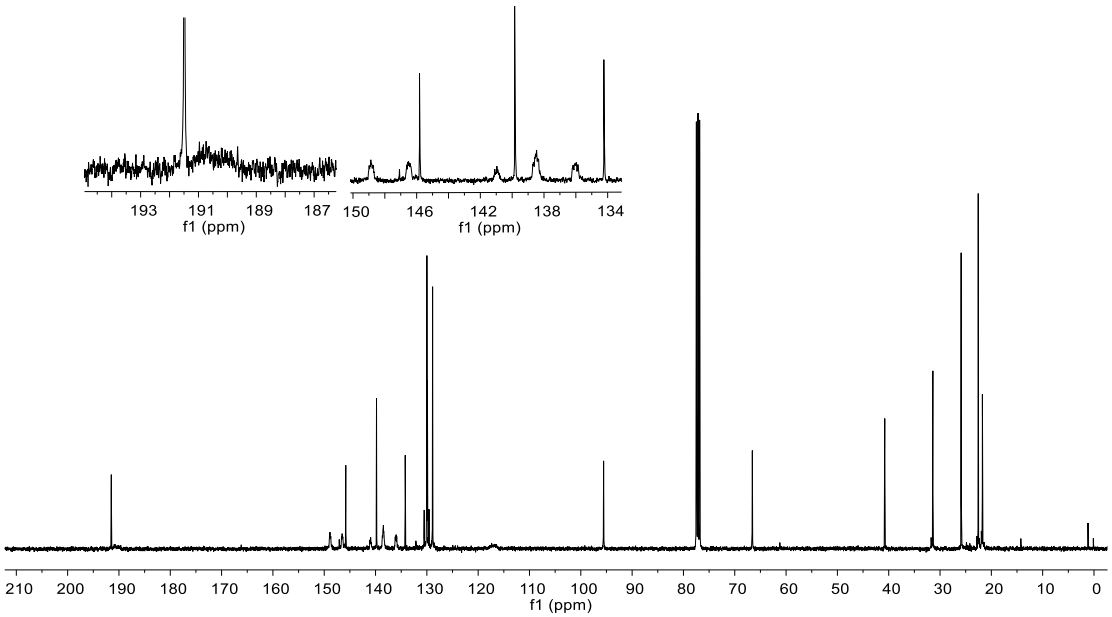


Fig. S32 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5e**.

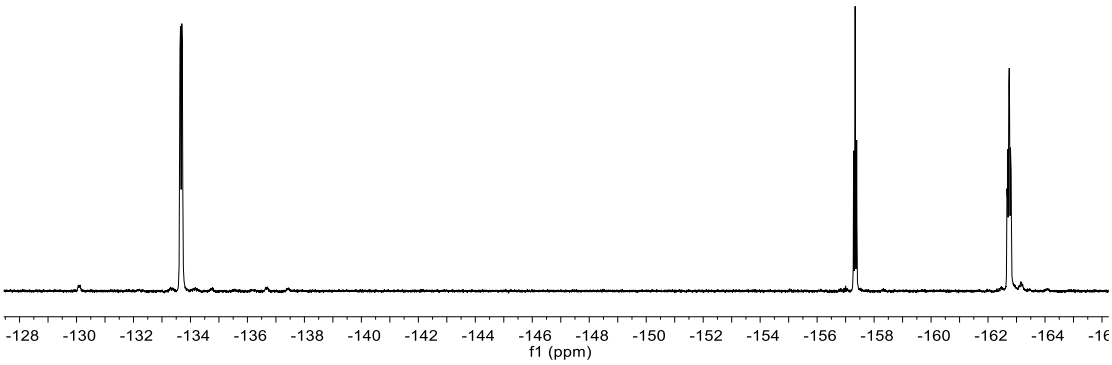


Fig. S33 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5e**.

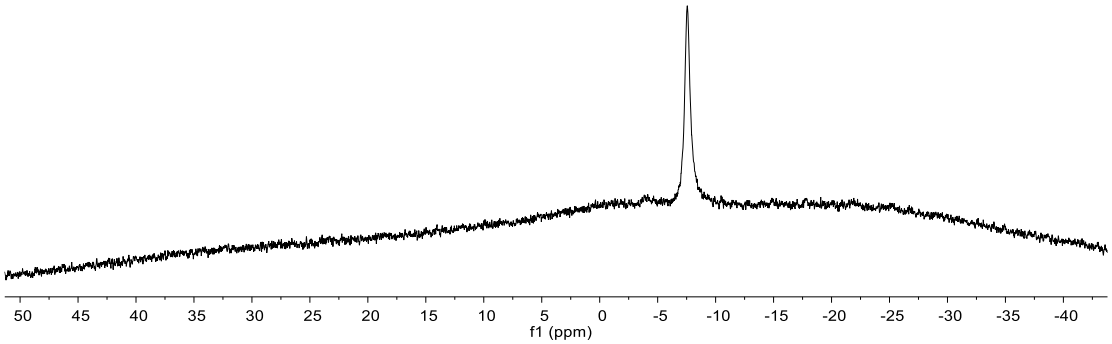
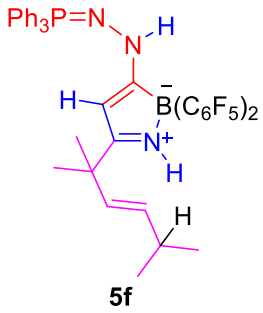


Fig. S34 ^{11}B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5e**.

Synthesis and characterization of compound 5f



5f

The compound **3a** was prepared in-situ according to the General

Procedure I. Then Ph_3P=N-N≡C **4f** (151.2 mg, 0.5 mmol) was added to give an orange solution immediately. The solution was stirred at room temperature for 18 h. After that, the reaction mixture was concentrated to 1 mL, which was added to *n*-hexane (20 mL) to give a yellow precipitate. After filtration, the obtained residue was dried in vacuo to give orange solid **5f**. Yield: 271.8 mg, 68%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.71 (br, 1H, N*H*N), 7.66-7.44 (m, 15H, Ph), 5.93 (br, 1H, N*H*), 5.64 (s, 1H, C*H*$^{C=N}$), 5.52 (dd, $^{3}J_{HH}$ = 15.6 and 6.4 Hz, 1H, =C*H*^{iPr}), 5.43 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H, =C*H*$^{-CMe_2}$), 2.31 (m, 1H, C*H*^{iPr}), 1.27 (s, 6H, CH_3^{C}), 0.99 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 188.5 (brm, B*C*), 187.3 (*C*$^{=N}$), 147.7 (dm, $^{1}J_{FC}$ = 238.9 Hz, *C*$_6F_5$), 139.1 (dm, $^{1}J_{FC}$ = 250.5 Hz, *C*$_6F_5$), 137.0 (dm, $^{1}J_{FC}$ = 255.2 Hz, *C*$_6F_5$), 137.4 (=*C*H^{iPr}), 132.8 (d, $^{3}J_{PC}$ = 9.1 Hz, *m*-Ph), 132.7 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Ph), 129.0 (d, $^{2}J_{PC}$ = 11.8 Hz, *m*-Ph), 127.7 (d, $^{1}J_{PC}$ = 93.7 Hz, *i*-Ph), 132.1 (=*C*H$^{-CMe_2}$), 119.7 (brm, *i*-*C*$_6F_5$), 92.3 (*C*H$^{C=N}$), 40.1 (*C*^{CH_3}), 31.3 (*C*H^{iPr}), 26.5 (*C*H_3^{C}), 22.7 (*C*H_3^{iPr}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.64/92.3 (*CH*$^{C=N}$), 5.52/137.4 (=*CH*^{iPr}), 5.43/132.1 (=*CH*$^{-CMe_2}$), 2.31/31.3 (*CH*^{iPr}), 1.27/26.5 (*CH*$_3^{C}$), 0.99/22.7 (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 7.71/(92.3, 187.3, 188.5) (N*H*N/*C*H$^{C=N}$, *C*$^{=N}$, B*C*), 5.93/(40.1, 92.3) (N*H*$^{=C}$/*C*^{CH_3}, =*C*H$^{-CMe_2}$), 5.64/187.3 (C*H*$^{C=N}$/*C*$^{=N}$), 5.52/(22.7, 40.1) (=C*H*^{iPr}/*C*H$_3$^{iPr}, *C*^{CH_3}), 5.43/(26.5, 31.3, 92.3) (=C*H*$^{-CMe_2}$/*C*H$_3$^{C}, *C*H^{iPr}, *C*H$^{C=N}$), 1.27/(40.1, 132.1, 187.3) (C*H*$_3$^{C}/*C*^{CH_3}, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 0.99/(31.3, 137.4) (C*H*$_3$^{iPr}/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.4 ($\nu_{1/2}$ ~ 62 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -134.4 (m, 4F, *o*-C_6F_5), -159.7 (t, $^{3}J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -164.2 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.5].

HRMS (ESI): m/z calcd for $C_{41}H_{33}BF_{10}N_3P$: 800.2418 $[M+H]^+$; found: 800.2417.

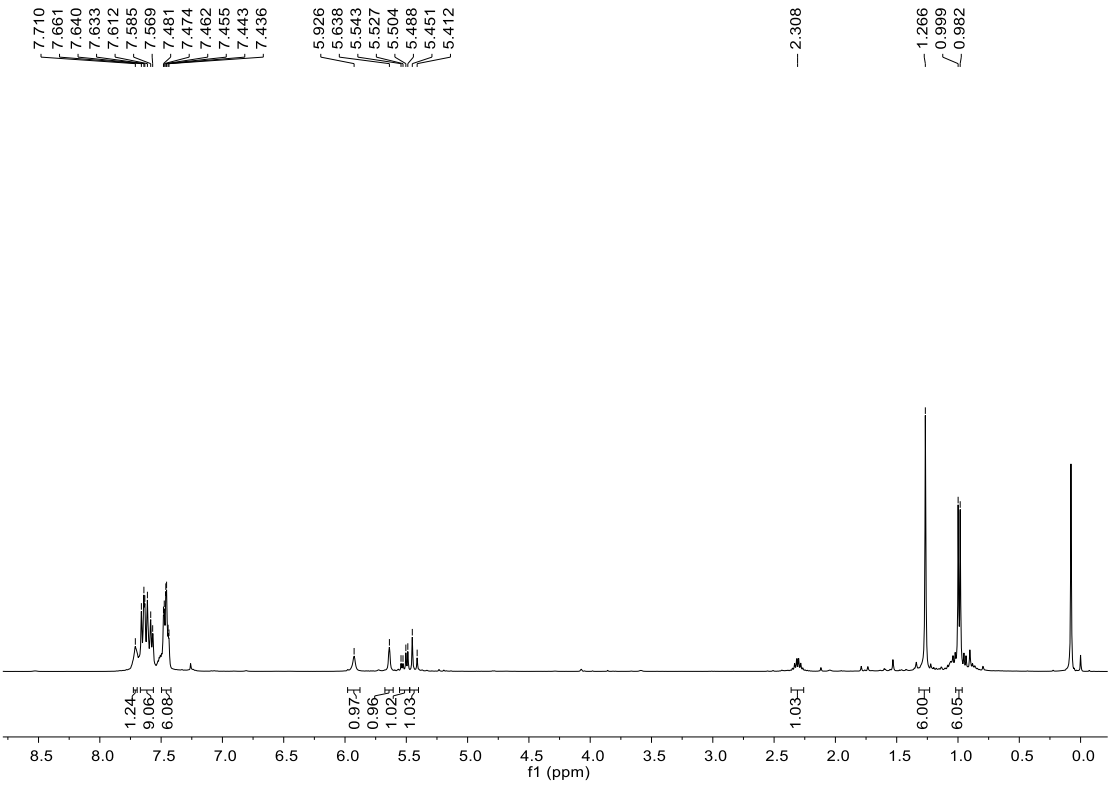


Fig. S35 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5f**.

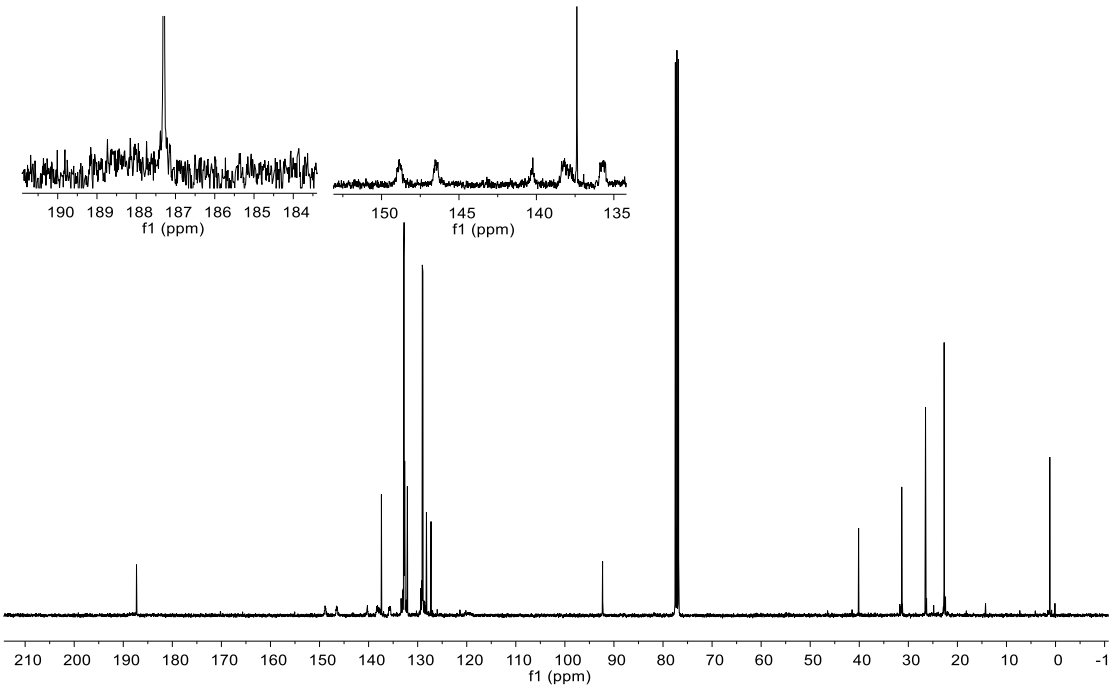


Fig. S36 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5f**.

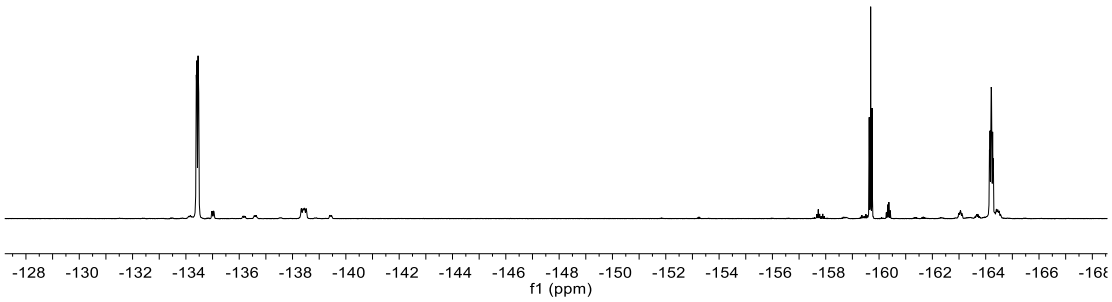


Fig. S37 ^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5f**.

