A Deprotonation Pathway to Reactive [B]=CH₂ Boraalkenes

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General Information

All experiments were carried out under a dry argon atmosphere using standard Schlenk-type glassware and/or in a glove box. Toluene, CH₂Cl₂, pentane, THF and Et₂O were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. NMR spectra were recorded on a Varian UNITY plus 600 MHz spectrometer (¹H 599 MHz, ¹¹B 192 MHz, ¹³C 151 MHz, ¹⁹F 564 MHz). ¹H and ¹³C NMR chemical shifts are given relative to tetramethylsilane (TMS) and referenced to the solvent signal. ³¹P, ²⁹Si, ¹⁹F and ¹¹B are referenced according to the proton resonance of TMS as the primary reference for the unified chemical shift scale (IUPAC recommendation 2001: R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* 2001, **73**, 1795-1818]. NMR assignment were supported by additional 2D-NMR experiments and ¹⁹F or ³¹P decoupled experiments. HRMS was recorded on GTC Waters Micromass (Manchester, UK) and melting points were measures on TA-instruments DSC-2010. Elemental analyses were performed on a Foss-Heraeus CHNO-Rapid. IR spectra were recorded on a Varian 3100 TF-IR (Excalibur Series).

Unless otherwise noted, all chemicals were purchased from commercially available sources (Sigma-Aldrich, TCI, ABCR, Alfa-Aesar, Fluorochem) and used as received unless stated otherwise. $B(C_6F_5)_3$ was obtained from Boulder Scientific and recrystallized from cold pentane prior to use. Deuterated solvents were dried over CaH₂, distilled under reduced pressure and stored over molecular sieves in argon atmosphere. Compounds IMes¹, FpxylBH₂SMe₂², IMesBH₂C₆F₅³ and HB(C₆F₅)₂⁴ were prepared according to the reported methods. **Warning**: Carbon monoxide is a toxic gas that must be handled with due care.

X-Ray diffraction: Data sets for compounds 3a, 6b, 7a, 8a, 8b, 9b, 10a, 10a-H₂O, 11b, 12a, 13a, 14b, 15b, 16b, 17b, 22a and 23a were collected with a Bruker D8 Venture Photon III Diffractometer. Data sets for compounds 10b und 20b were collected with a Bruker APEX II CCD Diffractometer. Programs used: data collection: APEX3 V2019.1-0⁵ (Bruker AXS Inc., 2019); cell refinement: SAINT V8.40A (Bruker AXS Inc., 2019); data reduction: SAINT V8.40A (Bruker AXS Inc., 2019); absorption correction, SADABS V2016/2 (Bruker AXS Inc., 2019); structure solution SHELXT-2015⁶ (Sheldrick, G. M. Acta Cryst., 2015, A71, 3-8); structure refinement SHELXL-2015⁷ (Sheldrick, G. M. Acta Cryst., 2015, C71 (1), 3-8) and graphics, XP⁸ (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 7a, 16b and 22a one C₆F₅ group, for compounds 8b, 11b and 17b one CF₃ group, for compound 8a two trifluoromethylsulfonylamid anions, for compound 9b three CF₃ groups, for compound **10a** the trifluoromethylsulfonylamid anion, for compound **13a** the bora- β -lactame like four-member ring, for compound 15b two CF₃ groups and the dichloromethane molecule were found disordered over two or three positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compound **3a** a half heptane molecule and for compound 23a a mixture of dichloromethane and pentane molecules 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 solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. Compound 11a was refined as a 2-component twin with BASF 0.46 using the HKLF5 option.

Preparation of compound 6b





A solution of borane **5b** (FpXylBH₂·SMe₂)(2.02 g, 7.0 mmol) in pentane (30 mL) was added into a stirred suspension of **4** (IMes)(2.13 g, 7.0 mmol) in pentane (30 mL). The resulting mixture was stirred overnight at room temperature to give the beige suspension. The liquid phase was filtered off via cannula and the solid residue was washed with pentane (3x10 mL). After drying the residue, compound **6b** was obtained as air-stable off-white solid (2.65 g, 5.0 mmol, 71% yield).

Melting point: 196.3 °C

IR (KBr): v(BH) 2420, 2276 cm⁻¹

Elemental analysis calculated for $C_{29}H_{29}BF_6N_2$ (530.4): C 65.67, H 5.51, N 5.28; found: C 65.33, H 5.48, N 5.32.

¹**H** NMR (599 MHz, 299K, CDCl₃): $\delta = [7.33 \text{ (d, } ^{3}J_{\text{HH}} = 8.1 \text{ Hz}, m), 7.19 \text{ (s, }o), 7.10 \text{ (d, }^{3}J_{\text{HH}} = 8.1 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), 6.94 \text{ (s, 2H, =CH)}, 6.84 \text{ (s, 4H, CH}^{\text{Mes}}), 2.28 \text{ (s, 6H, }p\text{-CH}_{3}^{\text{Mes}}), 2.12 \text{ (br m, 2H, BH}_{2}), 2.04 \text{ (s, 12H, }o\text{-CH}_{3}^{\text{Mes}}).$

¹³C{¹H} NMR (151 MHz, 299K, CDCl₃): $\delta = 171.9$ (br, BC^{IMes}), [151.4 (br, BC^{FpXyl}), 136.5 (q, ²*J*_{FC} = 28.9 Hz, *o*-C), 136.1 (q, ³*J*_{FC} = 3.8 Hz, *o*-CH), 129.9 (q, ²*J*_{FC} = 28.9 Hz, *m*-C), 125.1 (q, ¹*J*_{FC} = 274.8 Hz, *o*-CF₃), 124.3 (q, ¹*J*_{FC} = 272.9 Hz, *m*-CF₃), 124.0 (q, ³*J*_{FC} = 5.8 Hz, *m*-CH), 120.4 (q, ³*J*_{FC} = 3.7 Hz, *p*-CH)](FpXyl), [139.3 (*p*-C), 134.8 (*o*-C), 133.7 (NC), 129.0 (CH), 20.9 (*p*-CH₃), 17.6 (*o*-CH₃)](Mes), 121.4 (=CH).

¹¹B{¹H} NMR (192 MHz, 299K, CDCl₃): $\delta = -24.4 (v_{1/2} \approx 50 \text{ Hz})$

¹¹**B NMR** (192 MHz, 299K, CDCl₃): δ = -24.4 (t, ¹*J*_{BH} ≈ 88 Hz)

¹⁹**F** NMR (564 MHz, 299K, CDCl₃): δ = -59.3 (s, 1F), -62.8 (s, 1F)



Figure S1: ¹H NMR (599 MHz, CDCl₃, 299 K) spectrum of compound **6b** (* CHCl₃).



Figure S2: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CDCl₃, 299K) spectra of compound **6b**.





Figure S4: ¹⁹F NMR (564 MHz, CDCl₃, 299K) spectrum of compound **6b**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **6b** in dichloromethane covered with pentane at room temperature.

X-ray crystal structure analysis of compound 6b (erk9897): A colorless prism-like specimen of C₂₉H₂₉BF₆N₂, approximate dimensions 0.166 mm x 0.222 mm x 0.332 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 Mo Ims (MoK_a, $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 750 frames were collected. The total exposure time was 5.21 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 62824 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 5811 were independent (average redundancy 10.811, completeness = 99.3%, $R_{int} = 4.83\%$, $R_{sig} = 2.15\%$) and 5208 (89.62%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 21.6922(7) Å, <u>b</u> = 7.2551(2) Å, <u>c</u> = 35.0558(11) Å, β = 106.2820(10)°, volume = 5295.8(3) Å³, are based upon the refinement of the XYZ-centroids of 9915 reflections above 20 $\sigma(I)$ with 5.146° < 2 θ $< 54.92^{\circ}$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.945. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9650 and 0.9830. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C2/c, with Z = 8 for the unit, C₂₉H₂₉BF₆N₂. The full-matrix formula final anisotropic least-squares refinement on F^2 with 357 variables converged at R1 = 4.87%, for the observed data and wR2 = 12.04% for all data. The goodness-of-fit was 1.058. The largest peak in the final difference electron density synthesis was 0.562 e⁻ $/Å^3$ and the largest hole was -0.254 e⁻/Å³ with an RMS deviation of 0.047 e⁻/Å³. On the basis of the final model, the calculated density was 1.330 g/cm³ and F(000), 2208 e⁻. The hydrogens at B1 atom were refined freely. CCDC Nr.: 2108142.



Figure S5: Crystal structure of compound **6b** (thermal ellipsoids are set at 30% probability).

Preparation of compound 7a





Borane adduct **6a** [IMesBH₂C₆F₅] (96.8 mg, 0.2 mmol) was suspended in dichloromethane (3 mL) and a solution of triflic acid (29.8 mg, 0.2 mmol) in dichloromethane (2 mL) was added. Effervescence occurred immediately. The mixture was stirred for 30 minutes at room temperature, subsequently the volatiles were removed under reduced pressure. The residue was treated with pentane (5 mL) and vigorously stirred for 30 minutes at room temperature to yield a fine white suspension. The pentane fraction was carefully removed and the residue was washed with pentane (3x 2 mL). Drying the residue in vacuo provided compound **7a** as a fine white powder (108.6 mg, 0.172 mmol, 86% yield).

Melting point: 215.3 °C

Elemental analysis calculated for C₂₈H₂₅N₂BF₈SO₃ (632.4): C 53.18, H 3.99, N 4.43; found: C 53.36 H 4.40, N 4.58.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.17 (s, 2H, =CH), [6.942, 6.938](each s, each 2H, CH^{Mes}), 3.85 (br m, 1H, BH), 2.33 (s, 6H, *p*-CH₃^{Mes}), [2.05, 2.04](each s, each 6H, *o*-CH₃^{Mes})

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 159.2$ (br, BC^{IMes}), 140.8 (*p*-C^{Mes}), [135.0, 134.8](*o*-C^{Mes}), 133.0 (*i*-C^{Mes}), [129.5, 129.4](CH^{Mes}), 124.2 (=CH), 118.8 (q, ¹*J*_{CF} = 318.7, OTf), 21.0 (*p*-CH₃^{Mes}), [17.38, 17.36](*o*-CH₃^{Mes}), [C₆F₅ not listed].

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -7.5 (v_{1/2} \approx 200 Hz)

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -7.5 (br d, ¹*J*_{BH} \approx 80 Hz)

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = -77.7 (s, 3F, OTf), [-130.9 (m, 2F, *o*-), -159.2 (t, ³*J*_{FF} = 19.9 Hz, 1F, *p*-), -165.7 (m, 2F, *m*-)](C₆F₅) [Δδ¹⁹F_{m,p} = 6.5].



Figure S7: ¹¹B and ¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂) spectra of compound 7a.



Figure S8: ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K) spectrum and excerpt from excerpt from ¹H,¹³C gHMBC (599/151 MHz, CD₂Cl₂, 299K) spectrum of compound **7a**.



Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **7a** in dichloromethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 7a (erk9983): A colorless prism-like specimen of C₂₈H₂₅BF₈N₂O₃S, approximate dimensions 0.130 mm x 0.203 mm x 0.258 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK α (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 1259 frames were collected. The total exposure time was 5.09 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 50990 reflections to a maximum θ angle of 25.36° (0.83 Å resolution), of which 5245 were independent (average redundancy 9.722, completeness = 99.7%, R_{int} = 3.76%, R_{sig} = 1.96%) and 5076 (96.78%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 28.1536(10) Å, <u>b</u> = 14.3388(5) Å, <u>c</u> = 14.2090(6) Å, volume = 5736.0(4) Å³, are based upon the refinement of the XYZ-centroids of 9862 reflections above 20 σ (I) with $4.966^{\circ} < 2\theta < 50.65^{\circ}$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.957. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9510 and 0.9750. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Aba2, with Z = 8 for the formula unit, $C_{28}H_{25}BF_8N_2O_3S$. The final anisotropic full-matrix least-squares refinement on F^2 with 498 variables converged at R1 = 3.93%, for the observed data and wR2 = 9.77% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.787 e⁻ $/Å^3$ and the largest hole was -0.306 e⁻/Å³ with an RMS deviation of 0.048 e⁻/Å³. On the basis of the final model, the calculated density was 1.465 g/cm³ and F(000), 2592 e⁻. The hydrogen at B1 atom was refined freely. CCDC Nr.: 2108143.



