

Supporting Information

Introducing the Dihydro-1,3-azaboroles: Convenient Entry by a Three-Component Reaction, Synthetic and Photophysical Application

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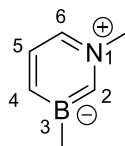
Experimental Procedures

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: elemental analyses: Foss–Heraeus CHNO-Rapid; HRMS: Thermo Scientific Orbitrap LTQ XL; NMR: Varian UNITY plus NMR spectrometer (^1H , 600 MHz; ^{13}C , 151 MHz; ^{11}B , 192 MHz; ^{19}F , 564 MHz). NMR chemical shifts are given relative to SiMe_4 and referenced to the respective solvent signal (^1H and ^{13}C) or an external standard [$\delta(\text{BF}_3\cdot\text{OEt}_2) = 0$ for ^{11}B NMR, $\delta(\text{CFCl}_3) = 0$ for ^{19}F NMR]. NMR assignments were supported by 2D NMR experiments.

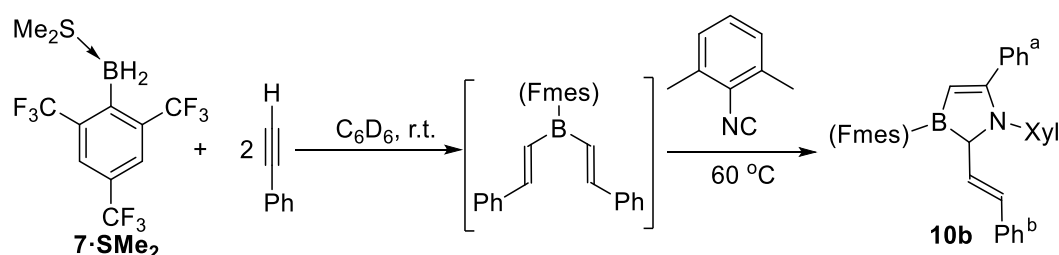
X-Ray diffraction: Data sets for compounds **13a**, **16e**, **16f**, **16g**, **18b**, **24d**, **25**, **26** and **28h** were collected with a Bruker D8 Venture CMOS diffractometer. For compounds **10b**, **11**, **15g**, **16b**, **16h**, **18a**, **24c**, **24e**, **28i** and **28k** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., 2016); cell refinement: SAINT V8.37A (Bruker AXS Inc., 2015); data reduction: SAINT V8.37A (Bruker AXS Inc., 2015); absorption correction, SADABS V2014/7 (Bruker AXS Inc., 2014); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.*, 2015, A71, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.*, 2015, C71 (1), 3-8). For compounds **16c**, **16d** and **24a** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hoof, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* 1997, 276, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* 2003, A59, 228-234); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.*, 2015, A71, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.*, 2015, C71 (1), 3-8) and graphics, *XP* (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features:* For compounds **11** and **28i** two CF_3 groups, for compounds **13a** and **16e** four CF_3 groups, for compound **16h** three CF_3 groups, for compound **15g** two CF_3 groups, the $\text{P}(\text{Mes})_2$ unit and one pentane molecule, for compounds **16b**, **24a**, **24c**, **24d** and **28k** one CF_3 group, for compound **16c** two CF_3 groups, for compound **16d** one ethyl group and two CF_3 groups, for compound **24e** one pentane molecule were found disordered over two positions in the asymmetric unit. For compound **28h** one CF_3 group was found disordered over three positions in the asymmetrical unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Additionally, compound **16e** was refined as a 2-component twin, whereby the BASF factor was refined to 0.40. For compound **16d** a badly disordered half pentane molecule, for compound **24c** a badly disordered pentane molecule, for compound **28h** two half badly disordered cyclopentane molecules and for compound **11** one-third pentane molecule were 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 solvents. The quoted formula and derived parameters are not included the squeezed solvent molecules.

Materials: Borane (**7**)₂ and **7-SMe**₂ were prepared according to a procedure described in the literature.⁸ **Warning:** Many isonitriles are toxic reagents, they should be used with due care. Organoalkalimetal compounds are strong bases and potentially ignite in contact with air and/or water. They should be used with due care.

Numbering of the azaborinine ring for the assignment of NMR signals:



Preparation of compound 10b



Scheme S1.

At room temperature, borane **7·SMe₂** (142.4 mg, 0.4 mmol, 1 eq.) was added to the solution of phenyl acetylene (81.6 mg, 0.8 mmol, 2 eq.) in C₆D₆ (2 mL) under argon atmosphere in a Schlenk tube. Then the mixture was stirred for 30 min at room temperature to give a light-yellow solution. Subsequently 2,6-dimethylphenylisocyanide (52.4 mg, 0.4 mmol, 1 eq.) was added to the mixture in one portion to give a brown solution. The resulting solution was stirred at 60 °C overnight. Then all volatiles were removed in vacuo, the residue was dissolved in heptane (1 mL) and stored at -35 °C to finally give the compound **10b** as a light yellow solid (174 mg, 69 % yield).

Elemental Analysis for C₃₄H₂₅BNF₉: calc. C (64.89 %), H (4.00 %), N (2.23 %); found: C (63.99 %), H (3.86 %), N (2.05%);

HRMS for C₃₄H₂₄BNF₉⁺ [M-H]⁺: calc. 628.1859, found: 628.1857.

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.14 (s, 1H, *m*-Fmes), 8.09 (s, 1H, *m'*-Fmes), 7.39 (m, 2H, *o*-Ph^a), 7.33 (m, 1H, *p*-Ph^a), 7.26 (m, 2H, *m*-Ph^a), 7.19 (m, 2H, *m*-Ph^b), 7.11 (m, 3H, *o*-Ph^b, *p*-Ph^b), 7.05 (m, 2H, *m*-Xyl, *p*-Xyl), 6.91 (dd, ³*J*_{HH} = 6.5 Hz, ⁴*J*_{HH} = 2.6 Hz, 1H, *m'*-Xyl), 6.20 (AB, ³*J*_{HH} = 15.6 Hz, 1H, Ph^bCH=), 6.12 (ABM, ³*J*_{HH} = 15.6 Hz, ³*J*_{HH} = 9.4 Hz, 1H, CH=), 5.68 (s, 1H, BCH=), 4.80 (m, 1H, NCH), 2.33 (s, 3H, *o'*-CH₃^{Xyl}), 2.13 (s, 3H, *o*-CH₃^{Xyl}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K)[selected resonances]: δ = 182.4 (NC=), 145.2 (br, *i*-Fmes), 139.7 (*i*-Xyl), [137.37, 137.36](*o*-Xyl, *o'*-Xyl), 137.3 (*i*-Ph^b), 134.8 (*i*-Ph^a), 134.5 (q, ²*J*_{FC} = 31.0 Hz, *o'*-Fmes), 133.8 (q, ²*J*_{FC} = 30.9 Hz, *o*-Fmes), 132.2 (Ph^bCH=), 130.5 (q, ²*J*_{FC} = 34.2 Hz, *p*-Fmes), 130.3 (*p*-Ph^a), 129.0 (*m*-Xyl), 128.85 (*m'*-Xyl), 128.78 (*m*-Ph^b), 128.6 (*o*-Ph^a), 128.4 (*m*-Ph^a), 127.9 (*p*-Xyl), 127.6 (*p*-Ph^b), 126.3 (*o*-Ph^b), 126.0 (br, *m'*-Fmes), 125.7 (br, *m*-Fmes), 124.6 (m, CH=), 109.3 (br, BCH=), 73.2 (br, NCH), 19.2 (*o'*-CH₃^{Xyl}), 18.6 (*o*-CH₃^{Xyl}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 59.6 (*v*_{1/2} ≈ 910 Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = [-56.7, -57.7](each s, each 1F, *o*-CF₃), -63.5 (*p*-CF₃).

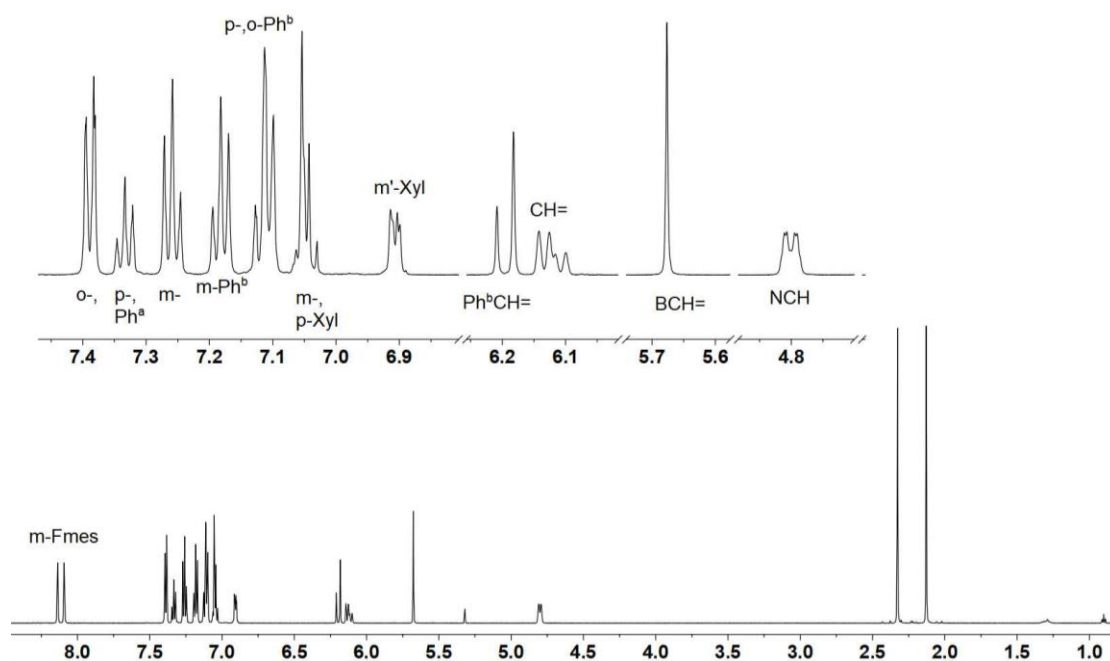


Figure S1. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **10b**.

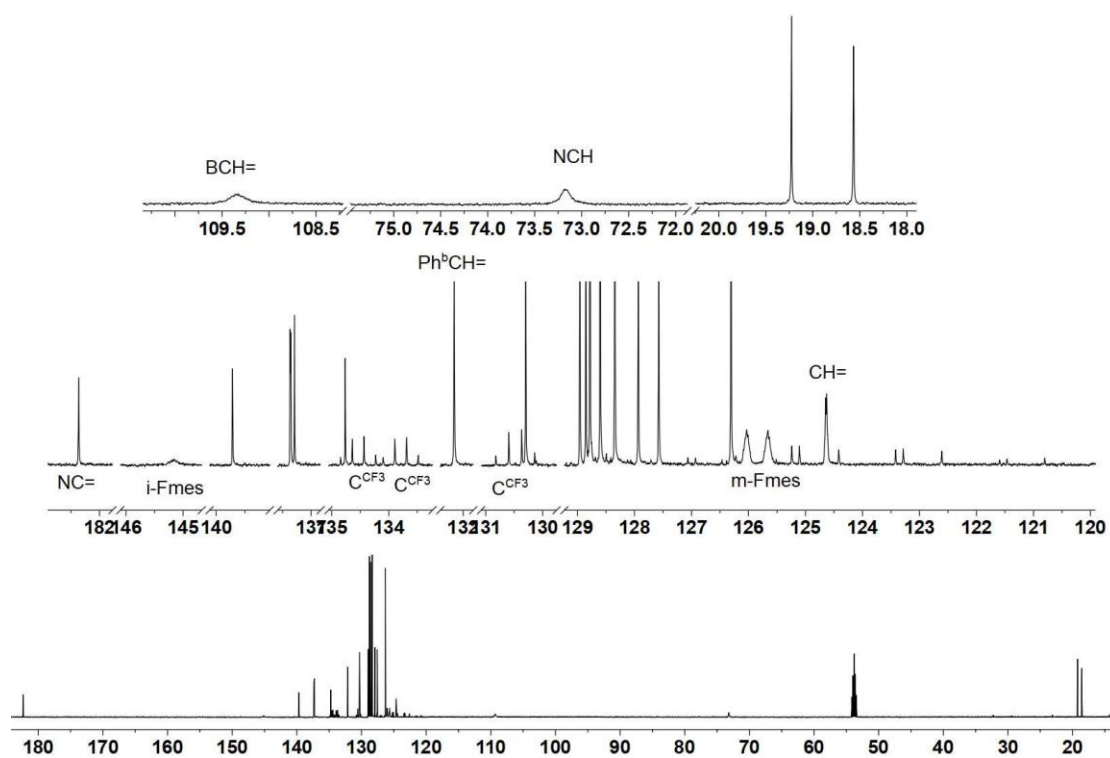


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **10b**.

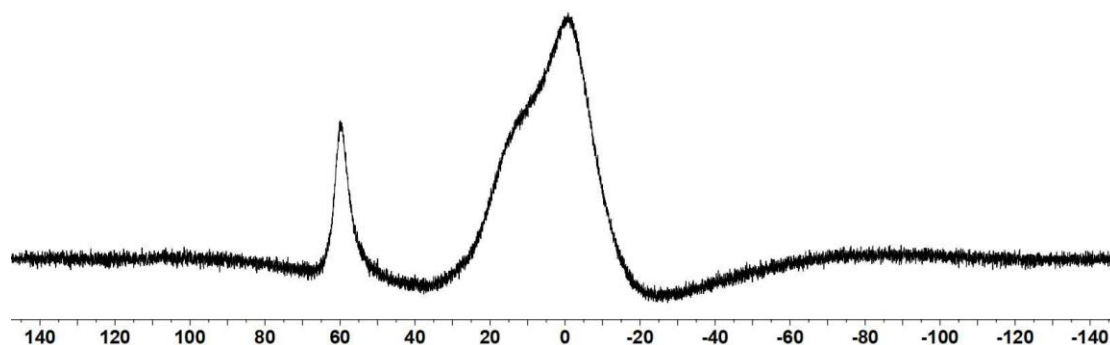


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **10b**.

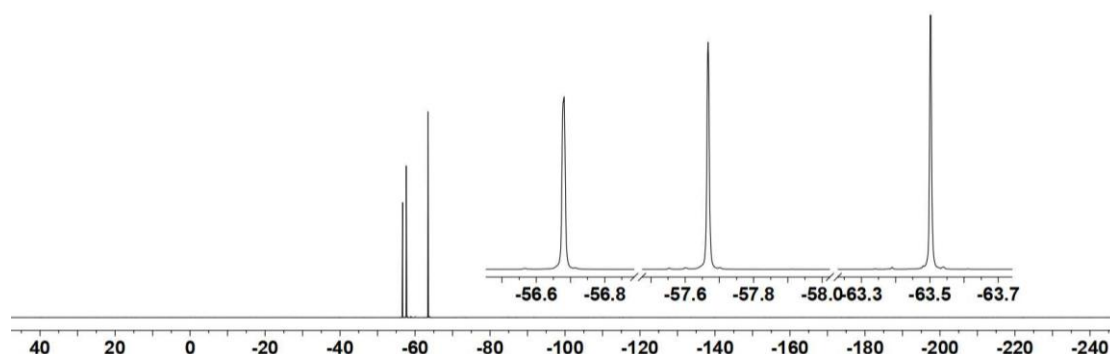


Figure S4. ^{19}F NMR (564 MHz, methylene chloride, 299 K) spectrum of compound **10b**.

The single crystal suitable for the X-ray crystal structure analysis was obtained from a solution of compound **10b** in heptane at room temperature.

X-ray crystal structure analysis of compound 10b (erk9655): A yellow prism-like specimen of $\text{C}_{34}\text{H}_{25}\text{BF}_9\text{N}$, approximate dimensions 0.100 mm x 0.140 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1459 frames were collected. The total exposure time was 19.84 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 39288 reflections to a maximum θ angle of 66.70° (0.84 \AA resolution), of which 5166 were independent (average redundancy 7.605, completeness = 99.8%, $R_{\text{int}} = 4.59\%$, $R_{\text{sig}} = 2.51\%$) and 4456 (86.26%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 17.0933(3) \text{ \AA}$, $b = 9.8292(2) \text{ \AA}$, $c = 17.4543(3) \text{ \AA}$, $\beta = 95.4300(10)^\circ$, volume = $2919.40(9) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9899 reflections above $20 \sigma(I)$ with $6.918^\circ < 2\theta < 133.2^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.868. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7840 and 0.9010. 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, $\text{C}_{34}\text{H}_{25}\text{BF}_9\text{N}$. The final anisotropic full-matrix least-squares refinement on F^2 with 408 variables converged at $R1 = 3.76\%$, for the observed data and $wR2 = 10.45\%$ for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was $0.244 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.239 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.045 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.432 g/cm^3 and $F(000)$, 1288 e^- . CCDC number: 2007631.

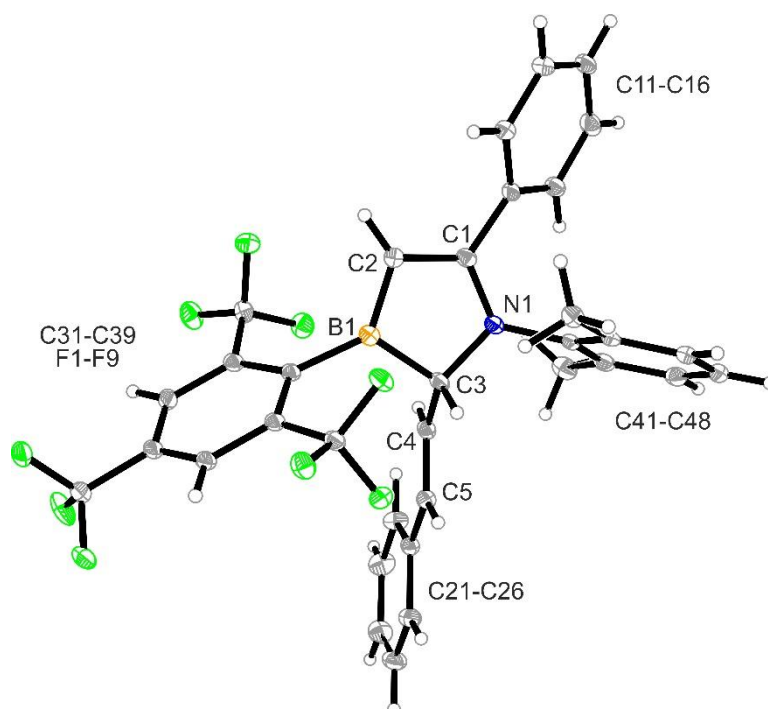
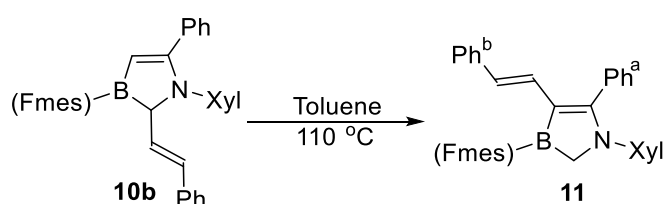


Figure S5. Crystal structure of compound **10b** (thermal ellipsoids at 30% probability).

Preparation of compound 11



Scheme S2.

At room temperature, azaborole **10b** (94.3 mg, 1.5 mmol) was dissolved in toluene (2 mL) under argon atmosphere in a J. Young tube. The resulting solution was stored at 110 °C for 7 days. Then all volatiles were removed in vacuo. Subsequently, the residue was dissolved in pentane (1 mL) and stored at -35 °C to finally give the compound **11** as a yellow solid (80 mg, 85% yield).

HRMS for $C_{34}H_{26}BNF_9^+$, $[M+H]^+$: calc. 630.2015; found: 630.2019.

1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.24 (s, 2H, *m*-Fmes), 7.34 (m, 5H, *o*-, *m*-, *p*-Ph^a), 7.11 (m, 2H, *m*-Ph^b), 7.06 (m, 1H, *p*-Xyl), 7.00 (m, 3H, *p*-Ph^b, *m*-Xyl), 6.95 (m, 2H, *o*-Ph^b), 6.74 (d, $^3J_{HH}$ = 16.1 Hz, 1H, CH=), 5.78 (d, $^3J_{HH}$ = 16.1 Hz, 1H, Ph^bCH=), 3.78 (m, 2H, CH₂), 2.20 (s, 6H, *o*-CH₃^{Xyl}).

$^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K)[selected resonances]: δ = 179.9 (NC=), 146.2 (br, *i*-Fmes), 140.9 (*i*-Xyl), 139.7 (*i*-Ph^b), 136.9 (*o*-Xyl), 133.8 (q, $^2J_{FC}$ = 31.4 Hz, *o*-Fmes), 132.8 (*i*-Ph^a), 130.8 (q, $^2J_{FC}$ = 34.3 Hz, *m*-Fmes), 129.9 (*p*-Ph^a), 129.2 (*m*-Ph^a), 128.7 (*m*-Xyl), 128.6 (*m*-Ph^b), 128.3 (*o*-Ph^a), 128.1 (*p*-Xyl), 126.8 (CH=), 126.3 (br, *m*-Fmes), 125.9 (*p*-Ph^b), 125.4 (*o*-Ph^b), 124.8 (Ph^bCH=), 119.1 (br, BC=), 56.9 (CH₂), 17.9 (*o*-CH₃^{Xyl}).

$^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 59.8 ($\nu_{1/2} \approx 1010$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -59.1 (s, 2F, *o*-CF₃^{Fmes}), -63.4 (s, 1F, *p*-CF₃^{Fmes}).

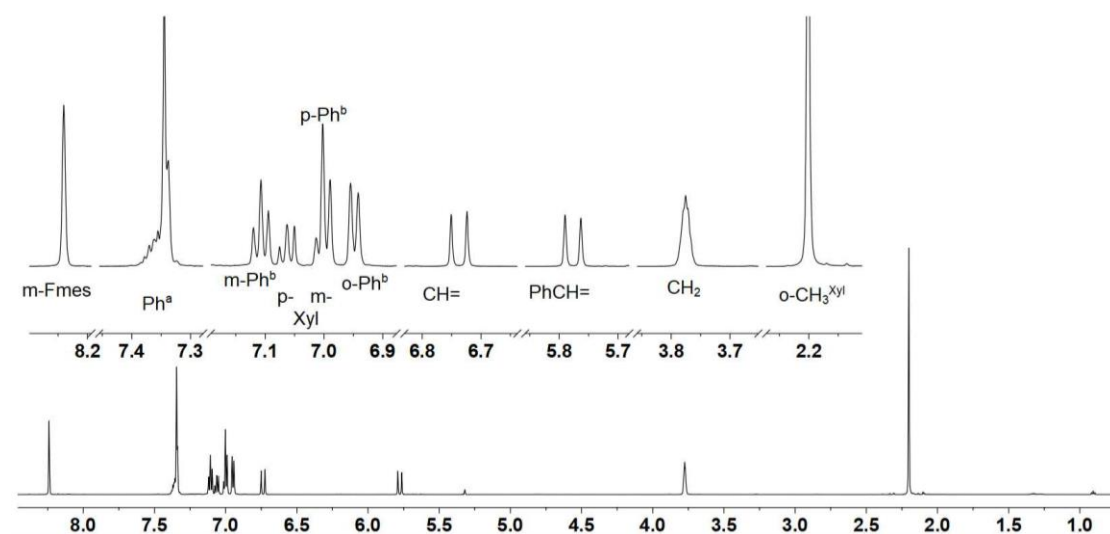


Figure S6. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **11**.

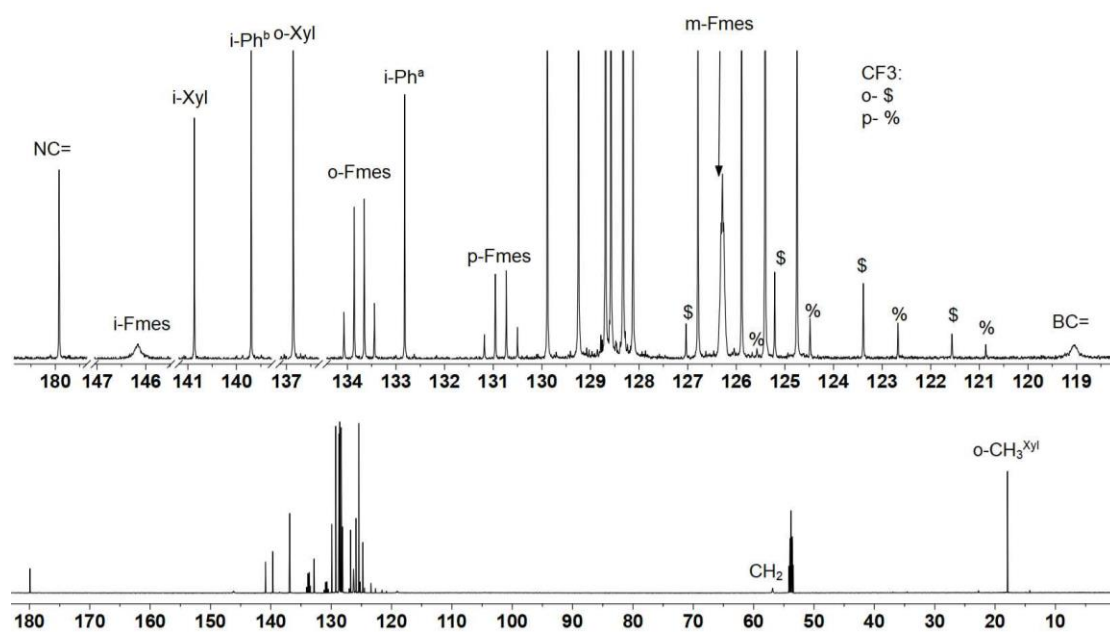


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **11**.

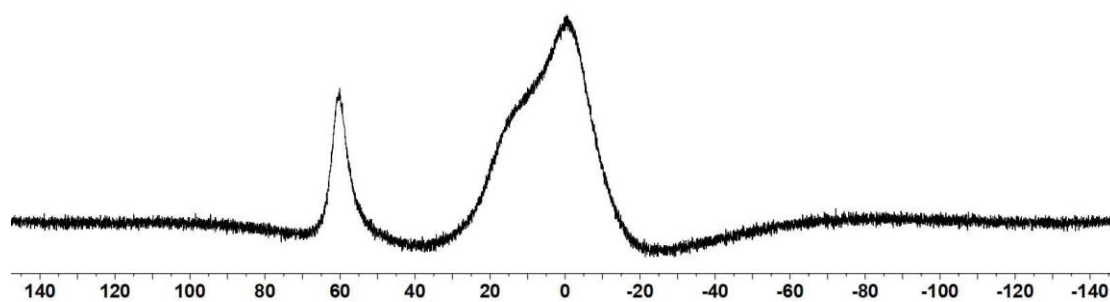


Figure S8. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **11**.

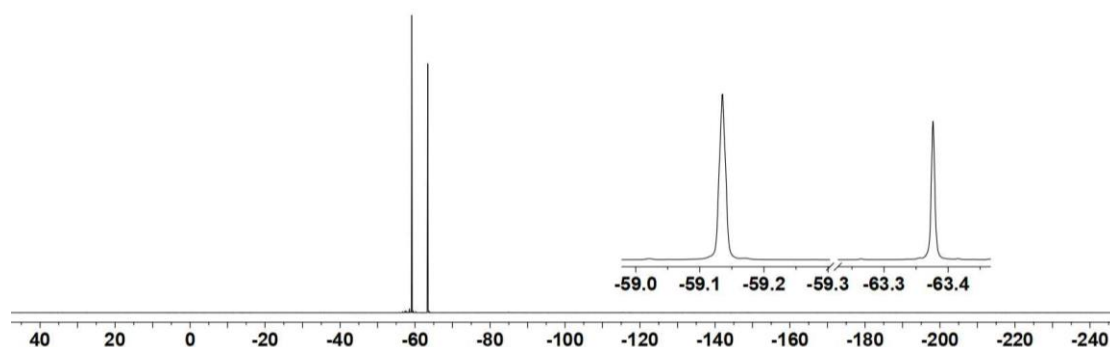


Figure S9. ^{19}F NMR (564 MHz, methylene chloride, 299 K) spectrum of compound **11**.

Single crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **10** in pentane at $-35\text{ }^{\circ}\text{C}$.

X-ray crystal structure analysis of compound 11 (erk9620): A pale yellow prism-like specimen of $\text{C}_{34}\text{H}_{25}\text{BF}_9\text{N}$, approximate dimensions $0.100\text{ mm} \times 0.120\text{ mm} \times 0.150\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2029 frames were collected. The total exposure time was 21.96 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a trigonal unit cell yielded a total of 62150 reflections to a maximum θ angle of 65.06° (0.85 \AA resolution), of which 5164 were independent (average redundancy 12.035, completeness = 99.8%, $R_{\text{int}} = 13.49\%$, $R_{\text{sig}} = 6.73\%$) and 3665 (70.97%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 34.991(3)\text{ \AA}$, $b = 34.991(3)\text{ \AA}$, $c = 12.8827(10)\text{ \AA}$, volume = 13660.2 \AA^3 , are based upon the refinement of the XYZ-centroids of 4849 reflections above $20\sigma(I)$ with $8.754^{\circ} < 2\theta < 130.5^{\circ}$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.779. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8620 and 0.9050. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $R\bar{3}$, with $Z = 18$ for the formula unit, $\text{C}_{34}\text{H}_{25}\text{BF}_9\text{N}$. The final anisotropic full-matrix least-squares refinement on F^2 with 465 variables converged at $R1 = 5.28\%$, for the observed data and $wR2 = 14.18\%$ for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was $0.280\text{ e}^{-}/\text{\AA}^3$ and the largest hole was $-0.244\text{ e}^{-}/\text{\AA}^3$ with an RMS deviation of $0.064\text{ e}^{-}/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.377 g/cm^3 and $F(000)$, 5796 e^{-} . CCDC number: 2007632.

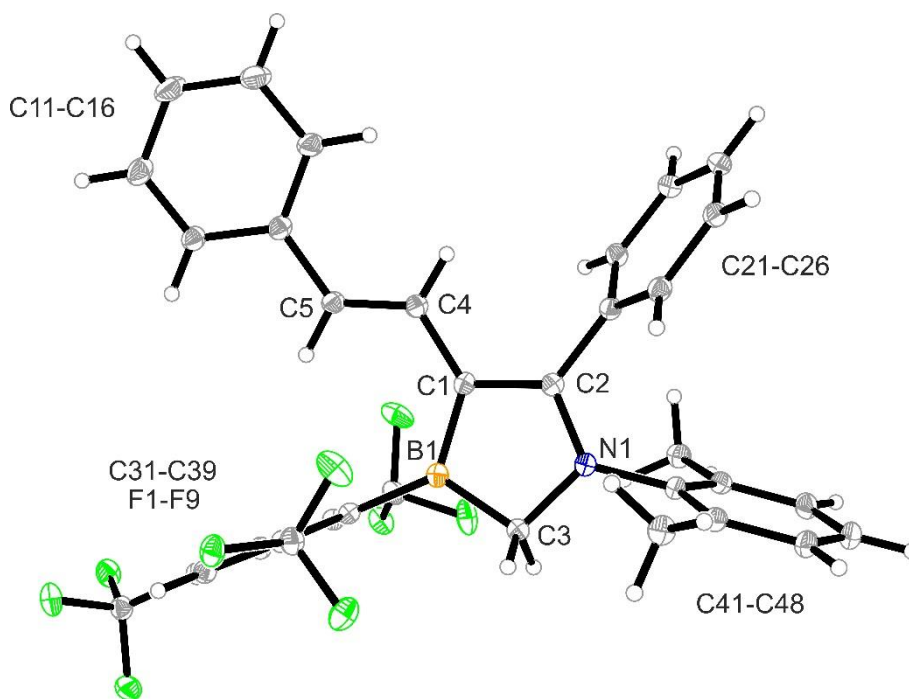
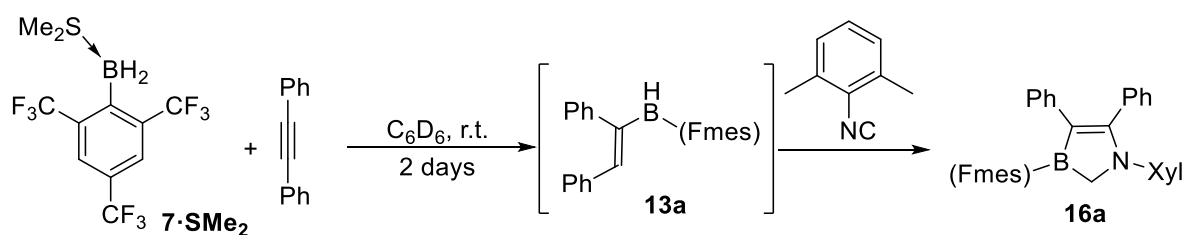


Figure S10. Crystal structure of compound **11** (thermal ellipsoids at 15% probability).

Preparation of compound **16a**

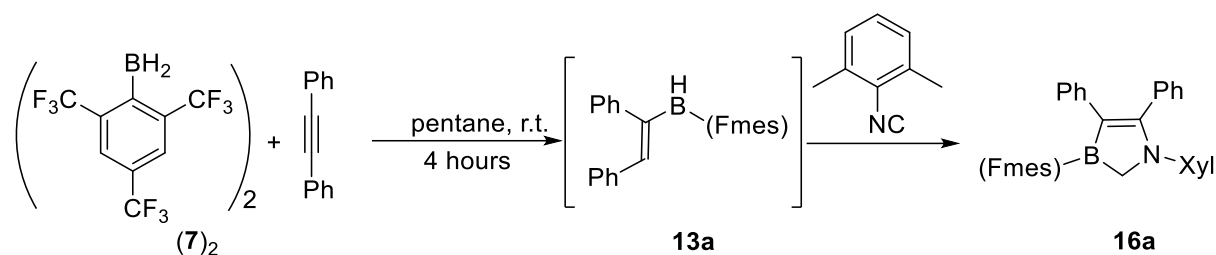


Scheme S3.

Experiment 1:

At room temperature, borane **7·SMe₂** (71.2 mg, 0.2 mmol, 1 equiv.) was added to a solution of diphenylacetylene (35.6 mg, 0.2 mmol, 1 equiv.) in C₆D₆ (1 mL) under argon atmosphere in a J. Young tube. Then the mixture was stored for 2 days at room temperature to give a light orange solution. The formation of the hydroboration product was monitored by an *in situ* NMR experiment. Then 2,6-dimethylphenylisocyanide (26.2 mg, 0.2 mmol, 1 equiv.) was added to the mixture in one portion to give a brown solution. The resulting solution was stored at 60 °C for 5 h. Then all volatiles were removed in vacuo, the residue was dissolved in pentane (1 mL) and stored at -35 °C to finally give the product **16a** as a light-yellow solid (95 mg, 77 % yield).

Experiment 2 (large scale reaction):



Scheme S4.

In a Schlenk tube, borane (**7**)₂ (588 mg, 2 mmol, 1 equiv.) and diphenylacetylene (356 mg, 2 mmol, 1 equiv.) was added subsequently to pentane (15 mL). The suspension was stirred for 4 hours at room temperature to give a clear solution. Then 2,6-dimethylphenylisocyanide (262 mg, 2 mmol, 1 equiv.) was added and the resulting mixture was stirred at room temperature for 2 days to give a red solution. Volatiles were removed in vacuo and the residue was purified by column chromatography on silica gel with pentane : dichloromethane (20:1) as the eluent to finally give compound **16a** as a light-yellow solid (1.12 g, 93% yield).

Elemental Analysis for C₃₂H₂₃BF₉N: calc. C (63.70 %), H (3.84 %), N (2.32 %); found: C (63.71 %), H (3.86 %), N (2.28 %).

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.10 (s, 2H, *m*-Fmes), 7.20 (m, 1H, *p*-Ph^N), 7.12 (m, 2H, *m*-Ph^N), 7.11 (m, 2H, *o*-Ph^N), 7.05 (m, 1H, *p*-Xyl), 6.99 (m, 2H, *m*-Xyl), 6.91 (m, 2H, *m*-Ph^B), 6.86 (m, 1H, *p*-Ph^B), 6.71 (m, 2H, *o*-Ph^B), 3.80 (sept., *J*_{FH} = 2.6 Hz, 2H, CH₂), 2.21 (s, 6H, *o*-CH₃^{Xyl}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K): δ = 179.2 (NC=), 145.5 (br, *i*-Fmes), 141.1 (*i*-Xyl), 140.2 (*i*-Ph^B), 137.0 (*o*-Xyl), 134.0 (q, ²*J*_{FC} = 31.1 Hz, *o*-Fmes), 133.5 (*i*-Ph^N), 130.5 (q, ²*J*_{FC} = 34.2 Hz, *p*-Fmes), 129.5 (*o*-Ph^B, BC=, *o*-Ph^N), 129.4 (*p*-Ph^N), 128.6 (*m*-Xyl), 128.00 (*p*-Xyl), 127.95 (*m*-Ph^N), 127.7 (*m*-Ph^B), 126.0 (br, *m*-Fmes), 124.2 (q, ¹*J*_{FC} = 274 Hz, *o*-CF₃^{Fmes}), 124.0 (*p*-Ph^N), 123.5 (q, ¹*J*_{FC} = 273 Hz, *p*-CF₃^{Fmes}), 56.7 (br, CH₂), 18.0 (*o*-CH₃^{Xyl}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 59.3 (*v*_{1/2} ≈ 770 Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = -58.3 (m, 2F, *o*-CF₃^{Fmes}), -63.5 (s, 1F, *p*-CF₃^{Fmes}).

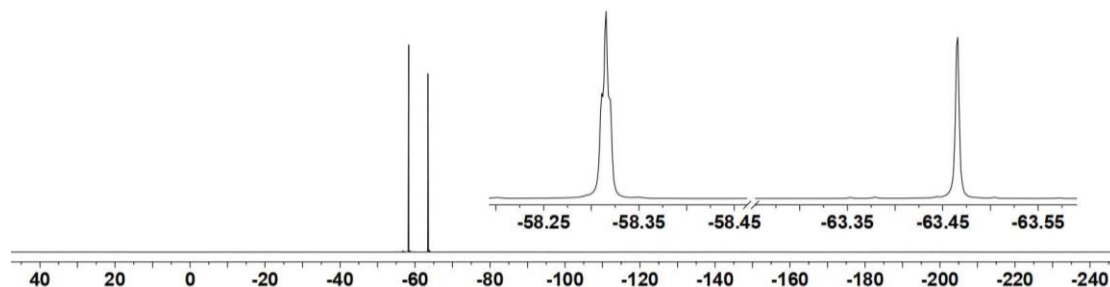


Figure S11. ¹⁹F NMR (564 MHz, methylene chloride, 299 K) spectrum of compound **16a**.

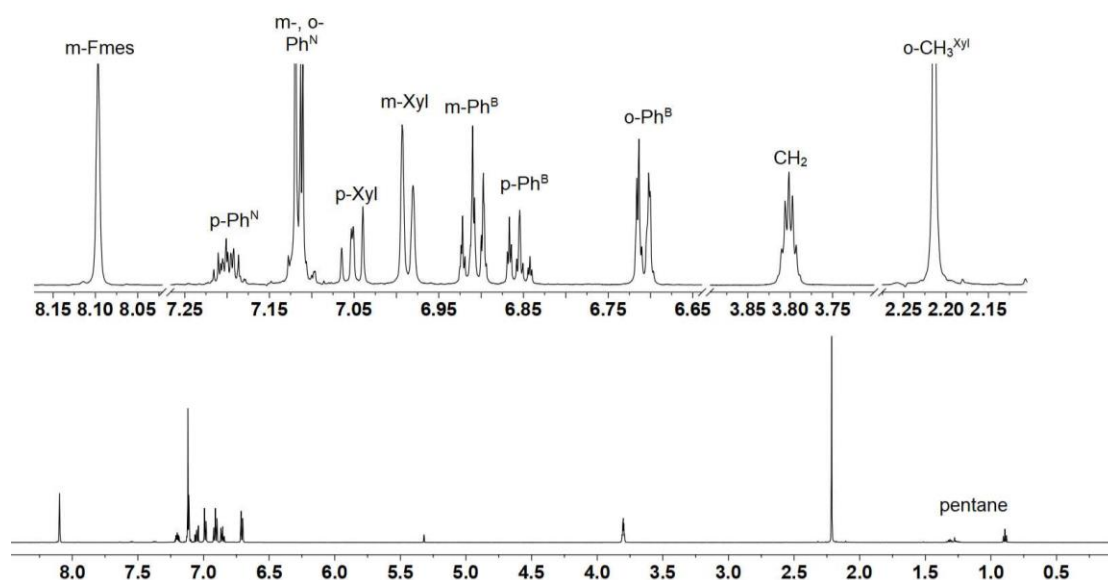


Figure S12. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16a**.

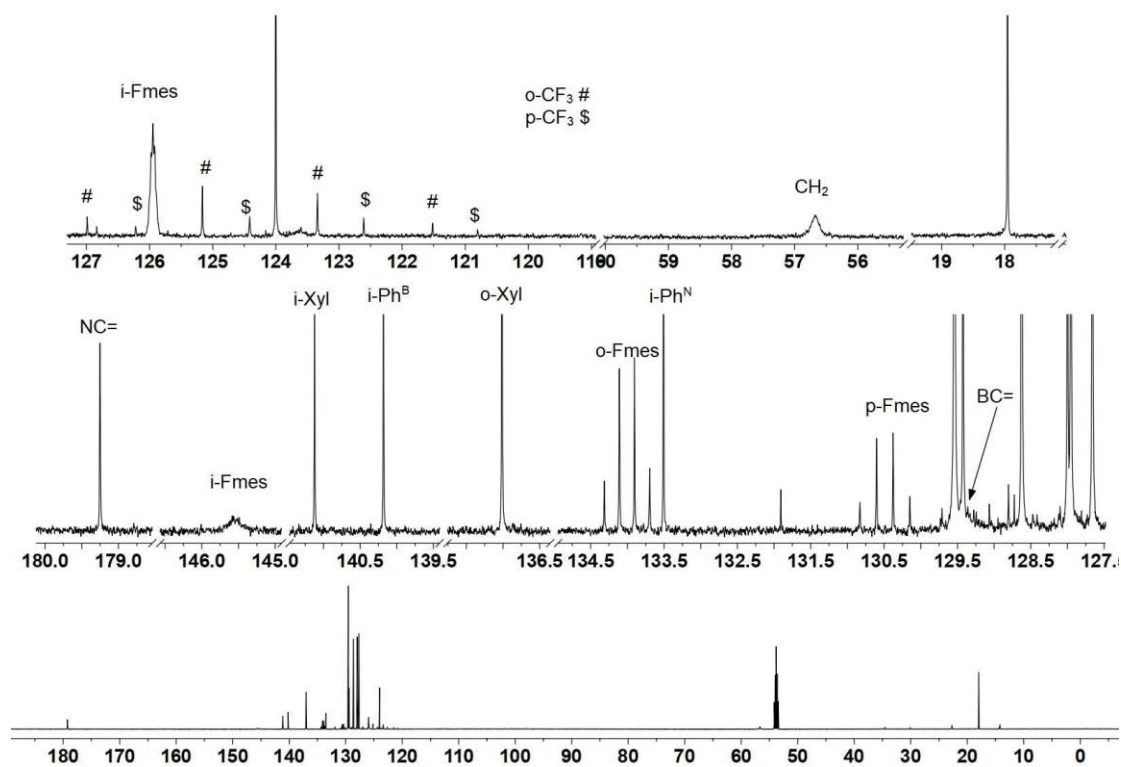


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16a**.

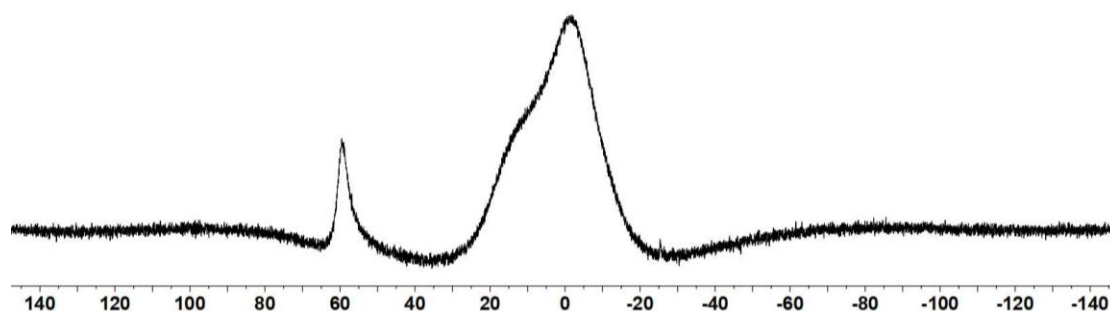
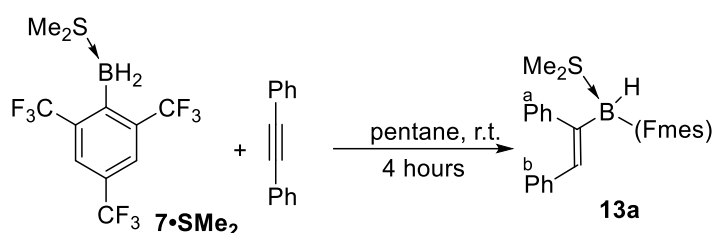


Figure S14. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16a**.

Preparation of Compound **13a**



Scheme S5.

In a Schlenk tube, borane **7-SMe₂** (356 mg, 1 mmol, 1 equiv.) and diphenylacetylene (178 mg, 1 mmol, 1 equiv.) were added subsequently to pentane (5 mL). The suspension was stirred for 4 hours at room temperature to give a clear solution. Then the mixture was stored at -35 °C for 1 day to give compound **13a** as a colorless crystalline solid (316 g, 59% yield).

Elemental Analysis for $\text{C}_{25}\text{H}_{20}\text{BF}_9\text{S}$: calc. C (56.20 %), H (3.77 %); found: C (56.85 %), H (3.29 %).

^1H NMR (600 MHz, benzene- d_6 , 299 K): δ = 7.79 (s, 2H, *m*-Fmes), 7.24 (br, 1H, CH=), 7.15 (m, 2H, *o*-Ph^a), 7.04 (m, 2H, *m*-Ph^a), 7.02 (m, 2H, *o*-Ph^b), 6.95 (m, 1H, *p*-Ph^a), 6.84 (m, 3H, *m*, *p*-Ph^b), 6.38 (br, BH), 1.49 (s, 6H, SCH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, benzene- d_6 , 299 K): δ = 152.4 (br, CH=), 148.3 (br, BC=), 146.3 (br, *i*-Fmes), 142.9 (*i*-Ph^a), 136.7 (*i*-Ph^b), 133.5 (q, $^2J_{\text{FC}}$ = 32.4 Hz, *o*-Fmes), 131.3 (d, $^2J_{\text{FC}}$ = 34.3 Hz, *p*-Fmes), 131.0 (*o*-Ph^b), 129.3 (*p*-Ph^b), 129.0 (*m*-Ph^a), 128.4 (*m*-Ph^b), 128.1 (*o*-Ph^a), 126.7 (*p*-Ph^a), 126.0 (br, *m*-Fmes), 124.5 (q, $^1J_{\text{FC}}$ = 275.0 Hz, *o*-CF₃), 123.2 (q, $^1J_{\text{FC}}$ = 271.0 Hz, *p*-CF₃), 19.4 (SCH₃).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, benzene- d_6 , 299 K): δ = 53.3 ($\nu_{1/2}$ \approx 1360 Hz).

^{19}F NMR (564 MHz, benzene- d_6 , 299 K): δ = -57.8 (s, 2F, *o*-CF₃), -63.0 (s, 1F, *p*-CF₃).

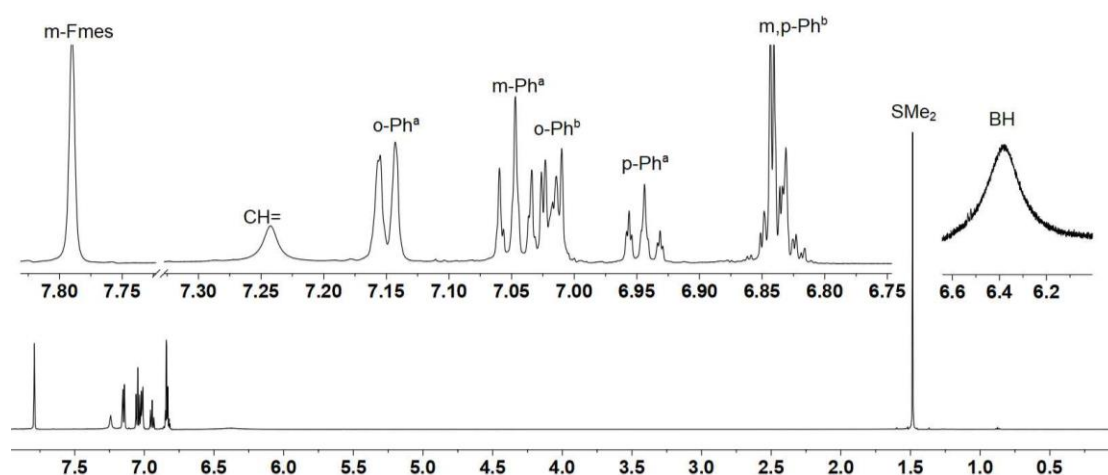


Figure S15. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectrum of compound **13a**.

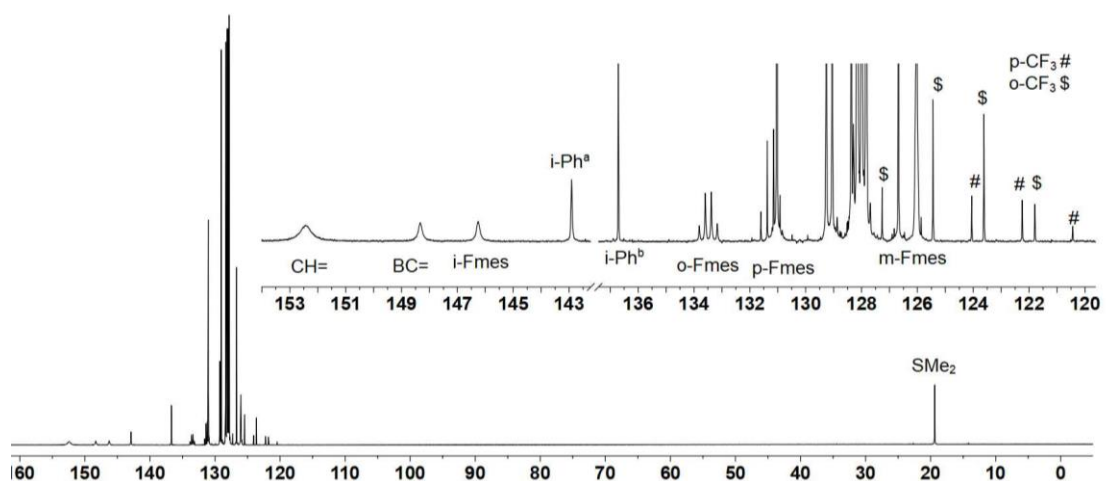


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 299 K) spectrum of compound **13a**.

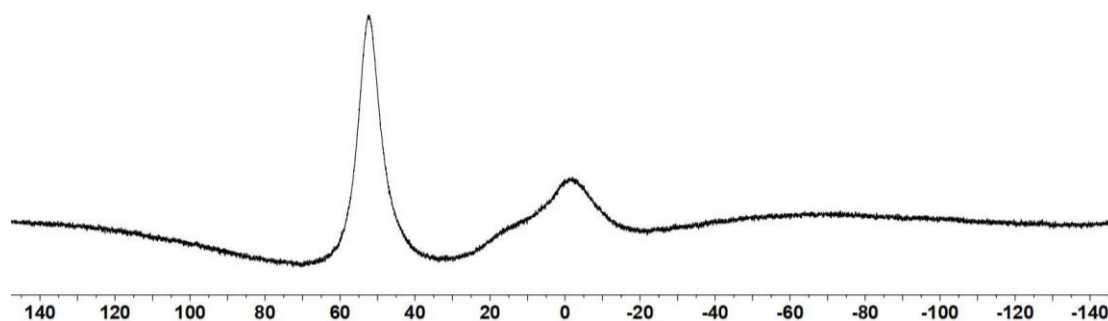


Figure S17. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6 , 299 K) spectrum of compound **13a**.

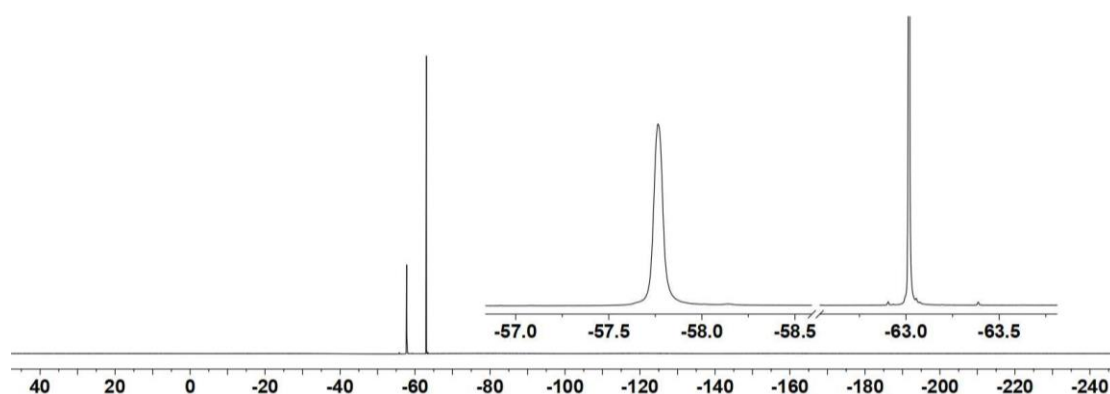


Figure S18. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectrum of compound **13a**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **13a** in cyclopentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 13a (erk9531): A colorless plate-like specimen of $\text{C}_{25}\text{H}_{20}\text{BF}_9\text{S}$, approximate dimensions $0.158\text{ mm} \times 0.189\text{ mm} \times 0.519\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The hydrogen's at P1 and P2 atoms were refined freely. A total of 801 frames were collected. The total exposure time was 6.53 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 157467 reflections to a maximum θ angle of 27.49° (0.77 \AA resolution), of which 17139 were independent (average redundancy 9.188, completeness = 99.8%, $R_{\text{int}} = 10.17\%$, $R_{\text{sig}} = 4.78\%$) and 13066 (76.24%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 28.1571(16)\text{ \AA}$, $b = 9.6190(5)\text{ \AA}$, $c = 28.4643(16)\text{ \AA}$, $\beta = 104.279(2)^\circ$, volume = $7471.2(7)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9813 reflections above $20\sigma(I)$ with $4.688^\circ < 2\theta < 54.82^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.861. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8990 and 0.9680. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with $Z = 12$ for the formula unit, $\text{C}_{25}\text{H}_{20}\text{BF}_9\text{S}$. The final anisotropic full-matrix least-squares refinement on F^2 with 1112 variables converged at $R1 = 6.98\%$, for the observed data and $wR2 = 14.42\%$ for all data. The goodness-of-fit was 1.131. The largest peak in the final difference electron density synthesis was $0.440\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.390\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.059\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.425 g/cm^3 and $F(000)$, 3264 e^- . The hydrogen's at B1A, B1B and B1C atoms were refined freely. CCDC number: 2007633.

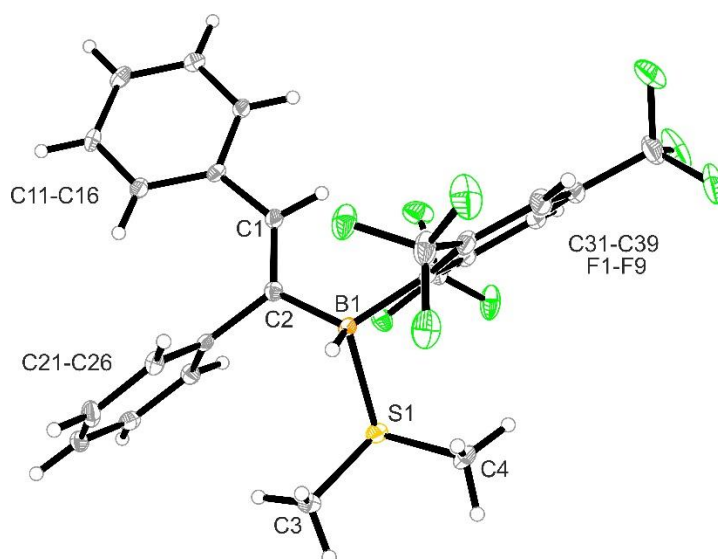
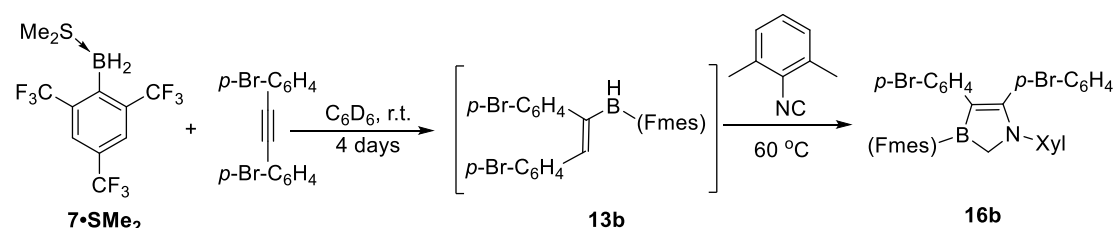


Figure S19. Crystal structure of compound **13a** (thermal ellipsoids at 30% probability).

Preparation of compound **16b**



Scheme S6.

At room temperature, borane **7·SMe₂** (106.8 mg, 0.3 mmol, 1 eq.) was added to a suspension of 1,2-bis(4-bromophenyl)ethyne **16b** (100.8 mg, 0.3 mmol, 1 eq.) in C₆D₆ (2mL) under argon atmosphere in a J. Young tube. The mixture was shaken for 4 days at room temperature to give a light red solution. The formation of the hydroboration product was monitored by an *in situ* NMR experiment. Then 2,6-dimethylphenylisocyanide (39.3 mg, 0.3 mmol, 1 eq.) was added to the mixture in one portion to give a brown solution. The resulting solution was stored at 60 °C for 5 h. All volatiles were removed in vacuo. Subsequently, the residue was dissolved in pentane (2 mL) and stored at -35 °C to finally give the compound **16b** as an olive solid (163 mg, 71 % yield).