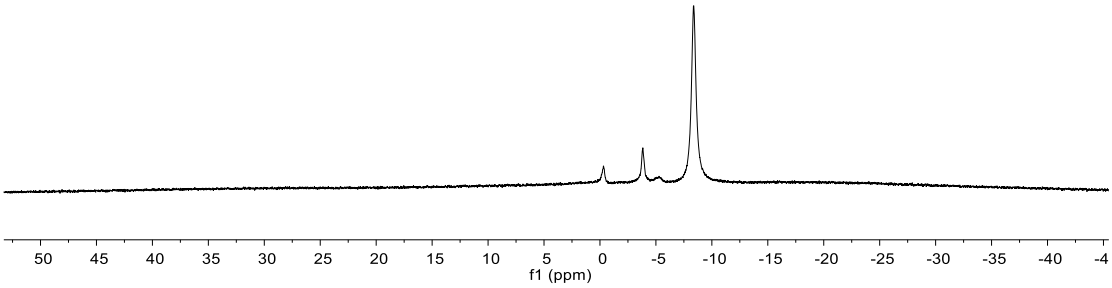
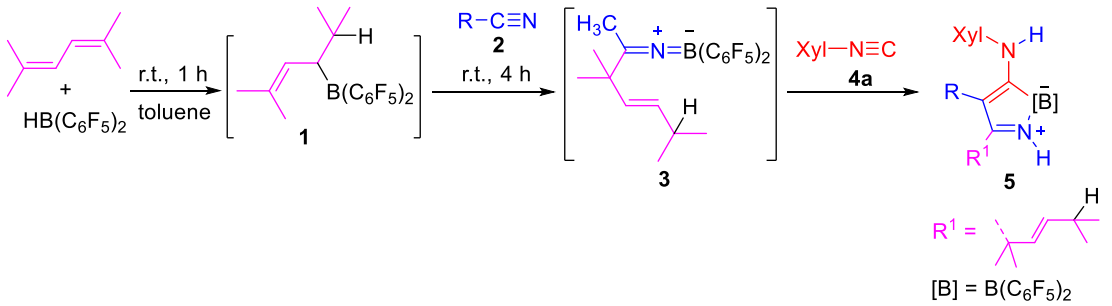


Fig. S38 ^{11}B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5f**.

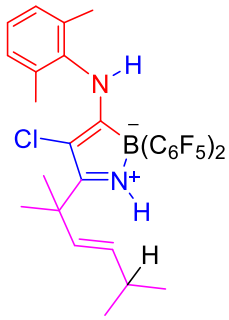
General Procedure II



Scheme S5

The compound **3** was *in-situ* prepared according to the General Procedure I [2,5-dimethylhexa-2,4-diene (0.5 mmol), $HB(C_6F_5)_2$ (0.5 mmol) and R-C≡N nitriles **2** (0.5 mmol) in toluene (2 mL)]. Then Xyl-N≡C **4a** (0.5 mmol) was added to the mixture. After completion, all the volatiles were removed in vacuo. The obtained residue was washed with *n*-hexane (2×1.5 mL) and dried in vacuo to afford target products.

Synthesis and characterization of compound 5g



5g

The compound **5g** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), $ClCH_2C{\equiv}N$ (37.8 mg, 0.5 mmol) and Xyl-N≡C (65.6 mg, 0.5 mmol) in toluene (2 mL)]. Xyl-N≡C was added to the solution of in-situ generated **3g** to give a pale yellow solution immediately. Then the mixture was stirred at room temperature for 43 h. The product **5g** was isolated as a gray solid. Yield: 210.7 mg, 61%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.36 and 7.33 (each br, each 1H, N*H*), 7.10 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, *p*-Ph), 7.05 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, *m*-Ph), 5.58 (dd, $^{3}J_{HH}$ = 16.0 and 5.6 Hz, 1H, =C*H*^{iPr}), 5.53 (d, $^{3}J_{HH}$ = 16.0 Hz, 1H, =C*H*$^{-CMe_2}$), 2.35 (m, 1H, C*H*^{iPr}), 2.02 (s, 6H, CH_3^{Ph}), 1.48 (s, 6H, CH_3^{C}), 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {H} NMR (101 MHz, 299K, $CDCl_3$): δ = 187.8 (*C*$^{=N}$), 182.1 (brm, B*C*), 147.9 (dm, $^{1}J_{FC}$ = 238.5 Hz, C_6F_5), 139.8 (dm, $^{1}J_{FC}$ = 251.9 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ = 277.6 Hz, C_6F_5), 139.9 (=C*H*^{iPr}), 136.7, 136.1,

127.7, 127.7 (Ph), 130.3 (=*C*H$^{-CMe_2}$), 117.3 (brm, *i*-*C*$_6$F$_5$), 97.5 (*C*^{Cl}), 41.6 (*C*^{CH_3}), 31.5 (*C*H^{iPr}), 24.6 (*C*H$_3^C$), 22.4 (*C*H$_3^{iPr}$), 18.2 (*C*H$_3^{Ph}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^1H/δ^{13}C: 5.58/139.9 (=*CH*^{iPr}), 5.53/130.3 (=*CH*$^{-CMe_2}$), 2.35/31.5 (*CH*^{iPr}), 2.02/18.2 (*CH*$_3^{Ph}$), 1.48/24.6 (*CH*$_3^C$), 1.01/22.4 (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^1H/δ^{13}C: 7.33/97.5 (N*H*/*C*^{Cl}), 5.53/24.6 (=C*H*$^{-CMe_2}$/*C*H$_3^C$), 5.58/41.6 (=C*H*^{iPr}/*C*^{CH_3}), 1.48/(41.6, 130.3, 187.8) (C*H*$_3^C$/*C*H$_3^C$, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 1.01/(31.5, 139.9) (C*H*$_3^{iPr}$/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.3 ($\nu_{1/2}$ ~ 69 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -134.0 (m, 4F, *o*-C_6F_5), -157.1 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -162.6 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.5].

HRMS (ESI): m/z calcd for $C_{31}H_{26}BClF_{10}N_2$: 661.1645 [M-H]$^-$; found: 661.1639.

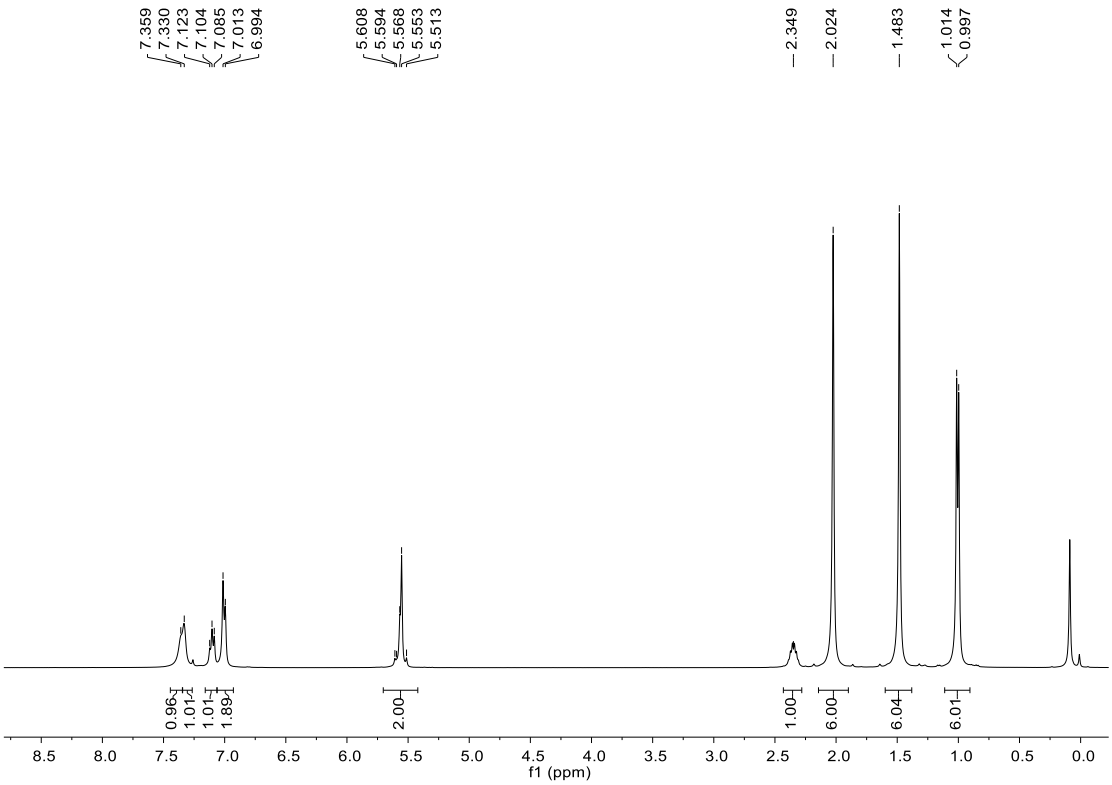


Fig. S39 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5g**.

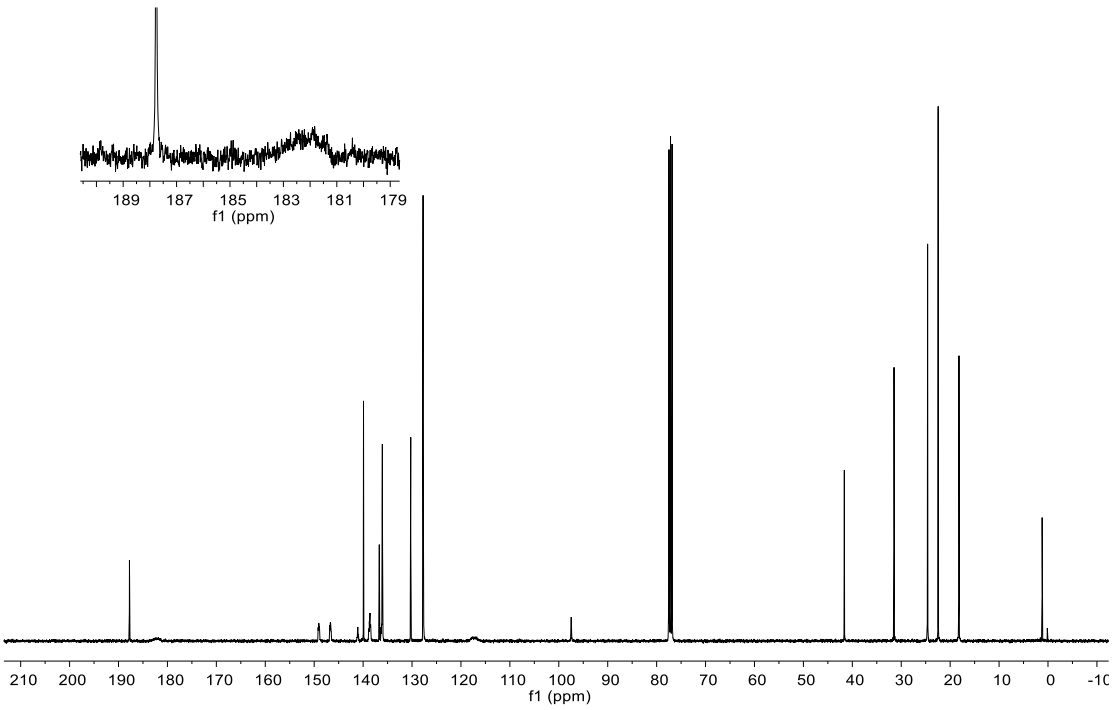


Fig. S40 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5g**.

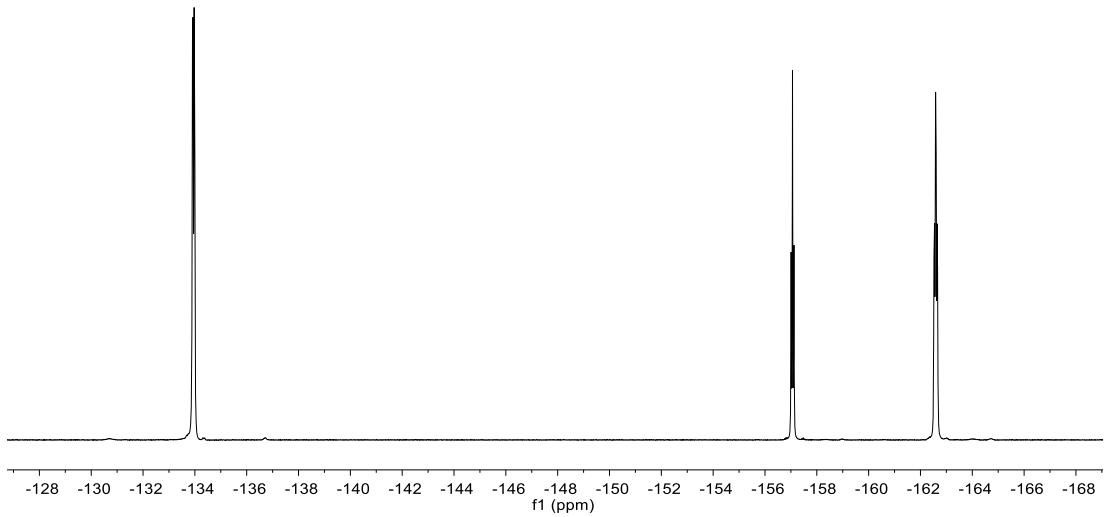


Fig. S41 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5g**.

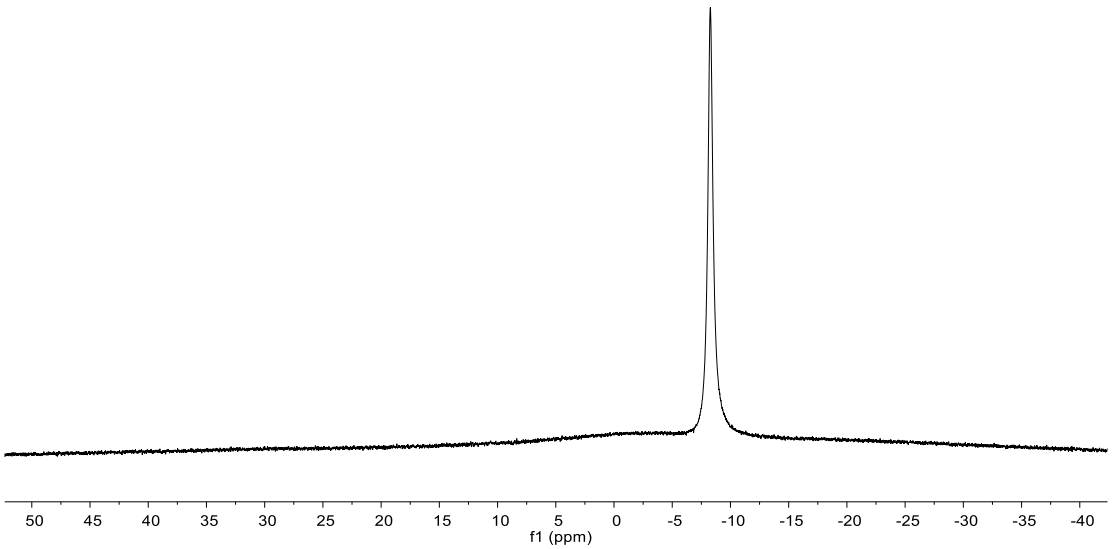
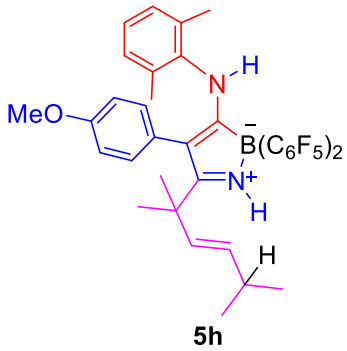


Fig. S42 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5g**.