Figure S10: Crystal structure of compound 7a (thermal ellipsoids are set at 30% probablility).

Preparation of compound **7b**





Borane adduct **6b** [IMesBH₂FpXyl] (106.0 mg, 0.2 mmol) was suspended in dichloromethane (3 mL) and a solution of triflic acid (29.8 mg, 0.2 mmol) in dichloromethane (2 mL) was added. Effervescence occurred immediately. The mixture was stirred for 30 minutes at room temperature, subsequently the volatiles were removed under reduced pressure. The residue was treated with pentane (5 mL) and vigorously stirred for 30 minutes at room temperature to give a fine white suspension. The pentane fraction was carefully removed and the residue was washed with pentane (3x 2 mL). Drying of the residue in vacuo provided compound **7b** as a fine white powder (113.2 mg, 0.167 mmol, 83% yield).

Melting point: 221.3 °C (melts with decomposition)

Elemental analysis calculated for $C_{30}H_{28}N_2BF_9SO_3$ (678.4): C 53.11, H 4.16, N 4.13; found: C 52.73 H 4.08, N 4.30.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.48 \text{ (d, } {}^{3}J_{\text{HH}} = 8.4 \text{ Hz}, m), 7.28 \text{ (d, } {}^{3}J_{\text{HH}} = 8.4 \text{ Hz}, p), 7.26 \text{ (s, } o)](\text{each 1H, CH}^{\text{FpXyl}}), 7.13 \text{ (s, 2H, =CH)}, [7.01, 6.78] (\text{each s, each 2H, CH}^{\text{Mes}}), [2.30 (p-), 2.17 (o-), 1.88 (o-)](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), 3.79 (br, 1H, BH).$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 159.6$ (br, BC^{IMes}), [140.7 (*p*-C), 135.03 (*o*-C), 134.99 (*o*-C), 133.1 (*i*-C), 129.8 (*m*-CH), 129.7 (*m*-CH), 21.0 (*p*-CH₃), 17.6 (q, $J_{FC} = 1.6$ Hz, *o*-CH₃), 17.4 (*o*-CH₃)](Mes), [144.3 (br, BC), 135.5 (q, $^2J_{FC} = 30.0$ Hz, o-C), 131.4 (br m, *o*-CH), 131.1 (q, $^2J_{FC} = 31.7$ Hz, *m*-C), 125.1 (q, $^1J_{FC} = 274.6$ Hz, *o*-CF₃), 125.0 (q, $^3J_{FC} = 5.8$ Hz, *m*-CH), 124.3 (q, $^1J_{FC} = 272.8$ Hz, *m*-CF₃), 123.3 (q, $^3J_{FC} = 3.6$ Hz, *p*-CH)](FpXyl), 124.3 (=CH), 119.0 (q, $^1J_{FC} = 318.6$ Hz, OTf).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -5.1 (v_{1/2} \approx 350 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -5.1 (v_{1/2} \approx 350 \text{ Hz})$

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): $\delta = [-58.5 \text{ (d, } J = 5.6 \text{ Hz}), -63.7 \text{ (s)}](\text{each 1F, FpXyl}), -77.5 \text{ (s, 1F, OTf)}.$







Figure S13: ¹¹B and ¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂) spectra of compound 7b.



Figure S14: ¹⁹F NMR (564 MHz, CD₂Cl₂) spectrum of compound 7b.

Preparation of compound 8a





A solution of bis(trifluoromethanesulfonyl)imide (84.3 mg, 0.3 mmol) in CH_2Cl_2 (5 mL) was added dropwise into a suspension of the borane adduct **6a** (145.2 mg, 0.3 mmol) in CH_2Cl_2 (5 mL). Effervescence occurred almost immediately. The homogenous off-yellow solution reacted for 30 minutes at room temperature. Subsequently the volatiles were removed under reduced pressure. The oily residue was treated with pentane (5 mL) and then vigorously stirred for 30 minutes at room temperature, resulting in the precipitation of a white solid. It was separated by decantation, washed with pentane (3x 3 mL) and dried in vacuo. Compound **8a** was obtained as a white solid (192.4 mg, 0.252 mmol, 84% yield).

Melting point: 139.3 °C

Elemental analysis calculated for $C_{29}H_{25}N_3BF_{11}O_4S_2$ (763.5): C 45.62, H 3.30, N 5.51; found: C 45.42 H 3.53, N 5.57.

The solution of the obtained white solid in CD_2Cl_2 shows of two diastereomers in ca 4:3 ratio (¹H, ¹⁹F) at 299 K.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): **major isomer** δ = 7.223 (s, 2H, =CH), 6.948 (m, 4H, CH^{Mes}), 4.00 (br, 1H, BH), 2.329 (s, 6H, *p*-CH₃^{Mes}), 2.039 (s, 12H, *o*-CH₃^{Mes}); **minor isomer** δ = 7.217 (s, 2H, =CH), 6.952 (m, 4H, CH^{Mes}), 4.00 (br, 1H, BH), 2.326 (s, 6H, *p*-CH₃^{Mes}), [2.046, 2.02] (each s, each 6H, *o*-CH₃^{Mes}).

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂)[selected resonances]: **major isomer** δ = 157.1 (br m, BC^{IMes}), 141.1 (*p*-C^{Mes}), [134.8, 134.6](*o*-C^{Mes}), 132.68 (*i*-C^{Mes}), [129.628, 129.6](CH^{Mes}), 124.6 (=CH), [119.3 (q, ¹J_{FC} = 320.4), 118.79 (q, ¹J_{FC} = 321.1)](CF₃), 21.02 (*p*-CH₃^{Mes}), 17.3(*o*-CH₃^{Mes}); **minor isomer** δ = 157.1 (br m, BC^{IMes}), 141.2 (*p*-C^{Mes}), [134.70, 134.66](*o*-C^{Mes}), 132.65 (*i*-C^{Mes}), [129.7, 129.632](CH^{Mes}), 124.7 (=CH), [119.4 (q, ¹J_{FC} = 320.6), 118.83 (q, ¹J_{FC} = 321.7)](CF₃), 21.01 (*p*-CH₃^{Mes}), 17.3 (*o*-CH₃^{Mes}).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -5.9 (v_{1/2} \approx 380 Hz)

¹¹**B NMR** (192 MHz, 299K, CD₂Cl₂): $\delta = -5.9 (v_{1/2} \approx 380 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): **major isomer** δ = [-77.1, -79.5](each s, each 3F, FpXyl), [-130.7 (m, 2F, *o*-), -158.0 (t, ³*J*_{FF} = 20.1 Hz, 1F, *p*-), -165.4 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 7.4]; **minor isomer** δ = [-76.8, -78.8](each s, each 3F, FpXyl), [-130.6 (m, 2F, *o*-), -157.9 (t, ³*J*_{FF} = 20.1 Hz, 1F, *p*-), -165.1 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 7.2].





Figure S18: ¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂) spectrum of compound 8a.



0 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -51

Figure S20: ¹¹B{¹H} NMR (243 MHz, C₆D₅Br) spectra of compound **8a** at various temperatures.



Figure S21: ¹⁹F NMR (564 MHz, C₆D₅Br) spectra of compound **8a** at various temperatures.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 8a in CH₂Cl₂/heptane at room temperature.

X-ray crystal structure analysis of compound 8a (erk10281): A colorless, plate-like specimen of C₂₉H₂₅BF₁₁N₃O₄S₂, approximate dimensions 0.052 mm x 0.092 mm x 0.202 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 0.71073$ Å). A total of 784 frames were collected. The total exposure time was 4.36 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 180894 reflections to a maximum θ angle of 26.78° (0.79 Å resolution), of which 13832 were independent (average redundancy 13.078, completeness = 99.4%, R_{int} = 11.84%, R_{sig} = 4.84%) and 9292 (67.18%) were greater than $2\sigma(F^2)$. The final cell constants of a = 17.1214(10) Å, b = 16.4782(7) Å, c = 23.4675(12) Å, β = 100.205(2)°, volume = 6516.1(6) Å³, are based upon the refinement of the XYZcentroids of 9884 reflections above 20 σ (I) with 4.307° < 2 θ < 49.91°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.871. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9480 and 0.9860. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P21/n, with Z = 8 for the formula unit, $C_{29}H_{25}BF_{11}N_3O_4S_2$. The final anisotropic fullmatrix least-squares refinement on F^2 with 1194 variables converged at R1 = 4.85%, for the observed data and wR2 = 13.02% for all data. The goodness-of-fit was 1.064. The largest peak in the final difference electron density synthesis was 0.739 e-/Å³ and the largest hole was -0.319 e-/Å³ with an RMS deviation of 0.071 e-/Å³. On the basis of the final model, the calculated density was 1.556 g/cm³ and F(000), 3104 e⁻. The hydrogen atoms at B1A and B1B atoms were refined freely. CCDC Nr.: 2156395.



Molecular B (rac- (R^{B}, R^{S}) -8a)

Figure S22: Crystal structure of compound **8a** (two diastereomers were found in the asymmetric unit (molecule "A" and molecule "B"; thermal ellipsoids are set at 30% probability).

Preparation of compound **8b**



Scheme S5

A solution of bis(trifluoromethanesulfonyl)imide (84.3 mg, 0.3 mmol) in CH_2Cl_2 (5 mL) was added dropwise into a suspension of borane adduct **6b** (159.0 mg, 0.3 mmol) in CH_2Cl_2 (5 mL). Effervescence occurred almost immediately. The homogenous pale-yellow solution reacted for 30 minutes at room temperature. Subsequently the volatiles were removed under reduced pressure. The oily residue was treated with pentane (5 mL) and then vigorously stirred for 30 minutes at room temperature, resulting in the precipitation of a white solid. It was separated by decantation, washed with pentane (3x 3 mL) and dried in vacuo to give compound **8b** as a white solid (211.1 mg, 0.261 mmol, 87% yield).

Decomposition point: 130.6 °C

Elemental analysis calculated for $C_{31}H_{28}N_3BF_{12}O_4S_2$ (809.5): C 45.99, H 3.49, N 5.19; found: C 45.32 H 3.51, N 5.15.

The obtained white solid in CD_2Cl_2 at 299K showed dynamic behaviour. At 213K the ratio of diastereomers was estimated to ca 4:3 (¹⁹F).