Elemental Analysis for C₃₂H₂₁BNF₉Br₂: calc. C (50.50 %), H (2.78 %), N (1.84 %); found: C (50.42 %), H (2.80 %), N (1.83 %);

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.11 (s, 2H, *m*-Fmes), 7.28 (m, 2H, *m*-C₆H₄Br^N), 7.09 (m, 1H, *p*-Xyl), 7.07 (m, 2H, *m*-C₆H₄Br^B), 7.01 (d, ³*J*_{HH} = 7.6 Hz, 2H, *m*-Xyl), 6.98 (m, 2H, *o*-C₆H₄Br^N), 6.58 (m, 2H, *o*-C₆H₄Br^B), 3.82 (s, 2H, CH₂), 2.19 (s, 6H, *o*-CH₃^{Xyl}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K): δ = 177.8 (CN=), 144.8 (br, *i*-Fmes), 140.6 (*i*-Xyl), 139.0 (*i*-C₆H₄Br^B), 136.8 (*o*-Xyl), 134.0 (q, ²*J*_{FC} = 31.1 Hz, *o*-Fmes), 132.0 (*i*-C₆H₄Br^N), 131.5 (*m*-C₆H₄Br^N), 131.25 (*o*-C₆H₄Br^N), 131.18 (*o*-C₆H₄Br^B), 131.0 (*m*-C₆H₄Br^B), 130.8 (q, ²*J*_{FC} = 34.3 Hz, *p*-Fmes), 128.8 (*m*-Xyl), 128.3 (*p*-Xyl), 126.0 (br, *m*-Fmes), 124.2 (q, ¹*J*_{FC} = 275.4 Hz, *o*-CF₃^{Fmes}), 123.4 (q, ¹*J*_{FC} = 269.7 Hz, *p*-CF₃^{Fmes}), 124.1 (*p*-C₆H₄Br^N), 122.3 (br, BC=), 117.9 (*p*-C₆H₄Br^B), 56.9 (br, CH₂),

17.9 (o -CH₃^{Xyl}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 59.4 ($\nu_{1/2} \approx 1080$ Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = -58.3 (s, 2F, o -CF₃^{Fmes}), -63.5 (s, 1F, p -CF₃^{Fmes}).

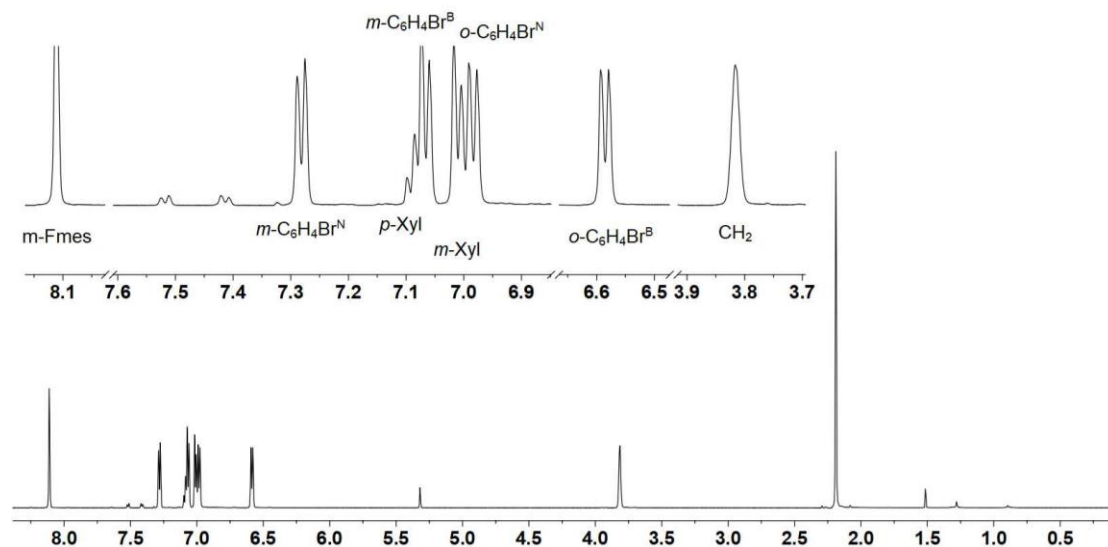


Figure S20. ¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16b**.

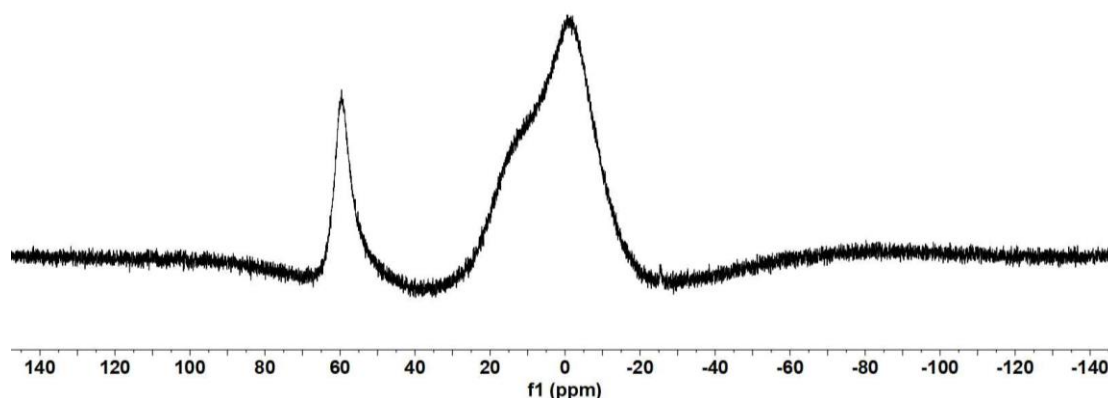


Figure S21. ¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16b**.

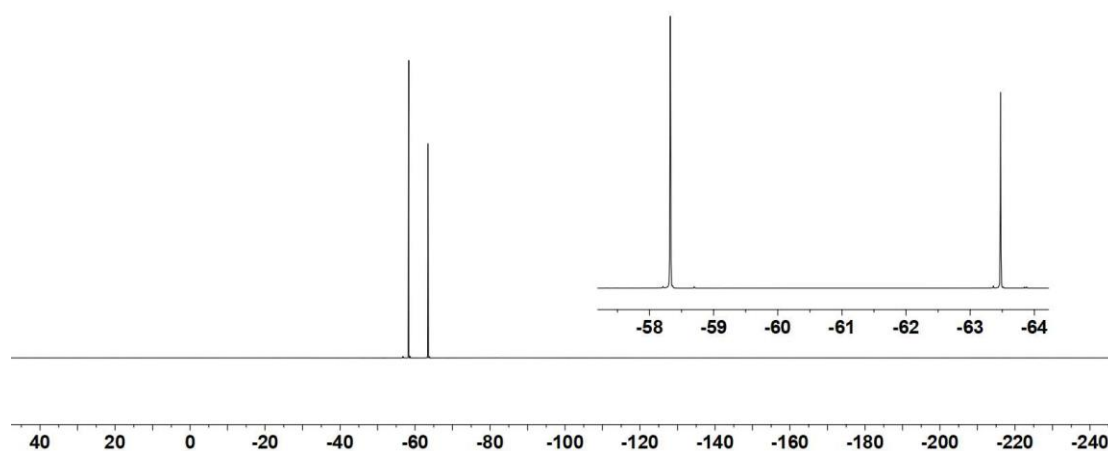


Figure S22. ¹⁹F NMR (564 MHz, methylene chloride, 299 K) spectrum of compound **16b**.

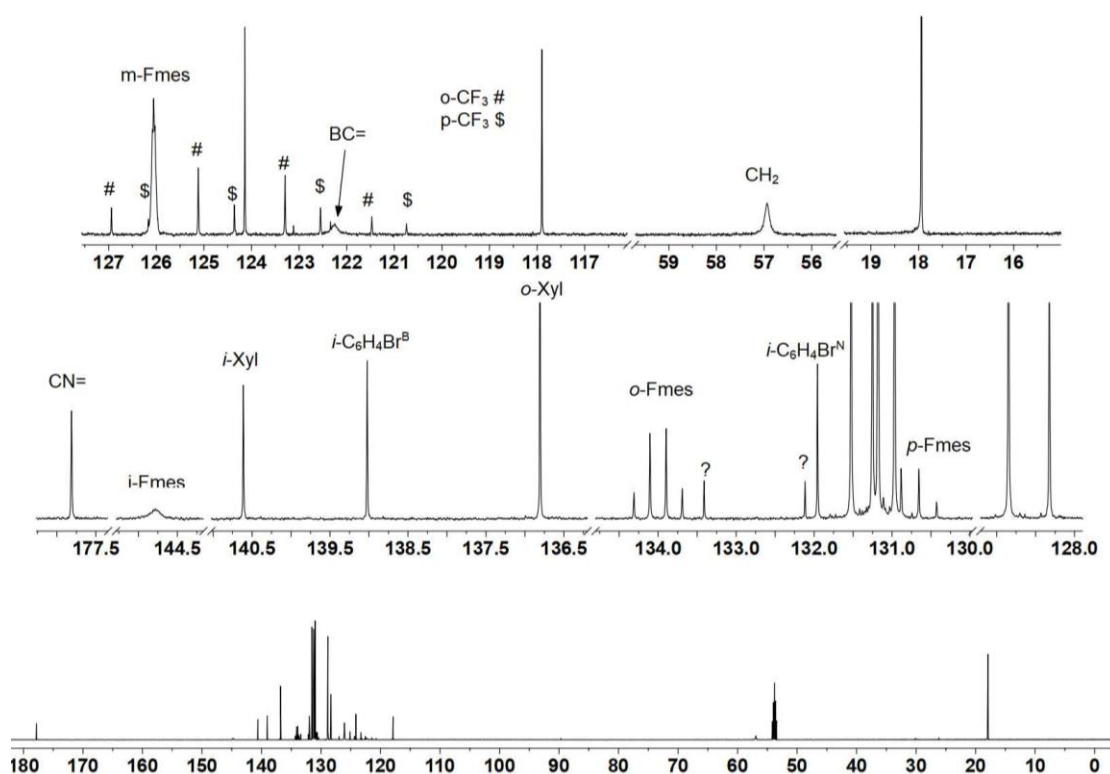


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16b**.

The *in situ* NMR spectra of the hydroboration product **13b** (with a small amount of starting material):

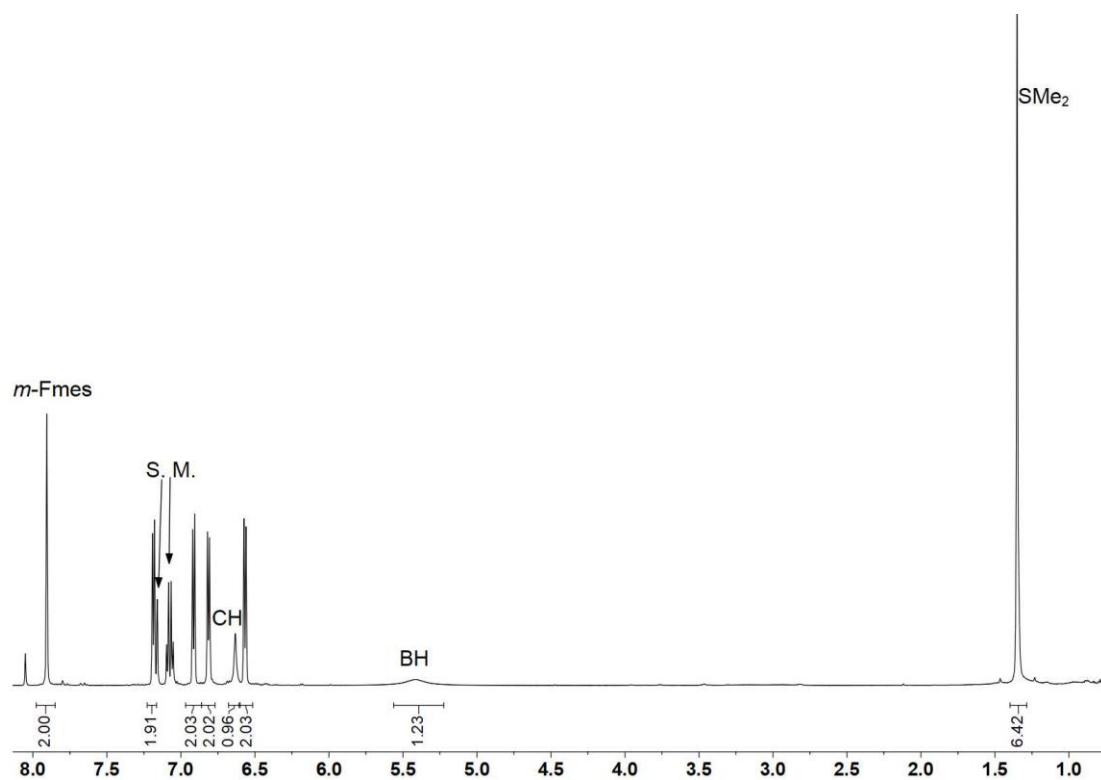


Figure S24. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectrum of compound **13b** (S.M. = 1,2-bis(4-bromophenyl)ethyne).

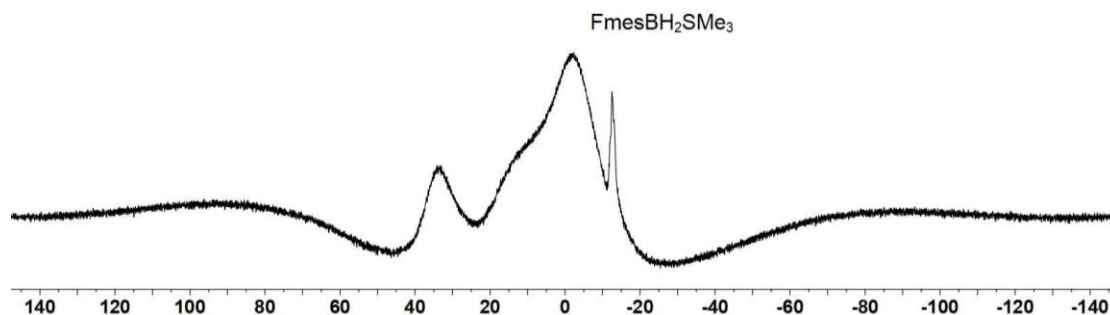


Figure S25. ^{11}B NMR (192 MHz, C_6D_6 , 299 K) spectrum of compound **13b**.

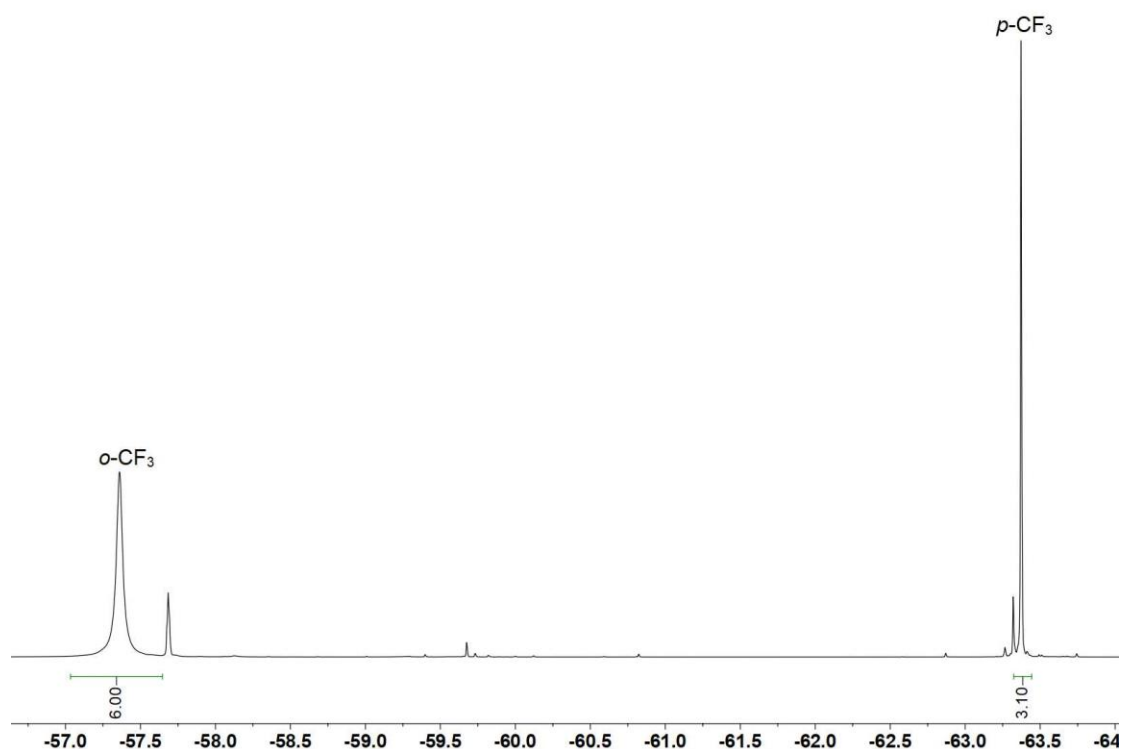


Figure S26. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectrum of compound **13b**.

Crystals suitable for X-ray crystal structure analysis were obtained from a solution of compound **16b** in cyclopentane at $-35\text{ }^{\circ}\text{C}$.

X-ray crystal structure analysis of compound 16b (erk9454): A colorless plate-like specimen of $\text{C}_{32}\text{H}_{21}\text{BBr}_2\text{F}_9\text{N}$, approximate dimensions $0.020\text{ mm} \times 0.050\text{ mm} \times 0.060\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1456 frames were collected. The total exposure time was 23.86 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 18923 reflections to a maximum θ angle of 66.70° (0.84 \AA resolution), of which 5217 were independent (average redundancy 3.627, completeness = 98.8%, $R_{\text{int}} = 8.71\%$, $R_{\text{sig}} = 8.18\%$) and 3539 (67.84%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 10.0146(6)\text{ \AA}$, $b = 11.7824(7)\text{ \AA}$, $c = 14.7823(9)\text{ \AA}$, $\alpha = 66.606(4)^{\circ}$, $\beta = 81.108(4)^{\circ}$, $\gamma = 68.680(4)^{\circ}$, volume = $1491.21(17)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 2399 reflections above $20\sigma(I)$ with $6.515^{\circ} < 2\theta < 133.1^{\circ}$. Data were corrected for absorption effects using the multi-scan

method (SADABS). The ratio of minimum to maximum apparent transmission was 0.804. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7870 and 0.9210. 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, $C_{32}H_{21}BBr_2F_9N$. The final anisotropic full-matrix least-squares refinement on F^2 with 465 variables converged at $R1 = 6.04\%$, for the observed data and $wR2 = 16.23\%$ for all data. The goodness-of-fit was 1.090. The largest peak in the final difference electron density synthesis was $0.623 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.625 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.115 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.695 g/cm^3 and $F(000)$, 752 e^- . CCDC number: 2007635.

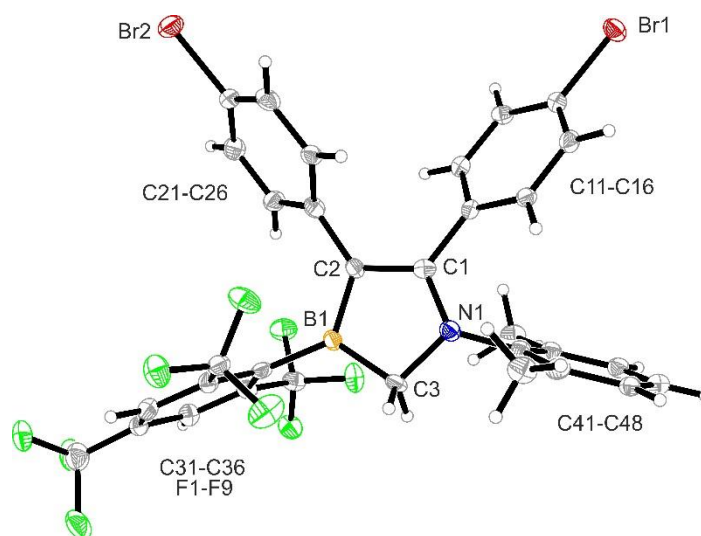
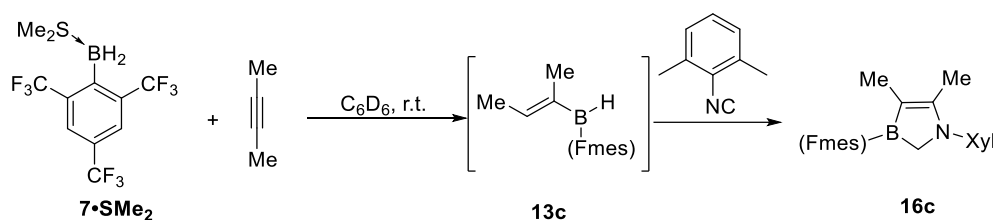


Figure S27. Crystal structure of compound **16b** (thermal ellipsoids at 30% probability).

Preparation of compound 16c



Scheme S7.

At room temperature, borane **7a**·**SMe**₂ (142.4 mg, 0.4 mmol, 1 eq.) was added to the solution of 2-butyne (21.6mg, 0.4 mmol, 1 eq.) in C_6D_6 (2mL) under argon atmosphere in a J. Young tube. Then the mixture was stored for 30 min to give a colorless solution. The formation of the hydroboration product was monitored by *in situ* NMR experiment. Then 2,6-dimethylphenylisocyanide (52.4 mg, 0.4 mmol, 1 eq.) was added to the mixture in one portion to give a brown solution. The resulting solution was stored at room temperature for 2 days. Then all volatiles were removed in vacuo. Subsequently, the residue was dissolved in pentane (1 mL) and stored at -35°C to finally give the compound **16c** as a light yellow solid (106 mg, 56 % yield).

Element Analysis for $C_{22}H_{19}BNF_9$: calc. C (55.14 %), H (4.00 %), N (2.92 %); found: C (54.73 %), H

(4.10 %), N (2.73 %);

HRMS for $C_{22}H_{22}BNF_9O^+$ $[M+H_3O]^+$: calc. 498.1649; found: 498.1669.

1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.12 (s, 2H, *m*-Fmes), 7.17 (m, 1H, *p*-Xyl), 7.13 (m, 2H, *m*-Xyl), 3.43 (m, 2H, CH_2), 2.10 (s, 6H, *o*- CH_3^{Xyl}), 1.86 (t, J = 1.9 Hz, 3H, CH_3^N), 1.67 (s, 3H, CH_3^B).

$^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 179.4 (NC=), 147.5 (br, *i*-Fmes), 141.1 (*i*-Xyl), 137.8 (*o*-Xyl), 134.1 (q, $^2J_{FC}$ = 30.8 Hz, *o*-Fmes), 130 (q, $^2J_{FC}$ = 34.0 Hz, *p*-Fmes), 128.7 (*m*-Xyl), 128.1 (*p*-Xyl), 125.5 (br, *m*-Fmes), 124.3 (q, $^1J_{FC}$ = 274.4 Hz, *o*-CF₃), 123.7 (q, $^1J_{FC}$ = 271.7 Hz, *p*-CF₃), 114.8 (br, BC=), 55.0 (br, CH_2), 17.3 (*o*- CH_3^{Xyl}), 13.7 (CH_3^N), 11.4 (CH_3^B).

$^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 57.5 ($\nu_{1/2}$ \approx 400 Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -59.4 (m, 2F, *o*-CF₃), -63.4 (s, 1F, *p*-CF₃).

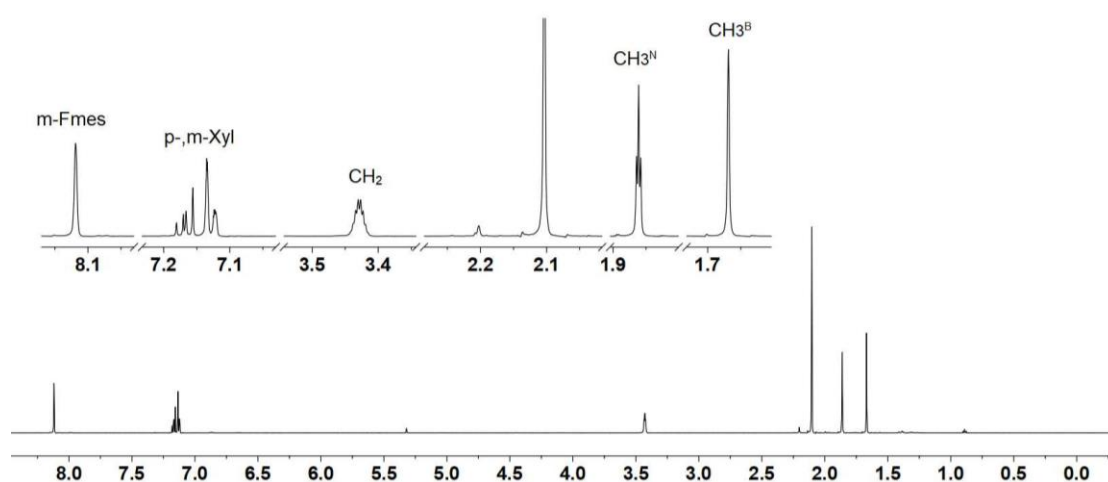


Figure S28. 1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16c**.

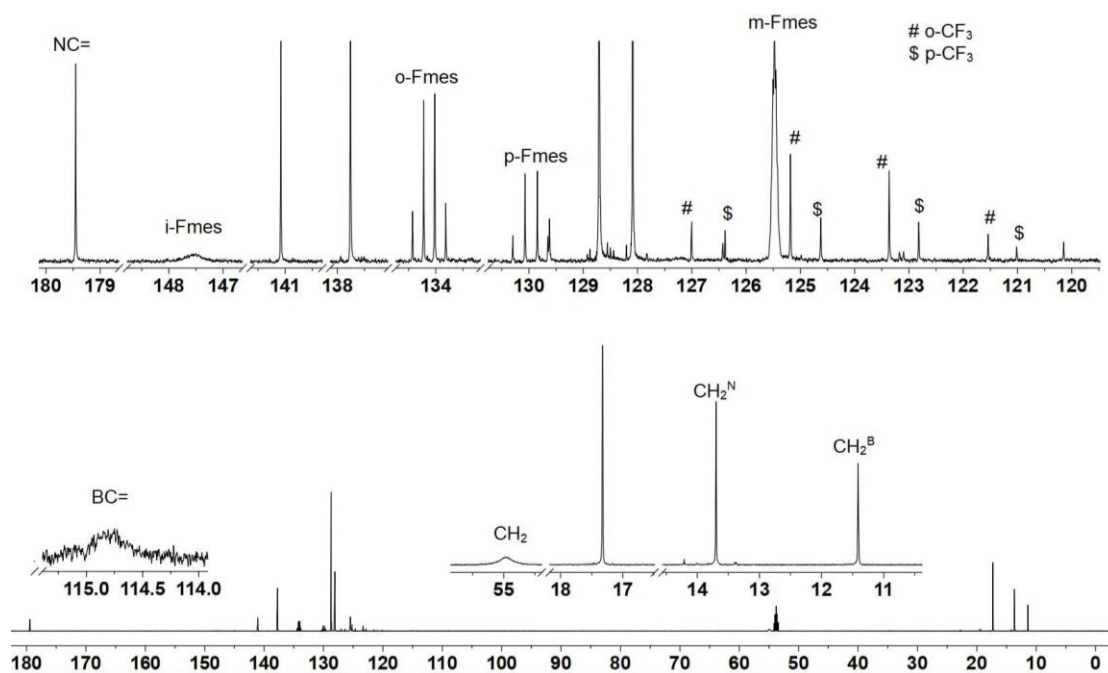


Figure S29. $^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16c**.

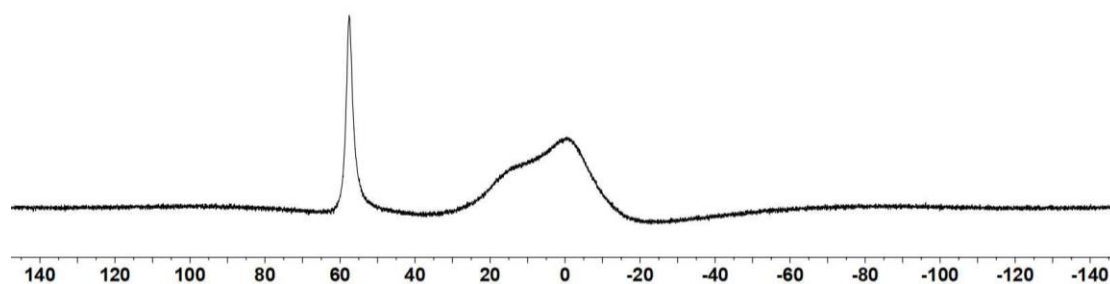


Figure S30. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16c**.

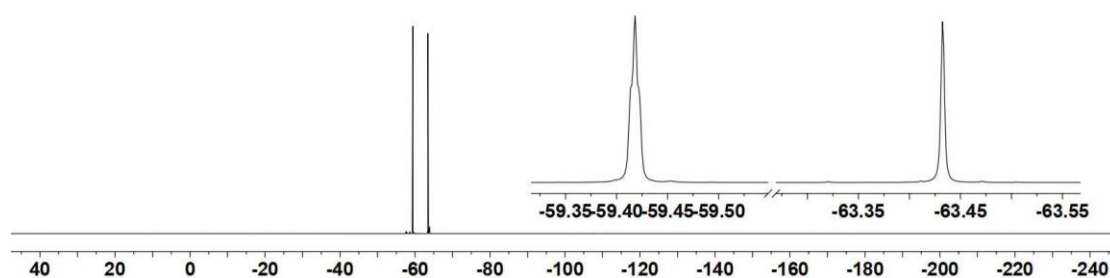


Figure S31. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16c**.

The *in situ* NMR spectra of the hydroboration product **13c** (with small amount di-hydroboration products):

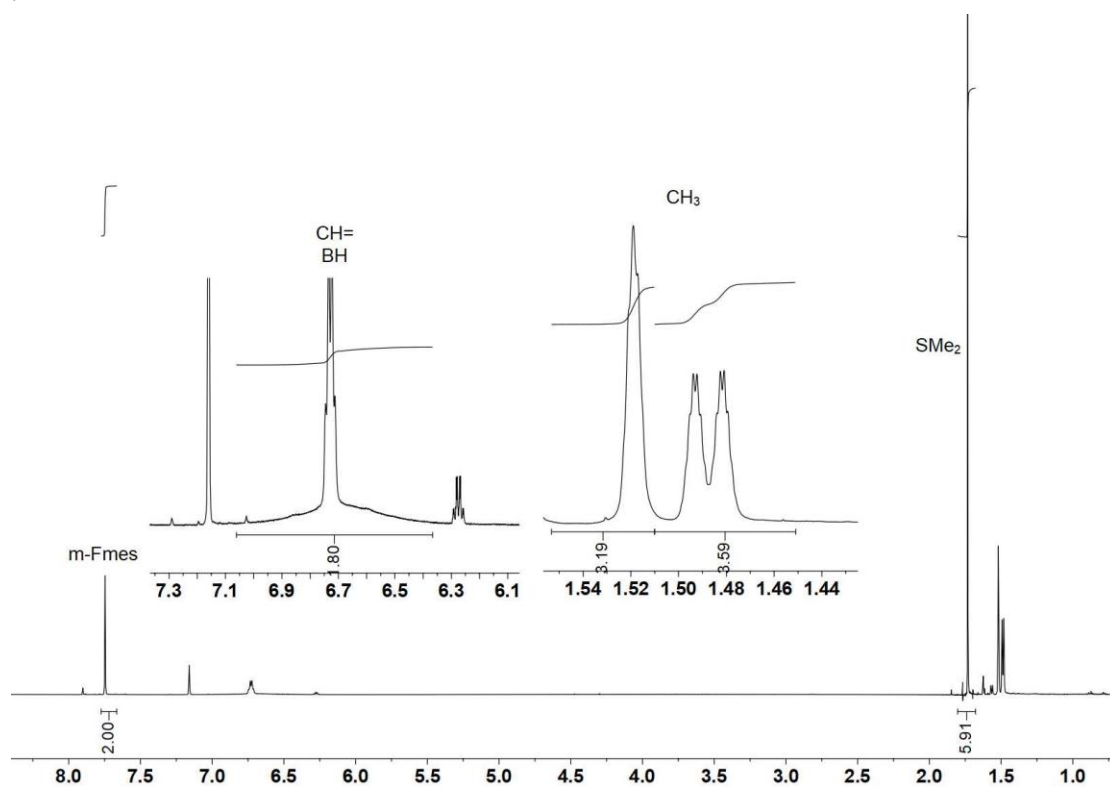


Figure S32. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectrum of compound **13c**.

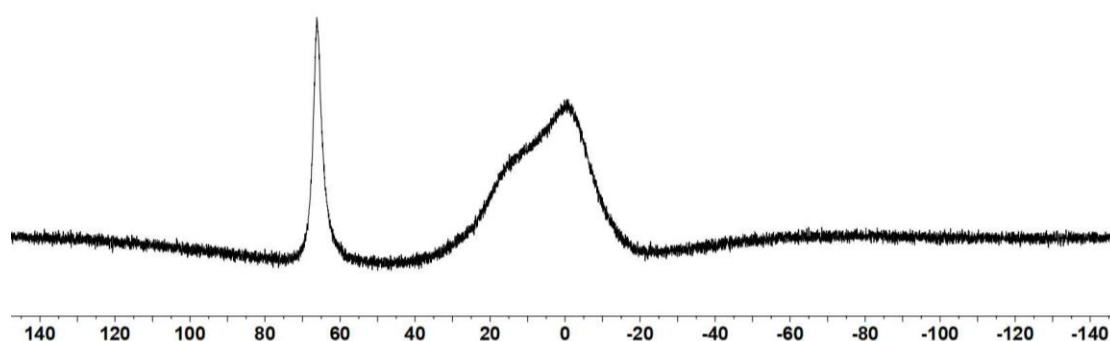


Figure S33. ^{11}B NMR (192 MHz, C_6D_6 , 299 K) spectrum of compound **13c**.

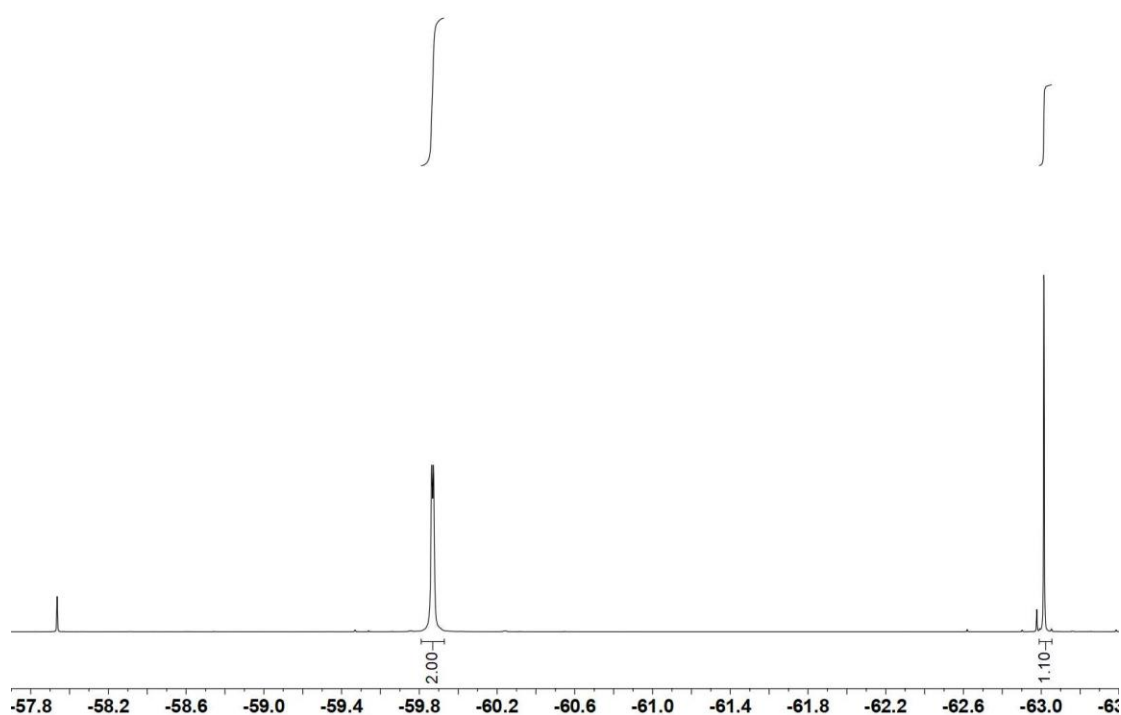


Figure S34. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectrum of compound **13c**.

Single crystals suitable for the X-ray diffraction analysis were obtained from a solution of compound **16c** in pentane at $-35\text{ }^{\circ}\text{C}$.

X-ray crystal structure analysis of compound 16c (erk9522): A colorless prism-like specimen of $\text{C}_{22}\text{H}_{19}\text{BF}_9\text{N}$, approximate dimensions $0.040\text{ mm} \times 0.080\text{ mm} \times 0.120\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 7426 reflections to a maximum θ angle of 25.00° (0.84 \AA resolution), of which 3781 were independent (average redundancy 1.964, completeness = 99.4%, $R_{\text{int}} = 4.92\%$, $R_{\text{sig}} = 4.99\%$) and 2915 (77.10%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.7614(2)\text{ \AA}$, $b = 29.9845(7)\text{ \AA}$, $c = 8.2980(2)\text{ \AA}$, $\beta = 97.1300(10)^{\circ}$, volume = $2163.08(9)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of reflections above $20\sigma(I)$. Data were corrected

for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9830 and 0.9940. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $C_{22}H_{19}BF_9N$. The final anisotropic full-matrix least-squares refinement on F^2 with 358 variables converged at $R1 = 7.19\%$, for the observed data and $wR2 = 20.99\%$ for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was $0.335\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.303\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.078\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.471 g/cm^3 and $F(000)$, 976 e^- . CCDC number: 2007636.

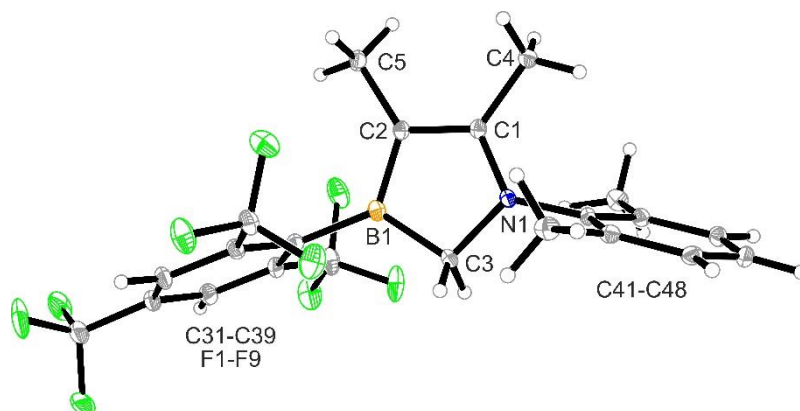
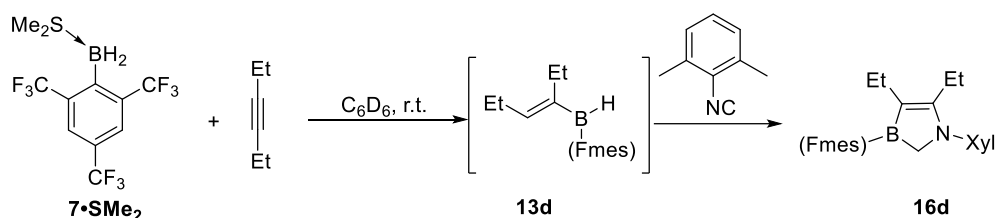


Figure S35. Crystal structure of compound **16c** (thermal ellipsoids at 15% probability).

Preparation of compound 16d



Scheme S8.

At room temperature, borane **7a·SMe₂** (142.4 mg, 0.4 mmol, 1 eq.) was added to a solution of hex-3-yne (32.8 mg, 0.4 mmol, 1 eq.) in C_6D_6 (2 mL) under argon atmosphere in a J. Young tube. Then the mixture was stored at room temperature for 30 min to give a colorless solution. The formation of the hydroboration product was monitored by an *in situ* NMR experiment. 2,6-dimethylphenylisocyanide (52.4 mg, 0.4 mmol, 1 eq.) was added to the mixture in one portion to give a brown solution. The resulting solution was stored at room temperature for 2 days. Then all volatiles were removed in vacuo and the residue was purified by column chromatography on silica gel with pentane as the eluents to finally give the compound **16d** as a light-brown oil (148 mg, 73 % yield).

HRMS for $C_{24}H_{26}BNF_9O^+$ [$M + H_3O$] $^+$: calc. 526.1963; found: 526.1968.

¹H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.11 (s, 2H, *m*-Fmes), 7.18 (m, 1H, *p*-Xyl), 7.13 (m, 2H, *m*-Xyl), 3.40 (m, 2H, CH_2), 2.28 (q, $^3J_{HH} = 7.6\text{ Hz}$, 2H, CH_2^N), 2.22 (q, $^3J_{HH} = 7.6\text{ Hz}$, 2H, CH_2^B), 2.14 (s, 6H, *o*- CH_3^{Xyl}), 1.00 (t, $^3J_{HH} = 7.6\text{ Hz}$, 3H, CH_3^N), 0.85 (t, $^3J_{HH} = 7.5\text{ Hz}$, 3H, CH_3^B).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 184.2 (NC=), 147.8 (br, *i*-Fmes), 141.2 (*i*-Xyl), 137.7 (*o*-Xyl), 134.0 (q, $^2J_{\text{FC}}$ = 30.7 Hz, *o*-Fmes), 130.1 (q, $^2J_{\text{FC}}$ = 34.1 Hz, *p*-Fmes), 128.9 (*m*-Xyl), 128.0 (*p*-Xyl), 125.7 (br, *m*-Fmes), 124.4 (q, $^1J_{\text{FC}}$ = 274.7 Hz, *o*-CF₃^{Fmes}), 123.8 (q, $^1J_{\text{FC}}$ = 272.5 Hz, *p*-CF₃^{Fmes}), 121.4 (br, BC=), 55.4 (br, CH₂), 21.4 (CH₂^N), 20.4 (CH₂^B), 17.6 (*o*-CH₃^{Xyl}), 16.5 (CH₃^B), 12.2 (CH₃^N).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 58.2 ($\nu_{1/2} \approx 470$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -58.5 (s, 2F, *o*-CF₃^{Fmes}), -63.5 (s, 1F, *p*-CF₃^{Fmes}).

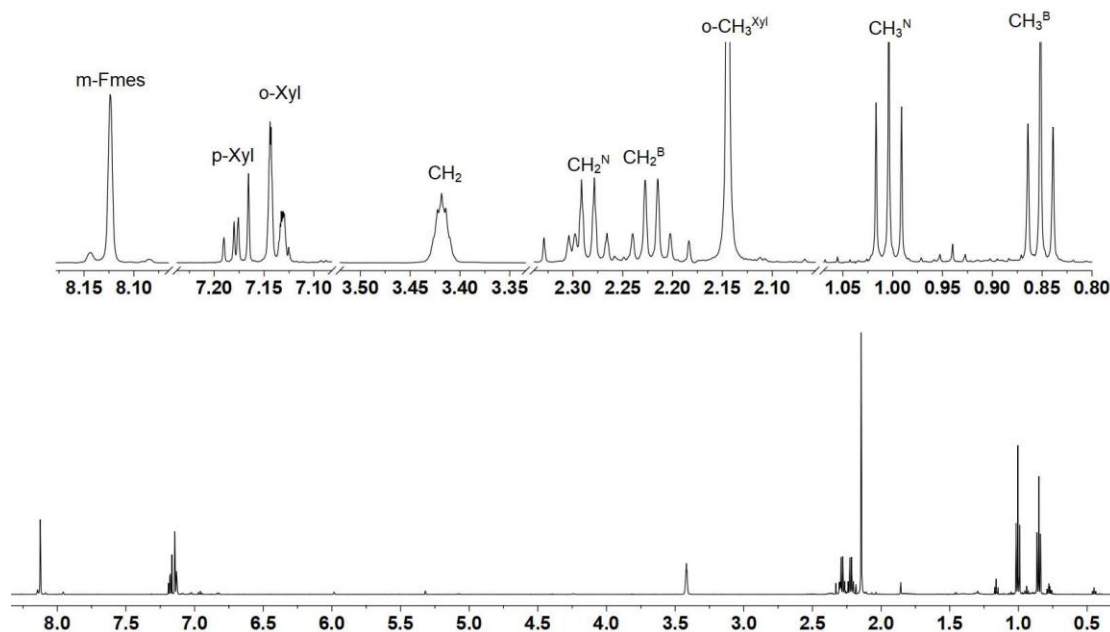


Figure S36. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16d**.

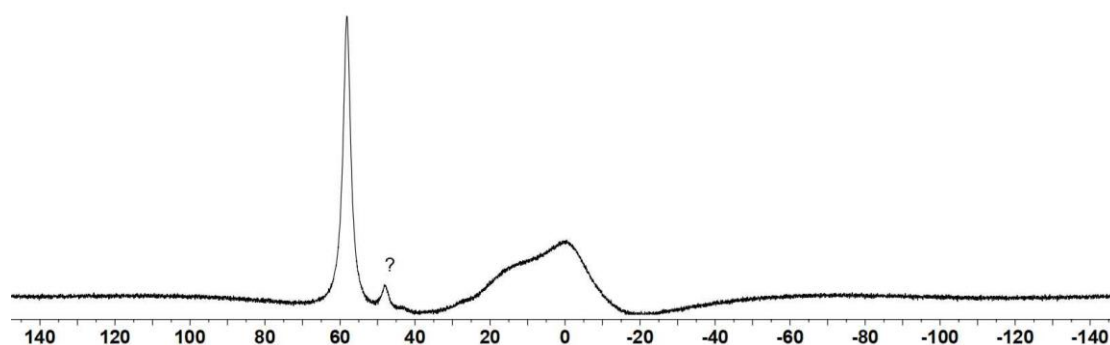


Figure S37. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16d**.

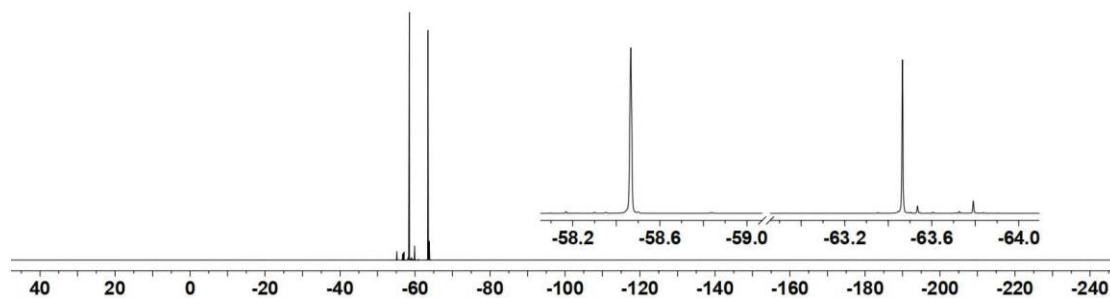


Figure S38. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16d**.

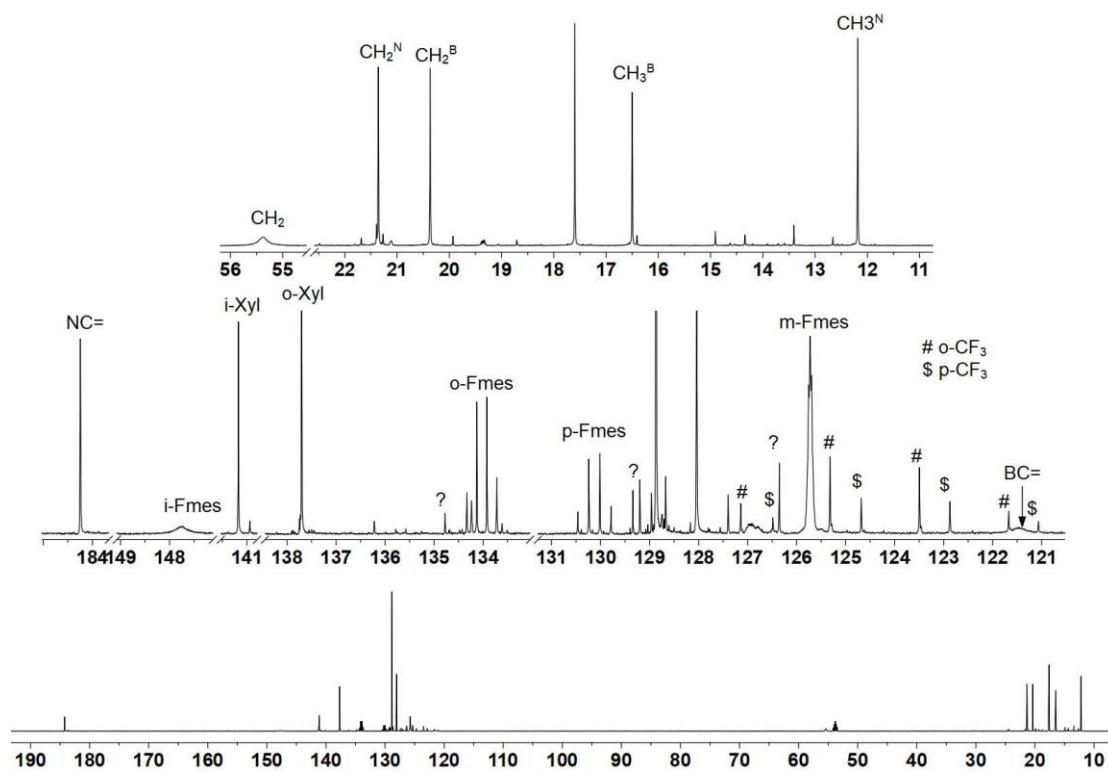


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16d**.

The *in situ* NMR spectra of the hydroboration product **13d** (with a small amount of impurities):

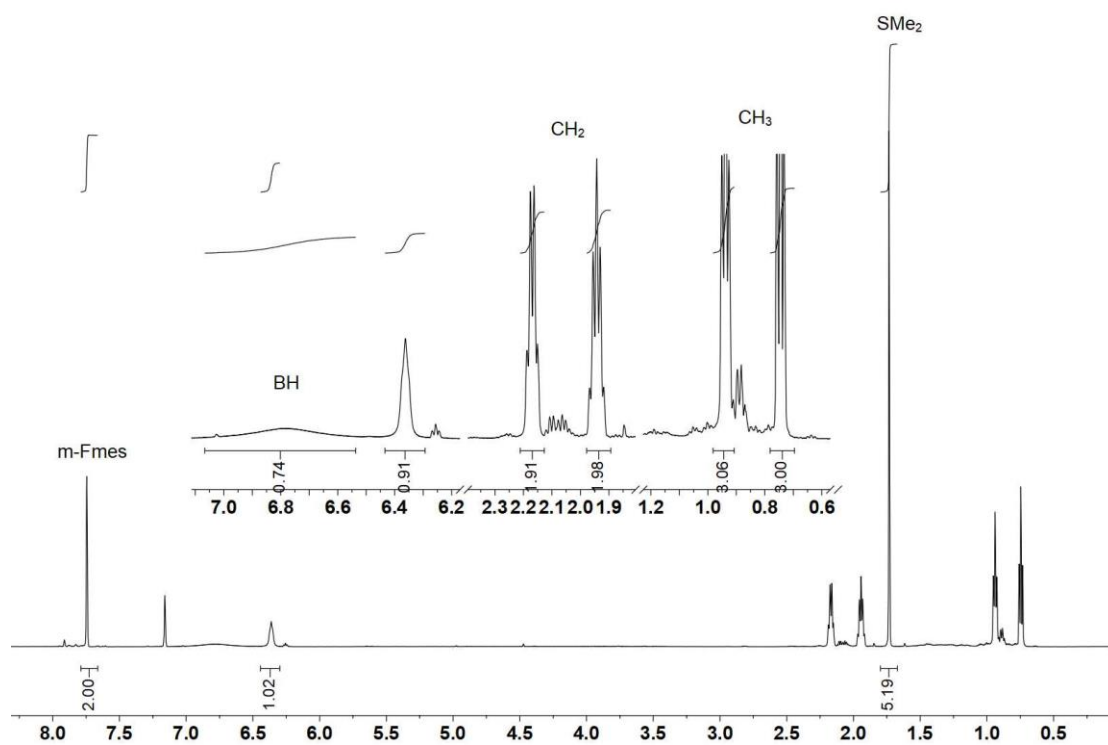


Figure S40. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectrum of hydroboration product **13d**.

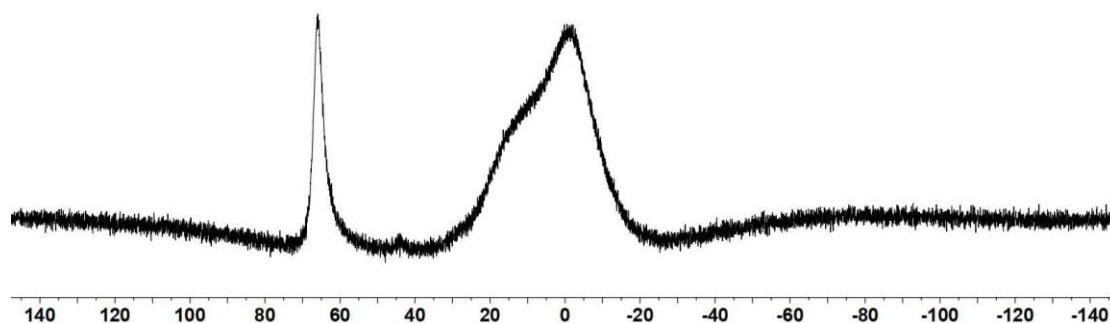


Figure S41. ^{11}B NMR (192 MHz, C_6D_6 , 299 K) spectrum of hydroboration product **13d**.

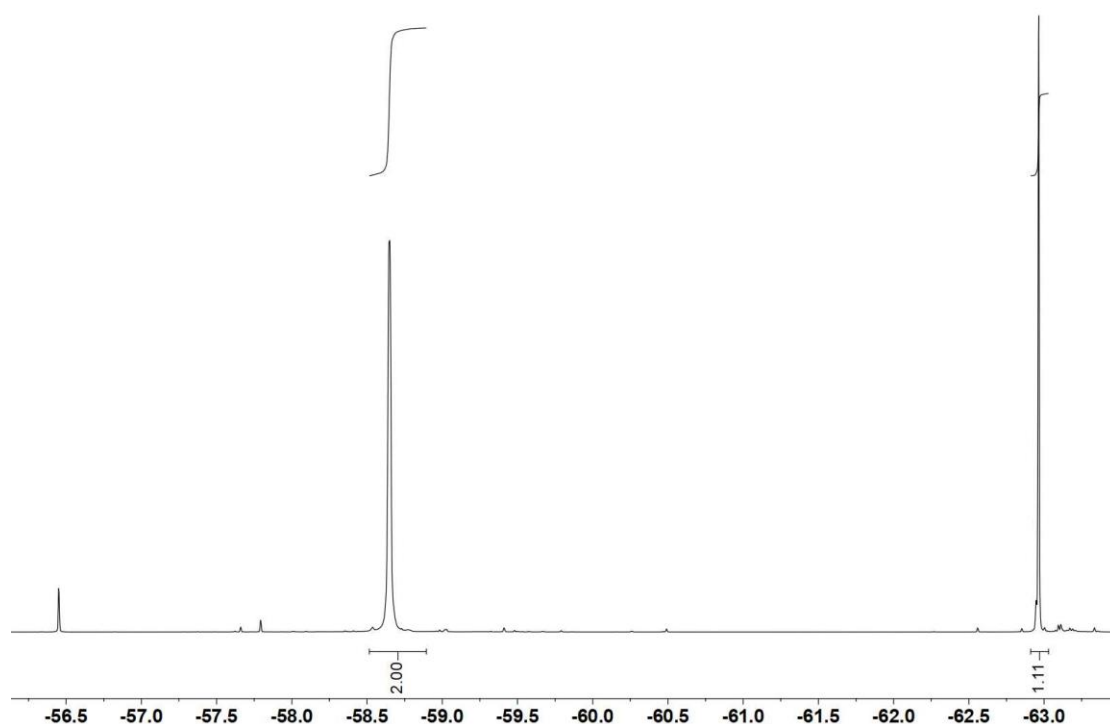


Figure S42. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectrum of hydroboration product **13d**.

Single crystals suitable for X-ray diffraction analysis were obtained from a solution of compound **16d**. in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 16d (erk9513): A colorless prism-like specimen of $\text{C}_{24}\text{H}_{23}\text{BF}_9\text{N}$, approximate dimensions $0.120\text{ mm} \times 0.200\text{ mm} \times 0.300\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 9145 reflections to a maximum θ angle of 25.00° (0.84 \AA resolution), of which 4711 were independent (average redundancy 1.941, completeness = 99.1%, $R_{\text{int}} = 4.56\%$, $R_{\text{sig}} = 4.54\%$) and 4088 (86.78%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 23.0146(5)\text{ \AA}$, $b = 14.3686(3)\text{ \AA}$, $c = 16.8760(4)\text{ \AA}$, $\beta = 104.4410(10)^\circ$, volume = $5404.4(2)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of reflections above $20\sigma(I)$. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and

maximum transmission coefficients (based on crystal size) are 0.9660 and 0.9860. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $C2/c$, with $Z = 8$ for the formula unit, $C_{24}H_{23}BF_9N$. The final anisotropic full-matrix least-squares refinement on F^2 with 416 variables converged at $R1 = 8.80\%$, for the observed data and $wR2 = 24.74\%$ for all data. The goodness-of-fit was 1.066. The largest peak in the final difference electron density synthesis was $0.422\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.438\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.097\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.247 g/cm^3 and $F(000)$, 2080 e⁻. CCDC: 2007637.