Synthesis and characterization of compound 5h



5h

The compound **5h** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), 4-OMe-$PhCH_2C{\equiv}N$ (73.6 mg, 0.5 mmol) and Xyl-N≡C (65.6 mg, 0.5 mmol) in toluene (2 mL)]. The solution of in-situ generated **3h** with Xyl-N≡C was stirred at 80°C for 28 h. The product **5h** was isolated as a gray solid. Yield: 235.0 mg, 64%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): 7.15 and 7.13 (each br, each 1H, N*H*), 6.73-6.33 (m, 7H, Ph), 5.43 (dd, $^3J_{HH}$ = 15.6 and 6.0 Hz, 1H, =C*H*^{iPr}), 5.36 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =C*H*$^{-CMe_2}$), 3.64 (s, 3H, CH_3^{OMe}), 2.25 (m, 1H, C*H*^{iPr}), 1.88 (s, 6H, CH_3^{Ph}), 1.11 (s, 6H, CH_3^{C}), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {H} NMR (101 MHz, 299K, $CDCl_3$): δ = 189.6 (*C*$^{=N}$), 188.4 (brm, B*C*), 148.0 (dm, $^1J_{FC}$ = 240.0 Hz, C_6F_5), 139.6 (dm, $^1J_{FC}$ = 242.8 Hz, C_6F_5), 137.4 (dm, $^1J_{FC}$ = 249.9 Hz, C_6F_5), 138.1 (=*C*H^{iPr}), 158.4, 137.1, 135.3, 132.9, 127.9, 127.1, 126.9, 112.5 (Ph), 132.1 (=*C*H$^{-CMe_2}$), 118.5

(brm, *i*-C_6F_5), 111.5 (C^{Ph}), 55.3 (CH_3^{OMe}), 42.3 (C^{CH_3}), 31.2 (CH^{iPr}), 26.1 (CH_3^{C}), 22.4 (CH_3^{iPr}), 18.3 (CH_3^{Ph}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 5.43/138.1 (=CH^{iPr}), 5.36/132.1 (=CH^{-CMe_2}), 3.64/55.3 (CH_3^{OMe}), 2.25/31.2 (CH^{iPr}), 1.88/18.3 (CH_3^{Ph}), 1.11/26.1 (CH_3^{C}), 0.96/22.4 (CH_3^{iPr}).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^1H/\delta^{13}C$: 7.15/111.5 (N*H*/C^{Ph}), 5.43/(31.2, 42.3) (=CH^{iPr}/CH^{iPr}, C^{CH_3}), 5.36/(26.1, 31.2) (=CH^{-CMe_2}/CH_3^{C}, CH^{iPr}), 3.64/158.4 (CH_3^{OMe}/Ph), 1.88/(127.9, 135.3, 137.1) (CH_3^{Ph}/Ph, Ph, Ph), 1.11/(42.3, 132.1, 189.6) (CH_3^{C}/C^{CH_3}, =CH^{-CMe_2}, $C^{=N}$), 0.96/(31.2, 138.1) (CH_3^{iPr}/CH^{iPr}, =CH^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.4 ($\nu_{1/2}$ ~ 72 Hz).

^{19}F{H} NMR (377 MHz, 299K, $CDCl_3$): δ = -133.8 (m, 4F, *o*-C_6F_5), -158.0 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -163.1 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.1].

HRMS (ESI): m/z calcd for $C_{38}H_{33}BF_{10}N_2O$: 733.2453 $[M-H]^-$; found: 733.2442.

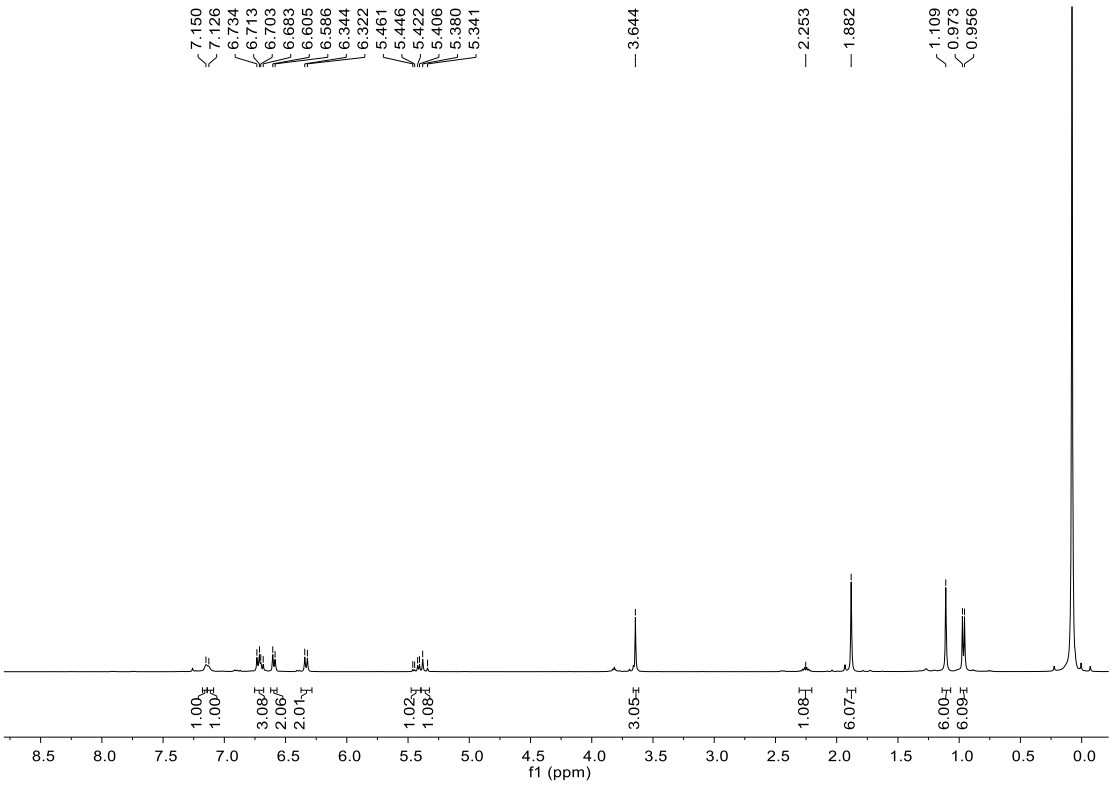


Fig. S43 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5h**.

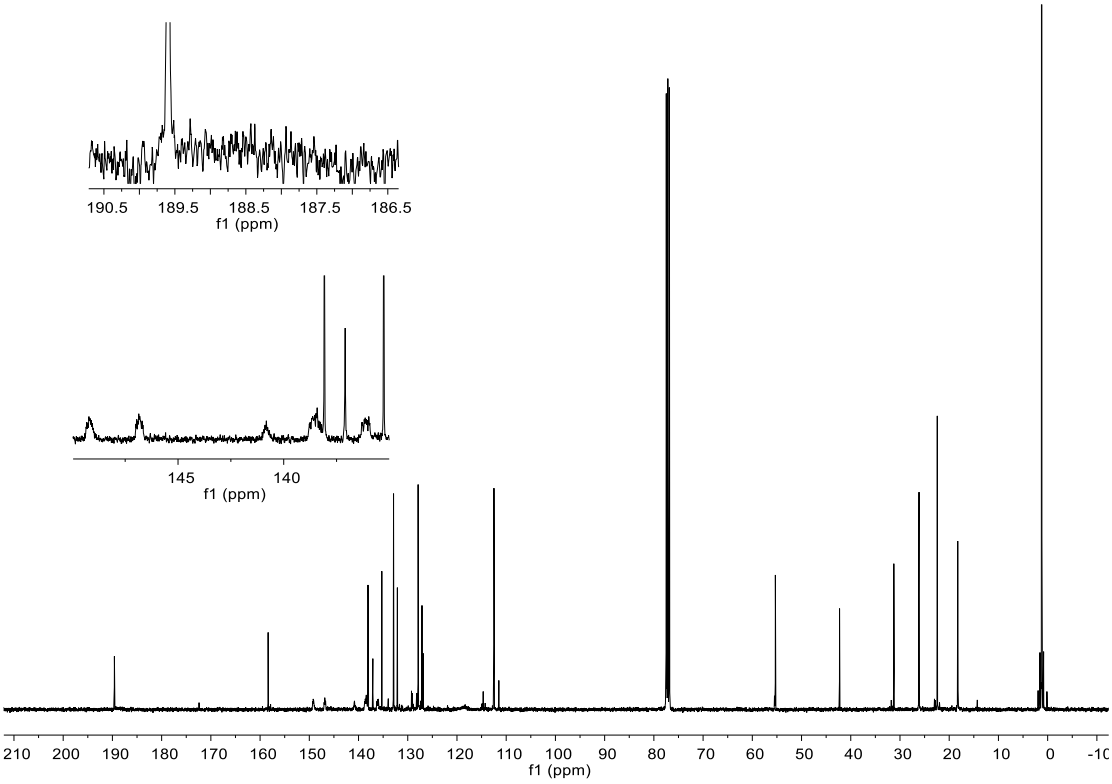


Fig. S44 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5h**.

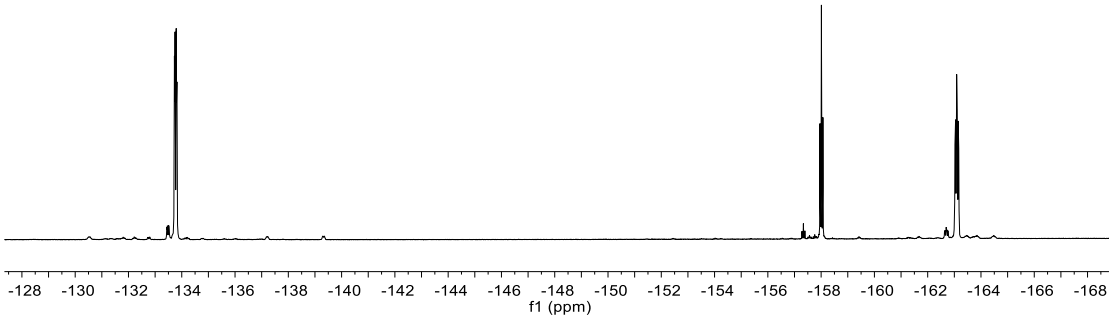


Fig. S45 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5h**.

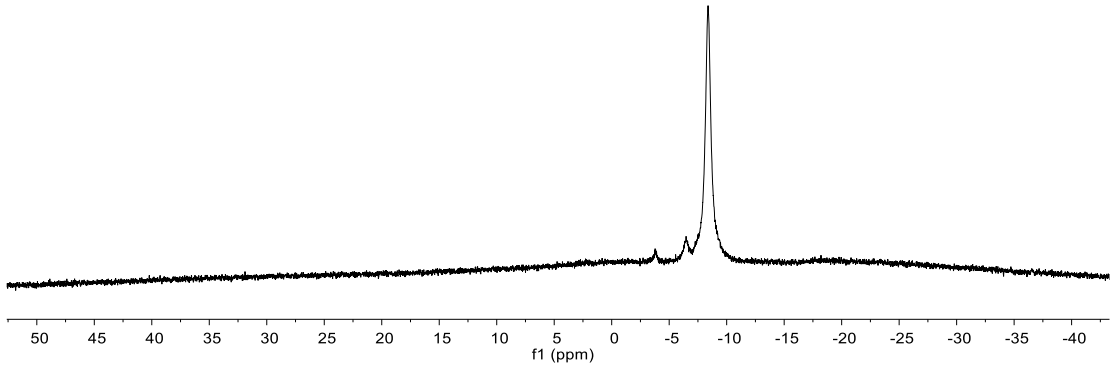
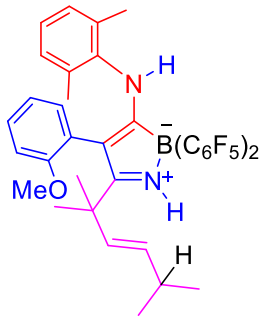


Fig. S46 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5h**.

Synthesis and characterization of compound 5i



5i

The compound **5i** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), 2-OMe-$PhCH_2C{\equiv}N$ (73.6 mg, 0.5 mmol) and Xyl-N≡C (65.1 mg, 0.5 mmol) in toluene (2 mL)]. The solution of in-situ generated **3i** with Xyl-N≡C was stirred at 80°C for 28 h. The product **5i** was isolated as a yellow solid. Yield: 275.4 mg, 75%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): 7.14 and 7.13 (each br, each 1H, N*H*), 6.91-6.22 (m, 7H, Ph), 5.46-5.38 (m, 2H, =C*H*^{iPr} and =C*H*$^{-CMe_2}$), 3.51 (s, 3H, C*H*$_3^{OMe}$), 2.23 (m, 1H, C*H*^{iPr}), 1.89 (s, 6H, C*H*$_3^{Ph}$), 1.07 and 1.05 (each s, each 3H, C*H*$_3^{C}$), 0.96 and 0.95 (each d, $^3J_{HH}$ = 6.4 Hz, each 3H, C*H*$_3^{iPr}$).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 189.9 (*C*$^{=N}$), 189.2 (brm, B*C*), 148.0 (dm, $^1J_{FC}$ = 238.1 Hz, *C*$_6F_5$), 139.5 (dm, $^1J_{FC}$ = 256.6 Hz, *C*$_6F_5$), 137.3 (dm, $^1J_{FC}$ = 248.8 Hz, *C*$_6F_5$), 137.7 (=*C*H^{iPr}), 157.9, 137.0, 135.9, 133.5, 128.7, 127.5, 127.1, 126.9, 123.7, 118.9, 108.5 (Ph), 132.2 (=*C*H$^{-CMe_2}$), 119.1 (brm, *i*-*C*$_6F_5$), 107.2 (*C*^{Ph}), 53.9 (*C*H$_3^{OMe}$), 42.3 (*C*^{CH_3}),

31.2 (*C*H^{iPr}), 25.5 and 25.2 (*C*H$_3^{C}$), 22.52 and 22.50 (*C*H$_3^{iPr}$), 18.6 and 17.9 (*C*H$_3^{Ph}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: 5.41/137.7 (=*CH*^{iPr}), 5.40/132.2 (=*CH*$^{-CMe_2}$), 3.51/53.9 (*CH*$_3^{OMe}$), 2.23/31.2 (*CH*^{iPr}), 1.89/18.2 (*CH*$_3^{Ph}$), (1.07, 1.05)/(25.5, 25.2) (*CH*$_3^{C}$), (0.96, 0.95)/(22.52, 22.50) (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^{1}H/\delta^{13}C$: 7.14/107.2 (N*H*/*C*^{Ph}), 3.51/157.9 (C*H*$_3^{OMe}$/Ph), 1.06/(42.3, 132.2, 189.9) (C*H*$_3^{C}$/*C*^{CH_3}, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 0.96/(31.2, 137.7) (C*H*$_3^{iPr}$/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.3 ($\nu_{1/2}$ ~ 68 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -133.6, 133.8 (each m, each 2F, *o*-C_6F_5), -158.3, 158.5 (each t, $^{3}J_{FF}$ = 20.7 and 20.4 Hz, each 1F, *p*-C_6F_5), -163.4 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.1 and 4.9].

HRMS (ESI): m/z calcd for $C_{38}H_{33}BF_{10}N_2O$: 733.2453 [M-H]$^{-}$; found: 733.2461.

