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# Electronic supplementary information

# for

# Metal-free *trans*-hydroboration without a B-H bond: reactions of propargyl amines with Lewis acidic boranes

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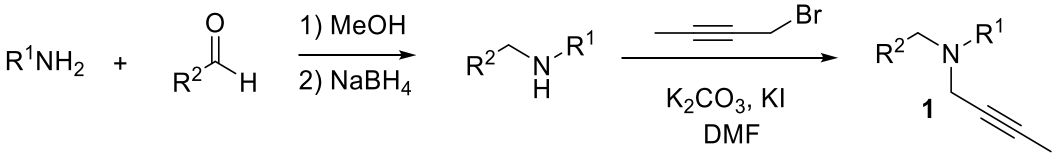
## General information

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.

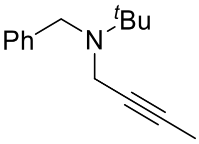
**X-Ray diffraction:** Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture CMOS-based diffractometer (compound **2a**) with graphite-monochromated $Mo_{Ka}$ radiation ($\lambda = 0.71073$ Å). All of the data were corrected for absorption effects using the multi-scan technique. 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-2160619 (**2a**) 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/.

## General procedure A



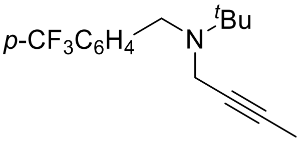
The secondary amine[1] (1.0 equiv.) was dissolved in DMF (40 mL), then $K_2CO_3$ (2.0 equiv.), KI (1.1 equiv.), and 1-Bromo-2-butyne (1.2 equiv.) were added successively. The mixture was stirred at room temperature for 12h. Then the solution was extracted with EA (30 mL) and washed with water (3x10 mL) for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated in vacuo to afford the crude material. The crude product was purified by silica gel column chromatography to give compound **1**.

## Synthesis and characterization of compound 1a



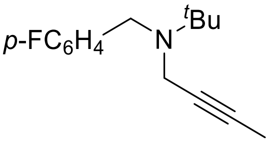
According to the procedure (A) from the corresponding secondary amine (1.63 g, 10 mmol), 1-Bromo-2-butyne (1.1 mL, 12 mmol), $K_2CO_3$ (2.76 g, 20 mmol), and KI (1.83 g, 11 mmol). The product was isolated as a brown oil (2.00 g, 93% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.20-7.39 (m, 5H), 3.79 (s, 2H), 3.30 (m, 2H), 1.82 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.26 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 141.4, 128.8, 128.3, 126.7, 79.8, 77.5, 55.0, 50.9, 36.6, 28.0, 3.7.

## Synthesis and characterization of compound 1b



According to the procedure (A) from the corresponding secondary amine (2.31 g, 10 mmol), 1-Bromo-2-butyne (1.1 mL, 12 mmol), $K_2CO_3$ (2.76 g, 20 mmol), and KI (1.83 g, 11 mmol). The product was isolated as a yellow oil (2.41 g, 85% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.48-7.56 (m, 4H), 3.84 (s, 2H), 3.28 (q, $^5J_{HH}$ = 2.7 Hz, 2H), 1.80 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.24 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 146.0, 129.0 (q, $^1J_{FC}$ = 32.2 Hz), 128.8, 125.1 (q, $^3J_{FC}$ = 3.8 Hz), 80.1, 77.1, 55.1, 50.8, 37.0, 27.9, 3.6.

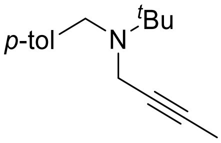
## Synthesis and characterization of compound 1c



According to the procedure (A) from the corresponding secondary amine (2.72 g, 15 mmol), 1-Bromo-2-butyne (1.6 mL, 18 mmol), $K_2CO_3$ (4.15 g, 30 mmol), and KI (2.74 g, 16.5 mmol). The product was isolated as a yellow oil (2.31 g, 66%

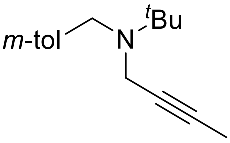
yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.35-6.95 (m, 4H), 3.75 (s, 2H), 3.27 (br, 2H), 1.81 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.24 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 161.9 (d, $^1J_{FC}$ = 244.7 Hz), 137.0 (d, $^4J_{FC}$ = 2.9 Hz), 130.1 (d, $^3J_{FC}$ = 8.0 Hz), 115.0 (d, $^2J_{FC}$ = 21.1 Hz), 79.9, 77.3, 55.0, 50.2, 36.5, 28.0, 3.7.

**Synthesis and characterization of compound 1d**



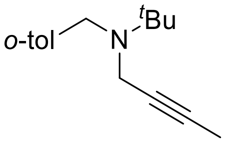
According to the procedure (A) from the corresponding secondary amine (2.66 g, 15 mmol), 1-Bromo-2-butyne (1.6 mL, 18 mmol), $K_2CO_3$ (4.15 g, 30 mmol), and KI (2.74 g, 16.5 mmol). The product was isolated as a colorless oil (2.20 g, 64% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.12-7.29 (m, 4H), 3.77 (s, 2H), 3.32 (q, $^5J_{HH}$ = 2.5 Hz, 2H), 2.35 (s, 3H), 1.84 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.27 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 138.2, 136.2, 129.0, 128.7, 79.7, 77.5, 54.9, 50.5, 36.4, 28.0, 21.2, 3.7.

**Synthesis and characterization of compound 1e**



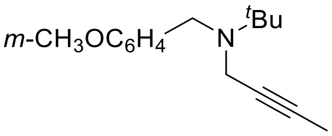
According to the procedure (A) from the corresponding secondary amine (2.66 g, 15 mmol), 1-Bromo-2-butyne (1.6 mL, 18 mmol), $K_2CO_3$ (4.15 g, 30 mmol), and KI (2.74 g, 16.5 mmol). The product was isolated as a brown oil (2.80 g, 81% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.04-7.21 (m, 4H), 3.79 (s, 2H), 3.34 (d, $^5J_{HH}$ = 2.5 Hz, 2H), 2.36 (s, 3H), 1.84 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.29 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 141.3, 137.8, 129.5, 128.1, 127.5, 125.9, 79.8, 77.5, 55.0, 50.8, 36.6, 28.0, 21.6, 3.7.

## Synthesis and characterization of compound 1f



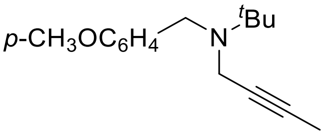
According to the procedure (A) from the corresponding secondary amine (2.35 g, 20 mmol), 1-Bromo-2-butyne (2.2 mL, 24 mmol), $K_2CO_3$ (5.53 g, 40 mmol), and KI (3.65 g, 22 mmol). The product was isolated as a brown oil (2.02 g, 44% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.11-7.48 (m, 4H), 3.81 (s, 2H), 3.29 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 2.40 (s, 3H), 1.84 (t, $^5J_{HH}$ = 2.3 Hz, 3H), 1.28 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 138.8, 137.1, 130.2, 129.5, 126.6, 125.8, 80.0, 77.9, 55.2, 48.3, 36.6, 27.9, 19.5, 3.7.

## Synthesis and characterization of compound 1g



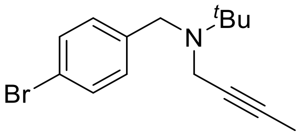
According to the procedure (A) from the corresponding secondary amine (2.50 g, 13 mmol), 1-Bromo-2-butyne (1.4 mL, 15.6 mmol), $K_2CO_3$ (3.57 g, 26 mmol), KI (2.36 g, 14.3 mmol). The product was isolated as a colorless oil (1.60 g, 50% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.48-6.73 (m, 4H), 3.86 (s, 5H), 3.39 (s, 2H), 1.88 (s, 3H), 1.32 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 159.6, 143.1, 129.1, 121.0, 114.2, 111.8, 79.6, 77.4, 55.1, 54.8, 50.8, 36.6, 27.9, 3.6.

## Synthesis and characterization of compound 1h



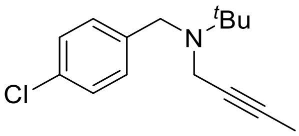
According to the procedure (A) from the corresponding secondary amine (2.50 g, 13 mmol), 1-Bromo-2-butyne (1.4 mL, 15.6 mmol), $K_2CO_3$ (3.57 g, 26 mmol), KI (2.36 g, 14.3 mmol). The product was isolated as a colorless oil (1.75 g, 55% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 6.84-7.30 (m, 4H), 3.79 (s, 3H), 3.72 (s, 2H), 3.28 (d, $^5J_{HH}$ = 2.4 Hz, 2H), 1.82 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.25 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 158.5, 133.2, 129.9, 113.7, 79.8, 77.5, 55.4, 54.9, 50.1, 36.2, 28.0, 3.7.

## Synthesis and characterization of compound 1i



According to the procedure (A) from the corresponding secondary amine (557.0 mg, 2.3 mmol), 1-Bromo-2-butyne (0.25 mL, 2.76 mmol), $K_2CO_3$ (0.32 g, 4.6 mmol), KI (0.38 g, 2.53 mmol). The product was isolated as a colorless oil (320.1 mg, 47% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 6.67-7.31 (m, 4H), 4.00 (s, 2H), 3.42 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 1.82 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.24 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 139.9, 132.2, 130.0, 128.3, 80.0, 77.2, 55.0, 50.3, 36.6, 28.0, 3.7.

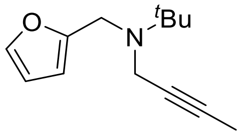
## Synthesis and characterization of compound 1j



According to the procedure (A) from the corresponding secondary amine (573.4 mg, 2.9 mmol), 1-Bromo-2-butyne (0.3 mL, 3.48 mmol), $K_2CO_3$ (0.40 g, 5.8

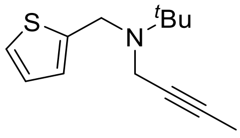
mmol), KI (0.48 g, 3.19 mmol). The product was isolated as a colorless oil (340.5 mg, 47% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.34 (m, 2H), 7.28 (m, 2H), 3.77 (s, 2H), 3.29 (m, 2H), 1.83 (m, 3H), 1.26 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 139.9, 132.2, 130.0, 128.3, 80.0, 77.2, 55.0, 50.3, 36.6, 27.9, 3.7.

### Synthesis and characterization of compound 1k



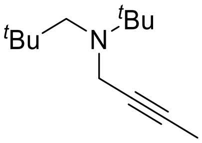
According to the procedure (A) from the corresponding secondary amine (5.06 g, 33 mmol), 1-Bromo-2-butyne (3.6 mL, 39.6 mmol), $K_2CO_3$ (9.12 g, 66 mmol), KI (6.03 g, 36.3 mmol). The product was isolated as a yellow oil (2.20 g, 32% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 6.26-7.36 (m, 3H), 3.85 (s, 2H), 3.40 (s, 2H), 1.82 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.20 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 154.0, 141.9, 110.2, 108.2, 80.1, 77.0, 55.0, 43.8, 37.0, 27.7, 3.8.

### Synthesis and characterization of compound 1l



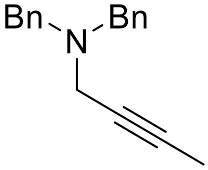
According to the procedure (A) from the corresponding secondary amine (4.23 g, 25 mmol), 1-Bromo-2-butyne (2.7 mL, 30 mmol), $K_2CO_3$ (6.91 g, 50 mmol), KI (4.56 g, 27.5 mmol). The product was isolated as a yellow oil (1.87 g, 56% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 6.67-7.31 (m, 3H), 4.00 (s, 2H), 3.42 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 1.82 (t, $^5J_{HH}$ = 2.4 Hz, 3H), 1.24 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 146.4, 126.5, 124.8, 124.3, 79.9, 77.2, 55.1, 45.9, 36.8, 28.0, 3.7.

### Synthesis and characterization of compound 1m



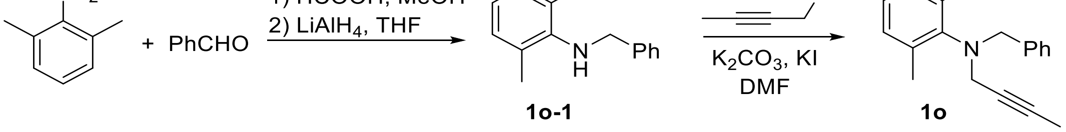
According to the procedure (A) from the corresponding secondary amine (2.58 g, 18 mmol), 1-Bromo-2-butyne (2.0 mL, 21.6 mmol), $K_2CO_3$ (4.98 g, 36 mmol), and KI (3.29g, 19.8 mmol). The product was isolated as a purple oil (2.31 g, 66% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 3.41 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 2.34 (s, 2H), 1.79 (t, $^5J_{HH}$ = 2.3 Hz, 3H), 1.10 (s, 9H), 0.89 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 79.4, 78.6, 59.6, 55.6, 40.7, 32.7, 29.0, 28.2, 3.8.

### Synthesis and characterization of compound 1n



According to the procedure (A) from Dibenzylamine (5.8 mL, 30 mmol), 1-Bromo-2-butyne (3.3 mL, 36 mmol), $K_2CO_3$ (8.30 g, 60 mmol), and KI (5.48 g, 33 mmol). The product was isolated as a brown oil (2.99 g, 40% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.26-7.46 (m,10H), 3.71 (s, 4H), 3.26 (q, $^5J_{HH}$ = 2.3 Hz, 2H), 1.95 (t, $^5J_{HH}$ = 2.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 139.3, 129.2, 128.4, 127.1, 81.1, 74.0, 57.6, 41.9, 3.7.

### Synthesis and characterization of compound 1o



i) Compound 2,6-dimethylaniline (1.0 mL, 10 mmol) was dissolved in

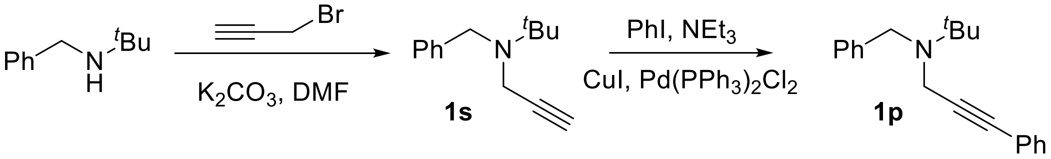
MeOH (8 mL), then PhCHO (1.06 g, 10 mmol) and HCOOH (0.5 mL, 5 mmol) were added successively. The mixture was refluxed at 100°C for 12h. After this time, the solution was concentrated at a low temperature, washed with cold methanol and filtered the supernatant, then concentration in vacuo afforded the crude material.

ii）The crude material was dissolved in anhydrous THF (15 mL) and added dropwise to a suspension of $LiAlH_4$ in anhydrous THF (5 mL, 12.5 mmol). The mixture was stirred at room temperature. After this time, the solution was added to water and extracted with $Et_2O$ (3x30 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography to give compound **1o-1** as a yellow oil (0.6 g, 31% yield).

iii) According to the procedure (A) from the corresponding secondary amine **1o** (0.6 g, 2.87 mmol), 1-Bromo-2-butyne (0.3 mL, 3.44 mmol), $K_2CO_3$ (0.79 g, 5.74 mmol), KI (0.52 g, 3.16 mmol). The product was isolated as a yellow oil (200.2 mg, 26% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.02-7.41 (m, 8H), 4.35 (s, 2H), 3.64 (m, 2H), 2.41 (s, 6H), 1.83 (t, $^5J_{HH}$ = 2.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 148.5, 140.1, 137.2, 129.1, 129.0, 128.3, 127.0, 125.2, 79.4, 76.9, 56.8, 41.2, 20.0, 3.7.

## Synthesis and characterization of compounds 1p and 1s



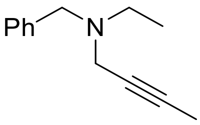
i) The secondary amine[1] (3.10 g, 19 mmol) was dissolved in DMF (40 mL), then $K_2CO_3$ (3.56 g, 22.8 mmol) and 3-bromoprop-1-yne (3.00 g, 22.8 mmol) were added successively. The mixture was stirred at room temperature for 12h. After this time, the solution was added to water and extracted with EA (3x30 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography to give compound **1s** as a colorless oil (3.37 g, 88% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.30 (m, 2H), 7.22 (m, 2H), 7.15 (m, 1H), 3.75 (s, 2H), 3.27 (d, $^4J_{HH}$ = 2.2 Hz, 2H), 2.09 (t, $^4J_{HH}$ = 2.2 Hz, 1H), 1.20 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 140.7, 128.6, 128.2, 126.7, 82.5, 72.4, 55.0, 50.6, 36.0, 27.8.

ii) The compound **1s** (194.0 mg, 0.96 mmol), PhI (203.3 mg, 1 mmol), CuI (7.4 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (11.7 mg, 0.02 mmol) were dissolved in anhydrous THF (5 mL), then $NEt_3$ (0.4 mL, 2.9 mmol) was added successively. The mixture was stirred at room temperature for 12h under $N_2$. After this time, the solution was added to water and extracted with EA (3x30 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography to give compound **1p** as a colorless oil (230.7mg, 86% yield).

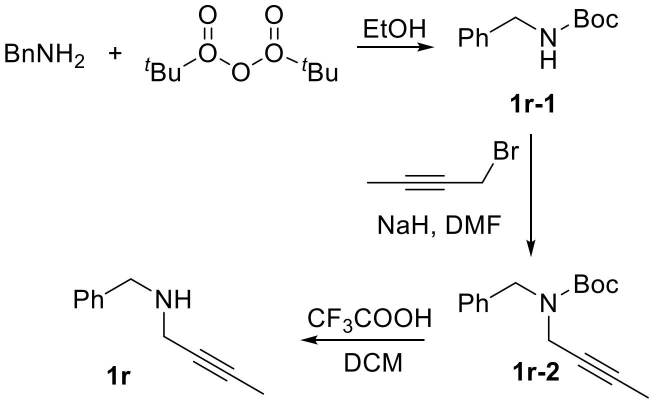
**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.28-7.50 (m, 10H), 3.95 (s, 2H), 3.63 (s, 2H), 1.39 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 141.0, 131.5, 128.8, 128.4, 128.3, 127.9, 126.9, 123.9, 88.4, 84.8, 55.1, 51.0, 37.0, 28.1.

**Synthesis and characterization of compound 1q**



According to the procedure (A) from N-Ethylbenzylamine (3.38g, 25 mmol), 1-Bromo-2-butyne (2.7 mL, 30 mmol), $K_2CO_3$ (6.91 g, 50 mmol), and KI (4.57 g, 27.5 mmol). The product was isolated as a brown oil (1.40 g, 30% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.21-7.36 (m, 5H), 3.61 (s, 2H), 3.27 (q, $^5J_{HH}$ = 2.3 Hz, 2H), 2.57 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 1.86 (t, $^5J_{HH}$ = 2.3 Hz, 3H), 1.09 (t, $^3J_{HH}$ = 7.1 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 139.2, 129.3, 128.3, 127.1, 80.7, 74.0, 57.8, 47.4, 41.6, 12.9, 3.6.

**Synthesis and characterization of compound 1r**

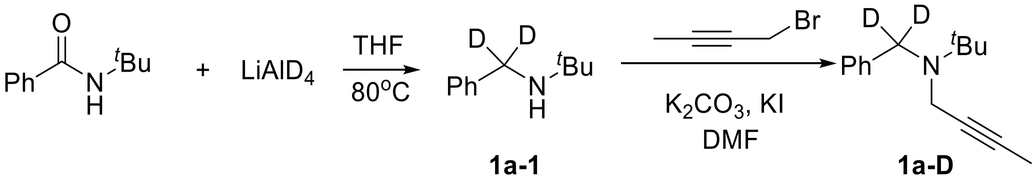


i) Compound **1r-1**[2] (1.04 g, 5 mmol) was dissolved in DMF (30 mL), then NaH (400 mg, 10 mmol) and 1-Bromo-2-butyne (0.46 mL, 5 mmol) were added successively. The mixture was stirred at room temperature for 4h. After this time, the solution was added saturated $NH_4Cl$ and extracted with DCM (3x30 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentration in vacuo afforded the crude material **1r-2**, which was used directly without other treatment.

ii） $CF_3COOH$ (1.1 mL, 15 mmol) was added dropwise to a suspension of compound **1r-2** in DCM (30 mL). The mixture was stirred at room temperature for 12h. After this time, the solution was added to water and extracted with DCM (3x30 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentration in vacuo to afford the crude material, which was then purified by silica gel column chromatography to give compound **1r** as a yellow liquid (300 mg, 38% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.19-7.32 (m, 5H), 3.81 (s, 2H), 3.33 (q, $^5J_{HH}$ = 2.4 Hz, 2H), 1.80 (t, $^5J_{HH}$ = 2.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 139.8, 128.5, 128.5, 127.2, 79.3, 77.2, 52.6, 38.0, 3.7.

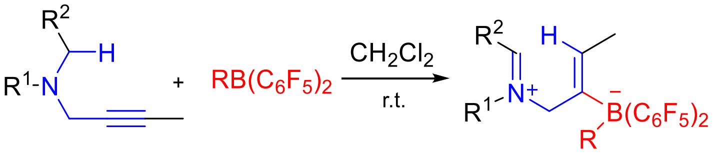
## Synthesis and characterization of compound 1a-D



i) The amide[2] (421.0 mg, 2.38 mmol) was dissolved in anhydrous THF (5 mL) and added dropwise to a suspension of $LiAlD_4$ (121.7 mg, 2.90 mmol) in anhydrous THF (10 mL). The mixture was refluxed at 80°C for 12h under $N_2$. Then the solution was extracted with EA (30 mL) and washed with water (3x10 mL) for three times. The combined organic layer was dried with $MgSO_4$, filtered and concentrated in vacuo to afford the crude material. The crude product was purified by silica gel column chromatography to give compound **1a-1** as an orange oil (119.7mg, 31% yield).

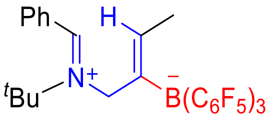
ii) According to the procedure (A) from compound **1a-1** (119.7mg, 0.72 mmol), 1-Bromo-2-butyne (115.6 mg, 0.87 mmol), $K_2CO_3$ (200.2 mg, 1.45 mmol), and KI (132.2 mg, 0.80 mmol). The product was isolated as a yellow oil (100.0 mg, 64% yield).

### General procedure B



To a Schlenk bottle equipped with a magnetic stirring bar, the solution of compound **1** (1.0 equiv.) and $RB(C_6F_5)_2$ (1.0 equiv.) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 4h. 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 the desired product **2**.

### Synthesis and characterization of compound 2a



According to the procedure (B) from $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol) and **1a** (65.6 mg, 0.3 mmol). The product was isolated as a white solid (206.1 mg, 93% yield).

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

**HRMS (ESI):** m/z calcd for $C_{33}H_{21}BF_{15}N$ $[M+Cl]^-$: 762.1222, found 762.1224.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): $\delta$ = 8.90 (s, 1H, N=C*H*), 7.67-8.11 (m, 5H, Ph), 5.24 (br, 1H, =C*H*), 4.88 (m, 2H, NC$H_2$), 1.62 (br, 9H, C$H_3^{tBu}$), 1.55 (d, $^3J_{HH}$ = 7.1 Hz, 3H, C$H_3$).

**$^{13}$C {H} NMR** (101 MHz, 299K, $CD_2Cl_2$): $\delta$ = 170.0 (N=*C*H), 137.5, 130.2, 126.7 (Ph), 128.7 (=*C*H), 72.0 (N$C^{tBu}$), 60.7 (N*C*H$_2$), 29.1 ($CH_3^{tBu}$), 16.1 (*C*H$_3$). [$C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): $\delta^1$H/$\delta^{13}$C: 8.90/170.0 (N=*CH*), 5.24/128.7 (=*C*H), 4.88/60.7 (N*CH*$_2$), 1.55/16.1 (*CH*$_3$).

**$^{19}$F{H} NMR** (377 MHz, 299K, $CD_2Cl_2$): $\delta$ = -126.6, -128.8, -129.6, -131.2, -131.6, -135.3 (each br, each 1F, *o*-$C_6F_5$), -161.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -

163.1 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -164.8 (t, $^3J_{FF}$ = 20.7 Hz, 1F) (*p*-$C_6F_5$), -163.4, -165.8, -166.2, -166.6, -167.1, -167.5 (each br, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -15.3 ($v_{1/2}$ ~ 30Hz).