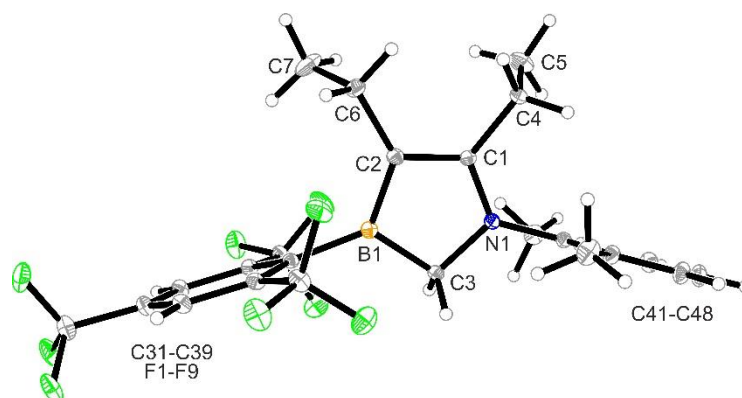
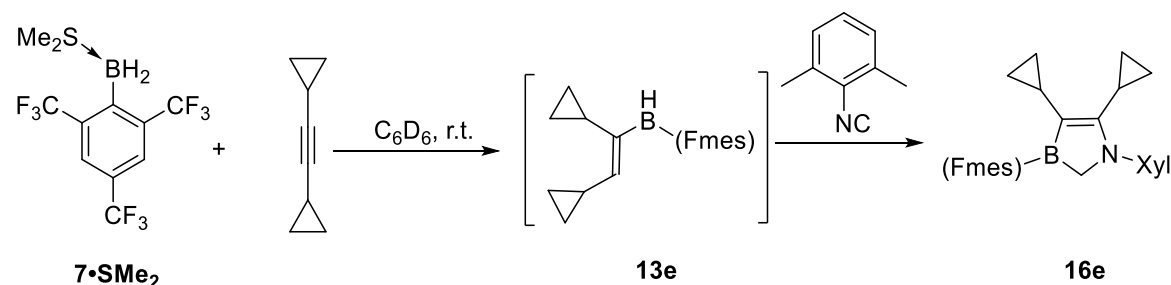


Figure S43. Crystal structure of compound **16d** (thermal ellipsoids at 15% probability).

Preparation of compound 16e.



Scheme S9.

At room temperature, borane **7•SMe₂** (142.4 mg, 0.4 mmol, 1 eq.) was added to a solution of 1,2-dicyclopropylethyne (42.4 mg, 0.4 mmol, 1 eq.) in C_6D_6 (2 mL) under argon atmosphere in a J. Young tube. The mixture was stored for 30 min to give a colorless solution. The formation of the hydroboration product **13e** was monitored by an *in situ* NMR experiment. Then 2,6-dimethylphenyl isocyanide (52.4 mg, 0.4 mmol, 1 eq.) was added to the mixture in one portion to give a brown solution. The resulting solution was stored at room temperature for 2 days. Then all volatiles were removed in vacuo, the residue was dissolved in pentane (1 mL) and stored at $-35\text{ }^\circ\text{C}$ to finally give the compound **16e** as a light yellow solid (138 mg, 65 % yield).

Elemental Analysis for $C_{26}H_{23}BNF_9$: calc. C (58.78 %), H (4.36 %), N (2.64 %); found: C (57.72 %), H (4.25 %), N (2.50 %);

HRMS for $C_{26}H_{26}BNF_9O^+$ $[M + H_3O]^+$: calc. 550.1963, found: 550.1967.

¹H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.08 (s, 2H, *m*-Fmes), 7.15 (m, 1H, *p*-Xyl), 7.11 (m, 2H, *m*-Xyl), 3.35 (m, 2H, CH₂), 2.15 (s, 6H, *o*-CH₃^{Xyl}), 1.53 (m, 1H, CH^{cpN}), 1.42 (m, 1H, CH^{cpB}),

[1.17, 0.74](each m, each 2H, CH₂^{cpN}), [0.38, -0.07](each m, each 2H, CH₂^{cpB}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K): δ = 184.2 (NC=), 148.1 (br, *i*-Fmes), 141.8 (*i*-Xyl), 137.4 (*o*-Xyl), 133.7 (q, ²*J*_{FC} = 30.6 Hz, *o*-Fmes), 129.9 (q, ²*J*_{FC} = 34.0 Hz, *p*-Fmes), 128.6 (*m*-Xyl), 127.9 (*p*-Xyl), 125.6 (br, *m*-Fmes), 124.3 (q, ¹*J*_{FC} = 274.8 Hz, *o*-CF₃^{Fmes}), 123.7 (q, ¹*J*_{FC} = 271.6 Hz, *p*-CF₃^{Fmes}), 121.2 (br, BC=), 55.7 (br, CH₂), 17.5 (*o*-CH₃^{Xyl}), 12.0 (CH^{cpN}), 9.1 (CH^{cpB}), 7.1 (CH₂^{cpB}), 6.4 (CH₂^{cpN}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 56.6 (*v*_{1/2} ≈ 380 Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = -58.4 (s, 2F, *o*-CF₃), -63.4 (s, 1F, *p*-CF₃).

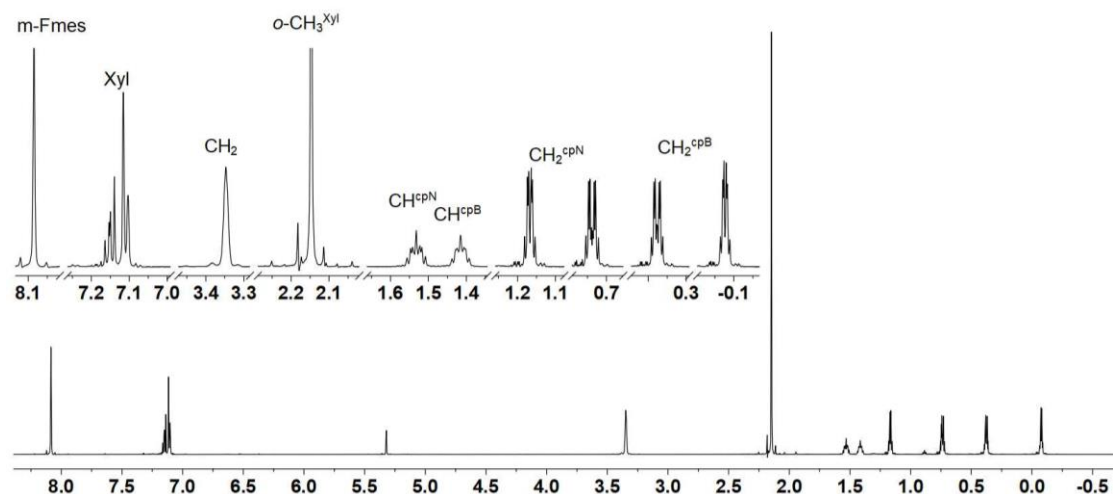


Figure S44. ¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16e**.

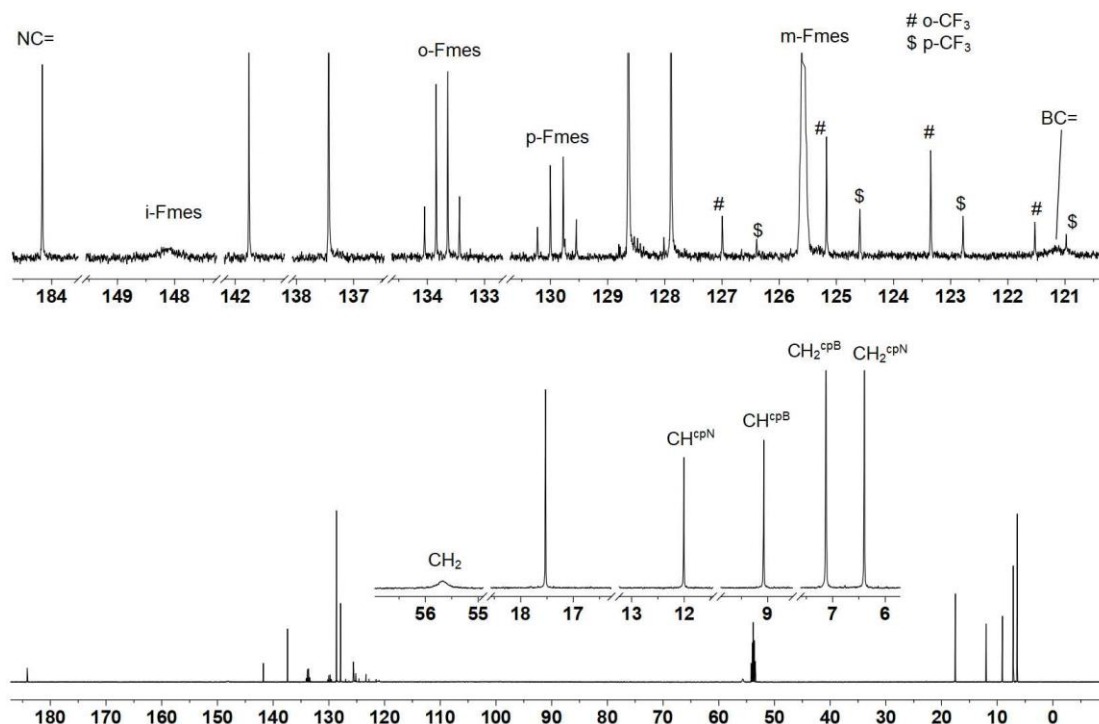


Figure S45. ¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16e**.

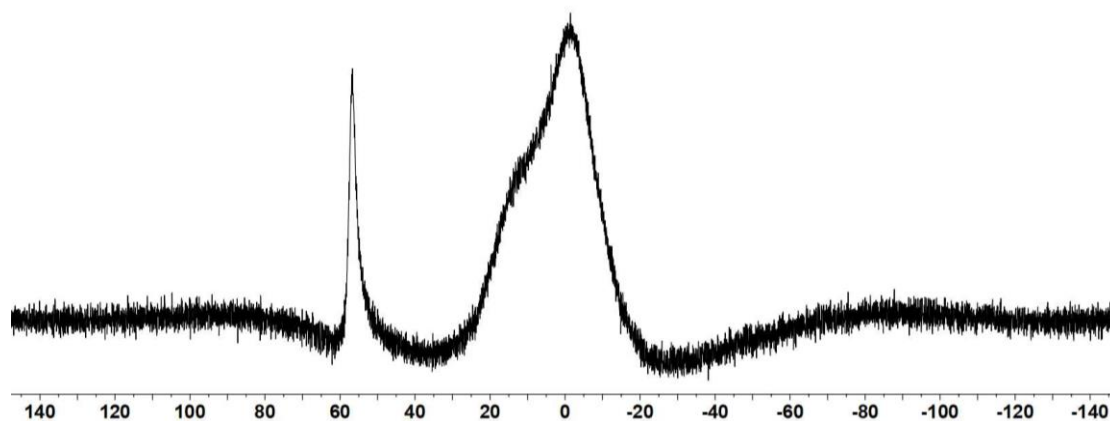


Figure S46. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16e**.

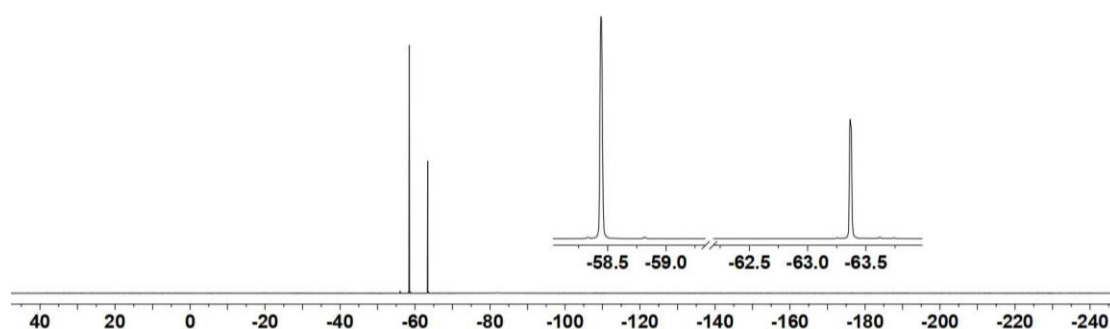


Figure S47. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16e**.

The *in situ* NMR spectra of the hydroboration product **13e** (with small amounts of impurities):

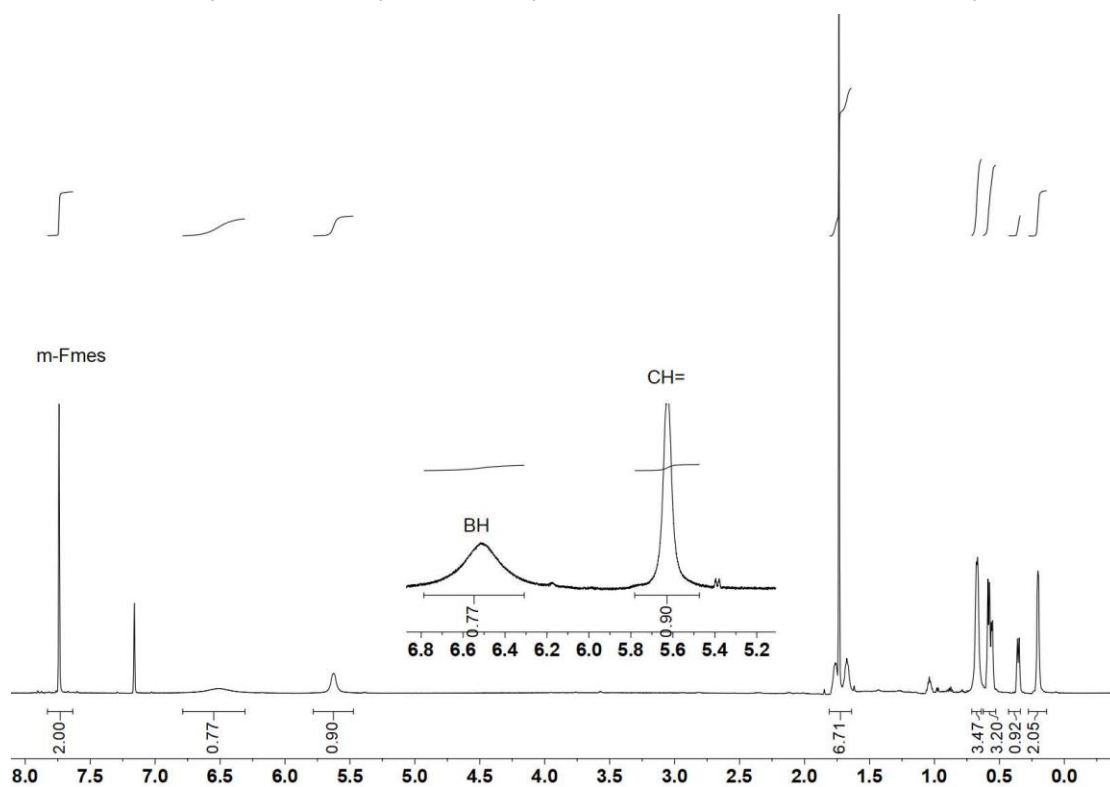


Figure S48. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectrum of hydroboration product **13e**.

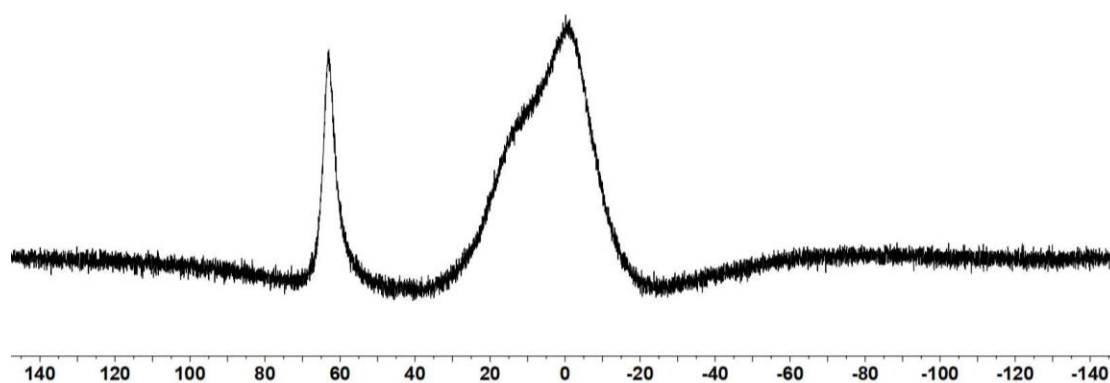


Figure S49. ^{11}B NMR (192 MHz, C_6D_6 , 299 K) spectrum of hydroboration product **13e**.

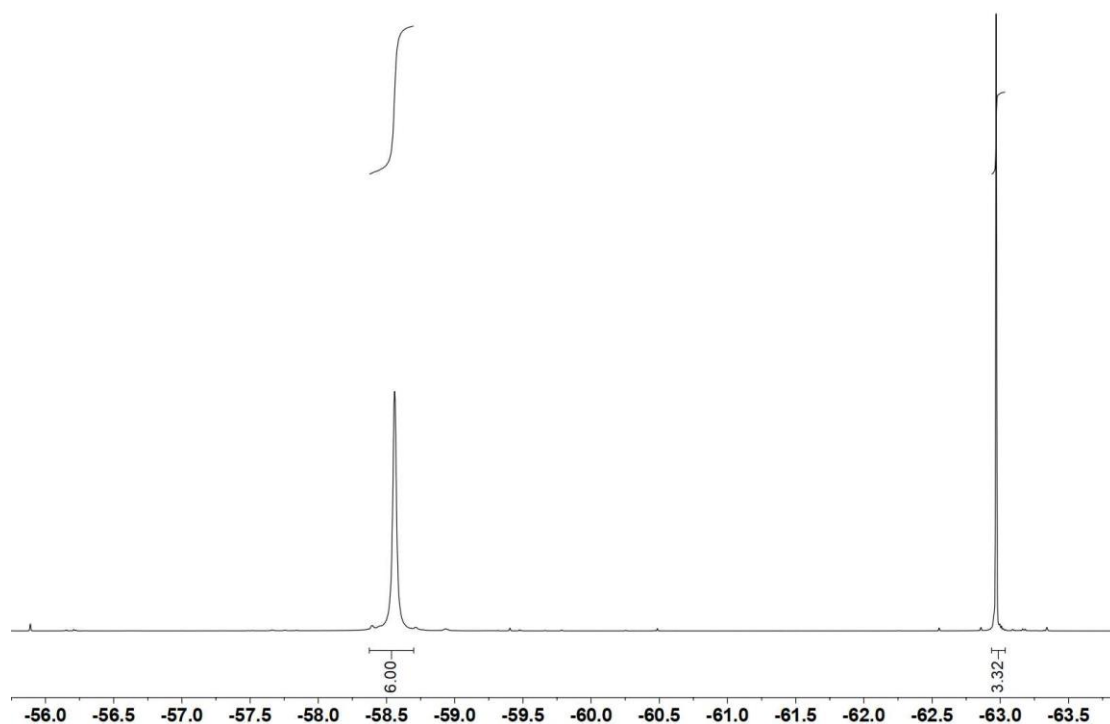


Figure S50. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectrum of hydroboration product **13e**.

Crystals suitable for X-ray diffraction analysis were obtained from a solution of compound **16e** in pentane at $-35\text{ }^{\circ}\text{C}$.

X-ray crystal structure analysis of compound 16e (erk9560): A colorless prism-like specimen of $\text{C}_{26}\text{H}_{23}\text{BF}_9\text{N}$, approximate dimensions $0.160\text{ mm} \times 0.173\text{ mm} \times 0.396\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 476 frames were collected. The total exposure time was 7.27 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 26762 reflections to a maximum θ angle of 25.03° (0.84 \AA resolution), of which 26762 were independent (average redundancy 1.000, completeness = 95.7%, $R_{\text{int}} = 9.50\%$, $R_{\text{sig}} = 14.46\%$) and 13868 (51.82%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 12.5513(8)\text{ \AA}$, $b = 19.8452(13)\text{ \AA}$, $c = 21.0373(15)\text{ \AA}$, $\alpha = 109.234(2)^{\circ}$, $\beta = 94.570(2)^{\circ}$, $\gamma = 93.812(2)^{\circ}$, volume = $4907.8(6)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9957 reflections above $20\sigma(I)$ with $4.992^{\circ} < 2\theta < 54.22^{\circ}$. Data were corrected for absorption effects using

the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.804. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9500 and 0.9790. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with *Z* = 8 for the formula unit, C₂₆H₂₃BF₉N. The final anisotropic full-matrix least-squares refinement on *F*² with 1458 variables converged at *R*1 = 8.25%, for the observed data and *wR*2 = 21.49% for all data. The goodness-of-fit was 1.005. The largest peak in the final difference electron density synthesis was 0.387 e⁻/Å³ and the largest hole was -0.460 e⁻/Å³ with an RMS deviation of 0.075 e⁻/Å³. On the basis of the final model, the calculated density was 1.438 g/cm³ and *F*(000), 2176 e⁻. CCDC number: 2007638.

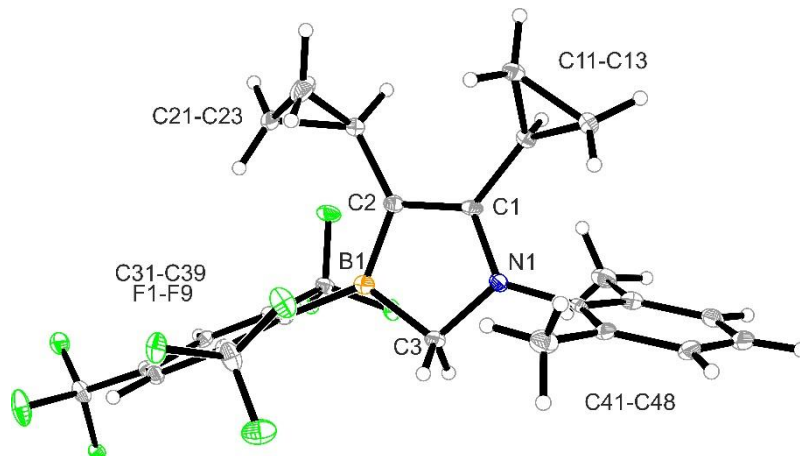
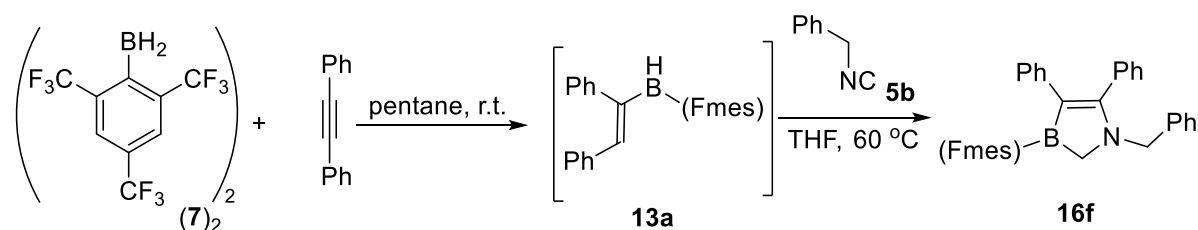


Figure S51. Crystal structure of compound **16e** (thermal ellipsoids at 30% probability).

Preparation of compound 16f



Scheme S10.

At room temperature, borane (**7**)₂ (441 mg, 1.5 mmol, 1 eq.) and diphenylacetylene (267 mg, 1.5 mmol, 1 eq.) were added subsequently to pentane (10 mL) under argon atmosphere in a Schlenk tube. The resulting suspension was stirred for 4h at room temperature to give a colorless solution. Volatiles were removed in vacuo. The residue was dissolved in THF (10 mL) and benzyl isocyanide (175.5 mg, 1.5 mmol, 1 eq.) was added as one portion to give a yellow solution. The resulting solution was stirred at 60 °C overnight. Volatiles were removed in vacuo and the residue was purified by column chromatography on silica gel with pentane: dichloromethane (10:1) as eluents to give the compound **16f** as white solid (460 mg, 52 % yield).

Elemental Analysis for C₃₁H₂₁BNF₉: calc. C (63.18 %), H (3.59 %), N (2.38 %); found: C (63.13%), H (3.59 %), N (2.22 %);

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.07 (s, 2H, *m*-Fmes), 7.36 (m, 7H, *o*-Ph^N, *m*-Ph^N, *p*-Ph^N, *m*-Ph^{Bn}), 7.29 (m, 1H, *p*-Ph^{Bn}), 7.13 (m, 2H, *o*-Ph^{Bn}), 6.88 (m, 2H, *m*-Ph^B), 6.83 (m, 1H, *p*-

Ph^B), 6.68 (m, 2H, *o*-Ph^B), 4.67 (s, 2H, CH₂^{Bn}), 3.55 (sept., *J*_{FH} = 2.5 Hz, 2H, CH₂).

¹³C{¹H} NMR (151 MHz, methylenechloride-*d*₂, 299 K): δ = 180.4 (NC=), 145.9 (br, *i*-Fmes), 140.2 (*i*-Ph^B), 138.6 (*i*-Ph^{Bn}), 134.02 (q, ²*J*_{FC} = 31.1 Hz, *o*-Fmes), 133.99 (*i*-Ph^N), 130.4 (q, ²*J*_{FC} = 34.2 Hz, *o*-Fmes), 129.6 (*p*-Ph^N), 129.34 (*o*-Ph^N), 129.32 (*o*-Ph^B), 129.1 (*m*-Ph^{Bn}), 128.9 (*m*-Ph^N), 127.7 (*p*-Ph^{Bn}), 127.6 (*m*-Ph^B), 127.0 (*o*-Ph^{Bn}), 125.9 (br, *m*-Fmes), 124.2 (q, ¹*J*_{FC} = 275.2 Hz, *o*-CF₃^{Fmes}), 123.9 (*p*-Ph^B) 123.8 (br, BC=), 123.5 (q, ¹*J*_{FC} = 272.2 Hz, *p*-CF₃^{Fmes}), 54.3 (br, CH₂), 53.3 (CH₂^{Bn}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 58.8 (*v*_{1/2} ≈ 720 Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = -58.4 (t, *J*_{HF} = 2.5 Hz, 2F, *o*-CF₃), -63.5 (s, 1F, *p*-CF₃).

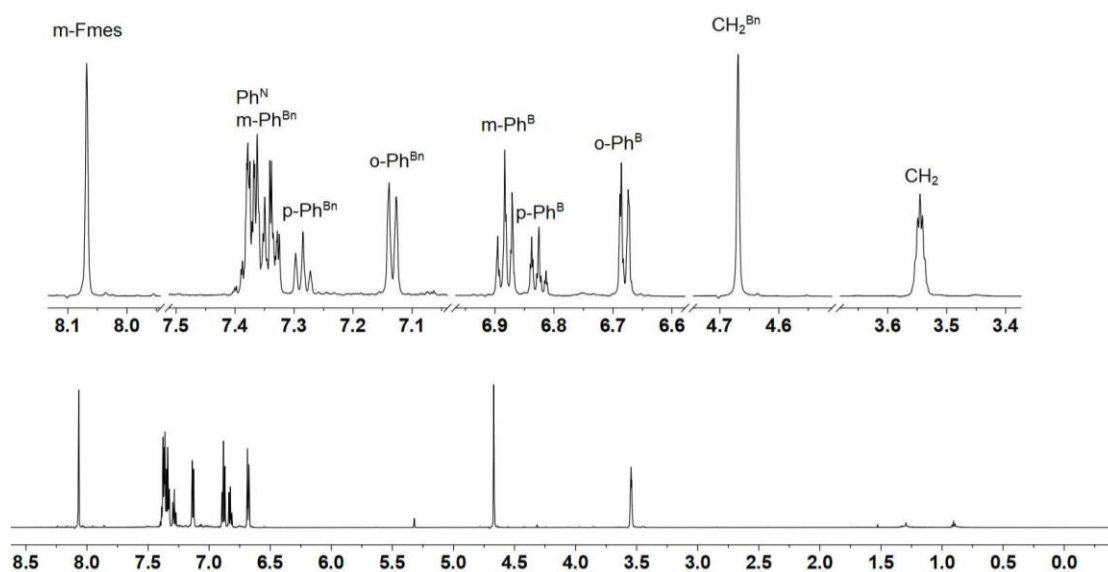


Figure S52. ¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16f**.

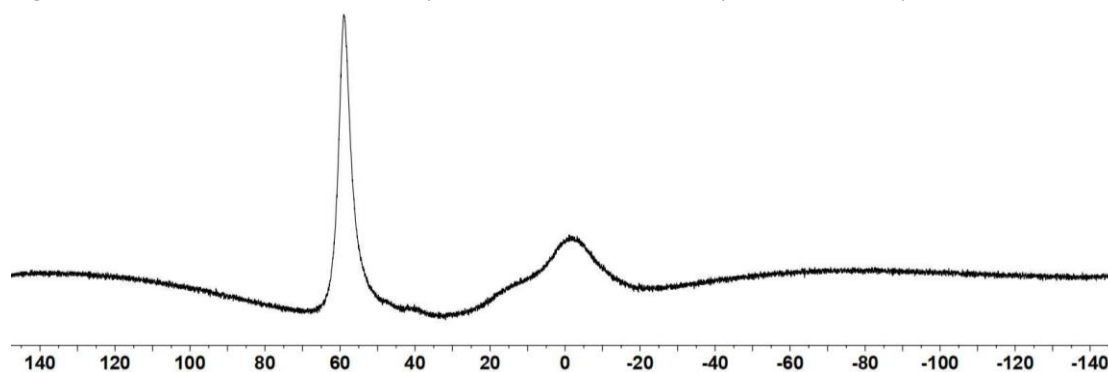


Figure S53. ¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16f**.

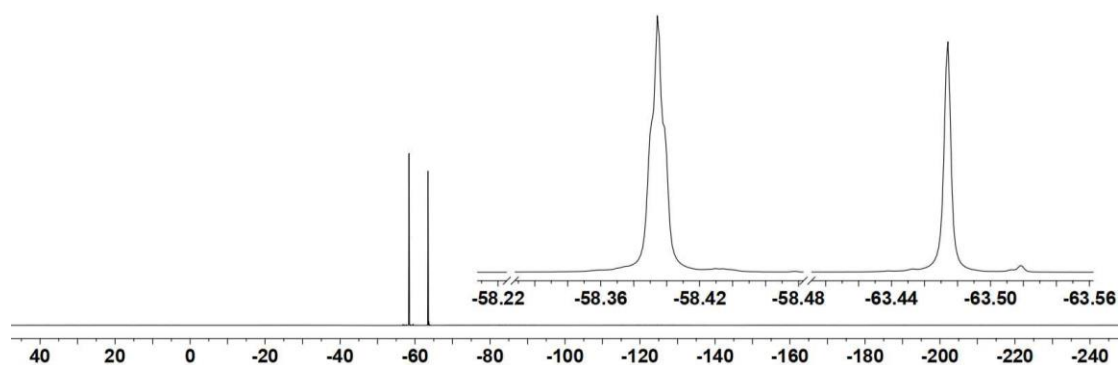


Figure S54. ¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **16f**.

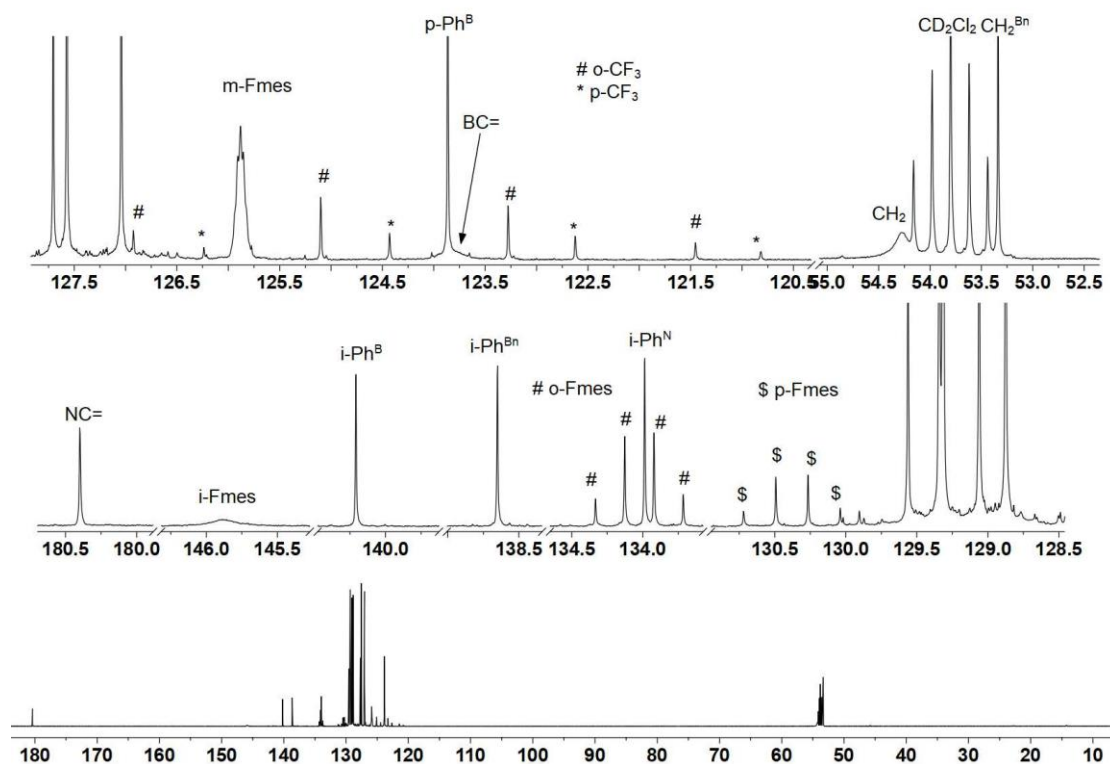


Figure S55. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16f**.

Crystals suitable for the X-ray diffraction analysis were obtained from a solution of compound **16f** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 16f (erk9729): A colorless prism-like specimen of $\text{C}_{31}\text{H}_{21}\text{BF}_9\text{N}$, approximate dimensions $0.092\text{ mm} \times 0.140\text{ mm} \times 0.148\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 468 frames were collected. The total exposure time was 3.25 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 52881 reflections to a maximum θ angle of 27.58° (0.77 \AA resolution), of which 6117 were independent (average redundancy 8.645, completeness = 99.4%, $R_{\text{int}} = 5.50\%$, $R_{\text{sig}} = 2.65\%$) and 5196 (84.94%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.0098(2)\text{ \AA}$, $b = 15.6527(4)\text{ \AA}$, $c = 21.2837(5)\text{ \AA}$, $\beta = 96.4280(10)^\circ$, volume = $2651.67(11)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9908 reflections above $20\sigma(I)$ with $4.648^\circ < 2\theta < 55.14^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.953. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9810 and 0.9880. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $\text{C}_{31}\text{H}_{21}\text{BF}_9\text{N}$. The final anisotropic full-matrix least-squares refinement on F^2 with 379 variables converged at $R1 = 4.71\%$, for the observed data and $wR2 = 11.16\%$ for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was $0.558\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.423\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.052\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.476 g/cm^3 and $F(000)$, 1200 e^- . CCDC number: 2007639.

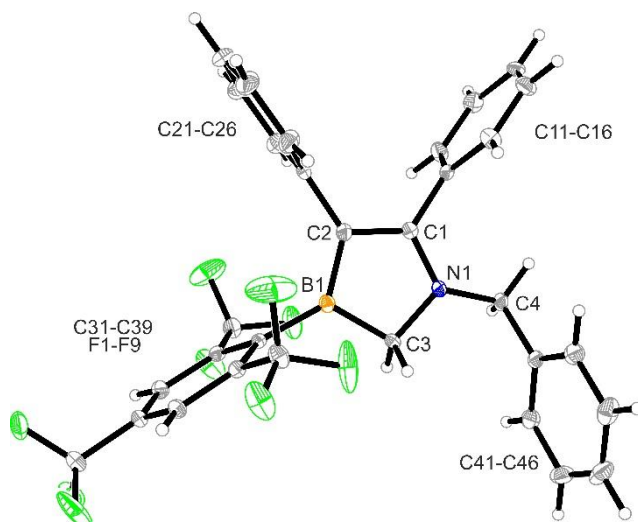
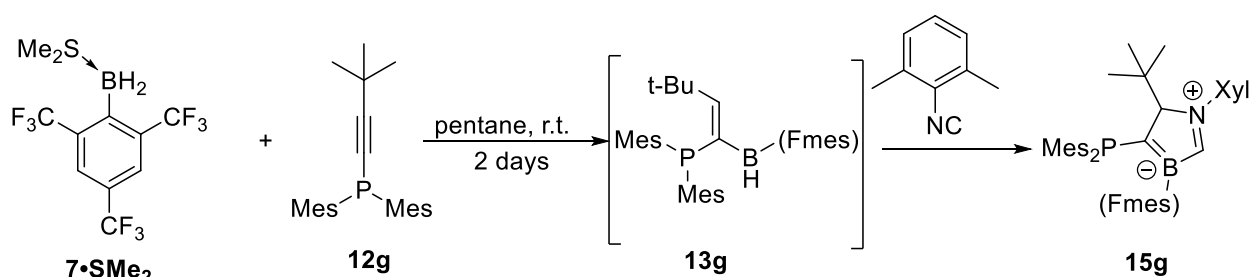


Figure S56. Crystal structure of compound **16f** (thermal ellipsoids at 50% probability).

Preparation of compound **15g**.



Scheme S11.

At room temperature, borane **7·SMe₂** (71.2 mg, 2 mmol, 1 eq.) was added to a solution of phosphane **12g** (70 mg, 2 mmol, 1 eq.) in pentane (5 mL) under argon atmosphere. The mixture was stirred for 2 days to give a yellow solution. The 2,6-dimethylphenyl isocyanide (26.2 mg, 2 mmol, 1 eq.) was added to the mixture in one portion to give a dark violet solution. The resulting solution was stored at -35 °C to finally give the compound **15g** as a violet crystalline solid (89 mg, 57 % yield).

Elemental Analysis for C₄₂H₄₄BNF₉P: calc. C (65.04 %), H (5.72 %), N (1.81 %); found: C (65.43 %), H (5.92 %), N (2.05 %)

¹H NMR (600 MHz, benzene-*d*₆, 299 K): δ = 7.83 (s, 1H, *m*-Fmes), 7.73 (s, 1H, CH=), 7.61 (s, 1H, *m*'-Fmes), 6.86 (s, 1H, *m*-Mes^a), 6.84 (t, ³J_{HH} = 7.4 Hz, 1H, *p*-Xyl), 6.73 (d, ³J_{HH} = 8.6 Hz, 1H, *m*-Xyl), 6.72 (d, ³J_{HH} = 8.3 Hz, 1H, *m*'-Xyl), 6.60 (d, *J* = 5.7 Hz, 2H, *m*'-Mes^a, *m*-Mes^b), 5.96 (s, 1H, *m*'-Mes^b), 5.28 (s, 1H, CH^t-Bu), 2.94 (s, 3H, *o*-CH₃^{Mesb}), 2.88 (s, 3H, *o*-CH₃^{Mesa}), 2.24 (s, 3H, *o*'-CH₃^{Mesa}), 2.10 (s, 6H, *p*-CH₃^{Mesa}, *o*'-CH₃^{Xyl}), 2.09 (s, 3H, *o*'-CH₃^{Xyl}), 1.96 (s, 3H, *p*-CH₃^{Mesb}), 1.95 (s, 3H, *o*'-CH₃^{Mesb}), 1.12 (s, 9H, CH₃^t-Bu).

¹³C{¹H} NMR (151 MHz, benzene-*d*₆, 299 K)[selected resonances]: δ = 189.1 (br, CH=), 151.0 (br, PC=), 146.6 (br, *i*-Fmes), 145.4 (*i*-Xyl), 145.3 (d, ²J_{PC} = 38.8 Hz, *o*-Mes^b), 144.2 (d, ²J_{PC} = 5.0 Hz, *o*'-Mes^b), [141.8 (d, ²J_{PC} = 15.3 Hz), 141.6 (d, ²J_{PC} = 16.2 Hz)](*o*-Mes^a, *o*'-Mes^a), 138.8 (d, ⁴J_{PC} = 1.7 Hz, *p*-Mes^b), 136.5 (*p*-Mes^a), 136.2 (d, ¹J_{PC} = 28.7 Hz, *i*-Mes^a), 133.2 (d, *J* = 2.4 Hz, *o*-Xyl), 132.9 (d, *J* =

3.4 Hz, *o'*-Xyl), 130.4 (d, $^1J_{PC}$ = 6.1 Hz, *i*-Mes^b), 130.1 (*m*-Mes^a), 130.0 (d, $^3J_{PC}$ = 7.0 Hz, *m'*-Mes^a), 129.7 (*m*-Xyl), 129.5 (*m'*-Mes^b), 129.4 (*m'*-Xyl), 129.1 (d, $^3J_{PC}$ = 9.8 Hz, *m*-Mes^b), 124.7 (br, *m*-Fmes), 124.0 (br, *m'*-Fmes), 91.5 (d, $^2J_{PC}$ = 33.0 Hz, CH^{t-Bu}), 38.0 (C^{t-Bu}), 28.2 (br, CH₃^{t-Bu}), 25.0 (*o*-CH₃^{Mesa}), 23.8 (d, $^3J_{PC}$ = 2.8 Hz, *o'*-CH₃^{Mesb}), 23.7 (dq, $^2J_{PC}$ = 30.9 Hz, J_{FC} = 3.8 Hz, *o*-CH₃^{Mesb}), 23.0 (d, $^2J_{PC}$ = 27.1 Hz, *o'*-CH₃^{Mesa}), , 20.8 (*p*-CH₃^{Mesa}), 20.4 (*p*-CH₃^{Mesb}), 19.1 (*o'*-CH₃^{Xyl}), 19.0 (*o*-CH₃^{Xyl}).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, benzene-*d*₆, 299 K): δ = 30.3 ($\nu_{1/2}$ \approx 430 Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, benzene-*d*₆, 299 K): δ = -17.7 (q, J_{FP} = 8.7 Hz).

^{19}F NMR (564 MHz, benzene-*d*₆, 299 K): δ = -55.4 (d, J_{PF} = 7.9 Hz, 1F, *o*-CF₃^{Fmes}), -55.8 (s, 1F, *o'*-CF₃^{Fmes}), -62.4 (s, 1F, *p*-CF₃^{Fmes}).

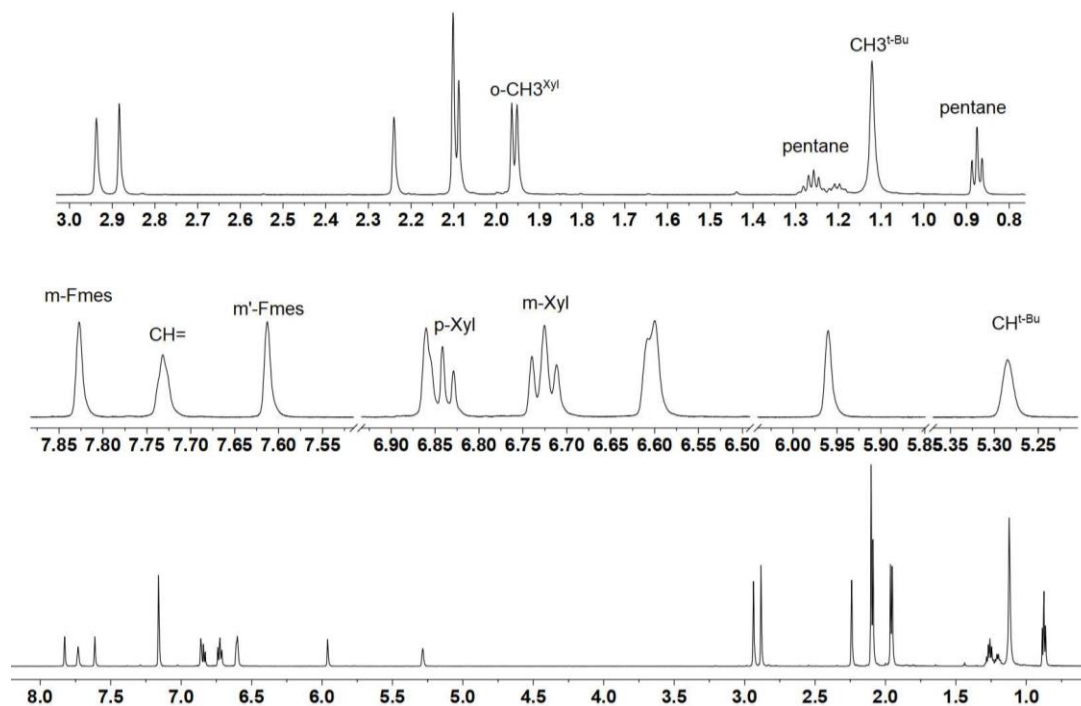


Figure S57. ^1H NMR (600 MHz, benzene-*d*₆, 299 K) spectrum of compound **15g**.

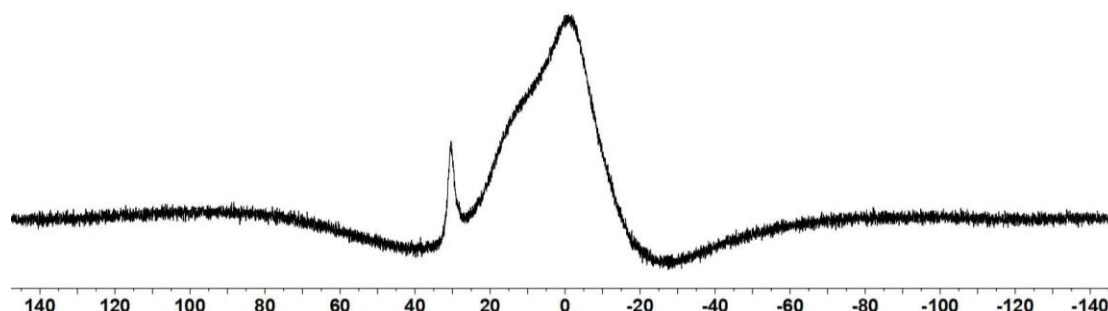


Figure S58. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, benzene-*d*₆, 299 K, 299 K) spectrum of compound **15g**.

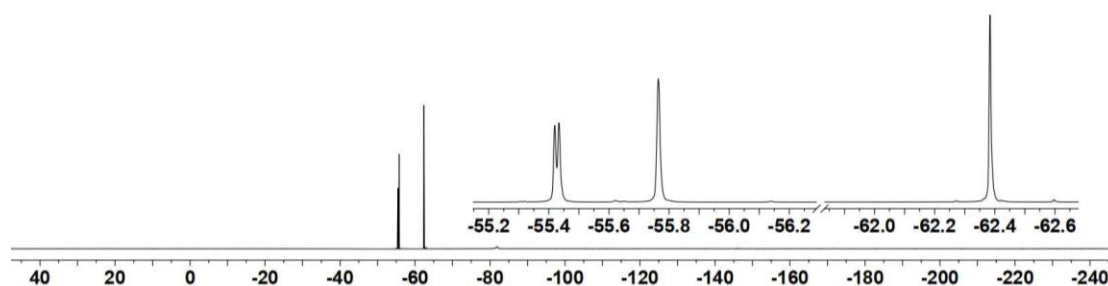


Figure S59. ^{19}F NMR (564 MHz, benzene-*d*₆, 299 K) spectrum of compound **15g**.

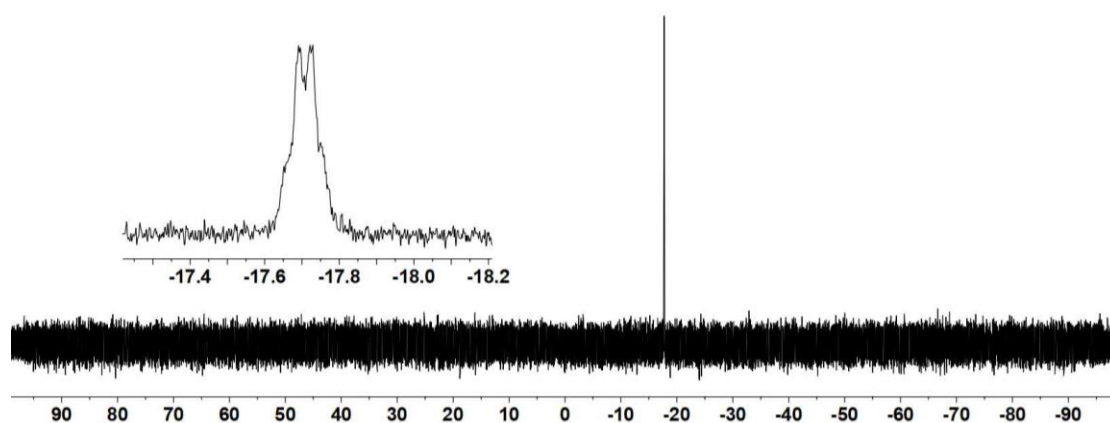


Figure S60. $^{31}\text{P}\{^1\text{H}\}$ NMR (192 MHz, benzene- d_6 , 299 K) spectrum of compound **15g**.

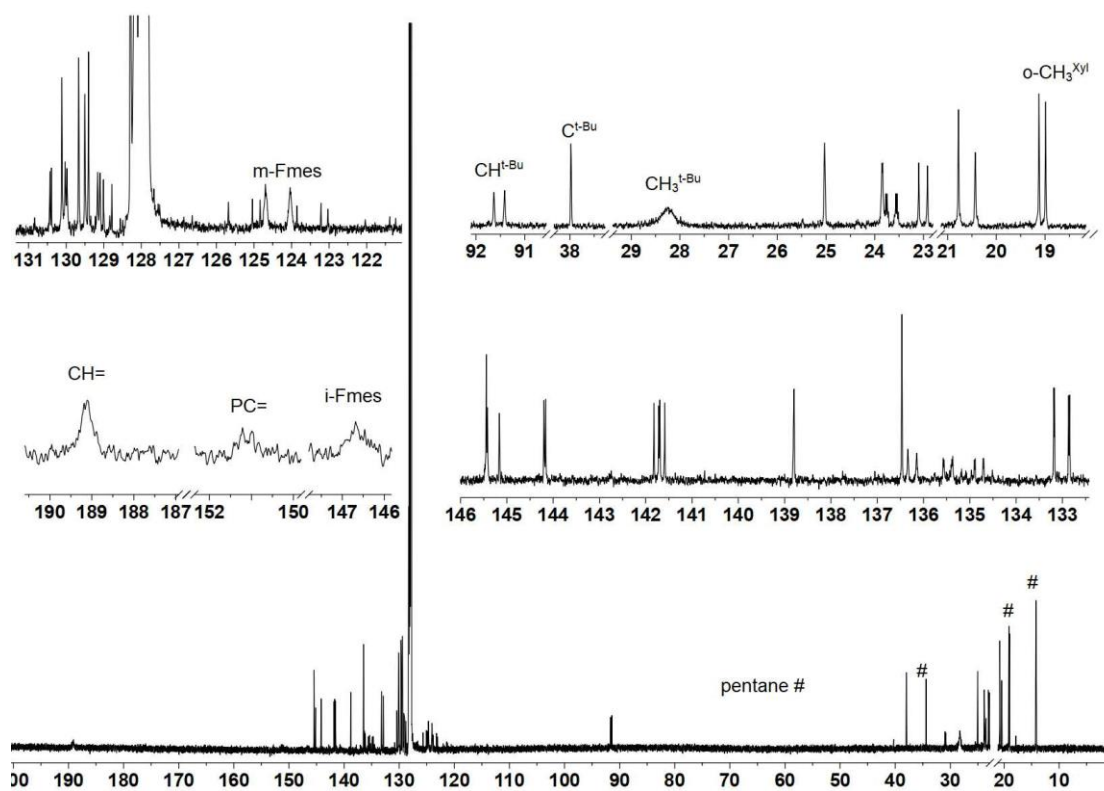


Figure S61. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, benzene- d_6 , 299 K) spectrum of compound **15g**.

The formation of the FLP intermediate **13g** was probed by NMR experiments (two days, 0.2 mmol scale in C_6D_6 (1 mL)); the sample contains some starting material.

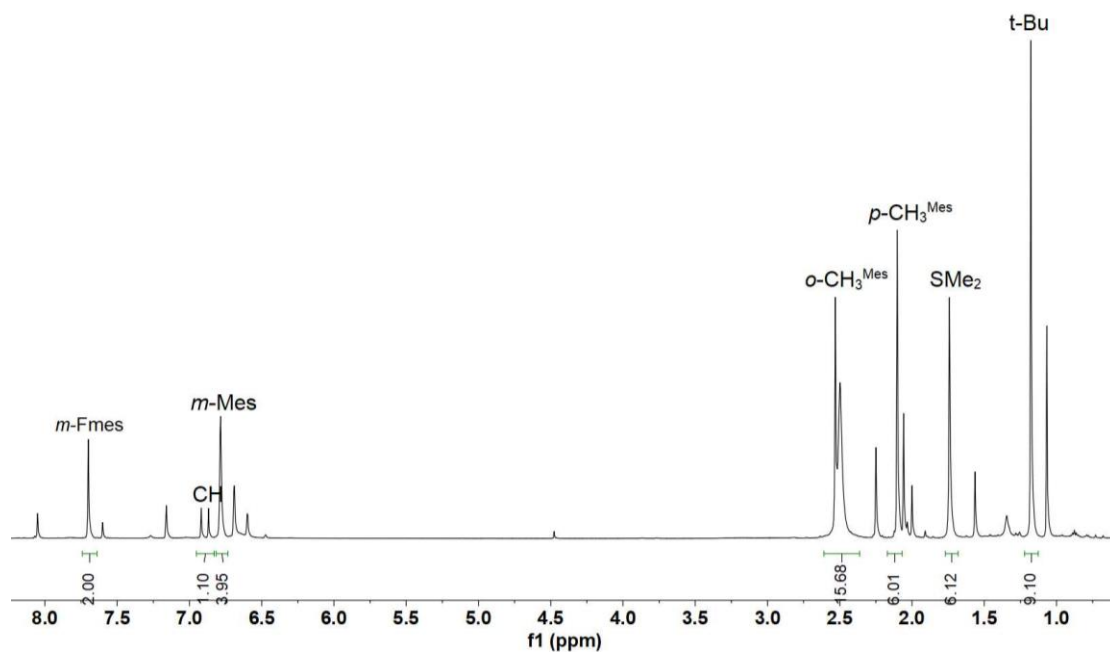


Figure S62. ^1H NMR (600 MHz, benzene- d_6 , 299 K) spectrum of FLP intermediate **13g**.

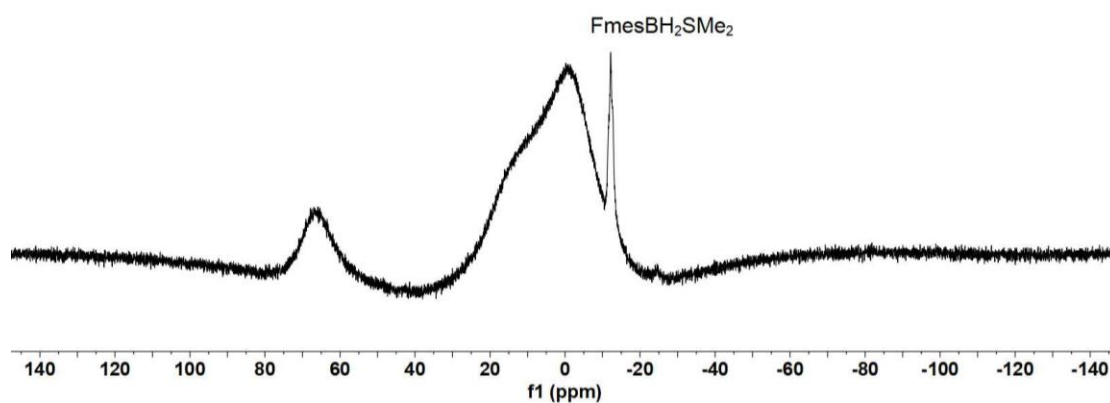


Figure S63. ^{11}B NMR (192 MHz, benzene- d_6 , 299 K, 299 K) spectrum of FLP intermediate **13g**.

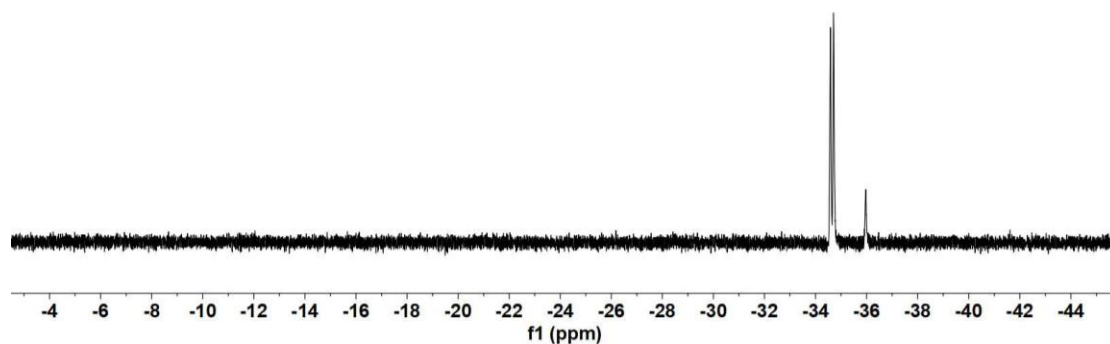


Figure S64. ^{31}P NMR (192 MHz, benzene- d_6 , 299 K) spectrum of FLP intermediate **13g**.

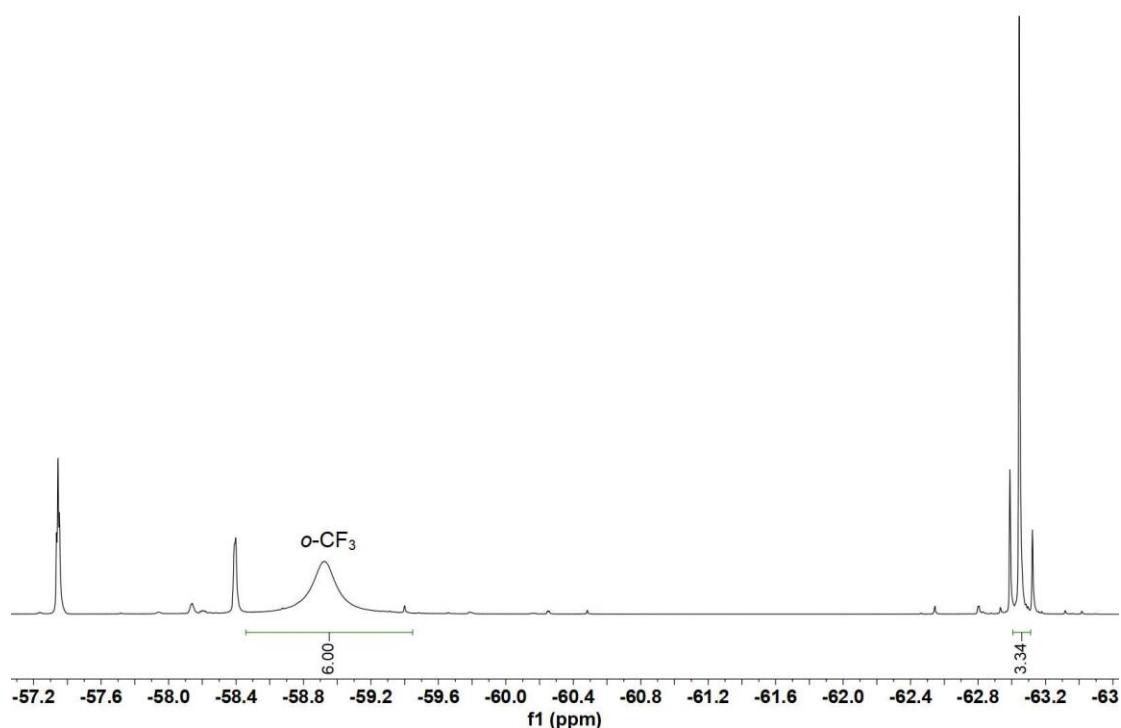


Figure S65. ^{19}F NMR (564 MHz, benzene- d_6 , 299 K) spectrum of FLP intermediate **13g**.