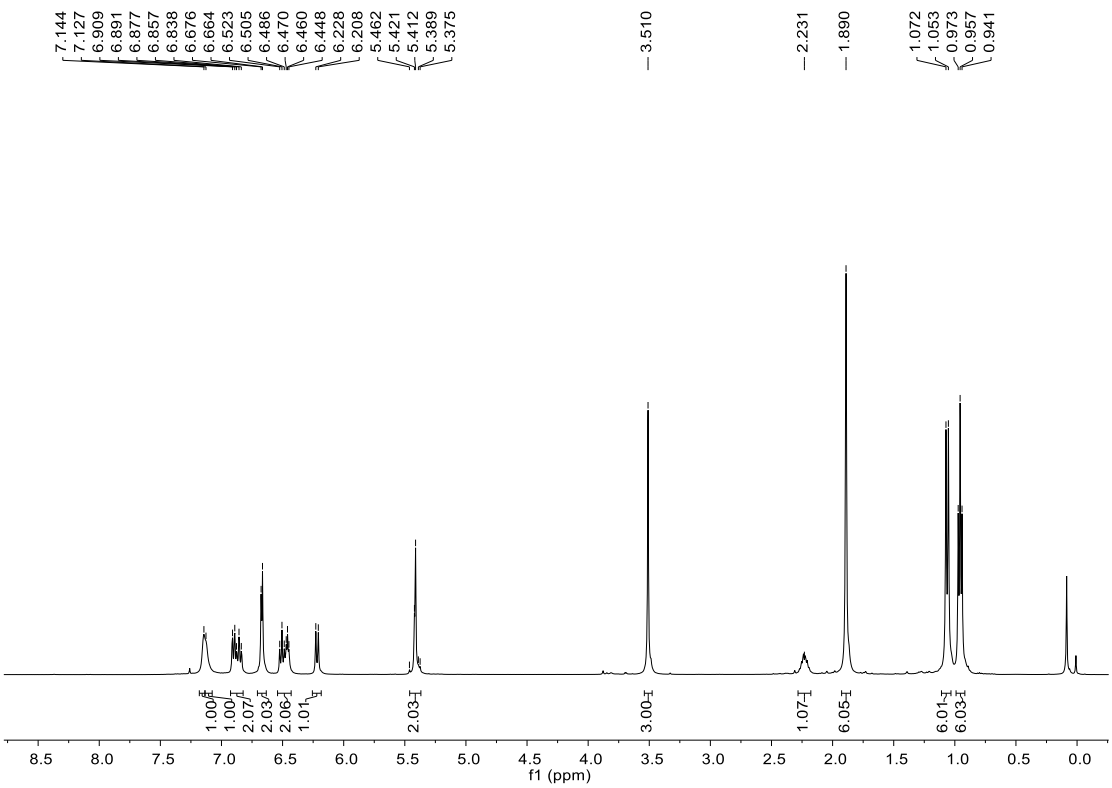


Fig. S47 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5i**.

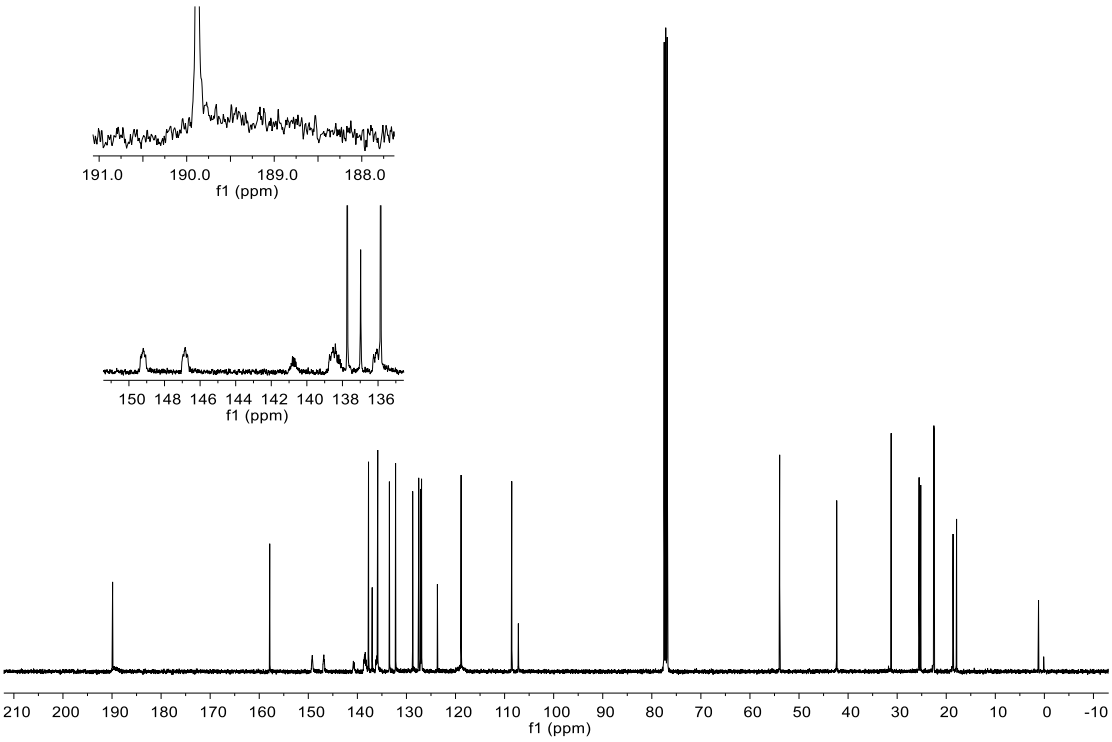


Fig. S48 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5i**.

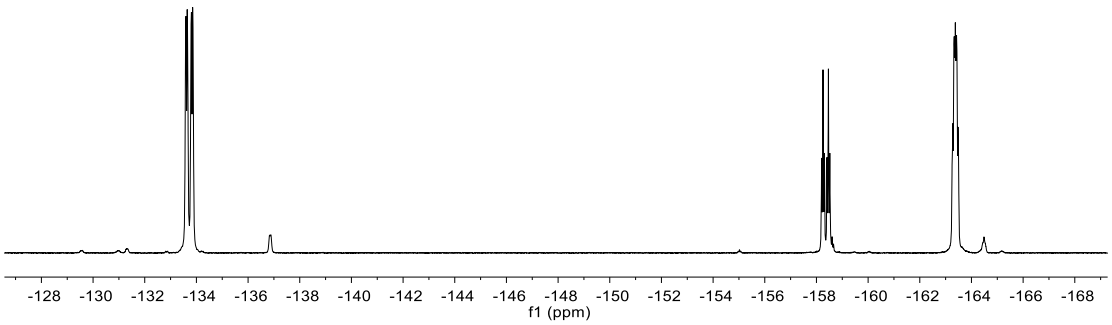


Fig. S49 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5i**.

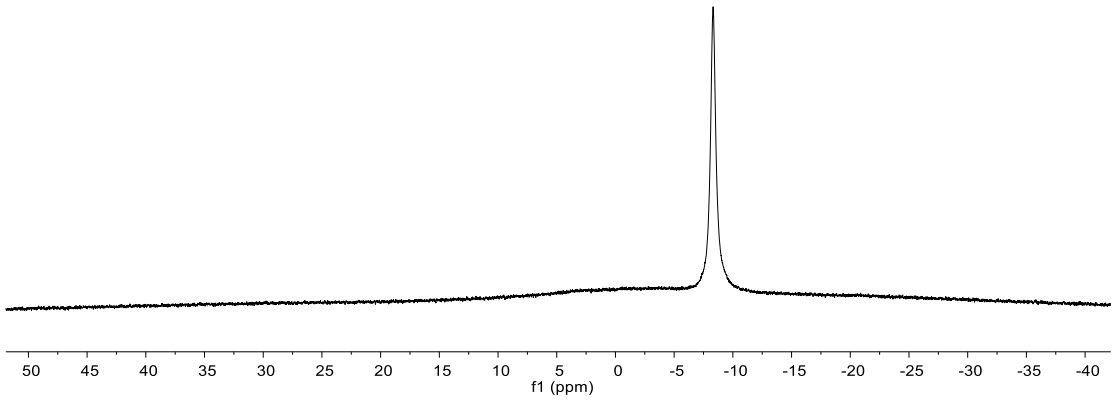
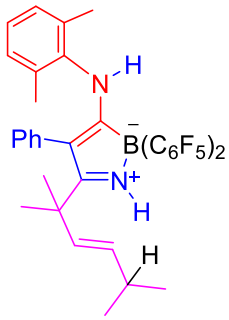


Fig. S50 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5i**.

Synthesis and characterization of compound 5j



5j

The compound **5j** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), $PhCH_2C{\equiv}N$ (58.6 mg, 0.5 mmol) and Xyl-N≡C (65.6 mg, 0.5 mmol) in toluene (2 mL)]. Xyl-N≡C was added to the solution of in-situ generated **3j** to give a pale yellow solution immediately. Then the solution was stirred at 80°C for 28 h. The product **5j** was isolated as a white solid. Yield: 239.5 mg, 68%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **5j** in CH_2Cl_2 covered with *n*-hexane at room temperature.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): 7.16 and 7.15 (each br, each 1H, N*H*), 6.86-6.56 (m, 8H, Ph), 5.42 (dd, $^3J_{HH}$ = 16.0 and 6.4 Hz, 1H, =C*H*^{iPr}), 5.34 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =C*H*$^{-CMe_2}$), 2.24 (m, 1H, C*H*^{iPr}), 1.88 (s, 6H, CH_3^{Ph}), 1.08 (s, 6H, CH_3^{C}), 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 189.3 (*C*$^{=N}$), 188.2 (brm, B*C*), 148.0 (dm, $^1J_{FC}$ = 238.1 Hz, C_6F_5), 139.6 (dm, $^1J_{FC}$ = 250.8 Hz,

C_6F_5), 137.4 (dm, $^1J_{FC}$ = 250.2 Hz, C_6F_5), 138.1 (=CH^{iPr}), 136.9, 135.3, 134.8, 131.9, 127.8, 127.3, 126.9, 126.8 (Ph), 132.1 (=CH$^{-CMe_2}$), 118.5 (brm, *i*-C_6F_5), 112.0 (C^{Ph}), 42.3 (C^{CH_3}), 31.2 (CH^{iPr}), 26.1 (CH$_3^C$), 22.4 (CH$_3^{iPr}$), 18.2 (CH$_3^{Ph}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^1H/δ^{13}C: 5.42/138.1 (=*CH*^{iPr}), 5.34/132.1 (=*CH*$^{-CMe_2}$), 2.24/31.2 (*CH*^{iPr}), 1.88/18.2 (*CH*$_3^{Ph}$), 1.08/26.1 (*CH*$_3^C$), 0.95/22.4 (*CH*$_3^{iPr}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^1H/δ^{13}C: 7.16/112.0 (N*H*/*C*^{Ph}), 5.42/42.3 (=C*H*^{iPr}/*C*^{CH_3}), 5.34/31.2 (=C*H*$^{-CMe_2}$/*C*H^{iPr}), 1.88/(127.8, 135.3, 136.9) (C*H*$_3^{Ph}$/Ph, Ph, Ph), 1.08/(42.3, 132.1, 189.3) (C*H*$_3^C$/*C*^{CH_3}, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 0.95/(31.2, 138.1) (C*H*$_3^{iPr}$/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.3 ($\nu_{1/2}$ ~ 68 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -133.8 (m, 4F, *o*-C_6F_5), -157.9 (t, $^3J_{FF}$ = 20.7 Hz, 2F, *p*-C_6F_5), -163.0 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.1].

HRMS (ESI): m/z calcd for $C_{31}H_{31}BF_{10}N_2$: 703.2348 $[M-H]^-$; found: 703.2338.

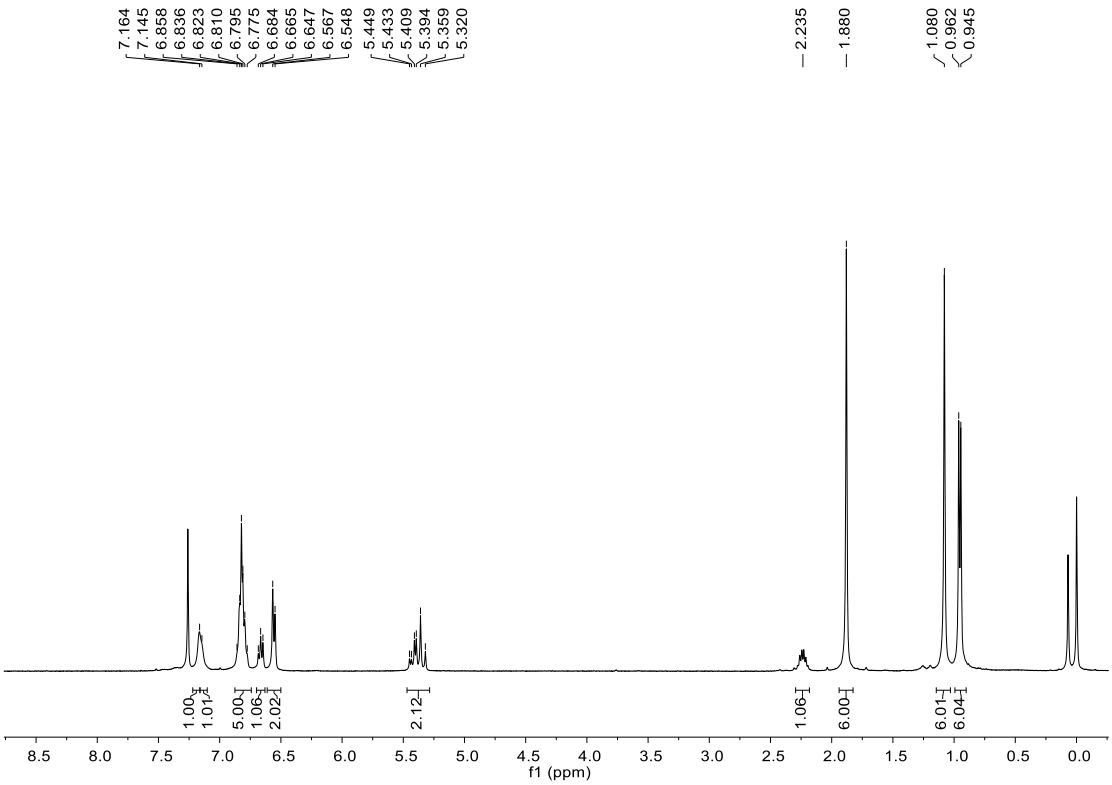


Fig. S51 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5j**.

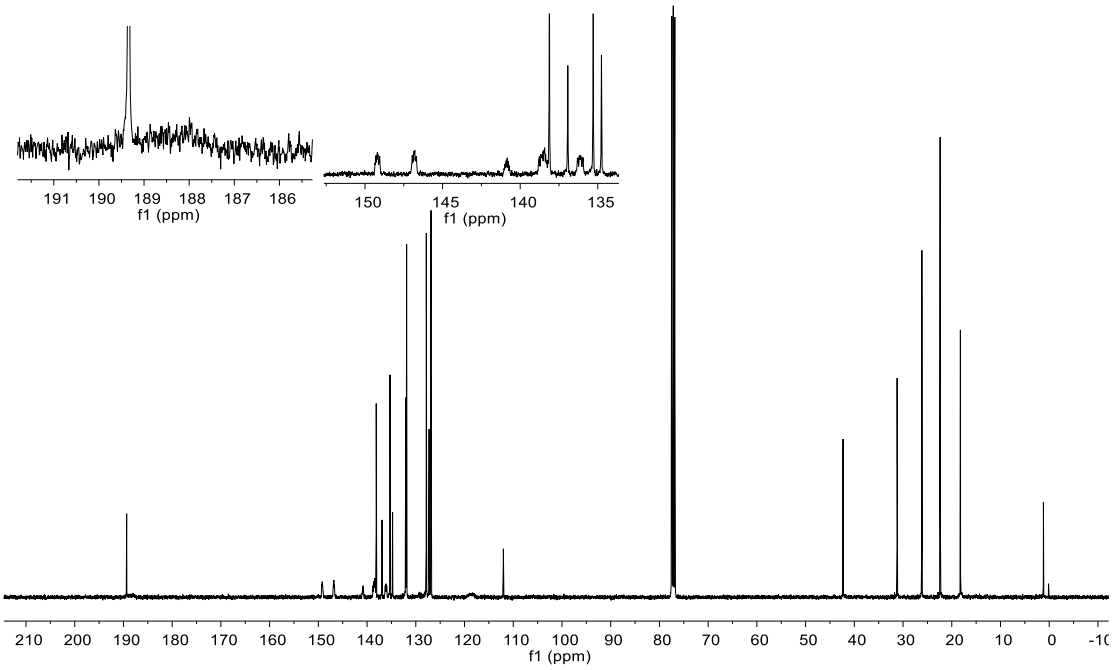


Fig. S52 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5j**.

