Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

An olefin-based multi-component reaction to yield 1,2-azaborolidine derivatives

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Content

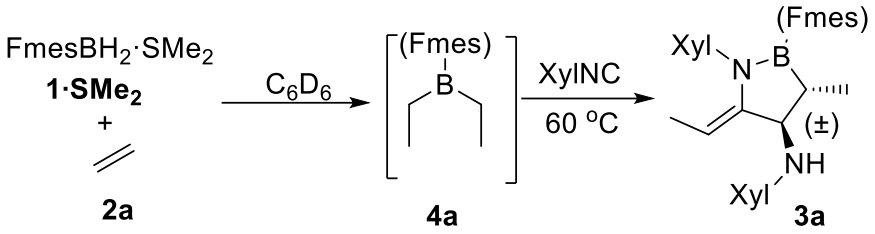
Experimental Procedures

General Information. All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. All solvents were dried and degassed before use, if necessary for the respective reaction. Chemicals: Unless otherwise noted all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: HRMS: Thermo Scientific Orbitrap LTQ XL; NMR: Varian UNITY plus. NMR: Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{11}B, 192 MHz; ^{19}F, 564 MHz). ^{1}H and ^{13}C NMR chemical shifts are given relative to tetramethylsilane (TMS) and referenced to the solvent signal. ^{19}F and ^{11}B are referenced according to the proton resonance of TMS as the primary reference for the unified chemical shift scale (IUPAC recommendation 2001: R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* 2001, **73**, 1795-1818]. NMR assignments were supported by 2D NMR experiments.

X-Ray diffraction: Data sets for compound **3e** were collected with a Bruker D8 Venture Photon III Diffractometer. Data sets for compounds **3a**, **3b**, **3d** und **3f** were collected with a Bruker APEX II CCD Diffractometer. Programs used: data collection: APEX3 V2019.1-0[1] (Bruker AXS Inc., **2019**); cell refinement: SAINT V8.40A (Bruker AXS Inc., **2019**); data reduction: SAINT V8.40A (Bruker AXS Inc., **2019**); absorption correction, SADABS V2016/2 (Bruker AXS Inc., **2019**); structure solution *SHELXT-2015*[2] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015*[3] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP*[4] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections. *Exceptions and special features*: For compound **3d** one $SiMe_3$ group, for compound **3e** a part of the BOB co-crystallized molecule and for compound **3f** one CF_3 group were found disordered over two or three positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Additionally, for compounds **3e** and **3f** a half badly disordered pentane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (**2015**). Acta Cryst. C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule.

Materials: Borane **1** was prepared according to a procedure described in the literature.[5]

Preparation of compound 3a



Scheme S1

At room temperature, the solution of borane **1·SMe$_2$** (71.2 mg, 0.2 mg, 1 equiv.) in C_6D_6 (1 mL) was added to a J. Young tube. The mixture was degassed and refilled with ethene (1.5 bar). Then the resulting mixture was shake at room temperature for 10 min. 2,6-dimethylphenyl isocyanide (52.4 mg, 0.4 mmol, 2 equiv.) was added to give a yellow solution. The yellow solution was stored at 60 ^{o}C overnight. All the volatiles were removed in vacuum, and the residue was dissolved in pentane (1 mL) and was stored at -35 ^{o}C to give the product as pale-yellow solid (45 mg, 37% yield).

HRMS for $C_{31}H_{30}BF_9N_2H^+$ $[M+H]^+$: calc. 613.2437, found: 613.2433.

^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K): δ = 8.11 (m, 1H, *m*-Fmes), 7.88 (m, 1H, *m*'-Fmes), 7.01 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, *m*-Xyl^a), 6.98 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-Xyl^b), 6.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-Xyl^a), 6.80 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ =1.6 Hz, 1H, *m*'-Xyl^a), 6.76 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-Xyl^b), 5.32 (qd, $^3J_{HH}$ = 7.4 Hz, *J* = 2.1 Hz, 1H, CH=), 4.14 (ddm, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 9.1 Hz, 1H, NCH), 3.30 (d, $^3J_{HH}$ = 11.0 Hz, 1H, NH), 2.37 (s, 6H, *o*-CH_3^{Xylb}), 2.27 (s, 3H, *o*-CH_3^{Xyla}), 1.96 (s, 3H, *o*'-CH_3^{Xyla}), 1.94 (m, 1H, BCH), 0.94 (dd, $^3J_{HH}$ = 7.4 Hz, *J* = 2.2 Hz, 3H, CH_3CH=), 0.73 (d, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3CH).

^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K): δ = 148.3 (NC=), 146.4 (*i*-Xyl^b), 140.4 (*i*-Xyl^a), 139.4 (br, *i*-Fmes), 136.1 (*o*-Xyl^a), 134.8 (m, *o*-Fmes, *o*'-Fmes), 133.2 (*o*'-Xyl^a), 131.9 (q, $^2J_{FC}$ = 34.5 Hz, *p*-Fmes), 129.3 (*m*-Xyl^b), 129.0 (*m*-Xyl^a), 128.9 (*m*'-Xyl^a), 128.1 (*o*-Xyl^b), 126.9 (br, *m*-Fmes), 126.8 (br, *m*'-Fmes), 126.4 (*p*-Xyl^a), [124.1 (q, $^1J_{FC}$ = 274.9 Hz), 123.5 (q, $^1J_{FC}$ = 273.8 Hz), 123.1 (q, $^1J_{FC}$ = 272.6 Hz)](CF_3), 121.0 (*p*-Xyl^b), 101.6 (CH=), 67.4 (NCH), 39.6 (br, BCH), 19.7 (q, J_{FC} = 2.9 Hz, *o*'-CH_2^{Xyla}), 19.1 (*o*-CH_3^{Xylb}), 18.9 (q, J_{FC} = 2.9 Hz, *o*-CH_2^{Xyla}), 13.4 (CH_3CH), 10.2 (CH_3CH=).

^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K): δ = 48.1 ($\nu_{1/2} \approx$ 700 Hz).

^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K): δ = -56.6 (d, *J* = 2.9 Hz, 1F, *o*-CF_3), -59. 8 (s, 1F, *o*'-CF_3), -63.8 (s, 1F, *p*-CF_3).

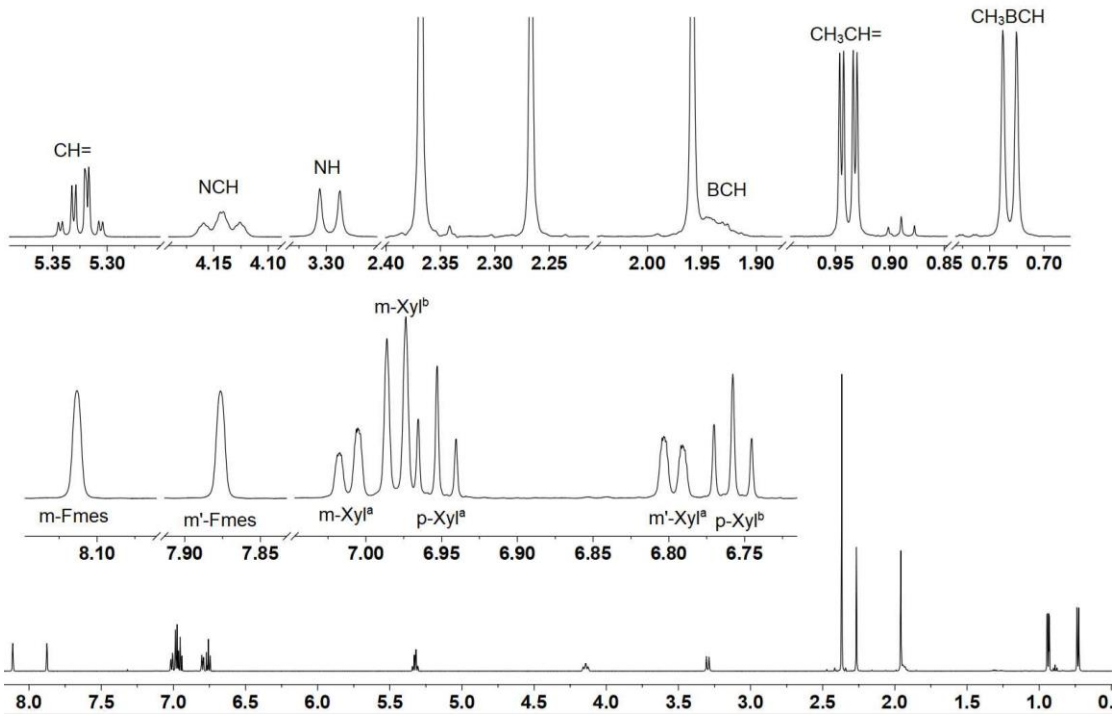


Figure S1. ^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3a**

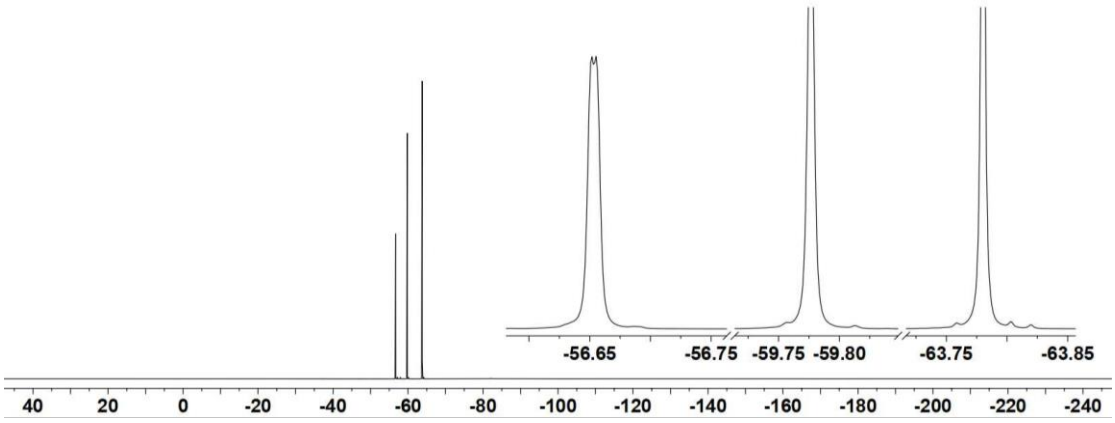


Figure S2. ^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3a**

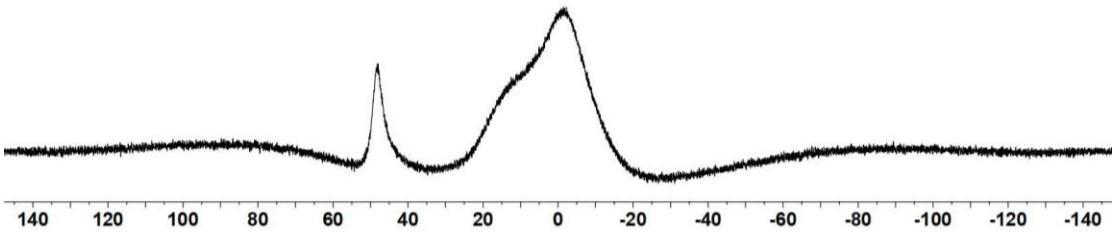


Figure S3. ^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3a**

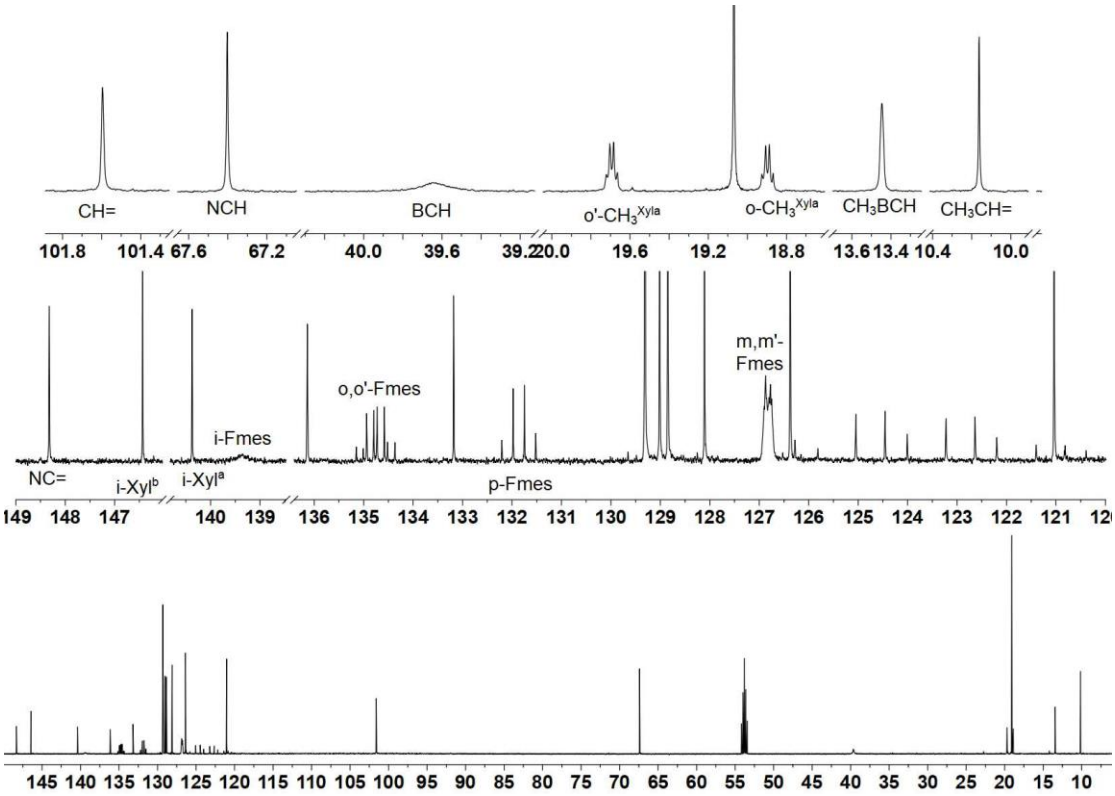


Figure S4. $^{13}C\{^{1}H\}$ NMR (151 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3a**

The crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **3a** in pentane at -35 °C.