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.50 \text{ (d, } ^{3}J_{\text{HH}} = 8.2 \text{ Hz}), 7.31 \text{ (d, } ^{3}J_{\text{HH}} = 8.2 \text{ Hz}), 7.17 \text{ (s)}](\text{each 1H, CH}^{\text{FpXyl}}), 7.18 \text{ (s, 2H, =CH)}, [6.98, 6.82] (\text{each br, each 2H, CH}^{\text{Mes}}), 3.98 \text{ (br, 1H, BH)}, [2.30 \text{ (s)}, 2.13 \text{ (br)}, 1.88 \text{ (br)}](\text{each 6H, CH}_{3}^{\text{Mes}}).$

¹**H** NMR (599 MHz, 213K, CD₂Cl₂): δ = major diastereomer δ = [7.47 (d, ³*J*_{HH} = 8.3 Hz), 7.27 (d, ³*J*_{HH} = 8.3 Hz), 6.98 (s)](each 1H, CH^{FpXyl}), 7.21 (s, 2H, =CH), [7.02, 6.72](each s, each 2H, CH^{Mes}), 3.80 (br, 1H, BH), [2.26, 2.11, 1.76](each s, each 6H, CH₃^{Mes}), minor diastereomer δ = [7.45 (d, ³*J*_{HH} = 8.3 Hz), 7.26 (d, ³*J*_{HH} = 8.3 Hz), 7.09 (s)](each 1H, CH^{FpXyl}), 7.20 (s, 2H, =CH), [7.00, 6.72](each s, each 2H, CH^{Mes}), 3.80 (br, 1H, BH), [2.24, 2.11, 1.75](each s, each 6H, CH₃^{Mes}).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -2.8 (v_{1/2} \approx 500 Hz)

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -2.8 (v_{1/2} \approx 550 Hz)

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): $\delta = [-58.6, -63.7](\text{each 3F, FpXyl}), [-76.8, -78.9, -79.7](\Sigma 6F, NTf_2)$

¹⁹**F NMR** (564 MHz, 213K, CD₂Cl₂): **major diastereomer** $\delta = [-58.6, -63.5]$ (each 1F, FpXyl), [-77.6, -80.3](each 1F, NTf₂), **minor diastereomer** $\delta = [-58.6, -63.3]$ (each 1F, FpXyl), [-77.3, -79.1](each 1F, NTf₂)



Figure S23: ¹H NMR (599 MHz, CD₂Cl₂) spectra of compound **8b** at various temperatures.



7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 4.5 4.3 4.1 3.9 3.7 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2

Figure S24: ¹H NMR (599 MHz, C₆D₅Br) spectra of compound **8b** at various temperatures.



Figure S25: ¹H NMR (599 MHz, CD₂Cl₂, 299K) spectrum of compound **8b**.



Figure S27: ¹¹B and ¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂) spectra of compound 8b.







6.5 -57.5 -58.5-62.0 -62.5 -63.0 -63.5 -74.5 -75.0 -75.5 -76.0 -76.5 -77.0 -77.5 -78.0 -78.5 -79.0 -79.5 -80.0 -80.5 -81.0 -81

Figure S29: ¹⁹F NMR (564 MHz, C₆D₅Br) spectra of compound **8b** at various temperatures [*: impurity].

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **8b** in dichloromethane covered with pentane at room temperature.

X-ray crystal structure analysis of compound 8b (erk9982): A colorless prism-like specimen of C₃₁H₂₈BF₁₂N₃O₄S₂, approximate dimensions 0.184 mm x 0.209 mm x 0.332 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK α (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 607 frames were collected. The total exposure time was 1.13 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 27155 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 6151 were independent (average redundancy 4.415, completeness = 99.3%, R_{int} = 4.77%, R_{sig} = 3.63%) and 5787 (94.08%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 11.6418(2) Å, <u>b</u> = 16.3588(4) Å, <u>c</u> = 18.4012(4) Å, volume = 3504.43(13) Å³, are based upon the refinement of the XYZ-centroids of 9916 reflections above 20 σ (I) with $4.427^{\circ} < 2\theta < 50.06^{\circ}$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.948. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9200 and 0.9540. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{31}H_{28}BF_{12}N_3O_4S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 515 variables converged at R1 = 2.88%, for the observed data and wR2 = 7.02% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 0.468 e⁻ $/Å^3$ and the largest hole was -0.221 e⁻/Å³ with an RMS deviation of 0.040 e⁻/Å³. On the basis of the final model, the calculated density was 1.534 g/cm³ and F(000), 1648 e⁻. The hydrogen at B1 atom was refined freely. CCDC Nr.: 2108144.



Figure S30: Crystal structure of compound 8b (thermal ellipsoids are set at 30% probability).

Preparation of compound 9a



Scheme S6

Method 1: IMesBH₂C₆F₅ (**6a**) (484 mg, 1.0 mmol) and triflic acid (151 mg, 1.0 mmol) were dissolved in toluene (50 mL) while effervescence occurred. After 30 minutes of stirring at room temperature, the mixture was cooled by using a CO₂(s) / i-PrOH bath. Then a solution of MeMgBr was added dropwise (0.4 mL of 3M solution of MeMgBr in diethyl ether, 1.2 mmol). The mixture was stirred for 30 minutes with cooling and then at room temperature for two hours. The reaction was quenched by slow addition of water (ca 20 mL). In a separatory funnel the organic phase was separated and the aqueous phase extracted with diethylether (3x 10 mL). The combined organic fractions were washed with brine and dried with MgSO₄. After filtration and removal of the volatiles, the product was purified by column chromatography on silica using diethylether / pentane mixture (1/1 vol.) as eluent. The first band eluted corresponded to compound **9a** and after removal of the volatiles it was isolated as a white solid (210 mg, 0.42 mmol, 42% yield). A second band eluted gave a white solid identified as IMesBH(Br)C₆F₅ (170 mg, 0.30 mmol, 30% yield).

Method 2: IMesBH₂C₆F₅ (**6a**) (484 mg, 1.0 mmol) and triflic acid (151 mg, 1.00 mmol) were dissolved in toluene (50 mL) while effervescence occurred. After 30 minutes of stirring at room temperature, the mixture was cooled by using a CO₂(s) / i-PrOH bath. Then a solution of MeLi was added dropwise (0.75 mL of 1.6M solution of MeLi in diethyl ether, 1.2 mmol). The mixture was stirred for 30 minutes with cooling and then for two hours at room temperature. The reaction was quenched by slow addition of water (ca 20 mL). In a separatory funnel the organic phase was separated and the aqueous phase extracted with diethylether (3x 10 mL). The combined organic fractions were washed with brine and dried with MgSO₄. After filtration and removal of the volatiles, the product was purified by column chromatography on silica using ethylacetate / pentane mixture (1/10 vol.) as eluent. A single band corresponding to IMesBH(Me)C₆F₅ (**9a**) was eluted. After removal of the volatiles, compound **9a** was isolated as a white solid (288 mg, 0.57 mmol, 57% yield).

Method 3: IMesBH₂C₆F₅ (**6a**) (1.94 mg, 4.0 mmol) and HNTf₂ (1.12 g, 4.0 mmol) were dissolved in toluene (100 mL) while effervescence occurred. After 30 minutes of stirring at room temperature, the mixture was cooled by using a CO₂ (s) / i-PrOH bath. Then a solution of MeLi was added dropwise (3.1 mL of 1.6M solution of MeLi in diethyl ether, 5.0 mmol). The mixture was stirred for 30 minutes with cooling and then for two hours at room temperature. The reaction was quenched by slow addition of water (ca 20 mL). In a separatory funnel the organic phase was separated and the aqueous phase extracted with diethylether (3x 10 mL). The combined organic fractions were washed with brine and dried with MgSO₄. After filtration and removal of the volatiles, the product was purified by column chromatography on silica using ethylacetate / pentane mixture (1/10 vol.) as eluent. A single band corresponded to IMesBH(Me)C₆F₅ (**9a**) was eluted. After removal of the volatiles, compound **9a** was isolated as a white solid (1.38 mg, 2.77 mmol, 69% yield).

NOTE: Performing the reaction under analogous conditions using diethyl ether as solvent and HCl (2.0M in Et_2O) or HNTf₂ as acid did not result in spontaneous gas evolution. After reaction workup the reaction, the unreacted starting material **6a** was obtained in almost quantitative yield.

Characterization of the white solid corresponding to compound 9a

Melting point: 178.9 °C

IR (KBr): v(BH) 2336 cm⁻¹

HRMS for C₂₈H₂₈BF₅N₂Na [M+Na⁺]: calculated 521.2163; found 521.2160

Elemental analysis calculated for C₂₈H₂₈BF₅N₂ (498.3): C 67.48, H 5.56, N 5.62; found: C 67.13, H 5.49, N 5.57.

¹**H NMR** (599 MHz, 299K, CD₂Cl₂): δ = 7.00 (s, 2H, =CH), 6.89 (s, 4H, CH^{Mes}), 2.46 (br m, BH), 2.31 (s, 6H, *p*-CH₃^{Mes}), [2.09, 2.07](each s, each 6H, *o*-CH₃^{Mes}), -0.52 (d, *J* = 6.1 Hz, 3H, BMe)

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 171.7$ (br m, BC^{IMes}), [148.0 (dm, ¹*J*_{FC} ≈ 235 Hz), 138.0 (dm, ¹*J*_{FC} ≈ 242 Hz), 136.4 (dm, ¹*J*_{FC} ≈ 245 Hz), 125.5 (br, *i*-)](C₆F₅), {[139.8 (*p*-), 135.5 (*o*-), 135.4 (*o*-), 134.5 (*i*-)](C^{Mes}), [129.0, 128.9](CH^{Mes}), [21.0 (*p*-), 17.7 (*o*-), 17.6 (*o*-)](CH₃^{Mes})}(Mes), 122.5 (=CH^{IMes}), 1.3 (br m, BCH₃)

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -23.7 (v_{1/2} \approx 50 Hz)

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -23.7 (d, ¹*J*_{BH} \approx 87 Hz)

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-129.4 (m, 2F, *o*-), -164.7 (t, ³*J*_{FF} = 20.0 Hz, 1F, *p*-), -167.4 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 2.7].



Figure S31: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **9a**.



Figure S32: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299K) spectra of compound **9a**.





Figure S34: ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K) spectrum of compound **9a**.

Characterization of the white solid corresponding to IMesBH(Br)C₆F₅ obtained from Method 1.

Melting point: 216.6 °C

IR (KBr): v(BH) 2467 cm⁻¹

HRMS for $C_{27}H_{25}B^{79}BrF_5N_2Na$ [M+Na⁺]: calculated 585.1112; found 585.1113, and for $C_{27}H_{25}B^{81}BrF_5N_2Na$ [M+Na⁺]: 587.1083; found 587.1090

Elemental analysis calculated for C₂₇H₂₅BBrF₅N₂ (563.2): C 57.58, H 4.47, N 4.98; found: C 57.52, H 4.64, N 4.75.

¹**H** NMR (599 MHz, 299K, CDCl₃): δ = 7.06, (s, 2H, =CH), [6.98, 6.83](each s, each 2H, CH^{Mes}), 3.51 (br m, 1H, BH), 2.33 (s, 6H, *p*-CH₃^{Mes}), [2.19, 2.02](each s, each 6H, *o*-CH₃^{Mes}).

¹³C{¹H} NMR (151 MHz, 299K, CDCl₃): $\delta = 161.2$ (br, B-C^{IMes}), [147.7 (dm, ${}^{1}J_{FC} \approx 241$ Hz), 139.1 (dm, ${}^{1}J_{FC} \approx 247$ Hz), 136.4 (dm, ${}^{1}J_{FC} \approx 250$ Hz), 116.7 (br, *i*-)](C₆F₅), {[140.1 (*p*-), 135.2 (*o*-), 134.6 (*o*-), 133.0 (*i*-)](C^{Mes}), [129.1, 128.7](CH^{Mes}), [20.9 (*p*-), 17.8 (*o*-), 17.7 (*o*-)](CH₃^{Mes})}(Mes), 123.0 (=CH^{IMes}).

¹¹B{¹H} NMR (192 MHz, 299K, CDCl₃): δ = -19.2 ($v_{1/2} \approx 220$ Hz)

¹¹**B** NMR (192 MHz, 299K, CDCl₃): $\delta = -19.2 (v_{1/2} \approx 300 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CDCl₃): δ = [-126.2 (m, 2F, *o*-), -160.2 (t, ³*J*_{FF} = 20.2 Hz, 1F, *p*-), -165.9 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹Fm,p = 5.7].