Crystals suitable for X-ray crystal structure analysis were obtained from a solution of compound **15g** in pentane at -35°C .

X-ray crystal structure analysis of compound 15g (erk9300): A pale red prism-like specimen of $\text{C}_{47}\text{H}_{56}\text{BF}_9\text{NP}$, approximate dimensions 0.180 mm x 0.180 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1986 frames were collected. The total exposure time was 19.54 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 64524 reflections to a maximum θ angle of 66.90° (0.84 \AA resolution), of which 7680 were independent (average redundancy 8.402, completeness = 99.6%, $R_{\text{int}} = 7.88\%$, $R_{\text{sig}} = 4.27\%$) and 6002 (78.15%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 12.9016(11) \text{ \AA}$, $b = 12.5211(11) \text{ \AA}$, $c = 27.465(2) \text{ \AA}$, $\beta = 102.563(5)^\circ$, volume = $4330.5(6) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9686 reflections above $20 \sigma(I)$ with $7.793^\circ < 2\theta < 131.2^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.798. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7640 and 0.8150. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $\text{C}_{47}\text{H}_{56}\text{BF}_9\text{NP}$. The final anisotropic full-matrix least-squares refinement on F^2 with 817 variables converged at $R1 = 8.51\%$, for the observed data and $wR2 = 17.76\%$ for all data. The goodness-of-fit was 1.123. The largest peak in the final difference electron density synthesis was $0.363 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.311 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.064 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.300 g/cm^3 and $F(000)$, 1784 e^- . CCDC number: 2007634.

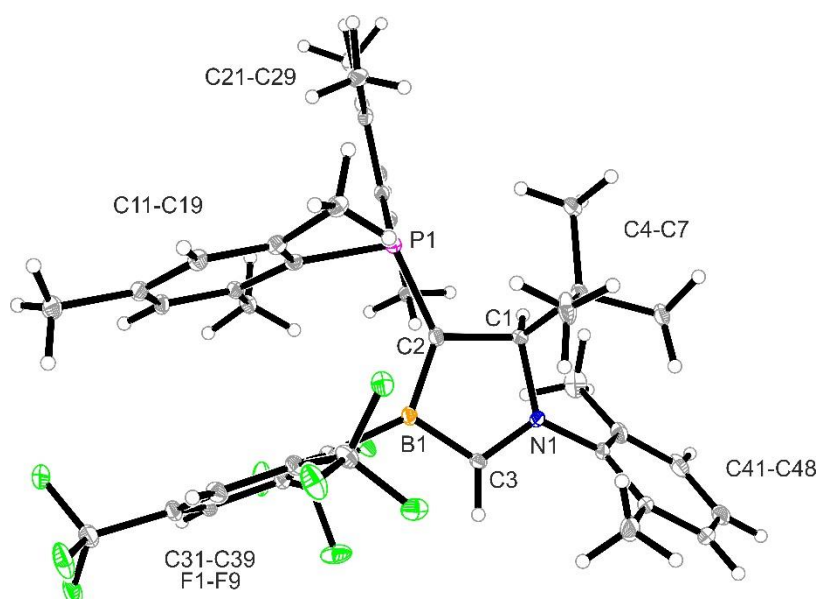
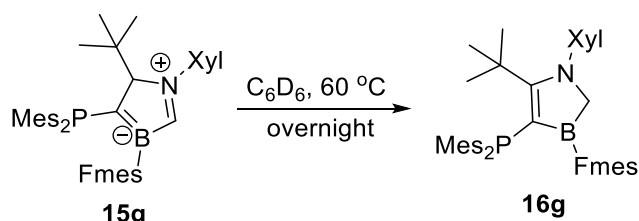


Figure S66. Crystal structure of compound **15g** (thermal ellipsoids at 15% probability).

Preparation of the compound **16g**



Scheme S12.

In a J. Young tube, compound **15g** (77.5 mg, 1 mmol) in C_6D_6 (1 mL) was heated at 60 °C overnight to give a brown solution. NMR monitoring shows all starting material was transformed to the product. Volatiles were removed in vacuo. The residue was dissolved in heptane (1 mL) and stored at -35 °C to finally give the compound **16g** as a brown crystalline solid (52 mg, 67% yield).

Elemental Analysis for $C_{42}H_{44}BNF_9P$: calc. C (65.04 %), H (5.72 %), N (1.81 %); found: C (65.61 %), H (5.69 %), N (1.87 %).

HRMS for $C_{42}H_{45}BNF_9P^+$ $[M + H]^+$: calc. 776.3241; found: 776.3249.

1H NMR (600 MHz, benzene- d_6 , 299 K): δ = 7.74 (s, 1H, *m*-Fmes), 7.38 (s, 1H, *m'*-Fmes), 6.89 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-Xyl), 6.83 (s, 1H, *m*-Mes^a), 6.79 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *m*-Xyl), 6.77 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *m'*-Xyl), 6.72 (d, $^4J_{PH}$ = 5.5 Hz, 1H, *m*-Mes^b), 6.58 (d, $^4J_{PH}$ = 4.0 Hz, 1H, *m'*-Mes^a), 5.77 (d, $^4J_{PH}$ = 1.9 Hz, 1H, *m'*-Mes^b), 3.21 (s, 2H, CH₂), 2.93 (s, 3H, *o*-CH₃^{Mesa}), 2.83 (d, $^4J_{PH}$ = 2.5 Hz, 3H, *o*-CH₃^{Mesb}), 2.10 (s, 3H, *p*-CH₃^{Mesa}), 2.084 (s, 6H, *o*-CH₃^{Xyl}, *o'*-CH₃^{Mesa}), 2.076 (s, 3H, *o'*-CH₃^{Xyl}), 1.98 (s, 3H, *p*-CH₃^{Mesb}), 1.64 (s, 3H, *o'*-CH₃^{Mesb}), 1.44 (d, $^5J_{PH}$ = 1.3 Hz, 9H, CH₃^{t-Bu}).

$^{13}C\{^1H\}$ NMR (151 MHz, benzene- d_6 , 299 K)[selected resonances]: δ = 193.9 (d, $^2J_{PC}$ = 39.1 Hz, NC=), 145.5 (*i*-Xyl), 144.5 (br, *i*-Fmes), 144.1 (d, $^2J_{PC}$ = 38.5 Hz, *o*-Mes^b), 142.8 (d, $^2J_{PC}$ = 4.4 Hz, *o'*-Mes^b), 141.4 (d, $^2J_{PC}$ = 1.8 Hz, *o*-Mes^a), 140.6 (d, $^2J_{PC}$ = 34.0 Hz, *o'*-Mes^a), 137.7 (*p*-Mes^b), 137.0 (d, $^1J_{PC}$ =

28.5 Hz, *i*-Mes^a), 135.43 (*p*-Mes^a), 135.40 (*o*-Xyl), 135.0 (*o'*-Xyl), 133.1 (d, $^1J_{PC} = 7.8$ Hz, *i*-Mes^b), 132.6 (br, BC=), 130.8 (*m*-Mes^a), 130.0 (d, $^3J_{PC} = 5.0$ Hz, *m'*-Mes^a), 129.8 (d, $^3J_{PC} = 9.2$ Hz, *m*-Mes^b), 129.4 (*m'*-Mes^b), 128.8 (*m*-Xyl), 128.5 (*m'*-Xyl), 127.7 (*p*-Xyl), 125.0 (br, *m*-Fmes), 124.6 (br, *m'*-Fmes), 59.2 (br, CH₂), 40.3 (C^t-Bu), 30.9 (d, $^4J_{PC} = 15.0$ Hz, CH₃^t-Bu), 25.5 (*o'*-CH₃^{Mesb}), 24.2 (d, $^3J_{PC} = 31.5$ Hz, *o*-CH₃^{Mesb}), 22.8 (d, $^3J_{PC} = 2.8$ Hz, *o*-CH₃^{Mesa}), 22.3 (d, $^3J_{PC} = 28.4$ Hz, *o'*-CH₃^{Mesa}), 20.7 (*p*-CH₃^{Mesa}), 20.4 (*p*-CH₃^{Mesb}), 17.9 (d, $J = 2.1$ Hz, *o*-CH₃^{Xyl}, *o'*-CH₃^{Xyl}).

¹¹B{¹H} NMR (192 MHz, benzene-*d*₆, 299 K): $\delta = 59.3$ ($\nu_{1/2} \approx 1270$ Hz).

³¹P{¹H} NMR (243 MHz, benzene-*d*₆, 299 K): $\delta = -35.0$ ($\nu_{1/2} \approx 6$ Hz).

¹⁹F NMR (564 MHz, benzene-*d*₆): $\delta = -55.0, -55.6$ (each s, each 1 F, *o*-CF₃^{Fmes}), -62.6 (s, 1F, *p*-CF₃^{Fmes}).

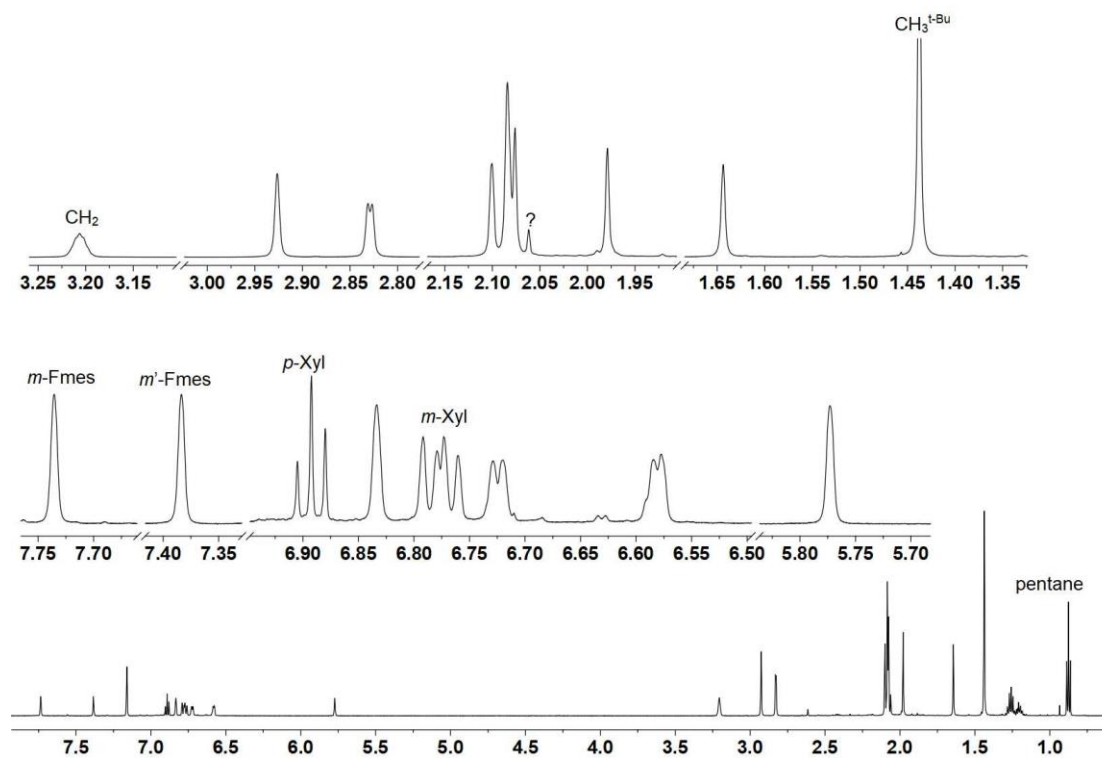


Figure S67. ¹H NMR (600 MHz, benzene-*d*₆, 299 K) spectrum of compound **16g**.

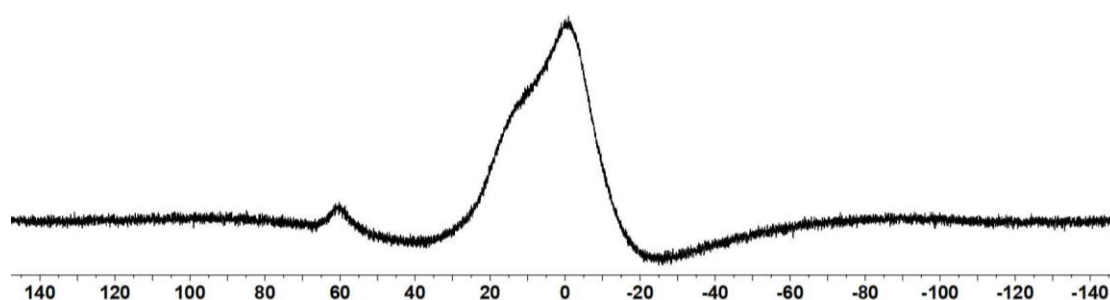


Figure S68. ¹¹B{¹H} NMR (192 MHz, benzene-*d*₆, 299 K) spectrum of compound **16g**.

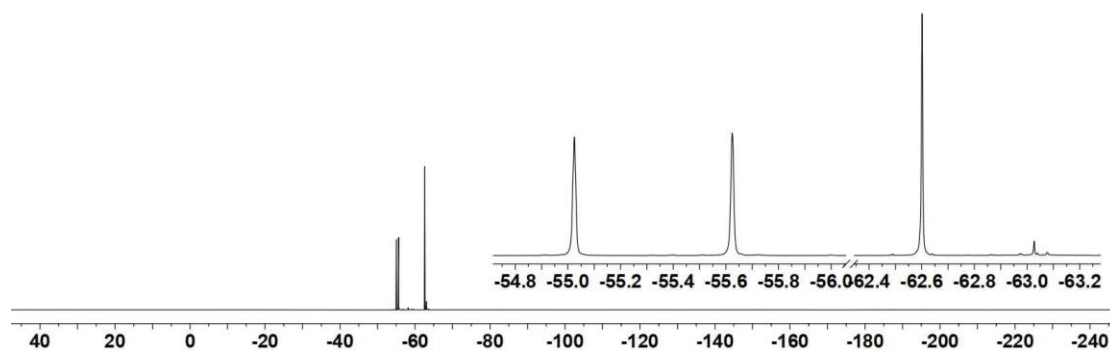


Figure S69. ^{19}F NMR (564 MHz, benzene- d_6 , 299 K) spectrum of compound **16g**.

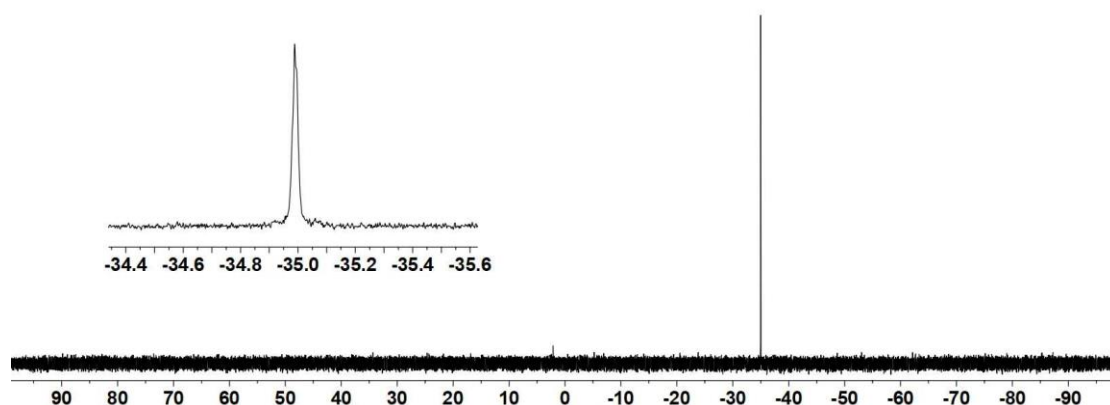


Figure S70. $^{31}\text{P}\{^1\text{H}\}$ NMR (192 MHz, benzene- d_6 , 299 K) spectrum of compound **16g**.

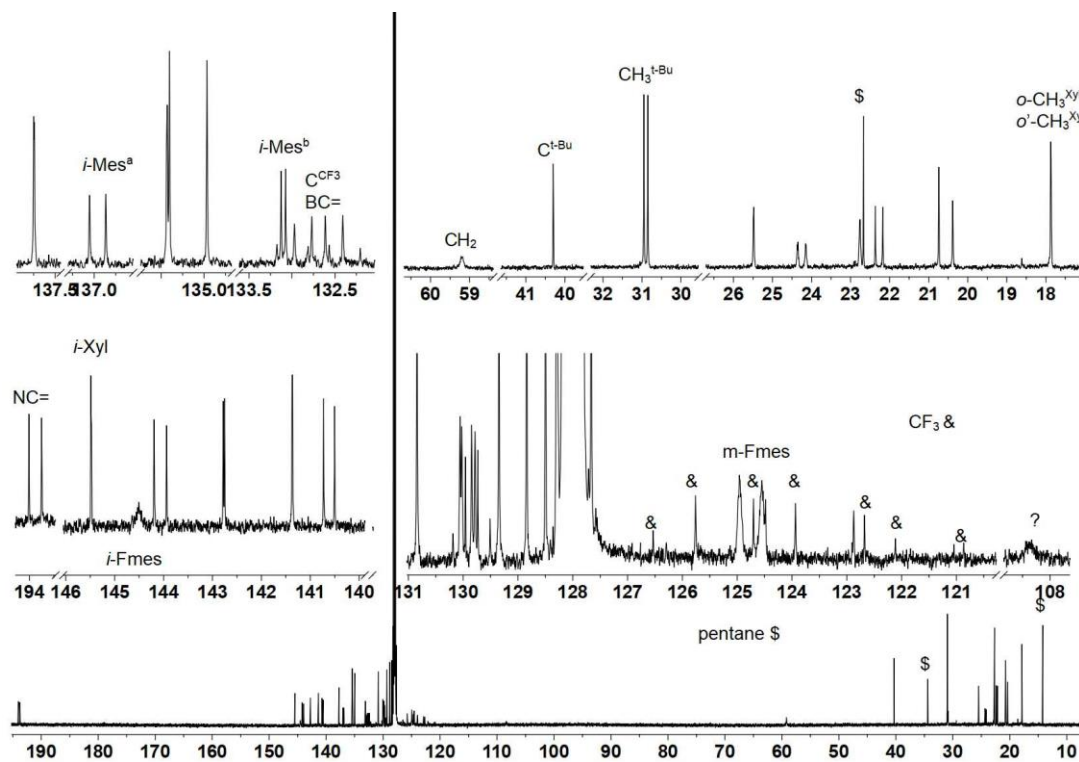


Figure S71. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, benzene- d_6 , 299 K) spectrum of compound **16g**.

Crystals suitable for X-ray crystal structure analysis were obtained from a solution of **16g** in pentane at -35°C.

X-ray crystal structure analysis of compound 16g (erk9226): A red prism-like specimen of $C_{47}H_{56}BF_9NP$, approximate dimensions 0.071 mm x 0.160 mm x 0.204 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1862 frames were collected. The total exposure time was 22.24 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 89324 reflections to a maximum θ angle of 26.73° (0.79 \AA resolution), of which 9311 were independent (average redundancy 9.593, completeness = 99.9%, $R_{\text{int}} = 6.00\%$, $R_{\text{sig}} = 3.52\%$) and 7230 (77.65%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 13.2994(6) \text{ \AA}$, $b = 12.6152(6) \text{ \AA}$, $c = 26.6795(11) \text{ \AA}$, $\beta = 101.2410(10)^\circ$, volume = $4390.3(3) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9883 reflections above $20 \sigma(I)$ with $4.491^\circ < 2\theta < 54.99^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.947. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9910. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $C_{47}H_{56}BF_9NP$. The final anisotropic full-matrix least-squares refinement on F^2 with 545 variables converged at $R1 = 5.36\%$, for the observed data and $wR2 = 12.61\%$ for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was $0.469 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.392 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.057 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.283 g/cm^3 and $F(000)$, 1784 e^- . CCDC number: 2007640.

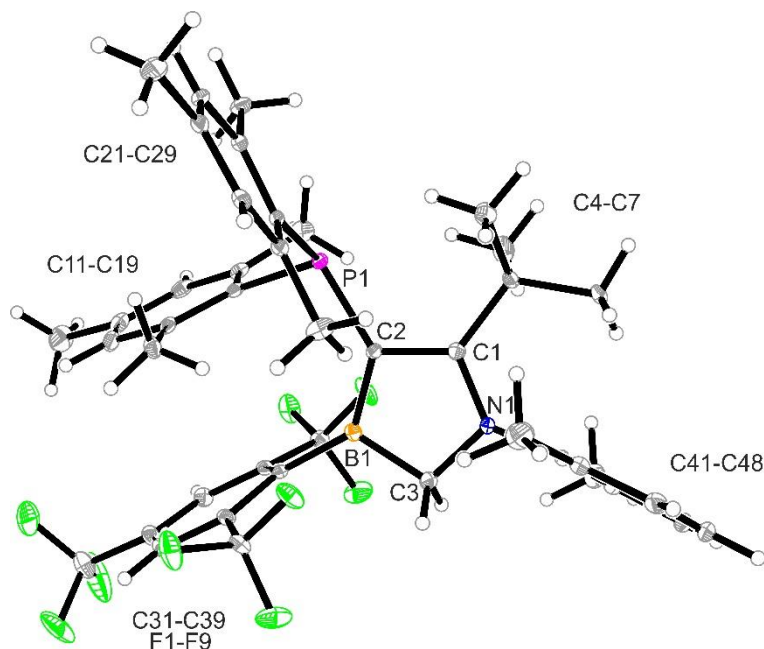
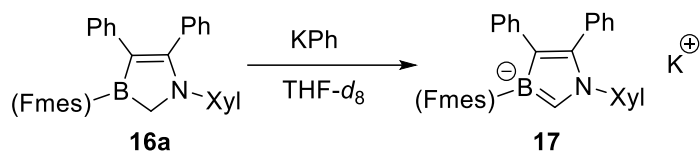


Figure S72. Crystal structure of compound **16g** (thermal ellipsoids at 30% probability).

Preparation of azaborolyl potassium **17** (*in situ* reaction)



Scheme S13.

In a J. Young tube, KPh (23.2 mg, 2 mmol, 2 equiv.) was added to a solution of azaborole **16a** (60.3 mg, 1 mmol, 1 equiv.) in THF- d_8 to give a deep brown solution. The resulting solution was stored at room temperature for 30 min., then it was used for NMR experiments.

[*Comments:* The deprotonation of compound **16a** works well with LiNMe₂, KTMP and KPh, but when LiTMP was employed as a base, the process progressed slowly concomitant with decomposition. t-BuLi (6 equiv.) furnished the product however, decomposition was observed.]

¹H NMR (600 MHz, THF- d_8 , 299 K): δ = 7.95 (s, 2H, *m*-Fmes), 6.84 (m, 2H, *o*-Ph^N), 6.82 (m, 1H, *p*-Xyl), 6.80 (m, 2H, *o*-Ph^B), 6.79 (m, 2H, *m*-Xyl), 6.77 (m, 2H, *m*-Ph^N), 6.74 (m, 2H, *m*-Ph^B), 6.67 (m, 1H, *p*-Ph^N), 6.57 (m, 1H, *p*-Ph^B), 5.58 (s, 1H, CH), 2.06 (s, 6H, *o*-CH₃^{Xyl}).

¹³C{¹H} NMR (151 MHz, THF- d_8 , 299 K): δ = 160.1 (br, *i*-Fmes), 147.8 (*i*-Ph^B), 146.8 (*i*-Xyl), 138.1 (*i*-Ph^N), 137.0 (*o*-Xyl), 133.3 (NC=), 130.4 (*o*-Ph^N), 129.9 (*o*-Ph^B), 127.8 (*m*-Xyl), 127.2 (*m*-Ph^B), 126.9 (*m*-Ph^N), 126.3 (br, BC=), 125.5 (*p*-Xyl), 124.2 (br, *m*-Fmes), 123.0 (*p*-Ph^N), 120.8 (CH, *p*-Ph^B), 18.3 (*o*-CH₃^{Xyl}).

¹¹B{¹H} NMR (192 MHz, THF- d_8 , 299 K): δ = 23.2 ($\nu_{1/2} \approx 380$ Hz).

¹⁹F NMR (564 MHz, THF- d_8 , 299 K): δ = -57.9 (s, 2F, *o*-CF₃^{Fmes}), -63.2 (s, 1F, *p*-CF₃^{Fmes})

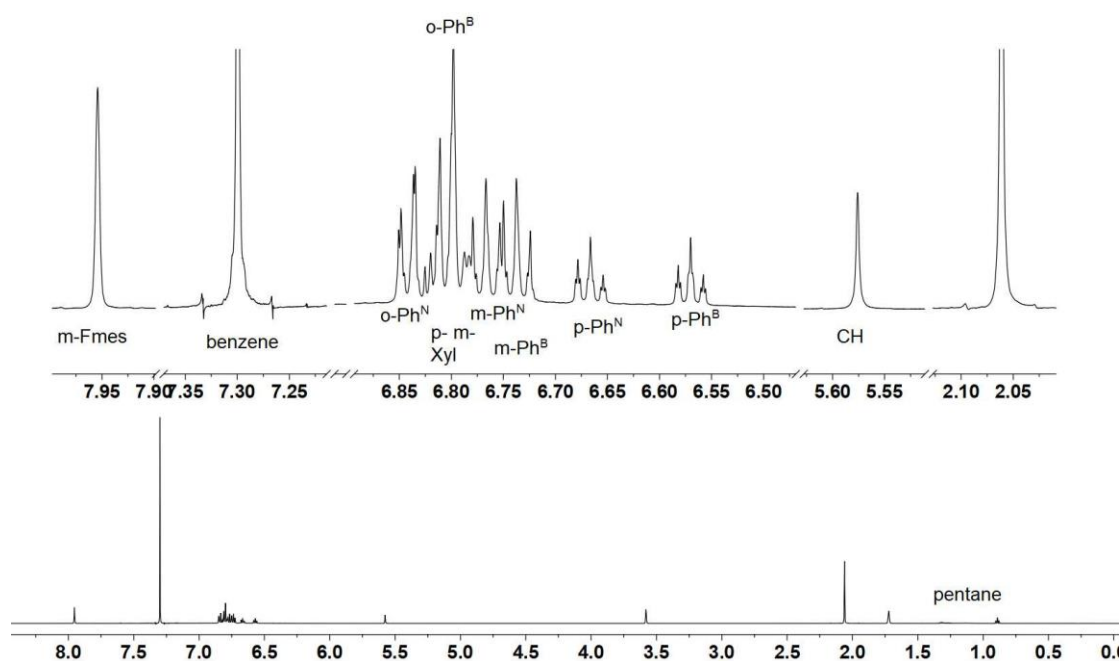


Figure S73. ¹H NMR (600 MHz, THF- d_8 , 299 K) spectrum of compound **17**.

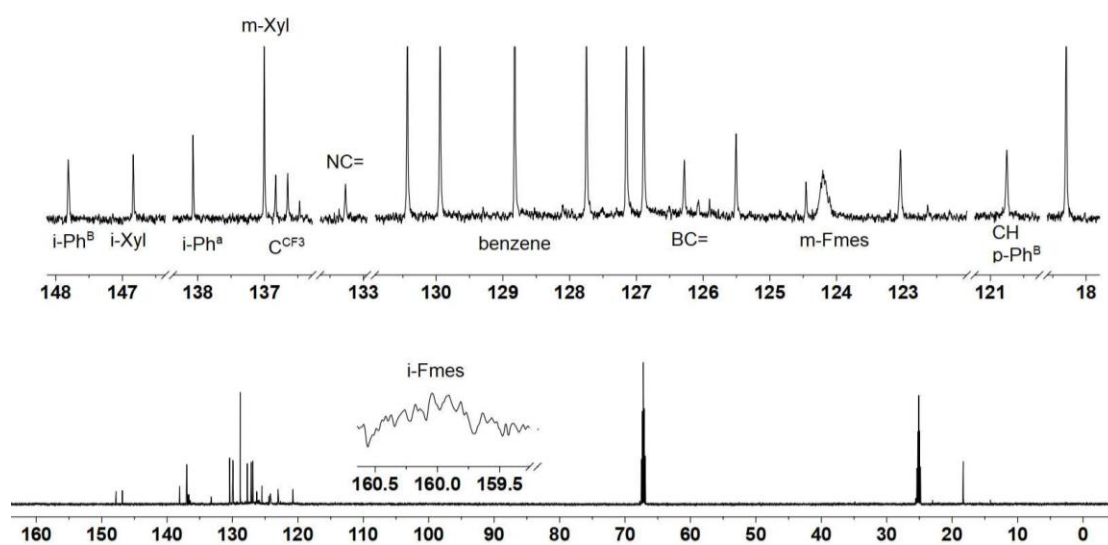


Figure S74. ¹³C{¹H} NMR (151 MHz, benzene-*d*₆, 299 K) spectrum of compound **17**.

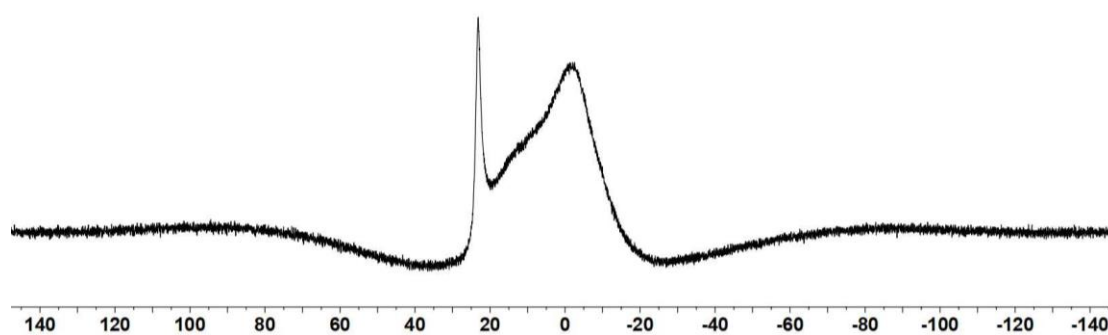


Figure S75. ¹¹B{¹H} NMR (192 MHz, THF-*d*₈, 299 K) spectrum of compound **17**.

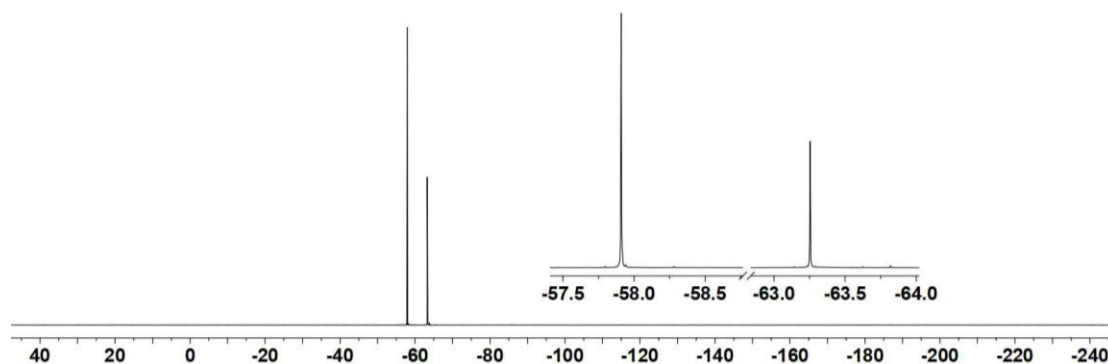
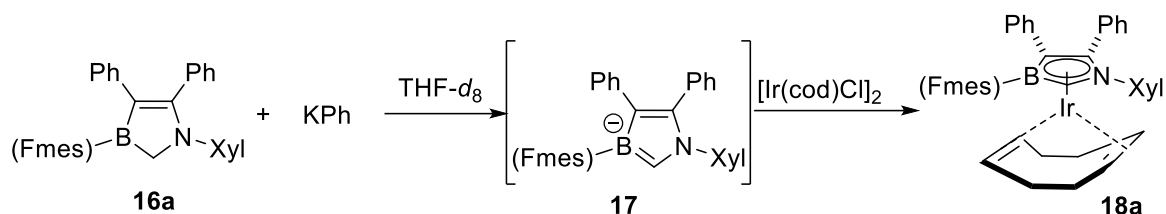


Figure S76. ¹⁹F NMR (564 MHz, THF-*d*₈, 299 K) spectrum of compound **17**.

Preparation of compound 18a



Scheme S14.

In a J. Young tube, KPh (23.2 mg, 2 mmol, 2 equiv.) was added to a solution of azaborole **16a** (60.3 mg, 1 mmol, 1 equiv.) in THF- d_8 to give a deep brown solution at room temperature. The resulting solution was stored at room temperature for 30 min. Then $[\text{Ir}(\text{cod})\text{Cl}]_2$ (33.6 mg, 0.5 mmol, 1 equiv.) was added and the resulting mixture was stored for overnight. All the volatiles were removed in vacuo. The residue was dispersed in pentane (20 mL) and the solid was filtered off. The solution was concentrated to ca. 1 mL and stored in $-35\text{ }^\circ\text{C}$ to finally give the compound **18a** as light-yellow crystalline solid (33 mg, 36% yield).

[Comments: As we show in the formation of compound **17**, the deprotonation works well with LiNMe_2 or KTMP. However, when the metal salt was added, compound **16a** was observed as the major component.]

Elemental Analysis for $\text{C}_{41}\text{H}_{36}\text{BNF}_9\text{IrCl}_2$ [$\text{M} + \text{CH}_2\text{Cl}_2$]: calc. C (49.86 %), H (3.67 %), N (1.42 %); found: C (50.12 %), H (3.58 %), N (1.20 %).

^1H NMR (600 MHz, methylene chloride- d_2 , 268 K): δ = 8.21 (s, 1H, *m*-Fmes), 8.04 (s, 1H, *m'*-Fmes), 7.13 (m, 1H, *m*-Xyl), 7.08 (m, 6H, *o*-Ph^N, *p*-Ph^N, *m*-Ph^B, *p*-Ph^B), 7.04 (m, 1H, *p*-Xyl), 6.98 (m, 2H, *m*-Ph^N), 6.87 (m, 2H, *o*-Ph^B), 6.72 (d, $^3J_{\text{HH}} = 7.6$, 1H, *m'*-Xyl), 4.71 (s, 1H, CH), [4.19, 4.03, 3.87, 3.73](each m, each 1H, $\text{CH}=\text{cod}$), 3.20 (s, 3H, *o*-CH₃^{Xyl}), [2.33 (m, 2H), 2.04 (m, 2H), 1.84 (m, 2H), 1.69 (m, 1H), 1.52 (m, 1H)](CH_2^{cod}), 1.77 (s, 3H, *o'*-CH₃^{Xyl}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 268 K)[selected resonances]: δ = 141.9 (br, *i*-Fmes), 139.2 (*i*-Ph^B), 136.9 (*o'*-Xyl), 134.5 (*p*-Xyl), 133.7 (*o*-Xyl), 132.0 (*o*-Ph^N), 129.9 (*i*-Ph^N), 129.4 (*o*-Ph^B), 129.0 (*m*-Xyl), 128.9 (*m'*-Xyl), 128.6 (*p*-Ph^N), 128.2 (*p*-Xyl), 127.8 (*m*-Ph^B, *m'*-Fmes), 127.1 (*m*-Ph^N), 126.2 (br, *m*-Fmes), 125.4 (*p*-Ph^B), 115.9 (NC=), 112.0 (br, BC=), 90.3 (br, CH), [69.1, 65.4, 55.4, 53.6]($\text{CH}=\text{cod}$), [34.0, 33.6, 32.1, 30.2](CH_2^{cod}), 19.4 (*o*-CH₃^{Xyl}), 18.4 (*o'*-CH₃^{Xyl}).

^{11}B NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 16.5 ($\nu_{1/2} \approx 350$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = [-52.7, -52.8](each s, each 1F, *o*-CF₃), -63.4 (s, 1F, *p*-CF₃).

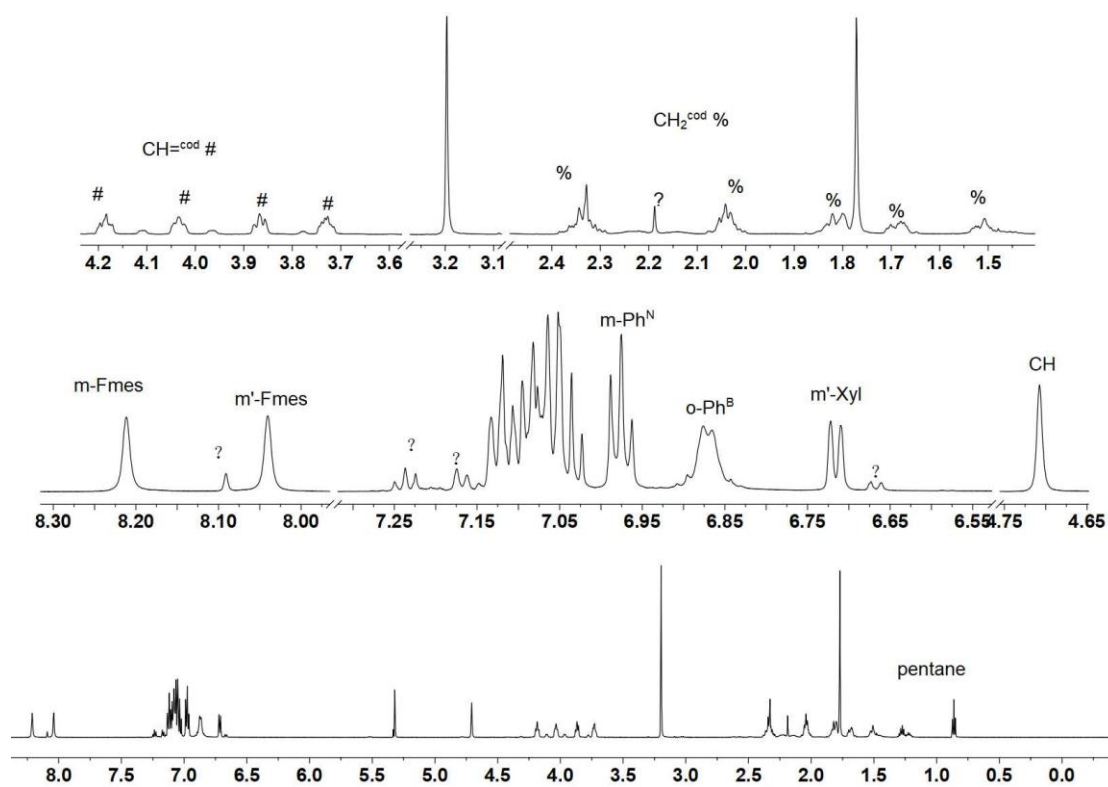


Figure 77. ^1H NMR (600 MHz, methylene chloride- d_2 , 268 K) spectrum of compound **18a**.

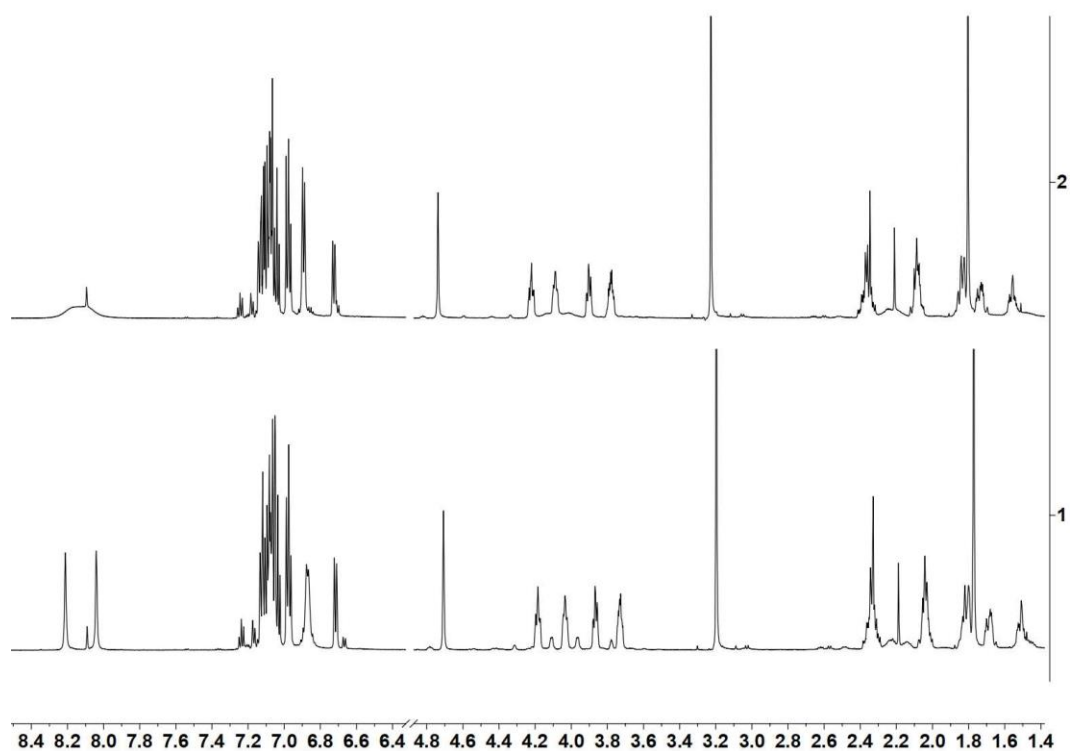


Figure 78. ^1H NMR (600 MHz, methylene chloride- d_2) spectra of compound **18a** (1) at 268 K, (2) at 299 K.

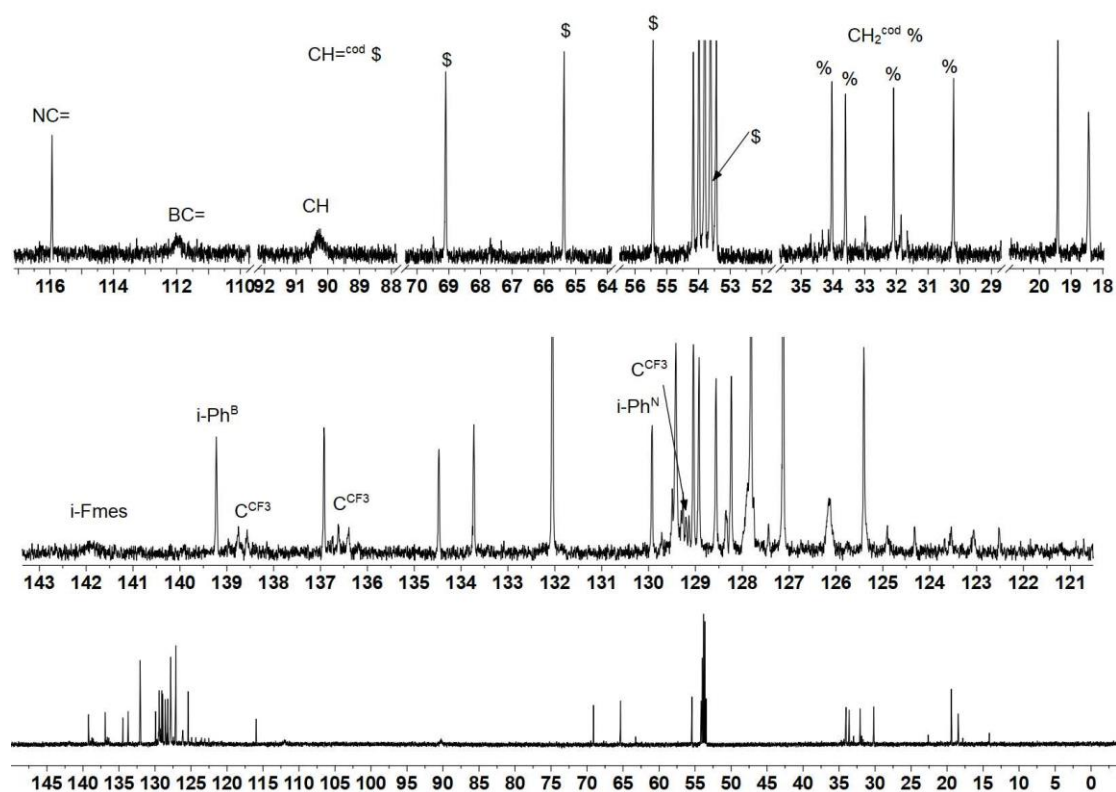


Figure 79. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 268 K) spectrum of compound **18a**.

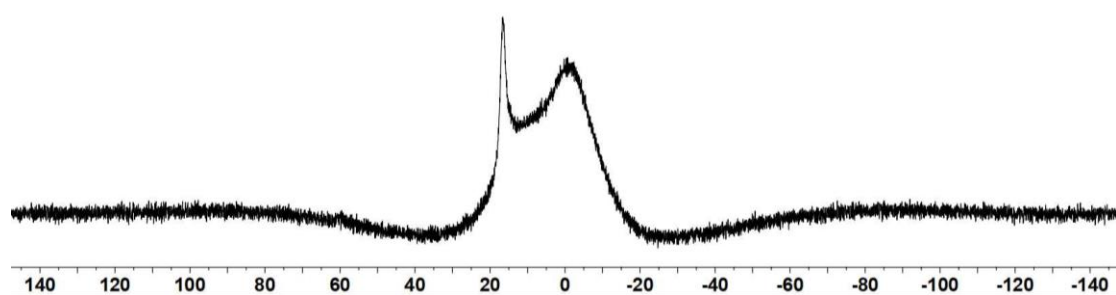


Figure 80. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **18a**.

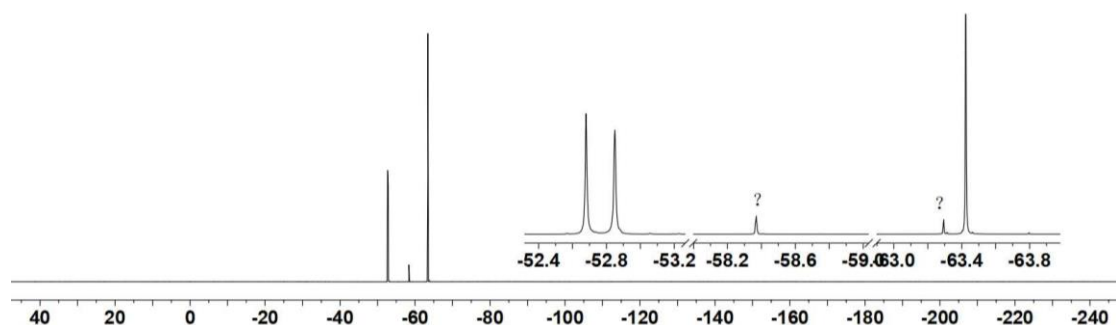


Figure 81. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 268 K) spectrum of compound **18a**.

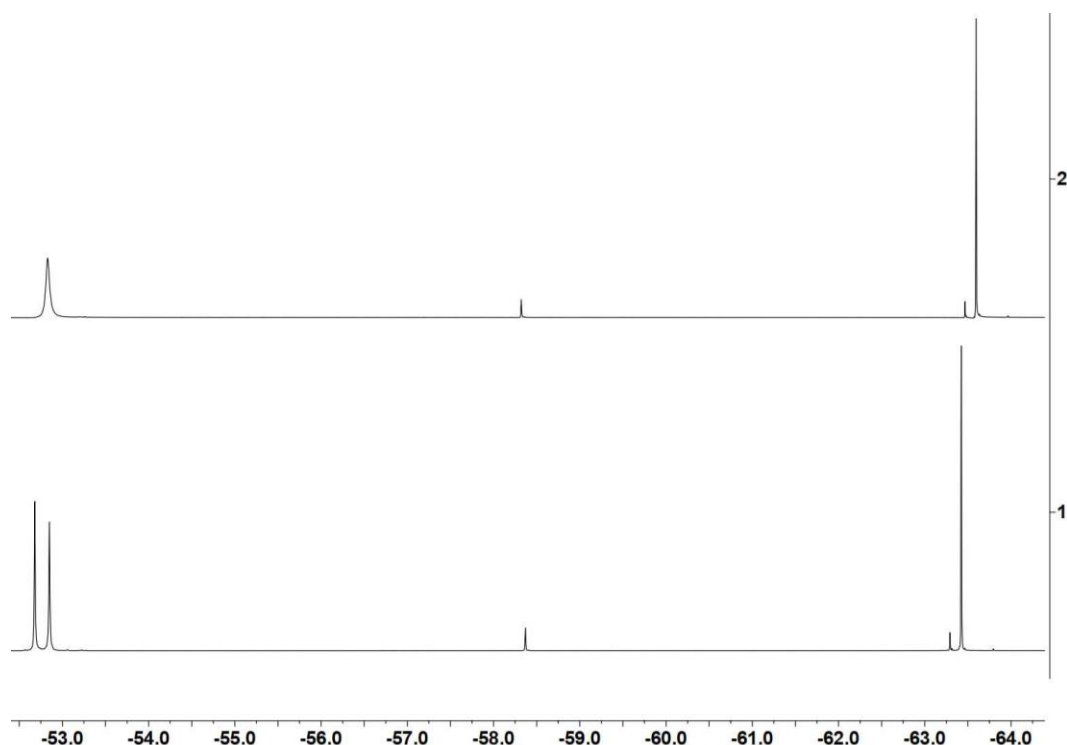


Figure 82. ^{19}F NMR (564 MHz, methylene chloride- d_2) spectra of compound **18a**, (1) at 268 K, (2) at 299 K.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of **18a** in pentane at room temperature.

X-ray crystal structure analysis of compound 18a (erk9646): A yellow plate-like specimen of $\text{C}_{40}\text{H}_{34}\text{BF}_9\text{IrN}$, approximate dimensions 0.030 mm x 0.120 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1514 frames were collected. The total exposure time was 19.86 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 25272 reflections to a maximum θ angle of 66.65° (0.84 \AA resolution), of which 5721 were independent (average redundancy 4.417, completeness = 99.2%, $R_{\text{int}} = 6.97\%$, $R_{\text{sig}} = 5.60\%$) and 5056 (88.38%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.6983(2) \text{ \AA}$, $b = 10.4210(2) \text{ \AA}$, $c = 19.0291(4) \text{ \AA}$, $\alpha = 77.0000(10)^\circ$, $\beta = 76.9460(10)^\circ$, $\gamma = 82.3110(10)^\circ$, volume = $1630.98(6) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9941 reflections above $20 \sigma(I)$ with $9.109^\circ < 2\theta < 133.2^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.614. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3770 and 0.7810. 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, $\text{C}_{40}\text{H}_{34}\text{BF}_9\text{IrN}$. The final anisotropic full-matrix least-squares refinement on F^2 with 471 variables converged at $R1 = 3.83\%$, for the observed data and $wR2 = 9.36\%$ for all data. The goodness-of-fit was 1.115. The largest peak in the final difference electron density synthesis was $0.955 \text{ e}/\text{\AA}^3$ and the largest hole was $-1.351 \text{ e}/\text{\AA}^3$ with an RMS deviation of $0.160 \text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was $1.838 \text{ g}/\text{cm}^3$ and $F(000)$, 888 e^- . CCDC number: 2007641.

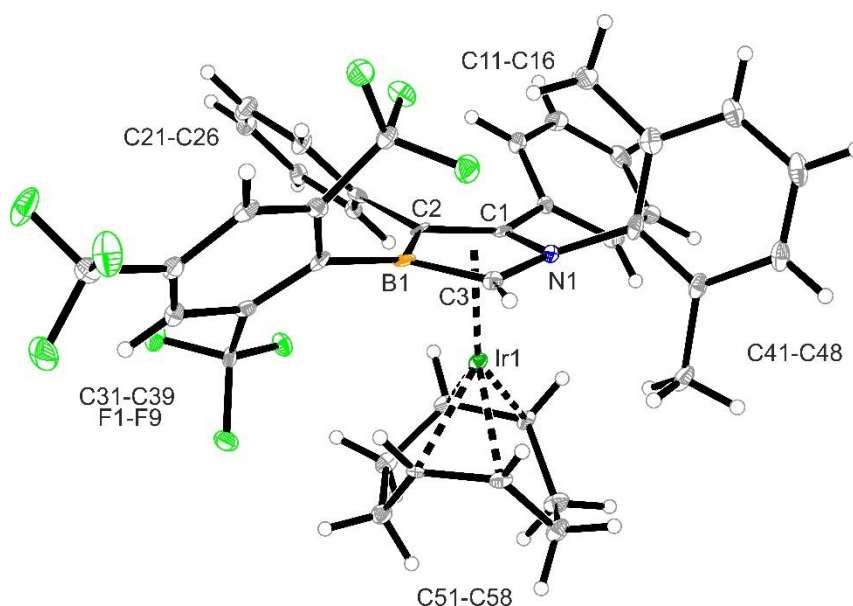
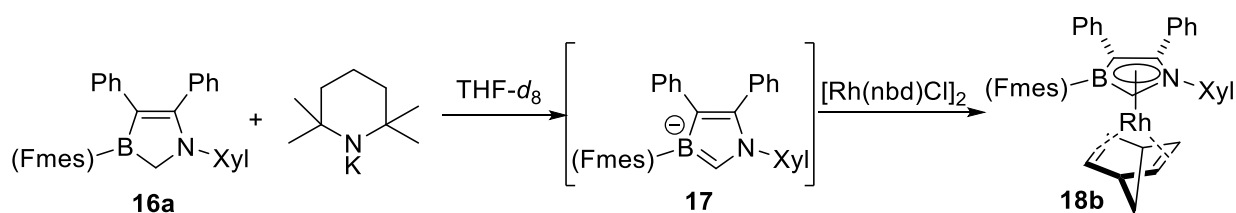


Figure S83. Crystal structure of compound **18a** (thermal ellipsoids at 30% probability).

Preparation of compound 18b



Scheme S15.

In a J. Young tube, KTMP (35.9 mg, 2 mmol, 2 equiv.) was added to a solution of azaborole **16a** (60.3 mg, 1 mmol, 1 equiv.) in THF- d_8 to give a deep brown solution. The resulting solution was stored at room temperature for 30 min. Then $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (23.0 mg, 0.5 mmol, 1 equiv.) was added and the resulting mixture was stored overnight. All the volatiles were removed in vacuo, the residue was dispersed in pentane (15 mL) and the solid was filtered off. The solution was concentrated to ca. 1 mL and stored in -35°C to finally give compound **18b** as yellow crystalline solid (34 mg, 42% yield).

Elemental Analysis for $\text{C}_{39}\text{H}_{30}\text{BNF}_9\text{Rh}$: calc. C (58.75 %), H (3.79 %), N (1.76 %); found: C (58.58 %), H (4.09 %), N (1.99 %)

^1H NMR (600 MHz, methylene chloride- d_2 , 183 K): δ = 8.16 (s, 1H, *m*-Fmes), 8.04 (s, 1H, *m'*-Fmes), 7.43 (m, 1H, *o*-Ph^N), 7.14 (d, $^3J_{\text{HH}}$ = 7.8 Hz, 1H, *o*-Xyl), [7.05 (m, 6H), 6.92 (m, 3H)](*p*-Xyl, *o'*-Ph^N, *m*-Ph^N, *m'*-Ph^N, *p*-Ph^N, *o*-Ph^B, *m*-Ph^B, *m'*-Ph^B, *p*-Ph^B), 6.70 (d, $^3J_{\text{HH}}$ = 7.6 Hz, 1H, *m'*-Xyl), 6.25 (m, 1H, *o'*-Ph^B), 4.28 (s, 1H, CH), [3.93, 3.33, 3.30, 3.17](each s, each 1H, CH=^{nbd}), [3.72, 3.42](each s, each 1H, CH^{nbd}), 3.47 (s, 3H, *o*-CH₃^{Xyl}), 1.60 (s, 3H, *o'*-CH₃^{Xyl}), [1.07 (AB, $^2J_{\text{HH}}$ = 8.3 Hz, 1H), 1.00 (AB, $^2J_{\text{HH}}$ = 8.1 Hz, 1H)](CH₂^{nbd}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 183 K)[selected resonances]: δ = 143.2 (br, *i*-Fmes), [139.6, 130.15](*i*-Ph^N, *i*-Ph^B), 136.9 (*o'*-Xyl), 134.6 (*o*-Xyl), 133.2 (*i*-Xyl), [132.1, 129.0, 127.47,

127.35, 126.5, 126.32, 126.25, 123.8][*p*-Xyl, *o*'-Ph^N, *m*-Ph^N, *m*'-Ph^N, *p*-Ph^N, *o*-Ph^B, *m*-Ph^B, *m*'-Ph^B, *p*-Ph^B] 130.05 (*o*-Ph^N), 128.22 (*m*'-Xyl), 128.16 (*m*-Xyl, *o*'-Ph^B), 127.41 (br, *m*-Fmes), 125.2 (br, *m*'-Fmes), , 117.7 (NC=), 111.6 (br, BC=), 92.7 (br, CH), 57.8 (CH₂^{nb}), [57.0, 51.2, 44.8, 38.9](CH=^{nb}), [49.0, 48.2](CH^{nb}), 18.6 (*o*-CH₃^{Xyl}), 17.0 (*o*'-CH₃^{Xyl}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 17.2 (ν_{1/2} ≈ 240 Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 263 K): δ = [-52.2, -53.6](each s, each 1F, *o*-CF₃), -63.3 (s, 1F, *p*-CF₃).