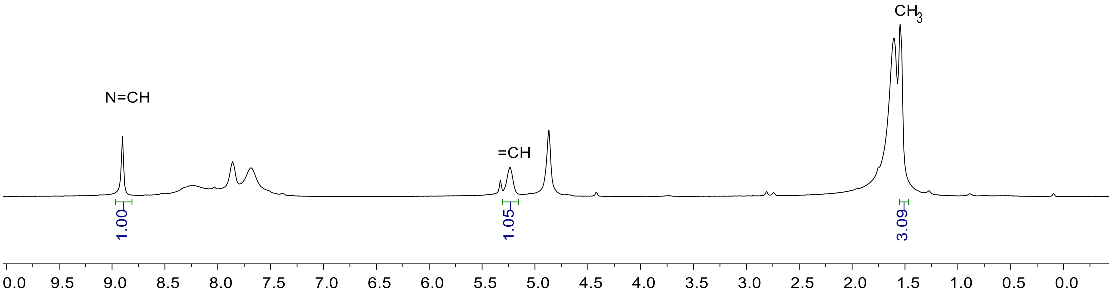


**Fig. S1** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2a**.

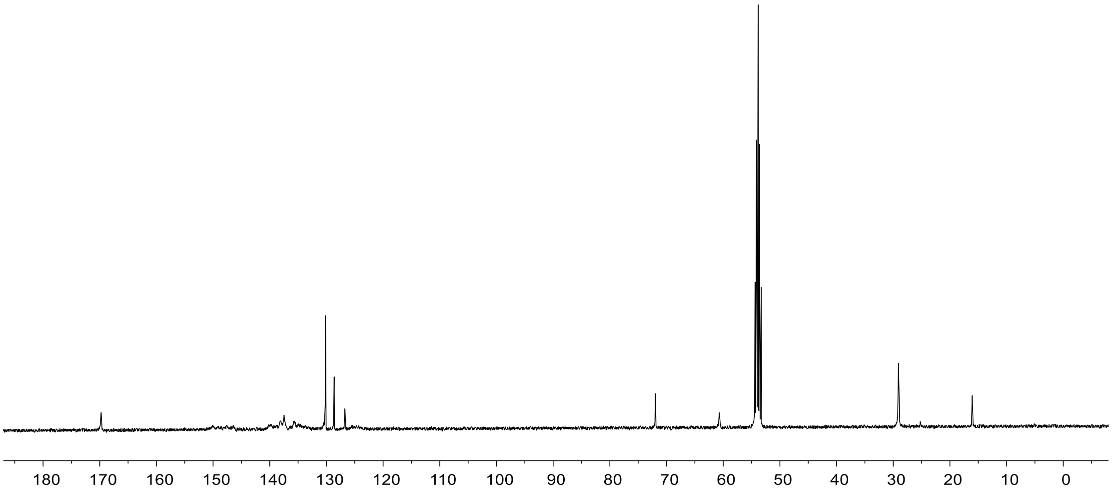


**Fig. S2** $^{13}$C {H} NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2a**.

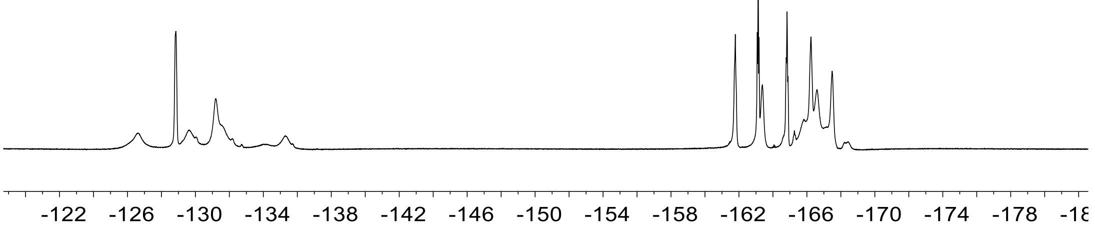


**Fig. S3** $^{19}$F{H} NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2a**.

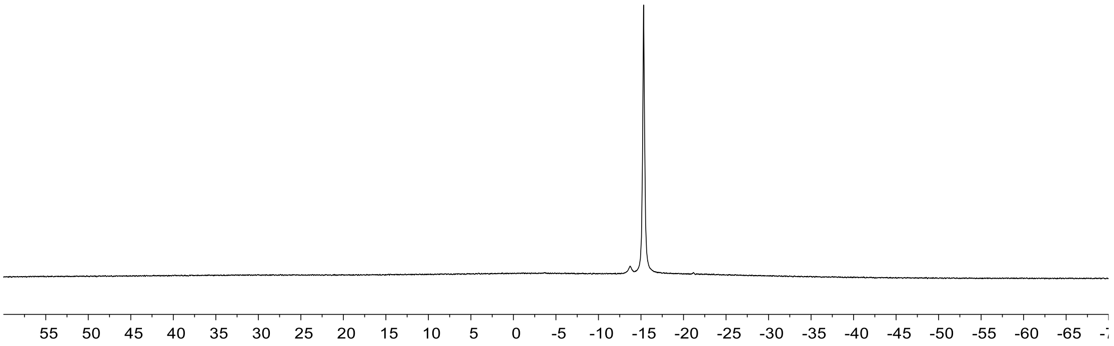


**Fig. S4** $^{11}$B NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2a**.

**X-ray crystal structure analysis of compound 2a:** formula $C_{36}H_{28}BF_{15}N$, $M$ = 770.40, colorless crystal, 0.1 × 0.1 × 0. 1 mm, $a$ = 11.053(5), $b$ = 16.413(7), $c$ = 18.289(9) Å, $\alpha = \gamma = 90^{o}$, $\beta = 90.900(14)^{o}$, $V$ = 3317(3) Å$^3$, $\rho_{calc}$ = 1.542 gcm$^{-3}$, $\mu$ = 0.148 mm$^{-1}$, empirical absorption correction (0.6041 ≤ T ≤ 0.7284), $Z$ = 4, monoclinic, space group $P2_1/n$, $\lambda$ = 0.71073 Å, $T$ = 150.15 K, $\omega$ and $\varphi$ scans, 38998 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7575 independent ($R_{int}$ = 0.1448) and 3472 observed reflections [$I>2\sigma(I)$], 483 refined parameters, $R$ = 0.0642, $wR^2$ = 0.1753, max. (min.) residual electron density 0.41 (-0.30) e.Å$^{-3}$, all the hydrogen atoms were calculated and refined as riding atoms.

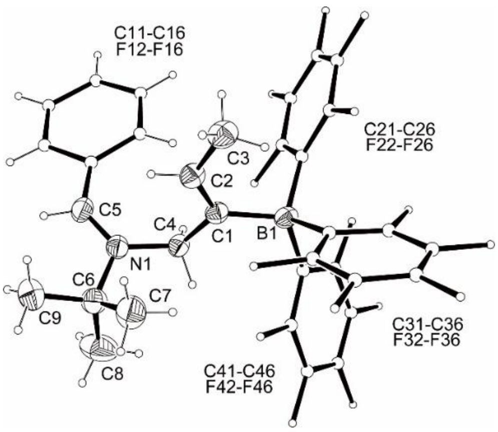
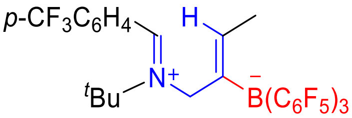


**Fig. S5** A view of the molecular structure of compound **2a**.

**Synthesis and characterization of compound 2b**



According to the procedure (B) from $B(C_6F_5)_3$ (158.7 mg, 0.31 mmol) and **1b** (86.5 mg, 0.31 mmol). The product was isolated as a yellow solid (218.5 mg, 90% yield).

**HRMS (ESI):** m/z calcd for $C_{34}H_{20}BF_{18}N$ $[M-H]^-$: 794.1328, found 794.1328.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): $\delta$ = 9.03 (s, 1H, N=C*H*), 7.91-8.30 (m, 4H, Ph), 5.18 (br, 1H, =C*H*), 4.90 (m, 2H, NC$H_2$), 1.63 (br, 9H, C$H_3^{tBu}$), 1.54 (d, $^3J_{HH}$ = 7.1 Hz, 3H, C$H_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): $\delta$ = 169.5 (N=*C*H), 128.7 (=*C*H), 73.2 (N$C^{tBu}$), 61.0 (N*C*$H_2$), 29.1 (*C*$H_3^{tBu}$), 16.1 (*C*$H_3$). [Ph, $C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): $\delta^1$H/$\delta^{13}$C: 9.03/169.5 (N=*CH*), 5.18/128.7 (=*CH*), 4.90/61.0 (N$CH_2$), 1.63/29.1 ($CH_3^{tBu}$), 1.54/16.1 ($CH_3$).

**$^1$H, $^{13}$C GHMBC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: $\delta^1$H/$\delta^{13}$C: 9.03/73.2 (N=C*H*/N$C^{tBu}$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): $\delta$ = -64.1 (s, 3F, $CF_3$), -127.1 (br, 1F), -129.4 (m, 2F), -131.1 (br, 1F), -131.6 (br, 1F), -136.0 (br, 1F) (*o*-$C_6F_5$), -161.5 (br, 1F), -162.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F), -164.6 (m, 1F) (*p*-

$C_6F_5$), -163.1, -165.4, -166.1, -166.5, -166.9, -167.4 (each m, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -15.4 ($v_{1/2}$ ~ 30Hz).

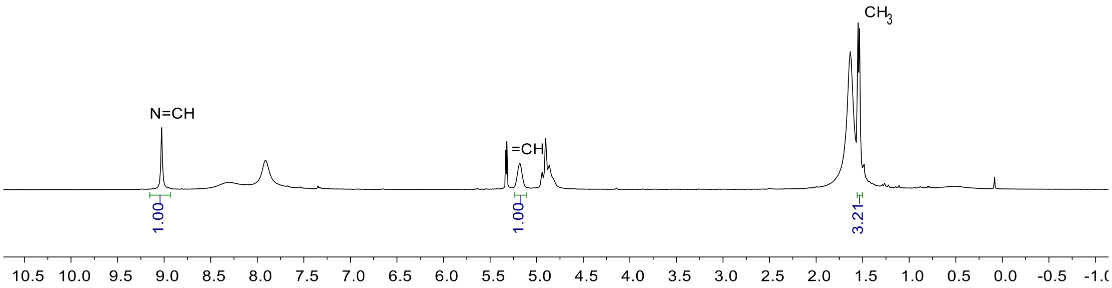


**Fig. S6** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2b**.

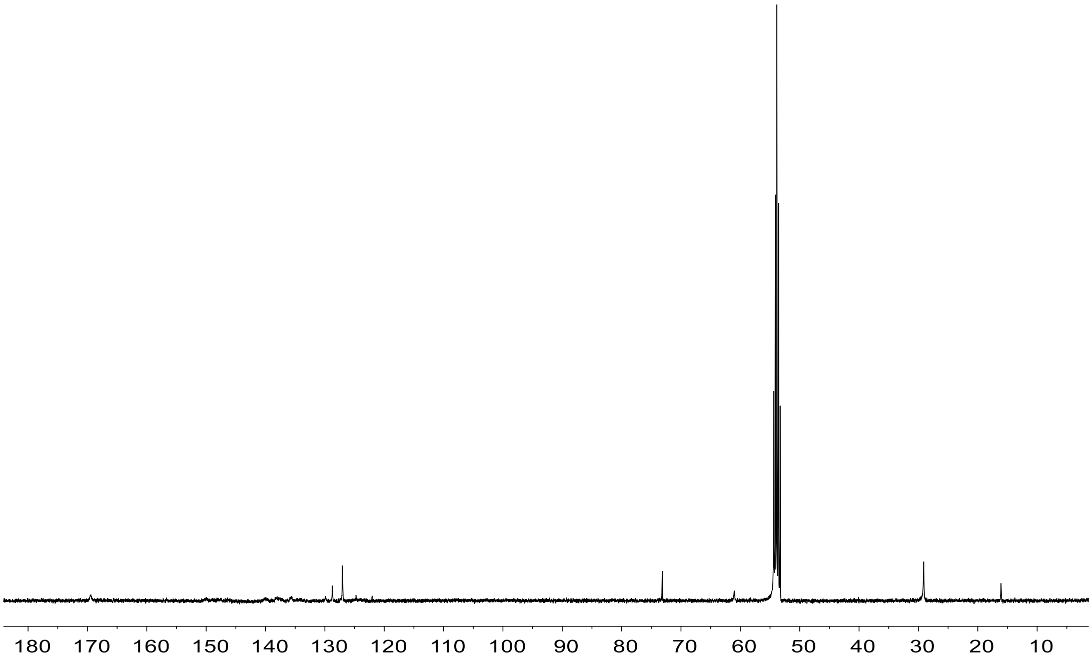


**Fig. S7** $^{13}$C{$^1$H} NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2b**.

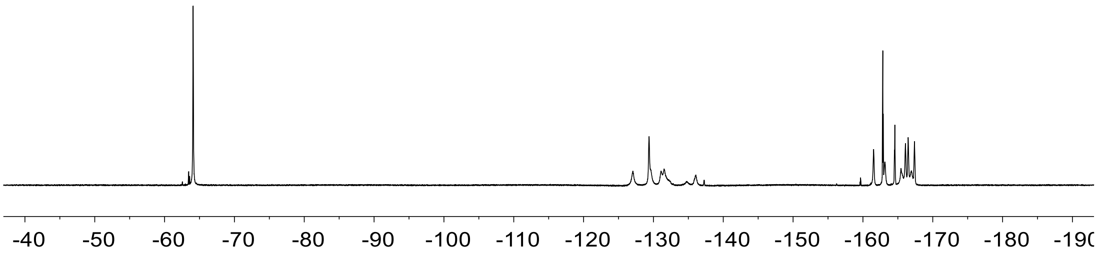


**Fig. S8** $^{19}$F{$^1$H} NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2b**.

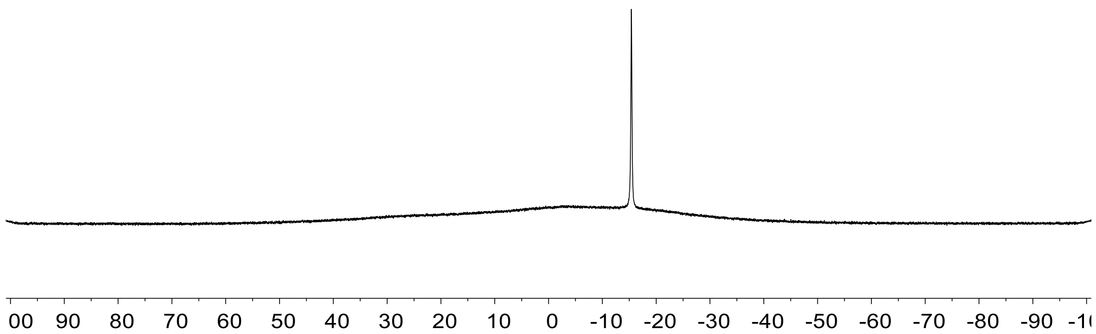
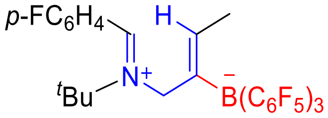


**Fig. S9** $^{11}$B NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2b**.

## Synthesis and characterization of compound 2c



According to the procedure (B) from $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol) and **1c** (70.8 mg, 0.3 mmol). The product was isolated as a yellow solid (212.9 mg, 94% yield).

**HRMS (ESI):** m/z calcd for $C_{33}H_{20}BF_{16}N$ $[M+Cl]^-$: 780.1127, found 780.1122.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): $\delta = 8.78$ (s, 1H, N=C*H*), 7.38 and 8.28 (each br, each 2H, Ph), 5.14 (br, 1H, =C*H*), 4.92 (m, 2H, $NCH_2$), 1.60 (br, 9H, $CH_3^{tBu}$), 1.52 (d, $^3J_{HH} = 7.1$ Hz, 3H, $CH_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): $\delta = 168.1$ (N=*C*H), 168.3 (d, $^1J_{FC} = 264.7$ Hz), 130.5, 123.2 (d, $^3J_{FC} = 2.0$ Hz), 117.9 (d, $^2J_{FC} = 22.3$ Hz) (Ph), 128.9 (=*C*H), 72.1 ($NC^{tBu}$), 60.7 ($NCH_2$), 29.0 ($CH_3^{tBu}$), 16.1 ($CH_3$). [$C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): δ$^1$H/δ$^{13}$C: 8.85/168.1 (N=*CH*), 5.22/128.9 (=*CH*), 4.89/60.7 (N*CH*$_2$), 1.60/29.0 (*CH*$_3^{tBu}$), 1.52/16.1 (*CH*$_3$).

**$^1$H, $^{13}$C GHMBC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: δ$^1$H/δ$^{13}$C: 8.85/72.1 (N=C*H*/N*C*$^{tBu}$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): δ =-94.1 (br, 1F, F), -127.1, -128.8, -129.7, -130.0, -130.9, -136.6 (each br, each 1F, *o*-$C_6F_5$), -160.4 (t, $^3J_{FF}$ = 21.2 Hz, 1F), -161.7 (t, $^3J_{FF}$ = 20.7 Hz, 1F), -163.3 (t, $^3J_{FF}$ = 22.5 Hz, 1F) (*p*-$C_6F_5$), -162.3, -164.5, -165.3, -165.6, -166.2, -166.8 (each br, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -15.4 ($\nu_{1/2}$ ~ 40Hz).

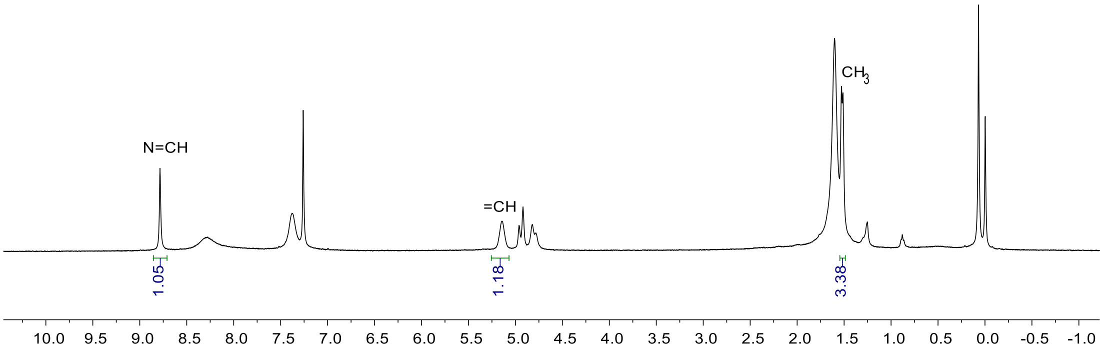


**Fig. S10** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2c**.

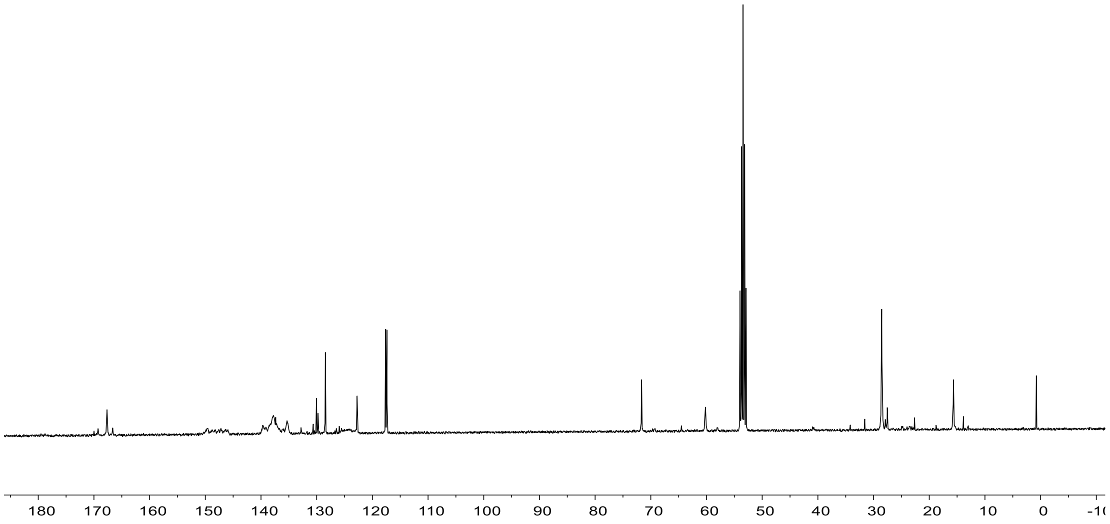


**Fig. S11** $^{13}C\{^{1}H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2c**.

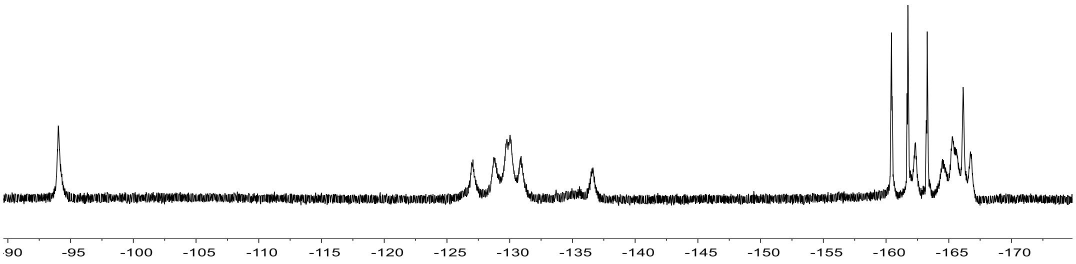


**Fig. S12** $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2c**..

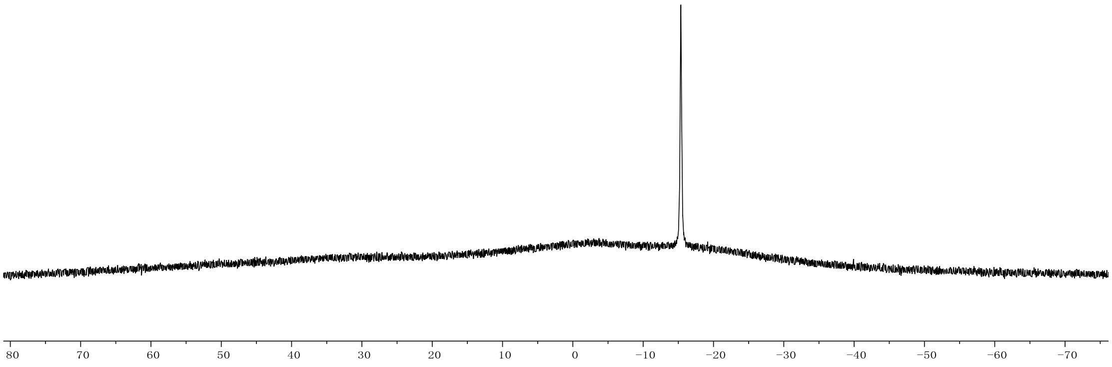
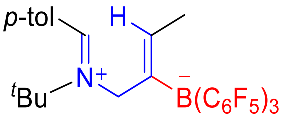


**Fig. S13** $^{11}B$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2c**.

## Synthesis and characterization of compound 2d



According to the procedure (B) from $B(C_6F_5)_3$ (163.8 mg, 0.32 mmol) and **1d** (72.9 mg, 0.32 mmol). The product was isolated as a white solid (225.8 mg, 96% yield).

**HRMS (ESI):** m/z calcd for $C_{34}H_{23}BF_{15}N$ $[M+Cl]^-$: 776.1378, found 776.1378.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): δ = 8.79 (s, 1H, N=C*H*), 7.47-8.09 (m, 4H, Ph), 5.21 (br, 1H, =C*H*), 4.84 (m, 2H, $NCH_2$), 2.53 (s, 3H, $CH_3^{Ph}$), 1.57 (br, 9H, $CH_3^{tBu}$), 1.51 (d, $^3J_{HH}$ = 7.2 Hz, 3H, $CH_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): δ = 168.9 (N=*C*H), 150.3, 135.7, 131.0, 124.1 (Ph), 128.6 (=*C*H), 71.4 ($NC^{tBu}$), 60.4 ($NCH_2$), 29.0 ($CH_3^{tBu}$), 22.4 ($CH_3^{Ph}$), 16.1 ($CH_3$). [$C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): δ$^1$H/δ$^{13}$C: 8.79/168.9 (N=*CH*), 5.21/128.6 (=*CH*), 4.84/60.4 ($NCH_2$), 2.53/22.4 ($CH_3^{Ph}$), 1.57/29.0 ($CH_3^{tBu}$), 1.51/16.1 ($CH_3$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): δ = -126.5, -128.9, -129.6, -131.1, -131.7, -135.4 (each br, each 1F, *o*-$C_6F_5$), -161.8 (t, $^3J_{FF}$ = 20.7 Hz, 1F), -163.1 (t, $^3J_{FF}$ = 20.5 Hz, 1F), -164.8 (m, 1F) (*p*-$C_6F_5$), -163.5, -165.8, -166.2, -166.6, -167.2, -167.5 (each br, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -15.3 ($\nu_{1/2}$ ~ 40Hz).