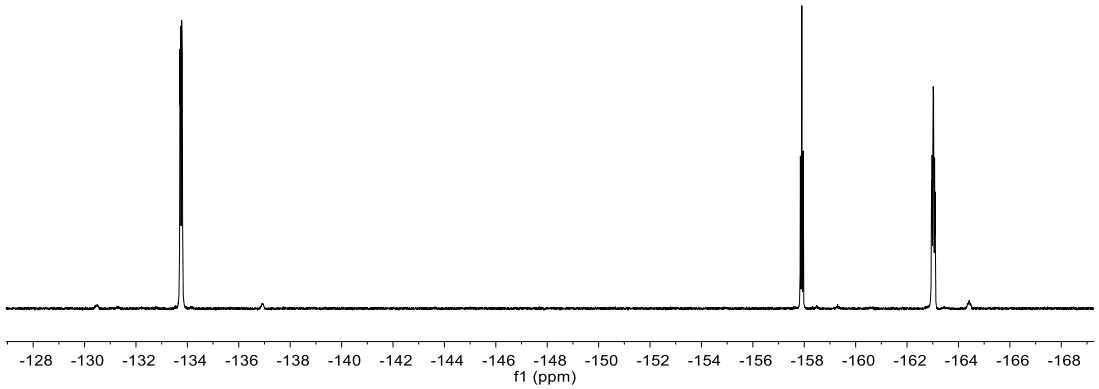


Fig. S53 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5j**.

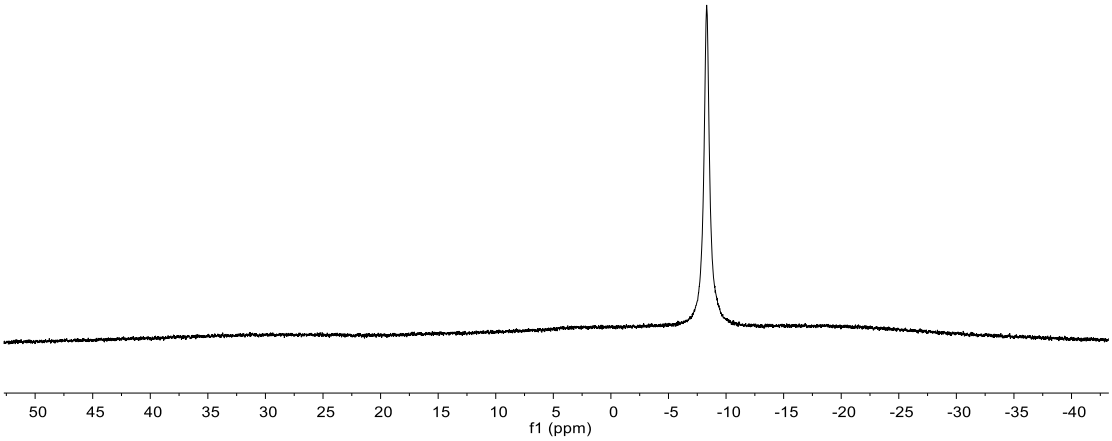


Fig. S54 ^{11}B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5j**.

X-ray crystal structure analysis of compound 5j: formula $C_{37}H_{31}BF_{10}N_2$, M = 704.45, colourless crystal, 0.31 × 0.23 × 0.10 mm, a = 11.60718(19), b = 14.4681(3), c = 20.6391(3) Å, α = γ = 90º, β = 90.6787(16)º, V = 3465.76(10) Å^3, ρ_{calc} = 1.350 gcm^{-3}, μ = 1.006 mm^{-1}, empirical absorption correction (0.39110 ≤ T ≤ 1.00000), Z = 4, monoclinic, space group $P2_1/n$, λ = 1.54184 Å, T = 296.22(11) K, ω and

φ scans, 19308 reflections collected (±*h*, ±*k*, ±*l*), 6102 independent (R_{int} = 0.0178) and 5176 observed reflections [$I>2\sigma(I)$], 460 refined parameters, R = 0.0643, wR^2 = 0.2051, max. (min.) residual electron density 0.41 (-0.39) e.Å^{-3}, all the hydrogen atoms were calculated and refined as riding atoms.

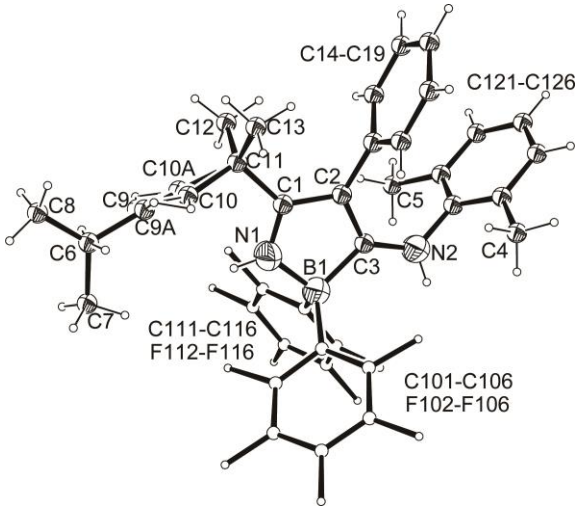
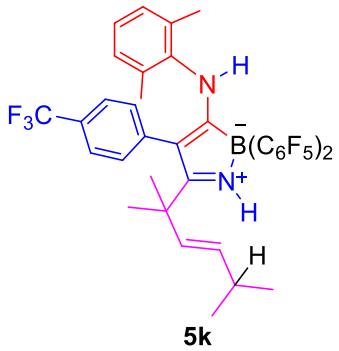


Fig. S55 A view of the molecular structure of compound **5j**.

Synthesis and characterization of compound 5k



5k

The compound **5k** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), 4-CF_3-$PhCH_2C{\equiv}N$ (92.6 mg, 0.5 mmol)

and Xyl-N≡C (65.6 mg, 0.5 mmol) in toluene (2 mL)]. The solution of in-situ generated **3k** with Xyl-N≡C was stirred at 80°C for 28 h. The product **5k** was isolated as a white solid. Yield: 258.8 mg, 67%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): 7.26 and 7.21 (each br, each 1H, N*H*), 7.04 (m, 2H, *m*-Ph^{CF3}), 6.95 (m, 2H, *o*-Ph^{CF3}), 6.69 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, *p*-Ph^{CH3}), 6.55 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, *m*-Ph^{CH3}), 5.40 (dd, $^{3}J_{HH}$ = 16.0 and 6.0 Hz, 1H, =C*H*^{iPr}), 5.32 (d, *J* = 16.0 Hz, 1H, =C*H*$^{-CMe_2}$), 2.21 (m, 1H, C*H*^{iPr}), 1.87 (s, 6H, CH_3^{Ph}), 1.12 (s, 6H, CH_3^{C}), 0.93 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, CH_3^{iPr}).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 189.3 (brm, B*C*), 188.9 (*C*$^{=N}$), 148.0 (dm, $^{1}J_{FC}$ = 238.3 Hz, C_6F_5), 139.7 (dm, $^{1}J_{FC}$ = 251.0 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ = 248.6 Hz, C_6F_5), 139.0 (*i*-Ph^{CF3}), 138.3 (=*C*H^{iPr}), 136.6 (*i*-Ph^{CH3}), 135.2 (*o*-Ph^{CH3}), 132.2 (*o*-Ph^{CF3}), 131.7 (=*C*H$^{-CMe_2}$), 128.9 (q, $^{2}J_{FC}$ = 32.0 Hz, *p*-Ph^{CF3}), 128.0 (*m*-Ph^{CH3}), 127.8 (*p*-Ph^{CH3}), 124.2 (q, $^{1}J_{FC}$ = 273.0 Hz, *C*F_3), 123.6 (q, $^{3}J_{FC}$ = 3.9 Hz, *m*-Ph^{CF3}), 118.2 (brm, *i*-C_6F_5), 110.4 (*C*^{Ph}), 42.3 (*C*^{CH_3}), 31.2 (*C*H^{iPr}), 26.3 (*C*H_3^{C}), 22.3 (*C*H_3^{iPr}), 18.2 (*C*H_3^{Ph}).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 7.04/123.6 (*m*-Ph^{CF3}), 6.95/132.2 (*o*-Ph^{CF3}), 6.71/127.8 (*p*-Ph^{CH3}), 6.53/128.0 (*m*-Ph^{CH3}), 5.40/138.3 (=*CH*^{iPr}), 5.32/131.7 (=*CH*$^{-CMe_2}$), 2.21/31.2 (*CH*^{iPr}), 1.87/18.2 (*C*H_3^{Ph}), 1.12/26.3 (*C*H_3^{C}), 0.93/22.3 (*C*H_3^{iPr}).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^1H/δ^{13}C: (7.26, 6.95/110.4 (N*H*/*C*^{Ph}), 7.06/(123.7, 139.0) (*m*-Ph^{CF3}/*m*-Ph^{CF3}, *i*-Ph^{CF3}), 6.95/128.9 (*o*-Ph^{CF3}/*p*-Ph^{CF3}), 6.70/135.2 (*p*-Ph^{CH3}/*o*-Ph^{CH3}), 6.55/(18.2, 136.6) (*m*-Ph^{CH3}/*C*H$_3$^{Ph}, *i*-Ph^{CH3}), 1.87/(128.0, 135.2) (C*H*$_3$^{Ph}/*m*-Ph^{CH3}, *o*-Ph^{CH3}), 1.12/(42.3, 131.7, 188.9) (C*H*$_3$^{C}/*C*^{CH_3}, =*C*H-^{CMe_2}, *C*$^{=N}$), 0.93/(31.2, 138.3) (C*H*$_3$^{iPr}/*C*H^{iPr}, =*C*H^{iPr}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.2 ($\nu_{1/2}$ ~ 75 Hz).

^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$): δ = -63.0 (s, CF_3), -133.7 (m, 4F, *o*-C_6F_5), -157.5 (t, $^3J_{FF}$ = 24.1 Hz, 2F, *p*-C_6F_5), -162.8 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.3].

HRMS (ESI): m/z calcd for $C_{38}H_{30}BF_{13}N_2$: 771.2221 $[M-H]^-$; found: 771.2212.

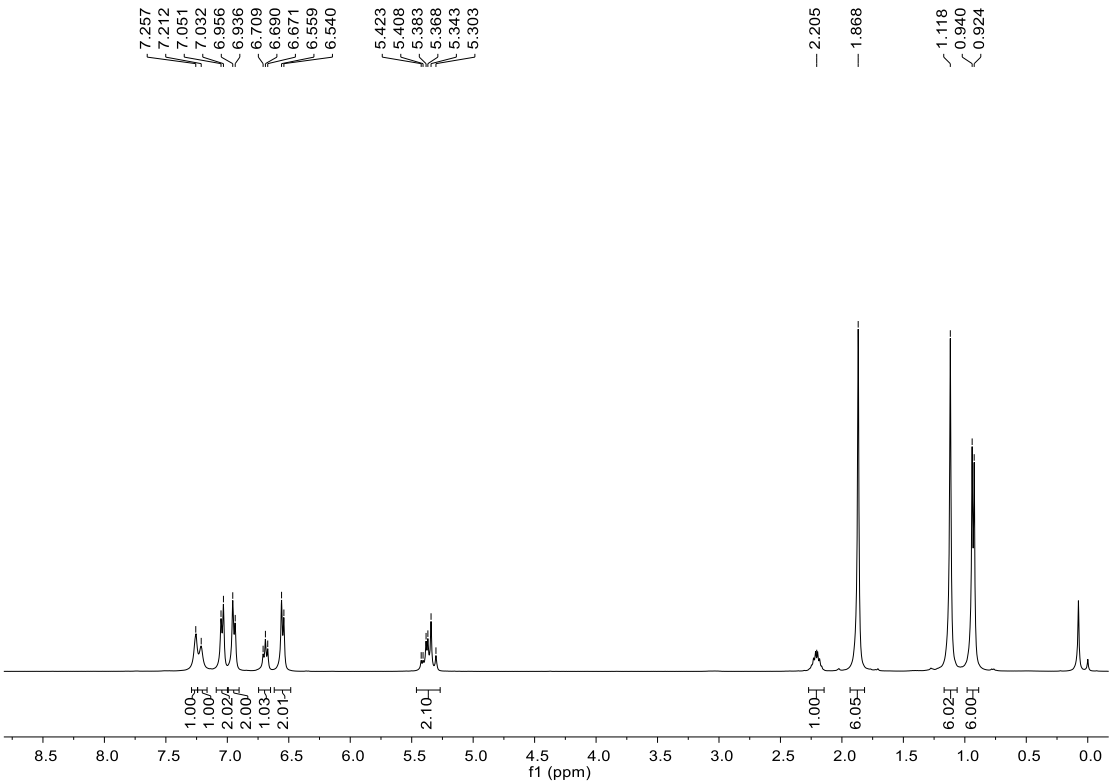


Fig. S56 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5k**.

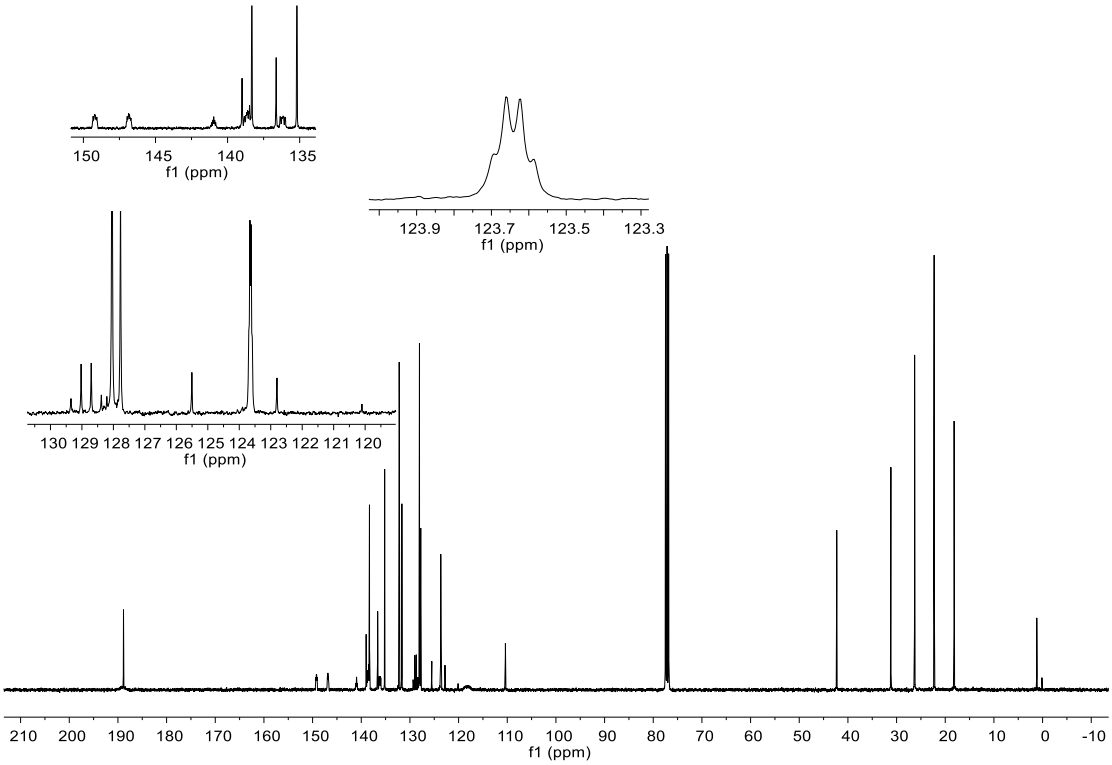


Fig. S57 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5k**.