Figure S35: ¹H NMR (599 MHz, CDCl₃*, 299 K) spectrum of IMesBH(Br)C₆F₅ [E: Et₂O]









Preparation of compound 9b



Scheme S7

Borane adduct IMesBH₂FpXyl (**6b**) (2.65 g, 5.0 mmol) and HNTf₂ (1.41 g, 5.0 mmol) were dissolved in diethylether (50 mL) while effervescence occurred. After 30 minutes of stirring at room temperature, the mixture was cooled by using a CO₂ (s) / i-PrOH bath. Then a solution of MeLi was added dropwise (3.5 mL of 1.6 M solution of MeLi in diethyl ether, 5.6 mmol). The mixture was stirred for 30 minutes with cooling and then for two hours at room temperature. The reaction was quenched by slow addition of water (ca 20 mL). In a separatory funnel the organic phase was separated and the aqueous phase extracted with diethylether (3x 10 mL). The combined organic fractions were washed with brine and dried with MgSO₄. After filtration and removal of the volatiles, the product was purified by flash column chromatography on silica using a dichloromethane / pentane mixture (1/1 vol.) as eluent. After removal of the volatiles, compound **9b** was isolated as an off-white solid (1.64 g, 3.0 mmol, 60% yield).

Melting point: 187.7 °C

IR (KBr): v(BH) 2358 cm⁻¹

Elemental analysis calculated for $C_{30}H_{31}BF_6N_2$ (544.4): C 66.19, H 5.74, N 5.15; found: C 65.94, H 5.63, N 5.21.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.35 \text{ (d, }^{3}J_{\text{HH}} = 8.2 \text{ Hz}, m), 7.32 \text{ (s, }p), 7.11 \text{ (d, }^{3}J_{\text{HH}} = 8.2 \text{ Hz}, o)](\text{each 1H, CH}^{\text{FpXyl}}), 6.92, (s, 2H, =CH), [6.86, 6.82](\text{each s, each 2H, CH}^{\text{Mes}}), 2.46 \text{ (br m, 1H, BH)}, 2.28 \text{ (s, 6H, }p\text{-CH}_{3}^{\text{Mes}}), [2.055, 2.048](\text{each s, each 6H, }o\text{-CH}_{3}^{\text{Mes}}), -0.44 \text{ (d, }J = 6.8 \text{ Hz}, 3H, BMe)$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 173.6$ (br m, BC^{IMes}), [157.9 (br m, BC^{FpXyl}), 136.0 (qm, ${}^{2}J_{FC} = 28.8$ Hz, *o*-C), 133.4 (q, ${}^{3}J_{FC} = 3.8$ Hz, *o*-CH^{FpXyl}), 130.3 (q, ${}^{2}J_{FC} = 31.0$ Hz, *m*-C), 125.6 (q, ${}^{1}J_{FC} = 275.1$ Hz, *o*-CF₃), 125.0 (q, ${}^{1}J_{FC} = 272.7$ Hz, *m*-CF₃), 124.6 (q, ${}^{3}J_{FC} = 6.2$ Hz, *m*-CH^{FpXyl}), 120.5 (q, ${}^{3}J_{FC} = 3.7$ Hz, *p*-CH^{FpXyl})[(FpXyl), {[139.6 (*p*-), 135.4 (*o*-), 135.2 (*o*-), 134.7 (*i*-)](C^{Mes}), 129.3 (CH^{Mes}), [21.0 (*p*-), 18.0 (*o*-), 17.9 (*o*-)](CH₃^{Mes})}(Mes), 122.7 (=CH^{IMes}), 4.6 (br m, BMe).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -20.0 (v_{1/2} \approx 55 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -20.0 (d, ¹*J*_{BH} \approx 87 Hz)

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): δ = -58.1 (d, J_{FH} = 6.8 Hz, 1F), -63.0 (s, 1F)



Figure S39: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **9b**.



Figure S40: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299K) spectra of compound **9b**, [* compound **6b**]



Figure S41: ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K) spectrum of compound **9b**.



Figure S42: ¹⁹F NMR (564 MHz, CD₂Cl₂, 299K) spectrum of compound 9b.

Crystals suitable for the the X-ray crystal structure analysis were obtained from a solution of compound **9b** in a diethyl ether (ca 2 mL) / heptane (ca 2 mL) mixture at ambient conditions.

X-ray crystal structure analysis of compound 9b (erk10067): A colorless plate-like specimen of C₃₀H₃₁BF₆N₂, approximate dimensions 0.063 mm x 0.108 mm x 0.276 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube CuK α (CuK α , $\lambda = 1.54178$ Å) and a MX mirror monochromator. A total of 1997 frames were collected. The total exposure time was 18.50 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 62174 reflections to a maximum θ angle of 66.67° (0.84 Å resolution), of which 9748 were independent (average redundancy 6.378, completeness = 99.6%, $R_{int} = 8.93\%$, $R_{sig} = 4.59\%$) and 6828 (70.05%) were greater than of a = 8.07210(10) Å, b = 17.2707(3) Å, c = 19.9694(4) Å, $2\sigma(F^2)$. The final cell constants $= 92.6730(10)^{\circ}$, $\beta = 97.0660(10)^{\circ}$, $\gamma = 90.3860(10)^{\circ}$, volume = 2759.58(8) Å³, are based upon the refinement of the XYZ-centroids of 9962 reflections above 20 σ (I) with 5.122° < 2 θ < 132.8°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.831. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7930 and 0.9460. 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, C₃₀H₃₁BF₆N₂. The final anisotropic full-matrix least-squares refinement on F² with 819 variables converged at R1 = 7.99%, for the observed data and wR2 = 21.27% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.517 e⁻/Å³ and the largest hole was -0.316 e^{-1}/A^3 with an RMS deviation of 0.054 e^{-1}/A^3 . On the basis of the final model, the calculated density was 1.310 g/cm³ and F(000), 1136 e⁻. The hydrogens at B1A and B1B atoms were refined freely, but with B-H distance restraints (SADI). CCDC Nr.: 2108145.


Figure S43: Crystal structure of compound **9b** (only one molecule (molecule "A") of two found in the asymmetric unit is shown.; thermal ellipsoids are set at 30% probability).

Preparation of compound 10a



Scheme S8

Compound IMesBH(Me)C₆F₅ (**9a**) (99.6 mg, 0.2 mmol) was dissolved in CH₂Cl₂ (3 mL) and a solution of HNTf₂ (54.6 mg, 0.2 mmol) in CH₂Cl₂ (3 mL) was added dropwise, resulting in effervescence. After the mixture was stirred for 15 minutes at room temperature, the volatiles were removed in vacuo. The colourless oily residue was treated with pentane (5 mL) and stirred vigorously at room temperature until a white suspension was formed. The white solid was separated by decantation, washed with pentane (3x 3 mL) and dried in vacuo to give compound **10a** as a white solid (131.5 mg, 1.69 mmol, 84% yield).

Melting point: 154.6 °C

Elemental analysis calculated for $C_{30}H_{27}BF_{11}N_3O_4S_2$ (777.5): C 46.34, H 3.50, N 5.41; found: C 46.08, H 3.65, N 5.22

¹**H NMR** (599 MHz, 299K, CD₂Cl₂): δ = 7.20 (s, 2H, =CH), 6.94 (s, 4H, CH^{Mes}), 2.32 (s, 6H, *p*-CH₃^{Mes}), 2.07 (s, 12H, *o*-CH₃^{Mes}), 0.53 (t, *J* = 2.9 Hz, 3H, BCH₃)

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): δ = 158.4 (br, BC^{IMes}), [147.9 (dm, ¹*J*_{FC} ≈ 241 Hz), 140.5 (dm, ¹*J*_{FC} ≈ 242 Hz), 137.2 (dm, ¹*J*_{FC} ≈ 253 Hz), 116.2 (br)](C₆F₅)], {[141.1 (*p*-), 134.8 (*o*-), 133.1 (*i*-)](C^{Mes}), 129.6 (CH^{Mes}), [21.0 (*p*-), 17.7 (*o*-)](CH₃^{Mes})}(Mes), 125.3 (=CH^{IMes}), 119.2 (q, ¹*J*_{FC} = 321.5 Hz, NTf₂), 7.7 (br, BCH₃).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 8.7 (v_{1/2} \approx 400 \text{ Hz})$

¹¹**B NMR** (192 MHz, 299K, CD₂Cl₂): $\delta = 8.7 (v_{1/2} \approx 400 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = -78.6 (s, 6F, NTf₂), [-129.2 (m, 2F, *o*-), -157.8 (t, ³*J*_{FF} = 20.1 Hz, 1F, *p*-), -165.0 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 7.2)



Figure S44: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **10a**.











-74 -75 -76 -77 -78 -79 -80 -81 -123 -125 -127 -129 -131 -133 -154 -156 -158 -160 -162 -164 -166 -168

Figure S50: ¹⁹F NMR (564 MHz, CD₂Cl₂) spectra of compound **10a** at various temperatures.





Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 10a in CH₂Cl₂/heptane at -35 °C.

X-ray crystal structure analysis of compound 10a (erk10279): A colorless, prism-like specimen of C₃₀H₂₇BF₁₁N₃O₄S₂, approximate dimensions 0.112 mm x 0.131 mm x 0.271 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoK α , λ = 0.71073 Å) and a MX mirror monochromator. A total of 546 frames were collected. The total exposure time was 4.55 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 67418 reflections to a maximum θ angle of 26.75° (0.79 Å resolution), of which 7004 were independent (average redundancy 9.626, completeness = 99.8%, $R_{int} = 8.04\%$, $R_{sig} = 3.34\%$) and 5351 (76.40%) were greater than $2\sigma(F^2)$. The final cell constants of a = 15.6564(5) Å, b = 11.3344(4) Å, c = 18.8248(6) Å, $\beta = 99.7730(10)^{\circ}$, volume = 3292.09(19) Å³, are based upon the refinement of the XYZ-centroids of 9941 reflections above 20 $\sigma(I)$ with 4.459° < 2 θ < 53.44°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.941. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9310 and 0.9710. 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, C₃₀H₂₇BF₁₁N₃O₄S₂. The final anisotropic full-matrix least-squares refinement on F² with 549 variables converged at R1 = 4.44%, for the observed data and wR2 = 11.86% for all data. The goodness-of-fit was 1.009. The largest peak in the final difference electron density synthesis was $0.825 \text{ e}^{-/\text{Å}^3}$ and the largest hole was -0.411 e⁻/Å³ with an RMS deviation of 0.057 e⁻/Å³. On the basis of the final model, the calculated density was 1.569 g/cm³ and F(000), 1584 e⁻. CCDC Nr.: 2156400.



Figure S52: Crystal structure of compound 10a (thermal ellipsoids are set at 30% probability).

Crystals suitable for the X-ray crystal structure analysis of compound $10a-H_2O$ were obtained via multiple recrystallization of compound 10a in CH₂Cl₂/heptane at room temperature.

X-ray crystal structure analysis of compound 10a-H₂O (erk10280): A colorless, prism-like specimen of C₃₀H₂₉BF₁₁N₃O₅S₂, approximate dimensions 0.109 mm x 0.111 mm x 0.155 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 1843 frames were collected. The total exposure time was 12.44 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 85471 reflections to a maximum θ angle of 26.08° (0.81 Å resolution), of which 6744 were independent (average redundancy 12.674, completeness = 99.1%, R_{int} = 5.34%, R_{sig} = 2.42%) and 6108 (90.57%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.9266(3) Å, b = 15.6701(4) Å, c = 20.3624(5) Å, β = 100.6230(10)°, volume = 3426.72(15) Å3, are based upon the refinement of the XYZ-centroids of 9702 reflections above 20 σ (I) with 5.199° < 2 θ < 52.09°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.964. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9610 and 0.9720. 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, C₃₀H₂₉BF₁₁N₃O₅S₂. The final anisotropic full-matrix least-squares refinement on F² with 484 variables converged at R1 = 4.18%, for the observed data and wR2 = 12.36% for all data. The goodness-of-fit was 1.066. The largest peak in the final difference electron density synthesis was 1.103 e-/Å³ and the largest hole was -0.476 e^{-1}/A^3 with an RMS deviation of 0.065 e^{-1}/A^3 . On the basis of the final model, the calculated density was 1.542 g/cm³ and F(000), 1624 e⁻. The hydrogens at O1 atom were refined freely. CCDC Nr.: 2156407.