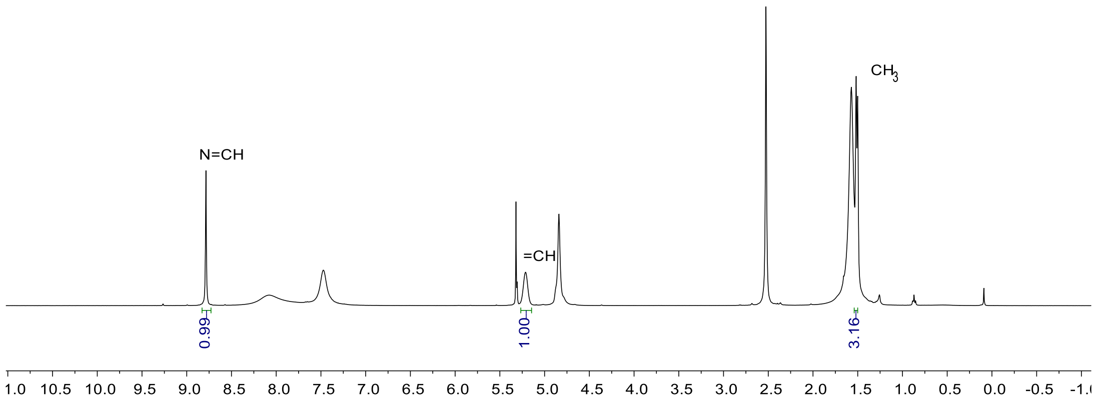


**Fig. S14** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d**.

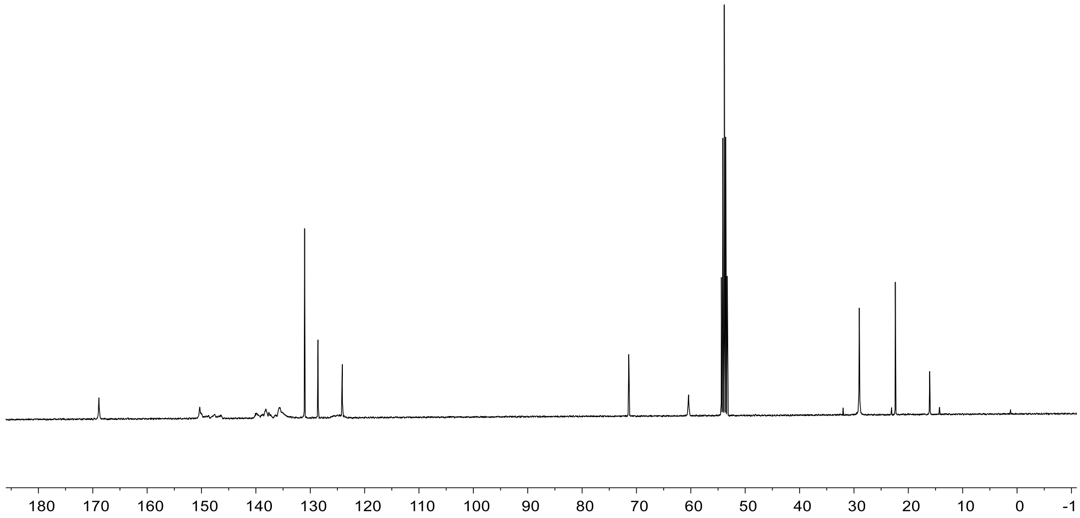


**Fig. S15** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d**.

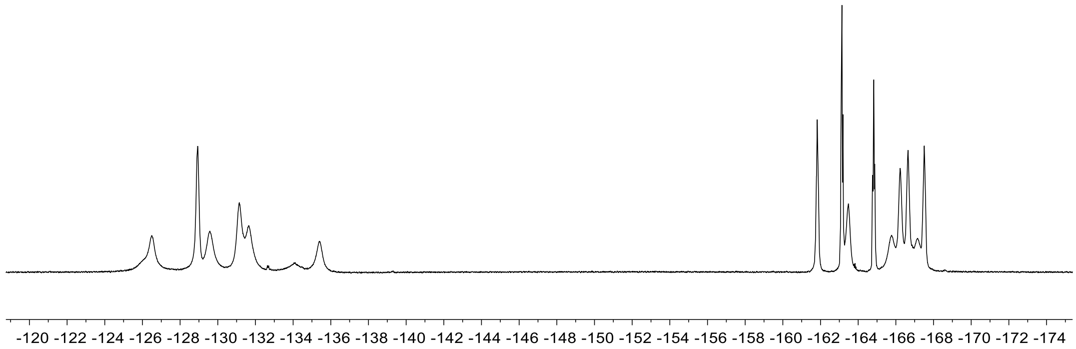


**Fig. S16** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d**.

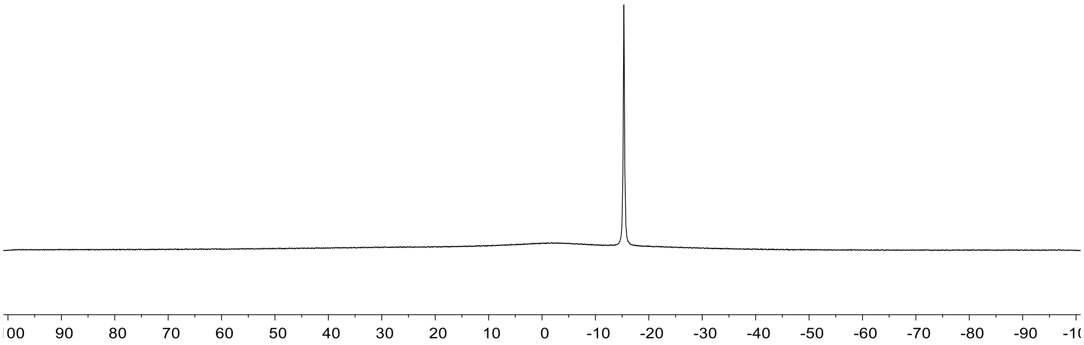
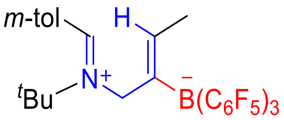


**Fig. S17** $^{11}$B NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d**.

## Synthesis and characterization of compound 2e



According to the procedure (B) from $B(C_6F_5)_3$ (158.7 mg, 0.31 mmol) and **1e** (70.0 mg, 0.31 mmol). The product was isolated as a white solid (218.5 mg, 97% yield).

**HRMS (ESI):** m/z calcd for $C_{34}H_{23}BF_{15}N$ $[M-H]^-$: 740.1611, found 740.1617.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): δ = 8.85 (s, 1H, N=C*H*), 7.55-7.95 (m, 4H, Ph), 5.22 (br, 1H, =C*H*), 4.85 (m, 2H, NC$H_2$), 2.50 (br, 3H, C$H_3^{Ph}$), 1.56 (br, 12H, C$H_3$ and C$H_3^{tBu}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): δ = 169.9 (N=*C*H), 141.1, 138.5, 134.4, 130.0, 126.9 (Ph), 128.4 (=*C*H), 71.8 (N$C^{tBu}$), 60.6 (N*C*$H_2$), 29.1 (*C*$H_3^{tBu}$), 21.0 (*C*$H_3^{Ph}$), 16.1 (*C*$H_3$). [$C_6F_5$ and BC not listed]

**$^1$H, $^1$H COSY** (400 MHz/400 MHz, 299K, $CD_2Cl_2$): δ$^1$H/δ$^{13}$C: 4.85/1.56 (NC$H_2$/C$H_3$).

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): $\delta^1$H/$\delta^{13}$C: 8.85/169.9 (N=$CH$), 5.22/128.4 (=$CH$), 4.85/60.6 (N$CH_2$), 2.50/21.0 ($CH_3^{Ph}$), 1.56/(29.1, 16.1) ($CH_3$ and $CH_3^{tBu}$).

**$^1$H, $^{13}$C GHMBC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: $\delta^1$H/$\delta^{13}$C: 8.85/71.8 (N=C$H$/N$C^{tBu}$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): $\delta$ = -126.9, -129.1, -129.9, -131.2, -133.2, -136.7 (each br, each 1F, *o*-$C_6F_5$), -161.9 (t, $^3J_{FF}$ = 18.1 Hz, 1F), -163.2 (t, $^3J_{FF}$ = 20.0 Hz, 1F), -164.9 (t, $^3J_{FF}$ = 18.9 Hz, 1F) (*p*-$C_6F_5$), -163.4 (1F), -165.5 (1F), -166.3 (1F), -166.8 (2F), -167.5 (1F) (each br, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): $\delta$ = -15.1 ($\nu_{1/2}$ ~ 30Hz).

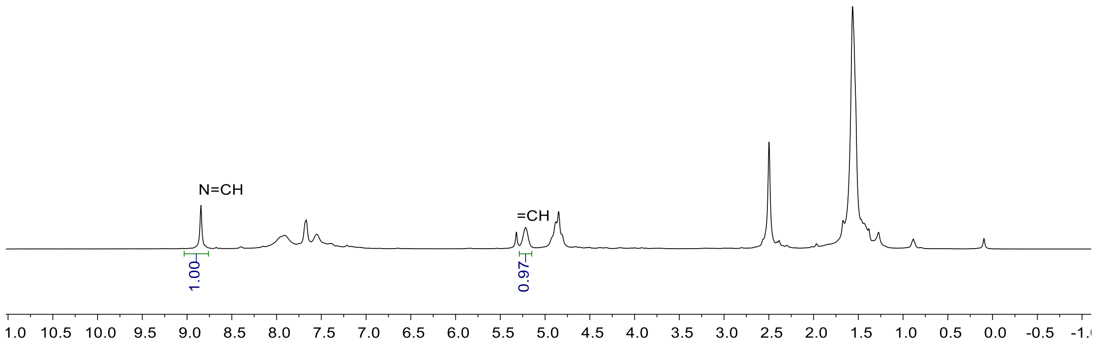


**Fig. S18** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2e**.

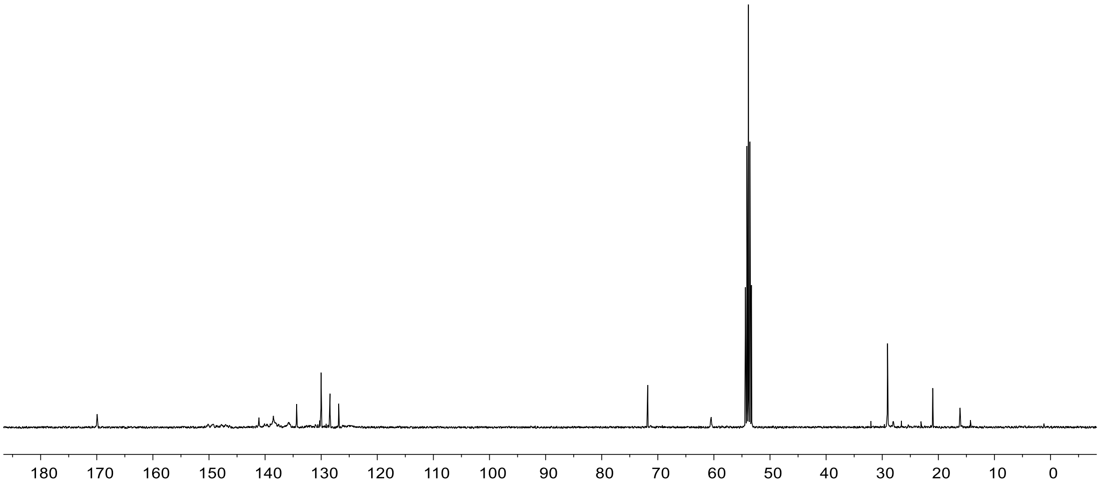


**Fig. S19** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2e**.

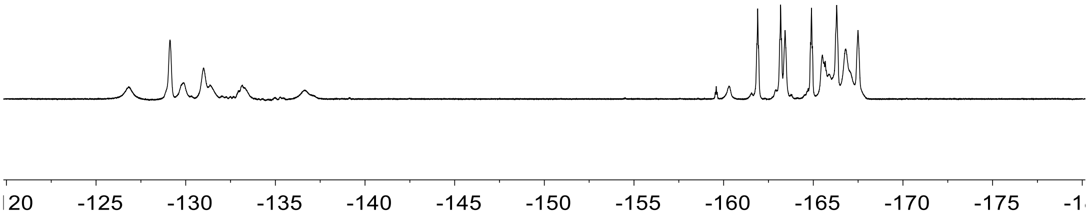


**Fig. S20** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2e**.

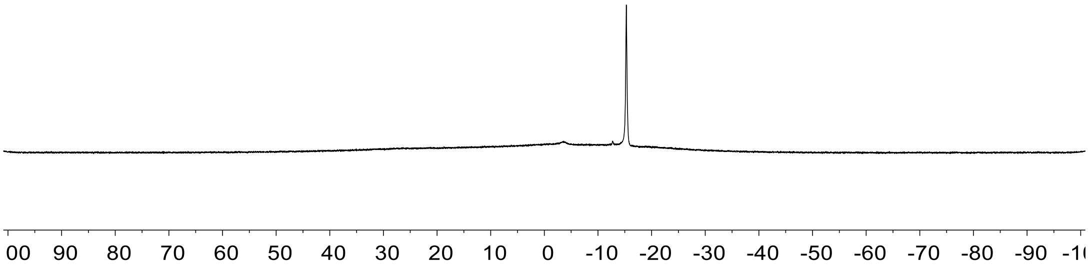
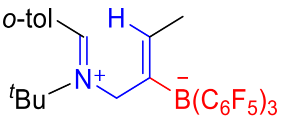


**Fig. S21** $^{11}B$ NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2e**.

## Synthesis and characterization of compound 2f



According to the procedure (B) from $B(C_6F_5)_3$ (153.6 mg, 0.3 mmol) and **1f** (68.8 mg, 0.3 mmol). The product was isolated as a yellow solid (218.0 mg, 98% yield).

**HRMS (ESI):** m/z calcd for $C_{34}H_{23}BF_{15}N$ $[M\text{-}H]^-$: 740.1611, found 740.1611.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): $\delta$ = 9.27 (s, 1H, N=C*H*), 7.38-8.35 (m, 4H, Ph), 5.19 (br, 1H, =C*H*), 4.79 (m, 2H, NC$H_2$), 2.40 (br, 3H, C$H_3^{Ph}$), 1.67 (br, 9H, C$H_3^{tBu}$), 1.53 (d, $^3J_{HH}$ = 7.0 Hz, 3H, C$H_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): $\delta$ = 171.4 (N=*C*H), 127.9 (=*C*H), 72.1 (N$C^{tBu}$), 60.7 (N*C*$H_2$), 29.5 (*C*$H_3^{tBu}$), 20.0 (*C*$H_3^{Ph}$), 16.1 (*C*$H_3$). [Ph, $C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): $\delta^1$H/$\delta^{13}$C: 5.19/127.9 (=*CH*), 4.79/60.7 (N*C*$H_2$), 2.40/20.0 (*C*$H_3^{Ph}$), 1.67/29.5 (*C*$H_3^{tBu}$), 1.53/16.1 (*C*$H_3$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): $\delta$ = -127.4 to -134.9 (br, *o*-$C_6F_5$), -161.9 (br), -163.4 (br, 2F) (*p*-$C_6F_5$), -165.0 to -167.6 (br, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): $\delta$ = -15.5 ($\nu_{1/2}$ ~ 40Hz).

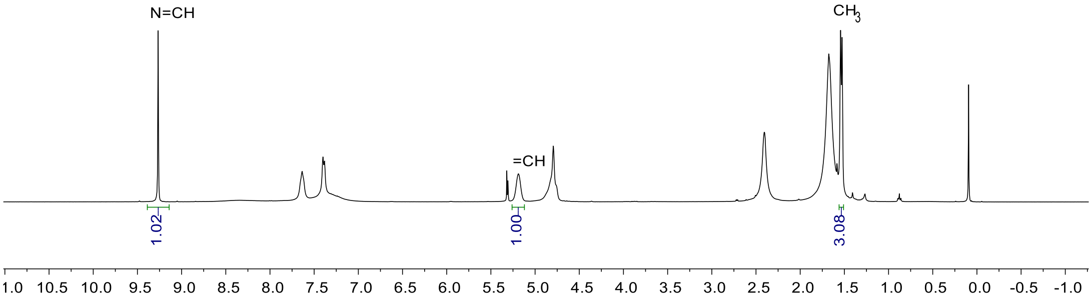


**Fig. S22** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2f**.

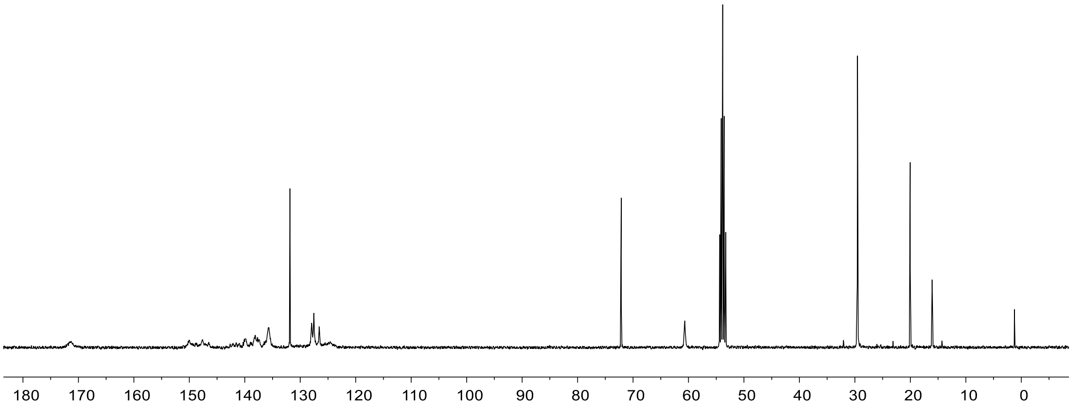


**Fig. S23** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2f**.

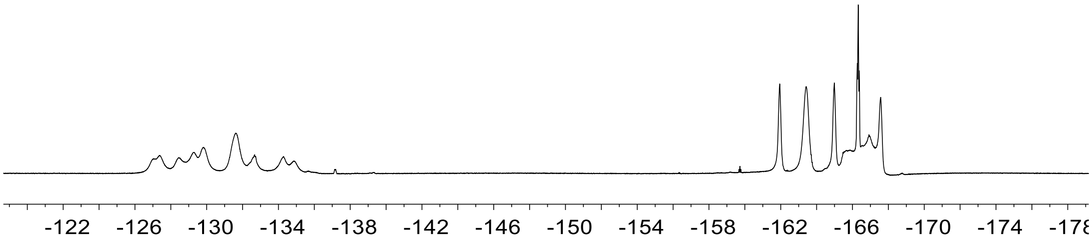


**Fig. S24** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2f**.

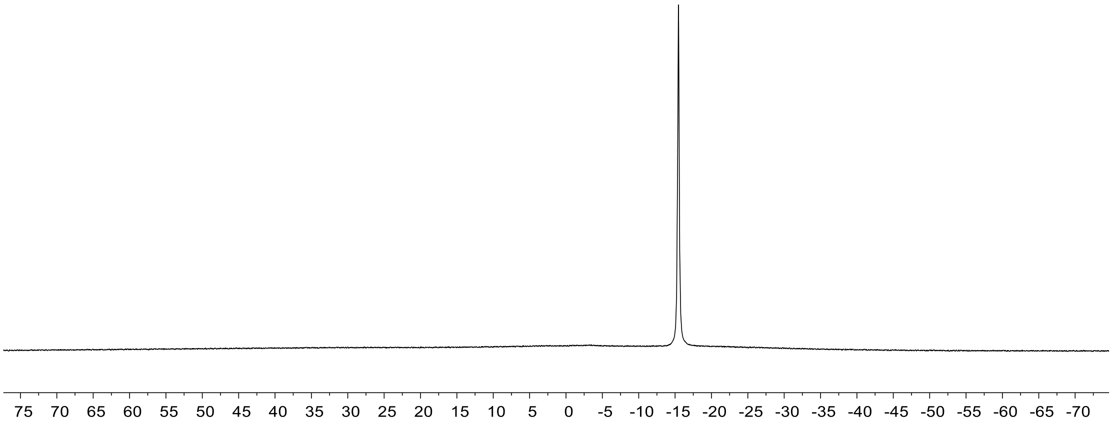
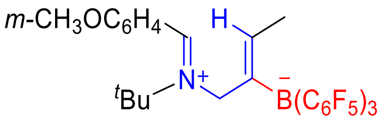


**Fig. S25** $^{11}B$ NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2f**.

## Synthesis and characterization of compound 2g



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1g** (48.9 mg, 0.2 mmol). The product was isolated as a white solid (143.3 mg, 95% yield).

**HRMS (ESI):** m/z calcd for $C_{34}H_{23}BF_{15}NO$ $[M+Na]^+$: 780.1525, found 780.1521.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): δ = 8.82 (s, 1H, N=C*H*), 7.21-8.04 (m, 4H, Ph), 5.16 (br, 1H, =C*H*), 4.86 (m, 2H, NC$H_2$), 3.86 (s, 3H, OC$H_3$), 1.63 (br, 9H, C$H_3^{tBu}$), 1.54 (d, $^3J_{HH}$ = 7.0 Hz, 3H, C$H_3$).

**$^{13}$C {$^1$H} NMR** (101 MHz, 299K, $CDCl_3$): δ = 169.5 (N=*C*H), 128.7 (=*C*H), 71.6 (N$C^{tBu}$), 60.6 (N$CH_2$), 55.8 (O$CH_3$), 29.2 ($CH_3^{tBu}$), 16.1 ($CH_3$). [$C_6F_5$, Ph, and BC not listed]

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): δ = -127.2, -129.0, -130.3, 130.8, 131.7, -134.7 (each br, each 1F, *o*-$C_6F_5$), -160.7, 162.2, -163.5 (each br, each 1F, *p*-$C_6F_5$), -162.2 (2F), -164.5 ~ -167.0 (br, 6F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -15.4 ($\nu_{1/2}$ ~ 40Hz).

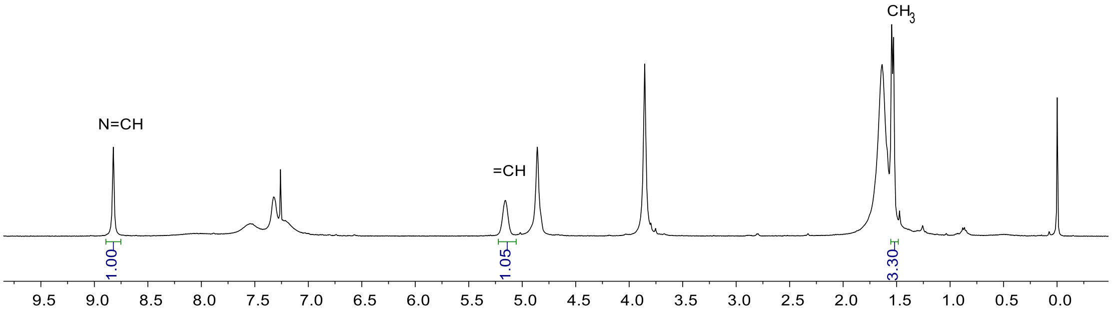


**Fig. S26** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2g**.

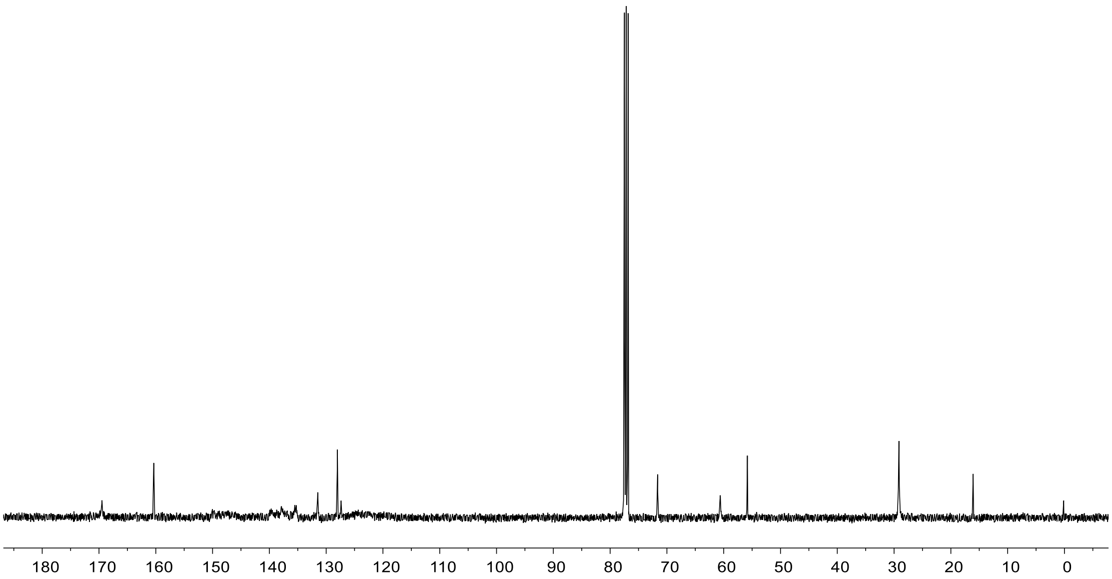


**Fig. S27** $^{13}$C {$^1$H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **2g**.

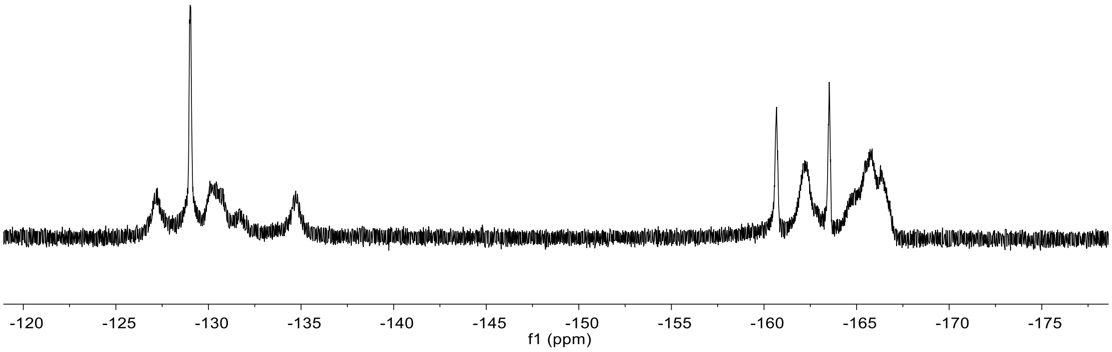


**Fig. S28** $^{19}$F{$^1$H} NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2g**.

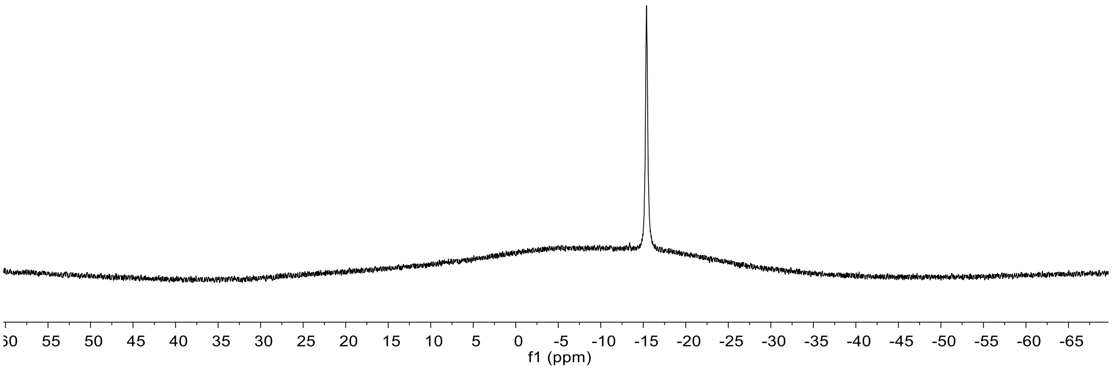
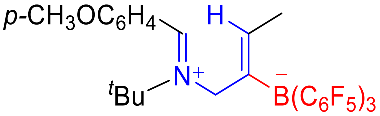


**Fig. S29** $^{11}$B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2g**.

## Synthesis and characterization of compound 2h



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1h** (48.9 mg, 0.2 mmol). The product was isolated as a white solid (140.0 mg, 93% yield).