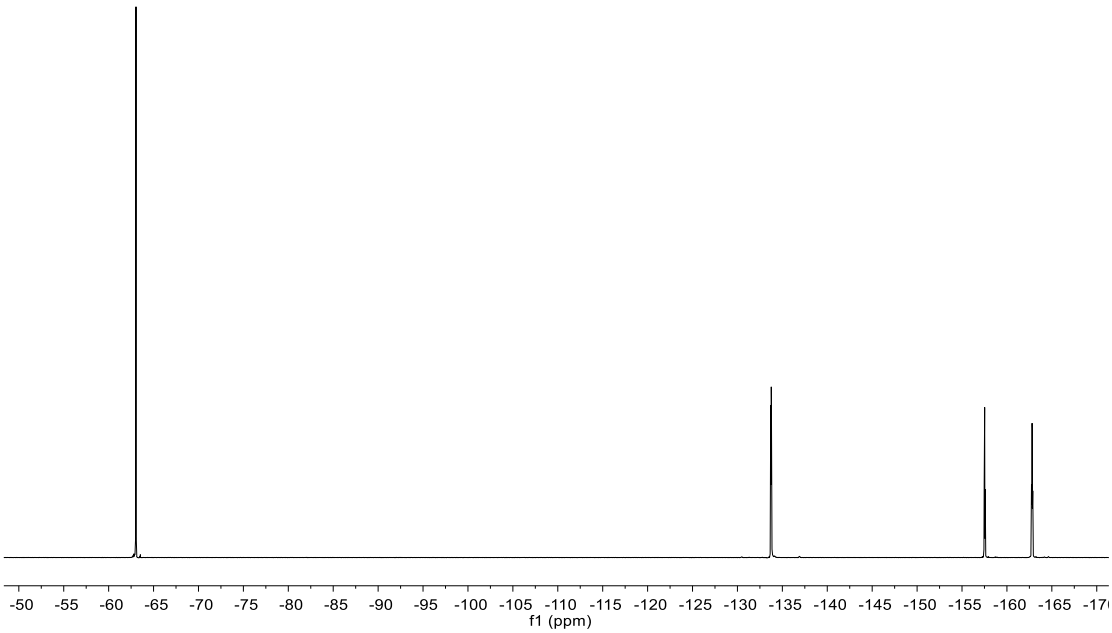


Fig. S58 ^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5k**.

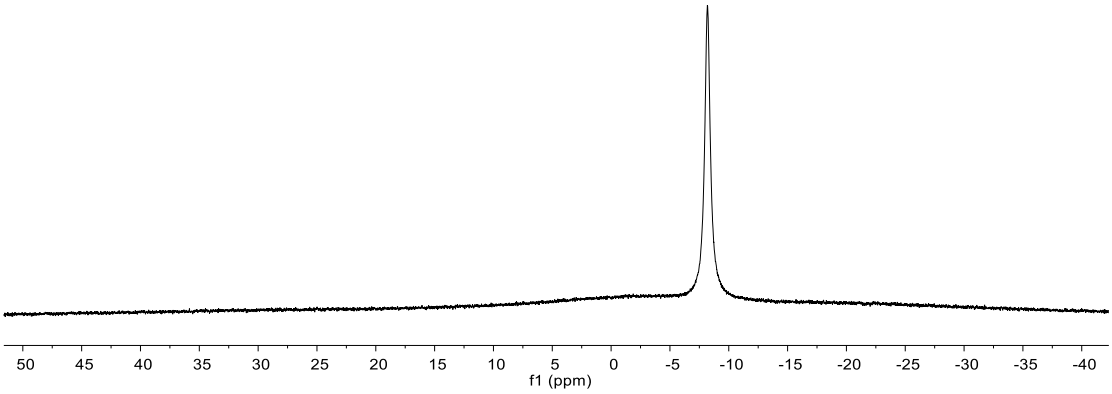
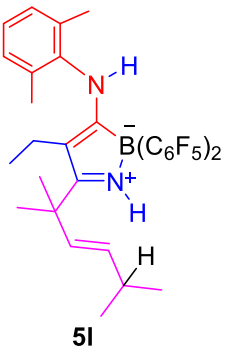


Fig. S59 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5k**.

Synthesis and characterization of compound 5l



5l

The compound **5l** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), $^{n}PrC{\equiv}N$ (34.6 mg, 0.5 mmol) and Xyl-N≡C (65.6 mg, 0.5 mmol) in toluene (2 mL)]. Xyl-N≡C was added to the solution of *in-situ* generated **3l** to give a pale yellow solution immediately. The mixture was stirred at 100°C for 31 h. The product **5l** was isolated as a gray solid. Yield: 200.2 mg, 61%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.18 (br, 1H, N*H*), 7.09-7.00 (m, 4H, N*H* and Ph), 5.55-5.46 (m, 2H, =C*H*^{iPr} and =C*H*$^{-CMe_2}$), 2.29 (m, 1H, C*H*^{iPr}), 2.00 (s, 6H, CH_3^{Ph}), 1.66 (q, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH_2^{Et}), 1.40 (s, 6H, CH_3^{C}), 0.97 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}), 0.41 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3^{Et}).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 190.2 (*C*$^{=N}$), 186.8 (brm, B*C*), 147.8 (dm, $^{1}J_{FC}$ = 237.8 Hz, *C*$_6$F$_5$), 139.5 (dm, $^{1}J_{FC}$ = 250.9 Hz, *C*$_6$F$_5$), 137.3 (dm, $^{1}J_{FC}$ = 251.3 Hz, *C*$_6$F$_5$), 137.6 (=*C*H^{iPr}), 137.6, 135.1, 128.1, 127.0 (Ph), 131.5 (=*C*H$^{-CMe_2}$), 119.1 (brm, *i*-*C*$_6$F$_5$), 113.0 (*C*^{Et}), 41.6 (*C*^{CH_3}), 31.3 (*C*H^{iPr}), 26.4 (*C*H$_3^{C}$), 22.4 (*C*H$_3^{iPr}$), 18.3 (*C*H$_2^{Et}$), 18.2 (*C*H$_3^{Ph}$), 15.0 (*C*H$_3^{Et}$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.50/137.6 (=*CH*^{iPr}), 5.49/131.5 (=*CH*$^{-CMe_2}$), 2.29/31.3 (*CH*^{iPr}), 2.00/18.2 (CH_3^{Ph}), 1.66/18.3 (*CH*$_2^{Et}$), 1.40/26.4 (*CH*$_3^{C}$), 0.97/22.4 (*CH*$_3^{iPr}$), 0.41/15.0 (*CH*$_3^{Et}$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 7.18/113.0 (N*H*/*C*^{Et}), 5.49/(26.4, 31.3) (=C*H*$^{-CMe_2}$/*C*H$_3^{C}$, *C*H^{iPr}), 5.50/41.6 (=C*H*^{iPr}/*C*^{CH_3}), 1.40/(41.6, 131.5, 190.2) (CH_3^{C}/*C*^{CH_3}, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 0.97/(31.3, 137.6) (CH_3^{iPr}/*C*H^{iPr}, =*C*H^{iPr}), 0.41/(18.3, 113.0) (CH_3^{Et}/*C*H$_2^{Et}$, *C*^{Et}).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.5 ($\nu_{1/2}$ ~ 67 Hz).

$^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$): δ = -133.9 (d, $^{3}J_{FF}$ = 18.5 Hz, 4F, *o*-C_6F_5), -158.2 (t, $^{3}J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -163.1 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.9].

HRMS (ESI): m/z calcd for $C_{33}H_{31}BF_{10}N_2$: 655.2348 $[M-H]^-$; found: 655.2357.

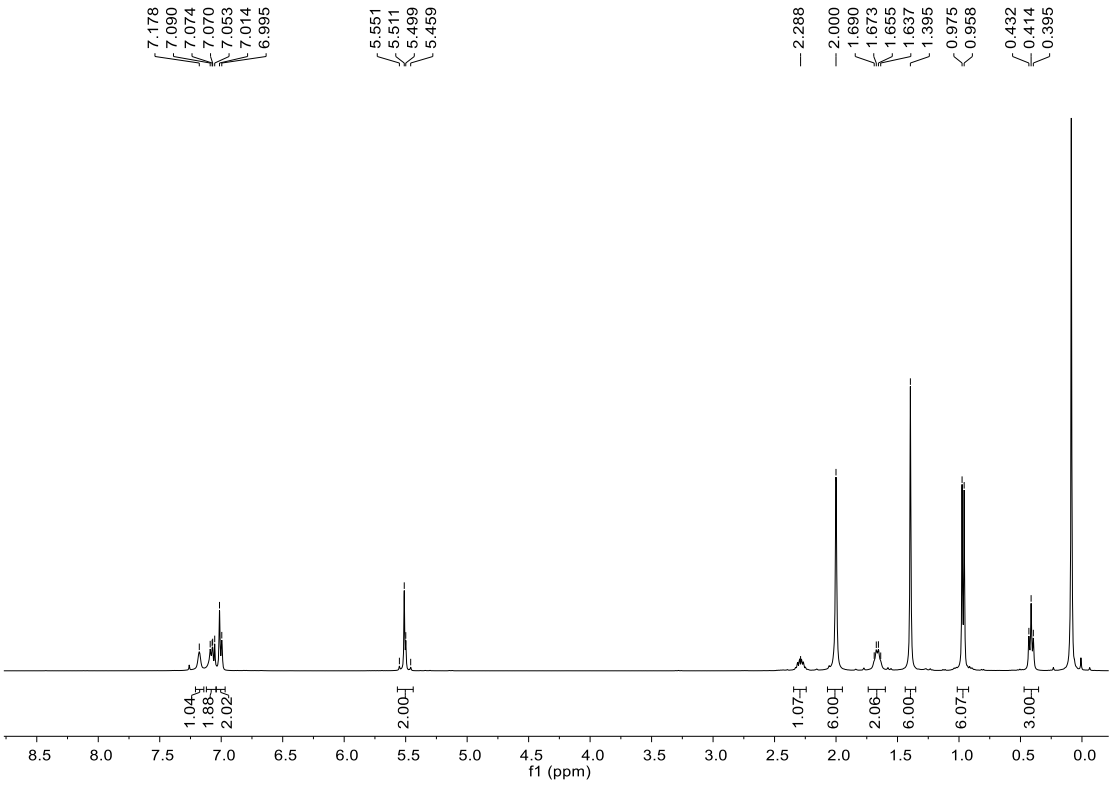


Fig. S60 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5l**.

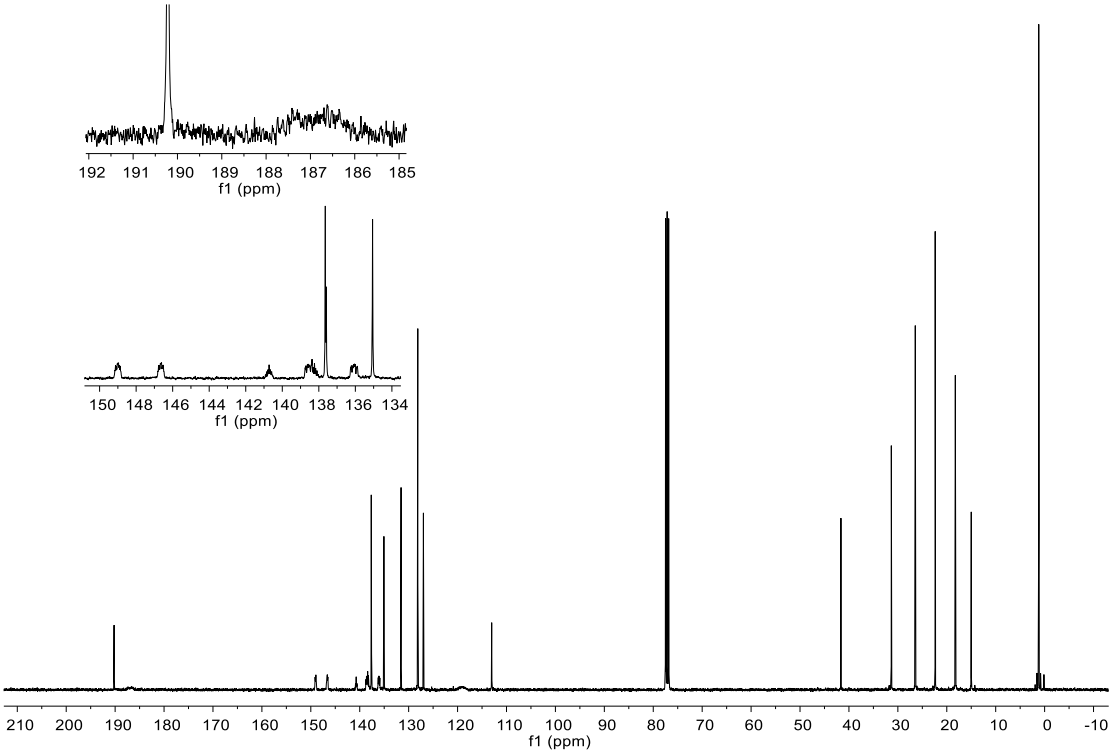


Fig. S61 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5l**.

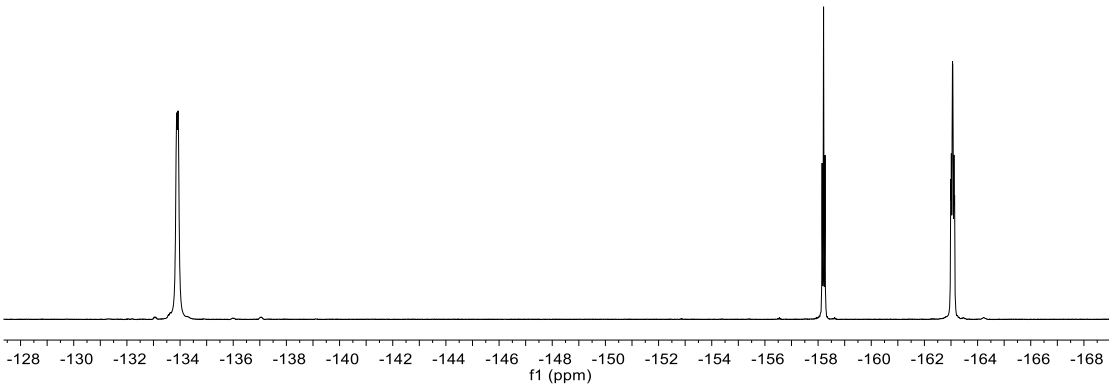


Fig. S62 ^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5l**.

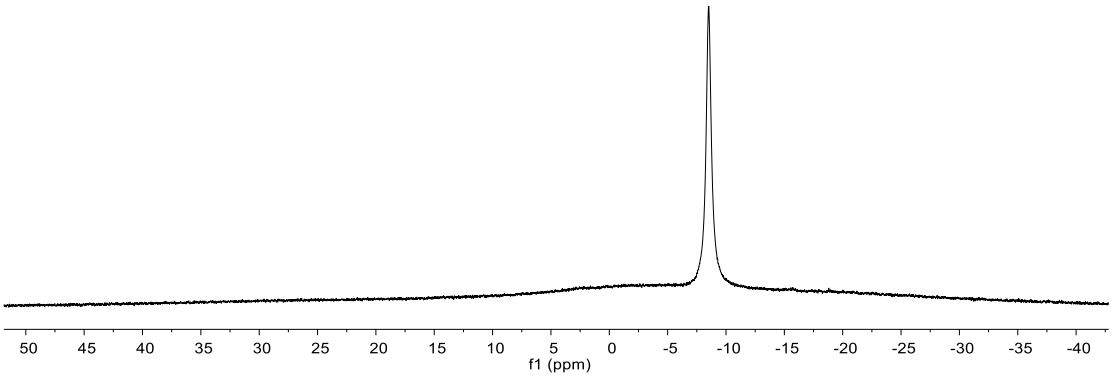
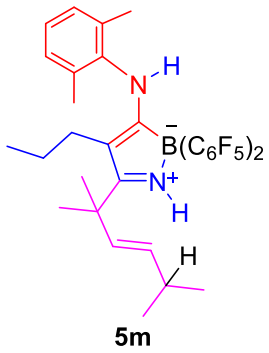


Fig. S63 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5l**.