Figure S53: Crystal structure of compound 10a-H₂O (thermal ellipsoids are set at 30% probability).

Preparation of compound 10b



Scheme S9

Compound IMesBH(Me)FpXyl (**9b**) (108.8 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (3 mL) and a solution of HNTf₂ (54.6 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) was added dropwise, resulting in effervescence. After the mixture was stirred for 15 minutes at room temperature, the volatiles were removed in vacuo. The colourless oily residue was treated with pentane (5 mL) and stirred vigorously at room temperature until a white suspension was formed. The white solid was separated by decantation, washed with pentane (3x 3 mL) and dried in vacuo to give compound **10b** as a white solid (145.0 mg, 1.76 mmol, 88% yield).

Melting point: 140.1 °C

Elemental analysis calculated for $C_{32}H_{30}BF_{12}N_3O_4S_2$ (823.5): C 46.67, H 3.67, N 5.10; found: C 4.35, H 3.75, N 4.99.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.94 (s, 2H, =CH), [7.59 (d, ³*J*_{HH} = 8.3 Hz, *p*), 7.53 (d, ³*J*_{HH} = 8.3 Hz, *m*), 7.04 (s, *o*)](each 1H, CH^{FpXyl}), 6.95 (m, 4H, CH^{Mes}), 2.29 (s, 6H, *p*-CH₃^{Mes}), 2.05 (s, 12H, *o*-CH₃^{Mes}), 0.79 (q, *J* = 2.6 Hz, 3H, BCH₃)

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 145.7$ (br, BC^{IMes}), {[142.8 (*p*-), 134.0 (*o*-), 132.3 (*i*-)] (C^{Mes}), 130.5 (CH^{Mes}), [21.1 (*p*-), 17.4 (*o*-)](CH₃^{Mes})}(Mes), {140.2 (br, BC^{FpXyl}), 132.9 (q, ²J_{FC} = 32.8 Hz, *m*-C), 131.9 (q, ²J_{FC} = 31.6 Hz, *o*-C), [127.1 (q, ³J_{FC} = 3.7 Hz, *m*), 126.5 (q, ³J_{FC} = 3.7 Hz, *p*), 122.6 (q, ³J_{FC} = 3.9 Hz, *o*)](CH^{FpXyl}), 124.8 (q, ¹J_{FC} = 274.1 Hz, *o*-CF₃), 123.4 (q, ¹J_{FC} = 274.1 Hz, *m*-CF₃)}(FpXyl), 131.0 (=CH^{IMes}), 120.2 (q, ¹J_{FC} = 321.6 Hz, NTf₂), 14.9 (br, BCH₃).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 67.2 (v_{1/2} \approx 900 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 67.2 (v_{1/2} \approx 900 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-56.7 (v_{1/2} \approx 7 Hz, 1F), -63.8 (s, 1F)](FpXyl), -79.6 (s, 2F, NTf₂).



Figure S54: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **10b**.







Figure S56: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299K) spectra of compound **10b**, [* unidentified]





8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 5.5 5.4 5.3 2.5 2.3 2.1 1.9 1.7 0.8 0.6 0.4 0.2

Figure S58: ¹H NMR (599 MHz, CD₂Cl₂) spectra of compound **10b** at various temperatures.





Figure S59: ¹H NMR (599 MHz, C₆D₅Br) spectra of compound **10b** at various temperatures.



-55.4 -55.8 -56.2 -56.6 -57.0 -57.4 -62.6 -63.0 -63.4 -63.8 -64.2 -79.0 -79.4 -79.8 -80.:

Figure S60: ¹⁹F NMR (564 MHz, CD₂Cl₂) spectra of compound **10b** at various temperatures.







Figure S61: ¹⁹F NMR (564 MHz, C₆D₅Br) spectra of compound **10b** at various temperatures.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of **10b** in pentane (ca 2 mL) / dichloromethane (ca 2 mL) mixture at -35°C.

X-ray crystal structure analysis of compound 10b (erk10111): A colorless plate-like specimen of C₃₂H₃₀BF₁₂N₃O₄S₂, approximate dimensions 0.090 mm x 0.200 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Kappa CCD APEXII Bruker APEXII Diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuK α , $\lambda = 1.54178$ Å) and a graphite monochromator. A total of 1795 frames were collected. The total exposure time was 20.93 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 61186 reflections to a maximum θ angle of 66.70° (0.84 Å resolution), of which 6315 were independent (average redundancy 9.689, completeness = 99.7%, $R_{int} = 8.94\%$, $R_{sig} = 4.54\%$) and 5174 (81.93%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 14.1451(4) Å, <u>b</u> = 11.7175(3) Å, <u>c</u> = 21.6932(5) Å, β = 94.299(2)°, volume = 3585.43(16) Å³, are based upon the refinement of the XYZ-centroids of 8749 reflections above 20 σ (I) with $6.266^{\circ} < 2\theta < 133.0^{\circ}$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.799. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6320 and 0.8200. 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, $C_{32}H_{30}BF_{12}N_3O_4S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 494 variables converged at R1 = 3.72%, for the observed data and wR2 = 9.23% for all data. The goodness-of-fit was 1.017. The largest peak in the final difference electron density synthesis was 0.324 e⁻ $/Å^3$ and the largest hole was -0.399 e⁻/Å³ with an RMS deviation of 0.054 e⁻/Å³. On the basis of the final model, the calculated density was 1.526 g/cm³ and F(000), 1680 e⁻. CCDC Nr.: 2108146.



Figure S62: Crystal structure of compound 10b (thermal ellipsoids are set at 30% probability).

Preparation compound 3a



Scheme S10

Compound IMesBH(Me)C₆F₅ (**9a**) (996 mg, 2.0 mmol) and HNTf₂ (562 mg, 2.0 mmol) were dissolved in dichloromethane (10 mL), resulting in effervescence. After 20 minutes of stirring at room temperature, the mixture was treated with a solution of IMes (608 mg, 2.0 mmol) in dichloromethane (5 mL). The mixture was stirred for 15 minutes and subsequently the volatiles were removed in vacuo to give a yellow foamy solid. The solid was extracted with a dichloromethane / pentane mixture (ca 1:5, ca 3x5 mL). The extracts were combined and after removal of the volatiles under reduced pressure, the beige residue was washed with pentane (3x 1 mL). The resulting off-white solid was dried in vacuo to give compound **3a** (620 mg, 1.25 mmol, 63% yield).

NOTE: The solid residue, insoluble in the dichloromethane/pentane mixture, was identified as $[IMesH^+][NTf_2^-]$ after drying in vacuo. It was obtained as an off-white solid (1.02 g, 1.74 mmol, 87% yield).

Characterization of the isolated off-white solid of compound 3a.

Melting point: 178.8 °C

Elemental analysis calculated for $C_{28}H_{26}N_2BF_5$ (496.3): C 67.75, H 5.28, N 5.65; found: C 67.27, H 5.35, N 5.55.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.05 (s, 2H, =CH), 6.90 (m, 4H, CH^{Mes}), [3.48, 3.39](each d, ²*J*_{HH} = 5.5 Hz, each 1H, =CH₂), 2.30 (s, 6H, *p*-CH₃^{Mes}), 2.12 (s, 12H, *o*-CH₃^{Mes}).

¹³C{¹H} **NMR** (151 MHz, 299K, CD₂Cl₂): $\delta = 160.9$ (br, BC^{IMes}), [146.1 (dm, ${}^{1}J_{FC} \approx 233$ Hz), 138.3 (dm, ${}^{1}J_{FC} \approx 248$ Hz), 136.5 (dm, ${}^{1}J_{FC} \approx 247$ Hz), 120.6 (br, *i*-)](C₆F₅), [140.0 (*p*-C), 135.3 (*o*-C), 134.3 (*i*-C), 129.3 (*m*-CH), 21.0 (*p*-CH₃), 17.8 (t, *J* = 1.3 Hz, *o*-CH₃)](Mes), 122.5 (=CH), 103.1 (br m, =CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 19.0 (v_{1/2} \approx 130 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 19.0 (v_{1/2} \approx 130 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-129.0 (m, 2F, *o*-), -163.3 (t, ³*J*_{FF} = 19.9 Hz, 1F, *p*-), -166.8 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 3.5].





Figure S65: ¹⁹F NMR (564 MHz, CD₂Cl₂, 299K) spectrum of compound **3a**.



Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 3a in dichloromethane covered with heptane at -35°C.

X-ray crystal structure analysis of compound 3a (erk10030): A colorless plate-like specimen of C₂₈H₂₆BF₅N₂, approximate dimensions 0.039 mm x 0.067 mm x 0.147 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK α (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 678 frames were collected. The total exposure time was 3.77 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 4945 reflections to a maximum θ angle of 25.06° (0.84 Å resolution), of which 4945 were independent (average redundancy 1.000, completeness = 99.7%, $R_{int} = 8.93\%$, $R_{sig} = 9.10\%$) and 3004 (60.75%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 7.1528(5) Å, <u>b</u> = 14.6225(9) Å, <u>c</u> = 15.3173(11) Å, $\alpha = 63.926(2)^\circ$, β $= 83.017(2)^{\circ}$, $\gamma = 75.844(2)^{\circ}$, volume = 1395.14(17) Å³, are based upon the refinement of the XYZcentroids of 5425 reflections above 20 σ (I) with 5.182° < 2 θ < 48.15°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.925. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9870 and 0.9960. 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, $C_{28}H_{26}BF_5N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 333 variables converged at R1 = 6.25%, for the observed data and wR2 = 16.59% for all data. The goodness-of-fit was 1.083. The largest peak in the final difference electron density synthesis was 0.600 e⁻/Å³ and the largest hole was -0.325 e⁻/Å³ with an RMS deviation of 0.072 e⁻ /Å³. On the basis of the final model, the calculated density was 1.181 g/cm³ and F(000), 516 e⁻. CCDC Nr.: 2108147.



Figure S67: Crystal structure of compound **3a** (thermal ellipsoids are set at 30% probablility).

Preparation of compound **3b**



Scheme S11

Compound IMesBH(Me)FpXyl (**9b**) (1.09 g, 2.0 mmol) and HNTf₂ (562 mg, 2.0 mmol) were dissolved in dichloromethane (10 mL), resulting in effervescence. After 20 minutes of stirring at room temperature, the mixture was treated with a solution of IMes (608 mg, 2.0 mmol) in dichloromethane (5 mL). The mixture was stirred for 15 minutes and subsequently the volatiles were removed in vacuo to give a yellow foamy solid. The solid was extracted with dichloromethane / pentane mixture (ca 1:10, ca 3x5 mL). Extracts were combined and after removal of the volatiles under reduced pressure, the beige residue was washed with pentane (3x 1 mL). The residue was dried in vacuo to give compound **3b** as a white solid (805 mg, 1.48 mmol, 74% yield).

NOTE: The solid residue, insoluble in the dichloromethane/pentane mixture, was identified as $[IMesH^+][NTf_2^-]$ after drying in vacuo. It was obtained as an off-white solid (1.08 g, 1.84 mmol, 92% yield).

Characterization of the isolated white solid of compound 3b.