**HRMS (ESI):** m/z calcd for $C_{34}H_{23}BF_{15}NO$ $[M+H]^+$: 758.1706, found 758.1719.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): δ = 8.60 (s, 1H, N=C*H*), 7.10-8.21 (m, 4H, Ph), 5.17 (br, 1H, =C*H*), 4.84 and 4.73 (each m, each 1H, NC$H_2$), 3.99 (s, 3H. OC$H_3$), 1.57 (br, 9H, C$H_3^{tBu}$), 1.49 (d, $^3J_{HH}$ = 7.0 Hz, 3H, C$H_3$).

**$^{13}$C {H} NMR** (101 MHz, 299K, $CDCl_3$): δ = 167.4 (N=*C*H), 128.0 (=*C*H), 70.2 (N$C^{tBu}$), 69.9 (N*C*$H_2$), 56.3 (O*C*$H_3$), 29.0 (*C*$H_3^{tBu}$), 16.1 (*C*$H_3$). [$C_6F_5$, Ph, and BC not listed]

**$^{19}$F{H} NMR** (377 MHz, 299K, $CDCl_3$): δ = -126.7, -128.8, -129.3, -130.1, -130.9, -135.7 (each br, each 1F, *o*-$C_6F_5$), -160.7, -162.6, -163.6 (each m, each 1F, *p*-$C_6F_5$), -162.2, -164.8, -165.5, -165.9, 166.3, -166.8 (each br, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -15.4 ($\nu_{1/2}$ ~ 40Hz).

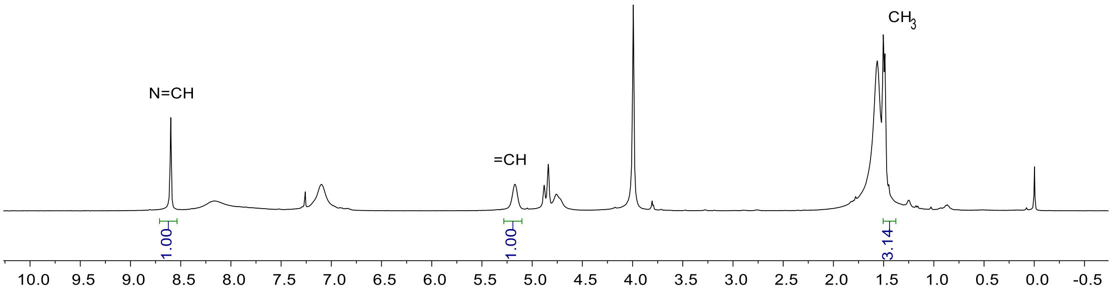


**Fig. S30** $^1$H NMR (400 MHz, 299K, CDCl$_3$) spectrum of compound **2h**.

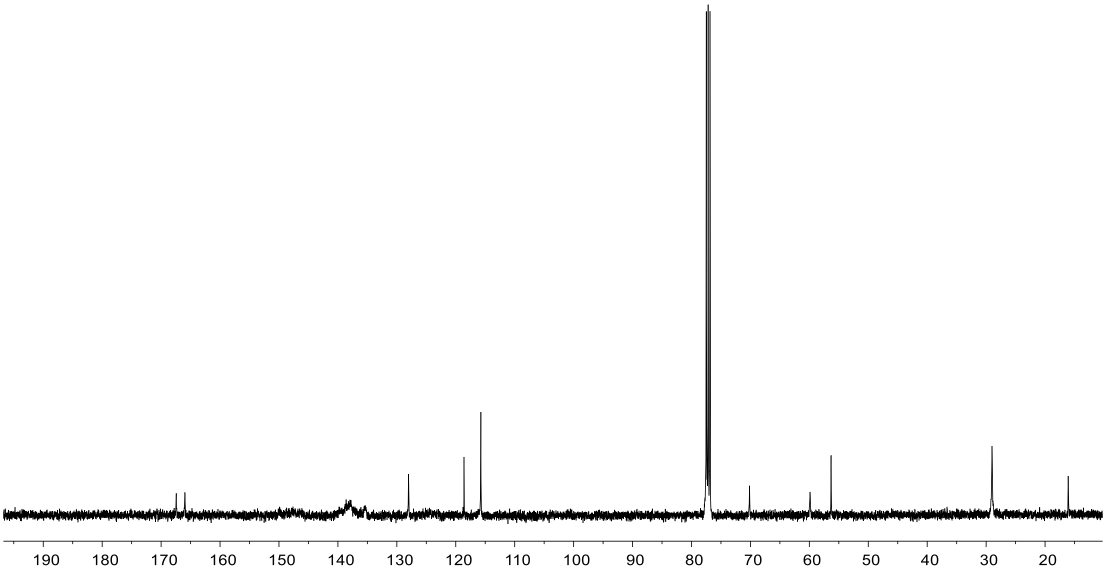


**Fig. S31** $^{13}$C {H} NMR (101 MHz, 299K, CDCl$_3$) spectrum of compound **2h**.

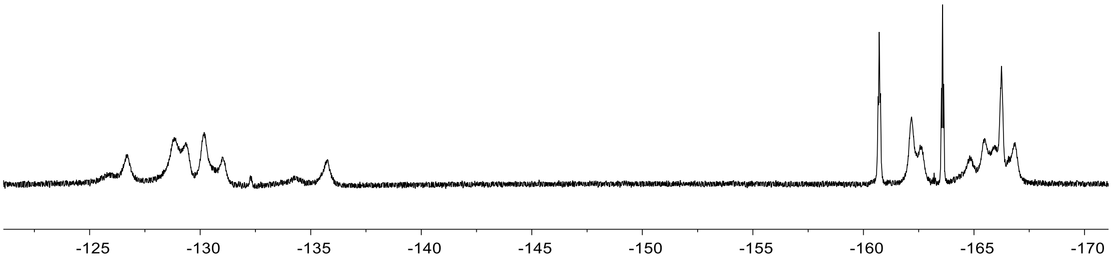


**Fig. S32** $^{19}$F{H} NMR (377 MHz, 299K, CDCl$_3$) spectrum of compound **2h**.

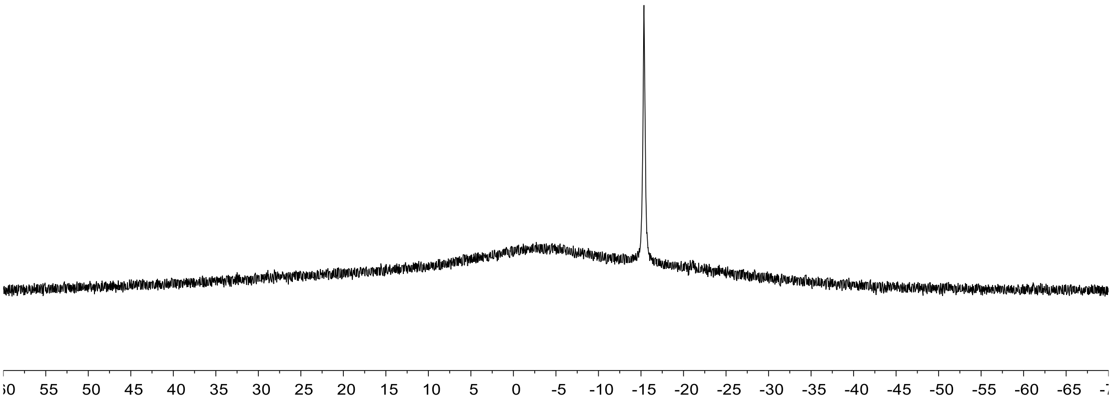
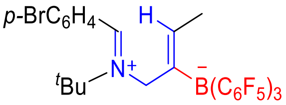


**Fig. S33** $^{11}$B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2h**.

## Synthesis and characterization of compound 2i



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1i** (58.8 mg, 0.2 mmol). The product was isolated as a white solid (156.4 mg, 97% yield).

**HRMS (ESI):** m/z calcd for $C_{33}H_{20}BBrF_{15}N$ $[M-H]^-$: 804.0560 found 804.0591.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): $\delta$ = 8.80 (s, 1H, N=C*H*), 7.50-8.30 (br, 4H, Ph), 5.16 (s, 1H, =C*H*), 4.82 (m, 2H, $NCH_2$), 1.56 (s, 9H, $CH_3^{tBu}$), 1.50 (d, $^3J_{HH}$ = 5.4 Hz, 3H, $CH_3$).

**$^{13}$C {$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): $\delta$ = 168.5 (N=*C*H), 128.8 (=*C*H), 72.4 ($NC^{tBu}$), 60.7 ($NCH_2$), 29.0 ($CH_3^{tBu}$), 16.1 ($CH_3$). [$C_6F_5$, Ph and BC not listed]

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): $\delta$ = -126.8 (1F), -129.4 (2F), -131.1 (1F), -131.6 (1F), -136.2 (1F) (each br, *o*-$C_6F_5$), -161.6 (br), -162.8

(t, $^3J_{FF}$ = 20.3 Hz), -164.6 (t, $^3J_{FF}$ = 21.8 Hz) (each 1F, *p*-$C_6F_5$), -163.3, -165.5, -166.0, -166.5, -167.0, -167.4 (each br, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -15.4 ($\nu_{1/2}$ ~ 60Hz).

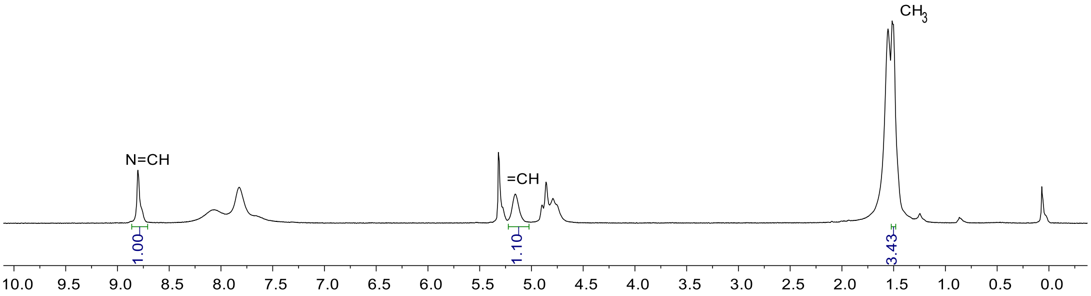


**Fig. S34** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2i**.

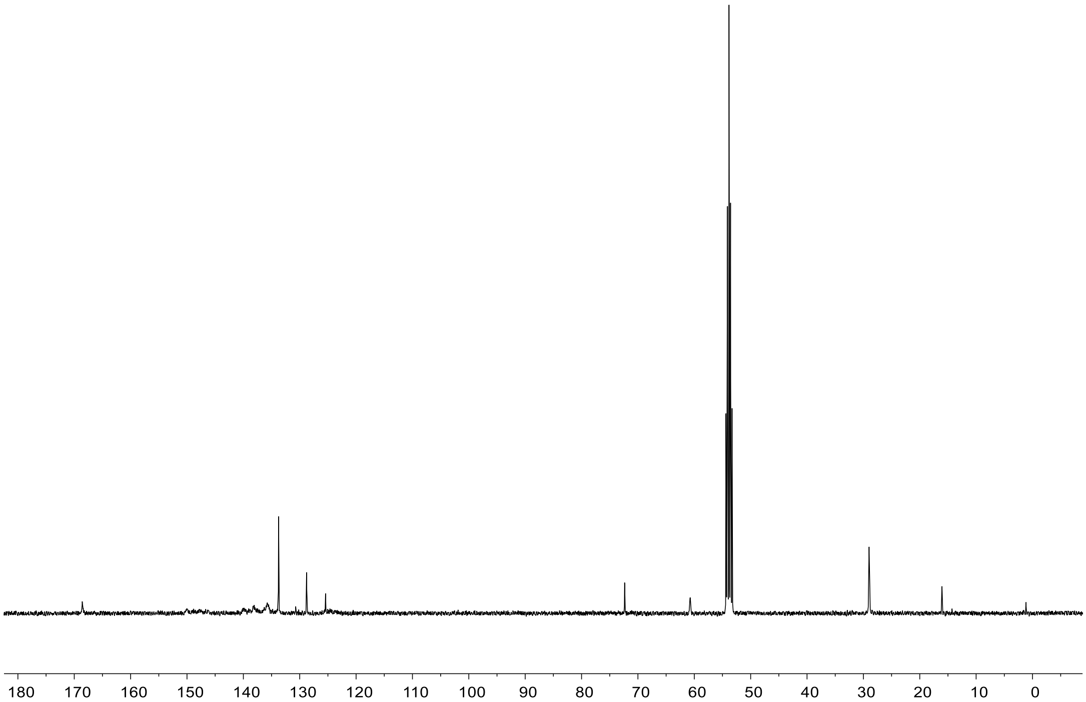


**Fig. S35** $^{13}$C {$^1$H} NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2i**.

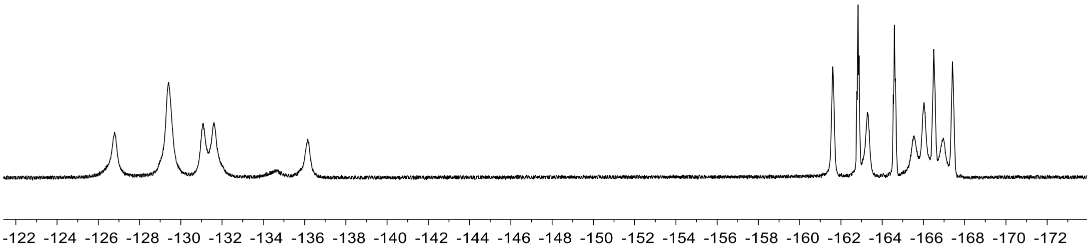


**Fig. S36** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2i**.

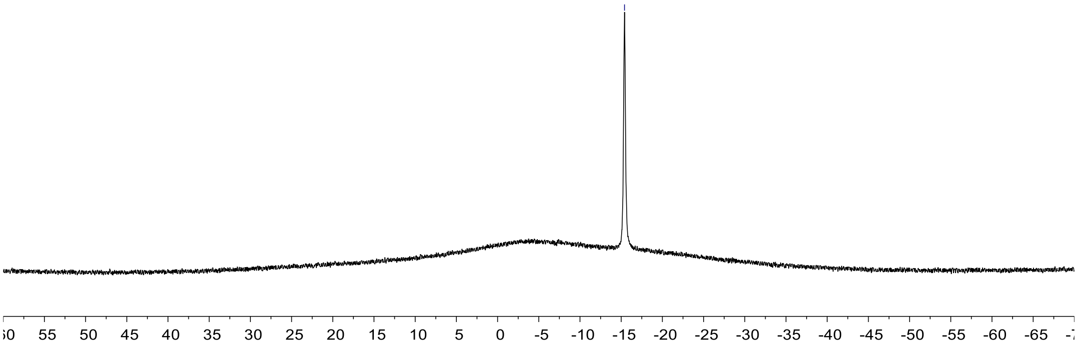
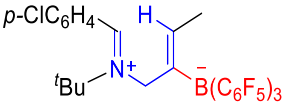


**Fig. S37** $^{11}B$ NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2i**.

## Synthesis and characterization of compound 2j



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1j** (50.0 mg, 0.2 mmol). The product was isolated as a white solid (146.3 mg, 96% yield).

**HRMS (ESI):** m/z calcd for $C_{33}H_{20}BClF_{15}N$ $[M-H]^-$: 760.1065 found 760.1051.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): $\delta = 8.79$ (s, 1H, N=C*H*), 7.60-8.30 (br, 4H, Ph), 5.14 (s, 1H, =C*H*), 4.89 (m, 2H, NC$H_2$), 1.59 (s, 9H, C$H_3^{tBu}$), 1.51 (d, $^3J_{HH} = 7.1$ Hz, 3H, C$H_3$).

**$^{13}$C {$^{1}$H} NMR** (101 MHz, 299K, CDCl$_3$): δ = 167.6 (N=*C*H), 128.4 (=*C*H), 71.9 (N*C*$^{tBu}$), 60.6 (N*C*H$_2$), 29.0 (*C*H$_3$$^{tBu}$), 16.1(*C*H$_3$). [C$_6$F$_5$, Ph, and BC not listed]

**$^{19}$F{$^{1}$H} NMR** (377 MHz, 299K, CDCl$_3$): δ = -126.8, -129.0, -129.5, -130.4, -131.0, -136.2 (each br, each 1F, *o*-C$_6$F$_5$), -160.4 (t, $^{3}J_{FF}$ = 20.2 Hz, 1F), -161.7 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F), -163.4 (t, $^{3}J_{FF}$ = 21.7 Hz, 1F) (*p*-C$_6$F$_5$), -162.3 (1F), -164.6 (1F), -164.9 (1F), -165.8 (2F), -166.6 (1F) (each br, *m*-C$_6$F$_5$).

**$^{11}$B NMR** (128 MHz, 299K, CDCl$_3$): δ = -15.4 ($\nu_{1/2}$ ~ 60Hz).

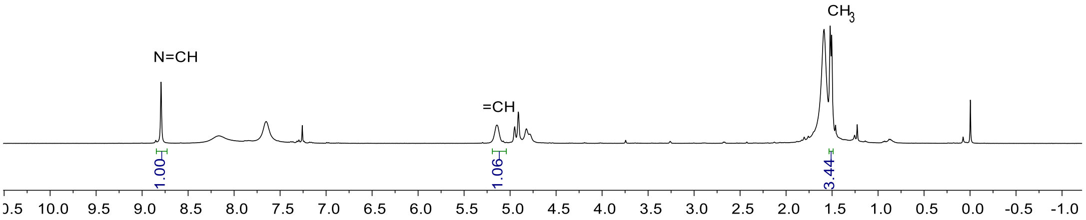


**Fig. S38** $^{1}$H NMR (400 MHz, 299K, CDCl$_3$) spectrum of compound **2j**.

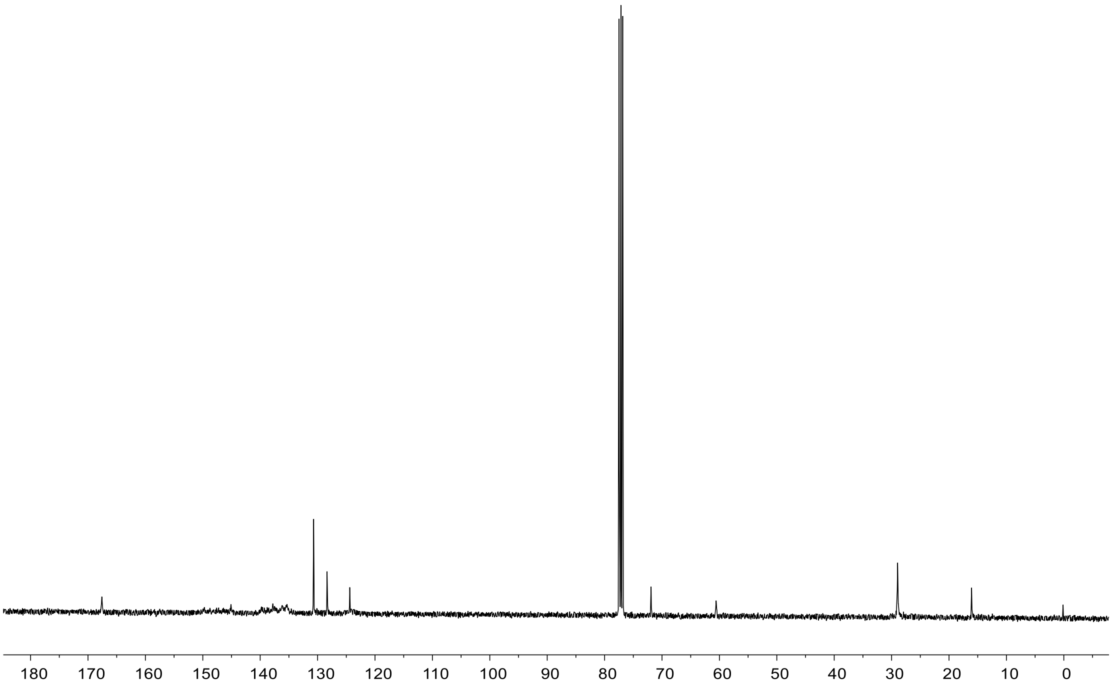


**Fig. S39** $^{13}$C {$^{1}$H} NMR (101 MHz, 299K, CDCl$_3$) spectrum of compound **2j**.

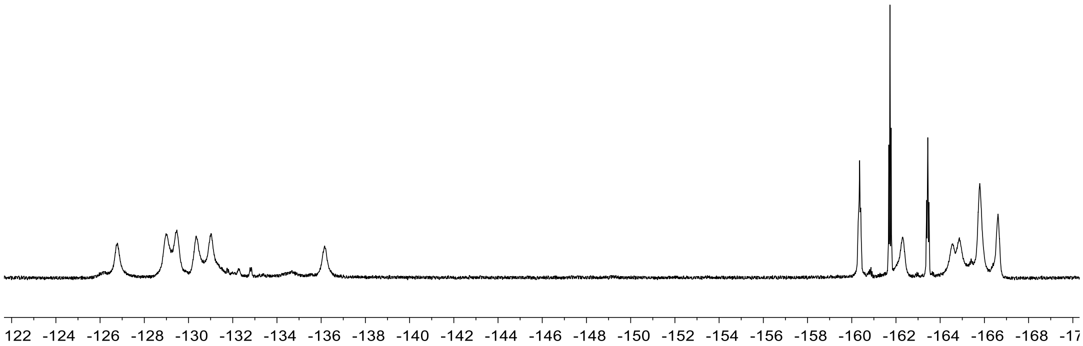


**Fig. S40** $^{19}$F{$^{1}$H} NMR (377 MHz, 299K, CDCl$_3$) spectrum of compound **2j**.

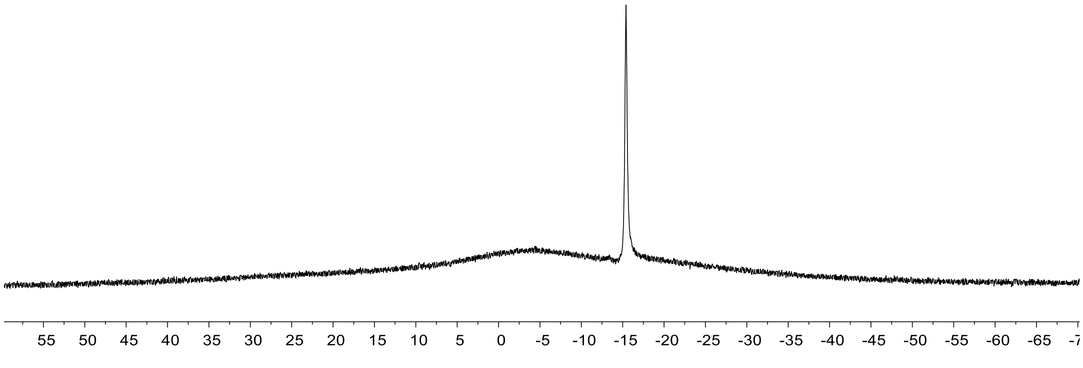
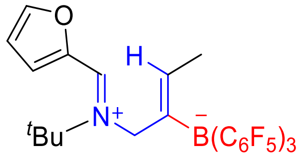


**Fig. S41** $^{11}$B NMR (128 MHz, 299K, CDCl$_3$) spectrum of compound **2j**.

## Synthesis and characterization of compound 2k



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1k** (41.1 mg, 0.2 mmol). The product was isolated as a white solid (134.9 mg, 94% yield).

**HRMS (ESI):** m/z calcd for $C_{31}H_{19}BF_{15}NO$ $[M+H]^+$: 718.1393, found 718.1396.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): $\delta$ = 8.55 (s, 1H, N=C*H*), 6.97-8.06 (br, 3H, furyl), 4.93 (m, 3H, =C*H* and NC$H_2$), 1.57 (br, 9H, C$H_3^{tBu}$), 1.39 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C$H_3$).

**$^{13}$C {$^1$H} NMR** (101 MHz, 299K, $CDCl_3$): $\delta$ = 154.3 (N=*C*H), 125.7 (=*C*H), 69.8 (N$C^{tBu}$), 59.9 (N$CH_2$), 28.6 ($CH_3^{tBu}$), 15.9 ($CH_3$). [$C_6F_5$, furyl, and BC not listed]

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): $\delta$ = -127.0, -129.0, -130.0, -130.3, -131.5, -134.7 (each br, each 1F, *o*-$C_6F_5$), -160.6 (t, $^3J_{FF}$ = 20.6 Hz), -162.1 (br), -163.5 (t, $^3J_{FF}$ = 20.5 Hz) (each 1F, *p*-$C_6F_5$), -162.7, -164.9, -165.5, -166.0, -166.5, -167.0 (each br, each 1F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): $\delta$ = -15.3 ($\nu_{1/2}$ ~ 40Hz).