Synthesis and characterization of compound 5m



5m

The compound **5m** was *in-situ* prepared according to the General Procedure II [2,5-dimethylhexa-2,4-diene (55.1 mg, 0.5 mmol), $HB(C_6F_5)_2$ (173.0 mg, 0.5 mmol), $^{n}BuC{\equiv}N$ (41.6 mg, 0.5 mmol) and Xyl-N≡C (65.6 mg, 0.5 mmol) in toluene (2 mL)]. Xyl-N≡C was added to the solution of *in-situ* generated **3m** to give a pale yellow solution immediately. Then the solution was stirred at 100°C for 31 h. The product **5m** was isolated as a pale yellow solid. Yield: 221.2 mg, 66%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.18 (br, 1H, N*H*), 7.08-7.00 (m, 4H, N*H* and Ph), 5.54-5.46 (m, 2H, =C*H*^{iPr} and =C*H*$^{-CMe_2}$), 2.28 (m, 1H, C*H*^{iPr}), 1.98 (s, 6H, CH_3^{Ph}), 1.53 (br, 2H, CH_2CH$_2$CH$_3$), 1.38 (s, 6H, CH_3^{C}), 0.96 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{iPr}), 0.83 (m, 2H, CH$_3$CH_2CH$_2$), 0.20 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH$_2$CH$_2$CH_3).

^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$): δ = 190.2 (*C*$^{=N}$), 186.9 (brm, B*C*), 147.8 (dm, $^{1}J_{FC}$ = 238.2 Hz, *C*$_6$F$_5$), 139.5 (dm, $^{1}J_{FC}$ = 250.8 Hz, *C*$_6$F$_5$), 137.3 (dm, $^{1}J_{FC}$ = 251.2 Hz, *C*$_6$F$_5$), 137.6 (=*C*H^{iPr}), 137.4, 135.1, 128.1, 126.9 (Ph), 131.5 (=*C*H$^{-CMe_2}$), 119.1 (brm, *i*-*C*$_6$F$_5$), 111.8 (*C*^{nPr}), 41.6 (*C*^{CH_3}), 31.3 (*C*H^{iPr}), 27.8 (*C*H$_2$CH$_2$CH$_3$), 26.4 (*C*H$_3^{C}$), 23.8 (CH$_2$*C*H$_2$CH$_3$), 22.4 (*C*H$_3^{iPr}$), 18.2 (*C*H$_3^{Ph}$), 13.8 (CH$_2$CH$_2$*C*H$_3$).

^{1}H, ^{13}C GHSQC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 5.50/137.6 (=*CH*^{iPr}), 5.49/131.5 (=*CH*$^{-CMe_2}$), 2.28/31.3 (*CH*^{iPr}), 1.98/18.2 (C*H*$_3^{Ph}$), 1.53/27.8 (*CH*$_2$CH$_2$CH$_3$), 1.38/26.4 (*CH*$_3^{C}$), 0.96/22.4 (*CH*$_3^{iPr}$), 0.83/23.8 (CH$_2$*CH*$_2$CH$_3$), 0.20/13.8 (CH$_2$CH$_2$*CH*$_3$).

^{1}H, ^{13}C GHMBC (400 MHz/101 MHz, 299K, $CDCl_3$): δ^{1}H/δ^{13}C: 7.18/111.8 (N*H*/*C*^{nPr}), 5.50/41.6 (=C*H*^{iPr}/*C*^{CH_3}), 5.49/(26.4, 31.3) (=C*H*$^{-CMe_2}$/*C*H$_3^{C}$, *C*H^{iPr}), 1.38/(41.6, 131.5, 190.2) (C*H*$_3^{C}$/*C*^{CH_3}, =*C*H$^{-CMe_2}$, *C*$^{=N}$), 0.96/(31.3, 137.6) (C*H*$_3^{iPr}$/*C*H^{iPr}, =*C*H^{iPr}), 0.20/(23.8, 27.8) (CH$_2$CH$_2$C*H*$_3$/CH$_2$*C*H$_2$CH$_3$, *C*H$_2$CH$_2$CH$_3$).

^{11}B {^{1}H} NMR (128 MHz, 299 K, $CDCl_3$): δ = -8.5 ($\nu_{1/2}$ ~ 69 Hz).

$^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$): δ = -133.9 (m, 4F, *o*-C_6F_5), -158.2 (t, $^{3}J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -163.1 (m, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.8].

HRMS (ESI): m/z calcd for $C_{34}H_{33}BF_{10}N_2$: 669.2504 $[M-H]^-$; found: 669.2513.

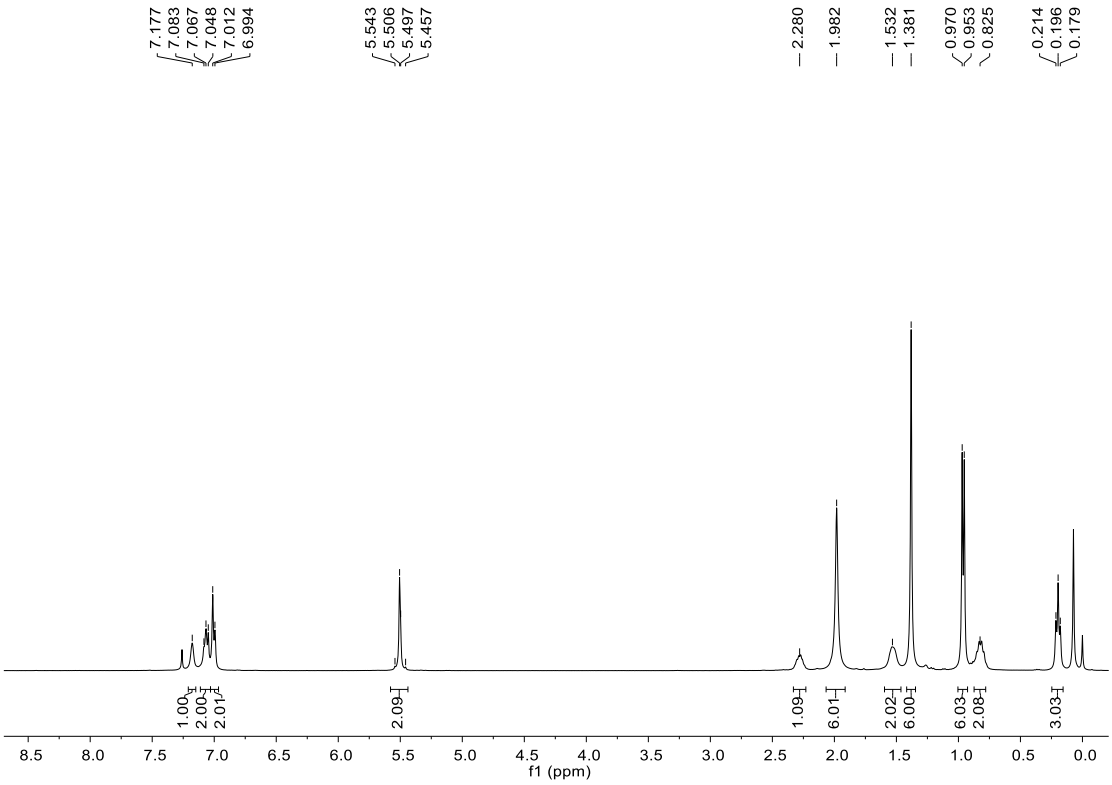


Fig. S64 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5m**.

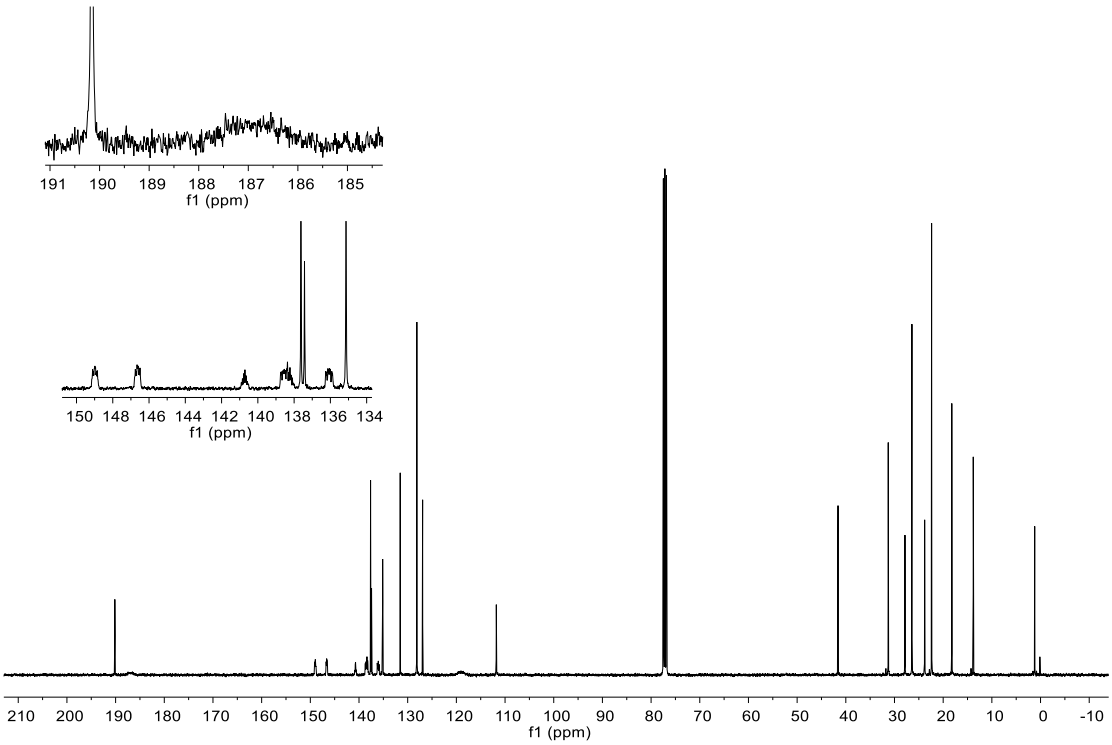


Fig. S65 ^{13}C {^{1}H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **5m**.

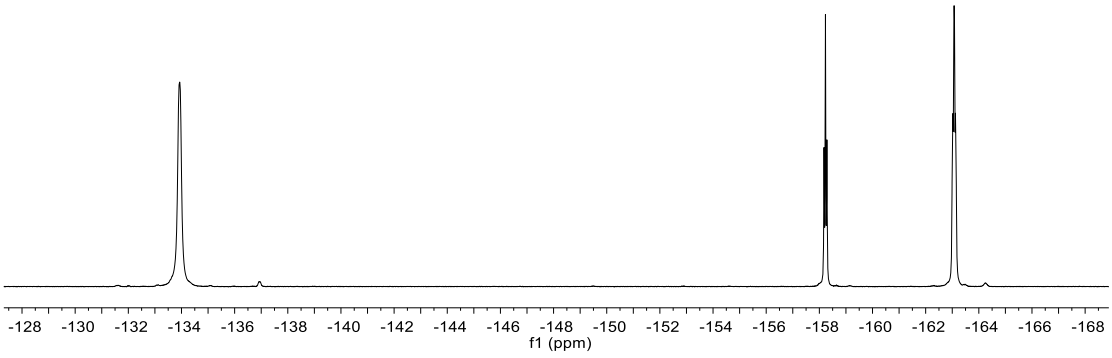


Fig. S66 ^{19}F{^{1}H} NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **5m**.

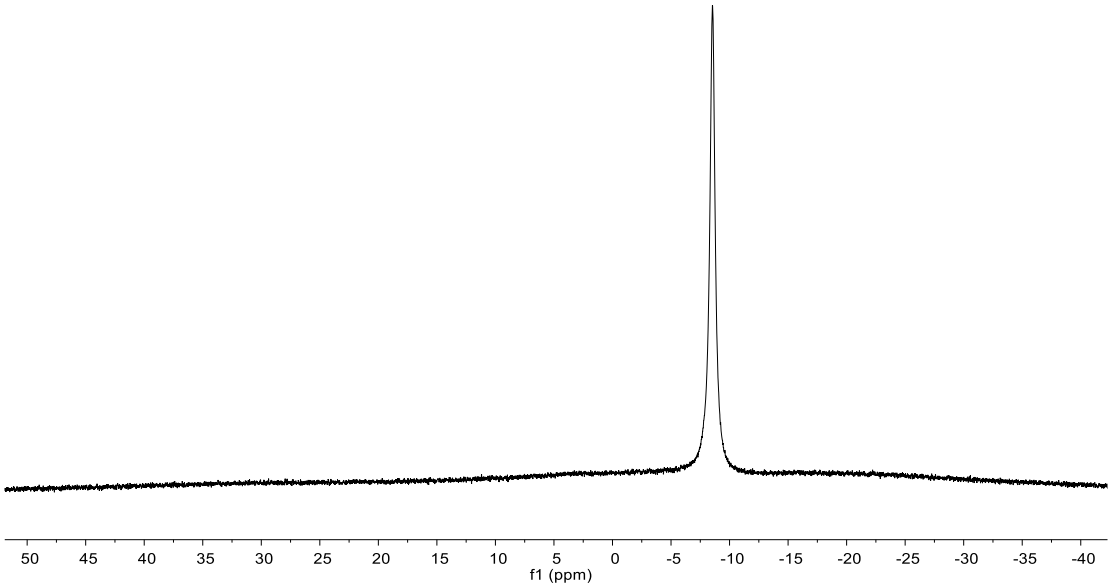
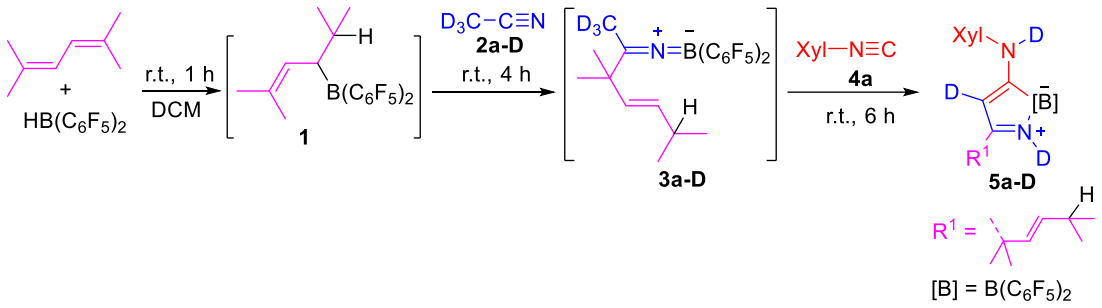


Fig. S67 $^{11}B\{^{1}H\}$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **5m**.

Control experiments



Scheme S6

Deuterium-labeled experiment: The compound **1** was prepared in-situ according to the General Procedure I. After that, **2a-D** (22.1 mg, 0.5 mmol) was added to give a colourless solution. The reaction mixture was stirred at room temperature for 4 h to *in-situ* generate compound **3a-D**.

Then Xyl-N≡C (65.6 mg, 0.5 mmol) was added and the mixture was stirred for another 6 h at room temperature. Atfer that, all the volatiles were removed in vacuo. The obtained residue was washed with *n*-hexane (1×2 mL) and dried in vacuo to give a white solid **5a-D**. Yield: 164.2 mg, 52%.