Melting point: 165.7 °C

Elemental analysis calculated for C₃₀H₂₉N₂BF₆ (542.4): C 66.43, H 5.39, N 5.17; found: C 66.80, H 5.49, 4.99.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.31 \text{ (d, }^{3}J_{\text{HH}} = 8.3 \text{ Hz}, m), 7.23 \text{ (s, }o), 7.15 \text{ (d, }^{3}J_{\text{HH}} = 8.3 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), 7.00 \text{ (s, }2\text{H}, =\text{CH}), 6.82 \text{ (s, }4\text{H}, \text{CH}^{\text{Mes}}), [3.23, 3.20](\text{each d, }^{2}J_{\text{HH}} = 5.3 \text{ Hz}, \text{ each 1H}, =\text{CH}_{2}), 2.24 \text{ (s, }6\text{H}, p\text{-CH}_{3}^{\text{Mes}}), 2.10 \text{ (s, }12\text{H}, o\text{-CH}_{3}^{\text{Mes}}).$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 162.1$ (br m, BC^{IMes}), [150.5 (br, BC), 134.2 (q, ²*J*_{FC} = 28.1 Hz, *o*-C), 133.3 (q, ³*J*_{FC} = 3.8 Hz, *o*-CH), 130.2 (q, ²*J*_{FC} = 31.3 Hz, *m*-C), 125.5 (q, ¹*J*_{FC} = 274.4 Hz, *o*-CF₃) 124.6 (q, ¹*J*_{FC} = 272.8 Hz, *m*-CF₃), 124.5 (q, ³*J*_{FC} = 5.3 Hz, *m*-CH), 121.2 (q, ³*J*_{FC} = 3.7 Hz, *p*-CH)] (FpXyl), [139.8 (*p*-C), 135.3 (*o*-C), 134.6 (*i*-C), 129.5 (*m*-CH), 21.0 (*p*-CH₃), 18.0 (q, *J* = 1.1 Hz, *o*-CH₃)](Mes), 122.6 (=CH), 100.4 (br m, =CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 25.6 (v_{1/2} \approx 180 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 25.6 (v_{1/2} \approx 180 \text{ Hz})$

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): δ = -57.5 (s, 1F), -63.2 (s, 1F)





Figure S70: ¹⁹F NMR (564 MHz, CD₂Cl₂, 299K) spectrum of compound **3b**.



Figure S71: ${}^{13}C{}^{1}H$ NMR (151 MHz, CD₂Cl₂*, 299 K) spectrum of compound **3b**.

Preparation of compound **11b**



Scheme S12

Boraalkene **3b** (54.2 mg, 0.1 mmol) and elemental sulfur (3.2 mg, 0.1 mmol) were combined in dichloromethane (3 mL) and stirred for 60 minutes at room temperature. The initially bright yellow solution quickly discoloured. Subsequently the volatiles were removed under reduced pressure. The resulting off-white residue was washed with pentane (3x1 mL) and dried in vacuo to give compound **11b** as a white solid (49.2 mg, 0.087 mmol, 87% yield).

Melting point: 151.5 °C

Elemental analysis calculated for C₃₀H₂₉N₂BF₆S (574.4): C 62.72, H 5.09, N 4.88; found: C 62.75, H 5.28, N 5.13

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.54 \text{ (s, }o) 7.35 \text{ (d, }^{3}J_{\text{HH}} = 8.3 \text{ Hz, }m), 7.18 \text{ (d, }^{3}J_{\text{HH}} = 8.3 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), [6.97, 6.69](\text{each s, each 2H, CH}^{\text{Mes}}), 6.95 \text{ (s, 2H, =CH)}, [2.28, 2.27, 1.96](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), [1.05, 0.92](\text{each d, }^{2}J_{\text{HH}} = 5.1 \text{ Hz}, \text{ each 1H, CH}_{2}).$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): δ = 165.0 (br, BC^{IMes}), [148.3 (br, BC), 137.1 (br m, *o*-CH), 135.5 (q, ²*J*_{FC} = 29.9 Hz, *o*-C), 130.2 (q, ²*J*_{FC} = 31.3 Hz, *m*-C), 125.7 (q, ¹*J*_{FC} = 274.7 Hz, *o*-CF₃), 124.5 (q, ¹*J*_{FC} = 272.2 Hz, *m*-CF₃), 123.8 (q, ³*J*_{FC} = 5.5 Hz, *m*-CH), 122.1 (q, ³*J*_{FC} = 3.6 Hz, *p*-CH)](FpXyl), {140.4 (*p*-C), [135.8, 135.7](*o*-C), 134.1 (*i*-C) [129.5, 129.4](*m*-CH), 21.0 (*p*-CH₃), [18.3 (q, *J* = 2.0 Hz), 18.2](*o*-CH₃)}(Mes), 123.6 (=CH), 18.8 (br, CH₂)

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -16.7 (v_{1/2} \approx 130 Hz)

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -16.7 (v_{1/2} \approx 130 Hz)

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): δ = -57.1 (s, 1F), -63.0 (s, 1F)



Figure S72: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **11b**.



Figure S73: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299K) spectra of compound **11b** [#: unidentified].



Figure S74: ¹⁹F NMR (564 MHz, CD₂Cl₂, 299K) spectrum of compound **11b** [#: unidentified].



Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **11b** in benzene covered with heptane at room temperature.

X-ray crystal structure analysis of compound 11b (erk10031): A colorless plate-like specimen of C₃₀H₂₉BF₆N₂S, approximate dimensions 0.064 mm x 0.072 mm x 0.222 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK α (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 510 frames were collected. The total exposure time was 4.96 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 44061 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 5898 were independent (average redundancy 7.470, completeness = 99.8%, $R_{int} = 8.34\%$, $R_{sig} = 4.41\%$) and 4507 (76.42%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 9.5906(3) Å, <u>b</u> = 20.3447(6) Å, <u>c</u> = 14.5376(4) Å, β = 101.3110(10)°, volume = 2781.45(14) Å³, are based upon the refinement of the XYZ-centroids of 8049 reflections above 20 σ (I) with 4.698° < 2 θ < 53.37°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.793. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9610 and 0.9890. 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, C₃₀H₂₉BF₆N₂S. The final anisotropic full-matrix least-squares refinement on F^2 with 424 variables converged at R1 = 4.57%, for the observed data and wR2 = 12.10% for all data. The goodness-of-fit was 1.027. The largest peak in the final difference electron density synthesis was 0.739 e⁻ $/Å^3$ and the largest hole was -0.390 e⁻/Å³ with an RMS deviation of 0.052 e⁻/Å³. On the basis of the final model, the calculated density was 1.372 g/cm³ and F(000), 1192 e⁻. CCDC Nr.: 2108148.



Figure S76: Crystal structure of compound 11b (thermal ellipsoids are set at 30% probability).

Preparation of compound 12a





Boraalkene **3a** (24.8 mg, 0.05 mmol) and elemental sulfur (16.0 mg, 0.5 mmol) were combined in C_6H_5Br (0.5 mL) and stirred for 60 minutes at room temperature. Then $Li[B(C_6F_5)_4]$ (29.3 mg, 0.05 mmol) and 4-ethynyltoluene (11.6 mg, 0.1 mmol) were added to the obtained mixture. After the resulted reaction mixture was stirred at r.t. for 14 days, it was purified by SiO_2 flash column chromatography (eluent pentane/ethyl acetate 5:1) to finally give compound **12a** as a white solid (10 mg, 31% yield).

Elemental analysis calculated for $C_{37}H_{34}N_2BF_5S$ (644.2): C 68.95, H 5.32, N 4.35; found: C 68.36, H 5.33, N 4.28

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.06 (s, 2H, =CH), [6.96, 6.78](each m, each 2H, CH^{Mes}), 6.95 (m, 4H, CH^{tol}), 5.75 (t, *J* = 3.6 Hz, 1H, =CH^B), [2.65, 2.29](each d, ²*J*_{HH} = 12.6 Hz, each 1H, CH₂), 2.26 (s, 3H, CH₃^{tol}), [2.26 (*p*), 2.12 (*o*), 2.01 (*o*)](each s, each 6H, CH₃^{Mes}).

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂)[selected resonances]: $\delta = 168.8$ (br, BC^{IMes}), [146.9, 135.9](*i*-tol, =CS), 140.3 (*p*-Mes), 136.3 (*p*-tol), [135.6, 135.3](*o*-Mes), 134.1 (*i*-Mes), 130.3 (br, =CH^B), [129.3, 129.0](*m*-Mes), 128.5 (*m*-tol), 126.2 (*o*-tol), 123.6 (=CH), 25.8 (br m, CH₂), 21.1 (CH₃^{tol}), 21.0 (*p*-CH₃^{Mes}), [17.9 (t, J = 2.0 Hz), 17.7](*o*-CH₃^{Mes}).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -8.2 (v_{1/2} \approx 45 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = -129.9 (m, 2F, *o*-C₆F₅), -163.2 (t, ³*J*_{FF} = 20.3 Hz, 1F, *p*-C₆F₅), 166.2 (m, 2F, *m*-C₆F₅) [Δδ¹⁹F_{m,p} = 3.0].



Figure S78: ${}^{11}B{}^{1}H{}$ NMR (192 MHz, CD₂Cl₂, 299K) spectra of compound 12a



Figure S79: ¹⁹F NMR (564 MHz, CD₂Cl₂, 299K) spectrum of compound 12a





Figure S80: (1) ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K) and (2) ¹H, ¹³C gHSQC NMR (599/151 MHz, CD₂Cl₂, 299K) spectra of compound **12a**

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 12a in CH₂Cl₂/heptane at room temperature.

X-ray crystal structure analysis of compound 12a (erk10261): A colorless, plate-like specimen of C₃₇H₃₄BF₅N₂S, approximate dimensions 0.063 mm x 0.075 mm x 0.242 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuK α , $\lambda = 1.54184$ Å) and a MX mirror monochromator. A total of 1171 frames were collected. The total exposure time was 16.00 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 82790 reflections to a maximum θ angle of 66.71° (0.84 Å resolution), of which 5585 were independent (average redundancy 14.824, completeness = 99.7%, $R_{int} = 12.86\%$, $R_{sig} = 3.80\%$) and 4269 (76.44%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.9516(3) Å, b = 16.2353(3) Å, c = 20.5299(4) Å, volume = 6316.7(2) Å3, are based upon the refinement of the XYZ-centroids of 7849 reflections above 20 $\sigma(I)$ with 8.364° < 2 θ < 132.6°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.885. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6662 and 0.7528. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pbca, with Z = 8 for the formula unit, C₃₇H₃₄BF₅N₂S. The final anisotropic full-matrix least-squares refinement on F² with 422 variables converged at R1 = 6.73%, for the observed data and wR2 = 17.89% for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 1.220 e⁻/Å³ and the largest hole was -0.388 e⁻/Å³ with an RMS deviation of 0.069 e⁻/Å³. On the basis of the final model, the calculated density was 1.355 g/cm³ and F(000), 2688 e⁻. CCDC Nr.: 2156427.



Figure S81: Crystal structure of compound 12a (thermal ellipsoids are set at 30% probability).

Preparation of compound 13a





Boraalkene **11a** (99.2 mg, 0.2 mmol) was dissolved in a mixture of dichloromethane (1 mL) and pentane (5 mL). The mixture was degassed, and subsequently treated with CO_2 (1.5 atm) for two hours at room temperature. During this time a white suspension was formed. The solvent was removed via cannula and the solid residue washed with pentane (3x1 mL) and dried in vacuo to give a white powder of compound **13a** (48.6 mg, 0.0828 mmol, 83% yield).

Decomposition point: 239.6 °C

IR (KBr): v(CO) 1757 cm⁻¹

HRMS for $C_{31}H_{30}N_3BF_5O_2$ [M + MeCN + H⁺]: calculated 582.2351; found 582.2347

HRMS for $C_{29}H_{26}N_2BClF_5O_2$ [M + Cl⁻]: calculated 575.1707; found 575.1704

Elemental analysis calculated for C₂₉H₂₆N₂BF₅O₂ (540.3): C 64.46, H 4.85, N 5.19; found: C 65.00, H 5.10, N 5.36.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.16 (s, 2H, =CH), [6.95, 6.91](each m, each 2H, CH^{Mes}), [2.33 (*p*-), 2.07 (*o*-), 2.06 (*o*-)](each s, each 6H, CH₃^{Mes}), [1.77, 1.63](each d, ²*J*_{HH} = 17.1 Hz, each 1H, CH₂).