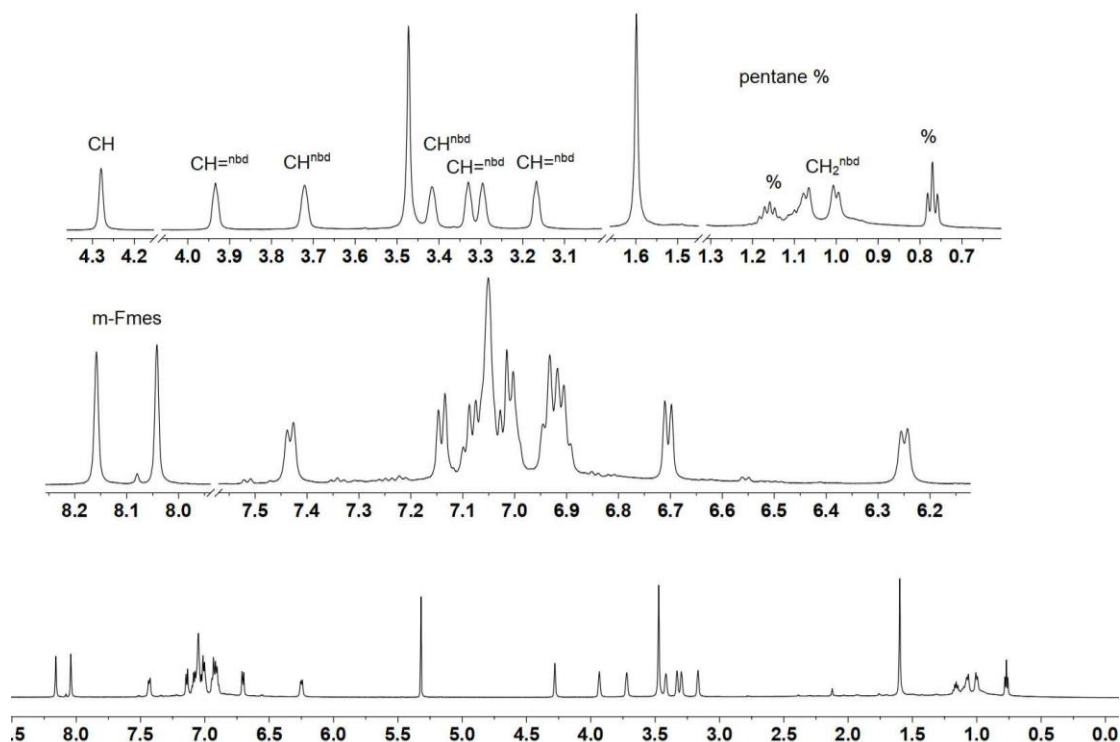


Figure S84. ¹H NMR (600 MHz, methylene chloride-*d*₂, 183 K) spectrum of compound **18b**.

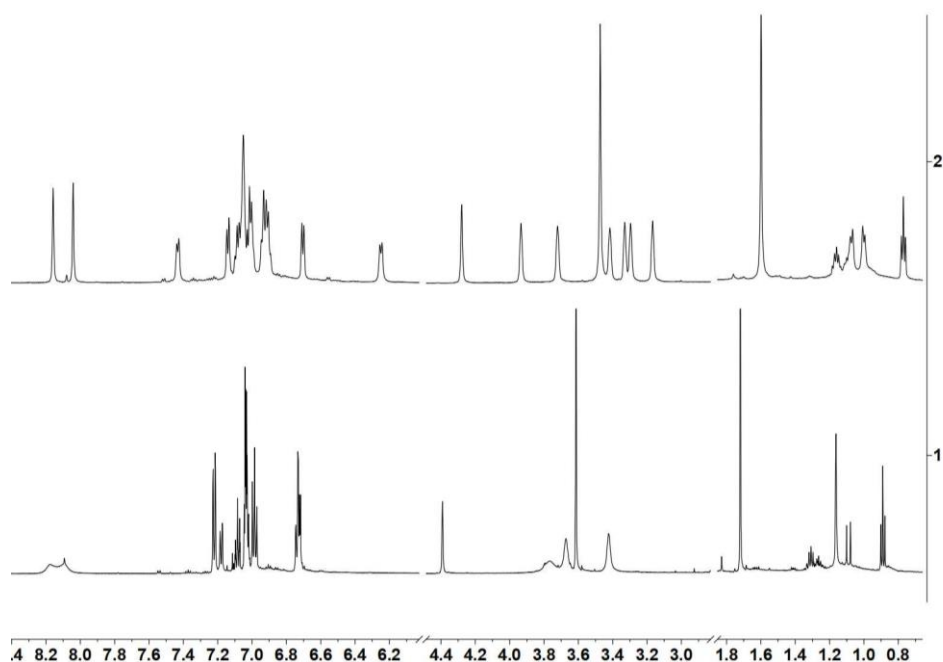


Figure S85. ¹H NMR (600 MHz, methylene chloride-*d*₂) spectra of compound **18b**: (1) at 299 K, (2) at 183 K.

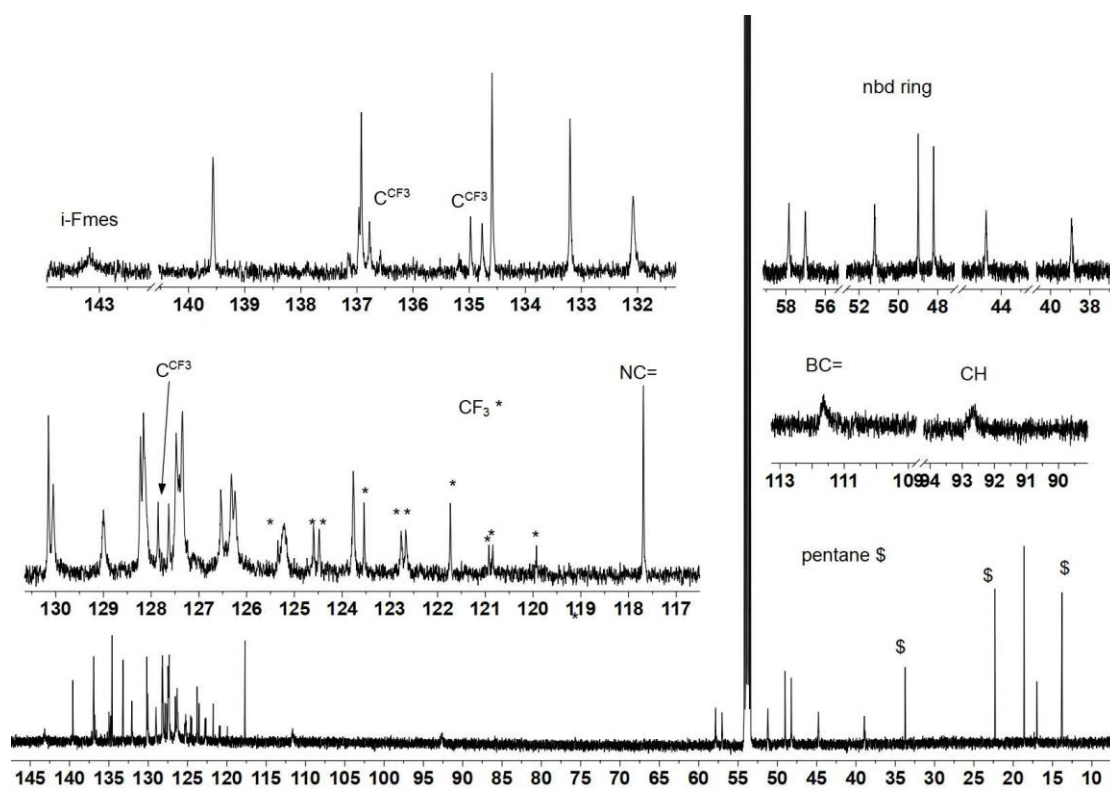


Figure S86. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 183 K) spectrum of compound **18b**.

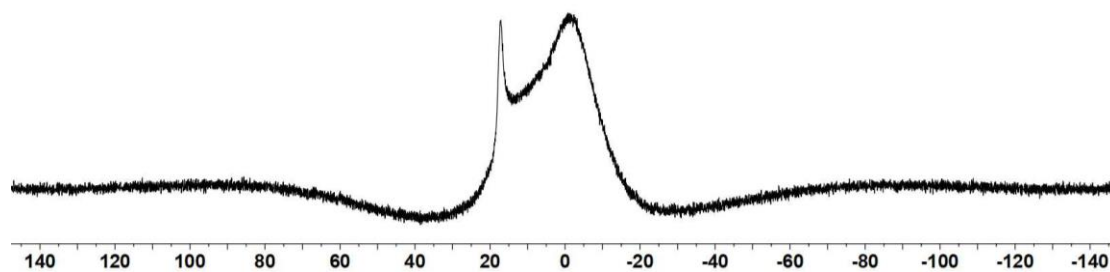


Figure S87. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **18b**.

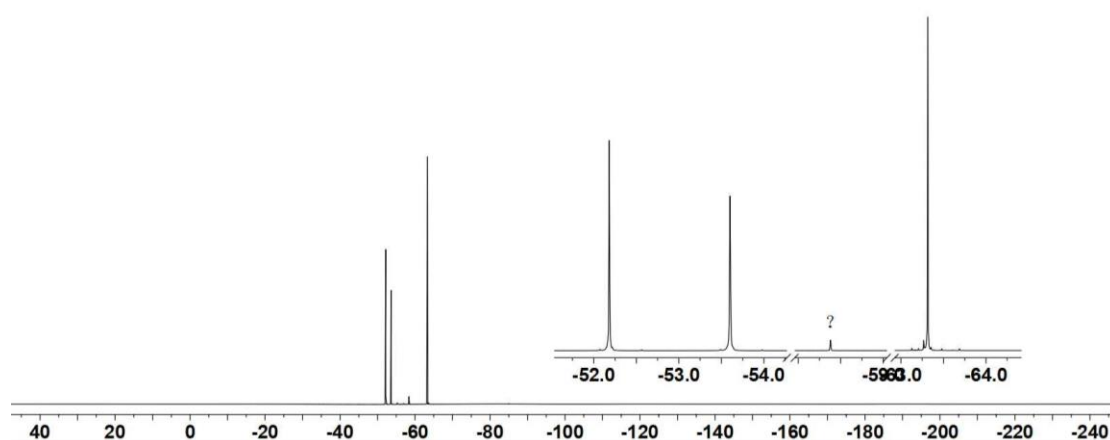


Figure S88. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 263 K) spectrum of compound **18b**.

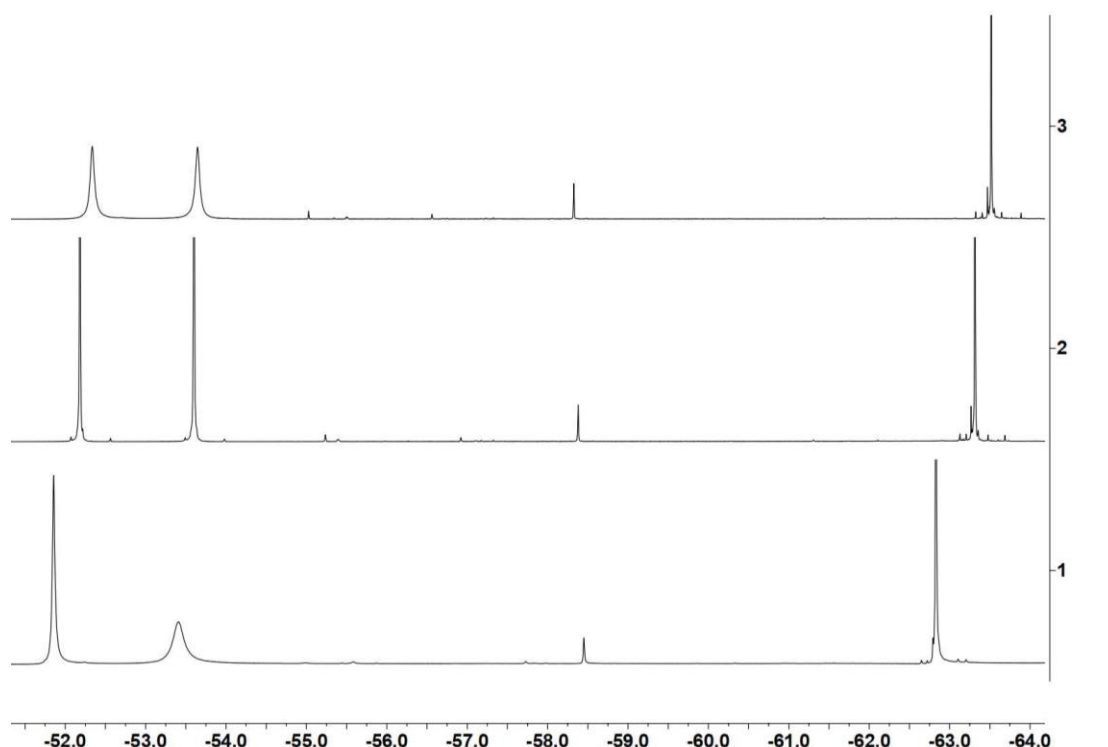


Figure S89. ^{19}F NMR (564 MHz, methylene chloride- d_2) spectra of compound **18b** (1) at 183 K, (2) at 263 K, 3) at 299 K.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of **18b** in pentane at room temperature.

X-ray crystal structure analysis of compound 18b (erk9633): A yellow needle-like specimen of $\text{C}_{39}\text{H}_{30}\text{BF}_9\text{NRh}$, approximate dimensions 0.043 mm x 0.084 mm x 0.261 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 622 frames were collected. The total exposure time was 3.97 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 133048 reflections to a maximum θ angle of 25.35° (0.83 \AA resolution), of which 12094 were independent (average redundancy 11.001, completeness = 99.9%, $R_{\text{int}} = 13.33\%$, $R_{\text{sig}} = 5.20\%$) and 9726 (80.42%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 25.8026(13) \text{ \AA}$, $b = 10.3993(5) \text{ \AA}$, $c = 26.3164(13) \text{ \AA}$, $\beta = 110.600(2)^\circ$, volume = $6609.9(6) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9916 reflections above $20 \sigma(I)$ with $4.737^\circ < 2\theta < 52.83^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.939. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8590 and 0.9750. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with $Z = 8$ for the formula unit, $\text{C}_{39}\text{H}_{30}\text{BF}_9\text{NRh}$. The final anisotropic full-matrix least-squares refinement on F^2 with 923 variables converged at $R1 = 4.32\%$, for the observed data and $wR2 = 8.82\%$ for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was $0.670 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.683 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.092 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.602 g/cm^3 and $F(000)$, 3216 e^- . CCDC number: 2007642.

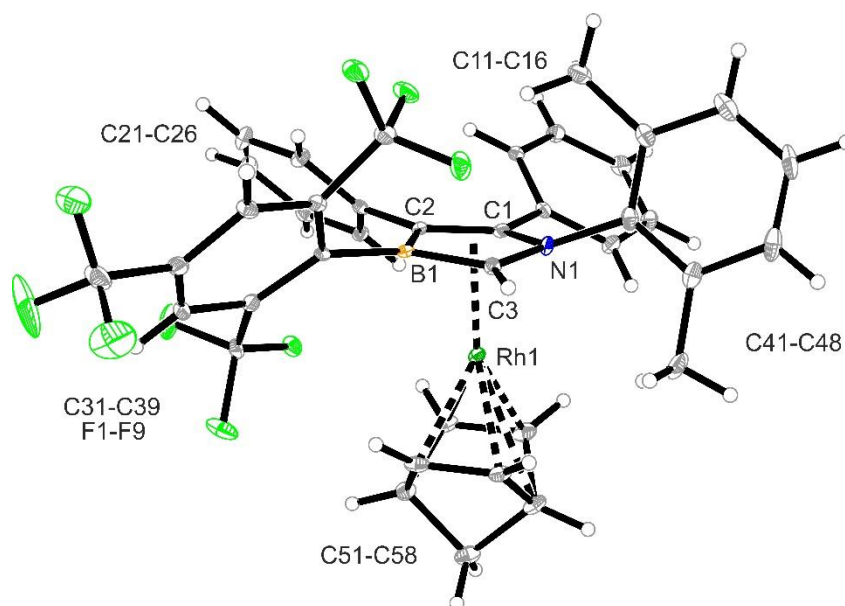
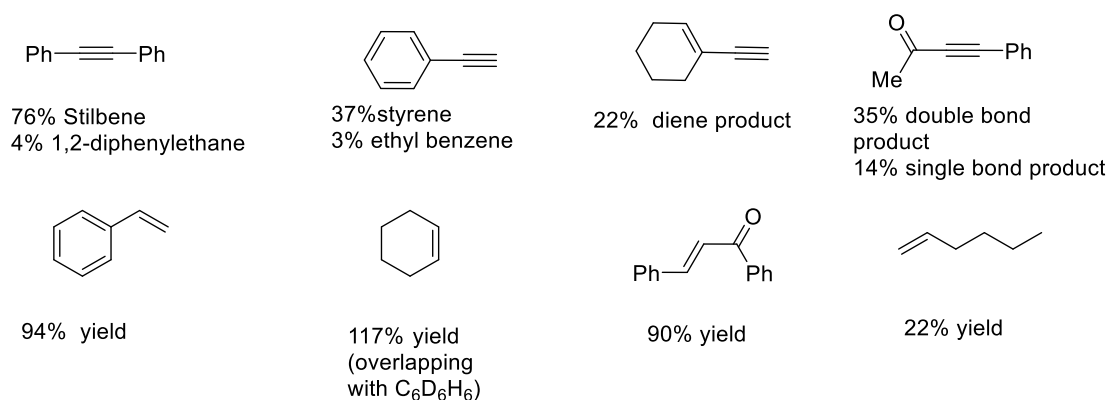


Figure S90. Crystal structure of compound **18b** (thermal ellipsoids at 30% probability).

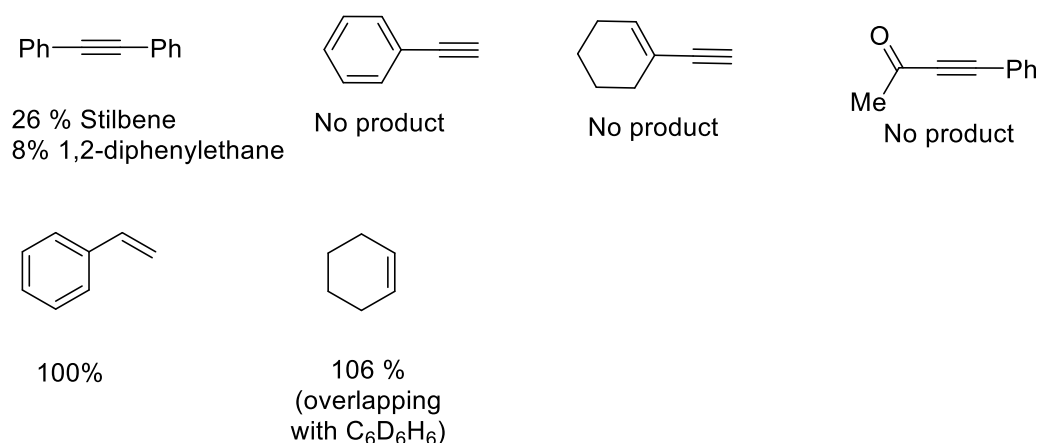
Catalytic hydrogenation of alkenes and alkynes using complexes **18a,b**

General procedure:

In a glovebox with an argon atmosphere, complex **18a** or **18b** (0.005 mmol, 1 mol%) and the respective unsaturated substrate (0.5 mmol), were mixed in C₆D₆ (1 mL). Then the reaction Schlenk tube was degassed and H₂ (1.0 bar, r.t.) was introduced and stirred overnight at room temperature. Subsequently, Ferrocene (18.6 mg, 0.1 mmol, 0.2 equiv.) was added as internal standard and the resulting mixture was transferred to an NMR tube and monitored by ¹H NMR. The conversion was determined by integration of a suitable ¹H NMR resonance relative to ferrocene.

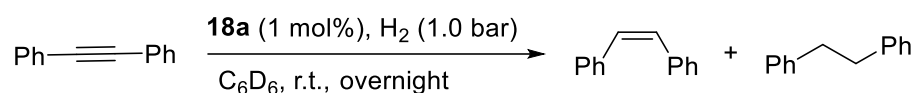


Scheme S16. Overview of catalytic hydrogenation of various substrates with complex **18a**.



Scheme S17. Overview of catalytic hydrogenation of various substrates with complex **18b**.

Experiment 1: Hydrogenation of 1,2-diphenylacetylene in the presence of the Ir complex **18a**.



Scheme S18.

Following the general procedure, the conversion to stilbene and 1,2-diphenylethane were 76% and 4% based on ¹H NMR relative to ferrocene, respectively.

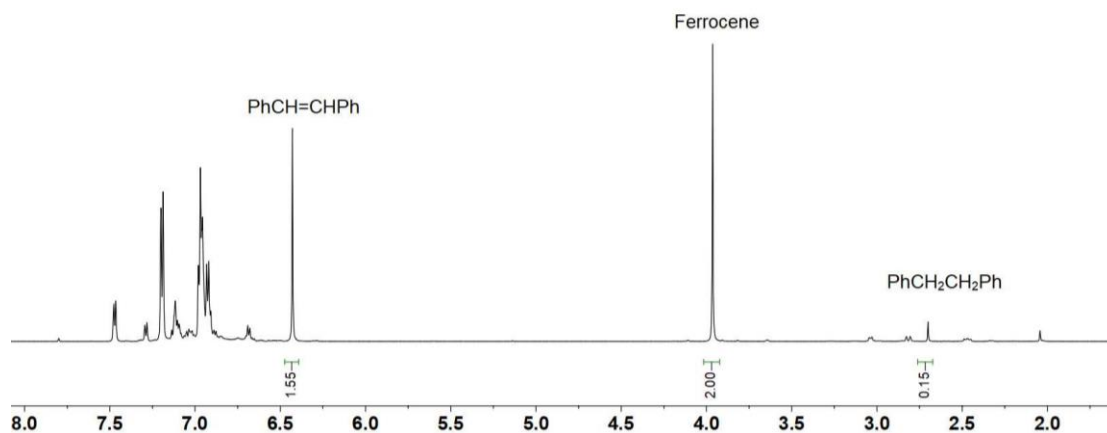
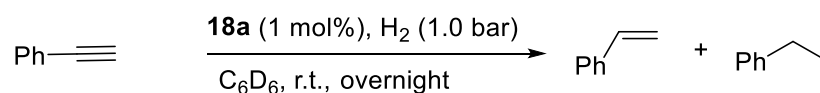


Figure S91. ¹H NMR (600 MHz, C₆D₆, 299 K) spectra of the obtained reaction mixture.

Experiment 2: Hydrogenation of phenylacetylene in the presence of the Ir complex **18a**.



Scheme S19.

Following the general procedure, the conversion to styrene and ethylbenzene were 35% and 3% based on ¹H NMR relative to ferrocene, respectively.

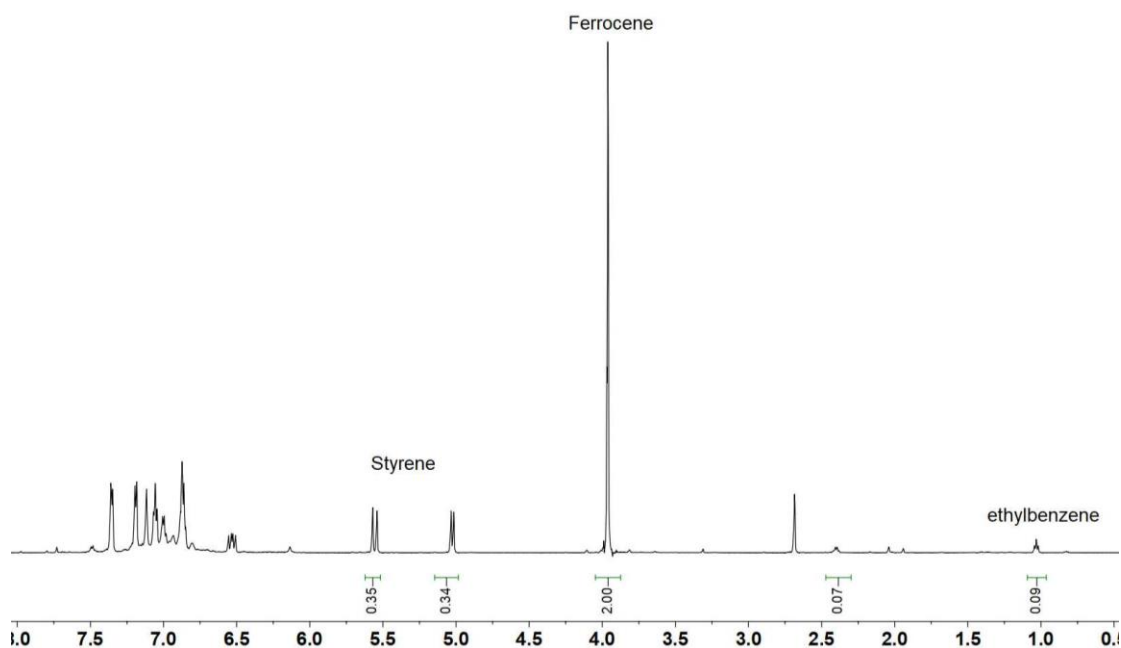
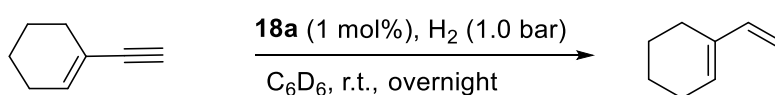


Figure S92. ¹H NMR (600 MHz, C₆D₆, 299 K) spectra of the obtained reaction mixture.

Experiment 3: Hydrogenation of 1-ethynylcyclohex-1-ene in the presence of the Ir complex **18a**.



Scheme S20.

Following the general procedure, the conversion to 1-vinylcyclohex-1-ene was 22% based on ¹H NMR relative to ferrocene.

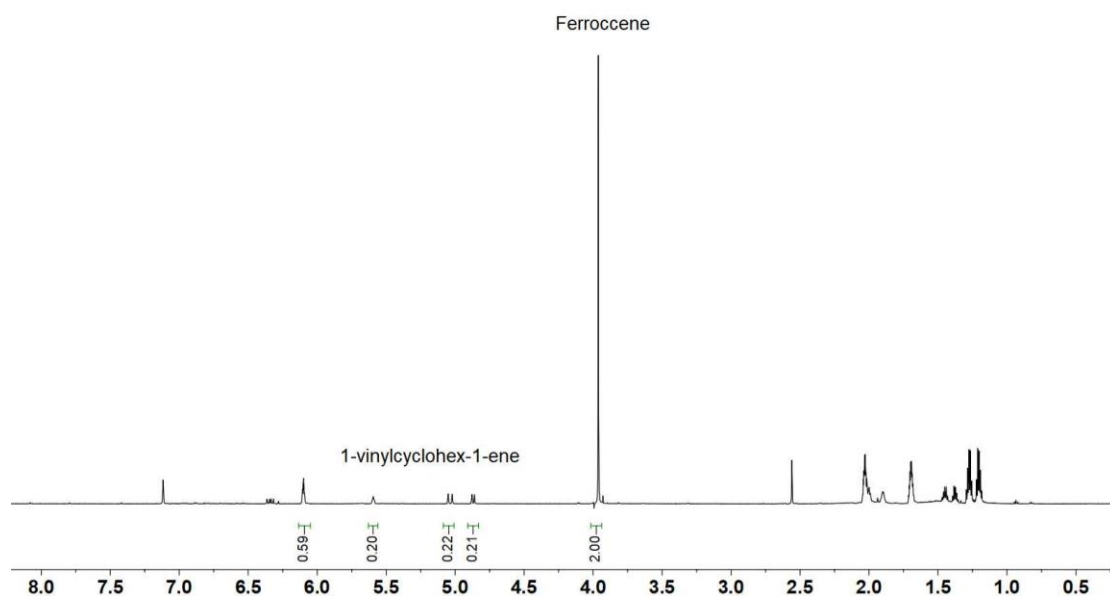
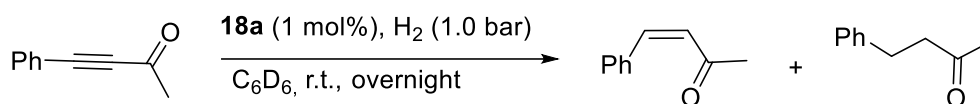


Figure S93. ¹H NMR (600 MHz, C₆D₆, 299 K) spectra of the obtained reaction mixture.

Experiment 4: Hydrogenation of 4-phenylbut-3-yn-2-one in the presence of the Ir complex **18a**.



Scheme S21.

Following the general procedure, the conversion to cis-4-phenylbut-3-yn-2-one ($-\text{CH}=\text{CH}-$ $^3J_{\text{HH}} = 12.75$ Hz) and 4-phenylbutan-2-one were 35% and 14% based on ^1H NMR relative to ferrocene, respectively.

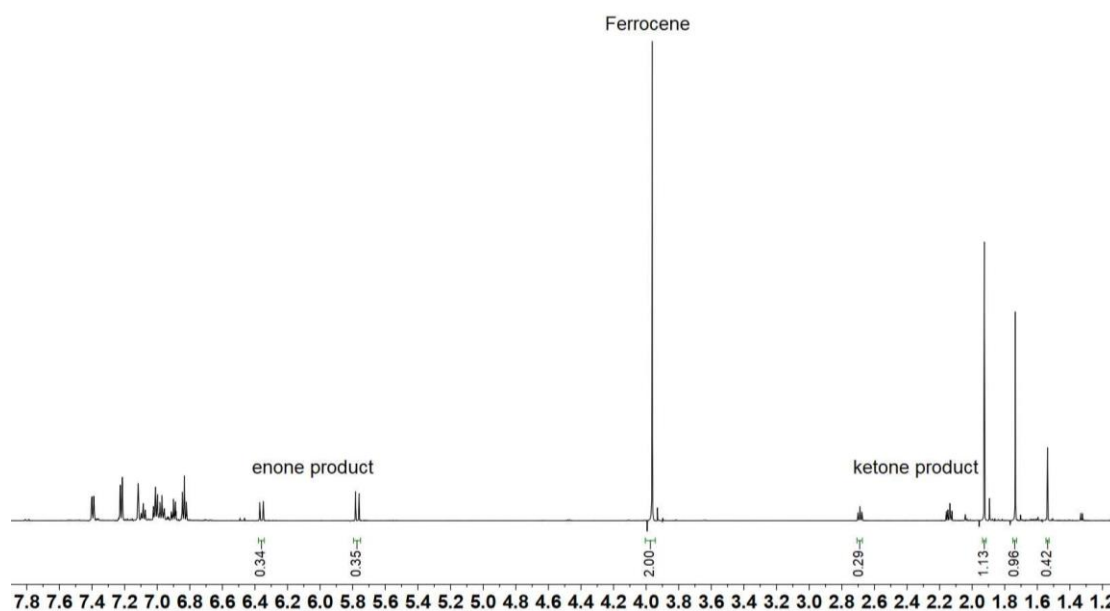
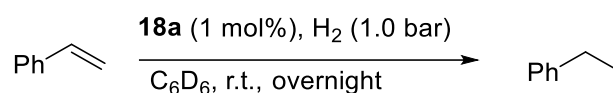


Figure S94. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 5: Hydrogenation of styrene in the presence of the Ir complex **18a**.



Scheme S22.

Following the general procedure, the conversion to ethylbenzene was 93% based on ^1H NMR relative to ferrocene.

[Comment: After the reaction, metal precipitate was observed.]

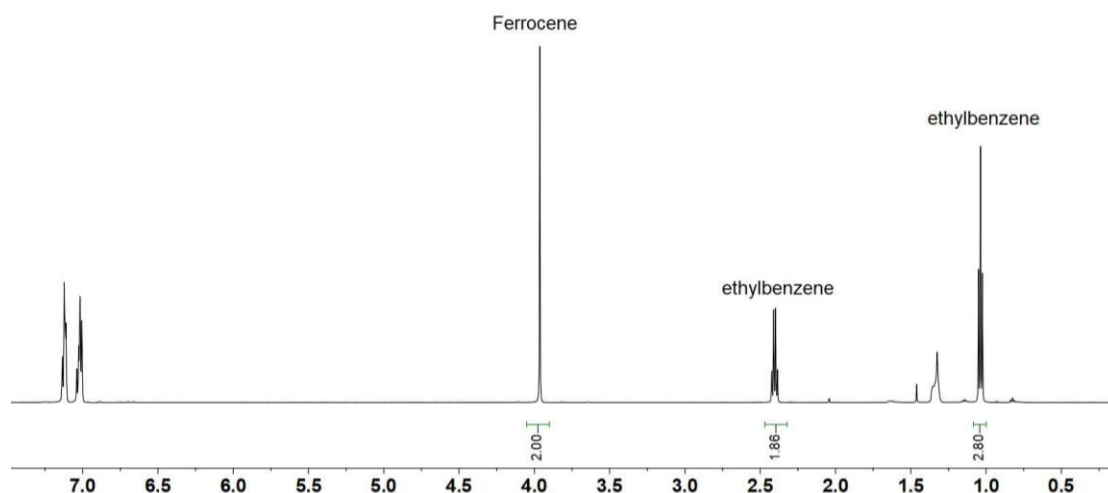
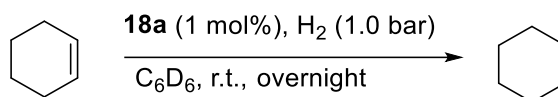


Figure S95. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 6: Hydrogenation of cyclohexene in the presence of the Ir complex **18a**.



Scheme S23.

Following the general procedure, the conversion to cyclohexane was 117% (overlapping with $\text{C}_6\text{H}_6\text{D}_6$) based on ^1H NMR relative to ferrocene.

[Comment: After the reaction, metal precipitate was observed.]

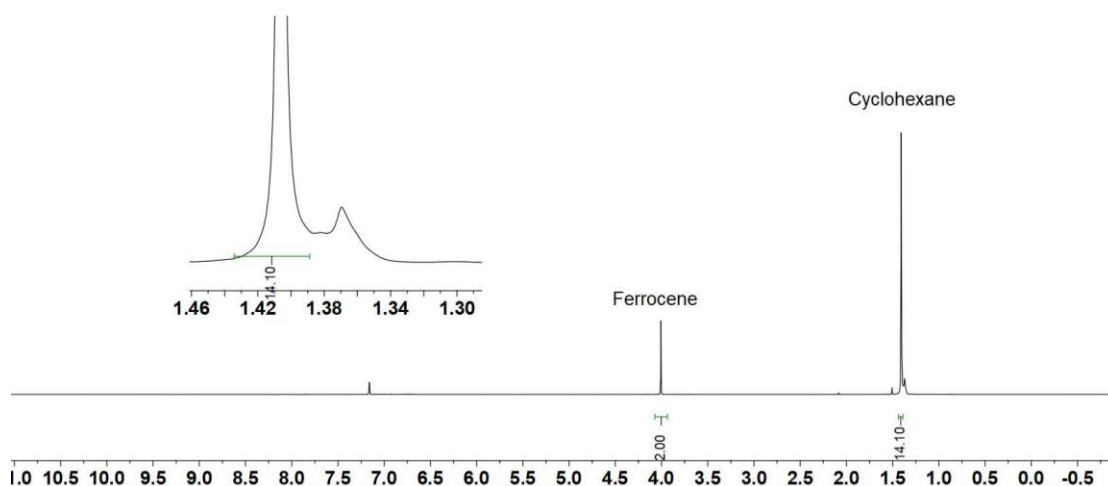
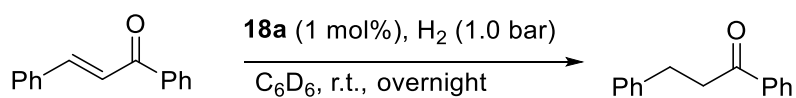


Figure S96. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 7: Hydrogenation of chalcone in the presence of the Ir complex **18a**.



Scheme S24.

Following the general procedure, the conversion to 1,3-diphenylpropan-1-one was 90% based on ^1H NMR relative to ferrocene.

[Comment: After the reaction, metal precipitate was observed.]

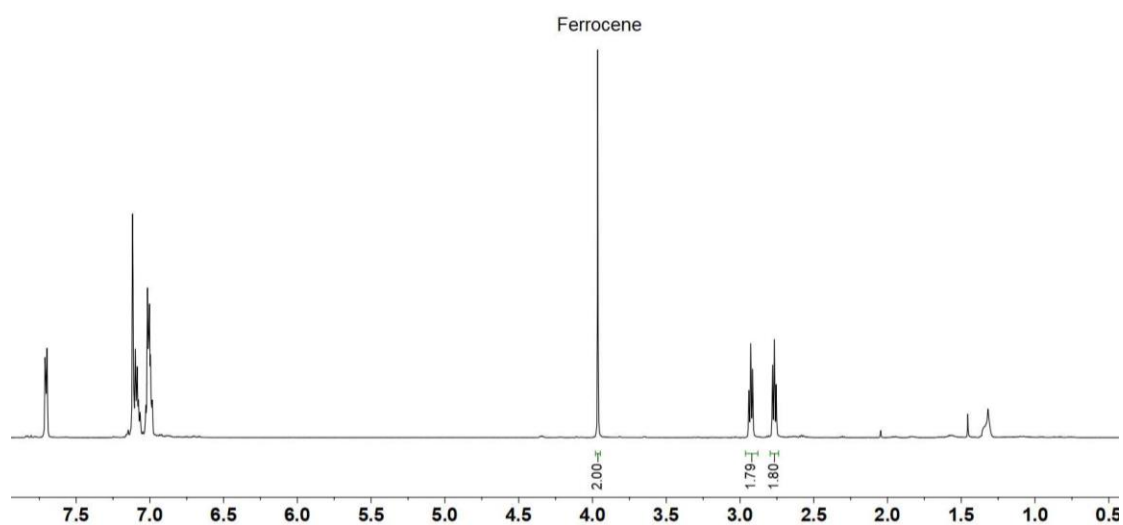
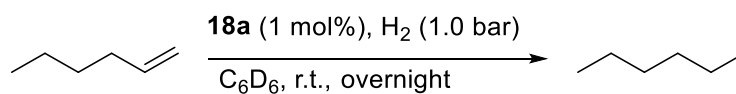


Figure S97. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 8: Hydrogenation of 1-hexene in the presence of the Ir complex **18a**.



Scheme S25.

Following the general procedure, the conversion to n-hexane was 22% based on ^1H NMR relative to ferrocene.

[Comment: After the reaction, metal precipitate was observed.]

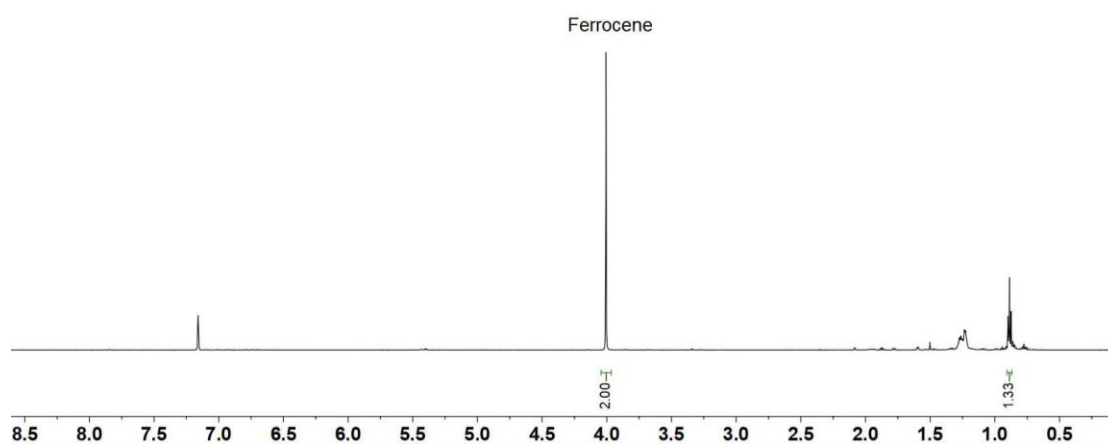
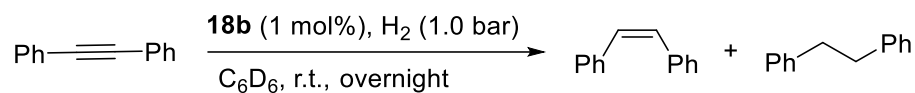


Figure S98. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 9: Hydrogenation of 1,2-diphenylacetylene in the presence of the Rh complex **18b**.



Scheme S26.

Following the general procedure, the conversion to stilbene and 1,2-diphenylethane were 27% and 8% based on ^1H NMR relative to ferrocene, respectively.

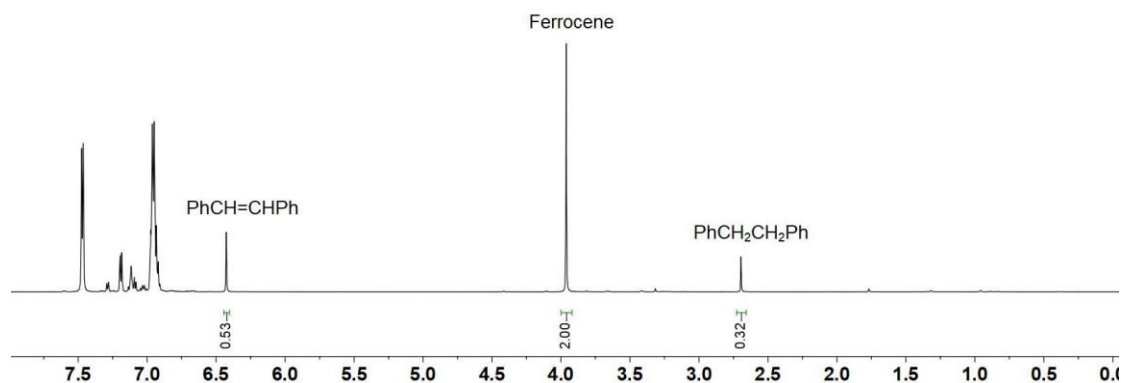
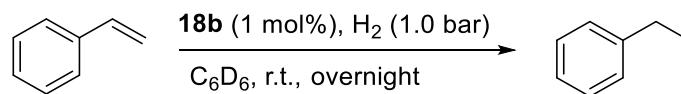


Figure S99. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 10: Hydrogenation of styrene in the presence of the Rh complex **18b**.



Scheme S27.

Following the general procedure, the conversion to ethylbenzene was quantitative based on ^1H NMR relative to ferrocene.

[Comment: After the reaction, a metal precipitate was observed.]

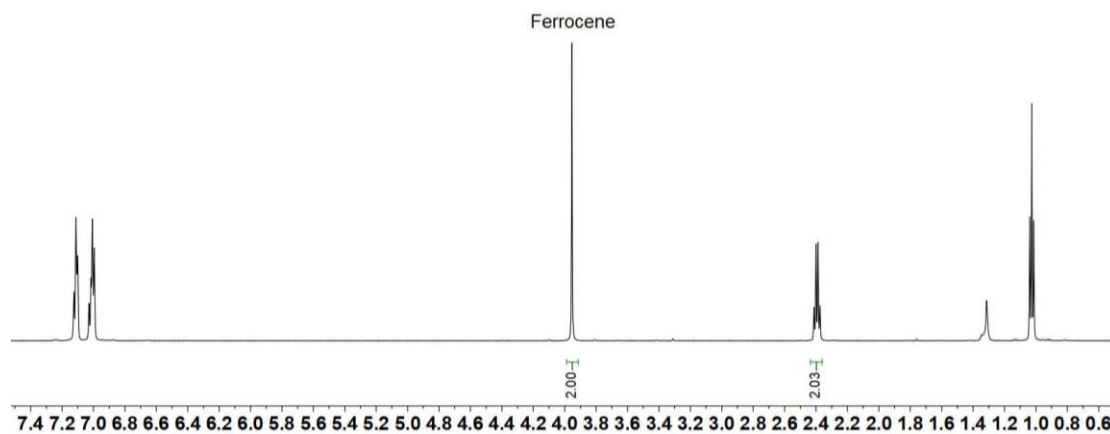
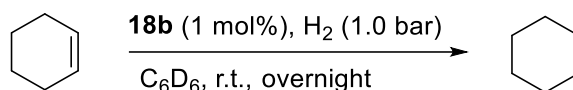


Figure S100. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Experiment 11: Hydrogenation of cyclohexene in the presence of the Rh complex **18b**.



Scheme S28.

Following the general procedure, the conversion to cyclohexane was quantitative based on 1H NMR relative to ferrocene.

[Comment: After the reaction, metal precipitate was observed.]

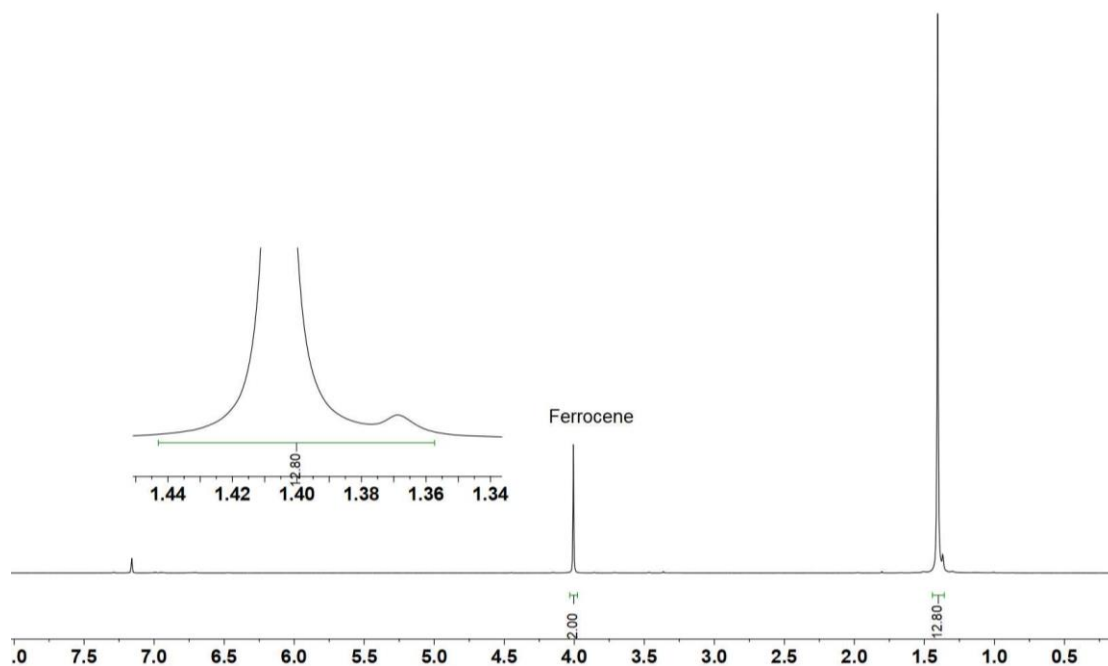
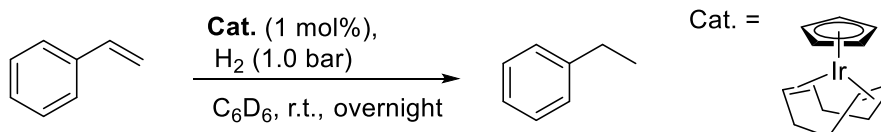


Figure S101. 1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Comparative experiment 1: Hydrogenation of cyclohexene in the presence of the Cplr(cod).



Scheme S29.

Following the general procedure, Cplr(cod) was used as the catalyst instead. No conversion was observed.

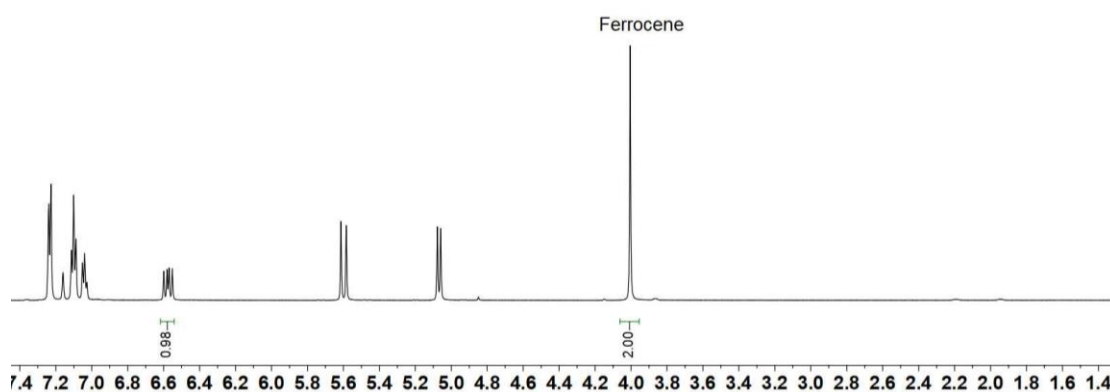
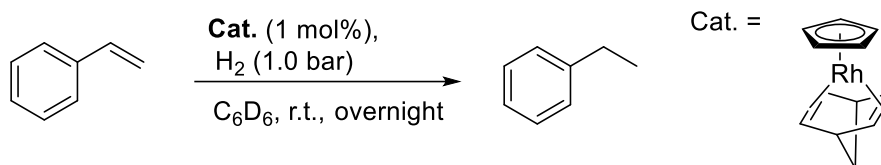


Figure S102. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Comparative experiment 2: Hydrogenation of cyclohexene in the presence of the $\text{CpRh}(\text{nbd})$.



Scheme S30.

Following the general procedure, $\text{CpRh}(\text{nbd})$ was used as the catalyst instead. No conversion was observed.

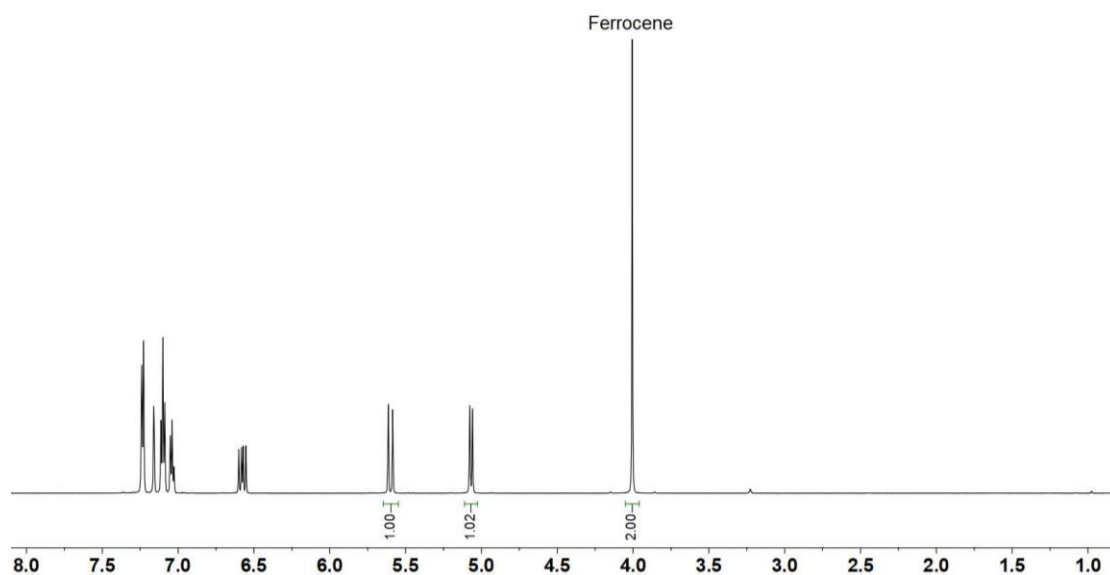
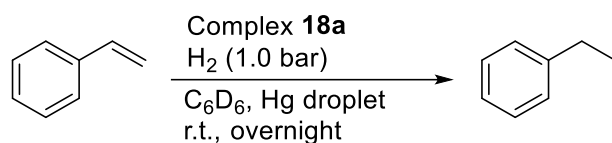


Figure S103. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of the obtained reaction mixture.

Mercury test with compound **18a**



Scheme S31.

In a glovebox with an argon atmosphere, a mixture of compound **18a** (4.5 mg, 0.005 mmol, 1 mol%) and styrene (52 mg, 0.5 mmol) was dissolved in C₆D₆ (1.0 mL). Then the obtained solution was transferred to a Schlenk tube. Then drops of Hg were added to the resulting mixture which was stirred vigorously for 30 min under argon atmosphere. After the mixture was degassed, it was stirred overnight at room temperature in a H₂ atmosphere (1.0 bar). A black metal precipitation was observed on the inside wall of the tube. Ferrocene (18.6 mg, 0.1 mmol, 0.2 equiv.) was added as internal standard. The obtained reaction mixture was characterized by ¹H NMR experiments: styrene was fully consumed and the conversion to ethylbenzene is determined by the integration relative to ferrocene (94%).

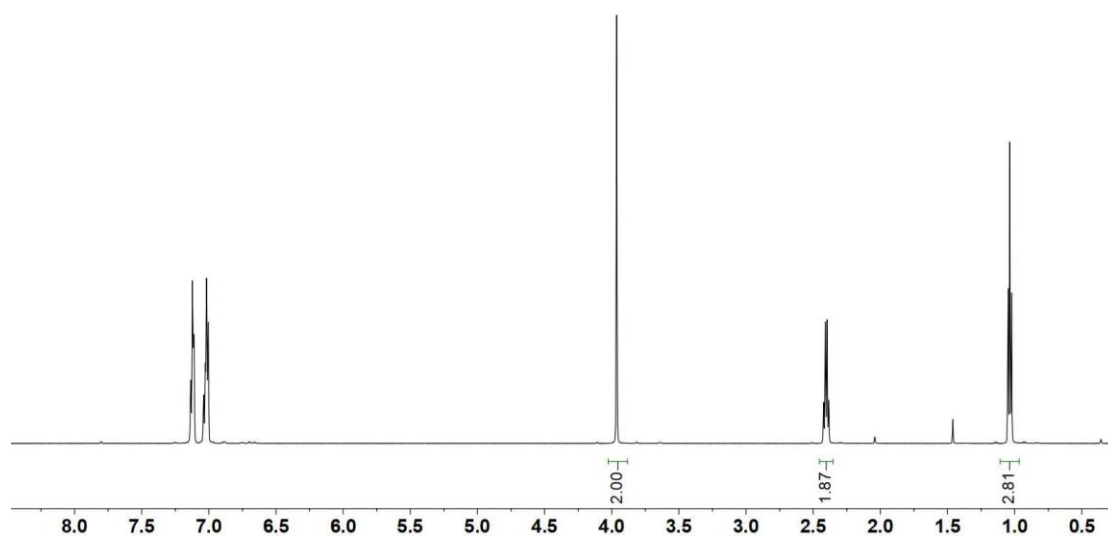


Figure S104. ¹H NMR (600 MHz, C₆D₆, 299 K) spectrum of the obtained mixture.

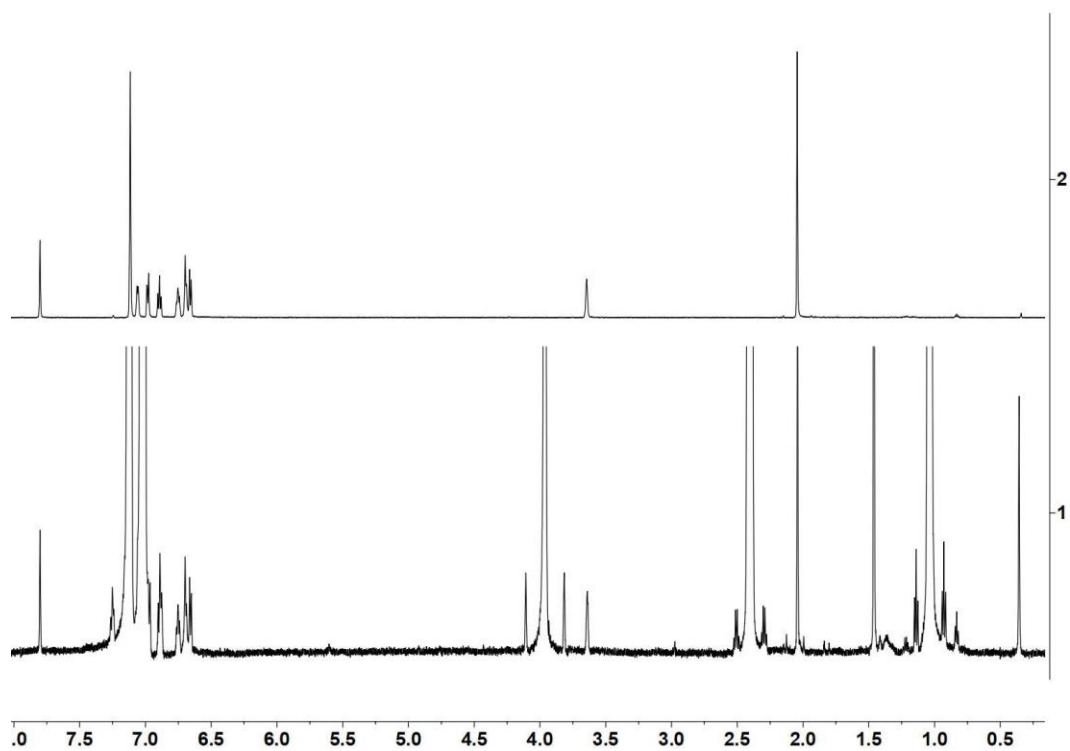


Figure S105. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of (1) the obtained mixture; (2) compound 16a.