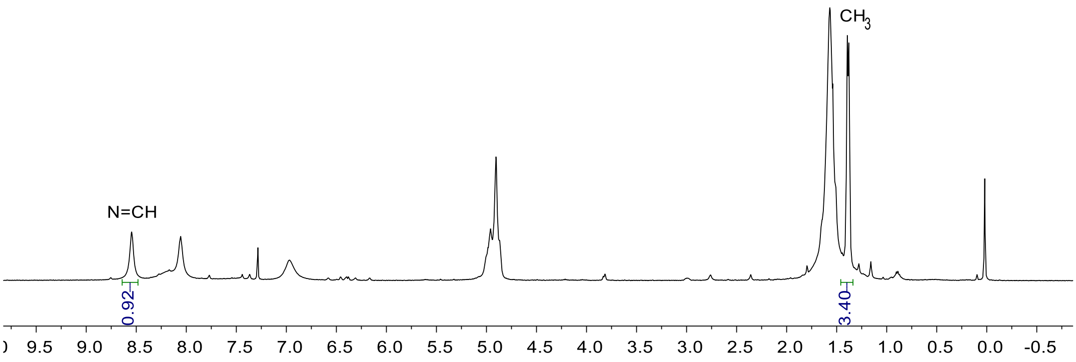


**Fig. S42** $^{1}$H NMR (400 MHz, 299K, CDCl$_3$) spectrum of compound **2k**.

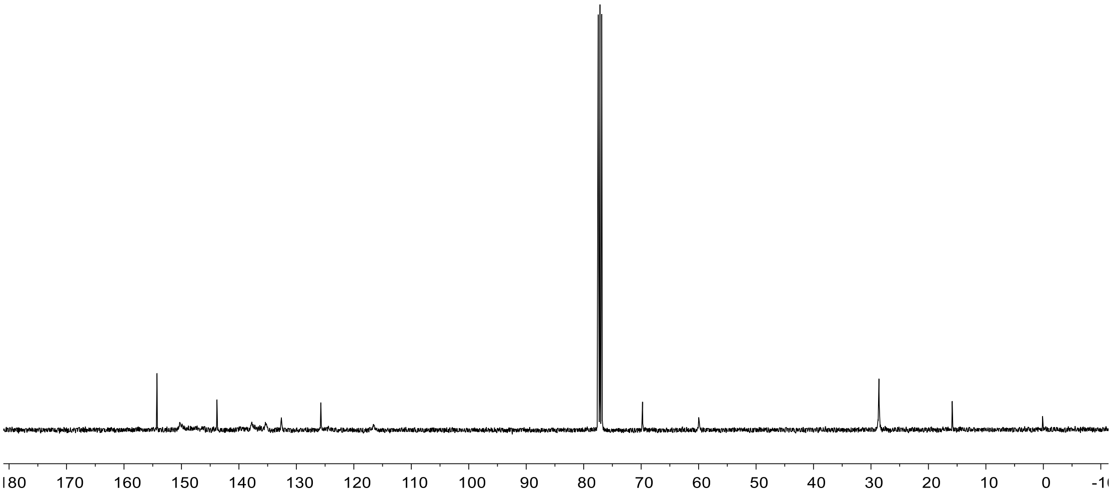


**Fig. S43** $^{13}$C {$^{1}$H} NMR (101 MHz, 299K, CDCl$_3$) spectrum of compound **2k**.

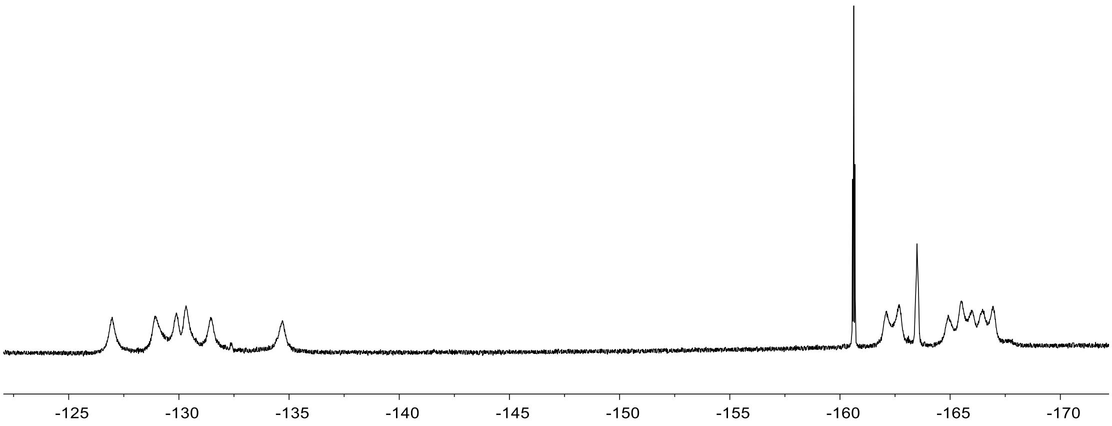


**Fig. S44** $^{19}$F{$^{1}$H} NMR (377 MHz, 299K, CDCl$_3$) spectrum of compound **2k**.

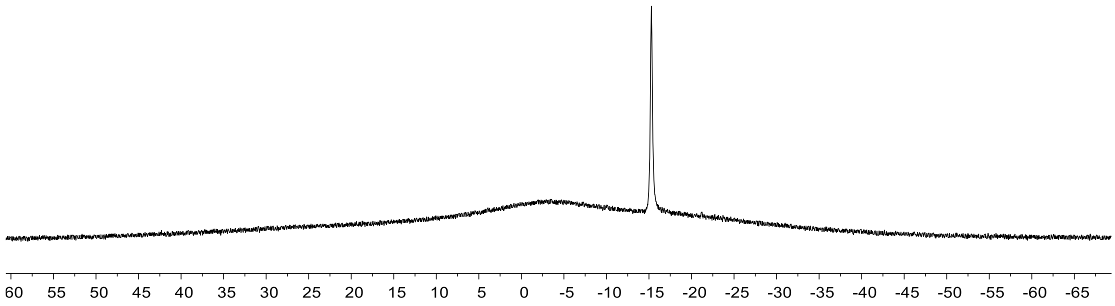
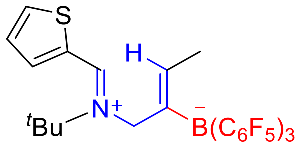


**Fig. S45** $^{11}$B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2k**.

## Synthesis and characterization of compound 2l



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1l** (44.3 mg, 0.2 mmol). The product was isolated as a yellow solid (135.0 mg, 92% yield).

**HRMS (ESI):** m/z calcd for $C_{31}H_{19}BF_{15}NS$ $[M+Na]^+$: 756.0984, found 756.1011.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): δ = 8.75 (s, 1H, N=C*H*), 7.49-8.28 (m, 3H, thienyl), 5.07 (br, 1H, =C*H*), 4.93 (m, 2H, NC$H_2$), 1.61 (br, 9H, C$H_3^{tBu}$), 1.46 (d, $^3J_{HH}$ = 7.0 Hz, 3H, C$H_3$).

**$^{13}$C {$^1$H} NMR** (101 MHz, 299K, $CDCl_3$): δ = 156.9 (N=*C*H), 127.3 (=*C*H), 70.3 (N$C^{tBu}$), 59.7 (N*C*$H_2$), 28.8 ($CH_3^{tBu}$), 15.9 ($CH_3$). [$C_6F_5$, thienyl, and BC not listed]

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): δ =-127.0 (br), -129.1 (m), -129.3 (br), -129.9 (m), -131.0 (br), -133.9 (br) (each 1F, *o*-$C_6F_5$), -160.6 (t, $^3J_{FF}$ = 20.6 Hz), -162.3 (br), -163.5 (t, $^3J_{FF}$ = 20.5 Hz) (each 1F, *p*-$C_6F_5$), -

162.4 (1F), -164.9 (1F), , -165.5 (2F) -166.3 (1F), -166.6 (1F) (each br, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -15.2 ($\nu_{1/2}$ ~ 50Hz).

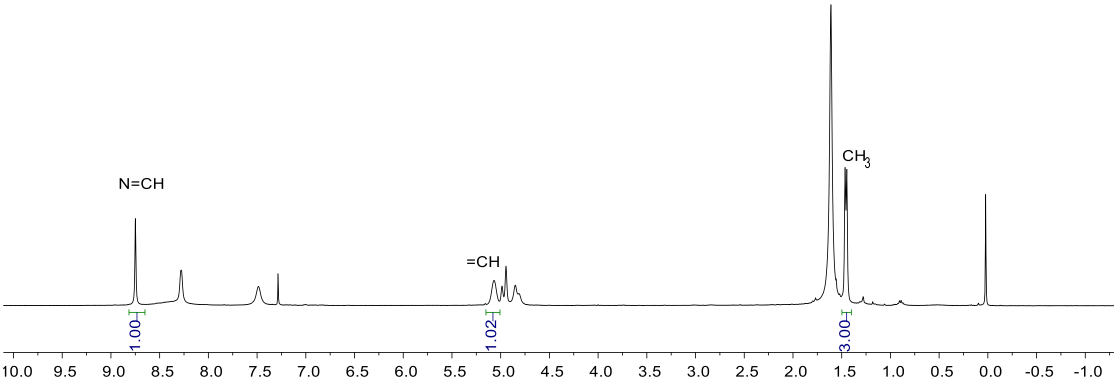


**Fig. S46** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2l**.

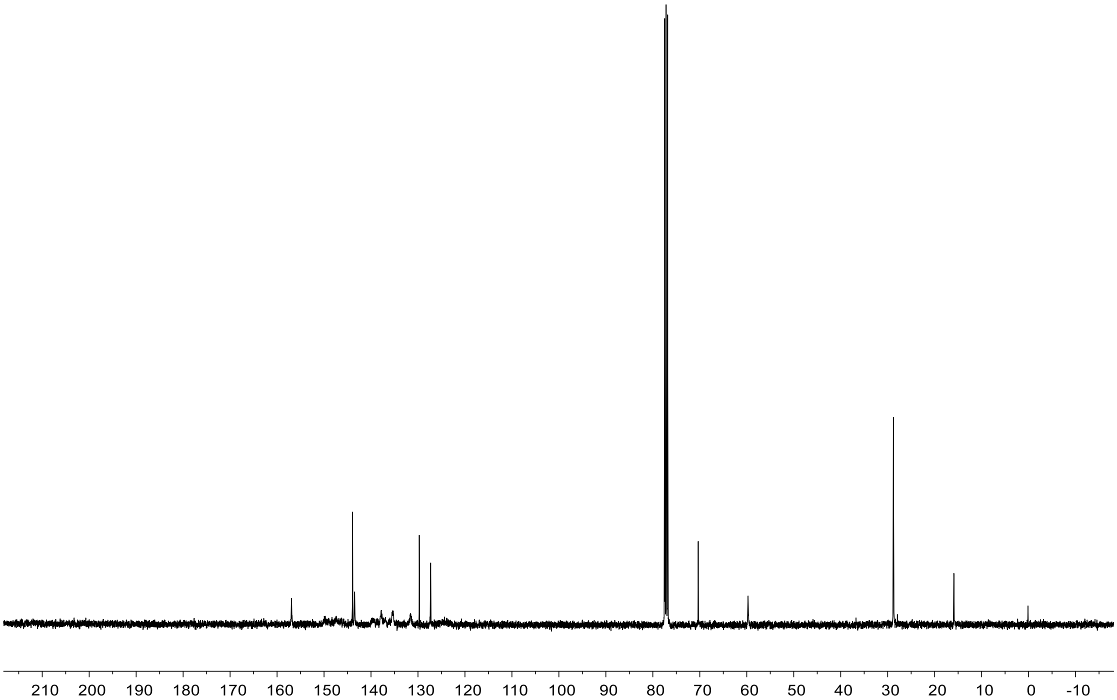


**Fig. S47** $^{13}$C {$^1$H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **2l**.

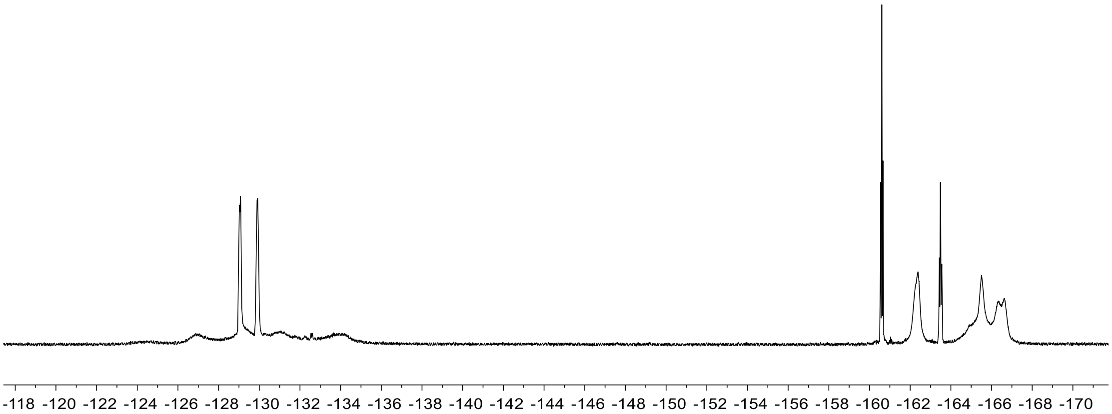


**Fig. S48** $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2l**.

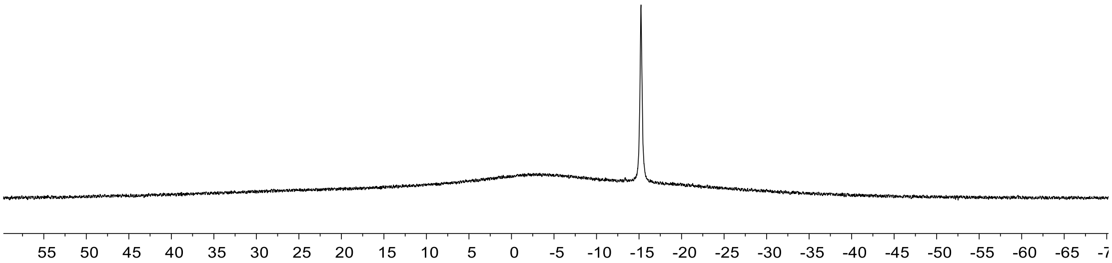
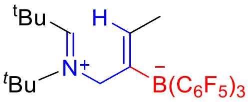


**Fig. S49** $^{11}B$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2l**.

## Synthesis and characterization of compound 2m



According to the procedure (B) from $B(C_6F_5)_3$ (169.0 mg, 0.33 mmol) and **1m** (65.0 mg, 0.33 mmol). The product was isolated as a white solid (215.3 mg, 91% yield).

**HRMS (ESI):** m/z calcd for $C_{31}H_{25}BF_{15}N$ $[M+Cl]^-$: 742.1535, found 742.1532.

$^{1}$**H NMR** (400 MHz, 299K, $CD_2Cl_2$): $\delta = 8.16$ (s, 1H, N=C*H*), 4.89 (br, 2H, NC$H_2$ and =C*H*), 4.62 (d,$^{3}J_{HH}$ = 16.6 Hz, 1H, NC$H_2$), 1.49 (m, 12H, $^{N}CH_3^{tBu}$ and C$H_3$), 1.33 (br, 9H, $CH_3^{tBu}$).

**$^{13}$C{$^{1}$H} NMR** (101 MHz, $CD_2Cl_2$): δ = 184.7 (N=*C*H), 127.7 (=*C*H), 73.6 (N$C^{\mathrm{tBu}}$), 59.1 (N$CH_2$), 38.9 ($C^{\mathrm{tBu}}$), 29.3 ($^{\mathrm{N}}CH_3^{\mathrm{tBu}}$), 27.5 ($CH_3^{\mathrm{tBu}}$), 15.9 ($CH_3$). [$C_6F_5$ and BC not listed]

**$^{1}$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): δ$^{1}$H/δ$^{13}$C: 8.16/184.7 (N=*CH*), 4.89/127.7 (=*C*H), (4.89, 4.62)/59.1 (N$CH_2$), 1.49/29.3 ($^{\mathrm{N}}CH_3^{\mathrm{tBu}}$), 1.33/27.5 ($CH_3^{\mathrm{tBu}}$), 1.49/15.9 ($CH_3$).

**$^{1}$H, $^{13}$C GHMBC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: δ$^{1}$H/δ$^{13}$C: 1.49/73.6 ($^{\mathrm{N}}\mathrm{C}H_3^{\mathrm{tBu}}$/N$C^{\mathrm{tBu}}$), 1.49/29.3 ($^{\mathrm{N}}\mathrm{C}H_3^{\mathrm{tBu}}$/$^{\mathrm{N}}C\mathrm{H}_3^{\mathrm{tBu}}$), 1.33/38.9 ($\mathrm{C}H_3^{\mathrm{tBu}}$/$C^{\mathrm{tBu}}$), 1.33/27.5 ($\mathrm{C}H_3^{\mathrm{tBu}}$/$C\mathrm{H}_3^{\mathrm{tBu}}$).

**$^{19}$F{$^{1}$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): δ = -126.7, -129.1, -129.7, -130.9, -131.9, -133.5 (each br, each 1F, *o*-$C_6F_5$), -161.8 (t, $^{3}J_{FF}$ = 20.6 Hz, 1F), -163.3 (br, 2F) (*p*-$C_6F_5$), -164.7 (m, 1F), -166.5 (m, 1F),-165.8 (br, 1F), -167.0 (br, 1F), -167.5 (br, 2F) (*m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -15.3 ($\nu_{1/2}$ ~ 30Hz).

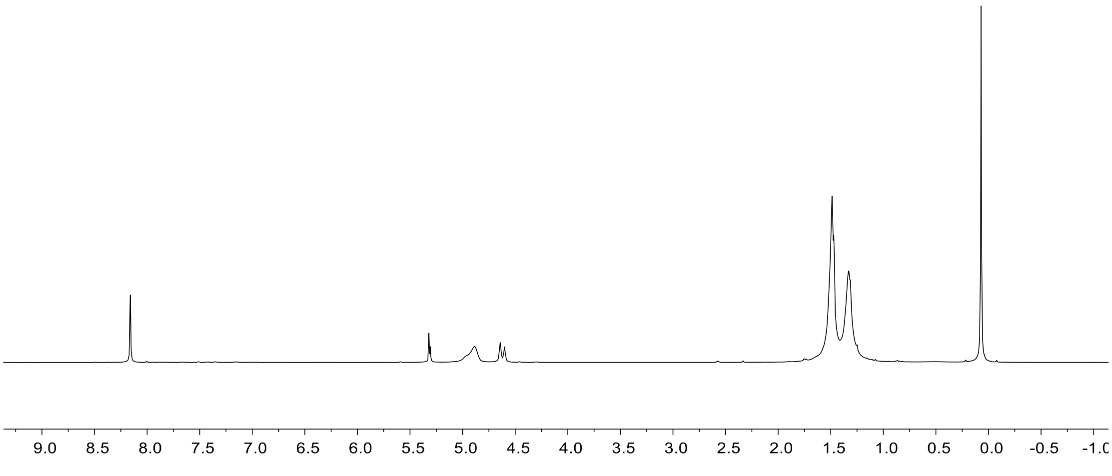


**Fig. S50** $^{1}$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2m**.

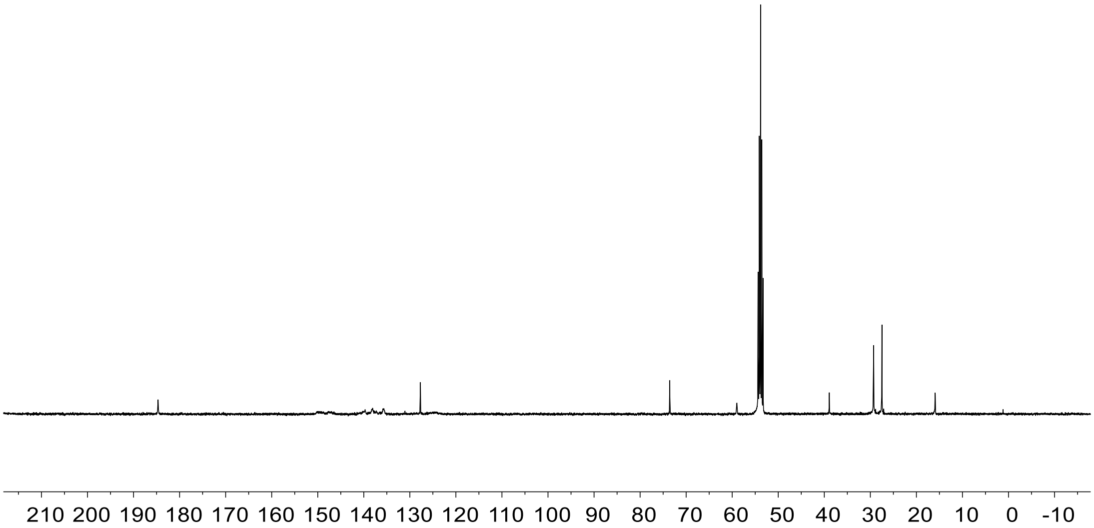


**Fig. S51** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2m** .

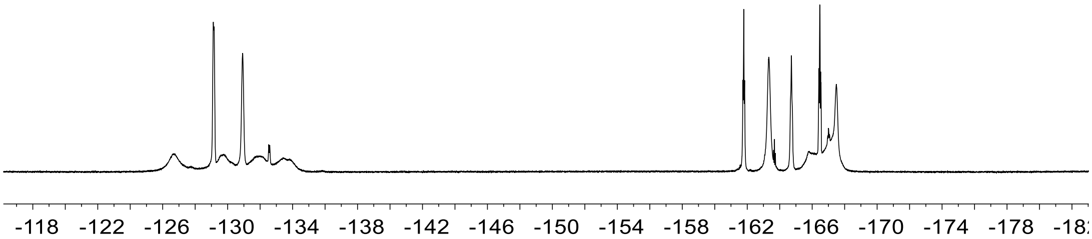


**Fig. S52** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2m** .

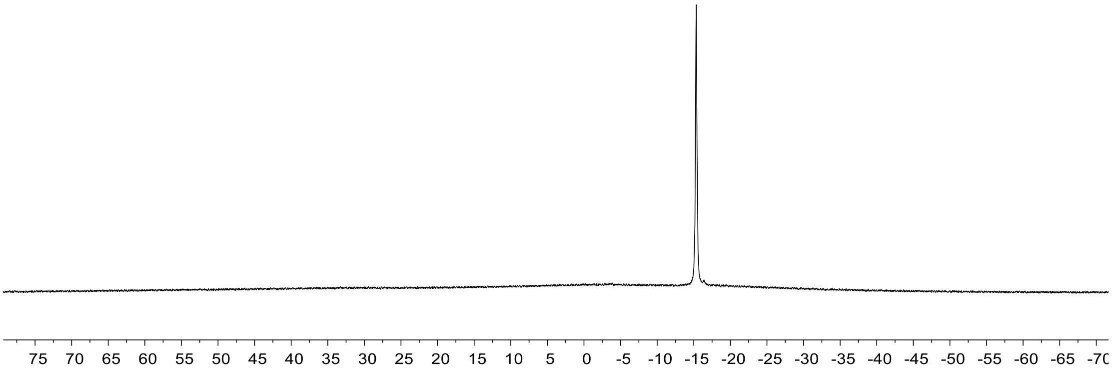
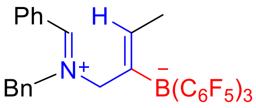


**Fig. S53** $^{11}B$ NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2m** .

## Synthesis and characterization of compound 2n



According to the procedure (B) from $B(C_6F_5)_3$ (138.2 mg, 0.27 mmol) and **1n** (66.6 mg, 0.27 mmol). The product was isolated as a yellow solid

(185.5 mg, 91% yield).

**HRMS (ESI):** m/z calcd for $C_{36}H_{19}BF_{15}N$ $[M-H]^-$: 760.1298, found 760.1295.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): δ = 8.51 (s, 1H, N=C*H*), 7.38-7.92 (m, 10H, Ph), 5.41 (br, 1H, =C*H*), 4.69-5.02 (m, 4H, NC$H_2$ and C$H_2$), 1.59 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C$H_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): δ = 170.3 (N=*C*H), 137.8, 133.2, 131.0, 130.5, 130.2, 130.1, 126.3 (Ph), 126.8 (=*C*H), 64.9 (N*C*$H_2$), 63.8 (*C*$H_2$), 16.3 (*C*$H_3$). [$C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$): δ$^1$H/δ$^{13}$C: 8.51/170.3 (N=*CH*), 5.41/126.8 (=*C*H), 5.02/64.9 (N*C*$H_2$), 4.69/63.8 (*C*$H_2$), 1.59/16.3 (*C*$H_3$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): δ = -129.6, -129.8, -130.3, -132.6, -133.6, -136.3 (each br, each 1F, *o*-$C_6F_5$), -161.5 (t, $^3J_{FF}$ = 20.5 Hz, 1F), -162.8 (d, $^3J_{FF}$ = 20.6 Hz, 1F), -163.3 (t, $^3J_{FF}$ = 20.7 Hz, 1F), (*p*-$C_6F_5$), -164.8 (m, 1F), -165.7 (m, 1F), -166.2 (m, 1F), -166.9 (m, 1F), -167.2 (br, 2F) (*m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -15.2 ($\nu_{1/2}$ ~ 40Hz).