X-ray crystal structure analysis of compound 3a (erk9527): A colorless prism-like specimen of $C_{31}H_{30}BF_9N_2$, approximate dimensions 0.090 mm x 0.090 mm x 0.160 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1033 frames were collected. The total exposure time was 9.40 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 21209 reflections to a maximum θ angle of 66.80° (0.84 Å resolution), of which 5020 were independent (average redundancy 4.225, completeness = 98.4%, R_{int} = 11.62%, R_{sig} = 14.66%) and 3131 (62.37%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.7127(9) Å, b = 33.713(3) Å, c = 9.8085(9) Å, β = 95.063(7)°, volume = 2869.8(5) Å^3, are based upon the refinement of the XYZ-centroids of 1718 reflections above 20 σ(I) with 10.46° < 2θ < 123.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.802. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8470 and 0.9100. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{31}H_{30}BF_9N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 399 variables converged at R1 = 7.03%, for the observed data and wR2 = 19.58% for all data. The goodness-of-fit was 1.051. The largest peak in the final difference electron density synthesis was 0.301 e^-/Å^3 and the largest hole was -0.307 e^-/Å^3 with an RMS deviation of 0.075 e^-/Å^3. On the basis of the final model, the calculated density was 1.417 g/cm^3 and F(000), 1264 e^-. The hydrogen at N2 atom was refined freely. CCDC Nr.: 2119779.

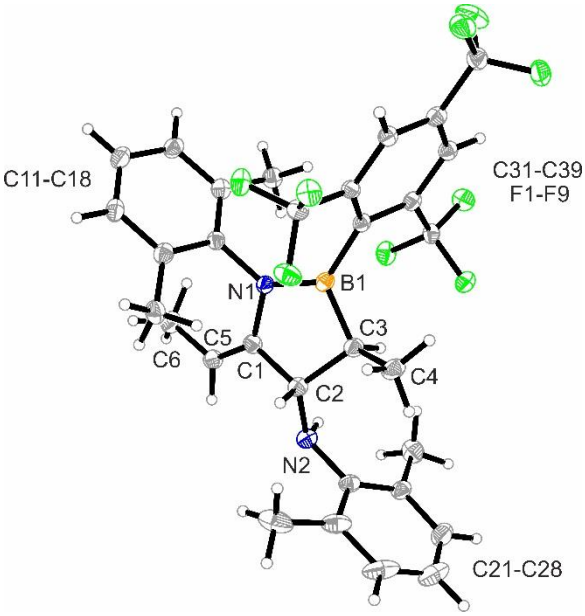


Figure S5. Crystal structure of compound **3a** (thermal ellipsoids are set at 30% probability).

In situ NMR spectra for compound 4a.

The sample from the above experiment was measured on a 600 MHz NMR spectrometer after filling with ethylene and shaking for 10 min to give the in-situ NMR spectra of compound **4a**.

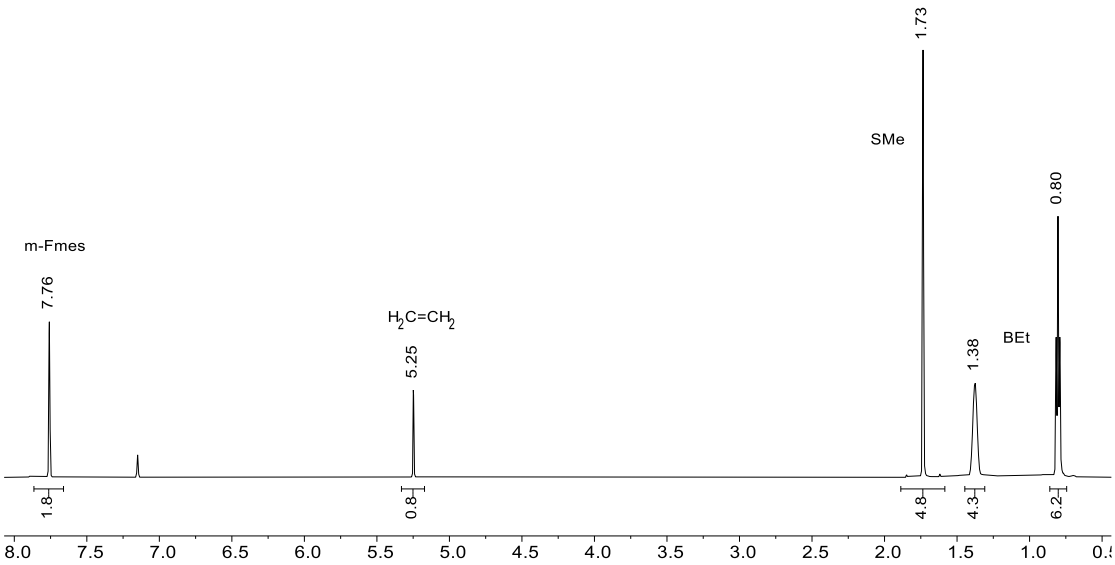


Figure S6. ^{1}H NMR (600 MHz, benzene-d_6, 299 K) spectrum of compound **4a**

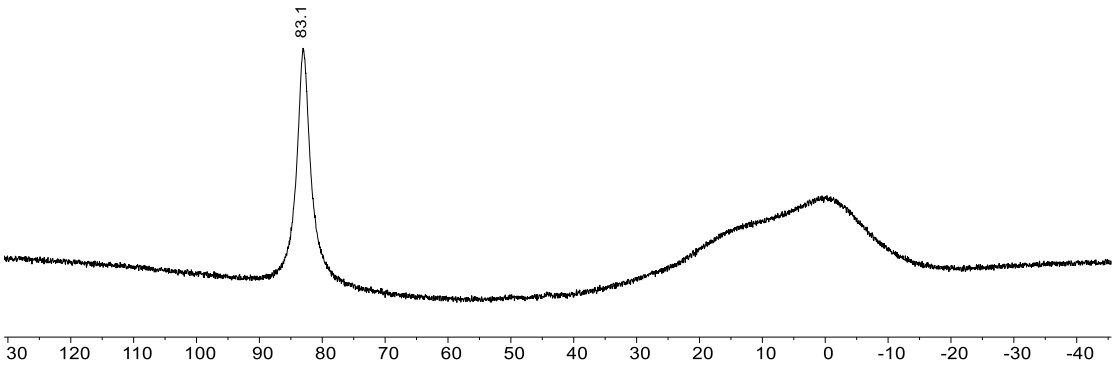


Figure S7. $^{11}B\{^{1}H\}$ NMR (192 MHz, benzene-d_6, 299 K) spectrum of compound **4a**

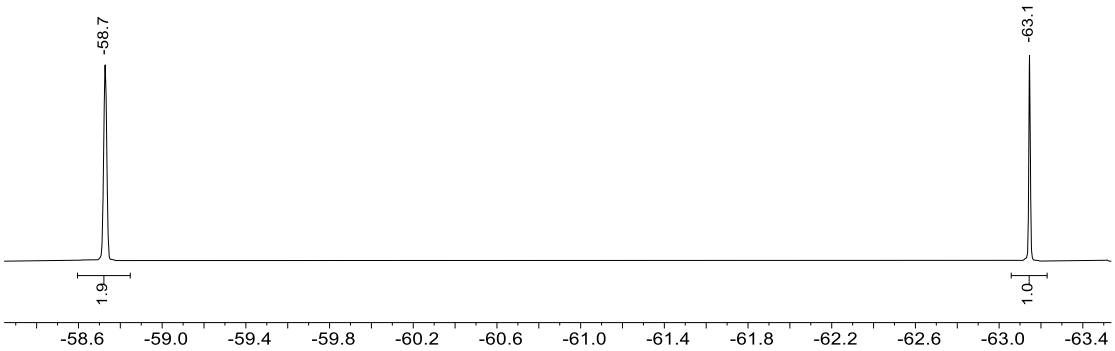
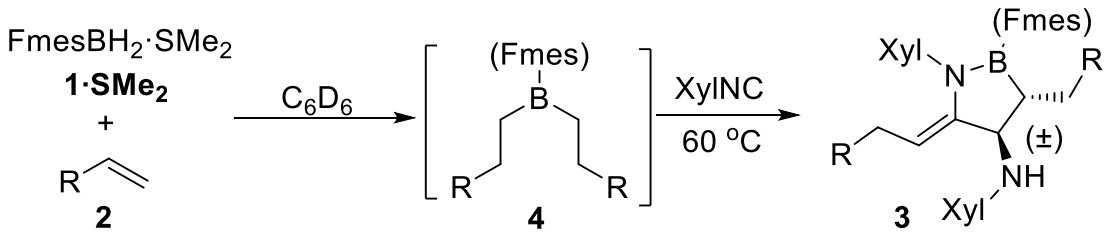


Figure S8. ^{19}F NMR (564 MHz, benzene-d_6, 299 K) spectrum of compound **4a**

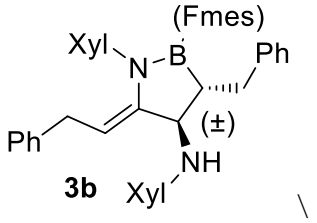
General Procedure for Preparation of compound 3b-f



Scheme S2

At room temperature, alkene **2** (0.4 mmol, 2 equiv.) was added to a solution of borane **1·SMe$_2$** (71.2 mg, 0.2 mg, 1 equiv.) in C_6D_6 (1 mL). The resulting mixture was stored at room temperature for 1 h. Then, 2,6-dimethylphenyl isocyanide (52.4 mg, 0.4 mmol, 2 equiv.) was added to give a yellow solution. The yellow solution was stored at 60 °C overnight. Then all volatiles were removed in vacuum and the residue was dissolved in pentane (1 mL). The solution was stored at -35 °C to give the respective product **3**.

Preparation of compound 3b



Following the general procedure, styrene (**2b**: 41.6 mg, 0.4 mmol, 2 equiv.) was used as the alkene substrate. Crystallization gave compound **3b** as a pale-yellow solid (36 mg, 24% yield).

[Note: We also tried to use benzyl isocyanide or tert.-butyl isocyanoacetate as the isonitrile components for this reaction, but these gave no clean results under our conditions].

HRMS for $C_{43}H_{38}BF_9N_2H^+$ $[M+H]^+$: calc. 765.3064, found: 765.3063.

^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K): δ = 7.78 (s, 1H, *m*-Fmes), 7.68 (s, 1H, *m*'-Fmes), 7.19 (m, 2H, *m*-Ph^a), 7.12 (m, 1H, *p*-Ph^a), 7.03 (m, 1H, *m*-Xyl^a), 6.98 (m, 3H, *m*-Xyl^b, *p*-Xyl^a), 6.92 (m, 2H, *o*-Ph^a), 6.81 (m, 4H, *m*'-Xyl^a, *m*-Ph^b, *p*-Ph^b), 6.75 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl^b), 6.59 (m, 2H, *o*-Ph^b), 5.48 (td, $^3J_{HH}$ = 7.5 Hz, *J* = 2.1 Hz, 1H, CH=), 4.45 (ddm, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, NCH), 3.43 (d, $^3J_{HH}$ = 11.0 Hz, 1H, NH), 2.73 (m, 2H, CH_2Ph^a, CH_2Ph^b), 2.55 (m, 1H, CH_2Ph^a), 2.40 (m, 7H, *o*-CH_3^{Xylb}, CH_2Ph^b), 2.32 (s, 3H, *o*-CH_3^{Xyla}), 2.28 (m, 1H, BCH), 1.97 (s, 3H, *o*'-CH_3^{Xyla}).

^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K): δ = 147.4 (NC=), 146.0 (*i*-Xyl^b), 141.9 (*i*-Ph^a), 140.6 (*i*-Ph^b), 140.2 (*i*-Xyl^a), 139.0 (br, *i*-Fmes), 136.1 (*o*-Xyl^a), 134.9 (q, $^2J_{FC}$ = 31.8 Hz, *o*-Fmes), 134.6 (q, $^2J_{FC}$ = 32.3 Hz, *o*'-Fmes), 133.4 (*o*'-Xyl^a), 131.6 (q, $^2J_{FC}$ = 34.5 Hz, *p*-Fmes), 129.5 (*m*-Xyl^b), 129.3 (*m*-Xyl^a), 129.0 (*m*'-Xyl^a), 128.7 (*o*-Ph^b), 128.55 (*m*-Ph^a), 128.47 (*o*-Ph^a), 128.1 (*m*-Ph^b), 127.8 (*o*-Xyl^b), 127.2 (br, *m*'-Fmes), 126.7 (*p*-Xyl^a), 126.4 (br, *m*-Fmes), 126.0 (*p*-Ph^a), 125.6 (*p*-Ph^b), [123.5 (q, $^1J_{FC}$ = 276.0 Hz), 123.3 (q, $^1J_{FC}$ = 275.1 Hz), 122.6 (q, $^1J_{FC}$ = 272.6 Hz)](CF_3), 121.1 (*p*-Xyl^b), 107.0 (CH=), 65.6 (NCH), 47.5 (br, BCH), 36.5 (CH_2Ph^b), 31.3 (CH_2Ph^a), 19.4 (q, *J* = 2.9 Hz, *o*'-CH_3^{Xyla}), 19.3 (*o*-CH_3^{Xylb}), 19.01 (q, J_{FC} = 3.0 Hz, *o*-CH_3^{Xyla}).

^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K): δ = 47.2 ($v_{1/2}$ ≈ 940 Hz).

^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K): δ = [-55.1, -59.4](each s, each 1F, *o*-CF_3), -63.9 (s, 1F, *p*-CF_3).