^{1}H NMR (400 MHz, 299 K, $CDCl_3$): δ = 7.18-7.10 (m, 3H, Ph), 5.58 (dd, $^3J_{HH}$ = 15.6 and 6.8 Hz, 1H, =C*H*^{iPr}), 5.43 (d, $^3J_{HH}$ = 16.0 Hz, 1H, =C*H*$^{-CMe_2}$), 2.34 (m, 1H, C*H*^{iPr}), 2.07 (s, 6H, CH_3^{Ph}), 1.28 (s, 6H, CH_3^{C}), 1.01 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH_3^{iPr}).

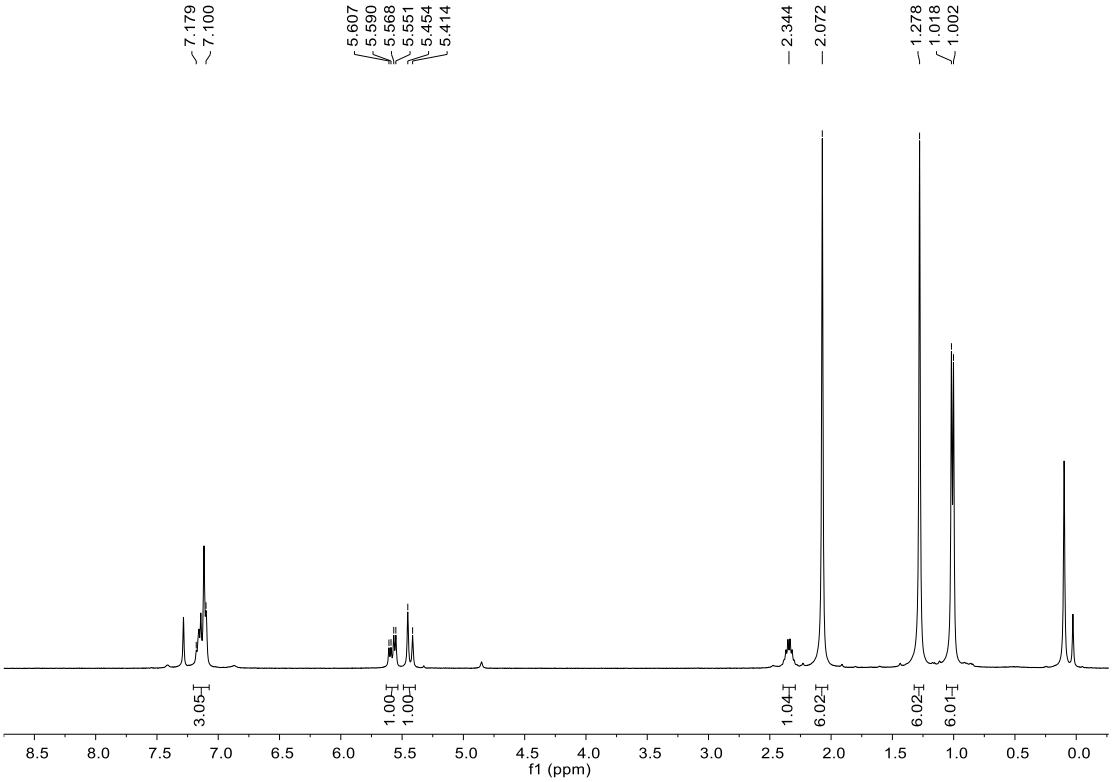


Fig. S68 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **5a-D**.

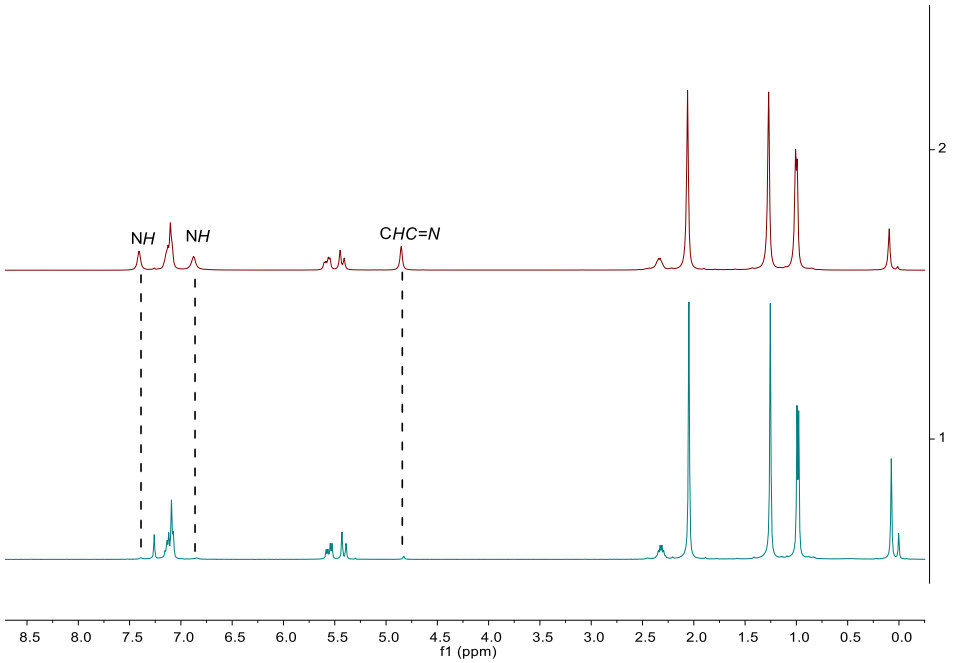


Fig. S69 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectra of (1) isolated compound **5a-D**, (2) isolated compound **5a**.

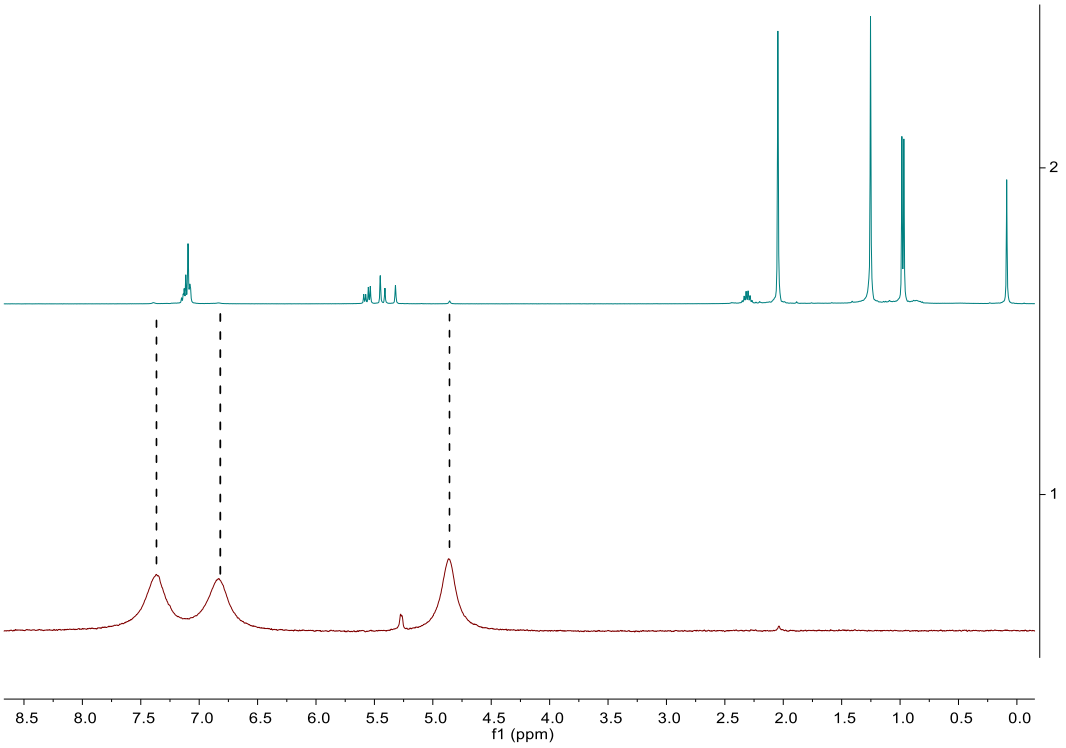
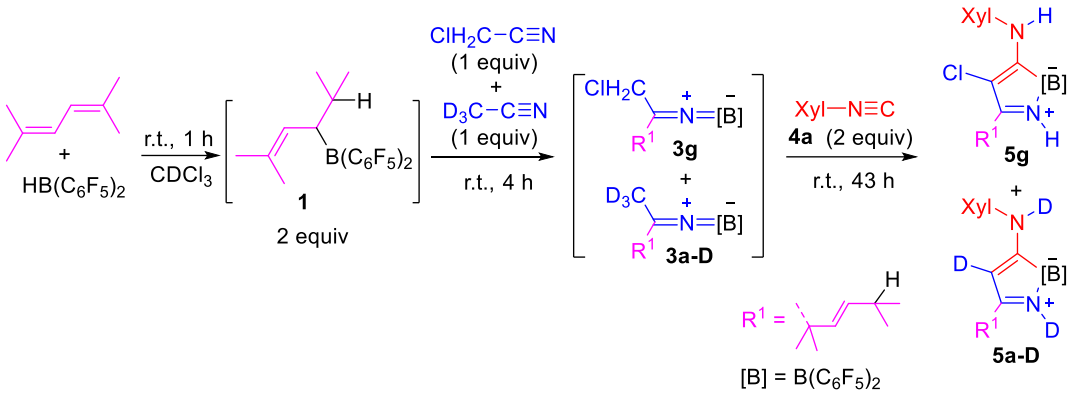


Fig. S70 (1) ^{2}H NMR (77 MHz, 299K, CH_2Cl_2) spectrum of isolated compound **5a-D**, (2) ^{1}H NMR (400 MHz, 299K, CD_2Cl_2) spectrum of isolated compound **5a-D**.



Scheme S7

Crossover experiment: In an NMR tube, 2,5-dimethylhexa-2,4-diene (15.5 mg, 0.14 mmol) and $HB(C_6F_5)_2$ (48.5 mg, 0.14 mmol) were dissolved in $CDCl_3$ (0.6 mL). The NMR tube was kept at room temperature for 1 h to *in-situ* generate compound **1**. After that, $ClCH_2C{\equiv}N$ (5.3 mg, 0.07 mmol) and $CD_3C{\equiv}N$ (3.1 mg, 0.07 mmol) were added to the solution. The reaction mixture was kept at room temperature for another 4 h to in-situ generate compounds **3g** and **3a-D**. Then Xyl-N≡C (18.4 mg, 0.14 mmol) was added to the mixture. After the NMR tube was kept at room temperature for 43 h, NMR experiments were conducted.

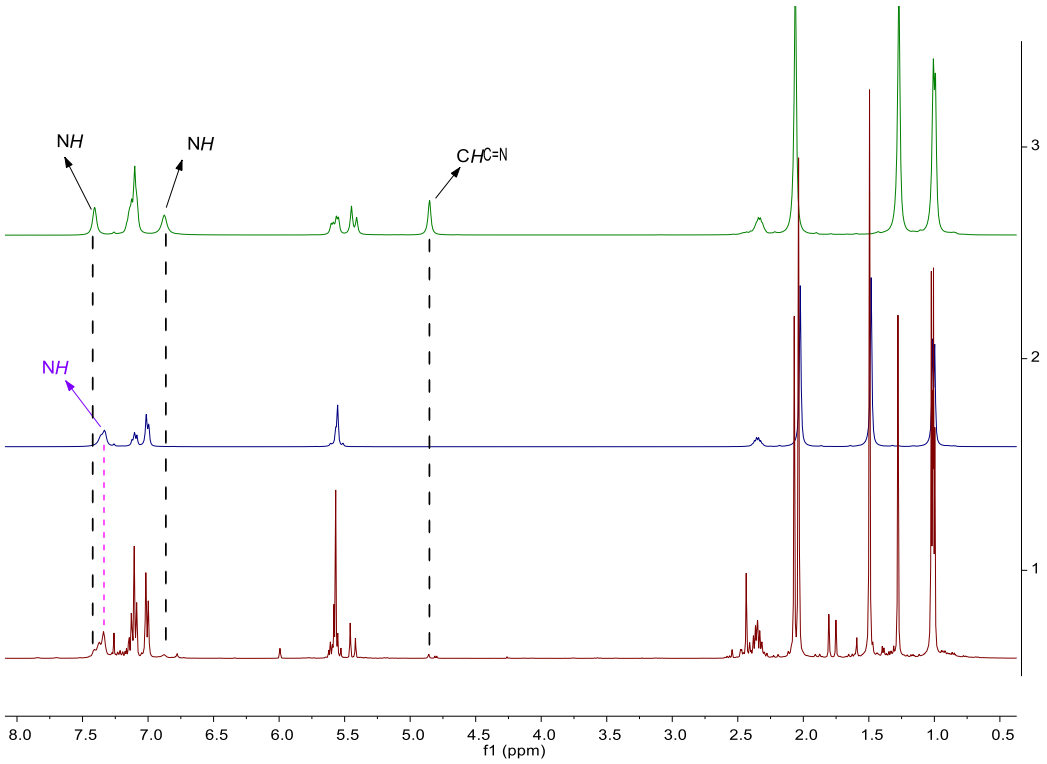
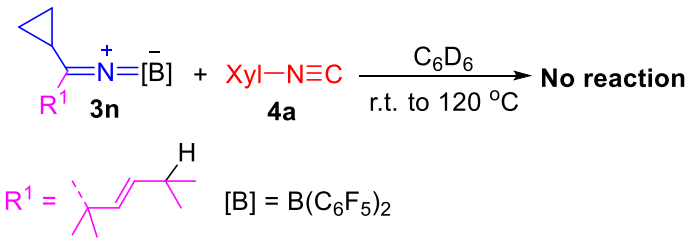


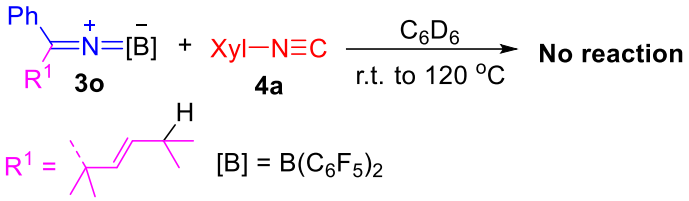
Fig. S71 ^{1}H NMR (400 MHz, 299K, $CDCl_3$) spectra of (1) *in-situ* crossover reaction, (2) isolated compound **5g**, (3) isolated compound **5a**.



Scheme S8

Investigation on reaction of 3n with 4a: In an NMR tube, The compound **3n** and **3o** was *in-situ* prepared according to the General Procedure I [2,5-dimethylhexa-2,4-diene (6.7 mg, 0.06 mmol), $HB(C_6F_5)_2$ (20.8 mg, 0.06 mmol) and $C_3H_5C{\equiv}N$ **2n** (4.1 mg, 0.06 mmol) in C_6D_6 (0.6 mL)]. Then Xyl-N≡C **4a** (7.9 mg, 0.06 mmol) was added to the

solution. Both of **3n** and **4a** remained unchanged when the mixture was changed from room temperature to 120 °C.



Scheme S9

Investigation on reaction of 3n with 4a: Reaction of 3n with 4a: In an NMR tube, The compound **3n** and **3o** was *in-situ* prepared according to the General Procedure I [2,5-dimethylhexa-2,4-diene (6.7 mg, 0.06 mmol), $HB(C_6F_5)_2$ (20.8 mg, 0.06 mmol) and PhC≡N **2o** (6.2 mg, 0.06 mmol) in C_6D_6 (0.6 mL)]. Then Xyl-N≡C **4a** (7.9 mg, 0.06 mmol) was added to the solution. Both of **3o** and **4a** remained unchanged when the mixture was changed from room temperature to 120 °C.