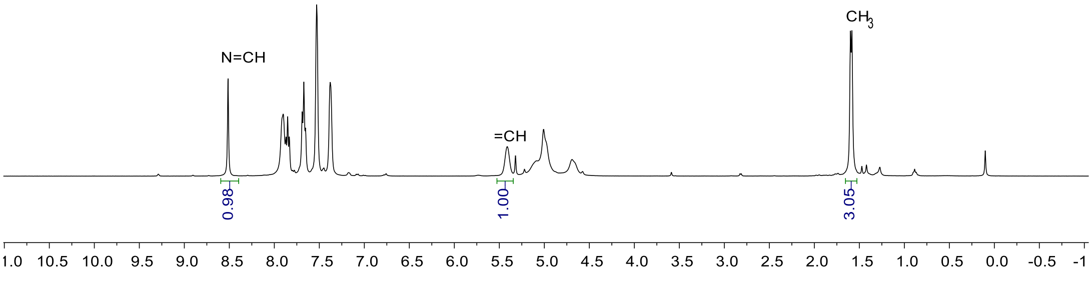


**Fig. S54** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2n**.

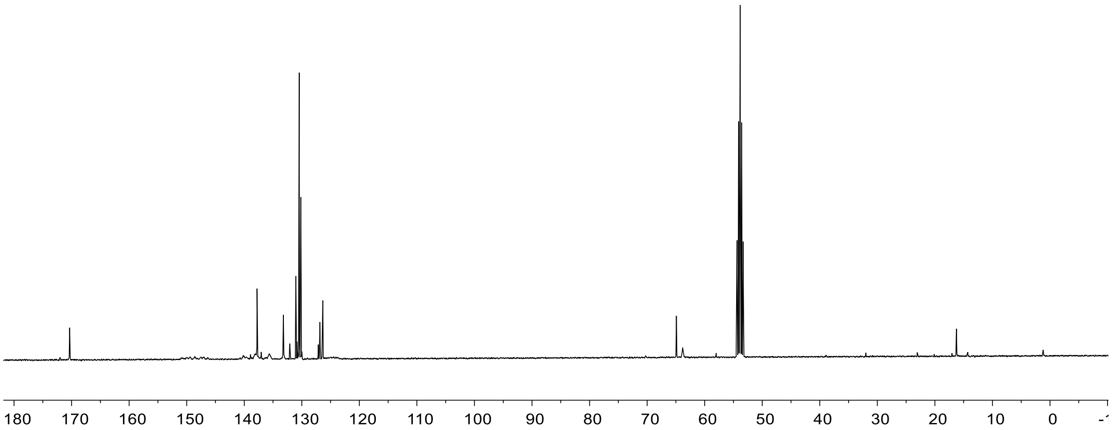


**Fig. S55** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2n**.

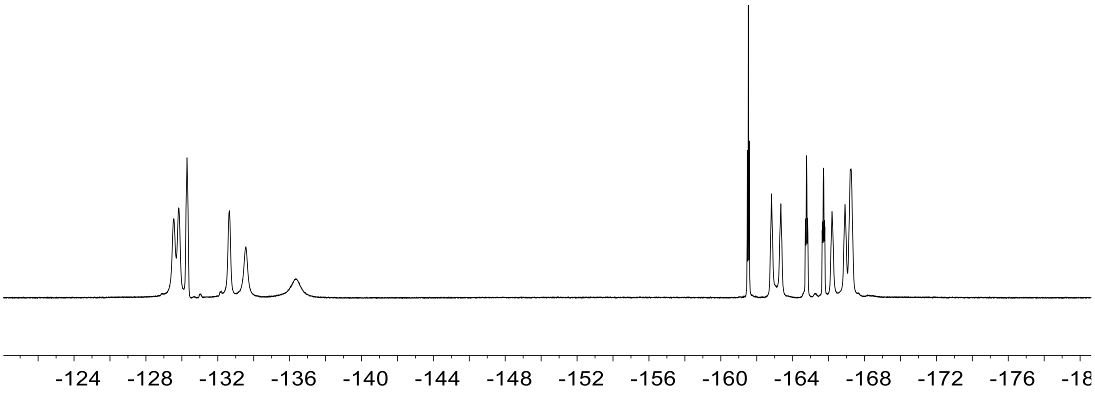


**Fig. S56** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2n**.

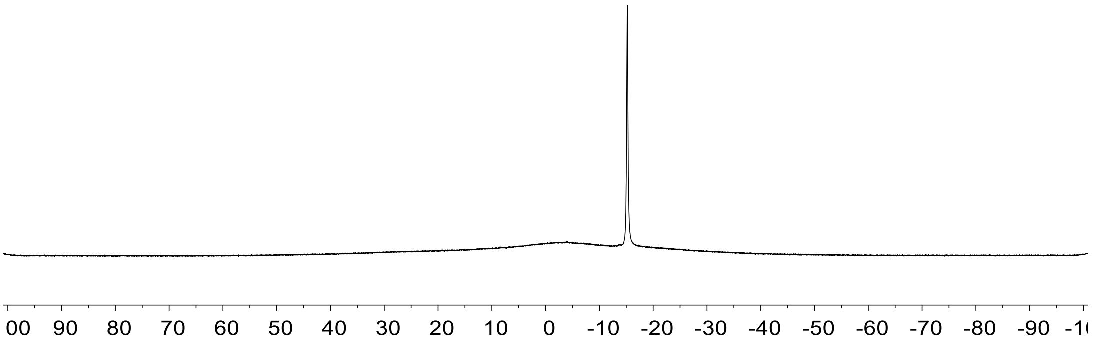
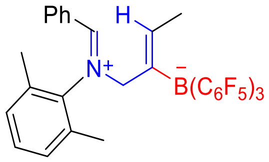


**Fig. S57** $^{11}B$ NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2n**.

## Synthesis and characterization of compound 2o



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and

**1o** (52.7 mg, 0.2 mmol). The product was isolated as a yellow solid (141.1 mg, 91% yield).

**HRMS (ESI):** m/z calcd for $C_{35}H_{25}BF_{15}N$ [M-H]$^-$: 754.1768 found 754.1772.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): δ = 8.44 (s, 1H, N=C*H*), 7.10-8.28 (m, 8H, Ph), 5.69 (br, 2H, NC$H_2$), 4.60 (br, 1H, =C*H*), 2.14 (s, 6H, C$H_3^{Ph}$), 1.54 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C$H_3$).

**$^{13}$C {$^1$H} NMR** (101 MHz, 299K, $CDCl_3$): δ = 173.9 (N=*C*H), 145.6, 139.6, 135.7, 131.2, 130.7, 129.1, 126.8 (Ph and =*C*H), 65.2 (N*C*$H_2$), 18.5 and 18.2 (*C*$H_3^{Ph}$), 15.7 (*C*$H_3$). [$C_6F_5$ and BC not listed]

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): δ = -129.2 (1F), -130.5 (1F), -130.9 (1F), -132.6 (1F), -133.5 (2F) (each m, *o*-$C_6F_5$), -160.9 (t, $^3J_{FF}$ = 20.6 Hz), -161.4 (m), -161.8 (m), (each 1F, *p*-$C_6F_5$), -164.2 (1F), -165.2 (2F), -165.3 (1F), -165.6 (1F), -165.8 (1F), -166.4 (1F) (each m, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -14.9 ($\nu_{1/2}$ ~ 50Hz).

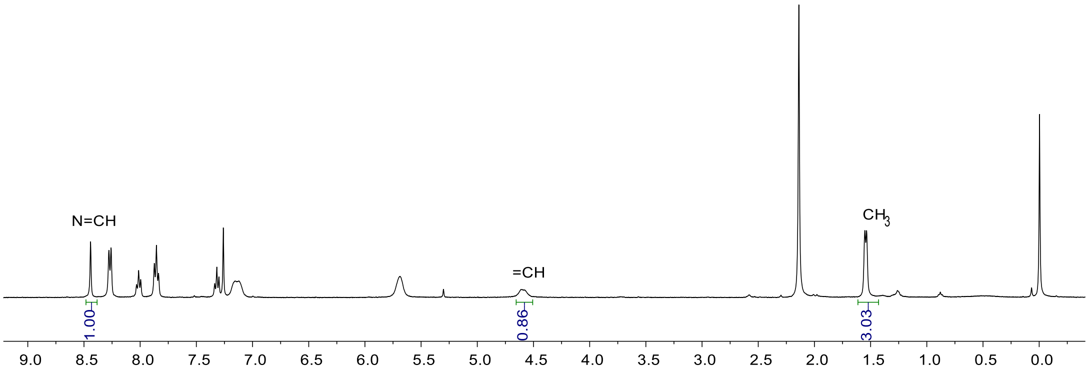


**Fig. S58** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2o**.

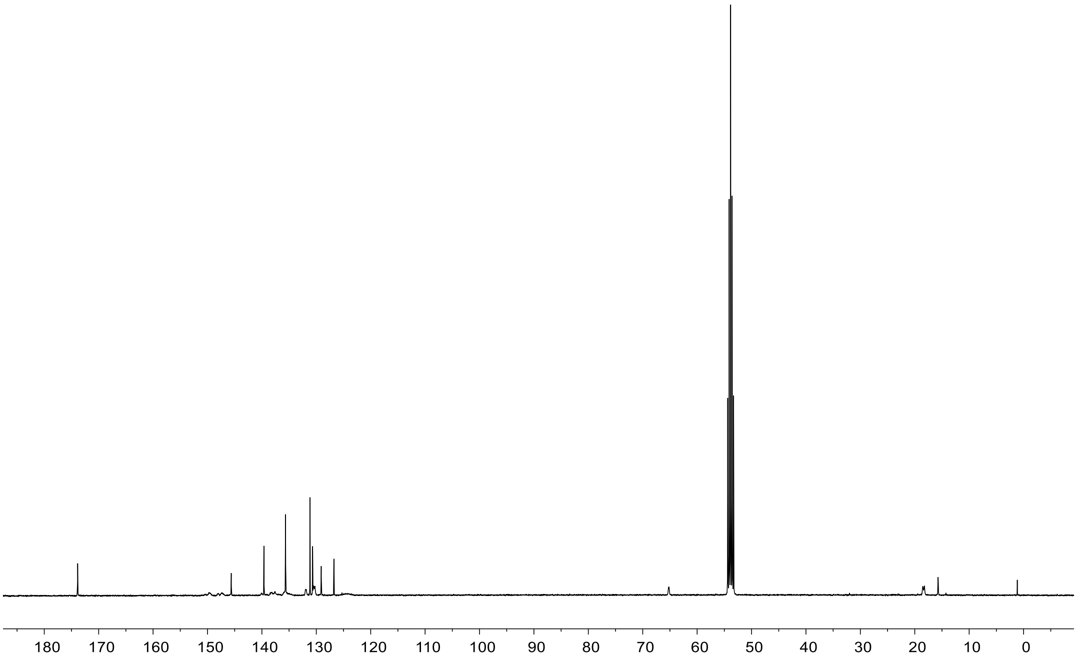


**Fig. S59** $^{13}C\ \{^{1}H\}$ NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **2o**.

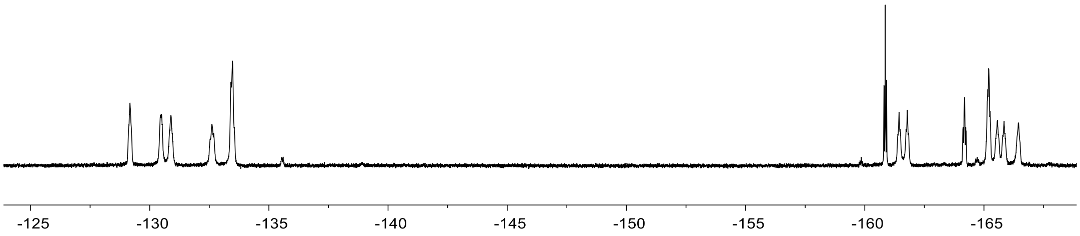


**Fig. S60** $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2o**.

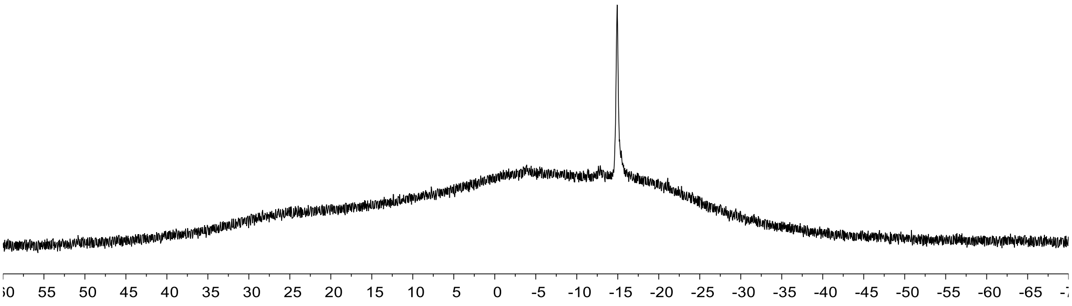
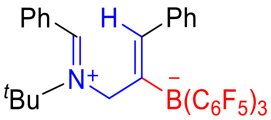


**Fig. S61** $^{11}B$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2o**.

## Synthesis and characterization of compound 2p



According to the procedure (B) from $B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) and **1p** (55.5 mg, 0.2 mmol). The product was isolated as a white solid (150.0 mg, 95% yield).

**HRMS (ESI):** m/z calcd for $C_{38}H_{23}BF_{15}N$ $[M+Na]^+$: 812.1576 found 812.1586.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): δ = 8.97 (s, 1H, N=C*H*), 8.08 (m, 2H), 7.88 (m, 1H), 7.74 (m, 2H), 7.00 (m, 3H), 6.81 (m, 2H) (Ph), 6.25 (br, 1H, =C*H*), 5.15 (m, 2H, NC*H*$_2$), 1.76 (s, 9H, C*H*$_3^{tBu}$),.

**$^{13}$C {$^1$H} NMR** (101 MHz, 299K, $CDCl_3$): δ = 170.1 (N=*C*H), 138.8, 137.6, 133.3, 132.1, 130.3, 127.7, 127.4, 126.3, 126.2 (Ph and =*C*H), 72.2 (N*C*$^{tBu}$), 61.0 (N*C*H$_2$), 29.5 (*C*H$_3^{tBu}$). [$C_6F_5$ and BC not listed]

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): δ = -128.1 (m, 1F), -129.0 (br, 2F), -129.6 (br, 2F), -130.6 (m, 1F) (*o*-$C_6F_5$), -160.2 (t, $^3J_{FF}$ = 20.7 Hz), -162.o (t, $^3J_{FF}$ = 20.5 Hz), -162.1 (t, $^3J_{FF}$ = 20.5 Hz) (each 1F, *p*-$C_6F_5$), -163.6 (m, 1F), -165.3 (m, 1F), -166.6 (br, 4F) (*m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -15.2 ($\nu_{1/2}$ ~ 40Hz).

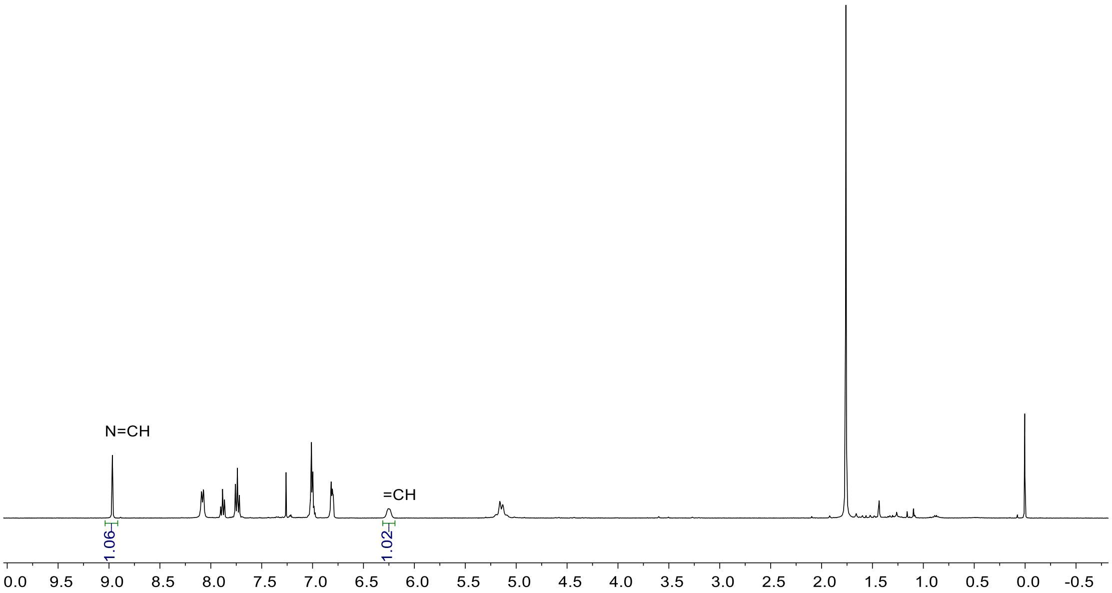


**Fig. S62** $^{1}H$ NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2p**.

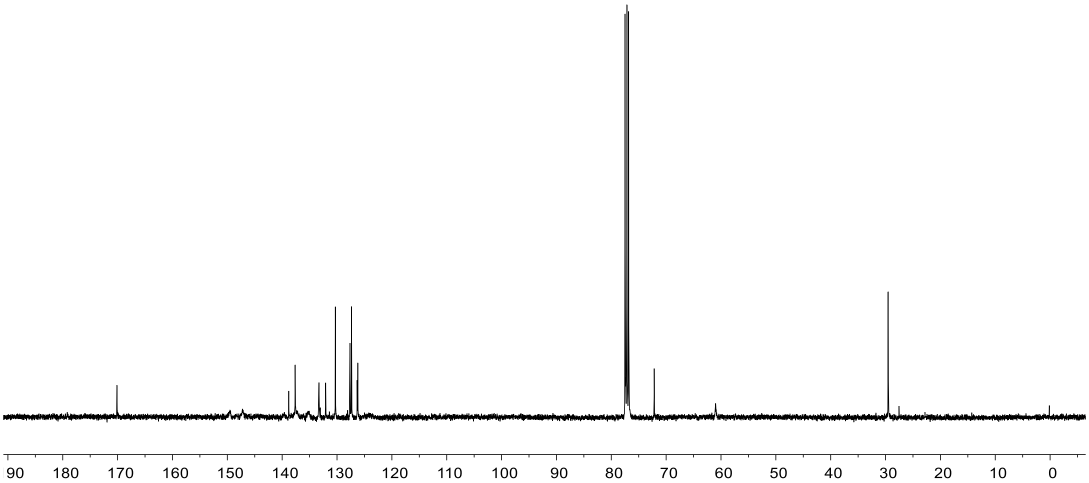


**Fig. S63** $^{13}C$ {$^{1}H$} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **2p**.

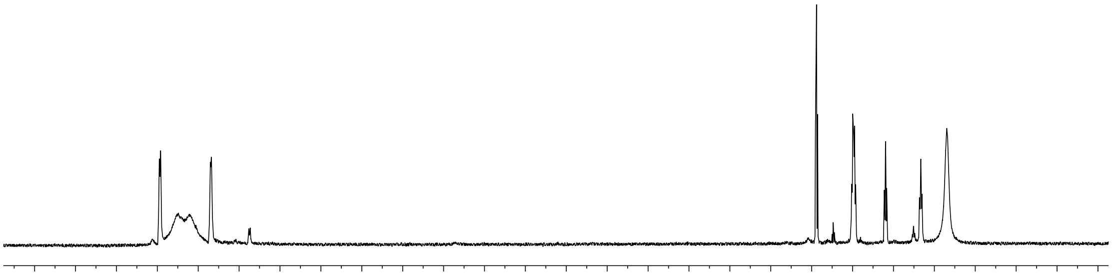


**Fig. S64** $^{19}F${$^{1}H$} NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2p**.

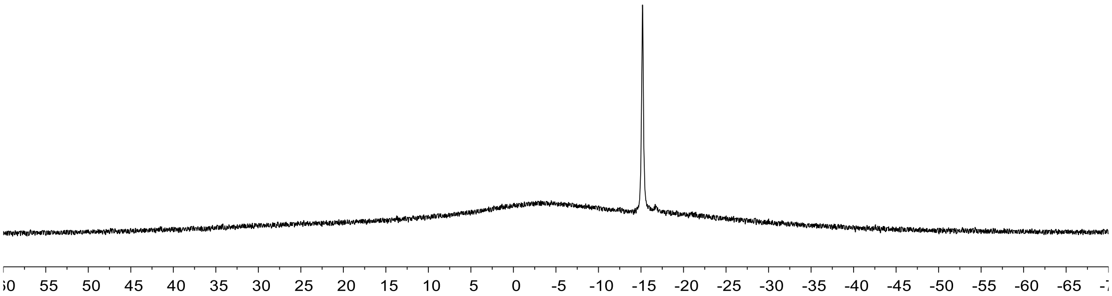
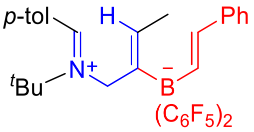


**Fig. S65** $^{11}$B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2p**.

## Synthesis and characterization of compound 2d-a



According to the procedure (B) from $Ph(CH)_2B(C_6F_5)_2$ (112.9 mg, 0.25 mmol) and compound **1d** (57.8 mg, 0.25 mmol). The product was isolated as a yellow solid (162.3 mg, 95% yield).

**HRMS (ESI):** m/z calcd for $C_{36}H_{30}BF_{10}N$ $[M+Na]^+$: 700.2204, found 700.2207.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): $\delta = 8.63$ (s, 1H, N=C*H*), 7.04-7.93 (m, 9H, Ph), 7.28 (br, 1H) and 6.15 (d, $^3J_{HH} = 17.9$ Hz, 1H) (C*H*=C*H*), 5.15 (q, $^3J_{HH} = 7.3$ Hz, 1H, =C*H*), 4.76 (br, 2H, NC$H_2$), 2.49 (s, 3H, $CH_3^{Ph}$), 1.58 (s, 12H, $CH_3^{tBu}$ and $CH_3$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CDCl_3$): $\delta = 166.8$ (N=*C*H), 149.9, 141.7, 134.8, 131.0, 128.3, 125.8, 123.9 (Ph), 131.9 and 125.6 (*C*H=*C*H), 125.5 (=*C*H), 69.9 ($NC^{tBu}$), 61.1 (N$CH_2$), 29.2 ($CH_3^{tBu}$), 22.3 ($CH_3^{Ph}$), 16.8 ($CH_3$). [$C_6F_5$ and BC not listed]

**$^{1}$H, $^{1}$H NOESY** (101 MHz/101 MHz, 299K, $CDCl_3$) [selected traces]: $\delta^{1}$H/$\delta^{1}$H: 8.63/1.58 (N=C*H*/C*H*$_3^{tBu}$), 6.15/1.58 (C*H*=C*H*/C*H*$_3$), 5.15/1.58 (=C*H*/C*H*$_3$), 4.76/1.58 (NC*H*$_2$/C*H*$_3^{tBu}$).

**$^{1}$H, $^{13}$C GHSQC** (400 MHz/101 MHz, 299K, $CDCl_3$): $\delta^{1}$H/$\delta^{13}$C: 8.63/166.8 (N=*CH*), (7.28, 6.15)/(131.9, 125.6) (*CH*=*CH*), 5.15/125.5 (=*CH*), 4.76/61.1 (N*CH*$_2$), 1.58/29.2 (*CH*$_3^{tBu}$), 1.58/16.8 (*CH*$_3$).

**$^{19}$F{$^{1}$H} NMR** (377 MHz, 299K, $CDCl_3$): δ = -130.1 (m, 4F, *o*-$C_6F_5$), -162.6 (m, 2F, *p*-$C_6F_5$), -165.7 (m, 4F, *m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -13.8 ($\nu_{1/2}$ ~ 60Hz).