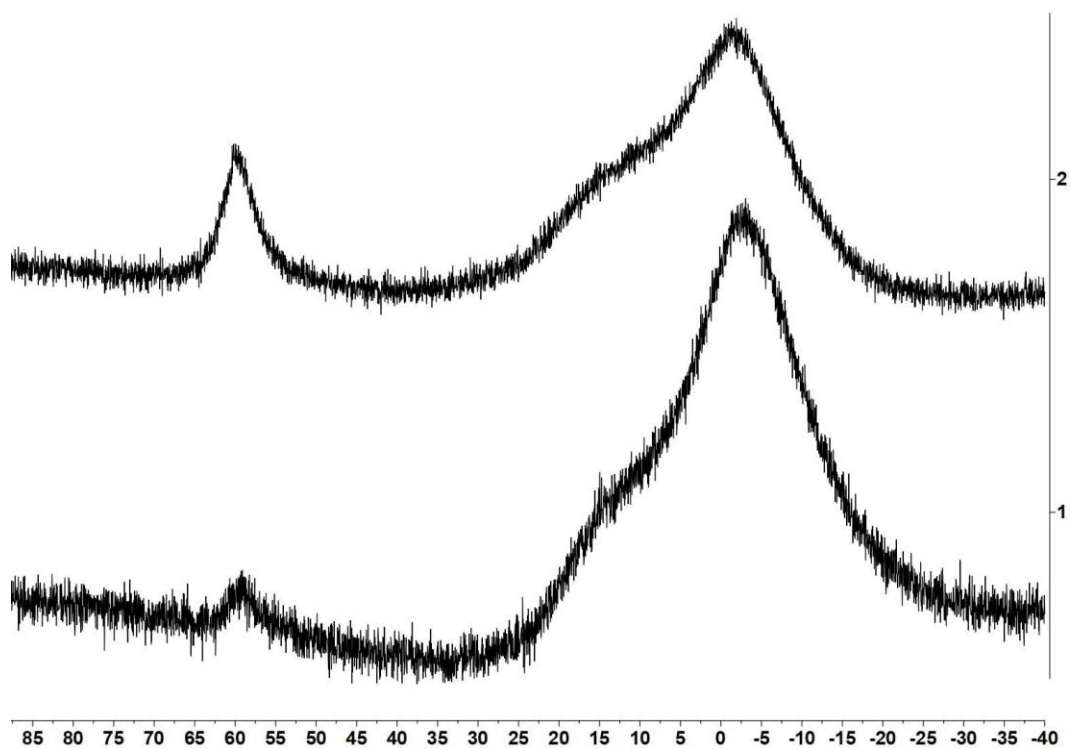


Figure S106. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6 , 299 K) spectra of (1) the obtained mixture; (2) compound 16a.

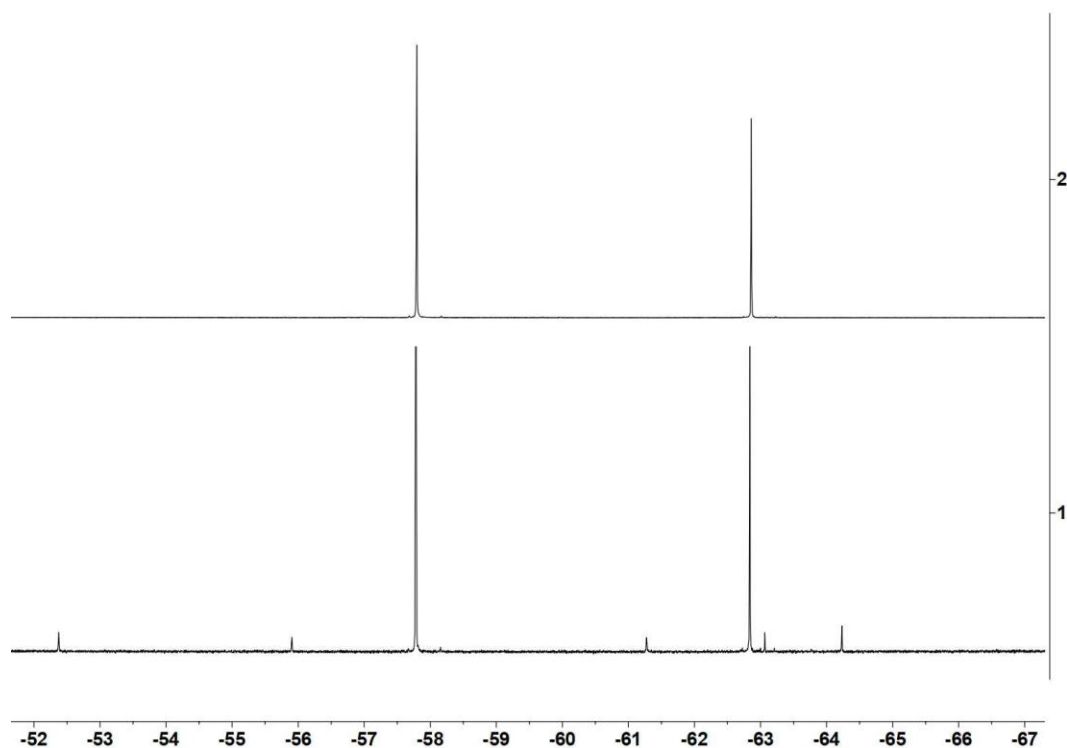
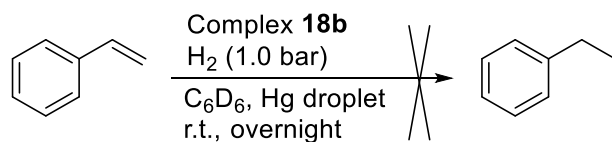


Figure S107. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectra of (1) the obtained mixture; (2) compound **16a**.

Mercury test with compound **18b**



Scheme S32.

In a glovebox with an argon atmosphere, a mixture of compound **18b** (4.0 mg, 0.005 mmol, 1 mol%) and styrene (52 mg, 0.5 mmol) was dissolved in C_6D_6 (1.0 mL). Then the obtained solution was transferred to a Schlenk tube. Then drops of Hg were added to the resulting mixture which was stirred vigorously for 30 min under argon atmosphere. After the mixture was degassed, it was stirred overnight at room temperature in a H_2 atmosphere (1.0 bar). Ferrocene (18.6 mg, 0.1 mmol, 0.2 equiv.) was added as internal standard. The obtained reaction mixture was characterized by ^1H NMR experiments: The sample contained unreacted styrene (92%) and trace amount (ca. 0.5 %) of ethylbenzene.

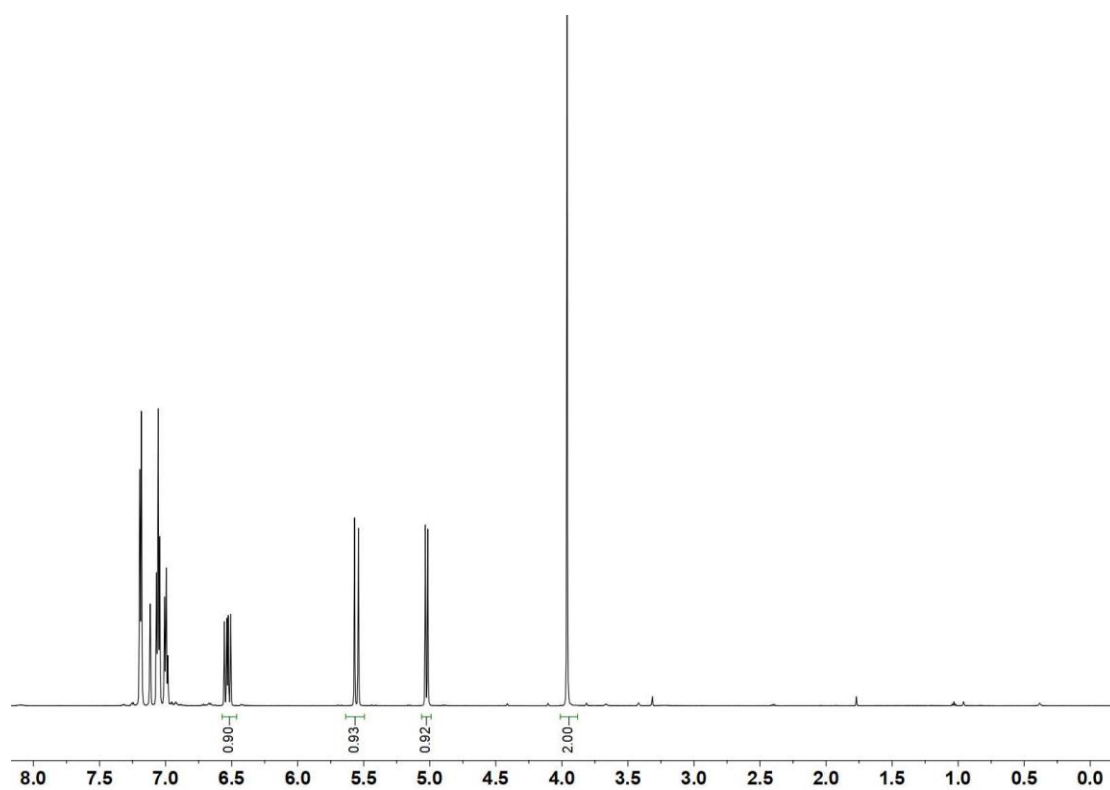


Figure S108. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectrum of the obtained mixture.

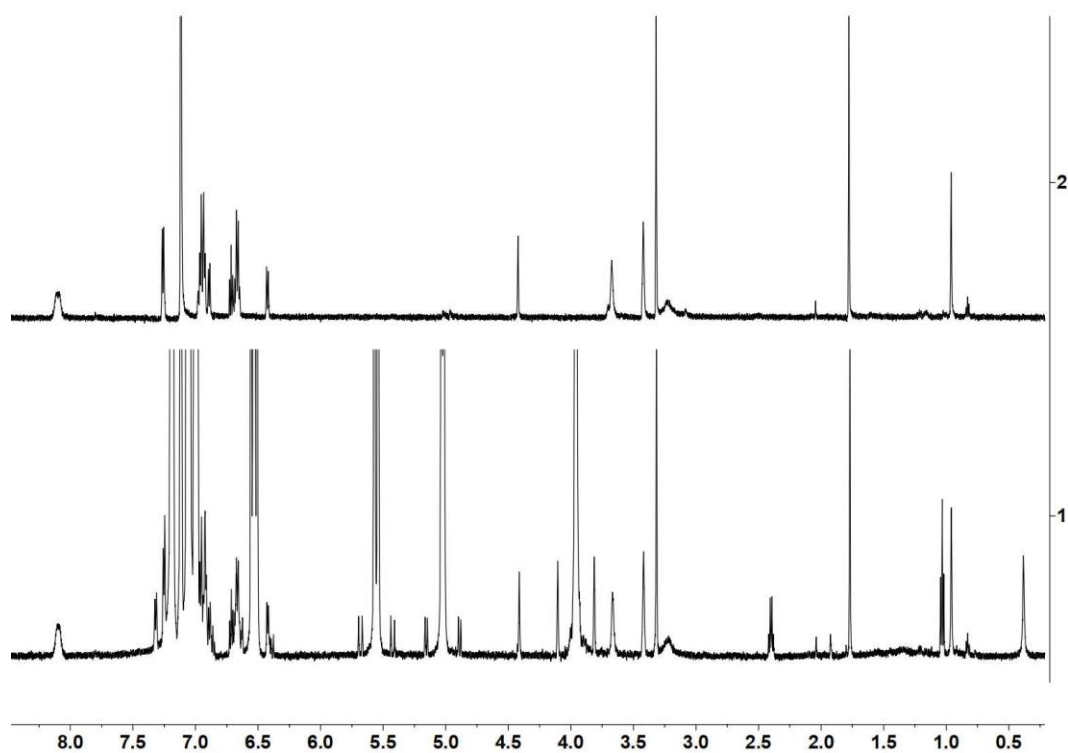


Figure S109. ^1H NMR (600 MHz, C_6D_6 , 299 K) spectra of (1) the obtained mixture; (2) compound **18b**.

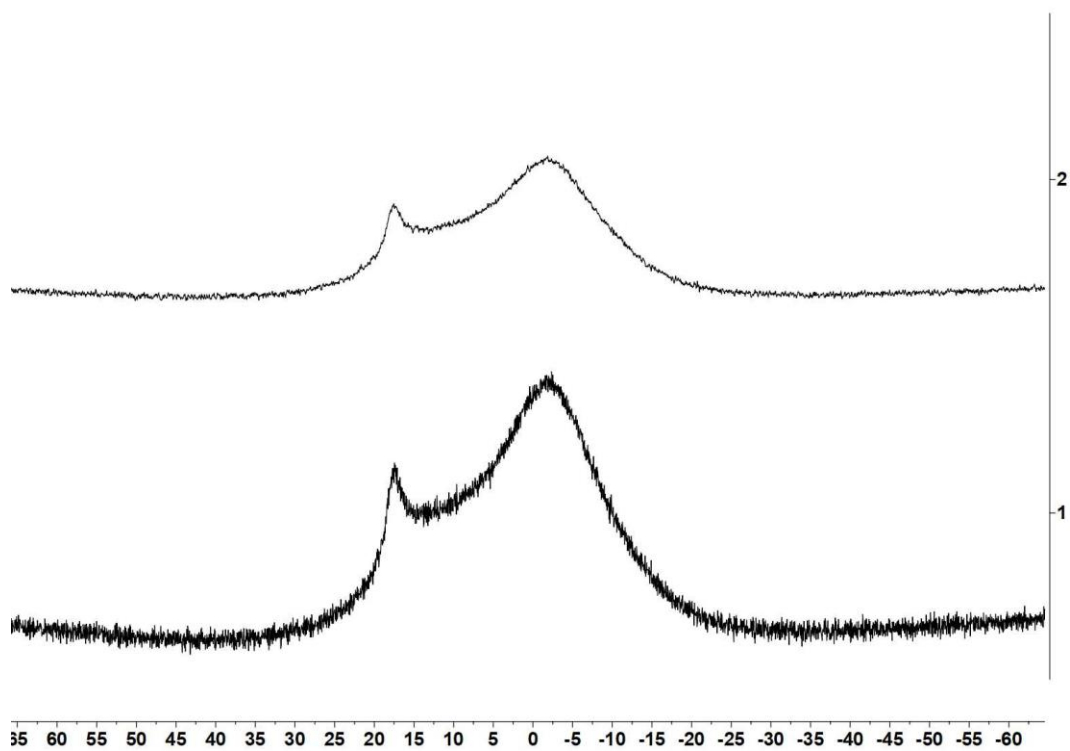


Figure S110. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6 , 299 K) spectra of (1) the obtained mixture; (2) compound **18b**.

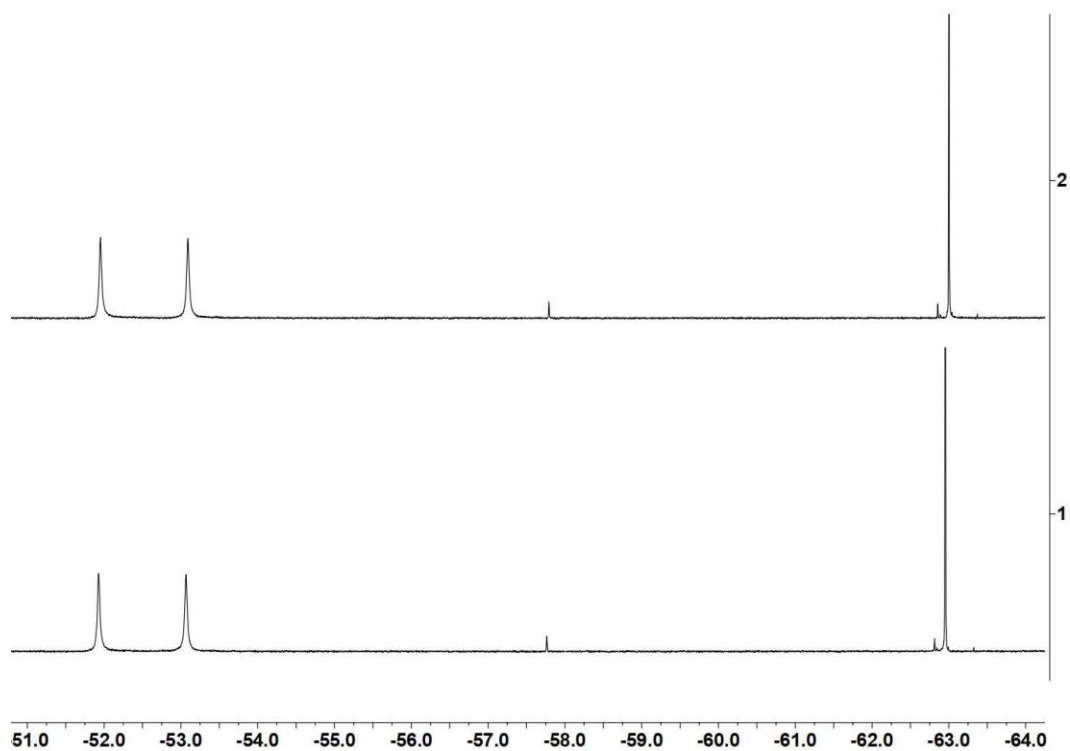
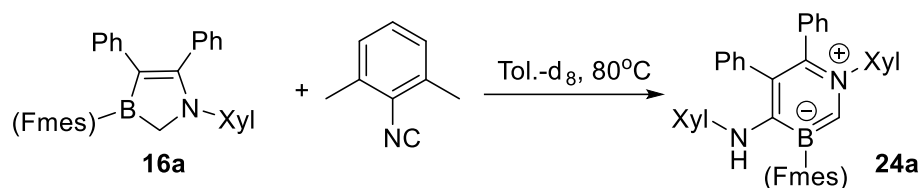


Figure S111. ^{19}F NMR (564 MHz, C_6D_6 , 299 K) spectra of (1) the obtained mixture; (2) compound **18b**.

Preparation of the azaborinine derivative 24a



Scheme S33.

At room temperature, the azaborole **16a** (60.3 mg, 0.1 mmol, 1 eq.) was added to a solution of 2,6-dimethylphenyl isocyanide (13.1 mg, 0.1 mmol, 1 eq.) in d_8 -toluene (1 mL) under an argon atmosphere in a J. Young tube. The resulting solution was stored at 80 °C for 14 days. Then all volatiles were removed in vacuo and the residue was dissolved in pentane (1 mL) and stored at -35 °C finally to give the compound **24a** as a yellow solid (57 mg, 78 % yield).

HRMS for $C_{41}H_{32}BN_2F_9^+$ $[M]^+$: calc. 734.2516; found: 734.2536.

1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 7.87 (s, 2H, *m*-Fmes), 7.08 (m, 2H, *o*-Ph⁽⁵⁾), 7.01 (m, 2H, *m*-Ph⁽⁵⁾), 6.97 (m, 3H, *o*-Ph⁽⁶⁾, *p*-Xyl⁽¹⁾), 6.93 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-Ph⁽⁵⁾), 6.90 (m, 3H, *p*-Ph⁽⁶⁾, *m*-Xyl⁽¹⁾), 6.87 (m, 2H, *m*-Ph⁽⁶⁾), 6.68 (s, 1H, C(2)H), 6.61 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-Xyl⁽⁴⁾), 6.54 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *m*-Xyl⁽⁴⁾), 5.38 (s, 1H, NH), 2.15 (s, 6H, *o*-CH₃^{Xyl(1)}), 2.02 (s, 6H, *o*-CH₃^{Xyl(4)}).

$^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 162.9 (br, C(4)), 149.0 (br, *i*-Fmes), 146.2 (*i*-Xyl⁽¹⁾), 140.2 (*i*-Xyl⁽⁴⁾), 138.6(C(6)), 138.3 (*i*-Ph⁽⁵⁾), 138.1 (br, C(2)H), 136.6 (*i*-Ph⁽⁶⁾, *o*-Xyl⁽⁴⁾), 135.6 (q, $^2J_{FC}$ = 29.1 Hz, *o*-Fmes), 134.2 (*o*-Xyl⁽¹⁾), 131.8 (*o*-Ph⁽⁵⁾), 130.4 (*o*-Ph⁽⁶⁾), 129.1 (q, $^2J_{FC}$ = 33.6 Hz, *p*-Fmes), 128.2 (*m*-Ph⁽⁵⁾), 128.1 (*m*-Xyl⁽¹⁾), 128.0 (*p*-Xyl⁽¹⁾), 127.9 (*m*-Xyl⁽⁴⁾), 127.4 (*p*-Ph⁽⁶⁾), 127.03 (br, C(5)), 126.95 (*m*-Ph⁽⁶⁾), 126.7 (*p*-Ph⁽⁵⁾), 126.0 (*p*-Xyl⁽⁴⁾), 124.9 (*m*-Fmes), 124.4 (q, $^1J_{FC}$ = 275.4 Hz, *o*-CF₃), 124.4 (q, $^1J_{FC}$ = 275.4 Hz, *o*-CF₃), 123.9 (q, $^1J_{FC}$ = 271.7 Hz, *p*-CF₃), 18.8 (q, J = 2.8 Hz, *o*-CH₃^{Xyl(1)}), 17.8 (*o*-CH₃^{Xyl(1)}).

$^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 26.2 ($\nu_{1/2}$ \approx 350 Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -57.1 (br, 2F, *o*-CF₃), -63.5 (s, 1F, *p*-CF₃).

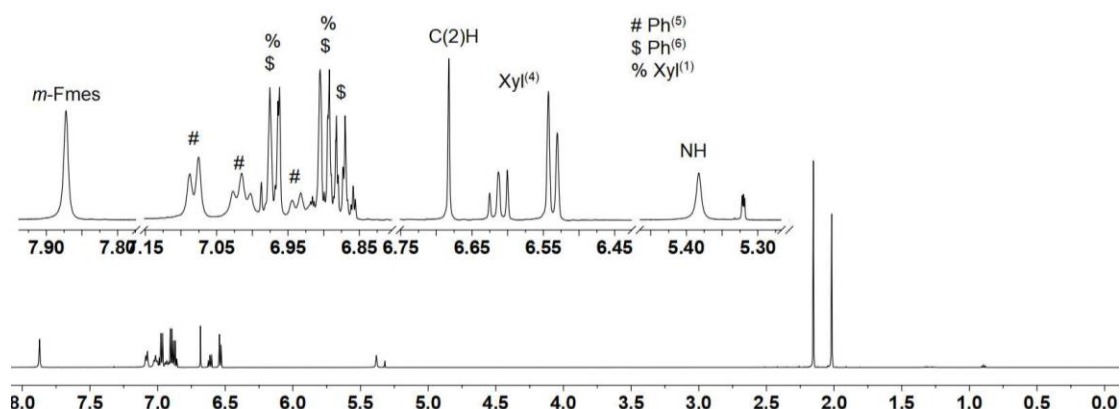


Figure S112. 1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24a**.

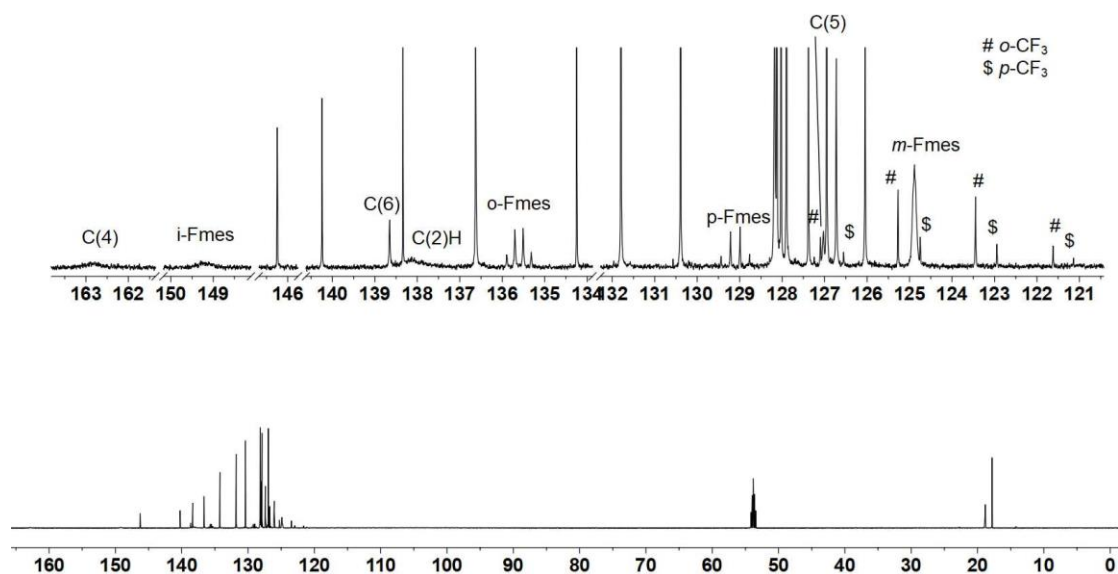


Figure S113. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24a**.

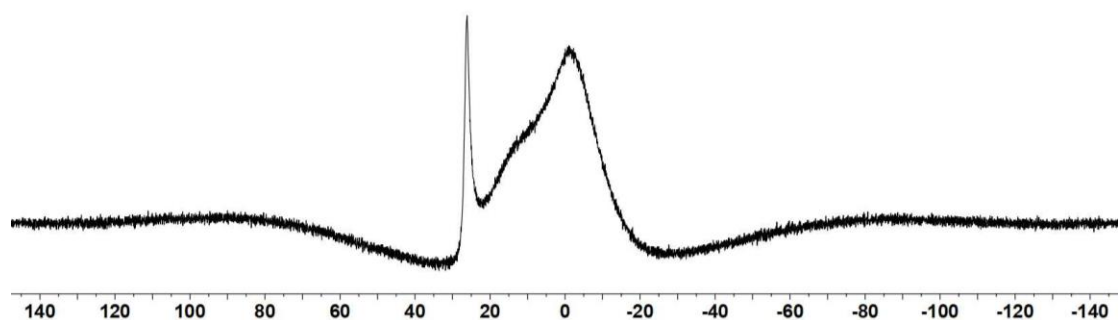


Figure S114. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24a**.

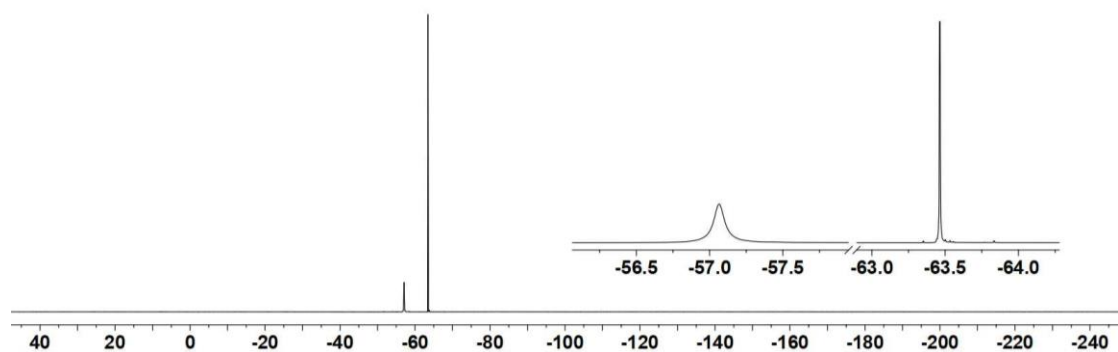


Figure S115. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24a**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **24a** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 24a (erk9501): A colorless plate-like specimen of $\text{C}_{41}\text{H}_{32}\text{BF}_9\text{N}_2$, approximate dimensions 0.030 mm x 0.130 mm x 0.160 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using

a monoclinic unit cell yielded a total of 12024 reflections to a maximum θ angle of 25.00° (0.84 \AA resolution), of which 6305 were independent (average redundancy 1.907, completeness = 98.9%, $R_{\text{int}} = 5.91\%$, $R_{\text{sig}} = 6.29\%$) and 4455 (70.66%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 9.3001(3) \text{ \AA}$, $b = 27.1592(10) \text{ \AA}$, $c = 14.5554(5) \text{ \AA}$, $\beta = 99.578(2)^\circ$, volume = $3625.2(2) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of reflections above $20 \sigma(I)$. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9830 and 0.9970. 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, $C_{41}H_{32}BF_9N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 514 variables converged at $R1 = 7.97\%$, for the observed data and $wR2 = 22.84\%$ for all data. The goodness-of-fit was 1.062. The largest peak in the final difference electron density synthesis was $0.389 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.262 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.064 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.346 g/cm^3 and $F(000)$, 1512 e^- . The hydrogen at N1 atom was refined freely. CCDC number: 2041296.

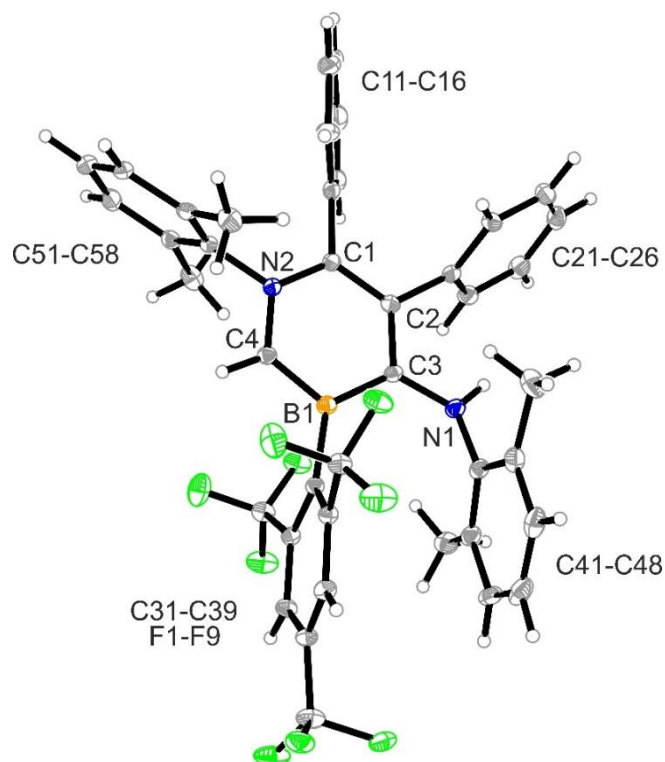
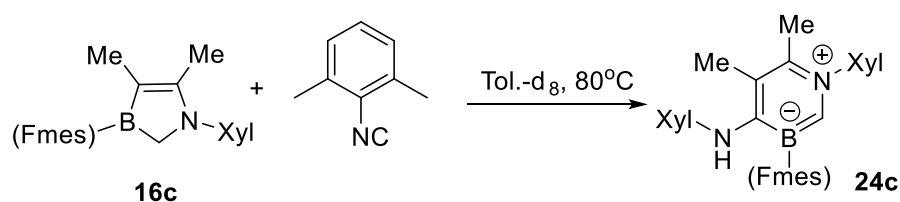


Figure S116. Crystal structure of compound **24a** (thermal ellipsoids are set at 15% probability).

Preparation of the azaborinine derivative **24c**



Scheme S34.

At room temperature, the azaborole **16c** (71.8 mg, 0.15 mmol, 1 eq.) was added to the solution of

2,6-dimethylphenyl isocyanide (19.6 mg, 0.15 mmol, 1 eq.) in d_8 -toluene (1 mL) under argon atmosphere in a J. Young tube. The resulting solution was stored at 80 °C for 7 day. Then all volatiles were removed in vacuo. Subsequently, the residue was dissolved in pentane (1 mL) and stored at -35 °C to give the compound **24c** as a yellow solid (65 mg, 71% yield).

HRMS for $C_{31}H_{28}BN_2F_9^+$ $[M]^+$: calc. 610.2202; found: 610.2205.

1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.11 (s, 2H, *m*-Fmes), 7.22 (m, 1H, *p*-Xyl⁽¹⁾), 7.16 (m, 2H, *m*-Xyl⁽¹⁾), 6.96 (m, 2H, *m*-Xyl⁽⁴⁾), 6.92 (m, 1H, *p*-Xyl⁽⁴⁾), 6.50 (s, 1H, C(2)H), 5.36 (s, 1H, NH), 2.09 (s, 6H, *o*-CH₃^{Xyl(4)}), 2.01 (s, 6H, *o*-CH₃^{Xyl(1)}), 1.98 (s, 3H, CH₃⁽⁶⁾), 1.62 (s, 3H, CH₃⁽⁵⁾).

$^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 163.0 (br, C(4)), 149.7 (br, *i*-Fmes), 146.5 (*i*-Xyl⁽¹⁾), 141.9 (*i*-Xyl⁽⁴⁾), 136.8 (q, $^2J_{FC}$ = 29.3 Hz, *o*-Fmes), 135.9 (br, C(2)H), 134.8 (C(6)), 134.3 (*o*-Xyl⁽⁴⁾), 134.0 (*o*-Xyl⁽¹⁾), 129.58 (q, $^2J_{FC}$ = 33.7 Hz, *p*-Fmes), 128.8 (*m*-Xyl⁽¹⁾), 128.33 (*p*-Xyl⁽¹⁾), 128.31 (*m*-Xyl⁽⁴⁾), 125.5 (br, *m*-Fmes), 124.8 (*p*-Xyl⁽⁴⁾), 124.3 (q, $^1J_{FC}$ = 275.3 Hz, *o*-CF₃), 123.8 (q, $^1J_{FC}$ = 272.7 Hz, *p*-CF₃), 118.6 (C(3)), 18.9 (q, J = 2.1 Hz, *o*-CH₃^{Xyl(4)}), 17.2 (CH₃⁽⁶⁾), 16.9 (*o*-CH₃^{Xyl(1)}), 16.3 (CH₃⁽⁵⁾).

$^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 26.3 ($\nu_{1/2}$ \approx 280 Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -58.6 (s, 2F, *o*-CF₃), -63.4 (s, 1F, *p*-CF₃).

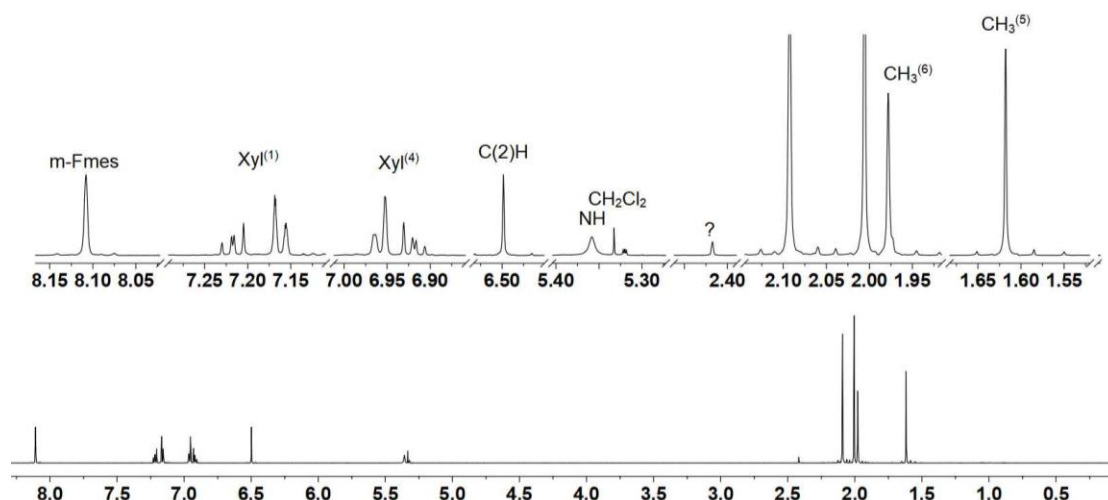


Figure S117. 1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24c**.

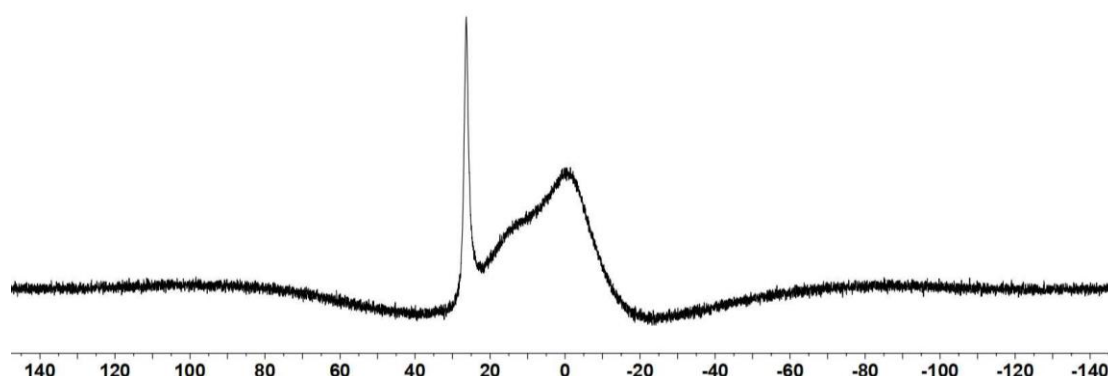


Figure S118. $^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24c**.

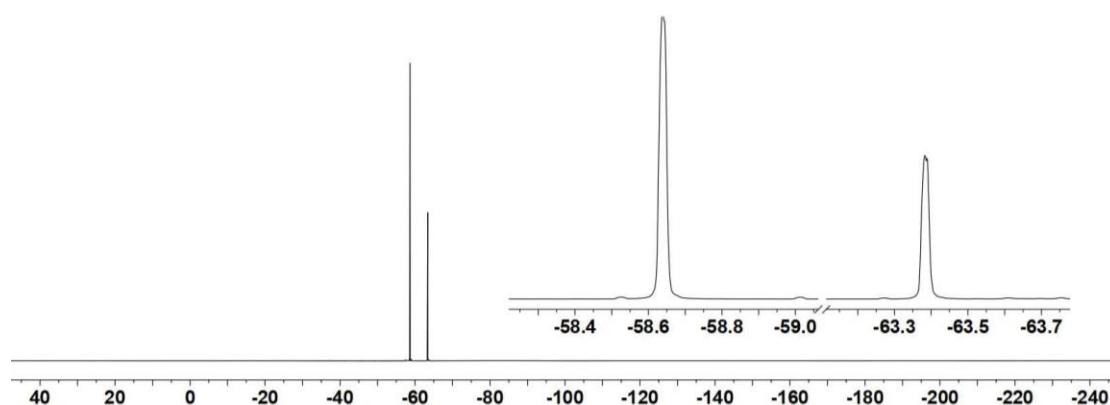


Figure S119. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24c**.

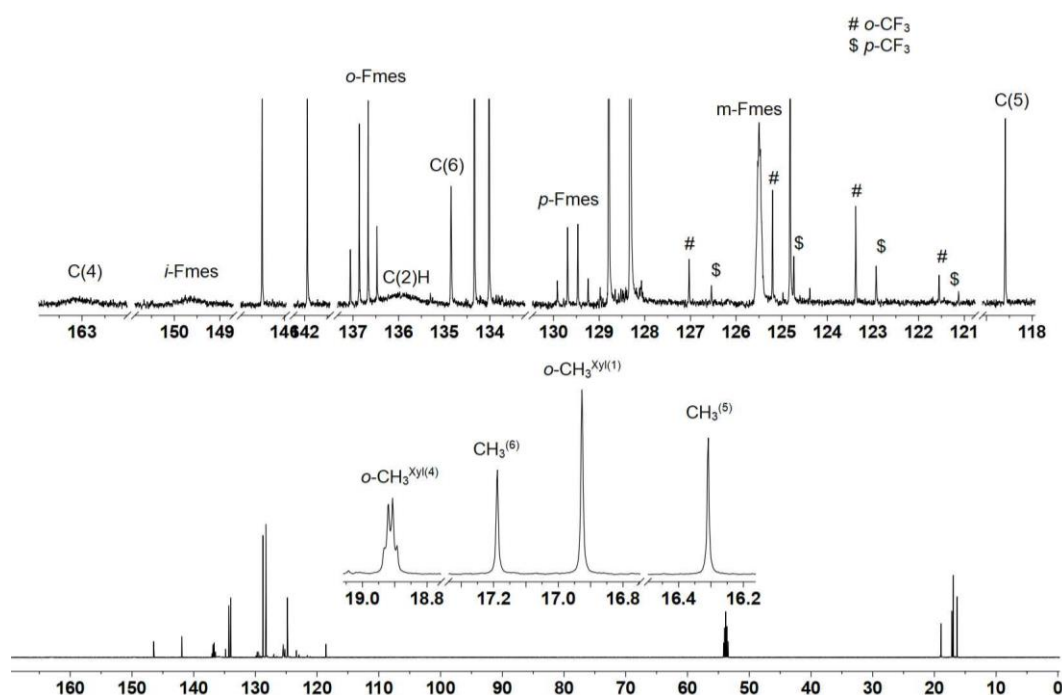


Figure S120. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24c**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of the compound **24c** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 24c (erk9568): A yellow prism-like specimen of $\text{C}_{31}\text{H}_{28}\text{BF}_9\text{N}_2$, approximate dimensions 0.140 mm x 0.160 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1643 frames were collected. The total exposure time was 23.61 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 24094 reflections to a maximum θ angle of 66.64° (0.84 \AA resolution), of which 5870 were independent (average redundancy 4.105, completeness = 99.4%, $R_{\text{int}} = 5.84\%$, $R_{\text{sig}} = 4.93\%$) and 4134 (70.43%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.6995(3)\text{ \AA}$, $b = 12.2055(4)\text{ \AA}$, $c = 15.8773(5)\text{ \AA}$, $\alpha = 95.526(2)^\circ$, $\beta = 90.646(2)^\circ$, $\gamma = 96.315(2)^\circ$, volume = $1667.45(10)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 4212 reflections above $20\sigma(I)$ with $7.322^\circ < 2\theta < 132.8^\circ$. Data were corrected for absorption effects using the multi-scan

method (SADABS). The ratio of minimum to maximum apparent transmission was 0.834. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7830 and 0.8820. 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, C₃₁H₂₈BF₉N₂. The final anisotropic full-matrix least-squares refinement on *F*² with 426 variables converged at *R*1 = 4.56%, for the observed data and *wR*2 = 12.11% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 0.207 e⁻/Å³ and the largest hole was -0.201 e⁻/Å³ with an RMS deviation of 0.041 e⁻/Å³. On the basis of the final model, the calculated density was 1.216 g/cm³ and *F*(000), 628 e⁻. The hydrogen at N1 atom was refined freely. CCDC number: 2041297.

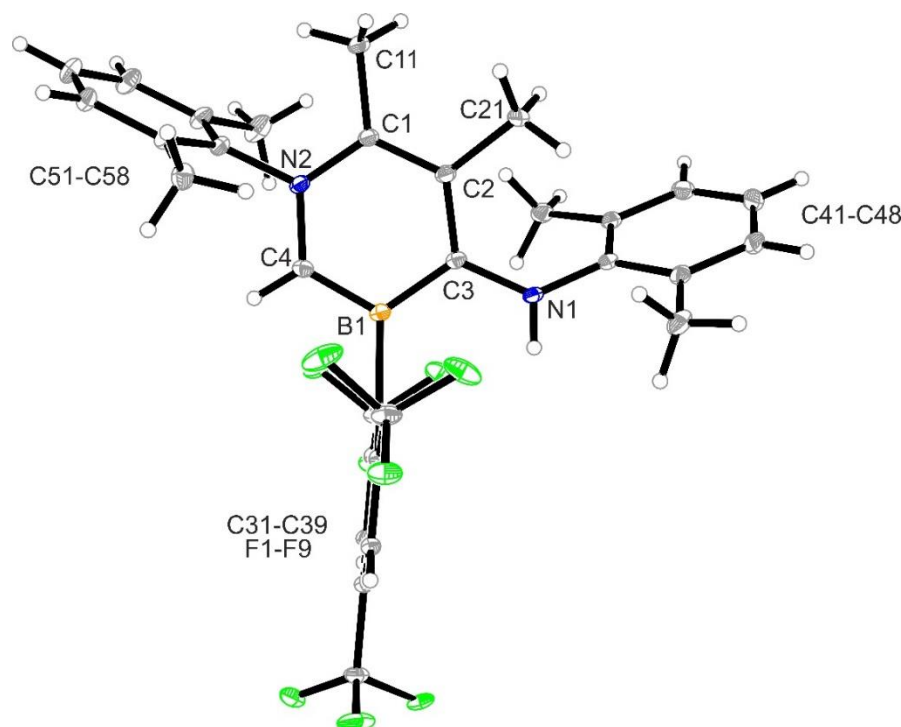
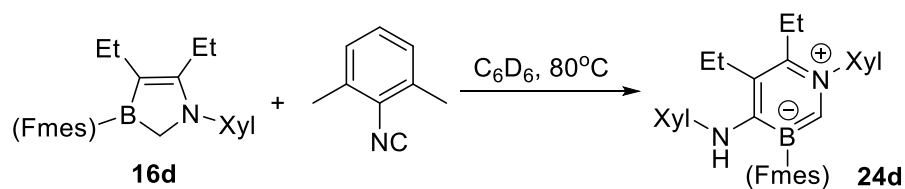


Figure S121. Crystal structure of compound **24c** (thermal ellipsoids are set at 15% probability).

Preparation of the azaborinine derivative **24d**



Scheme S35.

At room temperature, the azaborole **16d** (101.4 mg, 0.2 mmol, 1 eq.) was added to a solution of 2,6-dimethylphenyl isocyanide (26.2 mg, 0.2 mmol, 1 eq.) in C₆D₆ (2mL) under an argon atmosphere in a J. Young tube. The resulting solution was stored at 80 °C for 7 days. Then all volatiles were removed in vacuo. Subsequently, the residue was dissolved in pentane (1 mL) and stored at -35 °C to finally give the compound **24d** as a yellow solid (72 mg, 57 % yield).

HRMS for C₃₃H₃₂BF₉N₂⁺ [*M*]⁺: calc. 638.2515; found: 638.2517.

^1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 7.99 (s, 2H, *m*-Fmes), 7.23 (m, 1H, *p*-Xyl⁽¹⁾), 7.16 (m, 2H, *m*-Xyl⁽¹⁾), 6.86 (m, 3H, *m*-Xyl⁽⁴⁾, *p*-Xyl⁽⁴⁾), 6.42 (s, 1H, C(2)H), 5.42 (s, 1H, NH), 2.45 (q, $^3J_{\text{HH}}$ = 7.4 Hz, 2H, CH₂^{Et(6)}), 2.38 (q, $^3J_{\text{HH}}$ = 7.4 Hz, 2H, CH₂^{Et(5)}), 2.08 (s, 6H, *o*-CH₃^{Xyl(4)}), 2.04 (s, 6H, *o*-CH₃^{Xyl(1)}), 0.99 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 3H, CH₃^{Et(6)}), 0.94 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 3H, CH₃^{Et(5)}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 162.3 (br, C(4)), 149.8 (br, *i*-Fmes), 146.4 (*i*-Xyl⁽¹⁾), 141.1 (*i*-Xyl⁽⁴⁾), 139.4 (C(6)), 136.8 (br, C(2)H), 136.3 (q, $^2J_{\text{FC}}$ = 29.2 Hz, *o*-Fmes), 134.6 (*o*-Xyl⁽⁴⁾), 134.2 (*o*-Xyl⁽¹⁾), 129.3 (q, $^2J_{\text{FC}}$ = 33.8 Hz, *p*-Fmes), 128.8 (*m*-Xyl⁽¹⁾), 128.4 (*m*-Xyl⁽⁴⁾), 128.3 (*p*-Xyl⁽¹⁾), 125.9 (C(5)), 125.2 (br, *m*-Fmes), 124.9 (*p*-Xyl⁽⁴⁾), 23.7 (CH₂^{Et(6)}), 20.9 (CH₂^{Et(5)}), 19.0 (q, J_{FC} = 2.2 Hz, *o*-CH₃^{Xyl(4)}), 17.2 (*o*-CH₃^{Xyl(1)}), 14.4 (CH₃^{Et(5)}), 13.6 (CH₃^{Et(6)}).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 26.4 ($\nu_{1/2}$ \approx 310 Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -58.3 (s, 2F, *o*-CF₃^{Fmes}), -63.4 (s, 1F, *p*-CF₃^{Fmes}).

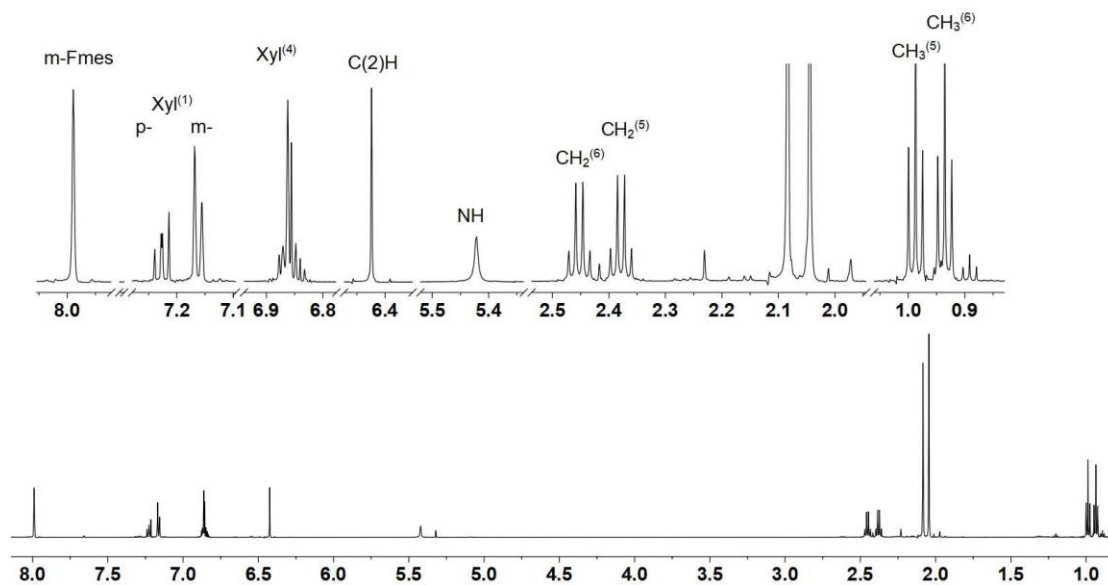


Figure S122. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24d**.

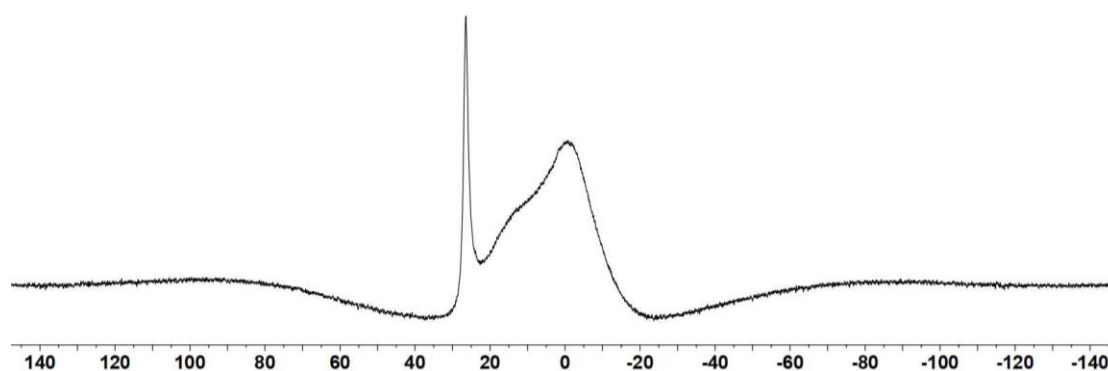


Figure S123. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24d**.

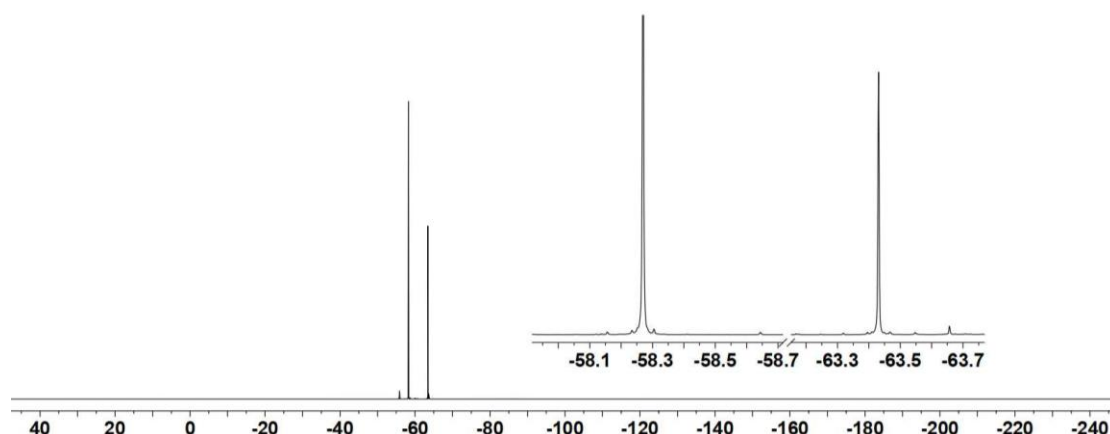


Figure S124. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24d**.

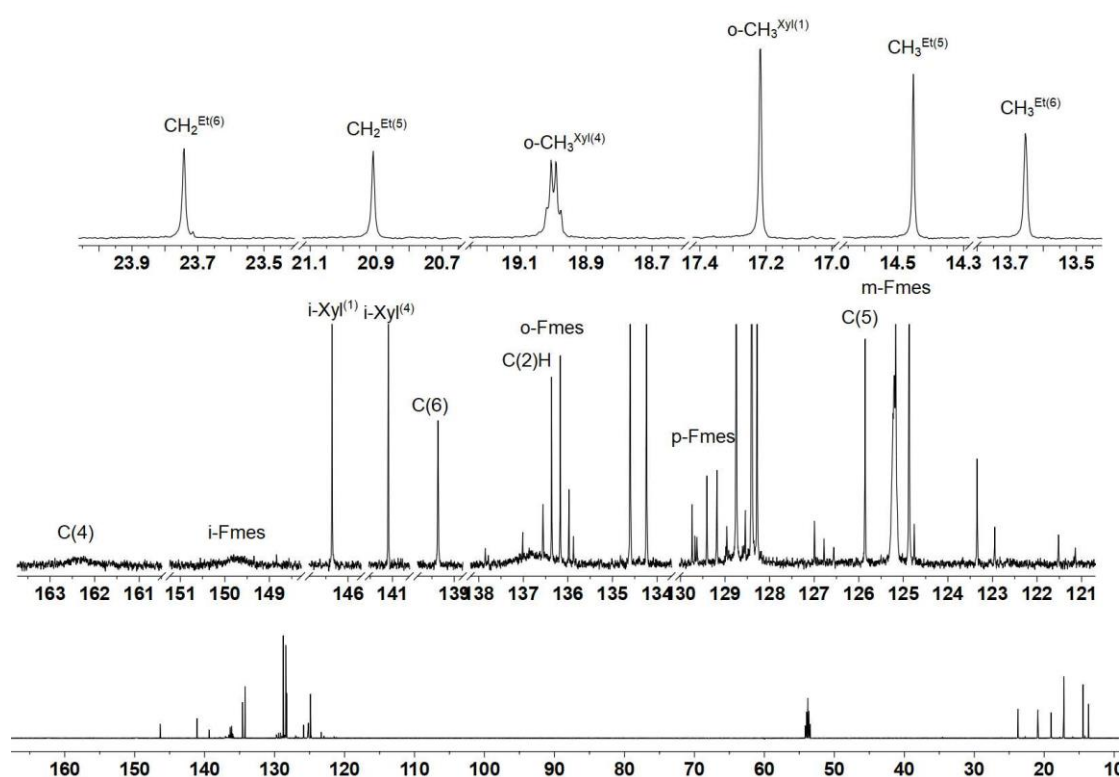


Figure S125. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24d**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **24d** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 24d (erk9597): A pale yellow plate-like specimen of $\text{C}_{33}\text{H}_{32}\text{BF}_9\text{N}_2$, approximate dimensions $0.041\text{ mm} \times 0.124\text{ mm} \times 0.156\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1479 frames were collected. The total exposure time was 27.67 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 45950 reflections to a maximum θ angle of 68.53° (0.83 \AA resolution), of which 5620 were independent (average redundancy 8.176, completeness = 99.2%,

$R_{\text{int}} = 7.85\%$, $R_{\text{sig}} = 4.41\%$ and 4126 (73.42%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.2377(3) \text{ \AA}$, $b = 11.1974(2) \text{ \AA}$, $c = 24.4577(6) \text{ \AA}$, $\beta = 90.739(2)^\circ$, volume = $3077.33(12) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 7201 reflections above $20 \sigma(I)$ with $7.229^\circ < 2\theta < 136.2^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.901. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8570 and 0.9590. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $\text{C}_{33}\text{H}_{32}\text{BF}_9\text{N}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 444 variables converged at $R1 = 5.59\%$, for the observed data and $wR2 = 14.89\%$ for all data. The goodness-of-fit was 1.030. The largest peak in the final difference electron density synthesis was $0.337 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.228 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.053 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.378 g/cm^3 and $F(000)$, 1320 e⁻. The hydrogen at N1 atom was refined freely. CCDC number: 2041298.

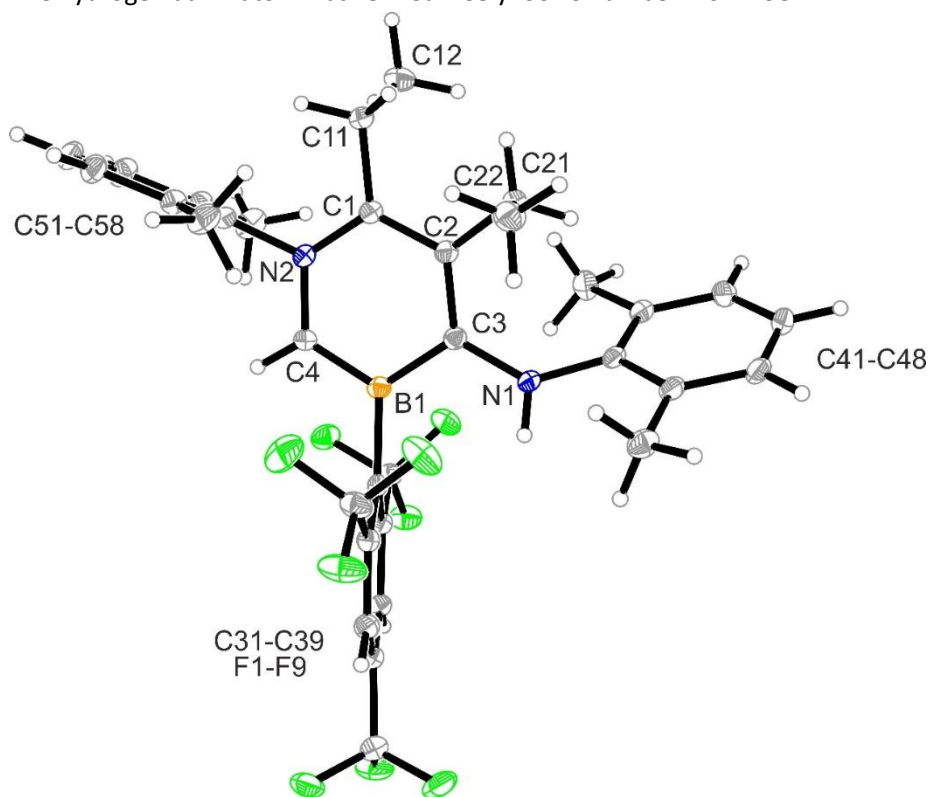
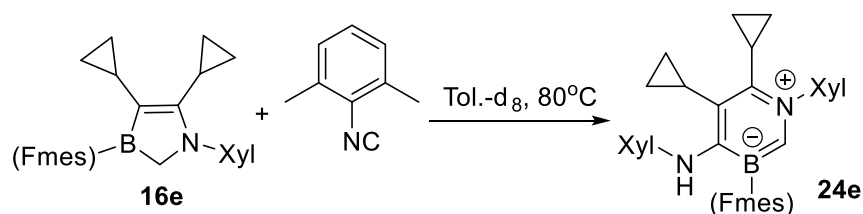


Figure S126. Crystal structure of compound **24d** (thermal ellipsoids are set at 15% probability).