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): δ = 176.1 (C=O), 161.5 (br, BC^{IMes}), [147.5 (dm, ¹*J*_{FC} ≈ 240 Hz), 139.5 (dm, ¹*J*_{FC} ≈ 246 Hz), 136.8 (dm, ¹*J*_{FC} ≈ 250 Hz), 118.8 (br, *i*)](C₆F₅), [140.7 (*p*-C), 135.6 (*o*-C), 134.6 (*o*-C), 133.6 (*i*-C), 129.5 (*m*-CH), 129.2 (*m*-CH), 21.0 (*p*-CH₃), 17.5 (*o*-CH₃), 17.4 (*o*-CH₃)](Mes), 124.4 (=CH), 29.1 (br, CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -6.8 (v_{1/2} \approx 90 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -6.8 (v_{1/2} \approx 90 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-130.6 (m, 2F, *o*-), -160.5 (t, ³*J*_{FF} = 19.9 Hz, 1F, *p*-), -165.8 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 5.3].



Figure S82: ¹**H NMR** (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **13a**. (# impurity originated from starting material).



Figure S83: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD_2Cl_2 , 299K) spectra of compound 13a.



Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **13a** in dichloromethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 13a (erk10112): A colorless plate-like specimen of C₃₀H₂₈BCl₂F₅N₂O₂, approximate dimensions 0.053 mm x 0.089 mm x 0.264 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube CuK α (CuK α , $\lambda = 1.54178$ Å) and a MX mirror monochromator. A total of 1479 frames were collected. The total exposure time was 18.36 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 31653 reflections to a maximum θ angle of 68.27° (0.83 Å resolution), of which 5196 were independent (average redundancy 6.092, completeness = 98.4%, R_{int} = 6.54%, R_{sig} = 4.66%) and 4124 (79.37%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 8.1301(2) Å, <u>b</u> = 53.7784(15) Å, <u>c</u> = 7.3365(2) Å, β = 115.797(2)°, volume = 2888.02(14) Å³, are based upon the refinement of the XYZ-centroids of 9944 reflections above $20 \sigma(I)$ with $6.574^{\circ} < 2\theta < 136.4^{\circ}$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.851. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5480 and 0.8750. 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, $C_{30}H_{28}BCl_2F_5N_2O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 422 variables converged at R1 = 4.70%, for the observed data and wR2 = 11.64% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.302 e⁻ $/Å^3$ and the largest hole was -0.407 e⁻/Å³ with an RMS deviation of 0.060 e⁻/Å³. On the basis of the final model, the calculated density was 1.438 g/cm³ and F(000), 1288 e⁻. CCDC Nr.: 2108149.



Figure S86: Crystal structure of compound 13a (thermal ellipsoids are set at 30% probability).

Preparation of **13b**





Boraalkene **3b** (108.2 mg, 0.2 mmol) was dissolved in a mixture of dichloromethane (1 mL) and pentane (5 mL). The mixture was degassed and subsequently treated with CO_2 (1.5 atm) for two hours at room temperature. A white suspension was formed. The solvent was removed via cannula and the solid residue washed with pentane (3x 1 mL) and dried in vacuo to give a white powder of compound **13b** (96.8 mg, 0.165 mmol, 83% yield).

IR (KBr): v(CO) 1742 cm⁻¹

HRMS for $C_{31}H_{29}N_2BClF_6O_2$ [M + Cl⁻]: calculated 621.1915; found 621.1918

Elemental analysis calculated for C₃₁H₂₉N₂BF₆O₂ (586.4): C 63.49, H 4.99, N 4.78; found: C 63.03, H 5.15, N 4.97.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.41 \text{ (s, } o), 7.42 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, m), 7.24 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), 7.10 \text{ (s, 2H, =CH)}, [6.96, 6.74](\text{each s, each 2H, CH}^{\text{Mes}}), [2.27 (p-), 2.19 (o-), 1.95 (o-)](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), 1.27 \text{ (s, 2H, CH}_{2}).$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 177.2$ (C=O), 162.3 (br, BC^{IMes}), [149.1 (br, BC), 134.4 (q, ²*J*_{FC} = 30.3 Hz, *o*-C), 131.2 (q, ²*J*_{FC} = 31.7 Hz, *m*-C), 131.0 (q, ³*J*_{FC} = 3.9 Hz, *o*-CH), 125.8 (q, ¹*J*_{FC} = 274.8 Hz, *o*-CF₃), 125.3 (q, ³*J*_{FC} = 5.2 Hz, *m*-CH), 124.4 (q, ¹*J*_{FC} = 274.9 Hz, *m*-CF₃), 122.6 (q, ³*J*_{FC} = 3.7 Hz, *p*-CH)](FpXyl), [140.7 (*p*-C), 135.5 (*o*-C), 135.1 (*o*-C), 134.0 (*i*-C), 129.9 (*m*-CH), 129.7 (*m*-CH), 21.0 (*p*-CH₃), 17.6 (q, *J*_{FC} = 1.6 Hz, *o*-CH₃), 17.4 (*o*-CH₃)](Mes), 124.2 (=CH), 28.7 (br, CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -5.6 (v_{1/2} \approx 120 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -5.6 (v_{1/2} \approx 120 \text{ Hz})$

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): δ = -57.8 (s, 1F), -63.2 (s, 1F)






Generation and preparation of compound 14b



Scheme S16

In situ experiment: Boraalkene **3b** (13.4 mg, 0.025 mmol) and DABSO (1,4-diazabicyclo[2.2.2]octan-bis sulfur dioxide adduct, 3.0 mg, 0.0125 mmol) dissolved in CD_2Cl_2 (0.6 mL) were vigorously shaken. NMR measurement after 30 minutes (room temperature) revealed complete consumption of the starting material and formation of two major components in ca 4:3 ratio (¹⁹F, see spectra below).

Preparative experiment: Boraalkene **3b** (54.2 mg, 0.1 mmol) and DABSO (1,4-diazabicyclo[2.2.2]octanbis sulfur dioxide adduct, 12.0 mg, 0.05 mmol) were combined in dichloromethane (3 mL) and stirred for 60 minutes at room temperature. Subsequently the volatiles were removed under reduced pressure. The solid residue was washed with pentane (3x1 mL), taken up in a small amount of dichloromethane (ca 1 mL) and layered with heptane (ca 5 mL). After five days colourless crystals were isolated by decantation, washed with pentane and dried in vacuo. Compound **14b** was obtained as a white solid (23.0 mg, 0.038 mmol, 35% isolated yield).

Characterization of the isolated white solid, which was identified as a single diastereomer of compound **14b** in solution (NMR) contaminated with a small amount of DABCO x 2 SO_2 .

Decomposition point: 194.1 °C

HRMS for C₃₀H₂₉N₂BF₆O₂SNa [M+Na⁺]: calculated 629.1844; found 629.1840

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.62 \text{ (br, } o), 7.38 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, m), 7.23 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, m)](\text{each 1H, CH}^{\text{FpXyl}}), 7.10 \text{ (s, 2H, =CH)}, [6.95, 6.75](\text{each s, each 2H, CH}^{\text{Mes}}), [2.26, 2.19, 2.00](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), [2.42, 1.67](\text{each d, } {}^{2}J_{\text{HH}} = 13.6 \text{ Hz}, \text{ each 1H, CH}_{2})$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 162.0$ (br, BC^{IMes}), [152.2 (br, BC^{FpXyl}), 132.7 (br q, ²*J*_{FC} = 31.3 Hz, *o*-C), 131.1 (q, ²*J*_{FC} = 31.2 Hz, *m*-C), 131.0 (q, ³*J*_{FC} = 3.9 Hz, *o*-CH), 125.8 (q, ¹*J*_{FC} = 274.9 Hz, *o*-CF₃), 125.5 (q, ³*J*_{FC} = 5.1 Hz, *m*-CH), 124.5 (q, ¹*J*_{FC} = 272.9 Hz, *m*-CF₃), 122.5 (q, ³*J*_{FC} = 3.8 Hz, *p*-CH)](FpXyl), {[140.8, 135.5, 135.1, 133.9](C^{Mes}), [129.9, 129.8](CH^{Mes}), [21.0, 17.7 (q, *J* = 1.5 Hz), 17.7](CH₃^{Mes})}(Mes), 124.2 (=CH), 49.5 (br, CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 0.0 (v_{1/2} \approx 100 \text{ Hz})$

¹¹**B NMR** (192 MHz, 299K, CD₂Cl₂): $\delta = 0.0 (v_{1/2} \approx 100 \text{ Hz})$

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): $\delta = [-57.7, -63.1]$ (each s, each 1F)



Figure S91: Comparison of ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectra of in situ generated mixture and isolated compound **14b**.



Figure S92:¹⁹F NMR (564 MHz, CD₂Cl₂, 299 K) spectra of in situ generated and isolated compound 14b.



Figure S93: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of isolated compound 14b [# impurity]



Figure S94:¹¹B and ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299 K) spectra of in situ generated and isolated compound **14b**.



Figure S95: ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K) spectrum of isolated compound **14b**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **14b** in dichloromethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 14b (erk10095): A colorless prism-like specimen of $C_{30}H_{29}BF_6N_2O_2S$, approximate dimensions 0.144 mm x 0.191 mm x 0.370 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK α (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 1398 frames were collected. The total exposure time was 11.65 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 120304 reflections to a maximum θ angle of 25.39° (0.83 Å resolution), of which 10584 were independent (average

redundancy 11.367, completeness = 99.6%, $R_{int} = 5.20\%$, $R_{sig} = 2.15\%$) and 9184 (86.77%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 40.6057(15) Å, <u>b</u> = 9.3758(4) Å, <u>c</u> = 30.7701(10) Å, β = 99.8210(10)°, volume = 11542.8(8) Å³, are based upon the refinement of the XYZ-centroids of 9864 reflections above 20 $\sigma(I)$ with 5.247° < 20 < 50.67°. 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 0.9360 and 0.9740. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 16 for the formula unit, $C_{30}H_{29}BF_6N_2O_2S$. The final anisotropic fullmatrix least-squares refinement on F² with 769 variables converged at R1 = 4.71%, for the observed data and wR2 = 11.95% for all data. The goodness-of-fit was 1.070. The largest peak in the final difference electron density synthesis was 0.676 e⁻/Å³ and the largest hole was -0.477 e⁻/Å³ with an RMS deviation of 0.051 e⁻/Å³. On the basis of the final model, the calculated density was 1.396 g/cm³ and F(000), 5024 e⁻. CCDC Nr.: 2108150.



Figure S96: Crystal structure of compound **14b**. (only one molecule (molecule "A") of two found in the asymmetric unit is shown; thermal ellipsoids are set at 30% probability).

Preparation of compound 15b





Boraalkene **3b** (54.2 mg, 0.1 mmol) and PhC(O)CF₃ (17.4 mg, 0.1 mmol) were combined in 3 mL of toluene and stirred for 60 minutes at 100 °C. Subsequently the volatiles were removed under reduced pressure, the residue was washed with pentane (3x2 mL). The solid residue was taken up in dichloromethane (2 mL), filtered and carefully layered with heptane (5 mL). After several days, white crystals of product have been formed. These were isolated by decantation, washed with pentane and dried in vacuo to give compound **15b** as white solid (40.5 mg, 0.057 mmol, 57% yield).