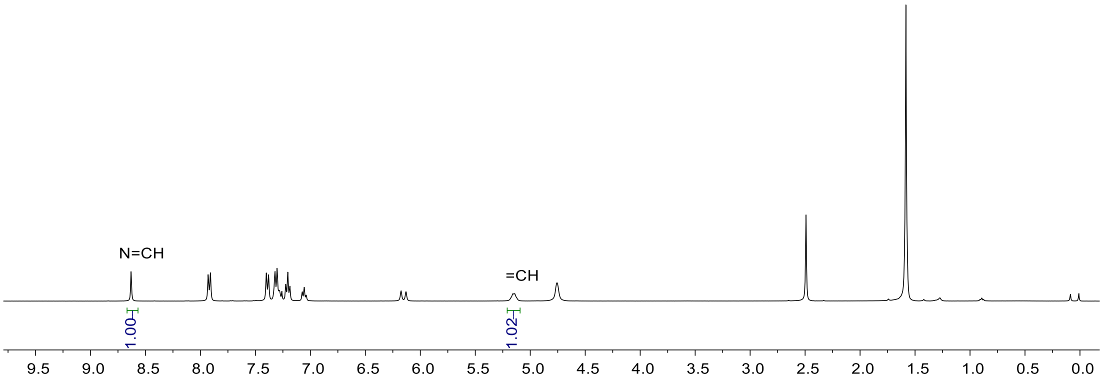


**Fig. S66** $^{1}$H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2d-a**.

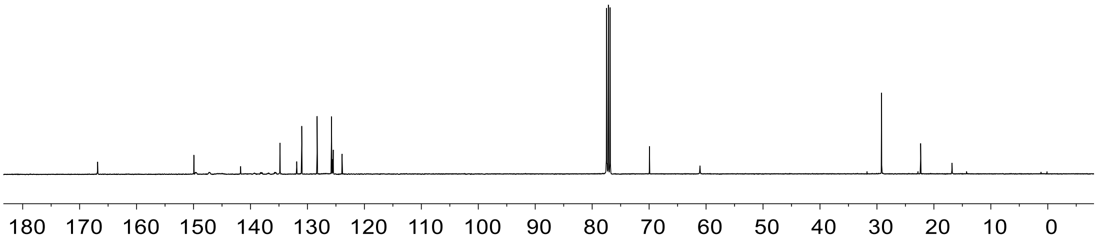


**Fig. S67** $^{13}$C{$^{1}$H} NMR (101 MHz, 299K, $CDCl_3$) spectrum of compound **2d-a**.

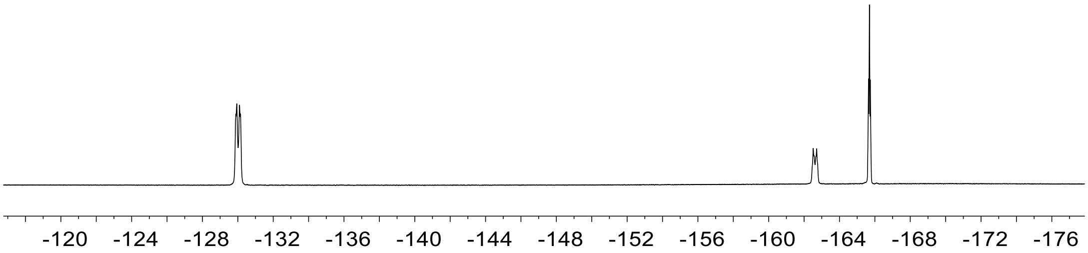


**Fig. S68** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2d-a**.

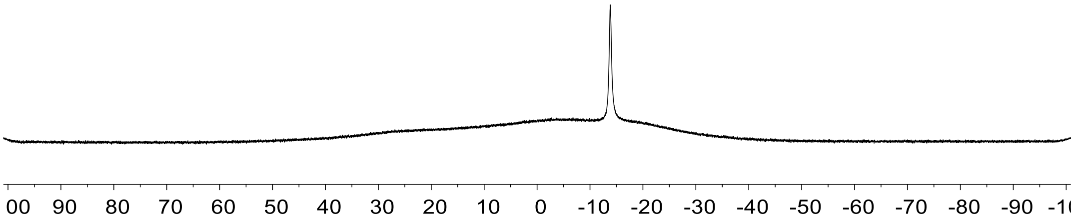
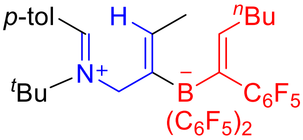


**Fig. S69** $^{11}B$ NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2d-a**.

## Synthesis and characterization of compound 2d-b



According to the procedure (B) from $^nBuCH(C_6F_5)B(C_6F_5)_2$ (110.4 mg, 0.25 mmol) and compound **1d** (57.3 mg, 0.25 mmol). The product was isolated as a yellow solid (153.3 mg, 91% yield).

**HRMS (ESI):** m/z calcd for $C_{40}H_{33}BF_{15}N$ $[M+Na]^+$: 846.2359, found 846.2357.

**$^1$H NMR** (400 MHz, 299K, $CD_2Cl_2$): $\delta = 8.72$ (s, 1H, N=C$H$), 7.85 (d, $^3J_{HH} = 8.0$ Hz, 2H) and 7.38 (d, $^3J_{HH} = 8.0$ Hz, 2H) (Ph), 5.89 (br, 1H, =C$H^{nBu}$), 5.19 (br, 1H, =C$H$), 4.92 (d, $^2J_{HH} = 16.8$ Hz, 1H) and 4.68 (d, $^2J_{HH} = 16.9$ Hz, 1H) (NC$H_2$), 2.51 (s, 3H, C$H_3^{Ph}$), 1.71 (m, 2H) and 1.11-1.23 (m, 4H)

($CH_2^{nBu}$), 1.60 (s, 9H, $CH_3^{tBu}$), 1.49 (d, $^3J_{HH}$ = 7.1 Hz, 3H, $CH_3$), 0.76 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $CH_3^{nBu}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): δ = 167.9 (N=*C*H), 150.2, 134.6, 131.0, 124.4 (Ph), 141.4 (=$CH^{nBu}$), 127.9 (=*C*H), 70.6 ($NC^{tBu}$), 61.3 (N$CH_2$), 31.7, 31.6, 22.7($CH_2^{nBu}$), 29.3 ($CH_3^{tBu}$), 22.3 ($CH_3^{Ph}$), 17.6 ($CH_3$), 14.0 ($CH_3^{nBu}$). [$C_6F_5$ and BC not listed]

**$^1$H, $^{13}$C GHMBC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: $\delta^1$H/$\delta^{13}$C: 8.72/61.3 (N=C*H*/N*C*$H_2$), 5.89/31.7 (=$CH^{nBu}$/$CH_2^{nBu}$), 4.92/127.9 (N$CH_2$/=*C*H), 1.71/141.4 ($CH_2^{nBu}$/=$CH^{nBu}$), 1.60/29.3 ($CH_3^{tBu}$/ $CH_3^{tBu}$), 1.60/70.6 ($CH_3^{tBu}$/$NC^{tBu}$).

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CD_2Cl_2$): δ = -127.2 (br, 2F), -128.8 (br, 2F), -138.4 (m, 1F), -138.5 (m, 1F) (*o*-$C_6F_5$), -162.1 (t, $^3J_{FF}$ = 20.9 Hz, 1F), -163.2 (t, $^3J_{FF}$ = 20.4 Hz, 1F), -163.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F) (*p*-$C_6F_5$), -165.9 (m, 1F), -166.3 (m, 1F), -167.1 (m, 2F), -167.3 (m, 2F) (*m*-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CD_2Cl_2$): δ = -12.0 ($\nu_{1/2}$ ~ 30Hz).

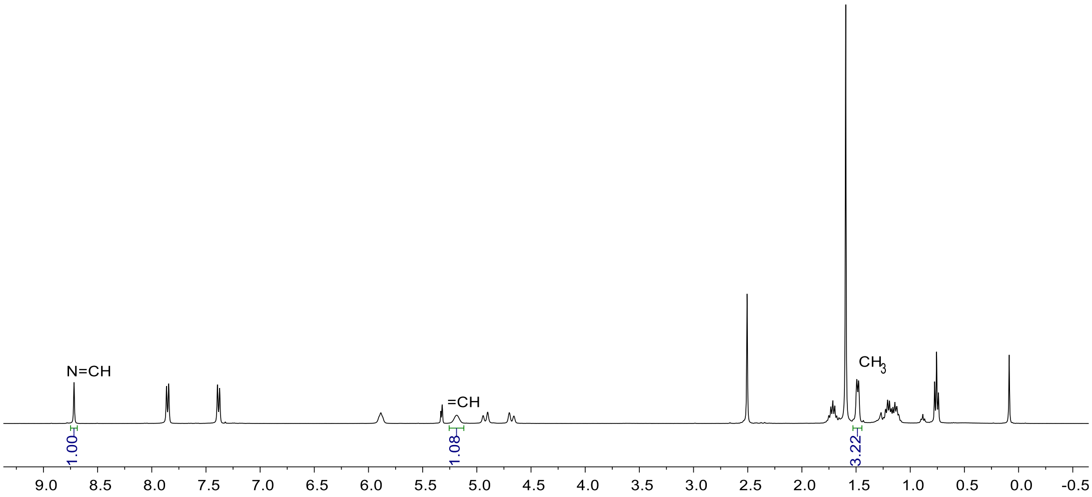


**Fig. S70** $^1$H NMR (400 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d-b**.

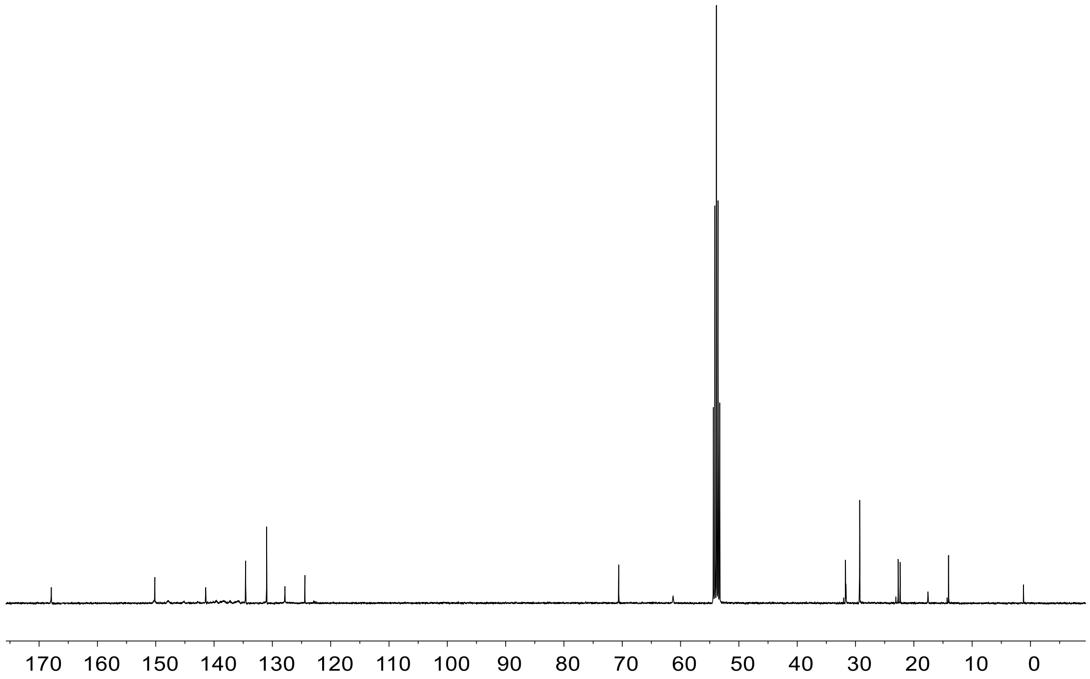


**Fig. S71** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d-b**.

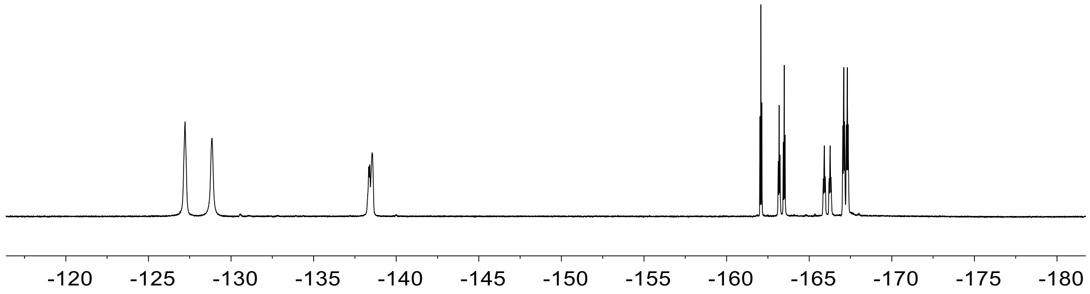


**Fig. S72** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d-b**.

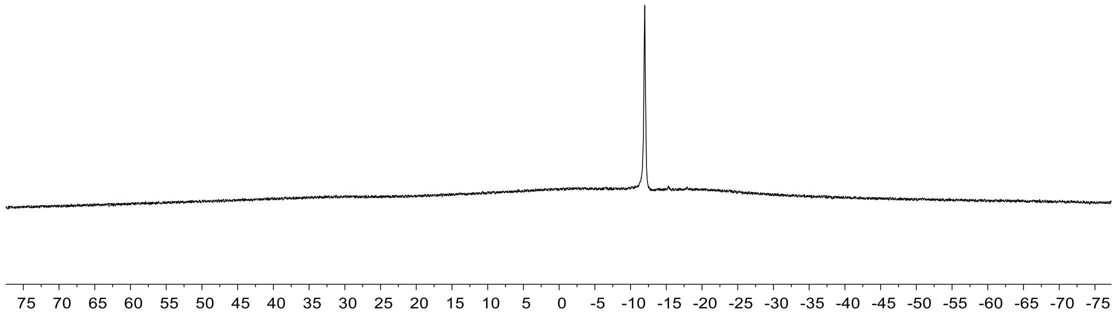
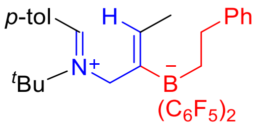


**Fig. S73** $^{11}B$ NMR (128 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d-b**.

## Synthesis and characterization of compound 2d-c



According to the procedure (B) from $Ph(CH_2)_2B(C_6F_5)_2$ (71.6 mg, 0.16 mmol) and compound **1d** (36.5 mg, 0.16 mmol). The product was isolated as a yellow solid (96.4 mg, 89% yield).

**HRMS (ESI):** m/z calcd for $C_{36}H_{32}BF_{10}N$ $[M+Na]^+$: 702.2360, found 702.2355.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): $\delta$ = 8.60 (s, 1H, N=C$H$), 7.91-6.86 (m, 9H, Ph), 4.90 (br, 1H, =C$H$), 4.72 (br, 2H, NC$H_2$), 2.49 (s, 3H, C$H_3^{Ph}$), 2.34, 2.05, 1.28 and 1.04 (each m, each 1H, C$H_2$C$H_2^{Ph}$), 1.54 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C$H_3$), 1.45 (s, 9H, C$H_3^{tBu}$).

**$^{13}$C{$^1$H} NMR** (101 MHz, 299K, $CD_2Cl_2$): $\delta$ = 167.6 (N=$C$H), 150.0, 148.9, 134.8, 131.0, 128.5, 128.3, 124.9, 124.4 (Ph), 123.4 (=$C$H), 70.1 (N$C^{tBu}$), 60.4 (N$C$H$_2$), 35.1 ($C$H$_2$), 28.8 ($C$H$_3^{tBu}$), 22.3 ($C$H$_3^{Ph}$), 16.4 ($C$H$_3$). [$C_6F_5$ and BC not listed]

**$^1$H, $^1$H NOESY** (101 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: $\delta^1$H/$\delta^1$H: 8.60/1.45 (N=C$H$/C$H_3^{tBu}$), 4.90/1.54 (=C$H$/C$H_3$), 4.72/1.45 (NC$H_2$/C$H_3^{tBu}$).

**$^1$H, $^{13}$C GHMBC** (400 MHz/101 MHz, 299K, $CD_2Cl_2$) [selected traces]: $\delta^1$H/$\delta^{13}$C: 8.60/60.4 (N=C$H$/N$C$H$_2$), 4.72/123.4 (NC$H_2$/=$C$H), 1.45/70.1 (C$H_3^{tBu}$/N$C^{tBu}$)

**$^{19}$F{$^1$H} NMR** (377 MHz, 299K, $CDCl_3$): $\delta$ = -131.4 (br, 2F), -131.8 (d, $^3J_{FF}$ = 25.0 Hz, 2F) ($o$-$C_6F_5$), -162.9 (t, $^3J_{FF}$ = 20.6 Hz, 1F), -163.4 (t, $^3J_{FF}$ = 20.6 Hz, 1F) ($p$-$C_6F_5$), -165.9 (m, 4F) ($m$-$C_6F_5$).

**$^{11}$B NMR** (128 MHz, 299K, $CDCl_3$): δ = -12.8 ($\nu_{1/2}$ ~ 50Hz).

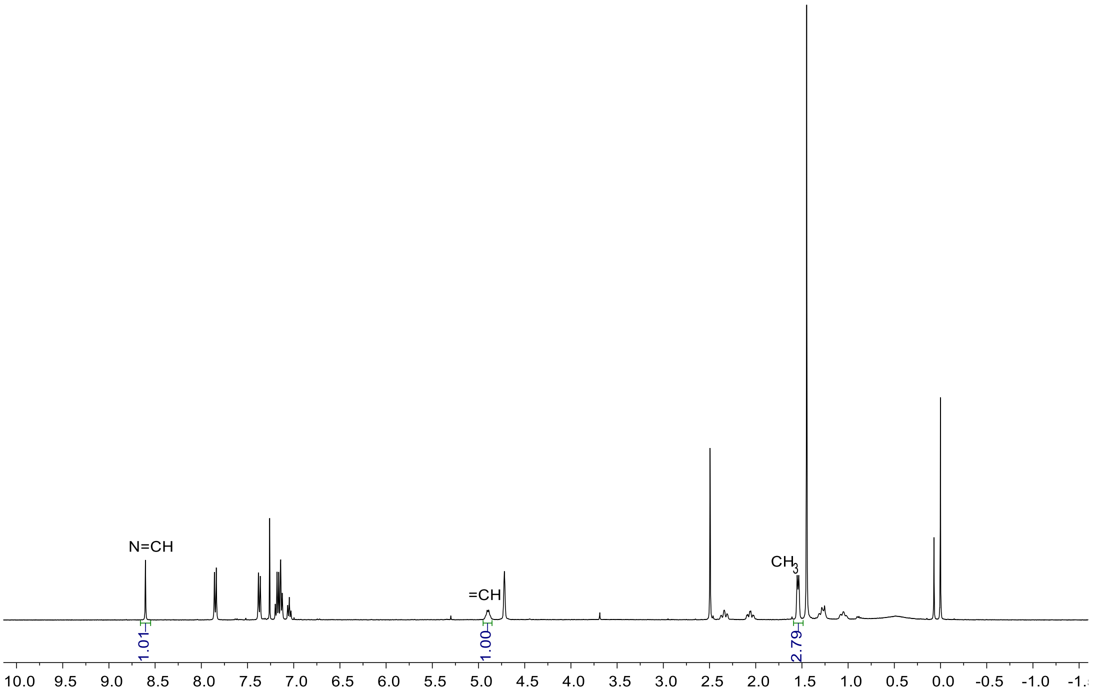


**Fig. S74** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectrum of compound **2d-c**.

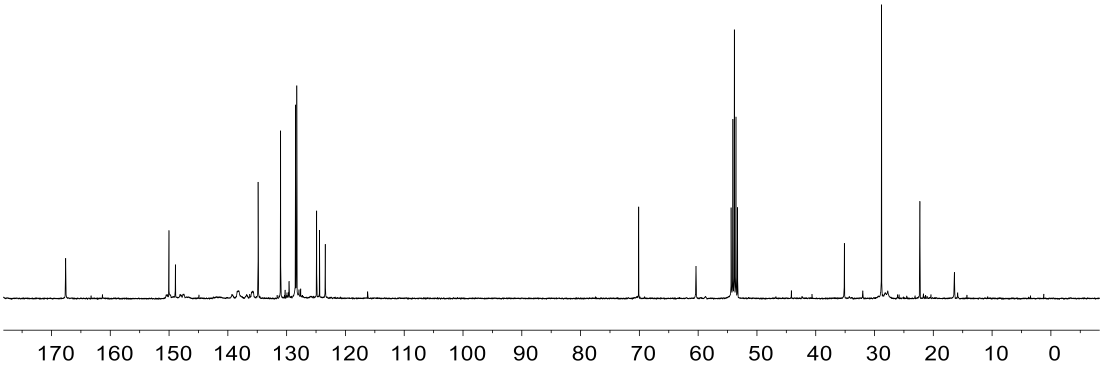


**Fig. S75** $^{13}C\{^1H\}$ NMR (101 MHz, 299K, $CD_2Cl_2$) spectrum of compound **2d-c**.

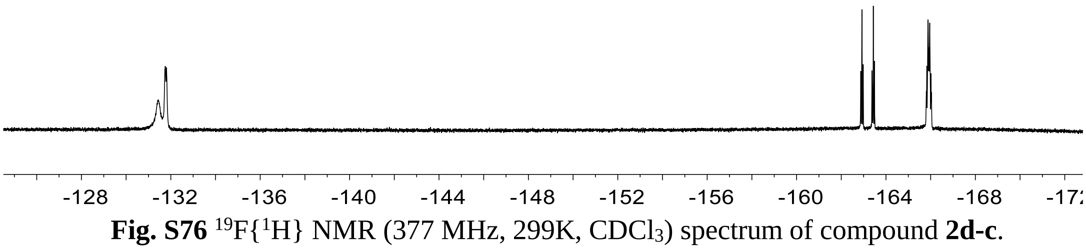


**Fig. S76** $^{19}F\{^1H\}$ NMR (377 MHz, 299K, $CDCl_3$) spectrum of compound **2d-c**.

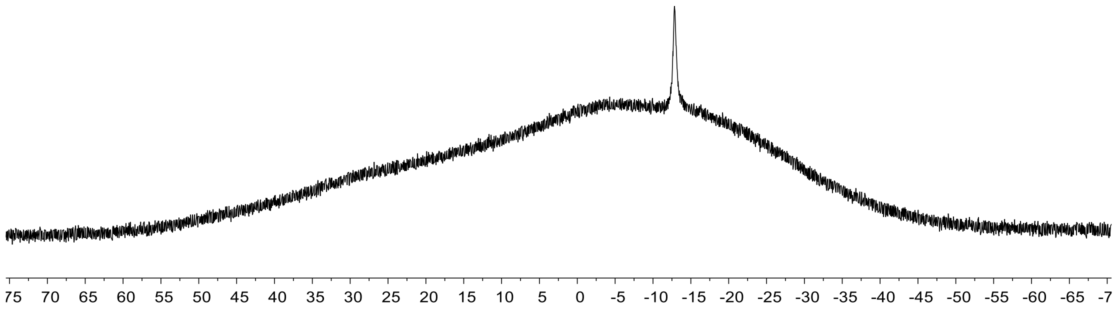
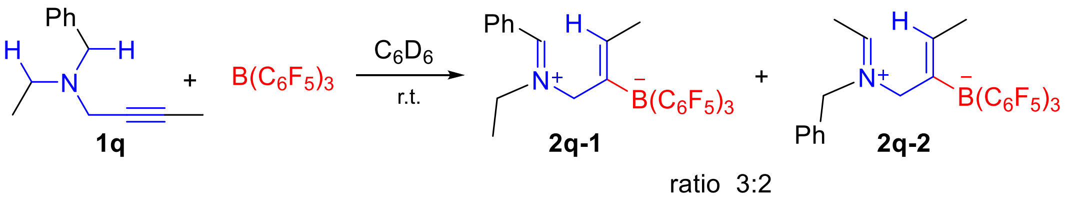


**Fig. S77** $^{11}$B NMR (128 MHz, 299K, $CDCl_3$) spectrum of compound **2d-c**.

## The reaction of 1q with $B(C_6F_5)_3$



A solution of $B(C_6F_5)_3$ (15.4 mg, 0.03 mmol) and **1q** (5.6 mg, 0.03 mmol) in $C_6D_6$ (0.6 mL) in the NMR tube was kept for 4 h at room temperature, then NMR experiments were conducted.

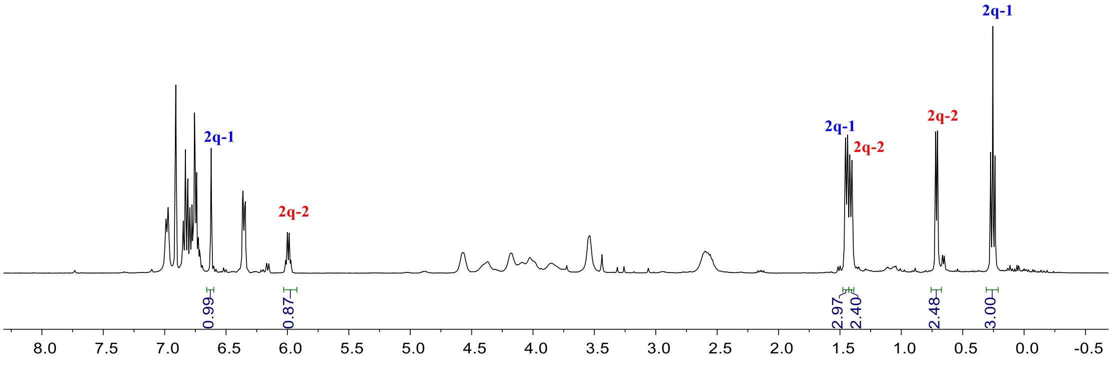


**Fig. S78** In-situ $^{1}$H NMR (400 MHz, 299K, $C_6D_6$) spectrum of reaction of **1q** with $B(C_6F_5)_3$.

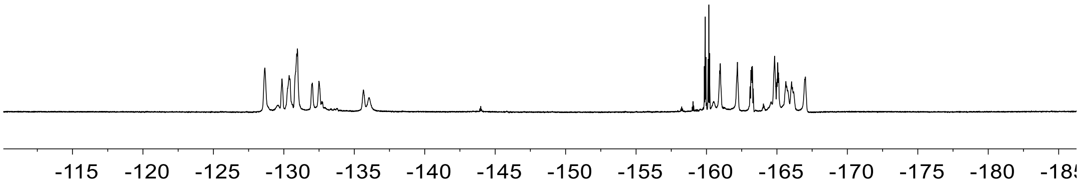


**Fig. S79** In-situ $^{19}F\{H\}$ NMR (377 MHz, 299K, $C_6D_6$) spectrum of reaction of **1q** with $B(C_6F_5)_3$.

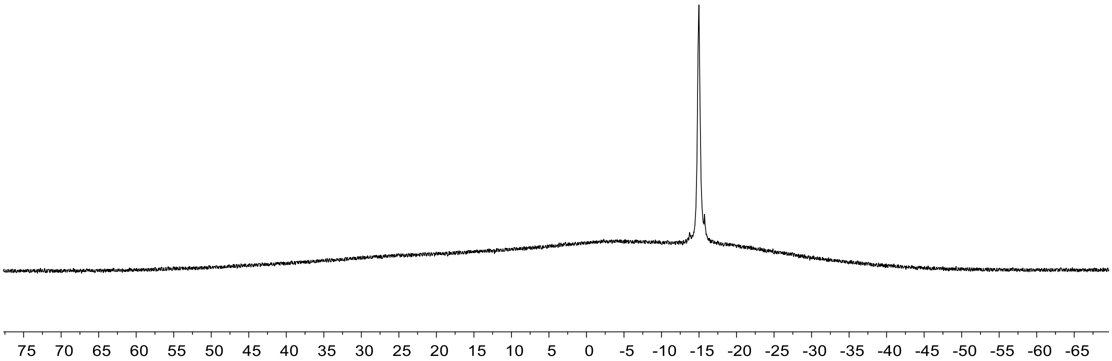
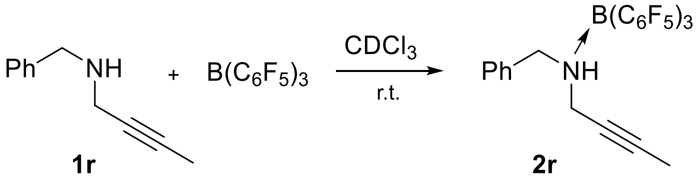


**Fig. S80** In-situ $^{11}B$ NMR (128 MHz, 299K, $C_6D_6$) spectrum of reaction of **1q** with $B(C_6F_5)_3$.

## Reactions of 1r with $B(C_6F_5)_3$



A solution of $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) and **1o** (3.2 mg, 0.02 mmol) in $CDCl_3$ (0.6 mL) in the NMR tube was kept for 4 h at room temperature, then NMR experiments were conducted.