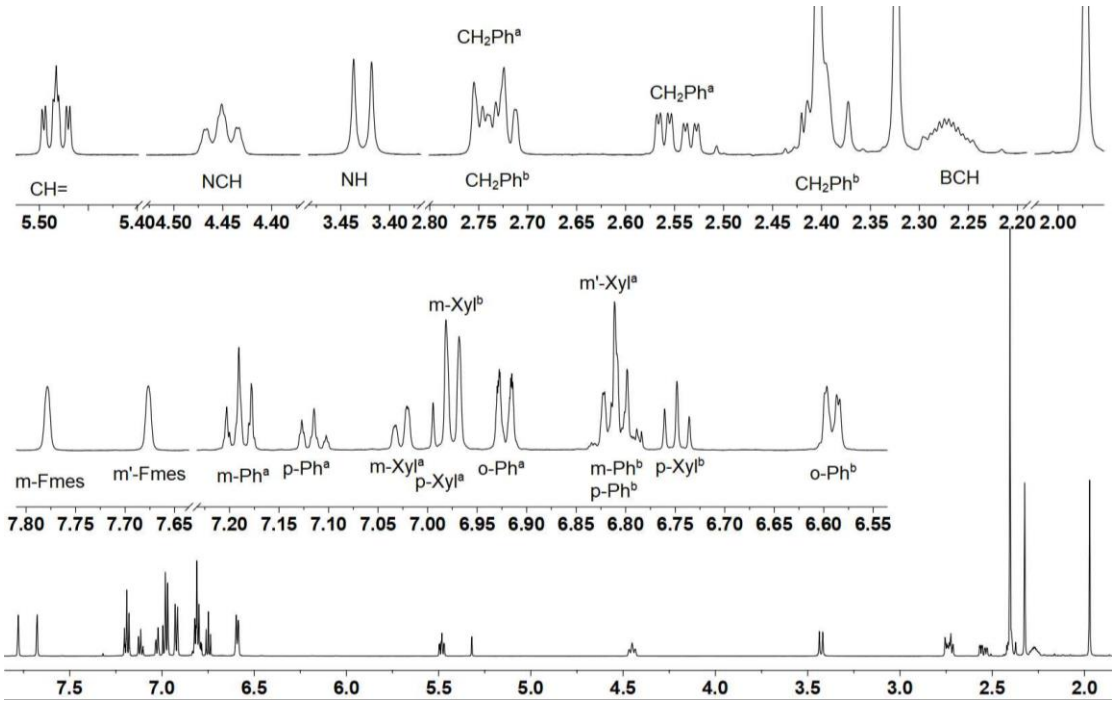


Figure S9. ^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3b**

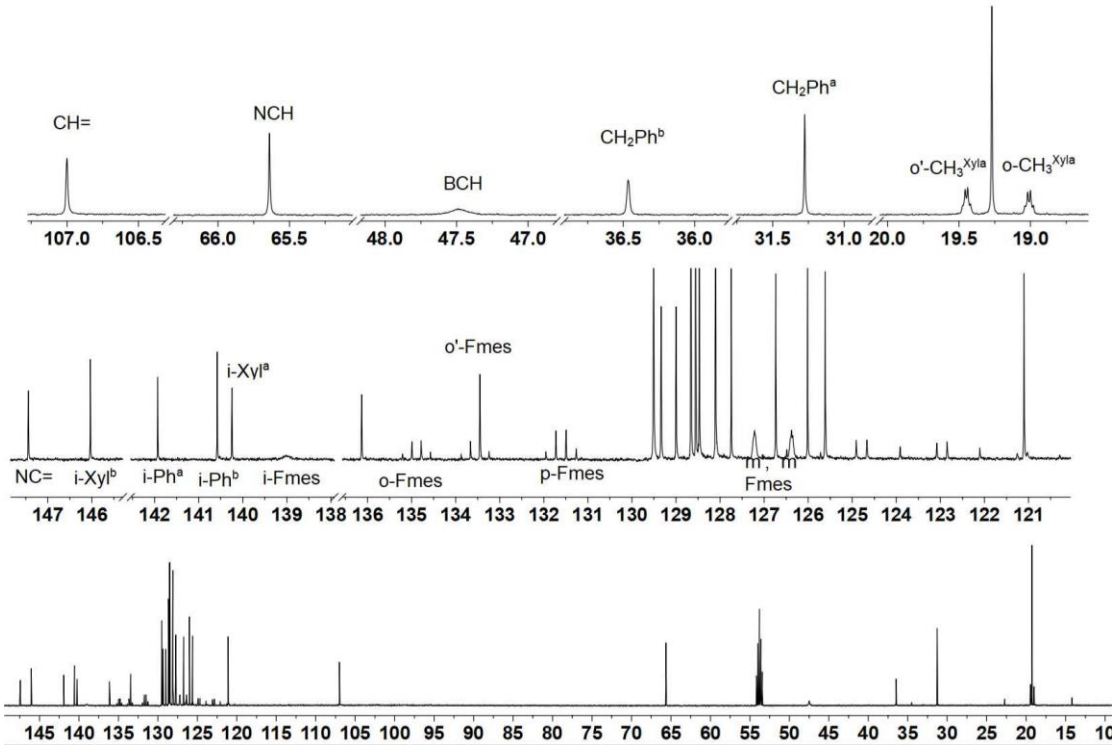


Figure 10. ^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3b**

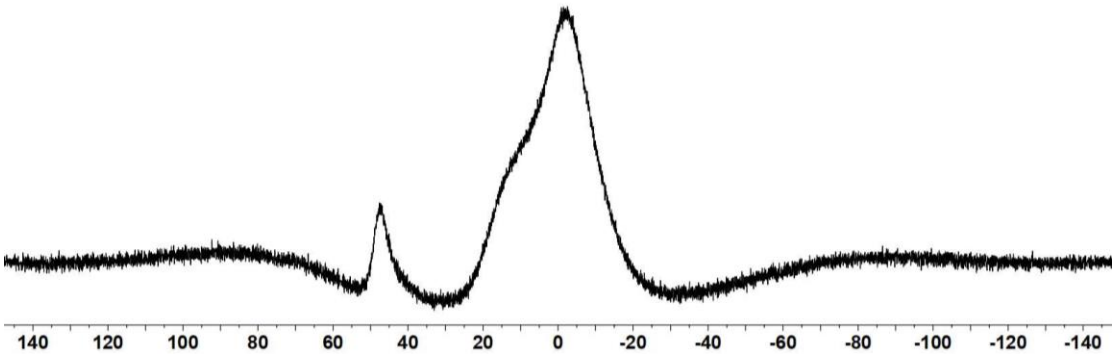


Figure 11. $^{11}B\{^{1}H\}$ NMR (192 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3b**

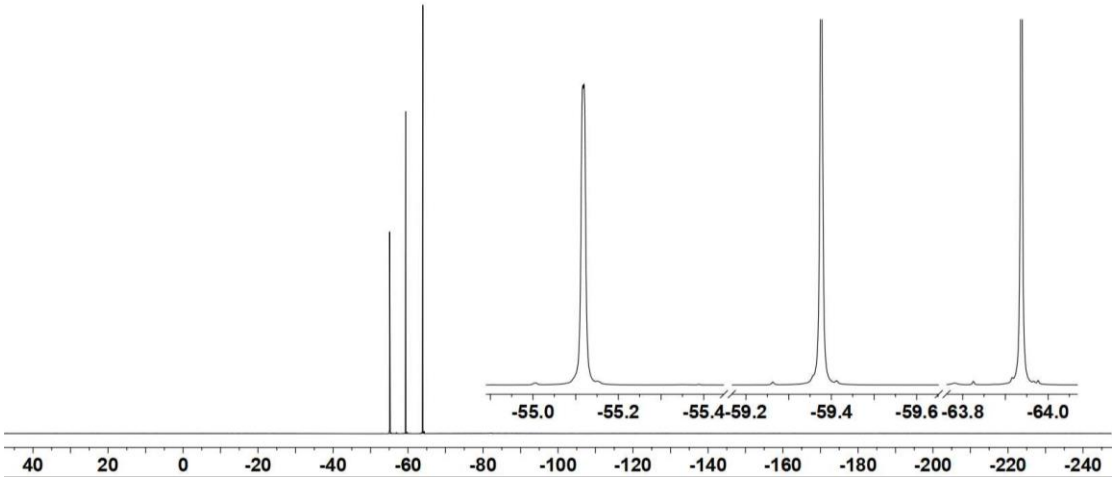


Figure 12. ^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3b**

The crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **3b** in pentane at -35 °C.

X-ray crystal structure analysis of compound 3b (erk9503): A colorless plate-like specimen of $C_{43}H_{38}BF_9N_2$, approximate dimensions 0.040 mm x 0.100 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1728 frames were collected. The total exposure time was 23.85 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 30770 reflections to a maximum θ angle of 66.64° (0.84 Å resolution), of which 6459 were independent (average redundancy 4.764, completeness = 99.2%, R_{int} = 5.66%, R_{sig} = 4.17%) and 5029 (77.86%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.2201(2) Å, b = 13.4877(3) Å, c = 15.2758(3) Å, α = 74.9650(10)°, β = 73.1130(10)°, γ = 67.9510(10)°, volume = 1840.51(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 8609 reflections above 20 σ(I) with 7.175° < 2θ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.875. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8780 and 0.9630. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{43}H_{38}BF_9N_2$. The final anisotropic full-matrix least-squares refinement on

F^2 with 504 variables converged at R1 = 4.32%, for the observed data and wR2 = 10.97% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 0.197 $e^-/Å^3$ and the largest hole was -0.231 $e^-/Å^3$ with an RMS deviation of 0.047 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.380 g/cm^3 and F(000), 792 e^-. The hydrogen at N2 atom was refined freely. CCDC Nr.: 2119780.

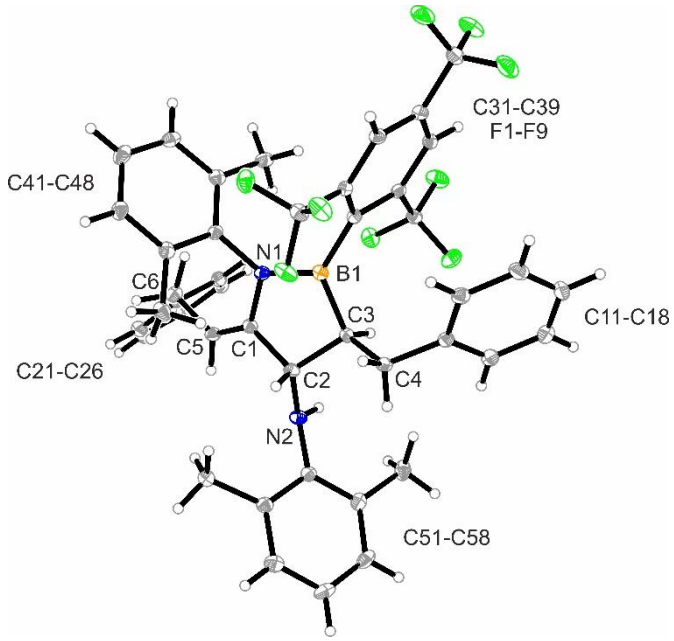
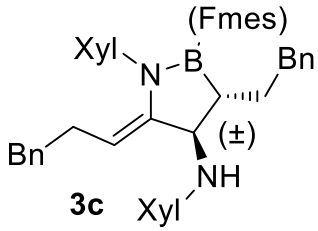


Figure S13. Crystal structure of compound **3b** (thermal ellipsoids are shown at 30% probability).

Preparation of compound 3c



Following the general procedure, allylbenzene (**2c**: 47.2 mg, 0.4 mmol, 2 equiv.) was used as the alkene substrate. Crystallization gave compound **3c** as an off-white solid (20 mg, 13% yield).

HRMS for $C_{45}H_{42}BF_9N_2H^+$ $[M+H]^+$: calc. 793.3378, found: 793.3378.

^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K): δ = 8.13 (s, 1H, *m*-Fmes), 7.91 (s, 1H, *m*'-Fmes), 7.17 (m, 2H, *m*-Ph^a), 7.10 (m, 3H, *p*-Ph^a, *m*-Ph^b), 7.01 (m, 5H, *m*-Xyl^a, *p*-Xyl^a, *m*-Xyl^b, *p*-Ph^b), 6.86 (m, 2H, *o*-Ph^a), 6.83 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ =2.0 Hz, 1H, *m*'-Xyl^a), 6.78 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl^b), 6.66 (m, 2H, *o*-Ph^b), 5.25 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH=), 4.37 (ddm, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 8.7

Hz, 1H, NCH), 3.35 (d, $^{3}J_{HH}$ = 11.0 Hz, 1H, NH), 2.37 (s, 6H, *o*-CH_3^{Xylb}), 2.35 (m, 2H, CH_2Ph^a), 2.25 (m, 1H, CH_2Ph^b), 2.21 (s, 3H, *o*-CH_3^{Xyla}), 1.96 (m, 2H, CH_2Ph^b, BCH), 1.94 (s, 3H, *o*'-CH_3^{Xyla}), 1.68 (m, 1H, CH_2CH=), 1.55 (m, 3H, CH_2CH=, CH_2CHB).

$^{13}C\{^{1}H\}$ NMR (151 MHz, methylene chloride-d_2, 299 K): δ = 148.0 (NC=), 146.0 (*i*-Xyl^b), 142.9 (*i*-Ph^b), 142.4 (*i*-Ph^a), 140.3 (*i*-Xyl^a), 139.7 (br, *i*-Fmes), 136.1 (*o*-Xyl^a), 135.0 (q, $^{2}J_{FC}$ = 31.5 Hz, *o*-Fmes), 134.3 (q, $^{2}J_{FC}$ = 32.1 Hz, *o*'-Fmes), 133.4 (*o*'-Xyl^a), 132.1 (q, $^{2}J_{FC}$ = 34.6 Hz, *p*-Fmes), 129.5 (*m*-Xyl^b), 129.4 (*m*-Xyl^a), 128.9 (*m*'-Xyl^a), 128.7 (*o*-Ph^a), 128.45 (*m*-Ph^b), 128.40 (*m*-Ph^a), 128.2 (*o*-Ph^b), 127.7 (*o*-Xyl^b), 127.2 (br, *m*-Fmes), 127.0 (br, *m*'-Fmes), 126.7 (*p*-Xyl^a), 126.0 (*p*-Ph^a), 125.9 (*p*-Ph^b), [124.2 (q, $^{1}J_{FC}$ = 274.7 Hz), 123.6 (q, $^{1}J_{FC}$ = 274.1 Hz), 123.1 (q, $^{1}J_{FC}$ = 272.7 Hz)](CF_3), 121.0 (*p*-Xyl^b), 107.3 (CH=), 65.6 (NCH), 45.6 (br, BCH), 36.5 (CH_2Ph^b), 36.2 (CH_2Ph^a), 33.3 (CH_2CHB), 27.1 (CH_2CH=), 19.5 (q, J_{FC} = 2.6 Hz, *o*'-CH_3^{Xyla}), 19.2 (*o*-CH_3^{Xylb}), 18.9 (q, *J* = 3.0 Hz, *o*-CH_3^{Xyla}).

$^{11}B\{^{1}H\}$ NMR (192 MHz, methylene chloride-d_2, 299 K): δ = 47.4 ($\nu_{1/2}$ ≈ 1040 Hz).

^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K): δ = [-55.5, -59.6](each s, each 1F, *o*-CF_3), -63.7 (s, 1F, *p*-CF_3).