Preparation of the azaborinine derivative **24e**



Scheme S36.

At room temperature, the azaborole **16e** (106 mg, 0.2 mmol, 1 eq.) was added to a solution of 2,6-dimethylphenyl isocyanide (26.2 mg, 0.2 mmol, 1 eq.) in d_8 -toluene (1 mL) under an argon atmosphere in a J. Young tube. The resulting solution was stored at 80 °C for 1 day. Then all volatiles were removed in vacuo and the residue was dissolved in pentane (1 mL) and stored at -35 °C to finally give the compound **24e** as a yellow solid (95 mg, 72% yield).

HRMS for $C_{35}H_{33}BN_2F_9^+$ [$M + H$] $^+$: calc. 663.2594; found: 663.2968.

1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.10 (s, 2H, *m*-Fmes), 7.19 (m, 1H, *p*-Xyl⁽¹⁾), 7.14 (m, 2H, *m*-Xyl⁽¹⁾), 6.92 (m, 2H, *m*-Xyl⁽⁴⁾), 6.86 (m, 1H, *p*-Xyl⁽⁴⁾), 6.49 (s, 1H, C(2)H), 5.60 (s, 1H, NH), 2.05 (s, 6H, *o*-CH₃^{Xyl(4)}), 2.01 (s, 6H, *o*-CH₃^{Xyl(1)}), 1.50 (*p*, $^3J_{HH}$ = 7.1 Hz, 1H, CH^{cp(6)}), 0.93 (m, 1H, CH^{cp(5)}), 0.58 (m, 4H, CH₂^{cp(6)}), 0.32 (m, 4H, CH₂^{cp(5)}).

$^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 164.9 (br, C(4)), 149.4 (br, *i*-Fmes), 146.8 (*i*-Xyl⁽¹⁾), 142.0 (*i*-Xyl⁽⁴⁾), 141.2 (C(6)), 137.3 (br, C(2)), 136.8 (q, $^2J_{FC}$ = 29.3 Hz, *o*-Fmes), 133.8 (*o*-Xyl⁽¹⁾), 133.0 (*o*-Xyl⁽⁴⁾), 129.6 (q, $^2J_{FC}$ = 33.8 Hz, *p*-Fmes), 128.7 (*m*-Xyl⁽¹⁾), 128.2 (*m*-Xyl⁽⁴⁾), 128.0 (*p*-Xyl⁽¹⁾), 127.7 (C(5)), 125.4 (br, *m*-Fmes), 124.2 (q, $^1J_{FC}$ = 275.5 Hz, *o*-CF₃^{Fmes}), 124.1 (*p*-Xyl⁽⁴⁾), 123.8 (q, $^1J_{FC}$ = 272.3 Hz, *p*-CF₃^{Fmes}), 19.1 (q, J_{FC} = 1.8 Hz, *o*-CH₃^{Xyl(4)}), 17.6 (*o*-CH₃^{Xyl(1)}), 15.0 (CH^{cp(6)}), 14.4 (CH^{cp(5)}), 10.8 (CH₂^{cp(5)}), 9.2 (CH₂^{cp(6)}).

$^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 26.2 ($\nu_{1/2}$ \approx 280 Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -59.0 (s, 2F, *o*-CF₃^{Fmes}), -63.4 (s, 1F, *p*-CF₃^{Fmes}).

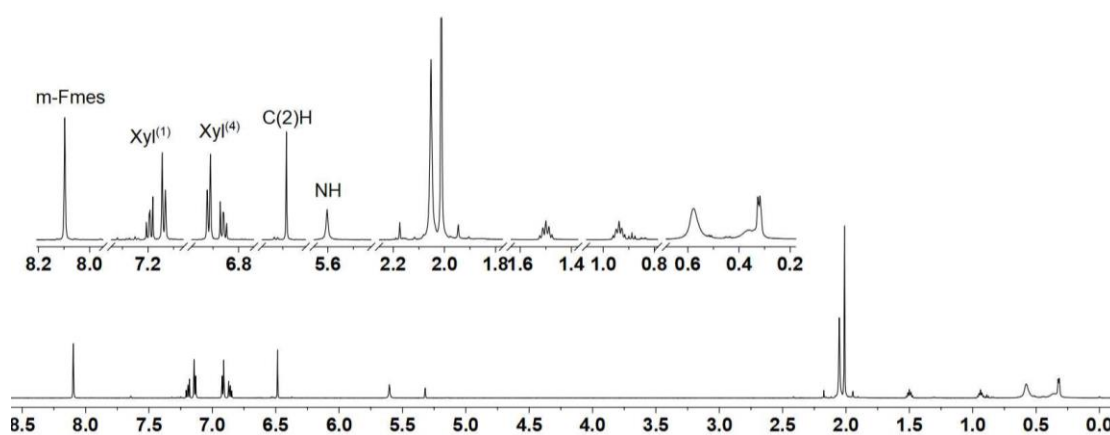


Figure S127. 1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24e**.

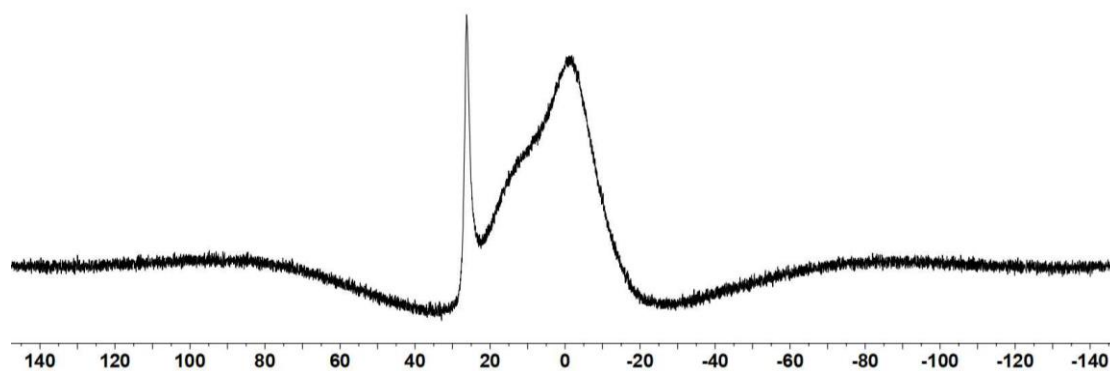


Figure S128. $^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24e**.

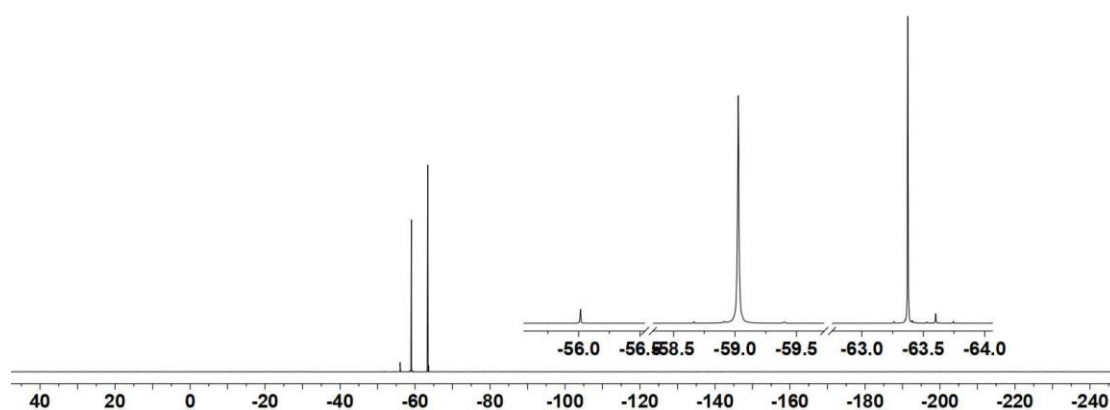


Figure S129. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24e**.

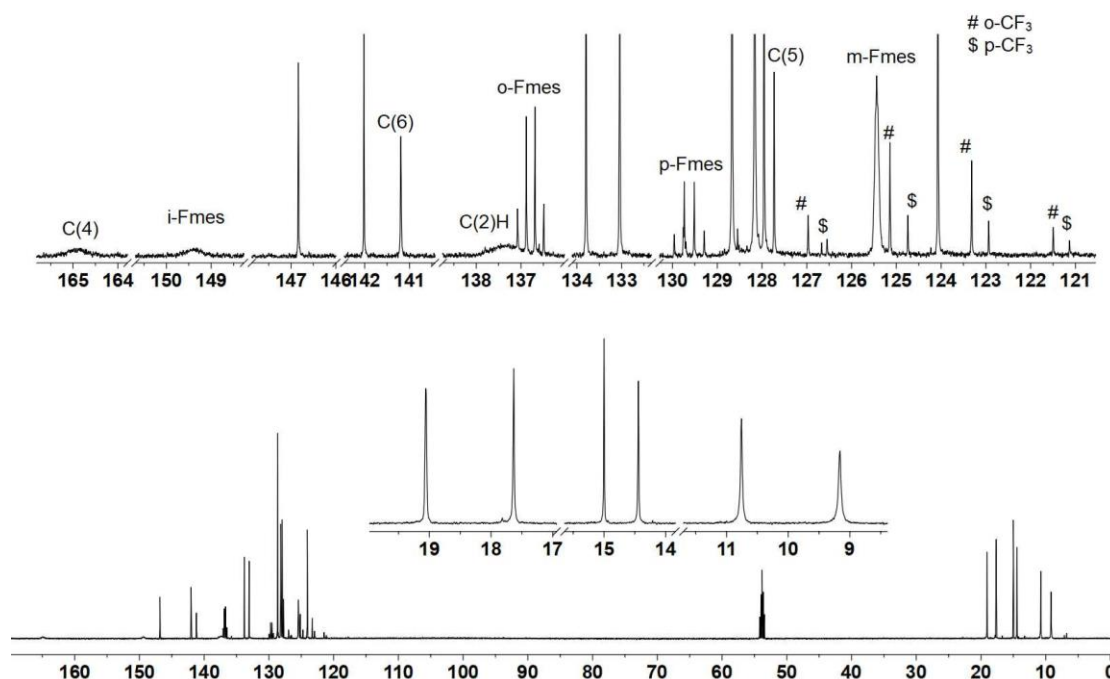


Figure S130. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **24e**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **24e** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 24e (erk9578): A pale yellow plate-like specimen of $\text{C}_{40}\text{H}_{44}\text{BF}_9\text{N}_2$, approximate dimensions $0.040\text{ mm} \times 0.080\text{ mm} \times 0.100\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1642 frames were collected. The total exposure time was 21.79 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 29287 reflections to a maximum θ angle of 66.67° (0.84 \AA resolution), of which 6493 were independent (average redundancy 4.511, completeness = 98.0%, $R_{\text{int}} = 10.13\%$, $R_{\text{sig}} = 10.40\%$) and 4026 (62.01%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.6311(7)\text{ \AA}$, $b = 14.6478(12)\text{ \AA}$, $c = 15.7274(12)\text{ \AA}$, $\alpha = 109.702(5)^\circ$, $\beta = 92.143(5)^\circ$, $\gamma = 92.957(6)^\circ$, volume = $1866.3(3)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 3062 reflections above $20\sigma(I)$ with $5.979^\circ < 2\theta < 124.7^\circ$. Data were corrected for absorption effects using the multi-scan method

(SADABS). The ratio of minimum to maximum apparent transmission was 0.778. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9140 and 0.9640. 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, C₄₀H₄₄BF₉N₂. The final anisotropic full-matrix least-squares refinement on *F*² with 528 variables converged at *R*1 = 6.15%, for the observed data and *wR*2 = 16.72% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 0.298 e⁻/Å³ and the largest hole was -0.263 e⁻/Å³ with an RMS deviation of 0.062 e⁻/Å³. On the basis of the final model, the calculated density was 1.307 g/cm³ and *F*(000), 768 e⁻. The hydrogen at N1 atom was refined freely. CCDC number: 2041299.

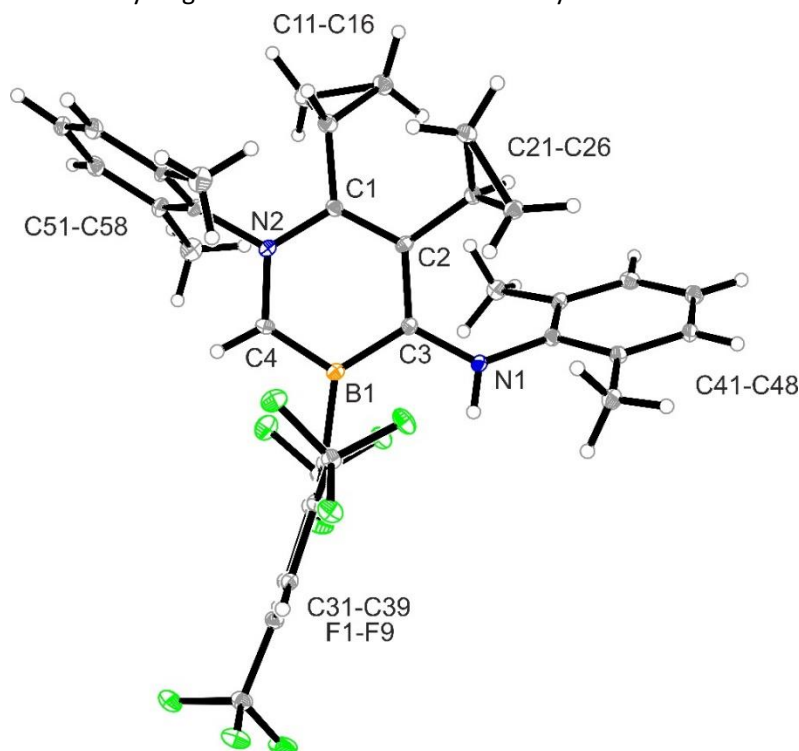
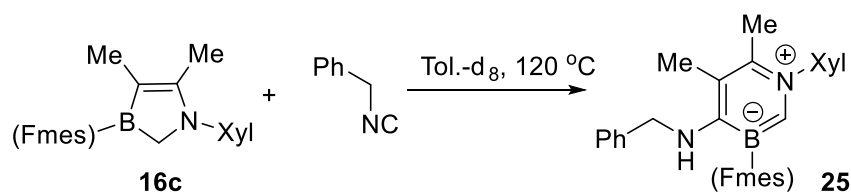


Figure S131. Crystal structure of compound **24e** (thermal ellipsoids are set at 15% probability).

Preparation of the azaborinine derivative **25**



Scheme S37.

At room temperature, (isocyanomethyl)benzene (17.6 mg, 0.15 mmol, 1 eq.) was added to the solution of the azaborole **16c** (62 mg, 0.15 mmol, 1 eq.) in *d*₈-toluene (1mL) under an argon atmosphere in a J. Young tube. The resulting solution was stored at 120 °C overnight. Then all volatiles were removed in vacuo. Subsequently, the residue was dissolved in pentane (1 mL) and stored at -35 °C to finally give compound **25** as a pale-yellow solid (68 mg, 76 % yield).

HRMS for C₃₀H₂₇BF₉N₂⁺ [*M* + *H*]⁺: calc. 597.2123; found: 597.2118.

^1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.05 (s, 2H, *m*-Fmes), 7.30 (m, 2H, *m*-Ph), 7.26 (m, 1H, *p*-Ph), 7.21 (m, 2H, *o*-Ph), 7.19 (m, 1H, *p*-Xyl), 7.14 (m, 2H, *m*-Xyl), 6.40 (s, 1H, C(2)H), 4.43 (t, $^3J_{\text{HH}}$ = 5.1 Hz, 1H, NH), 3.97 (d, $^3J_{\text{HH}}$ = 5.1 Hz, 2H, CH₂), 2.13 (s, 3H, CH₃⁽⁵⁾), 2.07 (s, 3H, CH₃⁽⁶⁾), 1.98 (s, 6H, *o*-CH₃^{Xyl}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 163.0 (br, C(4)), 153.8 (br, *i*-Fmes), 146.4 (*i*-Xyl), 140.2 (*i*-Ph), 138.1 (br, C(2)H), 135.7 (q, $^2J_{\text{FC}}$ = 28.6 Hz, *o*-Fmes), 134.3 (*m*-Xyl), 133.5 (C(6)), 128.92 (q, $^2J_{\text{FC}}$ = 33.9 Hz, *p*-Fmes), 128.91 (*m*-Ph), 128.7 (*m*-Xyl), 128.5 (*o*-Ph), 128.3 (*p*-Xyl), 127.8 (*p*-Ph), 124.9 (br, *m*-Fmes), 124.5 (q, $^1J_{\text{FC}}$ = 276.6 Hz, *o*-CF₃^{Fmes}), 123.9 (q, $^1J_{\text{FC}}$ = 271.3 Hz, *p*-CF₃^{Fmes}), 116.3 (C(5)), 51.4 (CH₂), 17.4 (CH₃⁽⁶⁾), 17.0 (*o*-CH₃^{Xyl}), 14.0 (CH₃⁽⁵⁾).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 22.9 ($\nu_{1/2} \approx 300$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -57.9 (s, 2F, *o*-CF₃^{Fmes}), -63.2 (s, 1F, *o*-CF₃^{Fmes}).

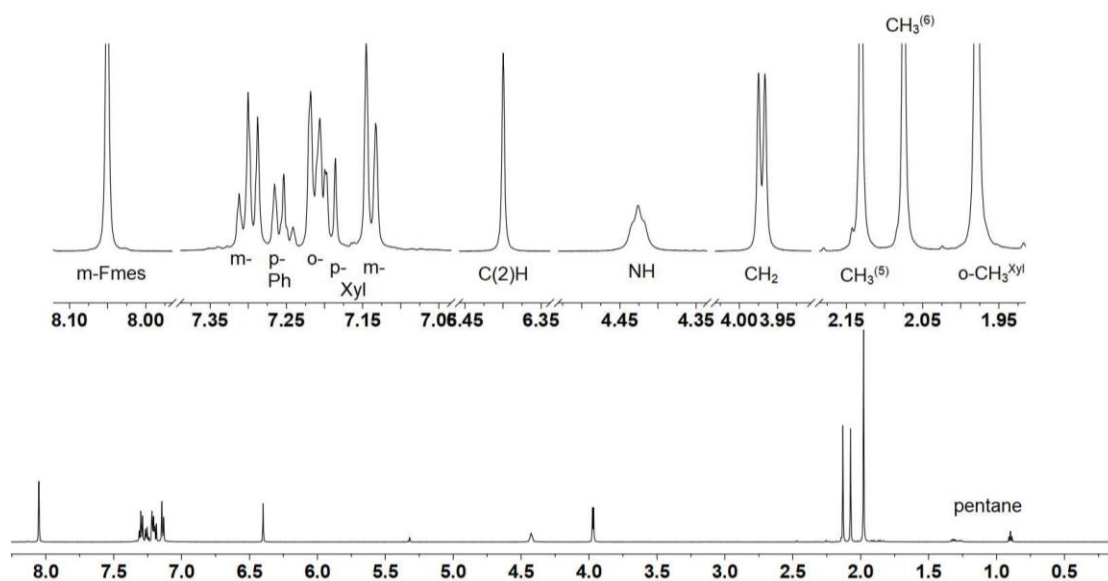


Figure S132. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **25**.

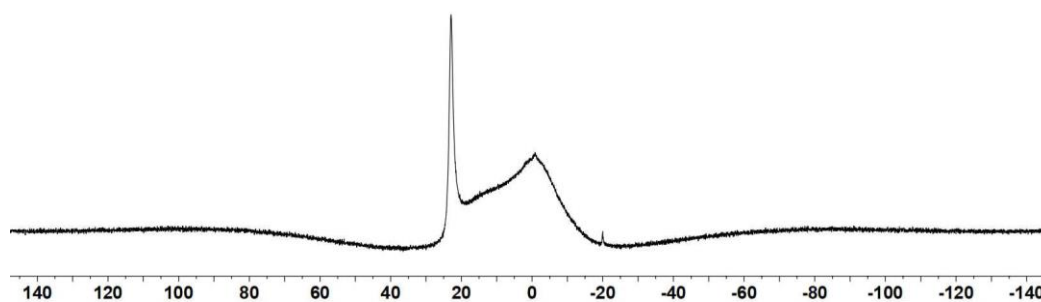


Figure S133. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **25**.

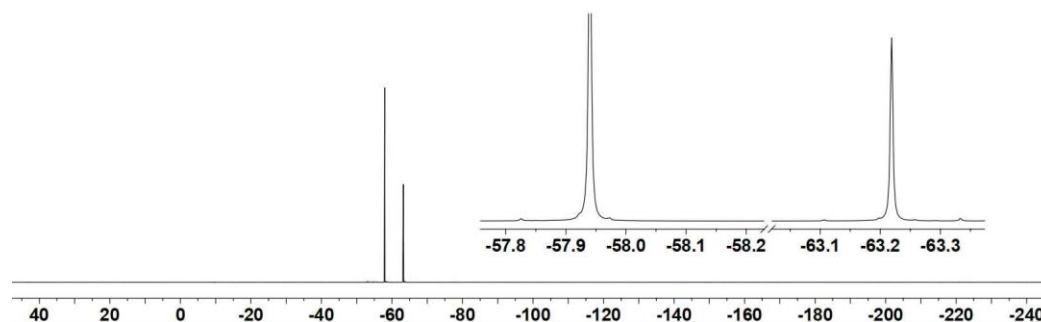


Figure S134. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **25**.

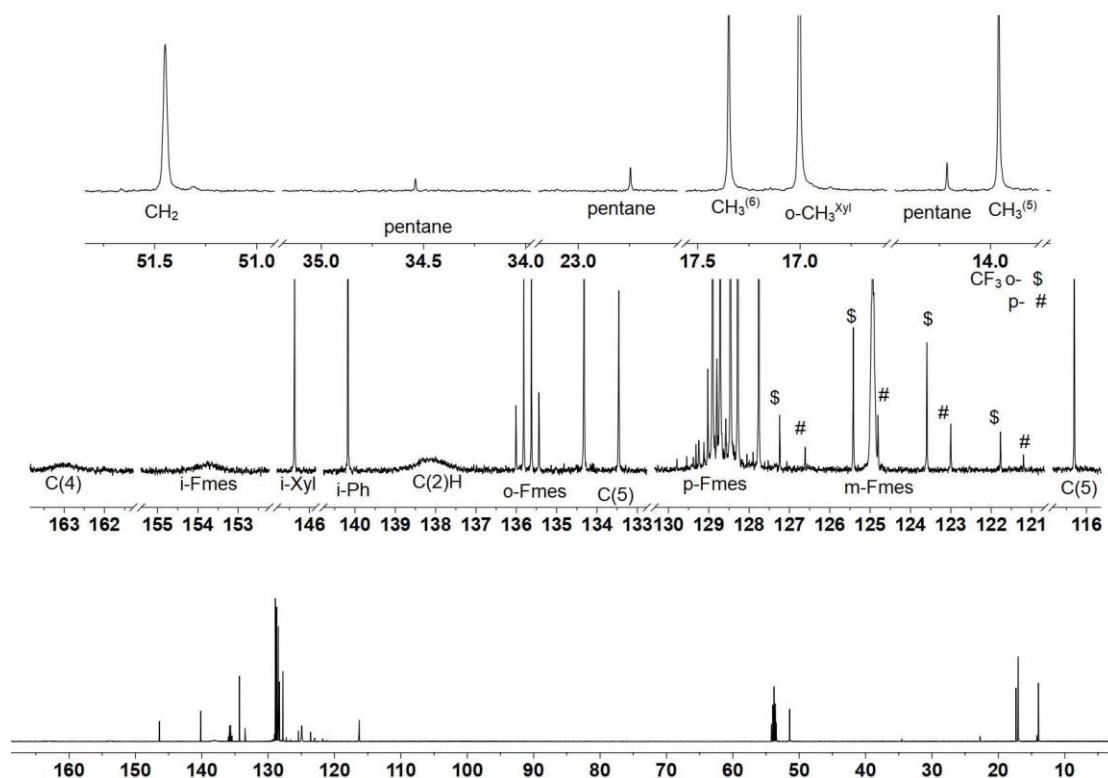


Figure 135. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **25**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **25** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 25 (erk9694): A pale yellow prism-like specimen of $\text{C}_{30}\text{H}_{26}\text{BF}_9\text{N}_2$, approximate dimensions $0.046\text{ mm} \times 0.100\text{ mm} \times 0.153\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 990 frames were collected. The total exposure time was 22.74 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 35855 reflections to a maximum θ angle of 66.94° (0.84 \AA resolution), of which 4886 were independent (average redundancy 7.338, completeness = 99.6%, $R_{\text{int}} = 5.72\%$, $R_{\text{sig}} = 3.14\%$) and 3957 (80.99%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 13.7751(3)\text{ \AA}$, $b = 11.5702(2)\text{ \AA}$, $c = 17.4052(4)\text{ \AA}$, $\beta = 97.6090(10)^\circ$, volume = $2749.63(10)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9940 reflections above $20\sigma(I)$ with $9.203^\circ < 2\theta < 133.6^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.882. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8490 and 0.9510.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $\text{C}_{30}\text{H}_{26}\text{BF}_9\text{N}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 387 variables converged at $R1 = 4.22\%$, for the observed data and $wR2 = 9.98\%$ for all data. The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was $0.235\text{ e}/\text{\AA}^3$ and the largest hole was $-0.208\text{ e}/\text{\AA}^3$ with an RMS deviation of $0.048\text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was $1.441\text{ g}/\text{cm}^3$ and $F(000)$, 1224 e^- . The hydrogen at N1 atom was refined freely. CCDC number: 2041300.

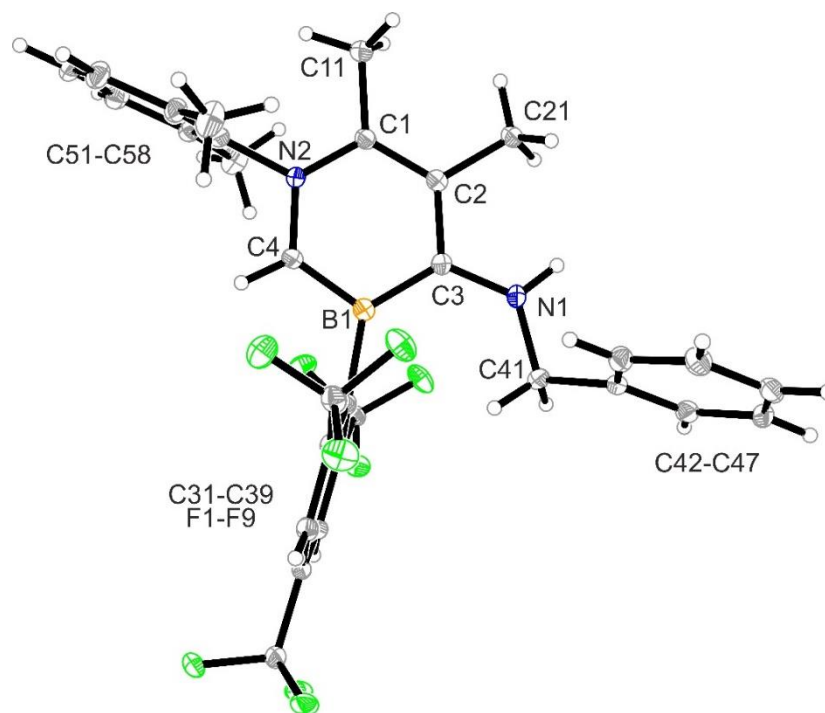
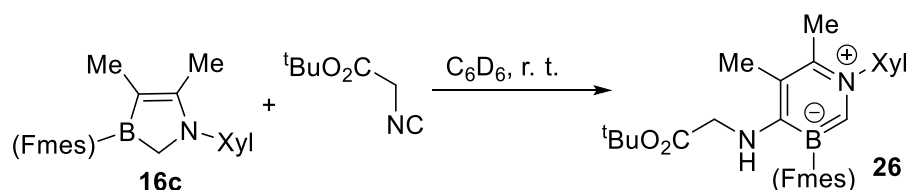


Figure S136. Crystal structure of compound **25** (thermal ellipsoids are set at 30% probability).

Preparation of the azaborinine derivative **26**



Scheme S38.

At room temperature, the azaborole **16c** (62 mg, 0.15 mmol, 1 eq.) was added to the solution of tert-butyl 2-isocyanoacetate (35.1 mg, 0.3 mmol, 2 eq.) in C_6D_6 (2 mL) under an argon atmosphere in a J. Young tube. The resulting solution was stored at room temperature for 7 days. Volatiles were removed in vacuo, the residue was dissolved in heptane (1 mL) and stored at room temperature for 15 days to finally give the products as a yellow solid (38 mg, 31 % yield).

HRMS for $C_{29}H_{30}BF_9N_2O_2Na^+$, $[M+Na]^+$: calc. 643.2154; Found: 643.2146.

1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.08 (s, 2H, *m*-Fmes), 7.18 (m, 1H, *p*-Xyl), 7.12 (m, 2H, *m*-Xyl), 6.36 (s, 1H, C(2)H), 4.98 (t, $^3J_{HH}$ = 4.9 Hz, 1H, NH), 3.43 (d, $^3J_{HH}$ = 4.9 Hz, 2H, CH_2), 2.22 (s, 3H, $CH_3^{(5)}$), 2.06 (s, 3H, $CH_3^{(6)}$), 1.94 (s, 6H, *o*- CH_3^{Xyl}), 1.39 (s, 9H, CH_3^{tBu}).

$^{13}C\{^1H\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 170.7 (C=O), 161.9 (br, C(4)), 153.3 (br, *i*-Fmes), 146.3 (*i*-Xyl), 138.3 (br, C(2)H), 135.8 (q, $^2J_{FC}$ = 28.7 Hz, *o*-Fmes), 134.3 (*o*-Xyl), 133.6 (C(6)), 129.1 (q, $^2J_{FC}$ = 33.8 Hz, *p*-Fmes), 128.7 (*m*-Xyl), 128.3 (*p*-Xyl), 125.0 (br, *m*-Fmes), 124.4 (q, $^1J_{FC}$ = 274.6 Hz, *o*- CF_3^{Fmes}), 123.9 (q, $^1J_{FC}$ = 272.0 Hz, *p*- CF_3^{Fmes}), 117.1 (C(5)), 82.2 (C^{tBu}), 48.4 (CH_2), 28.1 (CH_3^{tBu}), 17.3 ($CH_3^{(6)}$), 17.0 (*o*- CH_3^{Xyl}), 13.8 ($CH_3^{(5)}$).

$^{11}B\{^1H\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 19.5 ($\nu_{1/2} \approx 310$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -58.2 (s, 2F, *o*- CF_3^{Fmes}), -63.3 (s, 1F, *p*- CF_3^{Fmes}).

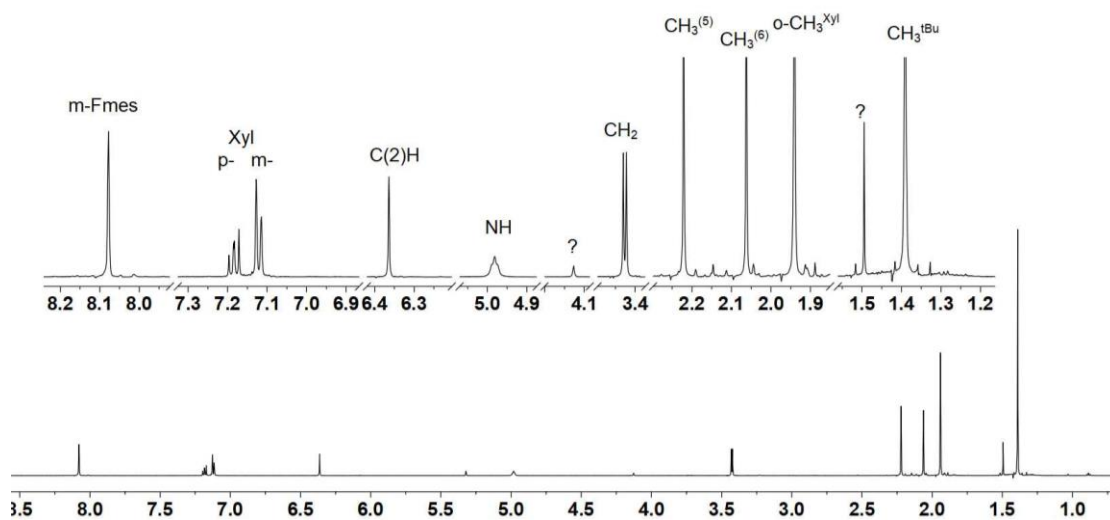


Figure S137. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **26**.

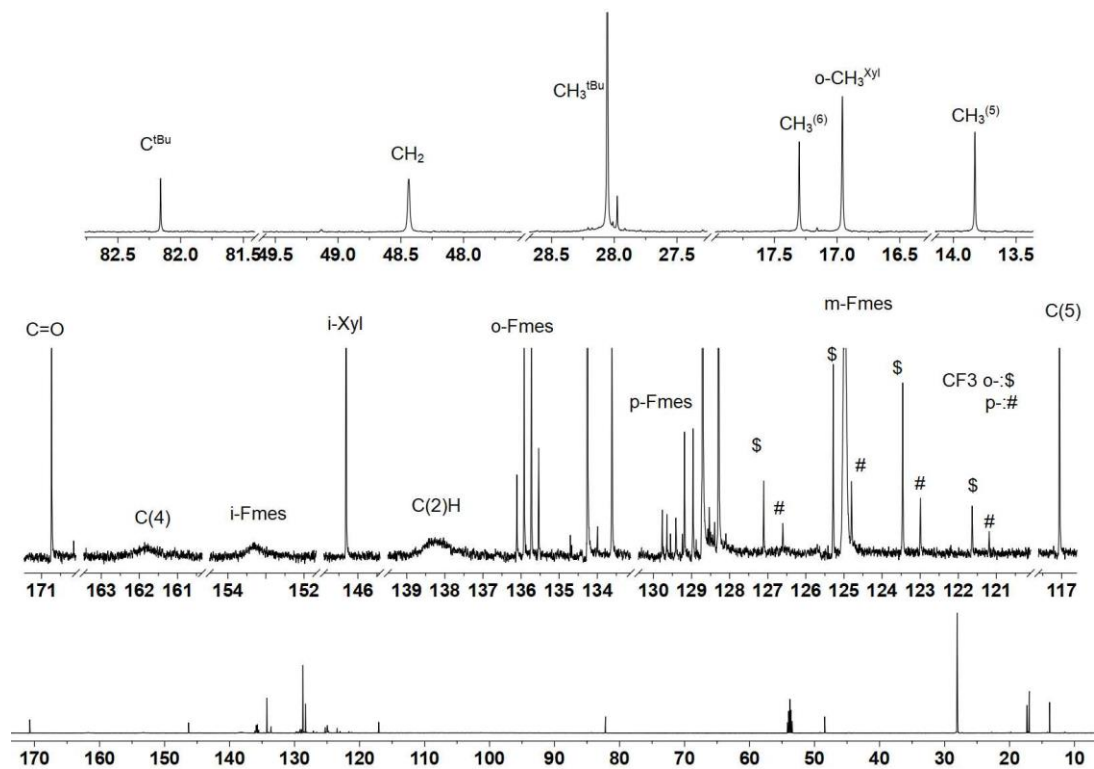


Figure S138. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **26**.

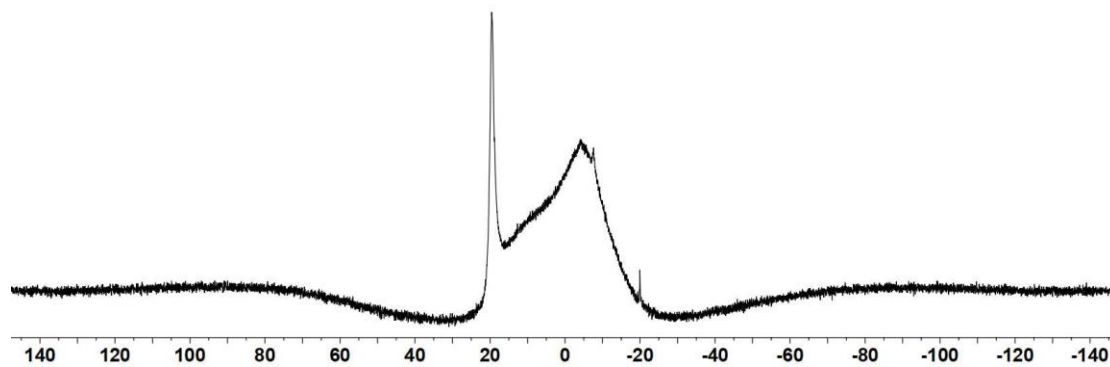


Figure S139. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **26**.

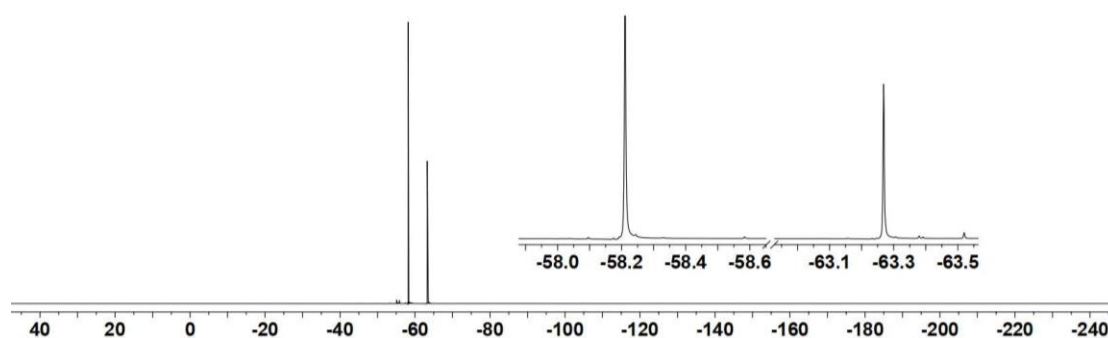


Figure S140. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **26**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **26** in heptane at room temperature.

X-ray crystal structure analysis of compound 26 (erk9641): A pale yellow prism-like specimen of $\text{C}_{29}\text{H}_{30}\text{BF}_9\text{N}_2\text{O}_2$, approximate dimensions 0.078 mm x 0.105 mm x 0.226 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1144 frames were collected. The total exposure time was 12.71 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 35028 reflections to a maximum θ angle of 27.47° (0.77 \AA resolution), of which 6836 were independent (average redundancy 5.124, completeness = 99.3%, $R_{\text{int}} = 3.27\%$, $R_{\text{sig}} = 2.22\%$) and 6230 (91.14%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 10.4043(3) \text{ \AA}$, $b = 11.6812(3) \text{ \AA}$, $c = 13.5156(3) \text{ \AA}$, $\alpha = 92.0810(10)^\circ$, $\beta = 94.3730(10)^\circ$, $\gamma = 113.2720(10)^\circ$, volume = $1500.61(7) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9890 reflections above $20 \sigma(I)$ with $4.69^\circ < 2\theta < 54.91^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.971. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9900. 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, $\text{C}_{29}\text{H}_{30}\text{BF}_9\text{N}_2\text{O}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 399 variables converged at $R1 = 4.12\%$, for the observed data and $wR2 = 9.60\%$ for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was $0.385 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.223 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.042 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.373 g/cm^3 and $F(000)$, 640 e^- . The hydrogen at N1 atom was refined freely. CCDC number: 2041301.

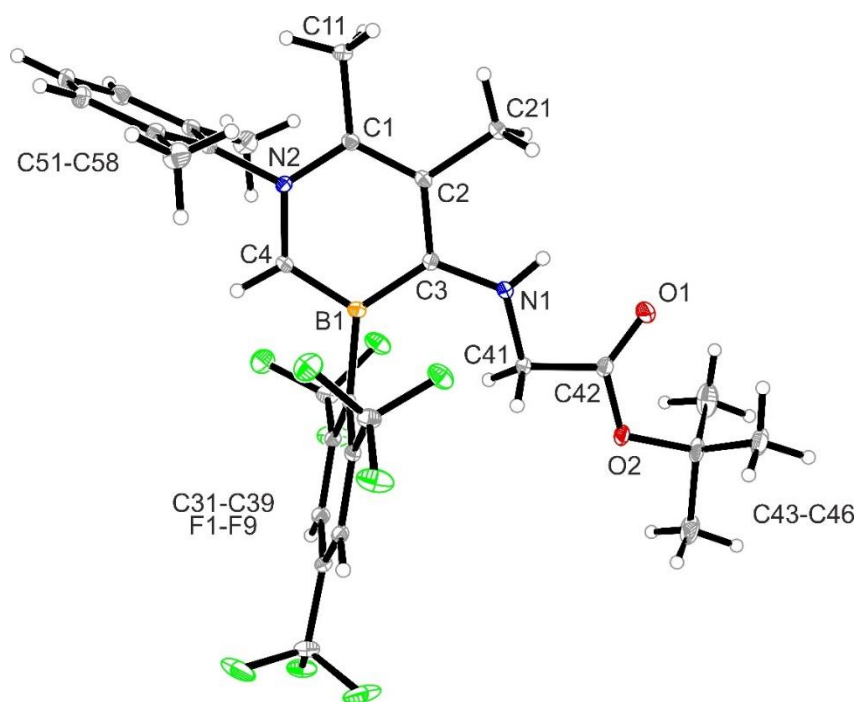
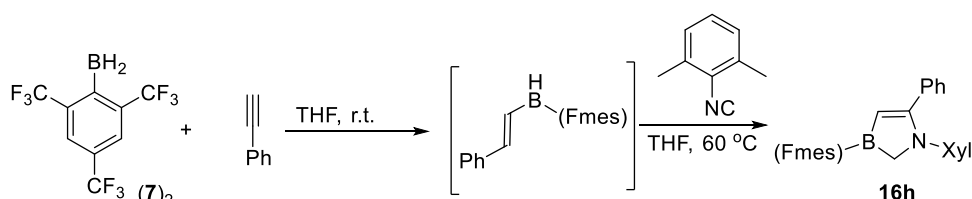


Figure S141. Crystal structure of compound **26** (thermal ellipsoids are set at 30% probability).

Preparation of azaborole derivative **16h**



Scheme S39.

At room temperature, phenylacetylene (102 mg, 1 mmol, 1 eq.) was added to the solution of borane (**7**)₂ (294 mg, 1.0 mmol, 1 eq.) in THF (10 mL) under an argon atmosphere in a Schlenk tube. The resulting mixture was stirred for 2h at room temperature to give a colorless solution. Then 2,6-dimethylphenyl isocyanide (131 mg, 1.0 mmol, 1 eq.) was added in one portion to give a yellow solution. The solution was stirred at 60 °C overnight. Then all volatiles were removed in vacuo and the residue was purified by column chromatography at silica gel with pentane as eluent to give compound **16h** as a white solid (160 mg, 30 % yield).

HRMS for C₂₆H₂₂BONF₉⁺ [M+H₃O]⁺: calc. 546.1450; found: 546.1446.

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.14 (s, 2H, *m*-Fmes), 7.36 (m, 2H, *o*-Ph), 7.31 (m, 1H, *p*-Ph), 7.24 (m, 2H, *m*-Ph), 7.08 (m, 1H, *p*-Xyl), 7.02 (m, 2H, *m*-Xyl), 5.62 (s, 1H, CH=), 3.77 (*sep*, *J*_{FH} = 2.5 Hz, 2H, CH₂^{NB}), 2.15 (s, 6H, *o*-CH₃^{Xyl}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K): δ = 182.2 (CN=), 146.4 (br, *i*-Fmes), 141.7 (*i*-Xyl), 137.0 (*o*-Xyl), 134.7 (*i*-Ph), 134.1 (q, ²*J*_{FC} = 30.9 Hz, *o*-Fmes), 130.3 (q, ²*J*_{FC} = 34.1 Hz, *p*-Fmes), 130.2 (*p*-Ph), 128.8 (*m*-Xyl), 128.6 (*o*-Ph), 128.3 (*m*-Ph), 127.9 (*p*-Xyl), 125.55 (br, *m*-Fmes), 124.3 (q, ¹*J*_{FC} = 274.7 Hz, *o*-CF₃^{Fmes}), 123.6 (q, ¹*J*_{FC} = 272.1 Hz, *p*-CF₃^{Fmes}), 109.1 (CH=), 58.2 (br, CH₂^{NB}), 17.9 (*o*-CH₃^{Xyl}).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): $\delta = 59.6$ ($\nu_{1/2} \approx 530$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): $\delta = -57.9$ (s, 2F, *o*-CF₃), -63.4 (s, 1F, *p*-CF₃).

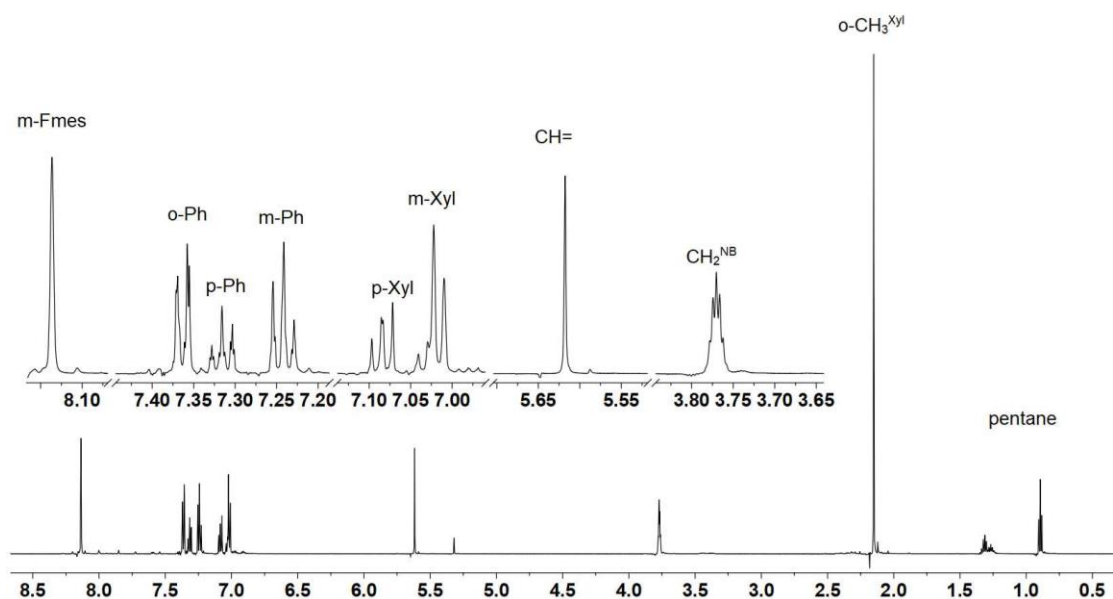


Figure S142. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16h**.

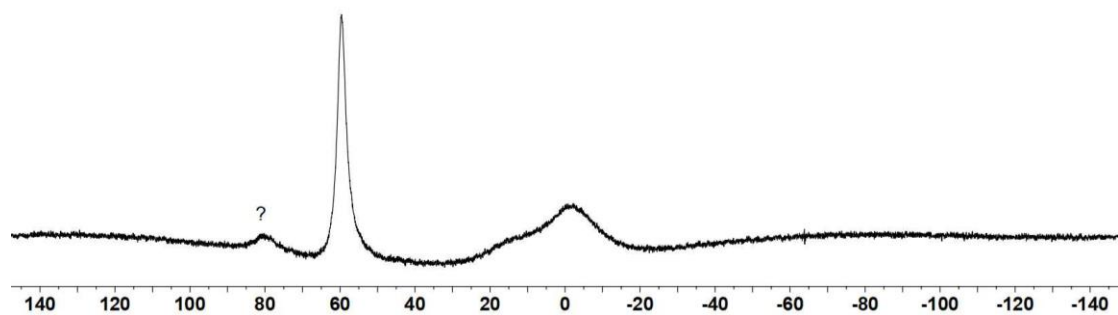


Figure S143. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16h**.

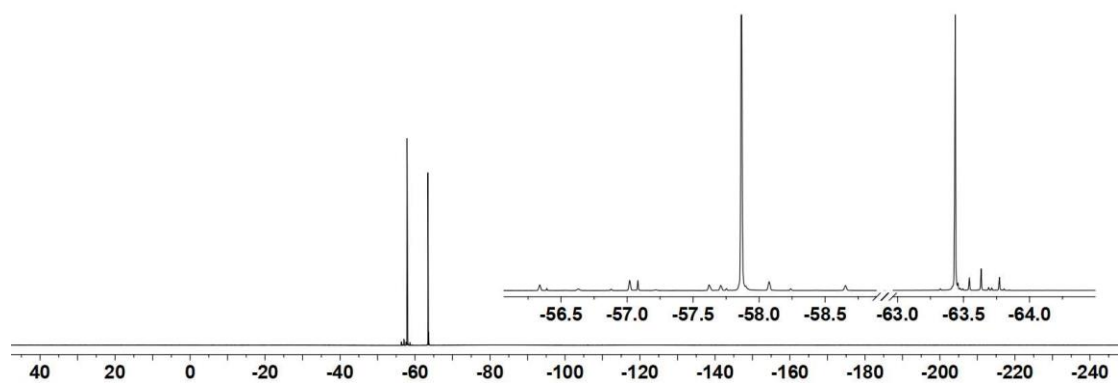


Figure S144. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16h**.

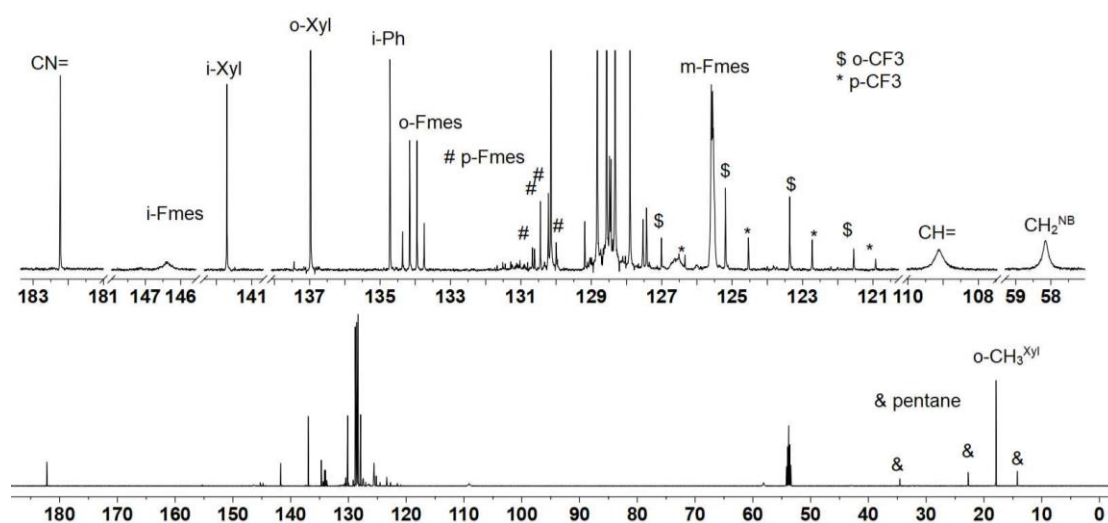


Figure S145. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **16h**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **16h** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 16h (erk9760): A colorless prism-like specimen of $\text{C}_{27.50}\text{H}_{20.50}\text{BF}_9\text{N}$, approximate dimensions $0.100\text{ mm} \times 0.100\text{ mm} \times 0.160\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1458 frames were collected. The total exposure time was 19.05 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 37024 reflections to a maximum θ angle of 66.67° (0.84 \AA resolution), of which 8689 were independent (average redundancy 4.261, completeness = 99.2%, $R_{\text{int}} = 8.86\%$, $R_{\text{sig}} = 7.00\%$) and 5636 (64.86%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.7841(3)\text{ \AA}$, $b = 14.7106(5)\text{ \AA}$, $c = 15.8655(5)\text{ \AA}$, $\alpha = 110.309(2)^\circ$, $\beta = 97.196(2)^\circ$, $\gamma = 100.853(2)^\circ$, volume = $2478.35(14)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 3127 reflections above $20\sigma(I)$ with $6.615^\circ < 2\theta < 133.1^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.847. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8360 and 0.8930. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P-1$, with $Z = 4$ for the formula unit, $\text{C}_{27.50}\text{H}_{20.50}\text{BF}_9\text{N}$. The final anisotropic full-matrix least-squares refinement on F^2 with 782 variables converged at $R1 = 5.48\%$, for the observed data and $wR2 = 15.44\%$ for all data. The goodness-of-fit was 1.013. The largest peak in the final difference electron density synthesis was $0.371\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.282\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.059\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.465 g/cm^3 and $F(000)$, 1114 e^- . CCDC number: 2041295.

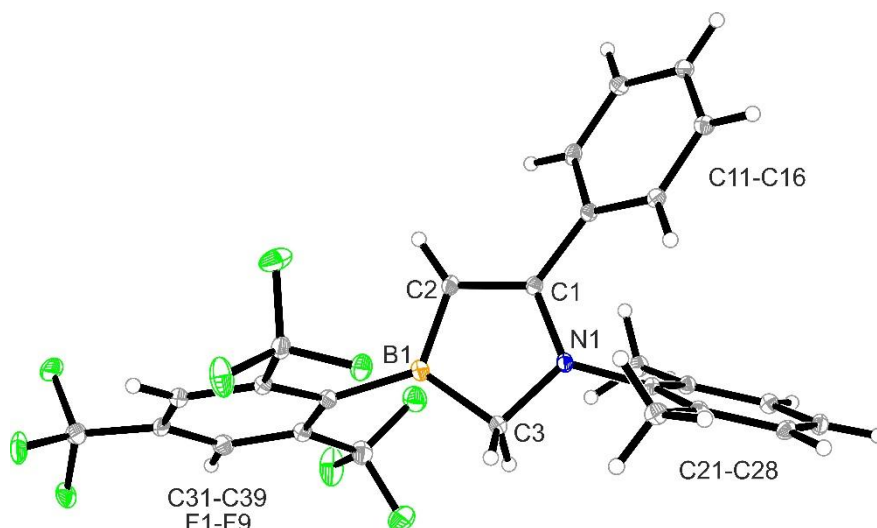
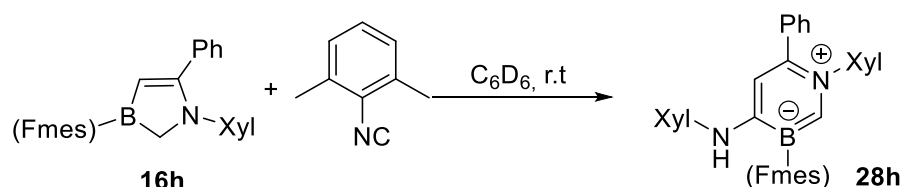


Figure S146. Crystal structure of compound **16h** (thermal ellipsoids are set at 15% probability).

Preparation of the azaborinine derivative **28h**



Scheme S40.

At room temperature, 2,6-dimethylphenyl isocyanide (13.1 mg, 0.1 mmol, 1 eq.) was added to a solution of the azaborole **16h** (53 mg, 0.10 mmol, 1 eq.) in C_6D_6 (1 mL) in a J. Young tube under an argon atmosphere. The resulting solution was stored at r. t. for overnight. Then all volatiles were removed in vacuo, the residue was dissolved in pentane (1 mL) and stored at $-35\text{ }^{\circ}\text{C}$ to finally give the product **28h** as a pale-yellow solid (32 mg, 48 % yield).

HRMS for $C_{35}H_{28}BN_2F_9^+ [M]^+$: calc. 658.2202; found: 658.2209.

^1H NMR (600 MHz, methylene chloride- d_2 , 299 K): δ = 8.20 (s, 2H, *m*-Fmes), 7.10 (m, 5H, *m*-Ph, *p*-Ph, *m*-Xyl⁽⁴⁾), 7.05 (m, 4H, *p*-Xyl⁽⁴⁾, *o*-Ph, *p*-Xyl⁽¹⁾), 6.95 (d, $^3J_{\text{HH}}$ = 7.6 Hz, 2H, *m*-Xyl⁽¹⁾), 6.63 (s, 1H, C(2)H), 6.11 (s, 1H, C(5)H), 5.48 (s, 1H, NH), 2.23 (s, 6H, *o*-CH₃^{Xyl(4)}), 2.05 (s, 6H, *o*-CH₃^{Xyl(1)}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K): δ = 163.7 (br, C(4)), 148.8 (br, *i*-Fmes), 145.7 (*i*-Xyl⁽¹⁾), 140.7 (C(6)), 139.3 (br, C(2)H), 137.8 (*i*-Ph), 137.6 (*i*-Xyl⁽⁴⁾), 137.1 (q, $^2J_{\text{CF}}$ = 29.8 Hz, *o*-Fmes), 137.0 (*o*-Xyl⁽⁴⁾), 134.5 (*o*-Xyl⁽¹⁾), 129.9 (q, $^2J_{\text{CF}}$ = 33.8 Hz, *p*-Fmes), 129.3 (*o*-Ph), 128.9 (*m*-Xyl⁽⁴⁾), 128.4 (*m*-Xyl⁽¹⁾), 128.2 (*p*-Xyl⁽¹⁾), 127.9 (*p*-Ph), 127.8 (*m*-Ph), 126.8 (*p*-Xyl⁽⁴⁾), 125.6 (brm, *m*-Fmes), 124.3 (q, $^1J_{\text{CF}}$ = 275.0 Hz, *o*-CF₃^{Fmes}), 123.8 (q, $^1J_{\text{CF}}$ = 272.8 Hz, *p*-CF₃^{Fmes}), 110.0 (C(4)H), 18.4 (*o*-CH₃^{Xyl(4)}), 17.7 (*p*-CH₃^{Xyl(4)}).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K): δ = 26.4 ($\nu_{1/2} \approx 330$ Hz).

^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K): δ = -59.0 (s, 2F, *o*-CF₃), -63.3 (s, 1F, *p*-CF₃).