**$^1$H NMR** (400 MHz, 299K, $CDCl_3$): $\delta$ = 7.44 (m, 5H, Ph), 6.21 (br, 1H, N$H$), 4.33 (d, $^3J_{HH}$ = 13.7 Hz, 1H) and 4.04 (t, $^3J_{HH}$ = 12.0 Hz, 1H) (PhC$H_2$), 3.66 (s, 2H, NC$H_2$), 1.60 (s, 3H, C$H_3$).

**$^{13}$C {H} NMR** (101 MHz, 299K, CDCl$_3$): δ = 139.8, 128.5, 128.5, 127.2 (Ph), 79.3 and 77.2 (*C*≡*C*), 52.6 (Ph*C*H$_2$), 38.0 (N*C*H$_2$), 3.7 (*C*H$_3$).[C$_6$F$_5$ not listed]

**$^{19}$F{H} NMR** (377 MHz, 299K, CDCl$_3$): δ = -125.8, -127.6, -128.2, -128.7, -137.0, -142.3 (each m, each 1F, *o*-C$_6$F$_5$), -155.3 (t, $^3J_{FF}$ = 20.3 Hz), -155.6 (t, $^3J_{FF}$ = 20.6 Hz), -156.2 (t, $^3J_{FF}$ = 20.5 Hz) (each 1F, *p*-C$_6$F$_5$), -160.2 (1F), -161.0 (1F), -162.3 (2F), -163.1 1F), -163.6 (1F) (each m, *m*-C$_6$F$_5$).

**$^{11}$B NMR** (128 MHz, 299K, CDCl$_3$): δ = -4.4 ($\nu_{1/2}$ ~ 300Hz).

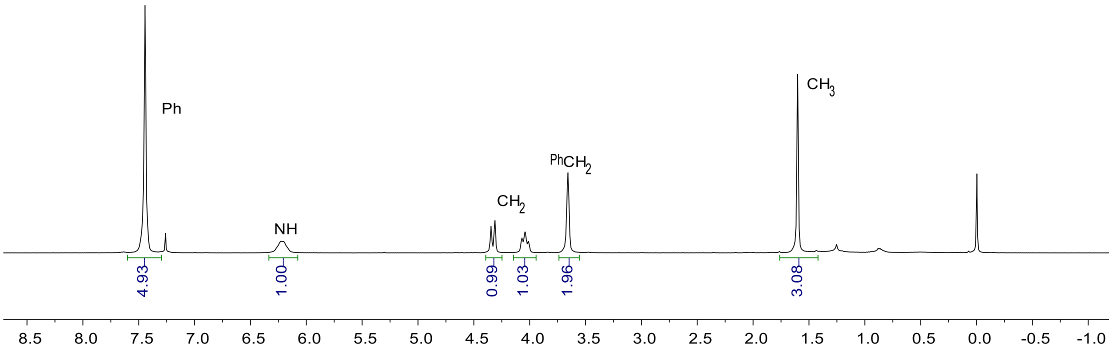


**Fig. S81** In-situ $^1$H NMR (400 MHz, 299K, C$_6$D$_6$) spectrum of the reaction of **1r** with B(C$_6$F$_5$)$_3$.

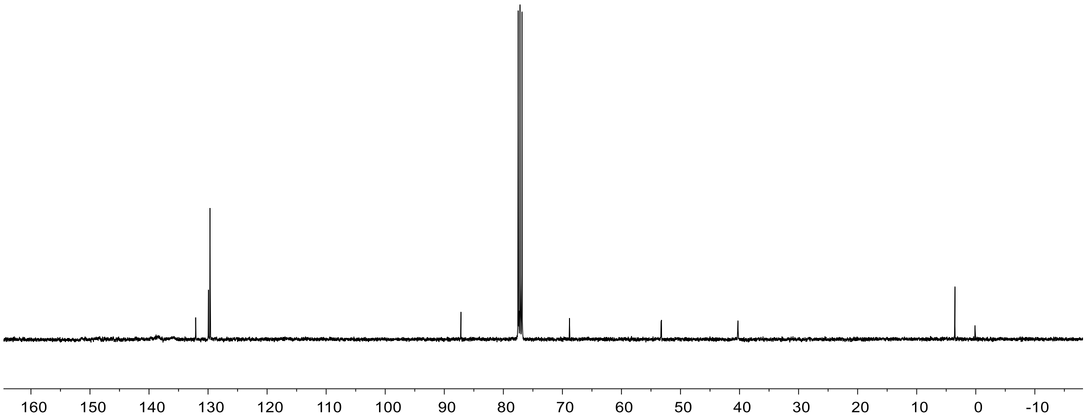


**Fig. S82** In-situ $^{13}$C {$^1$H} NMR (101 MHz, 299K, CDCl$_3$) spectrum of the reaction of **1r** with B(C$_6$F$_5$)$_3$.

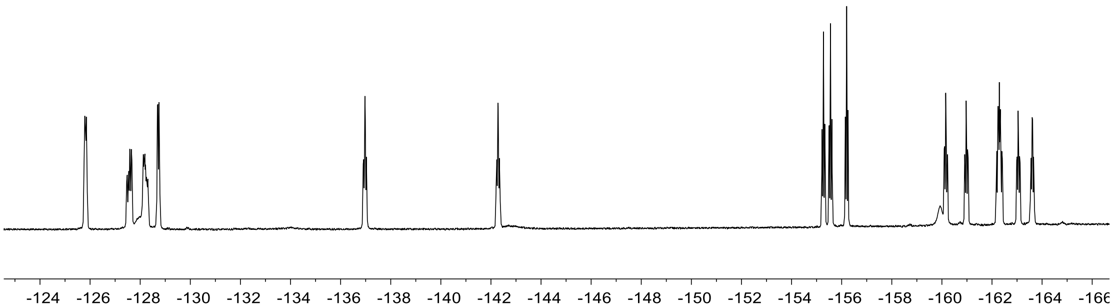


**Fig. S83** In-situ $^{19}F\{^{1}H\}$ NMR (377 MHz, 299K, $C_6D_6$) spectrum of the reaction of **1r** with $B(C_6F_5)_3$.

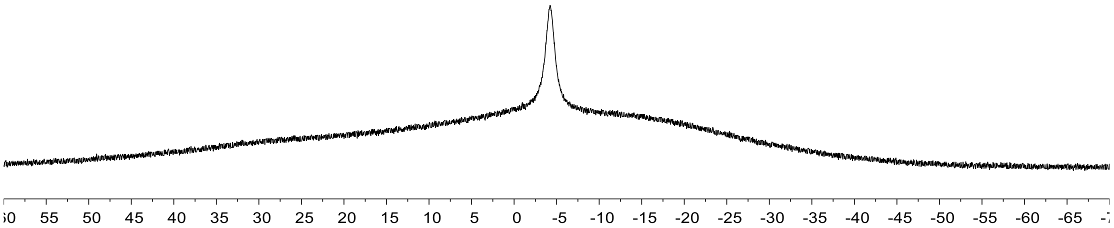
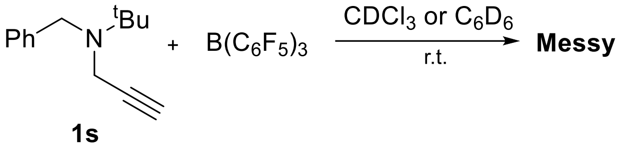


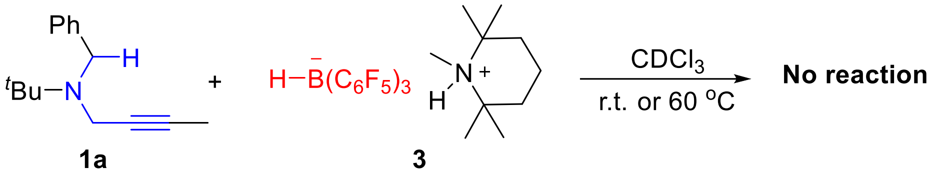
**Fig. S84** In-situ $^{11}B$ NMR (128 MHz, 299K, $C_6D_6$) spectrum of the reaction of **1r** with $B(C_6F_5)_3$.

## Reactions of 1s with $B(C_6F_5)_3$



In the NMR tube, a solution of $B(C_6F_5)_3$ (10.3 mg, 0.02 mmol) and **1s** (4.2 mg, 0.02 mmol) in $CDCl_3$ or $C_6D_6$ (0.6 mL). NMR studies showed that the reaction resulted in several products. Unfortunately, our efforts to isolate the products were not successful. We speculated that this reaction are messy due to several possible pathways which could lead to the 1,1-carboboration products, the deprotonation product and our desired *trans*-hydroboration product.

## Control experiments



**1$^{st}$ Experiment**: In an NMR tube, **1a** (4.5 mg, 1.0 equiv.) and **3**[3] (14.0 mg, 1.0 equiv.) were dissolved in CDCl$_3$ (0.6 mL). The NMR tube was kept at room temperature or heated to 60°C, then NMR experiments were conducted after 4 h.

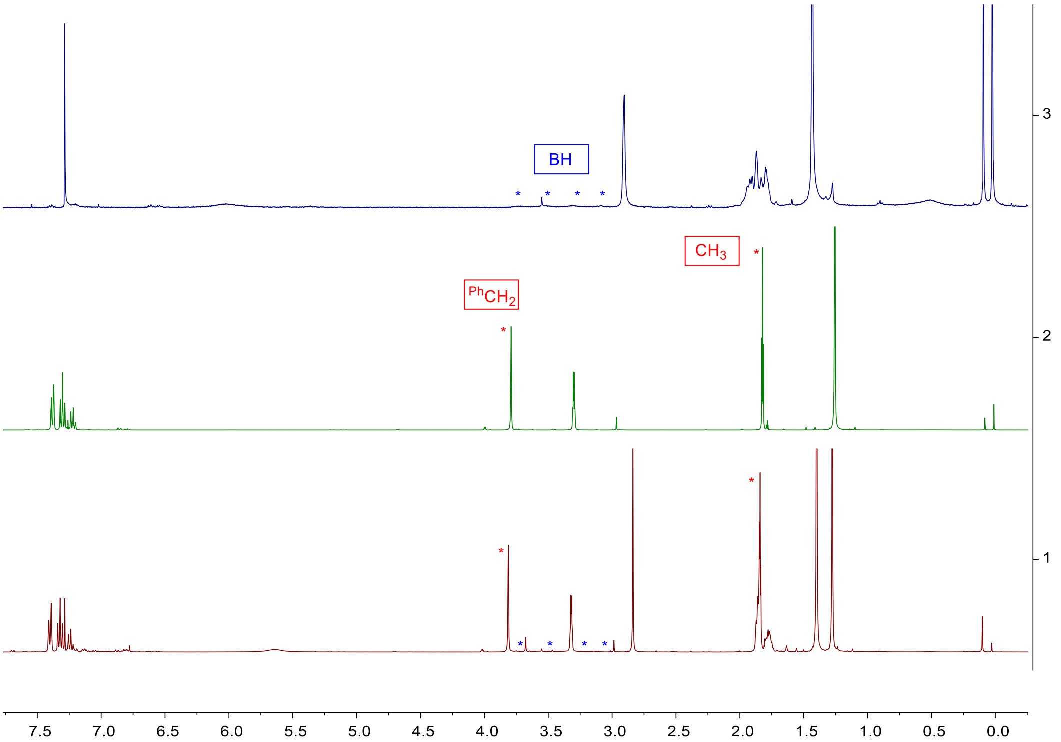
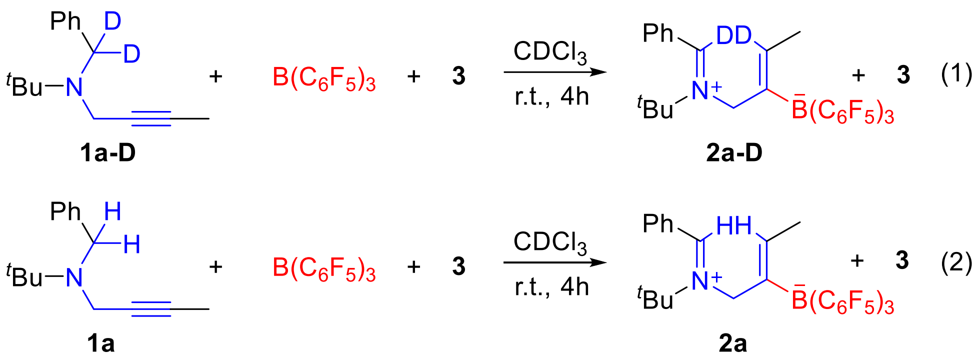


**Fig. S85** $^1$H NMR (400 MHz, 299K, CDCl$_3$) spectra of (1) in-situ reaction of **1a** and **3**, (2) compound **1a**, (3) compound **3**.



**2nd Experiments**: (1) In an NMR tube, $B(C_6F_5)_3$ (10.2 mg, 1.0 equiv.), **1a-D** (4.3 mg, 1.0 equiv.) and **3** (13.4 mg, 1.0 equiv.) were dissolved in $CDCl_3$ (0.6 mL). The NMR tube was kept at room temperature for 4 h, then NMR experiments were conducted.

(2) In an NMR tube, $B(C_6F_5)_3$ (10.2 mg, 1.0 equiv.), **1a** (4.3 mg, 1.0 equiv.) and **3** (13.4 mg, 1.0 equiv.) were dissolved in $CDCl_3$ (0.6 mL). The NMR tube was kept at room temperature for 4 h, then NMR experiments were conducted.

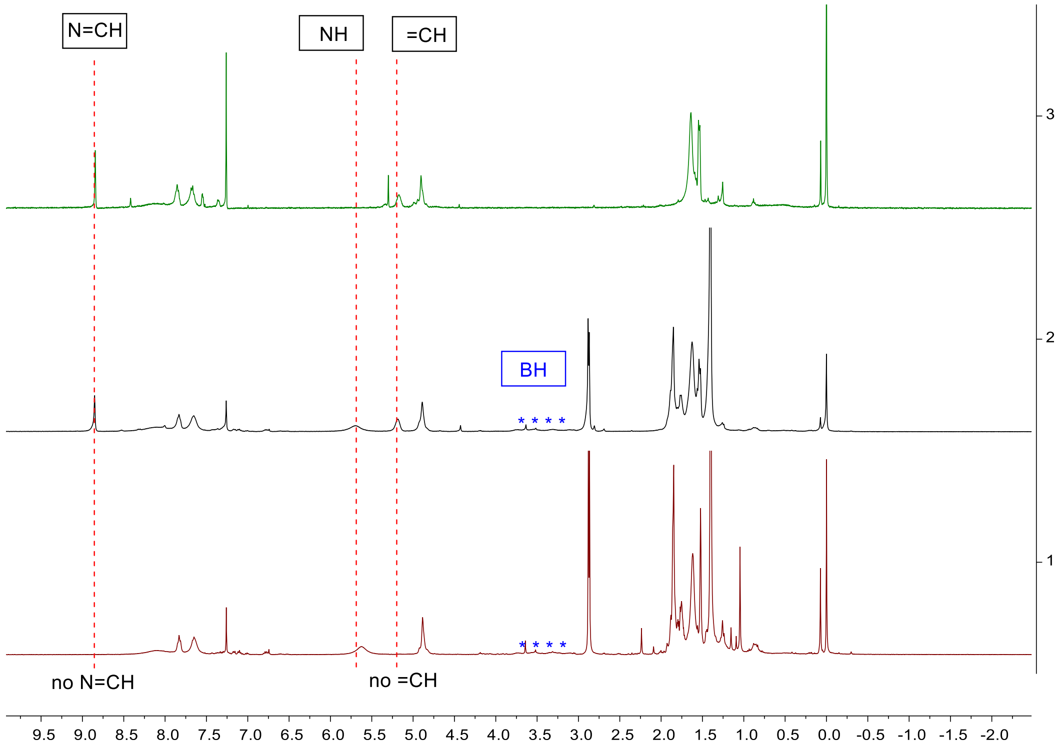
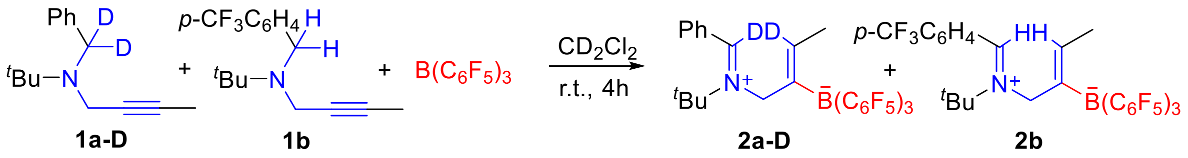


**Fig. S86** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectra of (1) in-situ reaction of **$B(C_6F_5)_3$**, **1a-D** and **3**, (2) in-situ reaction of **$B(C_6F_5)_3$**, **1a** and **3**, (3) isolated compound **2a**.



**3rd Experiment**: In an NMR tube, $B(C_6F_5)_3$ (10.3 mg, 2.0 equiv.), **1a-D** (2.2 mg, 1.0 equiv.) and **1b** (2.8 mg, 1.0 equiv.) were dissolved in $CD_2Cl_2$ (0.6 mL). The NMR tube was kept at room temperature for 4 h, then NMR experiments were conducted.

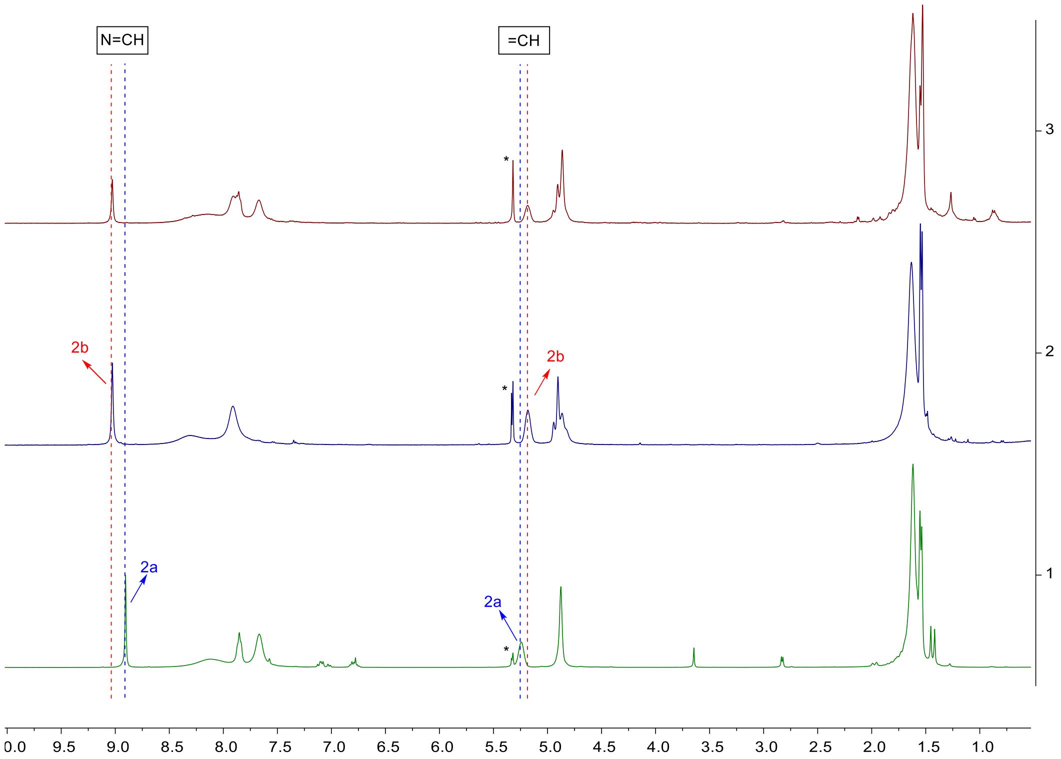
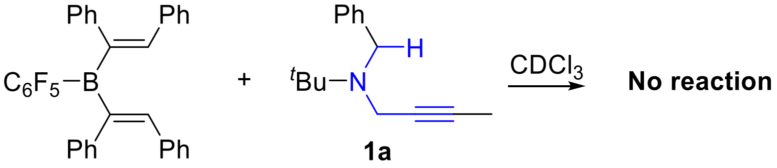
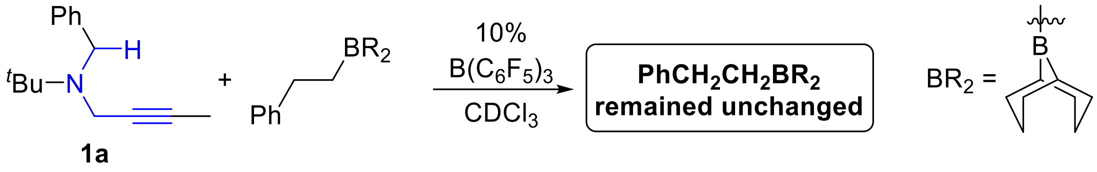


**Fig. S87** $^1$H NMR (400 MHz, 299K, $CDCl_3$) spectra of (1) isolated compound **2a**, (2) isolated compound **2b**, (3) in-situ reaction of $B(C_6F_5)_3$, **1a-D** and **1b**. (*$CD_2Cl_2$)

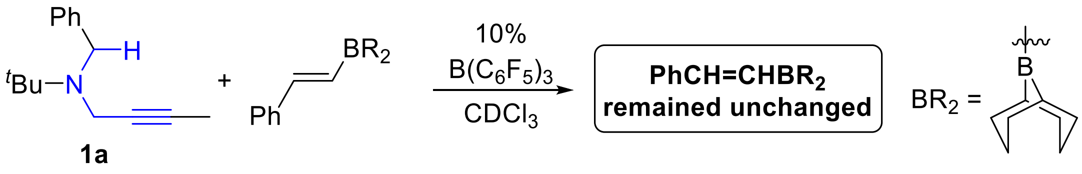
## Reactions of 1a with different boranes



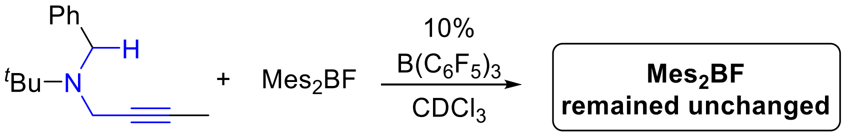
**1st Experiments**: In the NMR tube, a solution of $(PhCH{=}CPh)_2B(C_6F_5)$ was in-situ generated by the reaction of $C_6F_5BH_2{\cdot}SMe_2$ (10.0 mg, 0.04 mmol) and 1,2-diphenylethyne (14.8 mg, 0.08 mmol) at room temperature in $CDCl_3$ (0.6 mL), then **1a** (8.9 mg, 0.04 mmol) was added. NMR studies showed that both of the starting materials kept unchanged at room temperature or at elevated temperature (80 °C).



**2nd Experiment**: In the NMR tube, a solution of $PhCH_2CH_2BR_2$ was in-situ generated by the reaction of styrene (4.2 mg, 0.04 mmol) and 9-BBN dimer (4.9 mg, 0.02 mmol) at room temperature in $CDCl_3$ (0.6 mL), then $B(C_6F_5)_3$ (2.1 mg, 0.004 mmol) and **1a** (8.7 mg, 0.04 mmol) was added. NMR studies showed that (i) $PhCH_2CH_2BR_2$ remained unchanged at room temperature or at elevated temperature (80 °C), and (ii) **1a** were also unchanged except that a small part of **1a** reacted with the catalytic $B(C_6F_5)_3$.



**3rd Experiment**: In the NMR tube, a solution of $PhCH=CHBR_2$ was in-situ generated by the reaction of PhCCH (4.1 mg, 0.04 mmol) and 9-BBN dimer (4.8 mg, 0.02 mmol) at room temperature in $CDCl_3$ (0.6 mL), then $B(C_6F_5)_3$ (2.0 mg, 0.004 mmol) and **1a** (8.8 mg, 0.04 mmol) was added. NMR studies showed that (i) $PhCH=CHBR_2$ remained unchanged at room temperature or at elevated temperature (80 °C), and (ii) **1a** were also unchanged except that a small part of **1a** reacted with the catalytic $B(C_6F_5)_3$.



**1a**

**4th Experiment**:A solution of $Mes_2BF$ (10.8 mg, 0.04 mmol), $B(C_6F_5)_3$ (2.2 mg, 0.004 mmol) and **1a** (4.7 mg, 0.04 mmol) in $CDCl_3$ (0.6 mL) in the NMR tube. NMR studies showed that (i) $Mes_2BF$ remained unchanged at room temperature or at elevated temperature (80 °C), and (ii) **1a** were also unchanged except that a small part of **1a** reacted with the catalytic $B(C_6F_5)_3$.

## References:

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