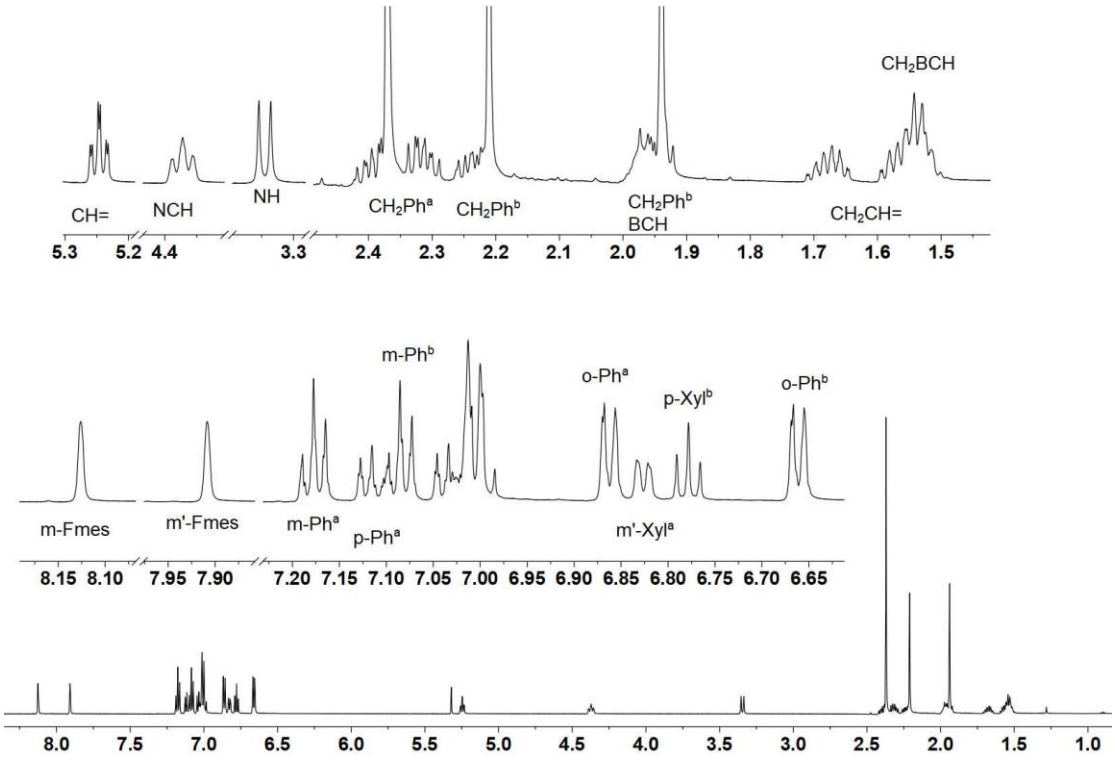


Figure S14. ^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3c**

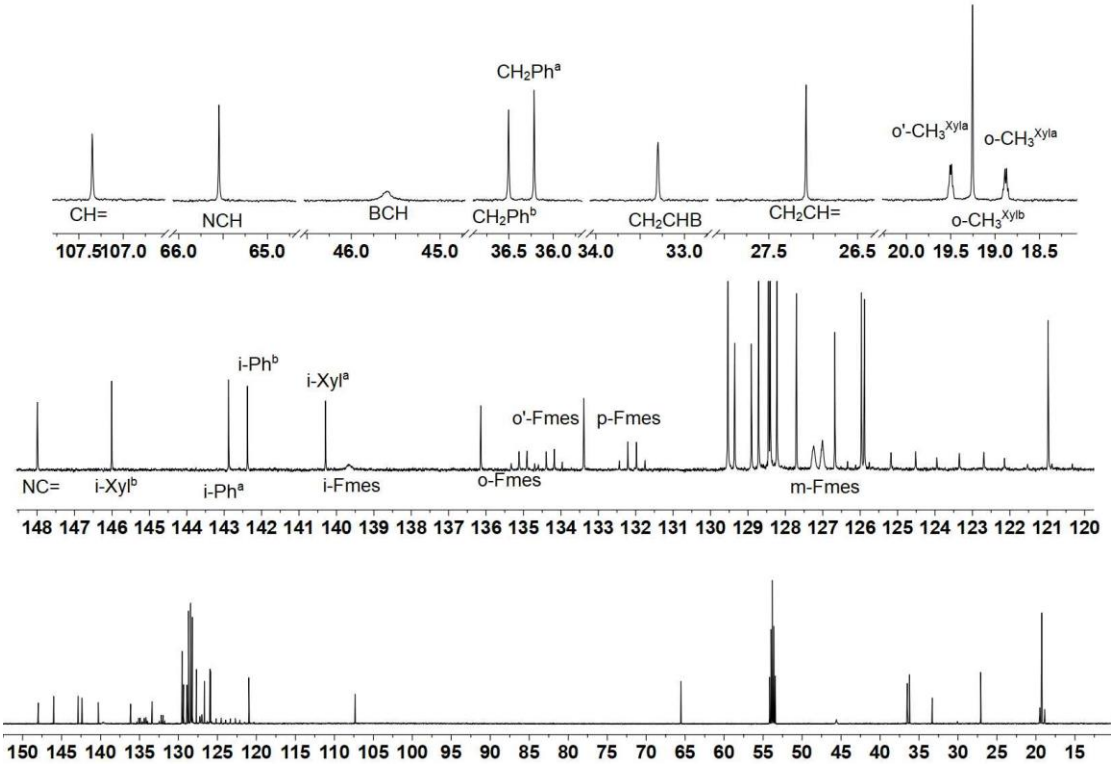


Figure S15. $^{13}C\{^{1}H\}$ NMR (151 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3c**

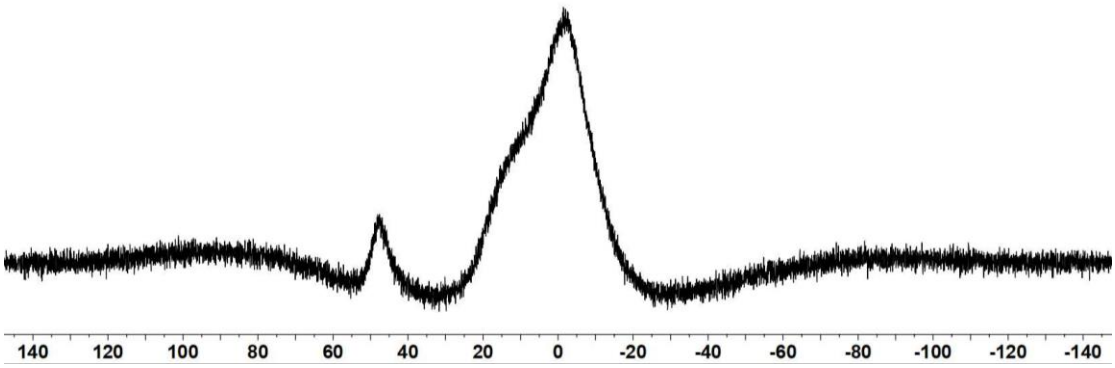


Figure S16. $^{11}B\{^{1}H\}$ NMR (192 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3c**

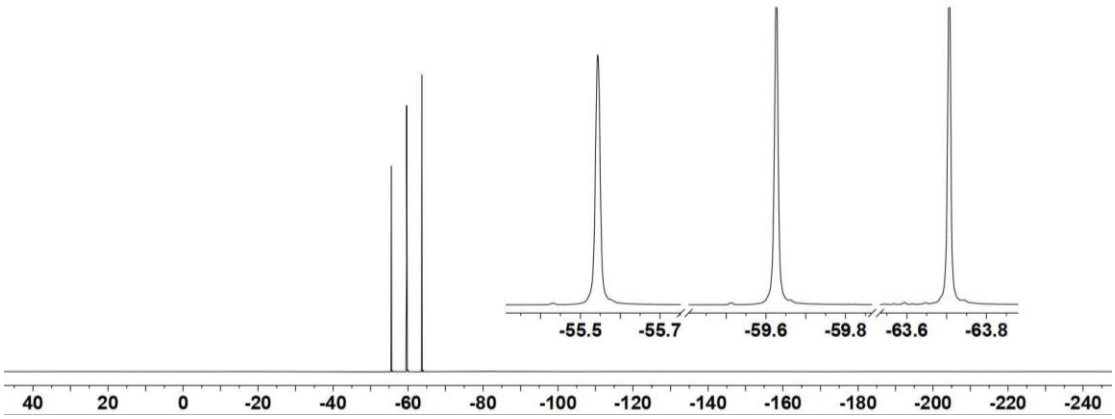
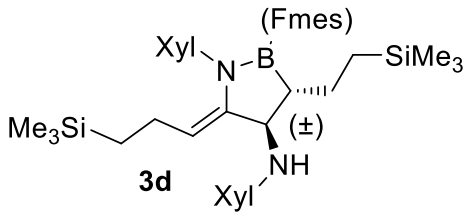


Figure S17. ^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3c**

Preparation of compound 3d



3d

Following the general procedure, allyltrimethylsilane (**3d**: 45.6 mg, 0.4 mmol, 2 equiv.) was used as the alkene substrate. Crystallization gave compound **3d** as a yellow solid (72 mg, 46% yield).

HRMS for $C_{39}H_{50}BF_9N_2Si_2H^+$ $[M+H]^+$: calc. 785.3542, found: 785.3541.

^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K): δ = 8.09 (s, 1H, *m*-Fmes), 7.86 (m, 1H, *m*'-Fmes), 6.99 (m, 1H, *m*-Xyl^a), 6.97 (m, 2H, *m*-Xyl^b), 6.94 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-Xyl^a), 6.78 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ =1.7 Hz, 1H, *m*'-Xyl^a), 6.75 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl^b), 5.22 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 6.6 Hz, *J* = 2.1 Hz, 1H, CH=), 4.20 (ddm, $^3J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, NCH), 3.27 (d, $^3J_{HH}$ = 10.9 Hz, 1H, NH), 2.36 (s, 6H, *o*-CH_3^{Xylb}), 2.27 (s, 3H, *o*-CH_3^{Xyla}), 1.95 (s, 3H, *o*'-CH_3^{Xyla}), 1.85 (m, 1H, BCH), 1.37 (m, 1H, CH_2CH=), 1.23 (m, 3H, CH_2CH=, CH_2CH), [0.37, 0.29](each m, each 1H, CH_2Si^a), [0.13, -0.29](each m, each 1H, CH_2Si^b), -0.23 [s, $^2J_{SiH}$ = 6.5 Hz(satellite, ^{29}Si-^{1}H), 9H, CH_3^{Sia}], -0.37 [s, $^2J_{SiH}$ = 6.5 Hz (satellite, ^{29}Si-^{1}H), 9H, CH_3^{Sib}].

^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K): δ = 146.5 (*i*-Xyl^b), 146.1 (NC=), 140.6 (*i*-Xyl^a), 140.3 (br, *i*-Fmes), 136.0 (*o*-Xyl^a), 135.2 (q, $^2J_{FC}$ = 31.6 Hz, *o*'-Fmes), 134.0 (q, $^2J_{FC}$ = 32.1 Hz, *o*-Fmes), 133.3 (*o*'-Xyl^a), 131.8 (q, $^2J_{FC}$ = 34.6 Hz, *p*-Fmes), 129.4 (*m*-Xyl^b), 129.1 (*m*-Xyl^a), 128.9 (*m*'-Xyl^a), 128.1 (*o*-Xyl^b), 127.1 (br, *m*-Fmes), 126.8 (br, *m*'-Fmes), 126.5 (*p*-Xyl^a), [124.4 (q, $^1J_{FC}$ = 275.1 Hz), 123.6 (q, $^1J_{FC}$ = 274.7 Hz), 123.1 (q, $^1J_{FC}$ = 272.9 Hz)](CF_3), 121.0 (*p*-Xyl^b), 111.1 (CH=), 65.6 (NCH), 49.7 (br, BCH), 24.2 (CH_2CH), 19.56 (q, J_{FC} = 2.7 Hz, *o*'-CH_3^{Xyla}), 19.52 (CH_2CH=), 19.1 (*o*-CH_3^{Xylb}), 19.0 (q, J_{FC} = 3.0 Hz, *o*-CH_3^{Xyla}), 17.3 [$^1J_{SiC}$ = 51.4 Hz(satellite, ^{29}Si-^{13}C), CH_2Si^a], 17.2 [$^1J_{SiC}$ = 51.5 Hz(satellite, ^{29}Si-^{13}C), CH_2Si^b], -1.8 [$^1J_{SiC}$ = 50.3 Hz(satellite, ^{29}Si-^{13}C), CH_3^{Sia}], -2.4 [$^1J_{SiC}$ = 50.5 Hz(satellite, ^{29}Si-^{13}C), CH_3^{Sib}[.

^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K): δ = 47.1 ($\nu_{1/2} \approx$ 1120 Hz).

^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K): δ = -55.4 (d, *J* = 3.1 Hz, 1F, *o*-CF_3), -59.8 (s, 1F, *o*'-CF_3), -63.8 (s, 1F, *p*-CF_3).