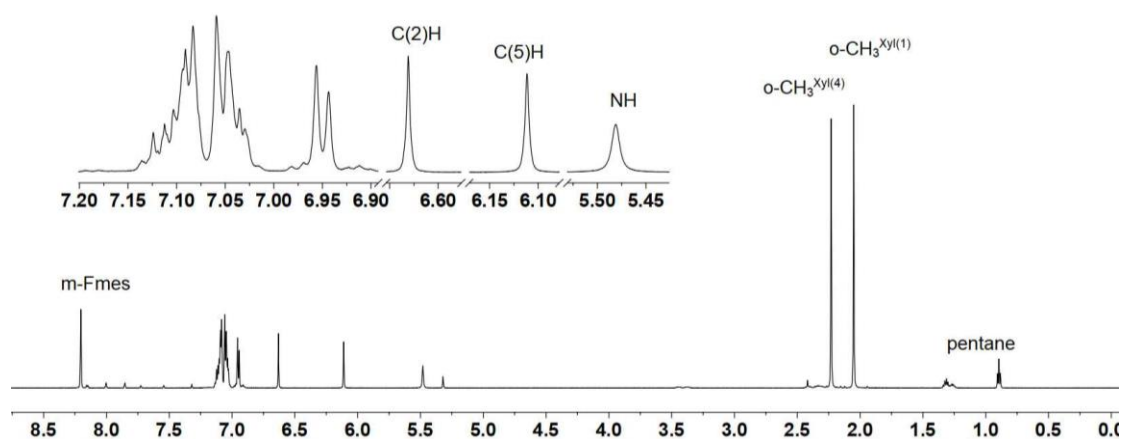


Figure S147. ^1H NMR (600 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **28h**.

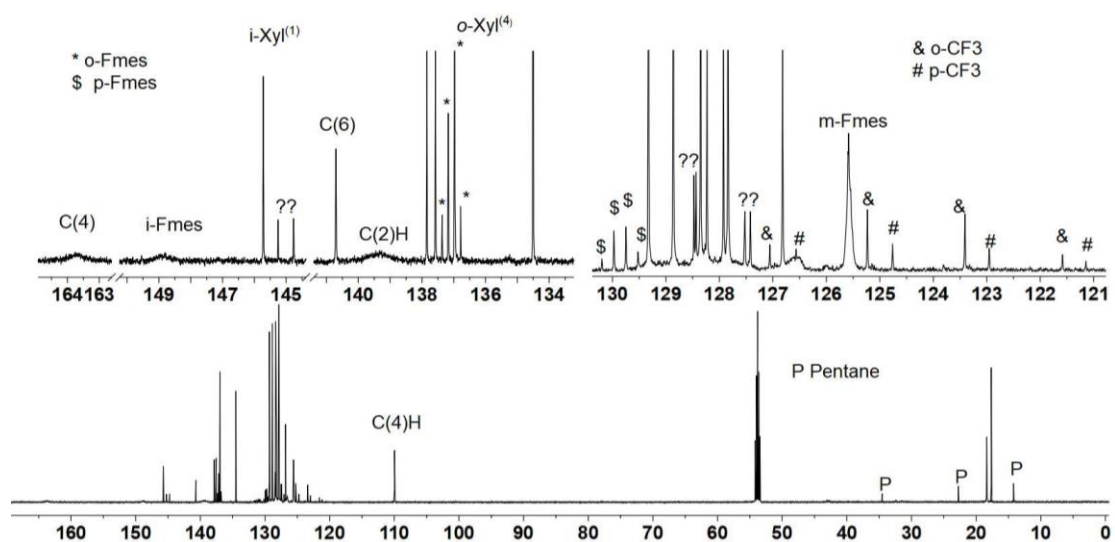


Figure S148. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **28h**.

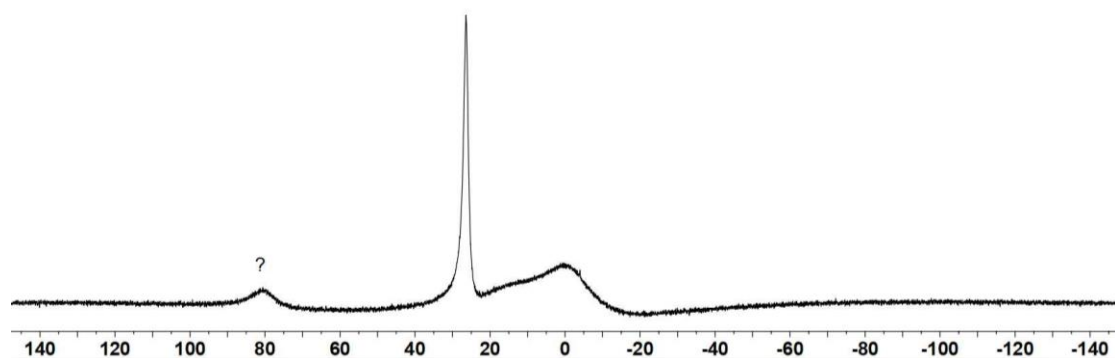


Figure S149. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **28h**.

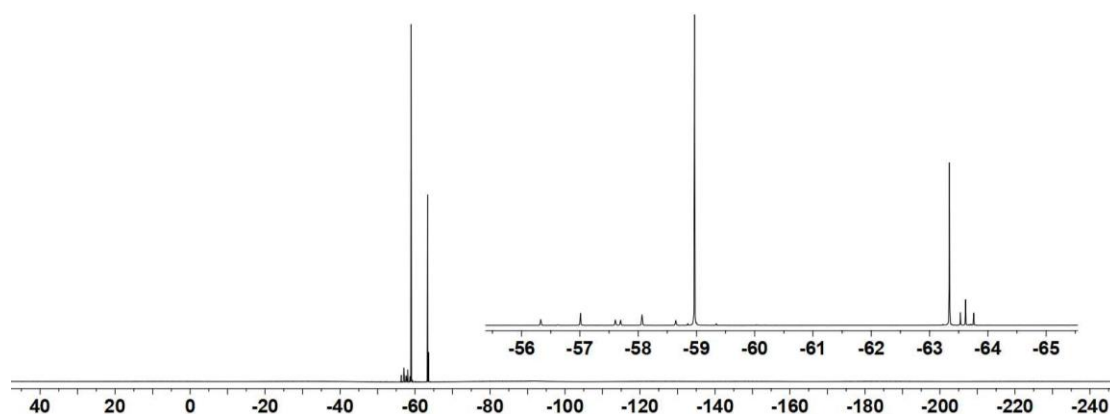


Figure S150. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **28h**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **28h** in heptane and methylene chloride at room temperature.

X-ray crystal structure analysis of compound 28h (erk9892): A pale yellow plate-like specimen of $\text{C}_{35}\text{H}_{28}\text{BF}_9\text{N}_2$, approximate dimensions 0.039 mm x 0.119 mm x 0.230 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims ($\text{CuK}\alpha$, $\lambda = 1.54178 \text{ \AA}$) and a MX mirror monochromator. A total of 1654 frames were collected. The total exposure time was 22.59 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 35269 reflections to a maximum θ angle of 66.78° (0.84 \AA resolution), of which 6347 were independent (average redundancy 5.557, completeness = 99.1%, $R_{\text{int}} = 7.09\%$, $R_{\text{sig}} = 4.45\%$) and 4836 (76.19%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.69690(10) \text{ \AA}$, $b = 11.9109(2) \text{ \AA}$, $c = 17.6858(3) \text{ \AA}$, $\alpha = 92.7280(10)^\circ$, $\beta = 95.6760(10)^\circ$, $\gamma = 97.7420(10)^\circ$, volume = $1802.98(5) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9958 reflections above $20 \sigma(I)$ with $5.030^\circ < 2\theta < 133.1^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.878. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8210 and 0.9660. 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, $\text{C}_{35}\text{H}_{28}\text{BF}_9\text{N}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 489 variables converged at $R1 = 5.04\%$, for the observed data and $wR2 = 12.67\%$ for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was $0.269 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.244 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.046 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.213 g/cm^3 and $F(000)$, 676 e^- . The hydrogen at N1 atom was refined freely. CCDC number: 2041302.

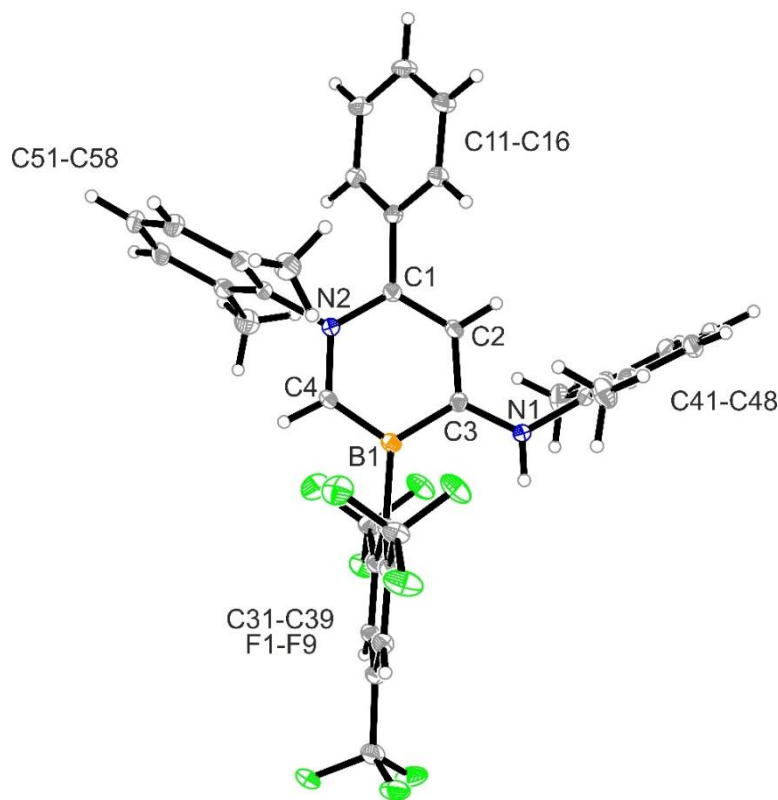
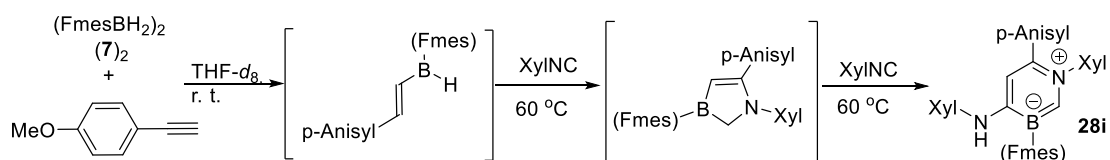


Figure S151. Crystal structure of compound **28h** (thermal ellipsoids are set at 30% probability).

Preparation of the azaborinine derivative **28i**



Scheme S41.

At room temperature, 1-ethynyl-4-methoxybenzene (26.4 mg, 0.2 mmol, 1 equiv.) was added to the solution of borane (**7**)₂ (58.8 mg, 0.2 mmol, 1 equiv.) in THF-*d*₈ (1 mL) in a J. Young tube under the argon atmosphere. The mixture was stored at room temperature for 1h, then 2,6-dimethylphenyl isocyanide (26.2 mg, 0.2 mmol, 1 equiv.) was added and the resulting solution was stored at 60 °C for 2 days. One more equivalent 2,6-dimethylphenyl isocyanide (26.2 mg, 0.2 mmol) was added and the mixture was stored at 60 °C for 1 day more. All volatiles were removed in vacuo and the residue was purified by flash chromatography with pentane: methylene chloride (10:1) as eluent to finally give compound **28i** as yellow solid (38 mg, 28 % yield).

HRMS for C₃₆H₃₃N₂BO₂F₉⁺ [M + H₃O]⁺: calc. 723.2441; found: 723.2438.

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.19 (s, 2H, *m*-Fmes), 7.06 (m, 4H, *m*-Xyl⁽⁴⁾, *p*-Xyl⁽⁴⁾, *p*-Xyl⁽¹⁾), 6.96 (m, 4H, *o*-Anisyl, *m*-Xyl⁽¹⁾), 6.61 (m, 2H, *m*-Anisyl), 6.59 (s, 1H, C(2)H), 6.07 (s, 1H, C(5)H), 5.45 (s, 1H, NH), 3.67 (s, 3H, OCH₃), 2.22 (s, 6H, *o*-CH₃^{Xyl(4)}), 2.03 (s, 6H, *o*-CH₃^{Xyl(1)}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K)[selected resonances]: δ = 163.8 (br, C(4)), 159.4 (*p*-Anisyl), 149.0 (br, *i*-Fmes), 145.8 (*i*-Xyl⁽¹⁾), 140.5 (C(6)), 139.0 (br, C(2)H), 137.6 (*i*-Xyl⁽⁴⁾), 137.0 (*o*-Xyl⁽⁴⁾), 134.4 (*o*-Xyl⁽⁴⁾), 130.5 (*o*-Anisyl), 130.2 (*i*-Anisyl), 128.8 (*m*-Xyl⁽⁴⁾), 128.4 (*m*-Xyl⁽¹⁾).

128.2 (*p*-Xyl⁽¹⁾), 126.8 (*p*-Xyl⁽⁴⁾), 125.5 (br, *i*-Fmes), 113.2 (*m*-Anisyl), 109.9 (C(5)H), 55.4 (OCH₃), 18.4 (*o*-CH₃^{Xyl(4)}), 17.6 (*o*-CH₃^{Xyl(1)}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 26.1 ($\nu_{1/2} \approx 330$ Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = -59.0 (s, 2F, *o*-CF₃), -63.3 (s, 1F, *p*-CF₃).

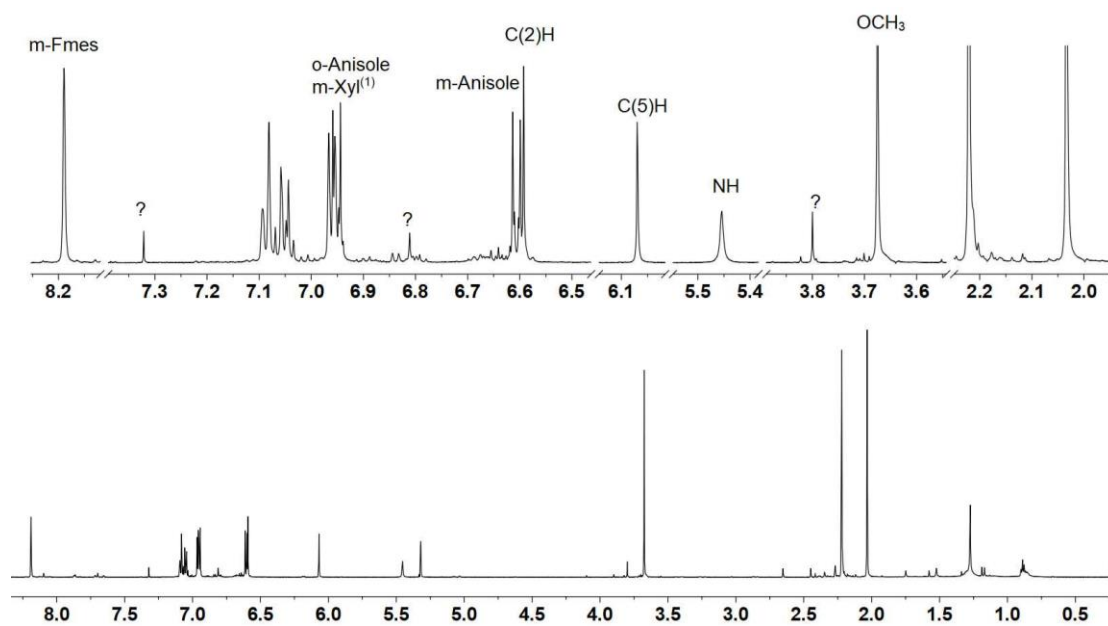


Figure S152. ¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **28i**.

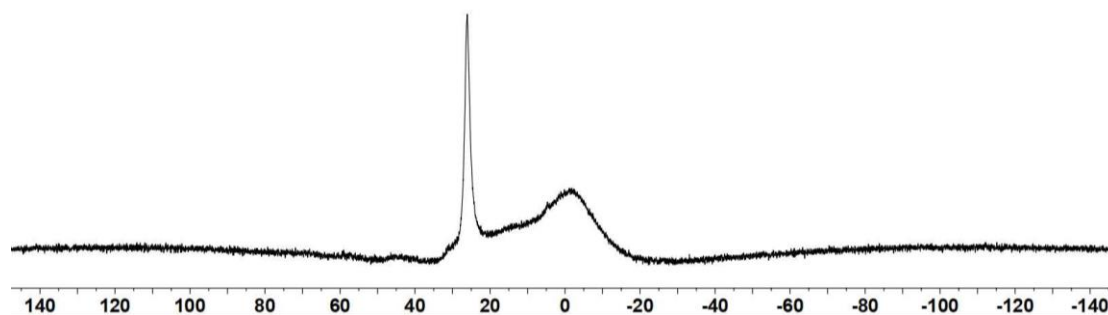


Figure S153. ¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **28i**.

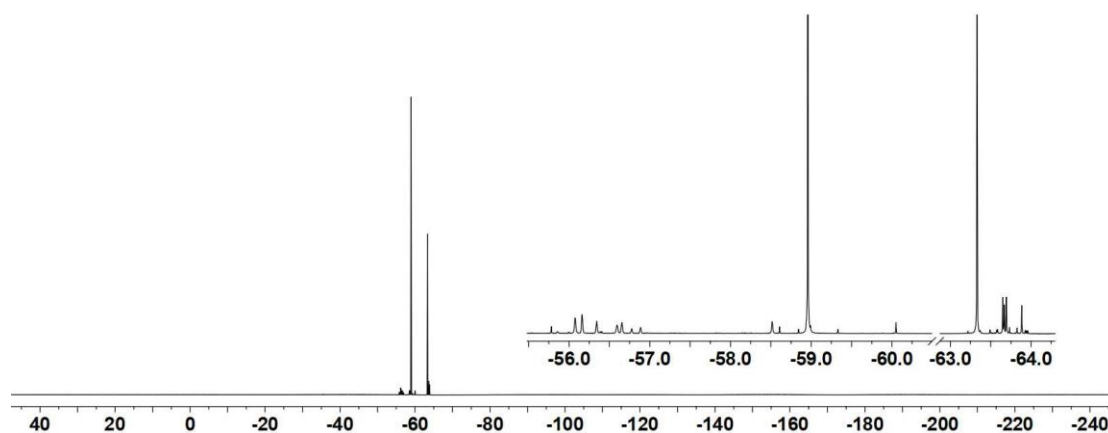


Figure S154. ¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **28i**.

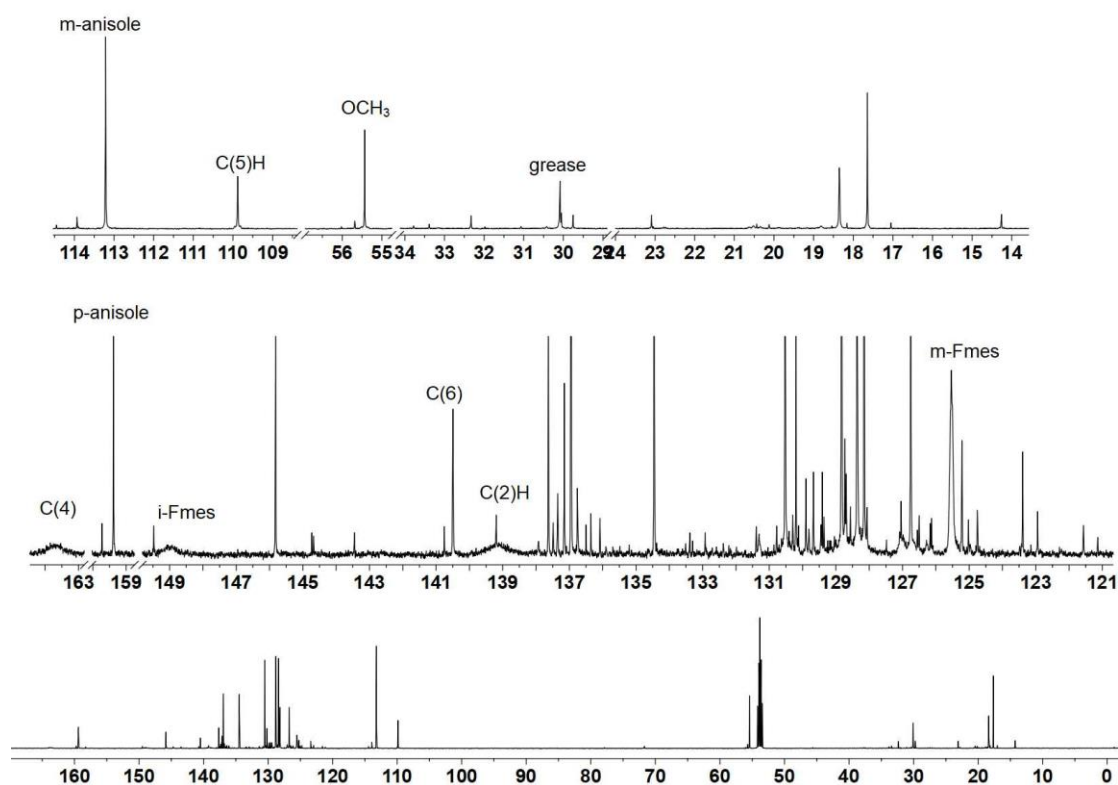


Figure S155. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **28i**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **28i** in pentane at 0 °C.

X-ray crystal structure analysis of compound 28i (erk9733): A yellow plate-like specimen of $\text{C}_{36}\text{H}_{30}\text{BF}_9\text{N}_2\text{O}$, approximate dimensions 0.080 mm x 0.200 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1395 frames were collected. The total exposure time was 20.18 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 56281 reflections to a maximum θ angle of 66.77° (0.84 \AA resolution), of which 10789 were independent (average redundancy 5.217, completeness = 99.2%, $R_{\text{int}} = 5.07\%$, $R_{\text{sig}} = 3.55\%$) and 9924 (91.98%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 22.8203(6) \text{ \AA}$, $b = 8.8132(3) \text{ \AA}$, $c = 31.8125(9) \text{ \AA}$, volume = $6398.1(3) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9695 reflections above $20 \sigma(I)$ with $8.232^\circ < 2\theta < 133.2^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.841. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8170 and 0.9200. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $Pca2_1$, with $Z = 8$ for the formula unit, $\text{C}_{36}\text{H}_{30}\text{BF}_9\text{N}_2\text{O}$. The final anisotropic full-matrix least-squares refinement on F^2 with 957 variables converged at $R1 = 3.30\%$, for the observed data and $wR2 = 8.10\%$ for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was $0.422 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.254 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.040 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.429 g/cm^3 and $F(000)$, 2832 e^- . The hydrogens at N1A and N1B atoms were refined freely. CCDC number: 2041303.

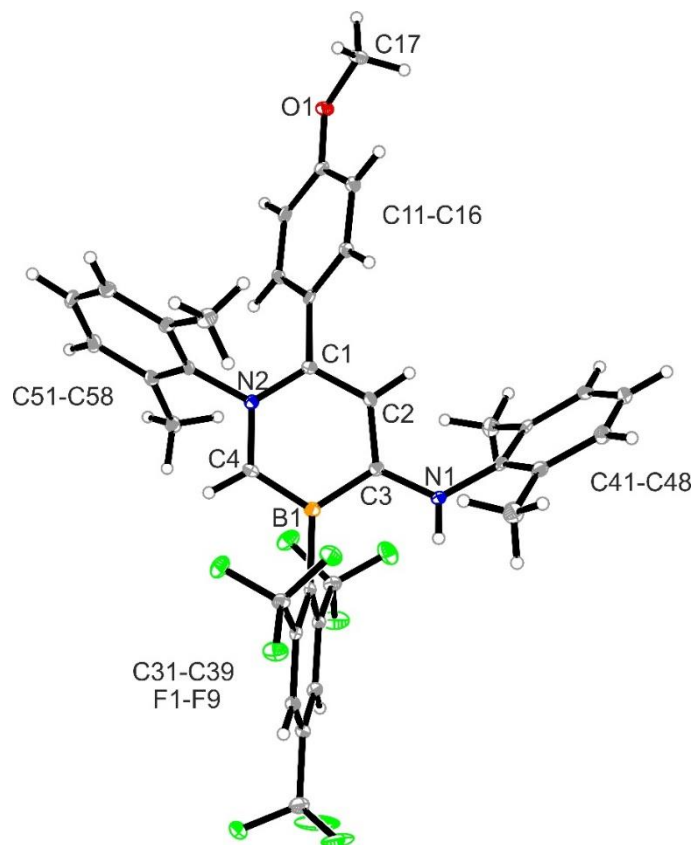
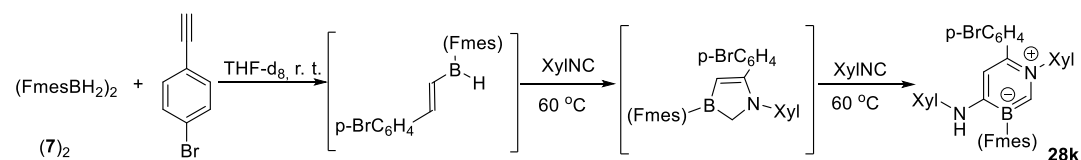


Figure S156. Crystal structure of compound **28i** (thermal ellipsoids are set at 30% probability).

Preparation of the azaborinine derivative **28k**



Scheme S42.

At room temperature, 1-bromo-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1 equiv.) was added to the solution of borane (**7**)₂ (58.8 mg, 0.2 mmol, 1 equiv.) in THF-*d*₈ (1 mL) in a J. Young tube under an argon atmosphere. The mixture was stored at room temperature overnight. Then 2,6-dimethylphenyl isocyanide (26.2 mg, 0.2 mmol, 1 equiv.) was added and the resulting mixture was stored at 60 °C for 2 days. One more equivalent 2,6-dimethylphenyl isocyanide (26.2 mg, 0.2 mmol) was added and the solution was stored at 60 °C for 1 day more. Then all volatiles were removed in vacuo and the residue was purified by flash chromatography with pentane: methylene chloride (20:1) as eluent to finally give the compound **28k** as yellow solid (59 mg, 40 % yield).

HRMS for C₃₅H₂₇N₂BBF₉⁺ [M]⁺: calc. 736.1308; found: 736.1319.

¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K): δ = 8.20 (s, 2H, *m*-Fmes), 7.22 (m, 2H, *m*-*p*-Br-C₆H₄), 7.08 (m, 4H, *m*-Xyl⁽⁴⁾, *p*-Xyl⁽⁴⁾, *p*-Xyl⁽¹⁾), 6.97 (m, 2H, *m*-Xyl⁽¹⁾), 6.91 (m, 2H, *o*-*p*-Br-C₆H₄), 6.64 (s, 1H, C(2)H), 6.08 (s, 1H, C(5)H), 5.50 (s, 1H, NH), 2.22 (s, 6H, *o*-CH₃^{Xyl(4)}), 2.03 (s, 6H, *o*-CH₃^{Xyl(1)}).

¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K): δ = 163.8 (br, C(4)), 148.6 (br, *i*-Fmes), 145.4 (*i*-Xyl⁽¹⁾), 139.6 (C(2)H), 139.4 (C(6)), 137.4 (*i*-Xyl⁽⁴⁾), 137.0 (q, ²J_{FC} = 29.4 Hz, *o*-Fmes) 136.9 (*o*-Xyl⁽⁴⁾),

136.8 (*i-p*-Br-C₆H₄), 134.4 (*o*-Xyl⁽¹⁾), 131.04 (*o-p*-Br-C₆H₄), 130.98 (*m-p*-Br-C₆H₄), 129.9 (q, ²J_{FC} = 33.8 Hz, *p*-Fmes), 128.9 (*p*-Xyl⁽⁴⁾), 128.52 (*m*-Xyl⁽¹⁾), 128.46 (*p*-Xyl⁽¹⁾), 126.9 (*m*-Xyl⁽⁴⁾), 125.6 (br, *m*-Fmes), 124.3 (q, ¹J_{FC} = 275.0 Hz, *o*-CF₃^{Fmes}), 123.8 (q, ¹J_{FC} = 272.1 Hz, *p*-CF₃^{Fmes}), 122.2 (*p-p*-Br-C₆H₄), 109.8 (C(5)H), 18.3 (q, J_{FC} = 1.3 Hz, *o*-CH₃^{Xyl(4)}), 17.6 (*o*-CH₃^{Xyl(1)}).

¹¹B{¹H} NMR (192 MHz, methylene chloride-*d*₂, 299 K): δ = 26.5 (ν_{1/2} ≈ 350 Hz).

¹⁹F NMR (564 MHz, methylene chloride-*d*₂, 299 K): δ = -59.0 (s, 2F, *o*-CF₃), -63.4 (s, 1F, *p*-CF₃).

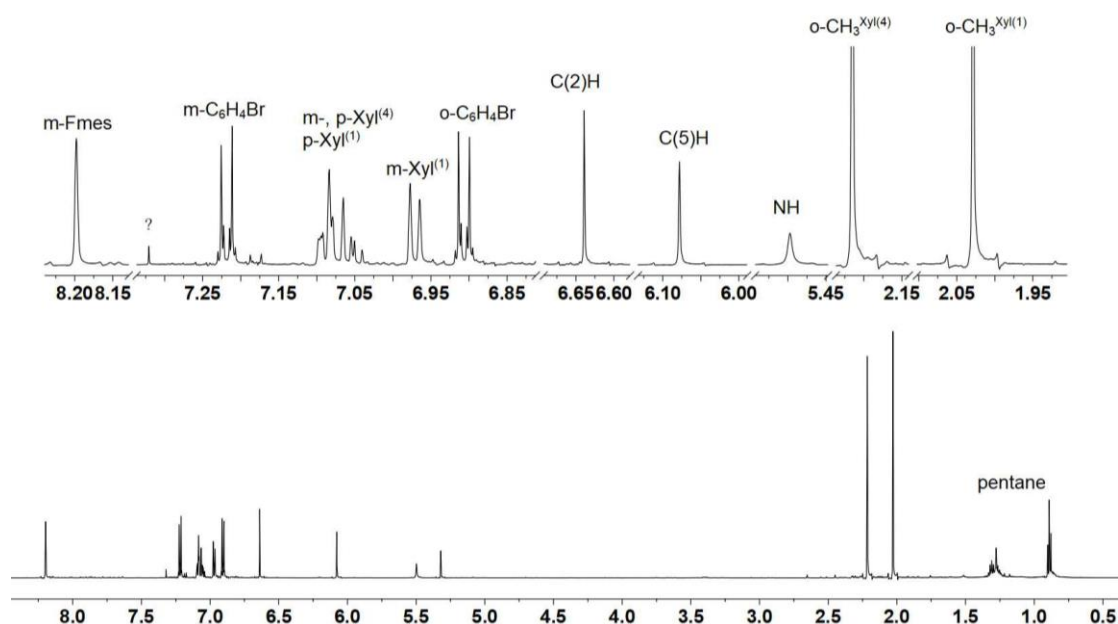


Figure S157. ¹H NMR (600 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **28k**.

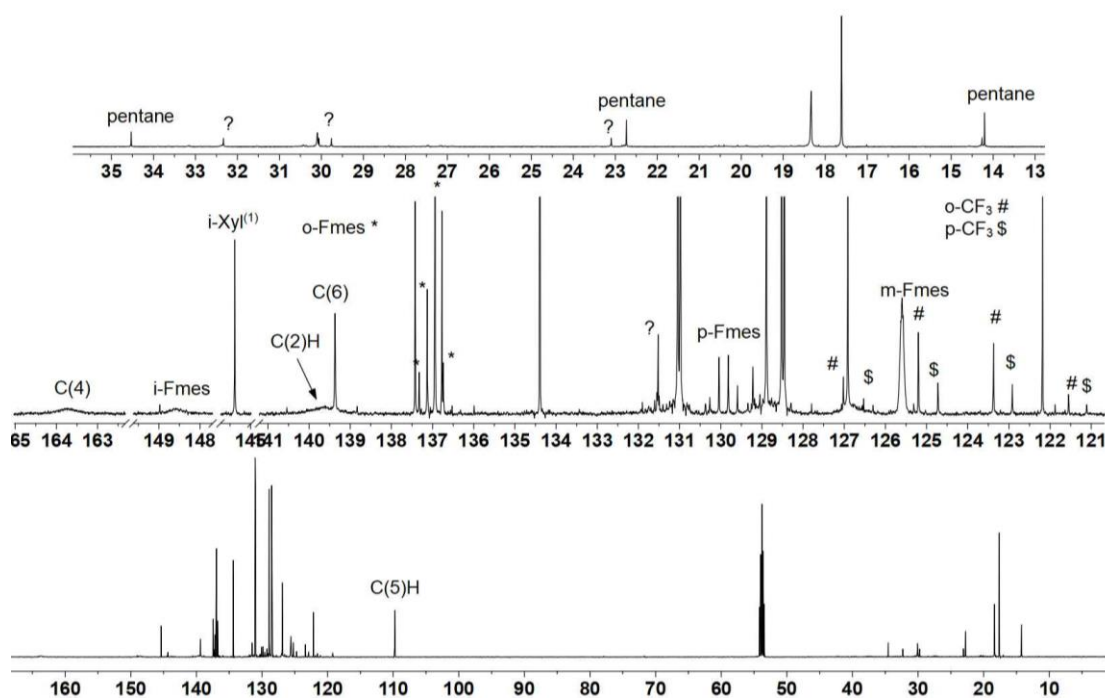


Figure S158. ¹³C{¹H} NMR (151 MHz, methylene chloride-*d*₂, 299 K) spectrum of compound **28k**.

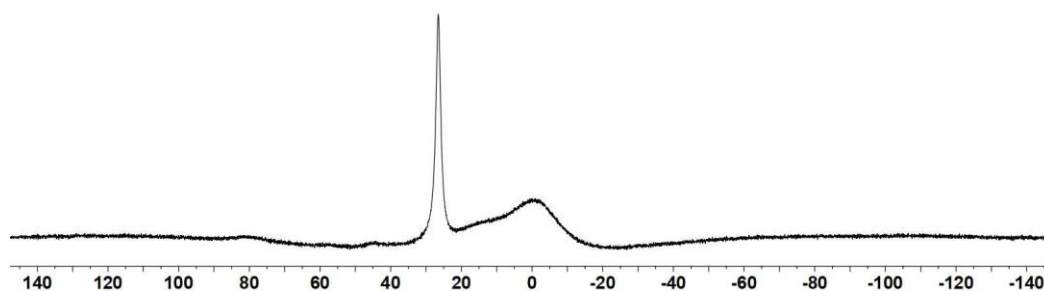


Figure S159. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **26k**.

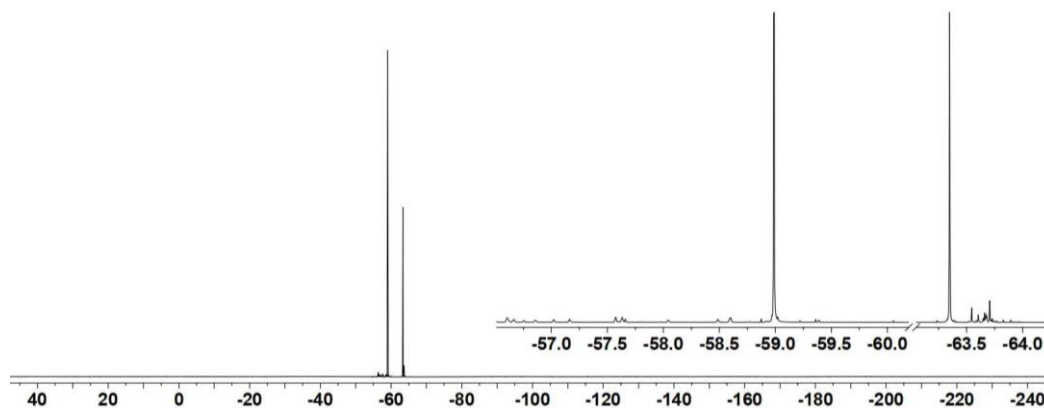


Figure S160. ^{19}F NMR (564 MHz, methylene chloride- d_2 , 299 K) spectrum of compound **28k**.

The crystal suitable for X-ray diffraction analysis was obtained from the solution of compound **28k** in pentane at 0 °C.

X-ray crystal structure analysis of compound 28k (erk9730): A yellow plate-like specimen of $\text{C}_{38}\text{H}_{34}\text{BBrF}_9\text{N}_2$, approximate dimensions 0.060 mm x 0.160 mm x 0.220 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 19.85 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 29496 reflections to a maximum θ angle of 66.84° (0.84 Å resolution), of which 6271 were independent (average redundancy 4.704, completeness = 98.8%, $R_{\text{int}} = 3.39\%$, $R_{\text{sig}} = 2.57\%$) and 5782 (92.20%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.7867(2)$ Å, $b = 12.7686(2)$ Å, $c = 16.8144(3)$ Å, $\alpha = 102.7230(10)^\circ$, $\beta = 103.3830(10)^\circ$, $\gamma = 91.8600(10)^\circ$, volume = 1783.25(6) Å³, are based upon the refinement of the XYZ-centroids of 9881 reflections above $20\sigma(I)$ with $7.125^\circ < 2\theta < 133.3^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.844. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6370 and 0.8770. 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, $\text{C}_{38}\text{H}_{34}\text{BBrF}_9\text{N}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 497 variables converged at $R1 = 3.16\%$, for the observed data and $wR2 = 8.23\%$ for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.341 e/Å³ and the largest hole was -0.656 e/Å³ with an RMS deviation of 0.060 e/Å³. On the basis of the final model, the calculated density was 1.453 g/cm³ and $F(000)$, 794 e⁻. The hydrogen at N1 atom was refined freely. CCDC number: 2041304.

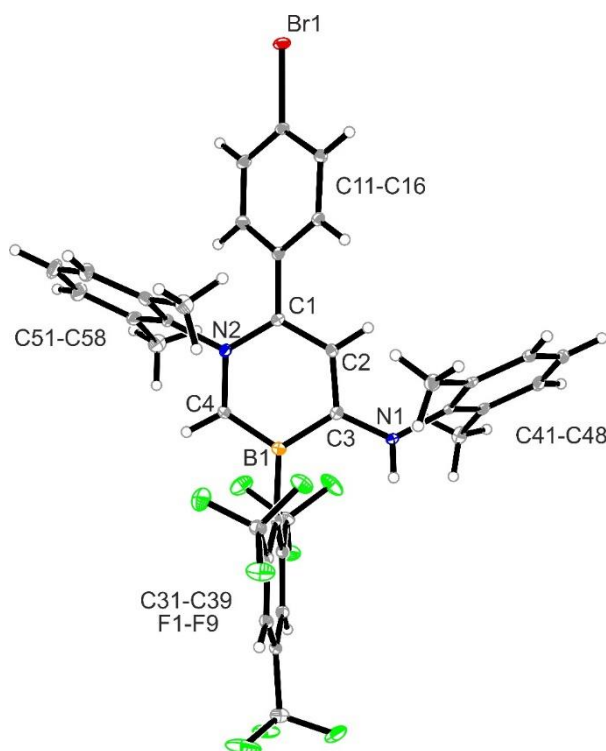


Figure S161. Crystal structure of compound **28k** (thermal ellipsoids are set at 30% probability).

Photophysical part

General Procedures

For UV-Vis and fluorescence measurements, spectroscopic grade solvents were used. Stock solutions of all compounds were prepared in THF ($c = 1 \times 10^{-3}$ M).

UV-Vis spectroscopy

UV-Vis absorption spectra were recorded on a JASCO V-750 with a spectral bandwidth of 1.0 nm and a scan rate of 400 nm min^{-1} . Glass cuvettes with an optical length of 1 cm were used.

Fluorescence spectroscopy

Fluorescence spectra were recorded on a JASCO Spectrofluorometer FP-8500 in quartz cuvettes with an optical length of 1 cm. The quantum yields (Φ_F) of all samples in water [refractive index (n) = 1.33] were measured by using quinine sulfate as a standard which was dissolved in 0.1 M H_2SO_4 [refractive index (n) = 1.33]. The absorbance intensities were kept below 0.1 in order to minimize re-absorption effects. Excitation wavelength (λ_{exc}): 325 nm for **16c-e** and 350 nm for the remaining compounds.

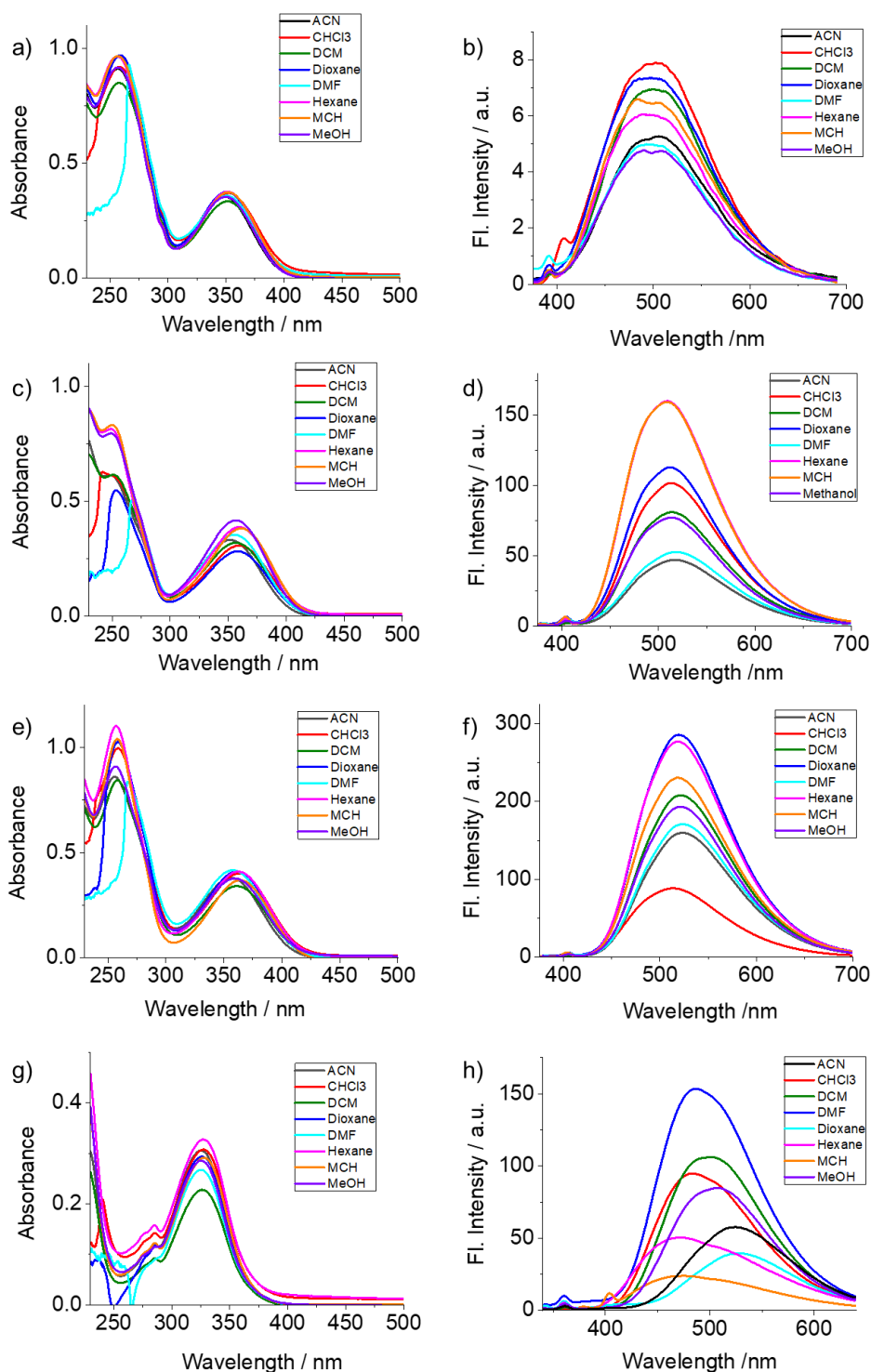


Figure S162. Absorption and emission changes of **10b** (a, b) **16a** (c, d), **16b** (e, f) and **16c** (g, h) in organic solvents of different polarity, conc. (c) = 10 μ M (1×10^{-5} M) and path length (*l*) = 1 cm.

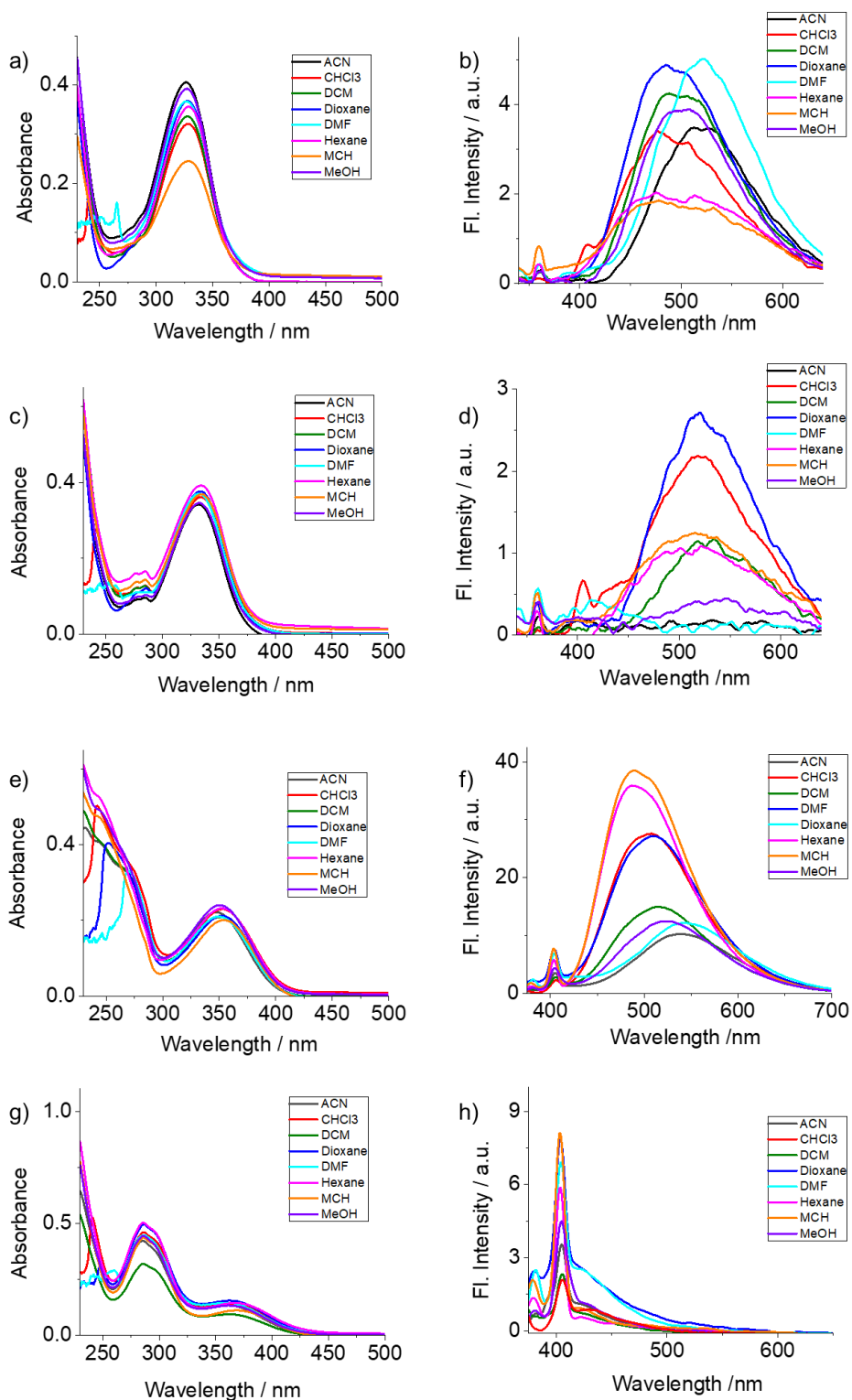


Figure S163. Absorption and emission changes of **16d** (a, b) **16e** (c, d), **16f** (e, f) and **16g** (g, h) in organic solvents of different polarity, conc. (c) = 10 μ M (1×10^{-5} M) and path length (l) = 1 cm.

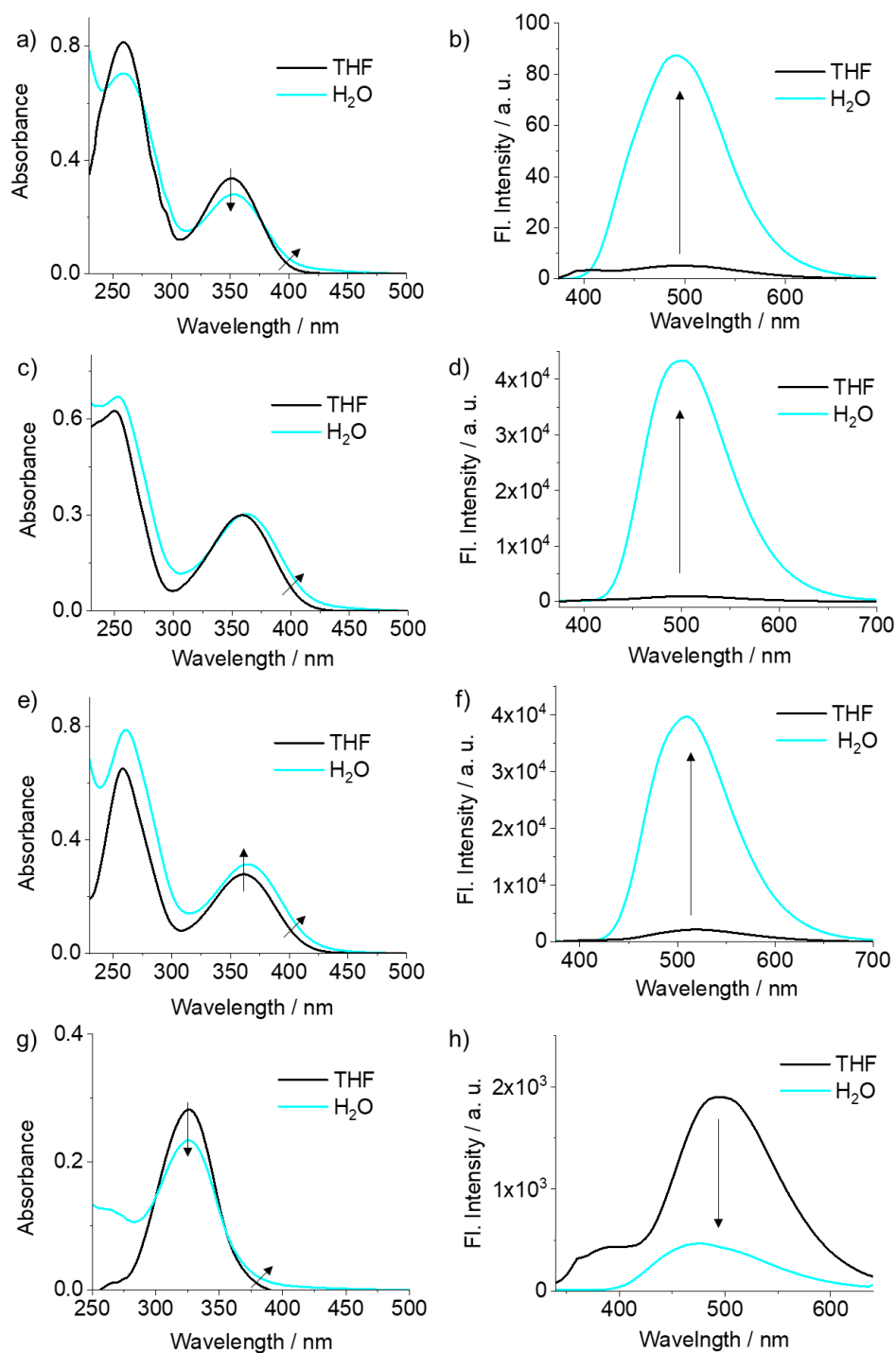


Figure S164. Absorption and emission changes of **10b** (a, b) **16a** (c, d), **16b** (e, f) and **16c** (g, h) in water (100%, cyan) and THF (100%, black), conc. (c) = 10 μ M (1×10^{-5} M) and path length (l) = 1 cm. The arrows indicate the spectral progression upon addition of water.

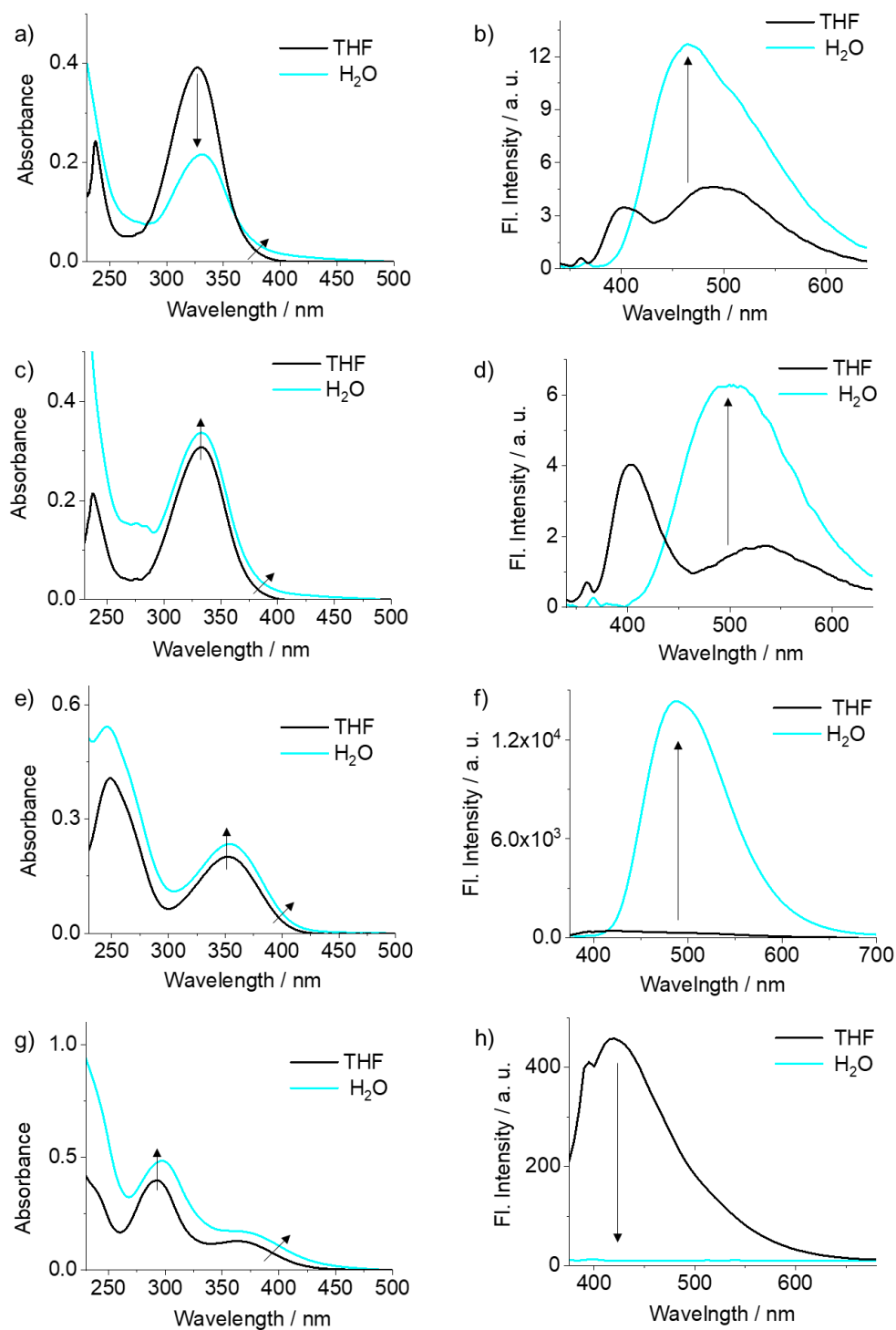


Figure S165. Absorption and emission changes of **16d** (a, b) **16e** (c, d), **16f** (e, f) and **16g** (g, h) in water (100%, cyan) and THF (100%, black), conc. (c) = 10 μ M (1×10^{-5} M) and path length (*l*) = 1 cm. The arrows indicate the spectral progression upon addition of water.

Table S1. Relative fluorescence quantum yields (Φ_F) of **16a-g** and **10b**, estimated using quinine sulfate in 0.05 M H₂SO₄ (Φ_F = 55 %) as a reference.

	Relative quantum yield (Φ_F) (%)	2 nd measurement with newly synthesized material
16a	68.6	65.1
16b	70.9	67.0
16c	4.2	
16d	0.38	
16e	0.22	
16f	64.8	63.2
16g	0.1	
10b	0.47	

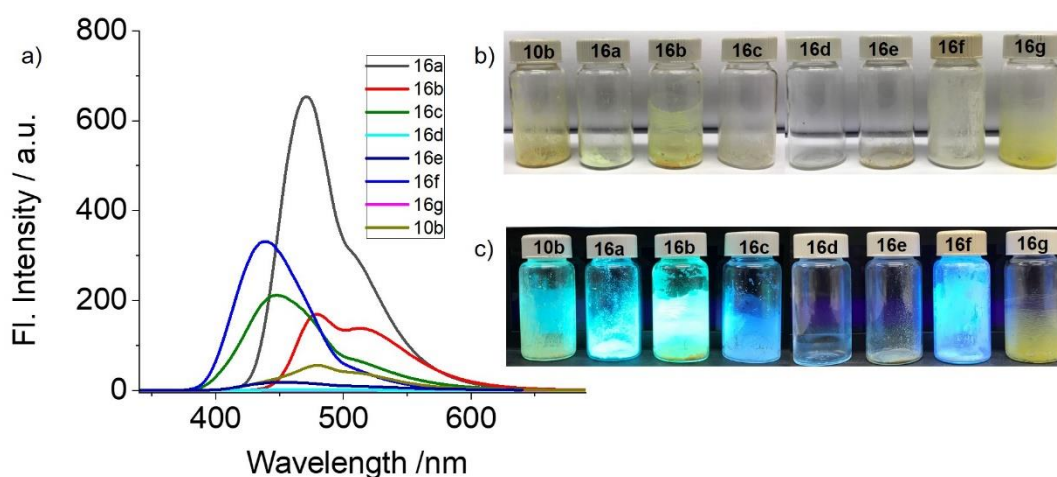


Figure S166. a) Solid-state emission spectra of **16a-g** (**16d** was a viscous oil in nature) and **10b** and corresponding photographs under daylight (b) and UV light (c).

References

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