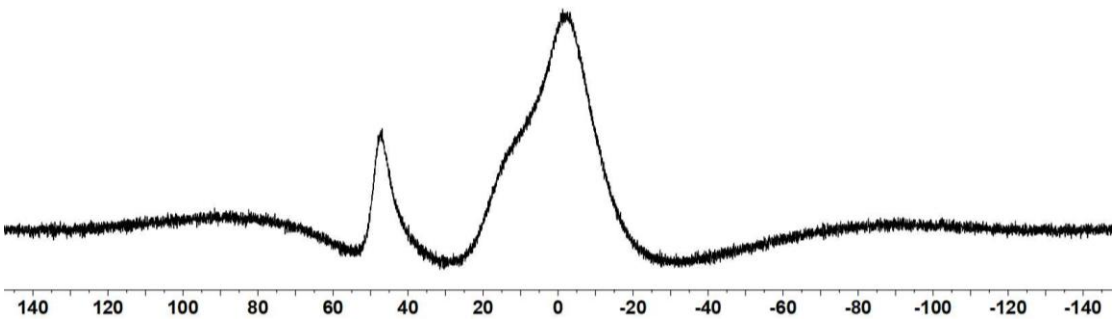


Figure S18. ^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3d**

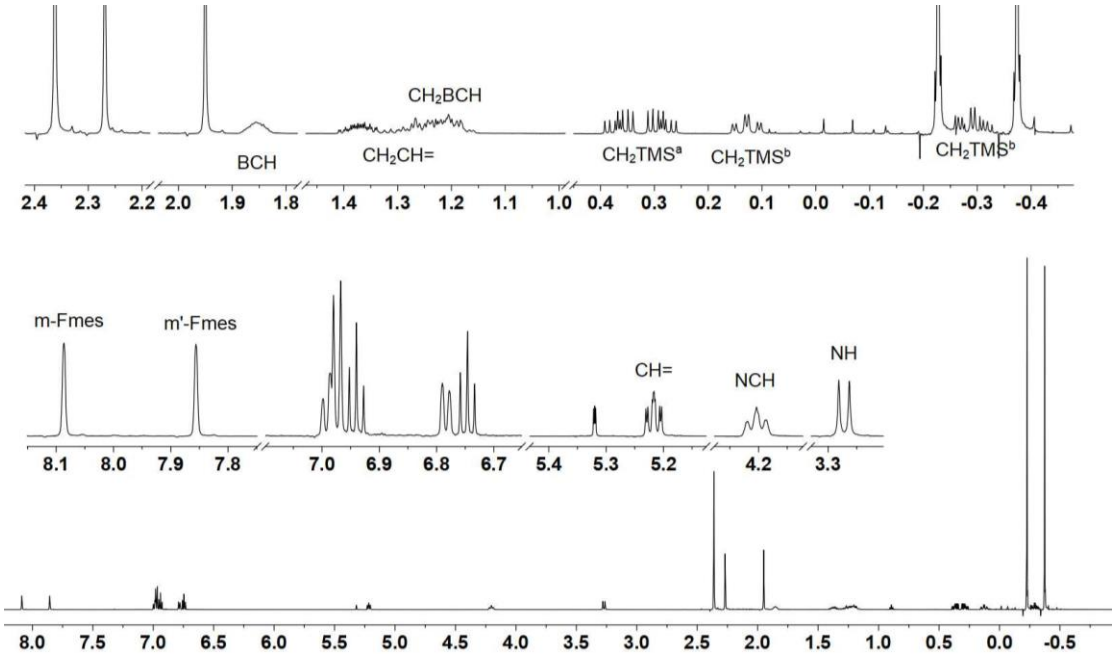


Figure S19. ^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3d**.

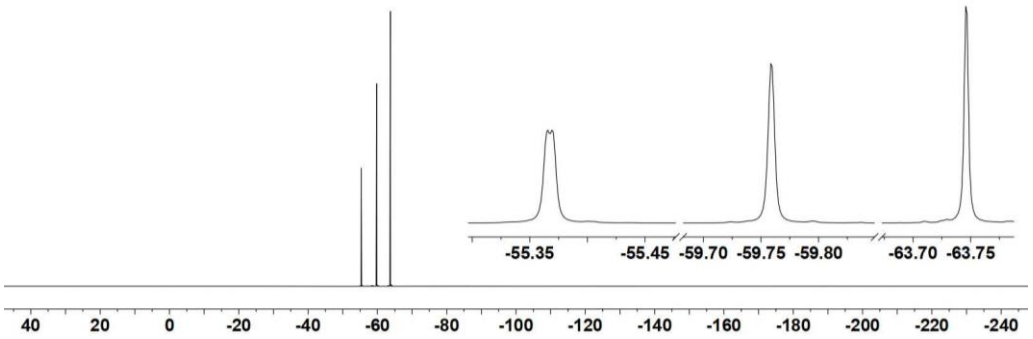


Figure S20. ^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3d**

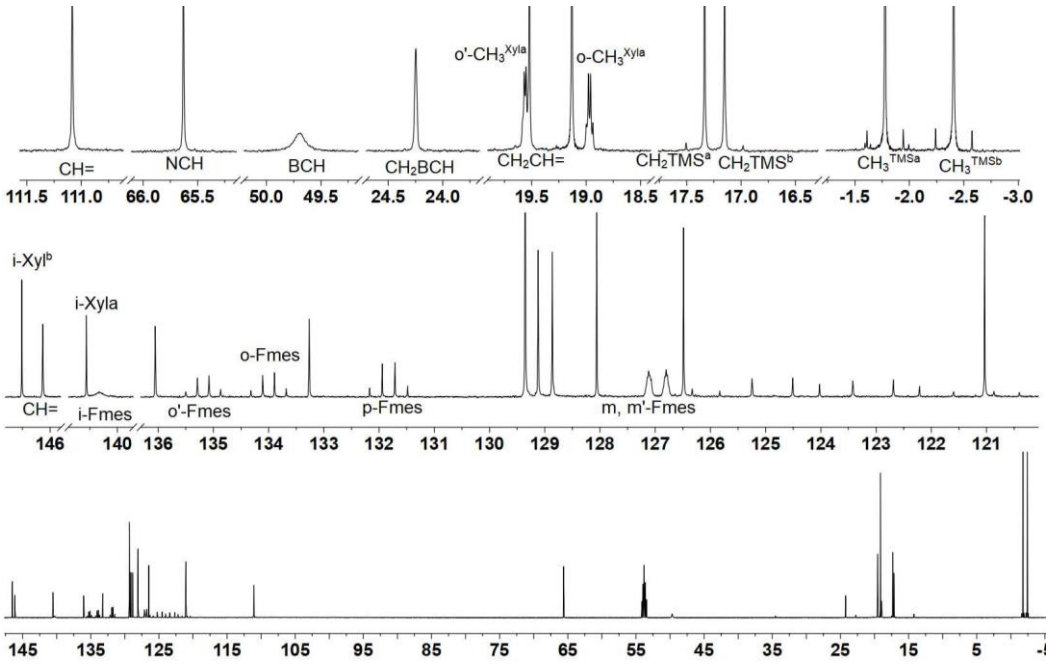


Figure S21. ^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3d**

The crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **3d** in pentane at -35 °C.

X-ray crystal structure analysis of compound 3d (erk9542): A colorless plate-like specimen of $C_{39}H_{50}BF_9N_2Si_2$, approximate dimensions 0.050 mm x 0.120 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1762 frames were collected. The total exposure time was 17.05 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 30815 reflections to a maximum θ angle of 66.85° (0.84 Å resolution), of which 7307 were independent (average redundancy 4.217, completeness = 98.7%, R_{int} = 4.95%, R_{sig} = 4.23%) and 5728 (78.39%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.2787(3) Å, b = 11.0652(3) Å, c = 18.3857(6) Å, α = 88.526(2)°, β = 86.347(2)°, γ = 86.166(2)°, volume = 2081.71(11) Å^3, are based upon the refinement of the XYZ-centroids of 8388 reflections above 20 σ(I) with 8.01° < 2θ < 132.8°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.873. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7700 and 0.9340. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{39}H_{50}BF_9N_2Si_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 517 variables converged at R1 = 4.43%, for the observed data and wR2 = 11.45% for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 0.459 e$^-$/Å^3 and the largest hole was -0.522 e$^-$/Å^3 with an RMS deviation of 0.051 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.252 g/cm^3 and F(000), 824 e$^-$. The hydrogen at N2 atom was refined freely. CCDC Nr.: 2119781.

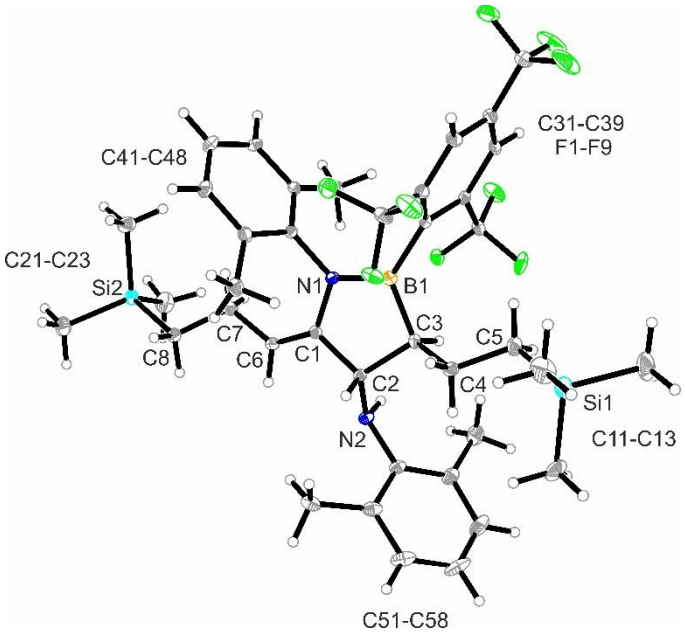


Figure S22. Crystal structure of compound **3d** (thermal ellipsoids are shown at 30% probability).

In situ NMR spectra of compound 4d.

The sample from the above experiment was measured on a 600 MHz NMR spectrometer 1h after adding allyltrimethylsilane to give the in-situ NMR spectra of compound **4d**.

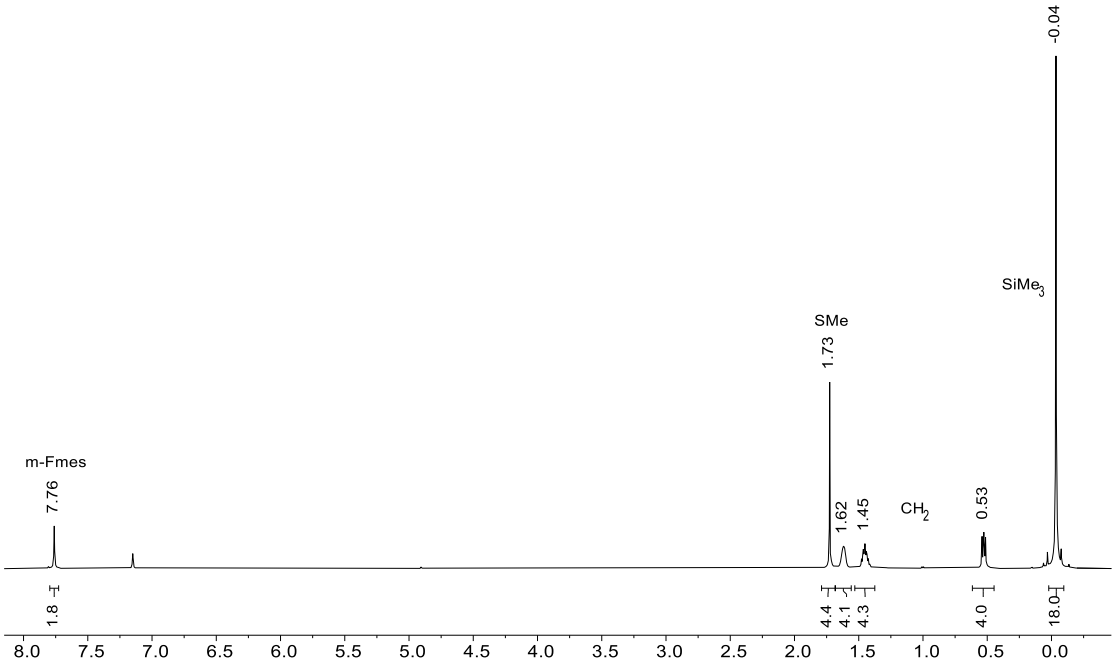


Figure S23. ^{1}H NMR (600 MHz, benzene-d_6, 299 K) spectrum of compound **4d**.

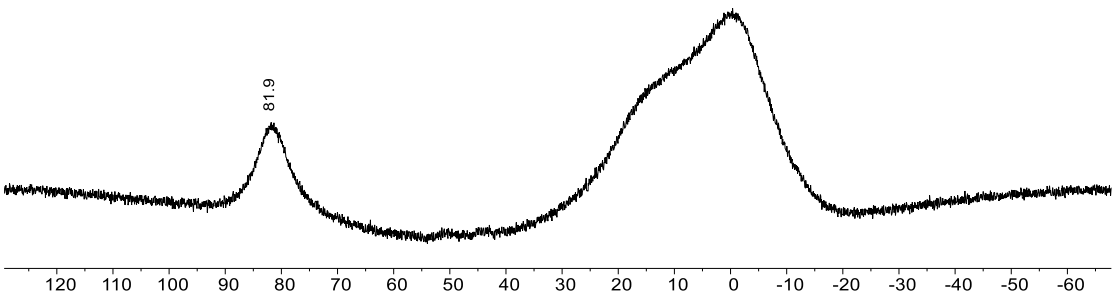


Figure S24. ^{11}B{^{1}H} NMR (192 MHz, benzene-d_6, 299 K) spectrum of compound **4d**

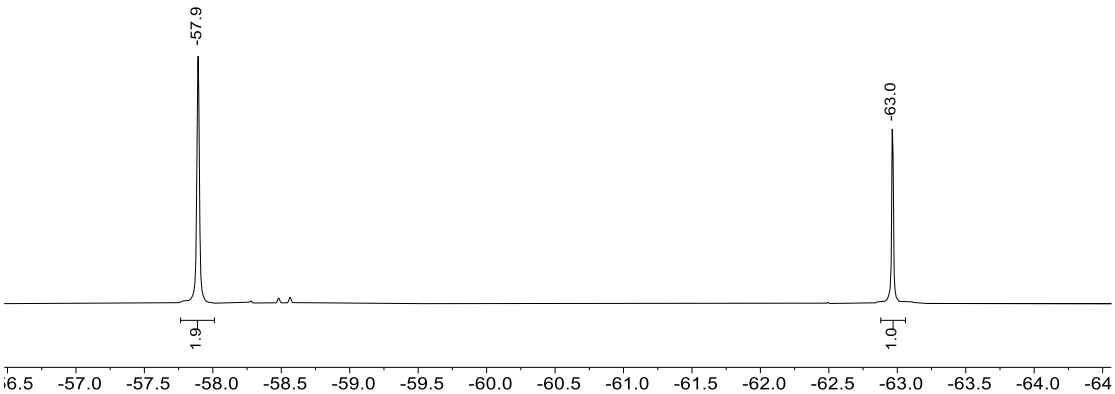
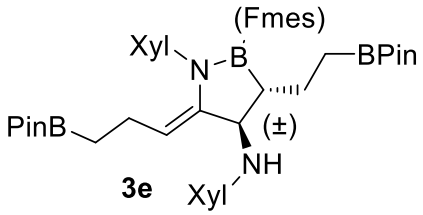


Figure S25 ^{19}F NMR (564 MHz, benzene-d_6, 299 K) spectrum of compound **4d**

Preparation of compound 3e



3e

Following the general procedure, 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**: 67.2 mg, 0.4 mmol, 2 equiv.) was used as the alkene substrate. (**1**)$_2$ (58.8 mg, 0.1 mmol, 1 equiv.) was used as the borane reagent. Crystallization gave compound **3e** as a light-yellow solid (56 mg, 31% yield).

HRMS for $C_{45}H_{56}B_3F_9N_2O_4H^+$ $[M+H]^+$: calc. 893.4469, found: 893.4468.

^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K): δ = 8.08 (s, 1H, *m*-Fmes), 7.85 (s, 1H, *m*'-Fmes), 6.97 (m, 3H, *m*-Xyl^a, *m*-Xyl^b), 6.93 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-Xyl^a), 6.76 (d, $^3J_{HH}$ = 7.5 Hz, 1H, *m*'-Xyl^a), 6.73 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl^b), 5.12 (ddm, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, CH=), 4.24 (br dd, $^3J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 8.5 Hz, 1H, NCH), 3.30 (d, $^3J_{HH}$ = 10.8 Hz, 1H, NH), 2.37 (s, 6H, *o*-CH_3^{Xylb}), 2.25 (s, 3H, *o*-CH_3^{Xyla}), 1.96 (s, 3H, *o*'-CH_3^{Xyla}), 1.87 (m, 1H, BCH), 1.42 (m, 2H, CH_2CH=, CH_2CH), 1.32 (m, 1H, CH_2CH), 1.21 (m, 1H, CH_2CH=), [1.146, 1.144](each s, each 6H, CH_3^{pina}), [1.09 , 1.08](each s, each 6H, CH_3^{pinb}), 0.50 (m, 2H, CH_2BPin^N), [0.36, 0.17](each m, each 1H, CH_2BPin^B).

^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K): δ = 146.8 (NC=), 146.4 (*i*-Xyl^b), 140.5 (*i*-Xyl^a), 140.1 (br, *i*-Fmes), 136.1 (*o*-Xyl^a), [135.1 (q, $^2J_{FC}$ = 31.5 Hz), 134.0 (q, $^2J_{FC}$ = 32.1 Hz)](*o*-Fmes), 133.4 (*o*'-Xyl^a), 131.8 (q, $^2J_{FC}$ = 34.9 Hz, *p*-Fmes), 129.4 (*m*-Xyl^b), 129.0 (*m*-Xyl^a), 128.7 (*m*'-Xyl^a), 127.5 (*o*-Xyl^b), 127.2 (br, *m*-Fmes), 126.9 (br, *m*'-Fmes), 126.4 (*p*-Xyl^a), [124.3 (q, $^1J_{FC}$ = 275.6 Hz), 123.6 (q, $^1J_{FC}$ = 273.8 Hz), 123.1 (q, $^1J_{FC}$ = 272.0 Hz)](CF_3), 120.6 (*p*-Xyl^b), 110.1 (CH=), 83.1 (C^{pina}), 83.0 (C^{pinb}), 65.7 (NCH), 48.1 (br, BCH), [24.94, 24.88](CH_3^{pina}), [24.90, 24.75](CH_3^{pinb}), 24.1 (br, CH_2CH), 19.6 (CH_2CH=), 19.5 (m, *o*'-CH_3^{Xyla}), 19.3 (*o*-CH_3^{Xylb}), 19.0 (m, *o*-CH_3^{Xyla}), 11.8 (br, CH_2^N) 11.2 (br, CH_2^B).

^{11}B{^{1}H} NMR (192 MHz, methylene chloride-d_2, 299 K): δ = 48.0 ($\nu_{1/2}$ ≈ 1000 Hz), 33.6 ($\nu_{1/2}$ ≈ 540 Hz).

^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K): δ = -55.2 (s, 1F, *o*-CF_3), -59.7 (s, 1F, *o*'-CF_3), -63.7 (s, 1F, *p*-CF_3).

[*Comments*: *commercially available allylBpin contained a small amount of pinBOBpin as impurity, which could not be removed from the product (ca. 6 mol% (^{1}H)*]

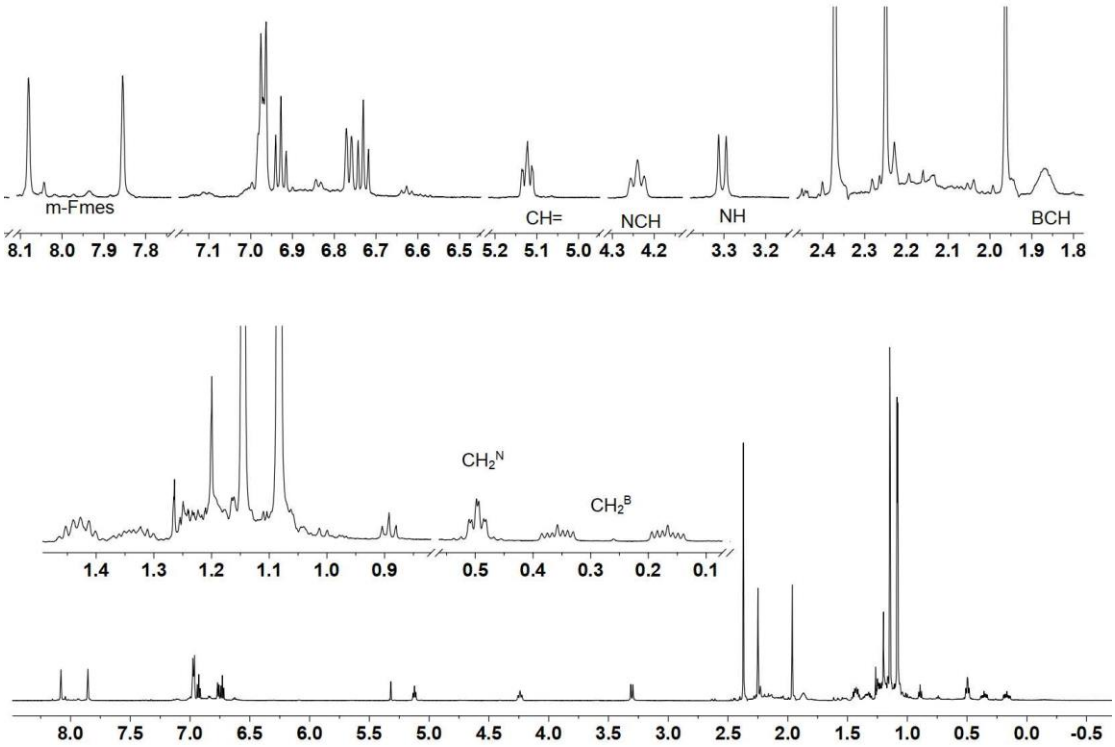


Figure S26. ^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3e**

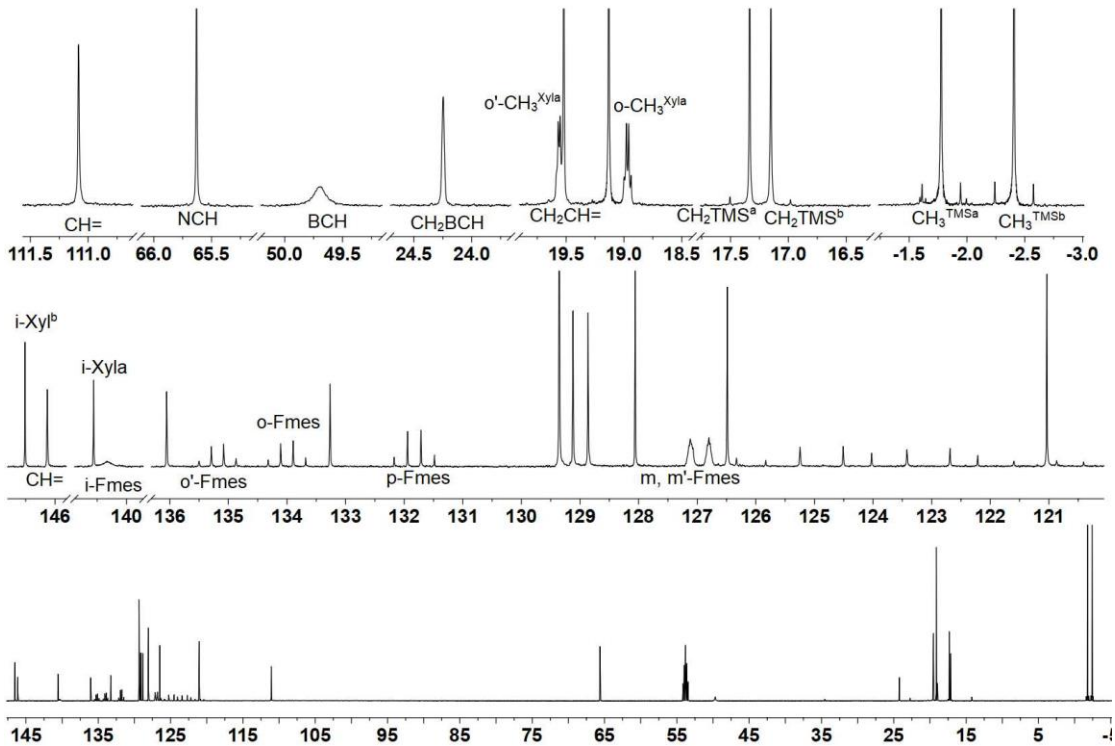


Figure S27. ^{13}C{^{1}H} NMR (151 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3e**

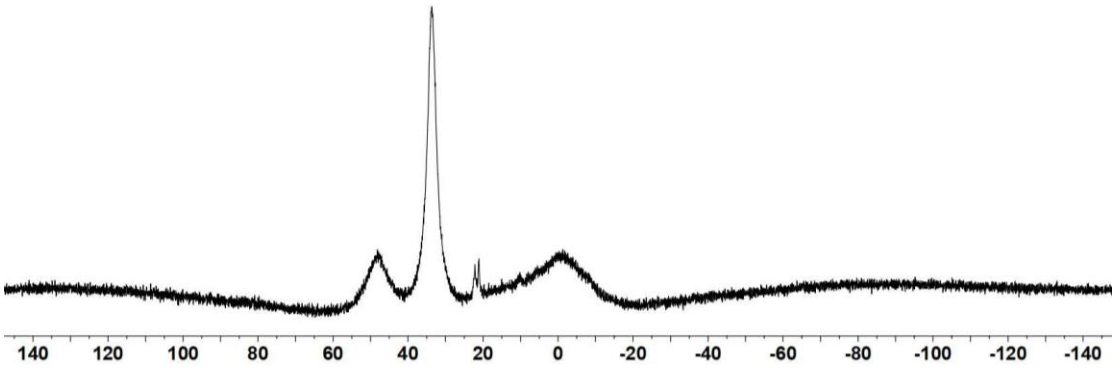


Figure S28. $^{11}B\{^{1}H\}$ NMR (192 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3e**

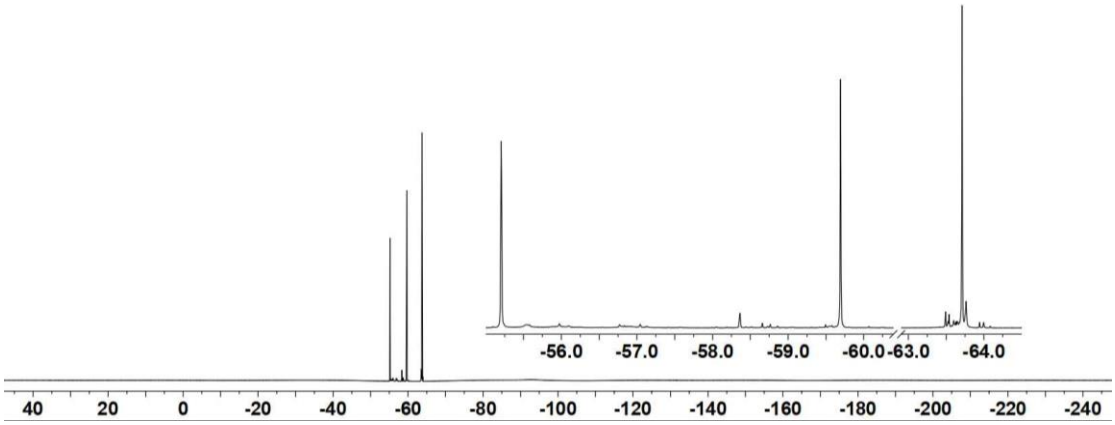


Figure S29. ^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3e**.

The crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **3e** in pentane at -35 °C.

X-ray crystal structure analysis of compound 3e (erk9557): A colorless prism-like specimen of $C_{57}H_{80}B_5F_9N_2O_9$, approximate dimensions 0.052 mm x 0.076 mm x 0.095 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1053 frames were collected. The total exposure time was 8.78 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 64068 reflections to a maximum θ angle of 27.19° (0.78 Å resolution), of which 14309 were independent (average redundancy 4.477, completeness = 99.0%, R_{int} = 8.39%, R_{sig} = 6.46%) and 10752 (75.14%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.6273(3) Å, b = 15.6946(6) Å, c = 19.7940(7) Å, α = 100.9550(10)°, β = 90.7880(10)°, γ = 90.5310(10)°, volume = 3240.76(19) Å^3, are based upon the refinement of the XYZ-centroids of 8733 reflections above 20 σ(I) with 4.630° < 2θ < 54.14°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.934. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9910 and 0.9950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{57}H_{80}B_5F_9N_2O_9$. The final anisotropic full-matrix least-squares refinement on F^2 with 860 variables converged at R1 = 6.96%, for the observed data and wR2 = 13.99% for all data. The goodness-of-fit was 1.077. The largest peak in the final difference electron density synthesis

was 0.335 $e^-/Å^3$ and the largest hole was -0.295 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.191 g/cm^3 and F(000), 1228 e^-. The hydrogen at N2 atom was refined freely. CCDC Nr.: 2119782.

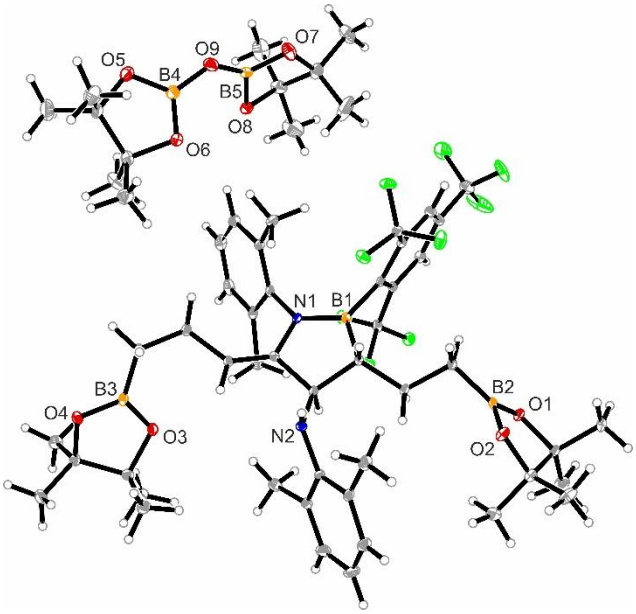


Figure S30. Crystal structure of 1:1 mixture of **3e** and **BOB** compounds found in the asymmetric unit. (thermal ellipsoids are shown at 30% probability).

In situ NMR spectra of compound 4e

The sample from the above experiment was measured in a 600 MHz NMR spectrometer ca. 1h after adding the allyl-Bpin reagent to give the in-situ NMR spectra of compound **4e**.

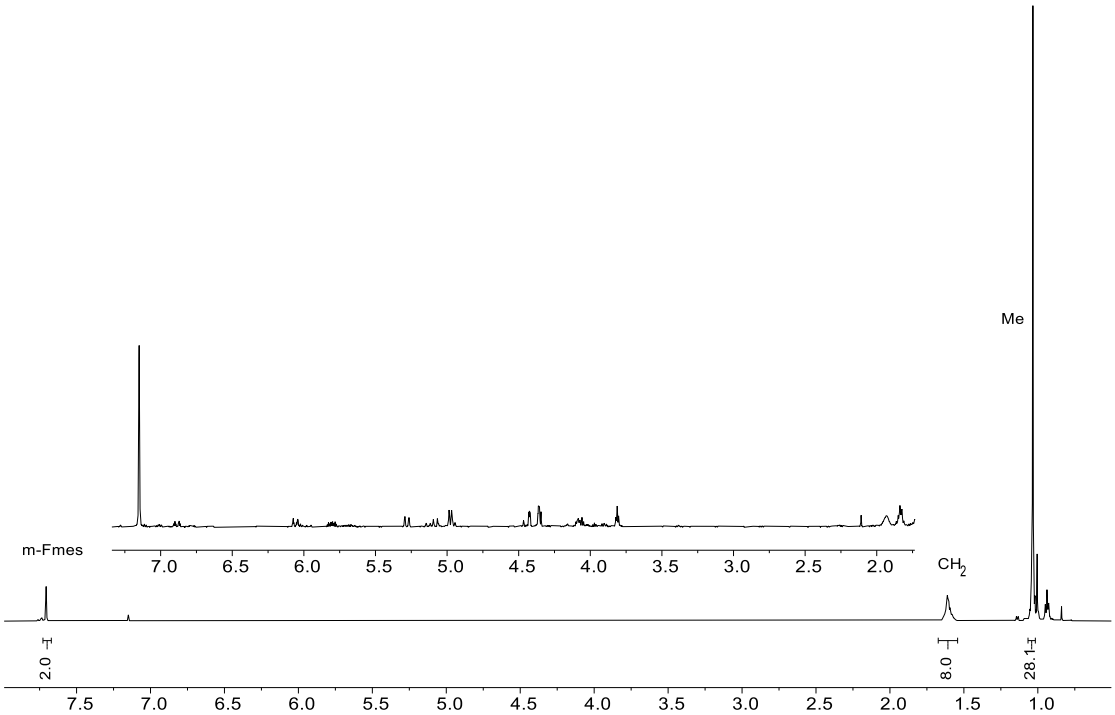


Figure S31. ^{1}H NMR (600 MHz, benzene-d_6, 299 K) spectrum of compound **4e**

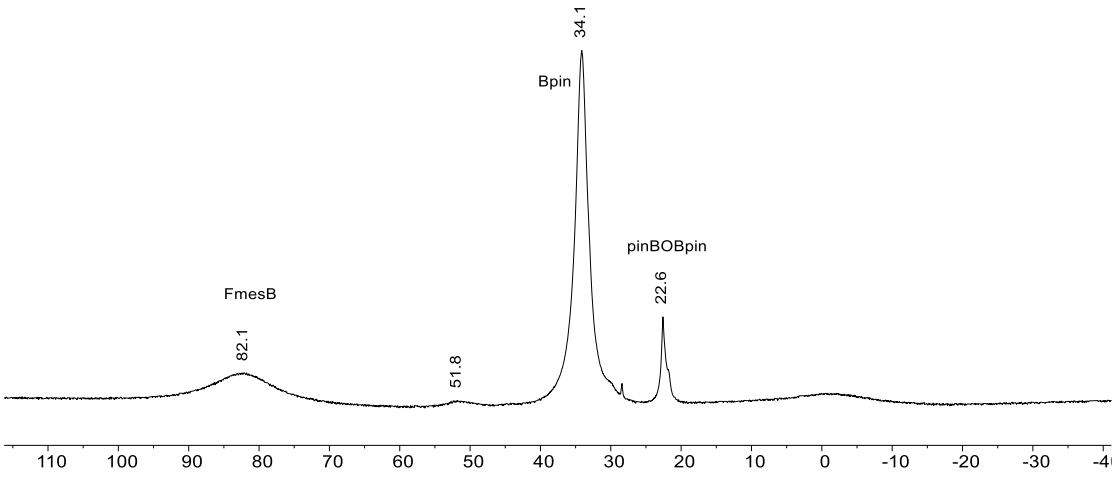


Figure S32. $^{11}B\{^{1}H\}$ NMR (192 MHz, benzene-d_6, 299 K) spectrum of compound **4e**

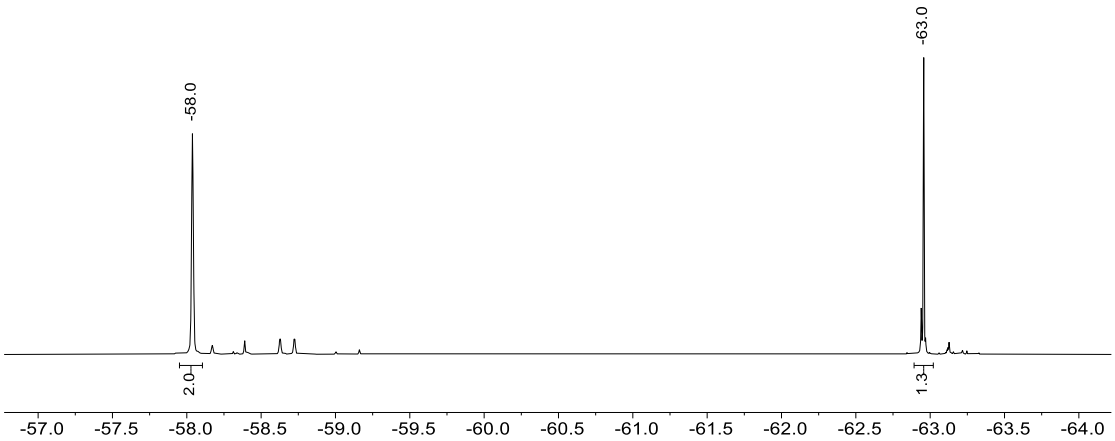
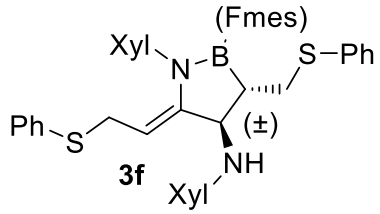


Figure S33. ^{19}F NMR (564 MHz, benzene-d_6,, 299 K) spectrum of compound **4e**.

Preparation of compound 3f



3f

Following the general procedure, phenyl(vinyl)sulfane (**2f**: 54.5 mg, 0.4 mmol, 2 equiv.) was used as the alkene substrate. Crystallization gave compound **3f** as a pale-yellow solid (42 mg, 25% yield).

HRMS for $C_{43}H_{38}BF_9N_2S_2H^+$ $[M+H]^+$: calc. 829.2506, found: 829.2505.

^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K): δ = 8.06 (s, 1H, *m*-Fmes), 7.84 (s, 1H, *m*'-Fmes), 7.22 (m, 2H, *m*-SPh^a), 7.16 (m, 1H, *p*-SPh^a), 7.11 (m, 2H, *o*-SPh^a), 7.09 (m, 2H, *m*-SPh^b), 7.06 (m, 1H, *p*-SPh^b), 7.03 (m, 2H, *m*-Xyl^a, *p*-Xyl^a), 7.01 (m, 2H, *m*-Xyl^b), 6.85 (m, 1H, *m*'-Xyl^a), 6.82 (m, 1H, *p*-Xyl^b),

6.72 (m, 2H, *o*-SPh^{b}), 5.33 (m, 1H, CH=), 4.46 (m, 1H, NCH), 3.31 (d, $^{3}J_{HH}$ = 11.4 Hz, 1H, NH), 2.97 (dd, $^{2}J_{HH}$ = 12.8 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, CH_2SPh^{b}), 2.87 (ddd, $^{2}J_{HH}$ = 14.2 Hz, $^{3}J_{HH}$ = 8.4 Hz, *J* = 1.5 Hz, 1H, CH_2SPh^{a}), 2.76 (dd, $^{2}J_{HH}$ = 12.8 Hz, $^{3}J_{HH}$ = 11.0 Hz, 1H, CH_2SPh^{b}), 2.74 (ddd, $^{2}J_{HH}$ = 14.2 Hz, $^{3}J_{HH}$ = 7.1 Hz, *J* = 2.0 Hz, 1H, CH_2SPh^{a}), (m, 2H, CH_2SPh^{a}, CH_2SPh^{b}), 2.30 (s, 6H, *o*-CH_3^{Xylb}), 2.26 (m, 4H, *o*-CH_3^{Xyla}, BCH), 1.98 (s, 3H, *o*'-CH_3^{Xyla}).

$^{13}C\{^{1}H\}$ NMR (151 MHz, methylene chloride-d_2, 299 K) [selected resonances]: δ = 149.7 (NC=), 145.0 (*i*-Xyl^{b}), 139.5 (*i*-Xyl^{a}), 138.8 (br, *i*-Fmes), 137.0 (*i*-SPh^{b}), 136.8 (*i*-SPh^{a}), 136.1 (*o*-Xyl^{a}), 135.2 (q, $^{2}J_{Fc}$ = 31.8 Hz, *o*'-Fmes), 133.9 (q, $^{2}J_{Fc}$ = 32.0 Hz, *o*-Fmes), 133.5 (*o*'-Xyl^{a}), 132.1 (q, $^{2}J_{Fc}$ = 34.5 Hz, *p*-Fmes), 130.0 (*o*-SPh^{a}), 129.63 (*m*-Xyl^{b}), 129.58 (*m*-Xyl^{a}), 129.2 (*m*'-Xyl^{a}), 129.1 (*m*-Ph^{a}), 129.0 (*m*-SPh^{b}), 128.5 (*o*-SPh^{b}), 128.3 (*o*-Xyl^{b}), 127.2 (br, *p*-Xyl^{a}, *m*-Fmes), 126.8 (br, *m*'-Fmes), 126.4 (*p*-SPh^{a}), 125.8 (*p*-SPh^{b}), [124.3 (q, $^{1}J_{FC}$ = 274.8 Hz), 123.8 (q, $^{1}J_{FC}$ = 274.6 Hz), 123.1 (q, $^{1}J_{FC}$ = 272.7 Hz)](CF_3), 121.8 (*p*-Xyl^{b}), 103.8 (CH=), 64.3 (NCH), 44.7 (br, BCH), 34.1 (CH_2SPh^{b}), 29.4 (CH_2SPh^{a}), 19.4 (q, J_{FC} = 2.6 Hz, o'-CH_3^{Xyla}), 19.2 (o-CH_3^{Xylb}), 18.98 (q, J_{FC} = 3.0 Hz, o-CH_3^{Xyla}).

$^{11}B\{^{1}H\}$ NMR (192 MHz, methylene chloride-d_2, 299K): δ = 47.2 ($\nu_{1/2} \approx$ 1080 Hz).

^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K): δ = -55.2 (d, *J* = 3.0 Hz, 1F, *o*-CF_3), -59.6 (s, 1F, *o*'-CF_3), -63.7 (s, 1F, *p*-CF_3).

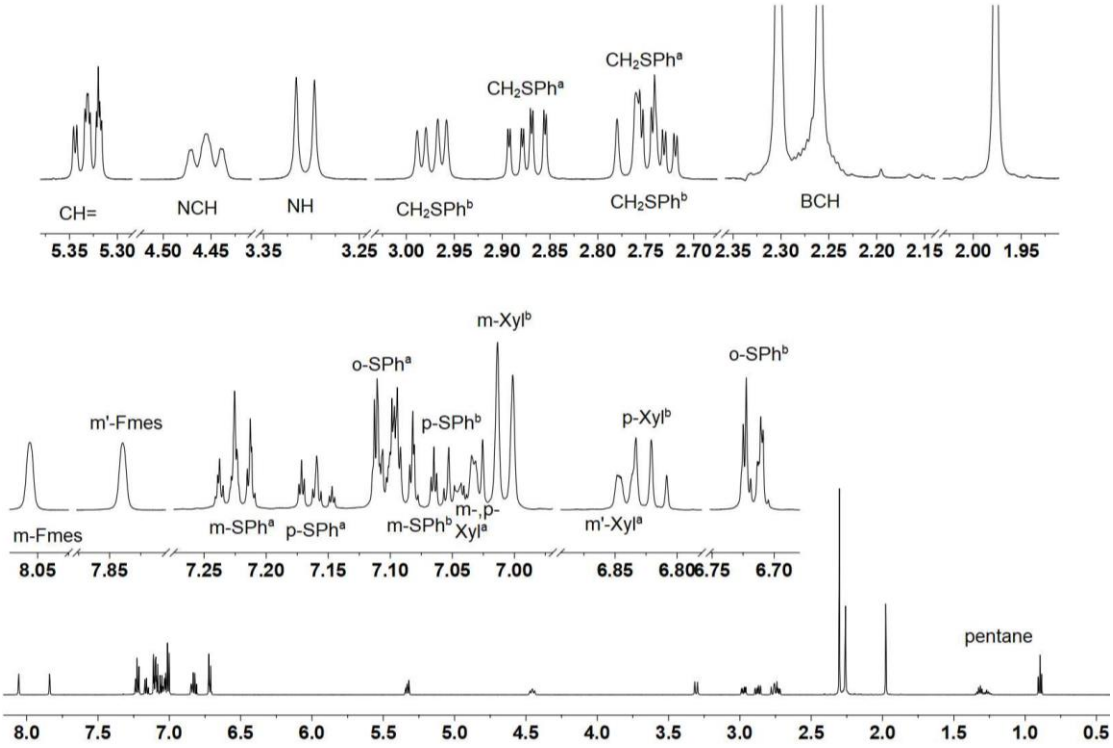


Figure S34. ^{1}H NMR (600 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3f**

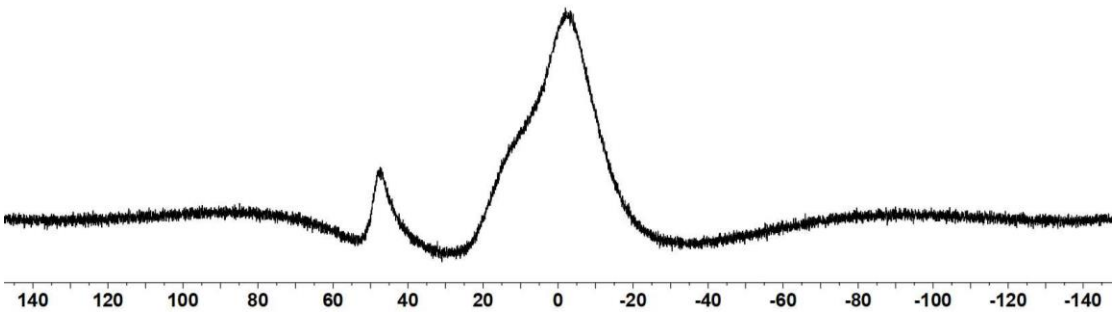


Figure S35. $^{11}B\{^{1}H\}$ NMR (192 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3f**

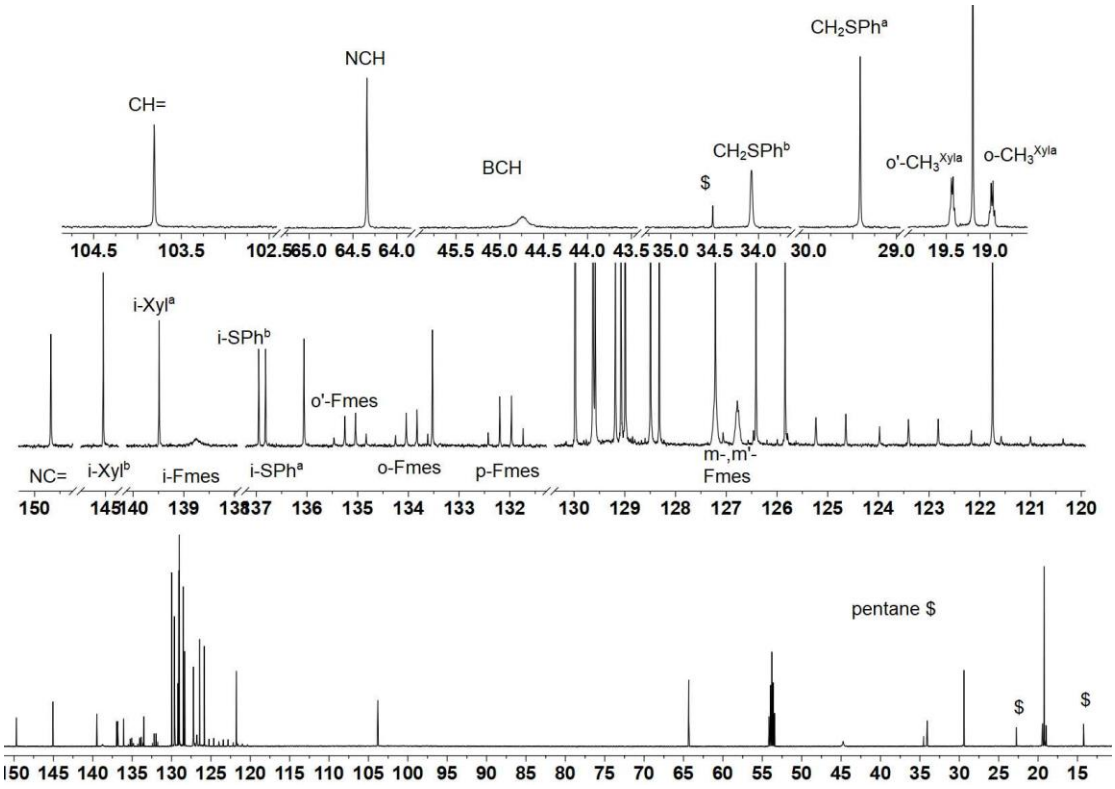


Figure S36. $^{13}C\{^{1}H\}$ NMR (151 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3f**

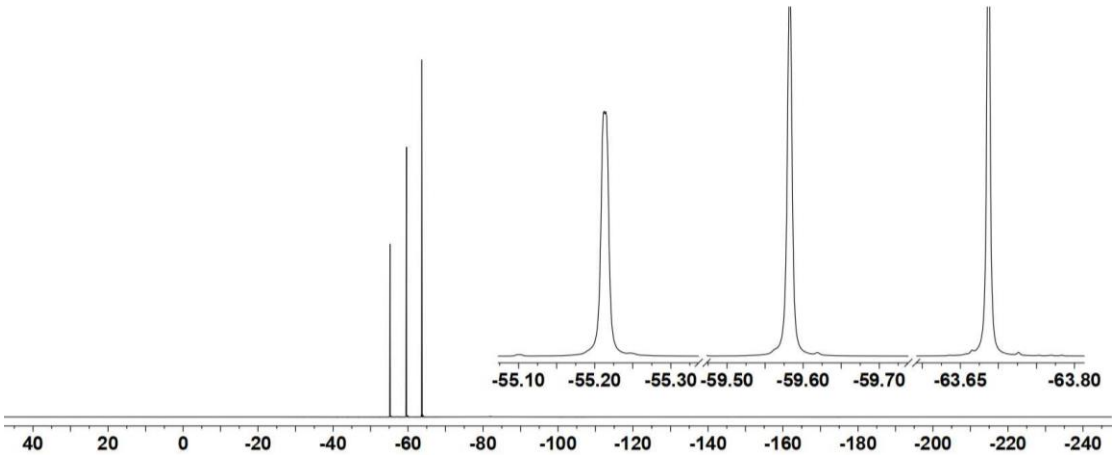


Figure S36.^{19}F NMR (564 MHz, methylene chloride-d_2, 299 K) spectrum of compound **3f**

The crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **3f** in pentane at -35 °C.

X-ray crystal structure analysis of compound 3f (erk9520): A colorless prism-like specimen of $C_{43}H_{38}BF_9N_2S_2$, approximate dimensions 0.180 mm x 0.200 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1805 frames were collected. The total exposure time was 21.42 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 35023 reflections to a maximum θ angle of 66.83° (0.84 Å resolution), of which 7416 were independent (average redundancy 4.723, completeness = 99.1%, R_{int} = 4.32%, R_{sig} = 3.23%) and 6301 (84.96%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.0047(2) Å, b = 12.1833(2) Å, c = 19.4720(4) Å, α = 85.1480(10)°, β = 81.4370(10)°, γ = 86.1730(10)°, volume = 2101.65(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9962 reflections above 20 σ(I) with 7.293° < 2θ < 133.6°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.857. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6750 and 0.7400. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{43}H_{38}BF_9N_2S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 550 variables converged at R1 = 3.85%, for the observed data and wR2 = 9.85% for all data. The goodness-of-fit was 1.088. The largest peak in the final difference electron density synthesis was 0.235 $e^-/Å^3$ and the largest hole was -0.313 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.310 g/cm^3 and F(000), 856 e^-. The hydrogen at N2 atom was refined freely. CCDC Nr.: 2119783.

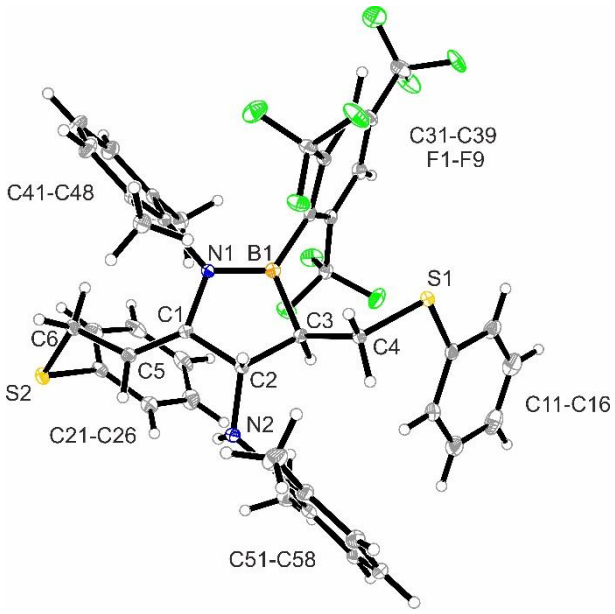


Figure S37. Crystal structure of compound **3f** (thermal ellipsoids are shown at 30% probability).

In situ NMR spectra of compound 4f

The sample from the above experiment was measured in a 600 MHz NMR spectrometer 1h after adding (phenylthio)ethylene to give the in-situ NMR spectra of compound **4f**.

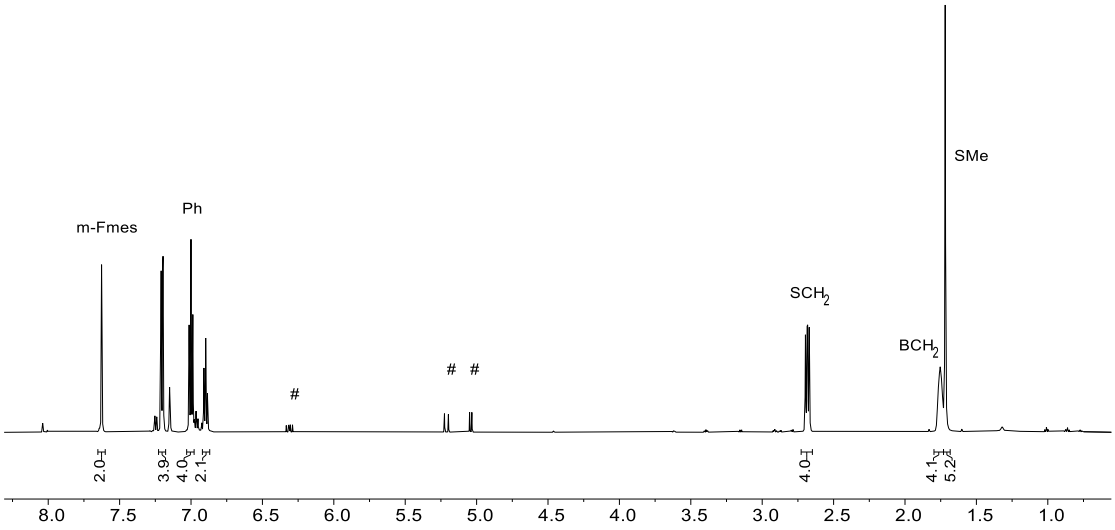


Figure S38. ^{1}H NMR (600 MHz, benzene-d_6, 299 K) spectrum of compound **4f** (#: compound **2f**)

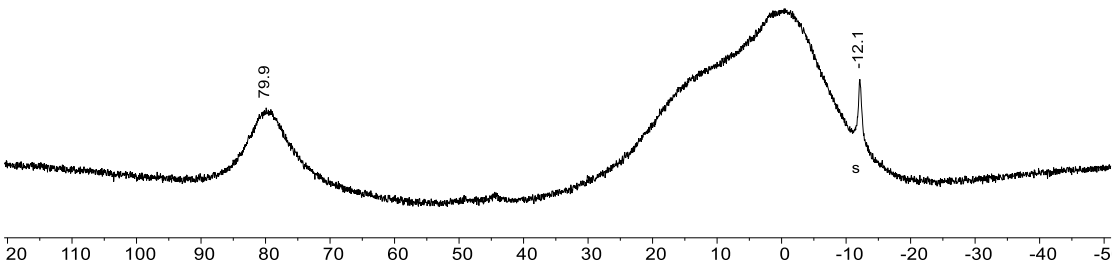


Figure S39. ^{11}B{^{1}H} NMR (192 MHz, benzene-d_6, 299 K) spectrum of compound **4f** (s: starting material)

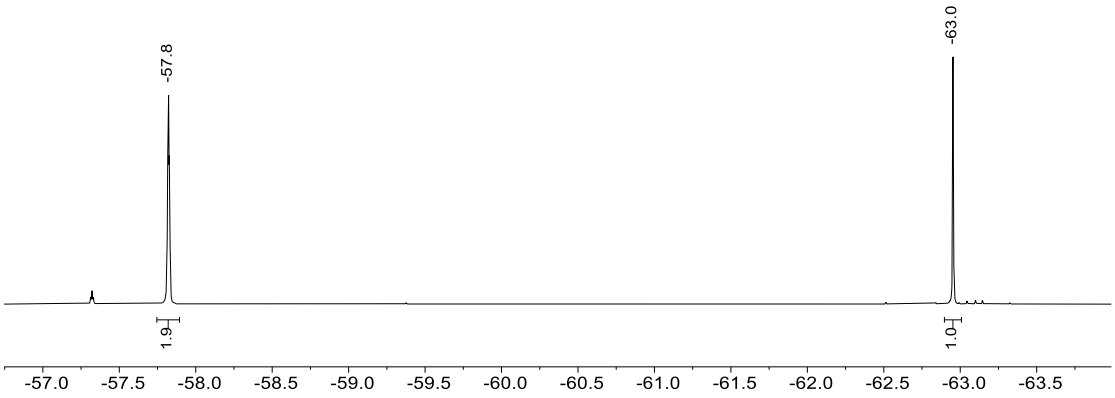


Figure S40.^{19}F NMR (564 MHz, benzene-d_6, 299 K) spectrum of compound **4f**

Reference

1. Bruker AXS (**2019**) *APEX3 Version 2019.1-0*, *SAINT Version 8.40A* and *SADABS Bruker AXS area detector scaling and absorption correction Version 2016/2*, Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M., *SHELXT – Integrated space-group and crystal-structure determination*, *Acta Cryst.,* **2015**, *A71*, 3-8.
3. Sheldrick, G.M., *Crystal structure refinement with SHELXL*, *Acta Cryst.*, **2015**, *C71 (1)*, 3-8.
4. Bruker AXS (**1998**) *XP – Interactive molecular graphics, Version 5.1,* Bruker AXS Inc., Madison, Wisconsin, USA.
5. J. Li, C. G. Daniliuc, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.* 2019, **58**, 6737-6741.