Melting point: 153.0 °C

HRMS for C₃₈H₃₄N₂BF₉ONa [M+Na⁺]: calculated 739.2519; found 739.2520.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.72 \text{ (s, } o), 7.40 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, m), 7.19 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), [7.27 \text{ (m, 1H, } p), 7.21 \text{ (m, 2H, } m), 7.12 \text{ (br, 2H, } o)](\text{Ph}), 6.86 \text{ (s, 2H, =CH)}, [6.93, 6.18](\text{each s, each 2H, CH}^{\text{Mes}}), [2.28, 2.21, 1.57](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), [1.36, 1.33](\text{each d, } {}^{2}J_{\text{HH}} = 13.4 \text{ Hz}, \text{ each 1H, CH}_{2})$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 164.7$ (br, BC^{IMes}), [154.3 (br, BC^{FpXyl}), 133.3 (q, ²*J*_{FC} = 30.5 Hz, *o*-C), 133.1 (br, *o*-CH), 129.9 (q, ²*J*_{FC} = 30.6 Hz, *m*-C), 126.2 (q, ¹*J*_{FC} = 273.9 Hz, *o*-CF₃), 124.9 (q, ¹*J*_{FC} = 273.0 Hz, *m*-CF₃), 124.6 (q, ³*J*_{FC} = 5.4 Hz, *m*-CH), 121.4 (q, ³*J*_{FC} = 5.4 Hz, *p*-CH)](FpXyl), [143.3 (*i*), 127.5 (*o*), 127.1 (*p*,*m*)](Ph), {[139.9, 135.2, 134.8, 134.6](C^{Mes}), [129.5, 129.4](CH^{Mes}), [20.9, 18.1 (q, *J* = 2.1 Hz), 17.9](CH₃^{Mes})}(Mes), 126.6 (q, ¹*J*_{FC} = 287.8 Hz, CF₃), 123.9 (=CH), 81.4 (br q, ²*J*_{FC} = 27.7 Hz, PhC(O)), 20.8 (br, CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = -1.4 (v_{1/2} \approx 90 \text{ Hz})$

¹¹**B NMR** (192 MHz, 299K, CD₂Cl₂): $\delta = -1.4 (v_{1/2} \approx 90 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): $\delta = [-55.6, -64.3, -79.5]$ (each s, each 1F)



Figure S97: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **15b** [# impurity, *P* Pentane]



Figure S98: ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K) spectrum of compound **15b** [*P* Pentane].





Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **15b** in dichloromethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 15b (erk10073): A colorless prism-like specimen of $C_{39}H_{36}BCl_2F_9N_2O$, approximate dimensions 0.079 mm x 0.143 mm x 0.181 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube CuK α (CuK α , $\lambda = 1.54178$ Å) and a MX mirror monochromator. A total of 1904 frames were collected. The total exposure time was 23.79 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 83131 reflections to a maximum θ angle of 68.37° (0.83 Å resolution), of which 6765 were independent (average redundancy 12.288, completeness = 99.5%, $R_{int} = 9.01\%$, $R_{sig} = 3.68\%$) and 5555 (82.11%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 13.2231(4) Å, <u>b</u> = 15.8615(5) Å, <u>c</u> = 17.6686(5) Å, $\beta = 91.414(2)^\circ$, volume = 3704.65(19) Å³, are based upon the refinement of the XYZ-centroids

of 9054 reflections above 20 $\sigma(I)$ with 7.491° < 2 θ < 136.3°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.840. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6820 and 0.8400. 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, $C_{39}H_{36}BCl_2F_9N_2O$. The final anisotropic full-matrix least-squares refinement on F² with 606 variables converged at R1 = 3.85%, for the observed data and wR2 = 9.64% for all data. The goodness-of-fit was 1.023. The largest peak in the final difference electron density synthesis was 0.512 e⁻/Å³ and the largest hole was -0.256 e⁻/Å³ with an RMS deviation of 0.045 e⁻/Å³. On the basis of the final model, the calculated density was 1.437 g/cm³ and F(000), 1648 e⁻. CCDC Nr.: 2108151.



Figure S101: Crystal structure of compound 15b (thermal ellipsoids are set at 30% probability).

Preparation of compound 16b



Scheme S18

Boraalkene **3b** (54.2 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51.1 mg, 0.1 mmol) were combined in dichloromethane (3 mL) and stirred for 90 minutes at room temperature. Subsequently the volatiles were removed under reduced pressure. The solid residue was washed with pentane (3x1 mL) and dried in vacuo to give compound **16b** as a white solid (90.5 mg, 0.086 mmol, 86% yield).

Decomposition point: 196.5 °C

Elemental analysis calculated for $C_{48}H_{29}N_2B_2F_{21}$ (1054.4): C 54.68, H 2.77, N 2.66; found: C 54.72, H 2.98, N 2.49.

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.49 (s, 2H, =CH), [7.22 (d, ³*J*_{HH} = 8.3 Hz, *p*), 7.16 (d, ³*J*_{HH} = 8.3 Hz, *m*), 6.86 (s, *o*)](each 1H, CH^{FpXyl}), [6.96, 6.77](each s, each 2H, CH^{Mes}), [2.21 (*p*-), 2.15 (*o*-), 1.96 (*o*-)](each s, each 6H, CH₃^{Mes}), [2.03 (br d, ²*J*_{HH} ≈ 14 Hz), 0.82 (br)](each 1H, CH₂)

¹³C{¹H} **NMR** (151 MHz, 299K, CD₂Cl₂): $\delta = 149.7$ (br, BC^{IMes}), [148.0 (dm, ¹*J*_{FC} ≈ 240 Hz), 138.2 (dm, ¹*J*_{FC} ≈ 250 Hz), 136.6 (dm, ¹*J*_{FC} ≈ 250 Hz), 126.2 (br, *i*-)](C₆F₅), [141.8 (*p*-C), 134.27 (*o*-C), 134.26 (*o*-C), 133.5 (*i*-C), 130.3 (*m*-CH), 130.1 (*m*-CH), 20.8 (*p*-CH₃), 17.5 (*o*-CH₃), 17.0 (*o*-CH₃)](Mes), [140.5 (br, BC^{FpXyI}), 131.9 (q, ²*J*_{FC} = 32.6 Hz, *m*-C), 130.9 (q, ²*J*_{FC} = 31.3 Hz, *o*-C), 125.9 (q, ³*J*_{FC} = 3.8 Hz, *m*-CH), 124.64 (q, ¹*J*_{FC} = 273.8 Hz, *o*-CF₃), 124.61 (q, ³*J*_{FC} = 3.2 Hz, *p*-CH), 124.1 (br, *o*-CH), 123.4 (q, ¹*J*_{FC} = 273.3 Hz, *m*-CF₃)](FpXyI), 128.5 (=CH), 29.8 (br m, CH₂)

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 70.1 (v_{1/2} \approx 1800 \text{ Hz}, \text{B}^+), -15.4 (v_{1/2} \approx 25 \text{ Hz}, \text{B}^-)$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = 70.1 (v_{1/2} \approx 1800 Hz, B⁺), -15.4 (v_{1/2} \approx 25 Hz, B⁻)

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-55.6, -64.3](each s, each 1F, FpXyl), [-131.9 (br, 2F, *o*-), 163.6 (t, ³*J*_{FF} = 20.2 Hz, 1F, *p*-), -167.3 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 3.7]



Figure S102: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **16b** [# impurity, *P* Pentane]



 ∇ C^{Mes} ▼ CH^{Mes} ♦ =CH • CH^{FpXyl} \bigcirc_{FpXyl} ($^{2}J_{FC} \approx 30$ Hz) \frown_{Fg} CF₃^{FpXyl} ($^{1}J_{FC} \approx 274$ Hz) $\frown_{F_{c}}$ C₆F₅ ($^{1}J_{FC} \approx 250$ Hz)



S86

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **16b** in dichloromethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 16b (erk10094): A colorless plate-like specimen of C₄₈H₂₉B₂F₂₁N₂, approximate dimensions 0.065 mm x 0.158 mm x 0.175 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube CuK α (CuK α , $\lambda = 1.54178$ Å) and a MX mirror monochromator. A total of 1779 frames were collected. The total exposure time was 22.58 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 79383 reflections to a maximum θ angle of 66.75° (0.84 Å resolution), of which 7573 were independent (average redundancy 10.482, completeness = 99.3%, $R_{int} = 6.68\%$, $R_{sig} = 3.21\%$) and 6051 (79.90%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 22.1581(5) Å, <u>b</u> = 10.6732(3) Å, <u>c</u> = 18.8029(5) Å, β = $105.0880(10)^\circ$, volume = 4293.55(19) Å³, are based upon the refinement of the XYZ-centroids of 9728 reflections above 20 σ (I) with 9.542° < 2 θ < 133.2°. 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 0.7890 and 0.9130. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{48}H_{29}B_2F_{21}N_2$. The final anisotropic fullmatrix least-squares refinement on F^2 with 764 variables converged at R1 = 4.16%, for the observed data and wR2 = 9.15% for all data. The goodness-of-fit was 1.038. The largest peak in the final difference electron density synthesis was 0.281 e⁻/Å³ and the largest hole was -0.274 e⁻/Å³ with an RMS deviation of 0.044 e^{-1} Å³. On the basis of the final model, the calculated density was 1.631 g/cm³ and F(000), 2120 e⁻. CCDC Nr.: 2108152.



Figure S106: Crystal structure of compound 16b (thermal ellipsoids are set at 30% probability).

Preparation of compound 17b



Scheme S19

Boraalkene **3b** (54.2 mg, 0.1 mmol) and $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol) were combined in dichloromethane (5 mL) and stirred for three hours at room temperature, while a white precipitate was formed. It was isolated by cannula filtration, washed with dichloromethane (1 mL), pentane (3x1 mL) and subsequently dried in vacuo to give compound **17b** as a white solid (62.2 mg, 0.068 mmol, 68% yield).

Decomposition point: 225.3 °C

Elemental analysis calculated for $C_{42}H_{30}N_2B_2F_{16}$ (916.3): C 56.78, H 3.40, N 3.20; found: C 56.90, H 3.52, N 3.50

Measurement of partially dissolved and filtered sample of compound 17b in CD_2Cl_2 (poorer solubility than in d_8 -thf):

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.36 \text{ (d, }^{3}J_{\text{HH}} = 8.3 \text{ Hz}), 7.08 \text{ (s)}, 7.04 \text{ (m)](each 1H, CH^{FpXyl})}, 7.07 \text{ (s, 2H, =CH)}, [6.99, 6.33](s, 2H, CH^{\text{Mes}}), [2.42, 2.20, 1.70](each s, each 6H, CH₃^{\text{Mes}}), 2.15 \text{ (br, BH)}^{t}, [0.63 \text{ (br t, }^{3}J_{\text{HH}} \approx 10 \text{ Hz}), 0.04 \text{ (br d, }^{2}J_{\text{HH}} \approx 10 \text{ Hz})](each 1H, CH_{2}), [^{t} \text{ tentatively assigned}].$

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -14.7 (v_{1/2} \approx 300 Hz), -18.9 (v_{1/2} \approx 300 Hz)

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -14.0 (v_{1/2} \approx 300 Hz), -18.9 (v_{1/2} \approx 300 Hz)

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-55.4, -63.8](each s, each 3F, FpXyl), [-129.5 (br, 4F, *o*-), -161.8 (t, ³*J*_{FF} = 20.5 Hz, 2F, *p*-), -165.3 (m, 4F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 4.8]

Measurement of compound **17b** in d₈-thf (better solubility than in CD₂Cl₂):

¹**H** NMR (599 MHz, 299K, *d*₈-thf): δ = 7.54 (s, 2H, =CH), [7.40 (d, ³*J*_{HH} = 8.2 Hz, *m*), 7.10 (d, ³*J*_{HH} = 8.2 Hz, *p*), 7.08 (s, *o*)](each 1H, CH^{FpXyl}), [7.02, 6.37](s, 2H, CH^{Mes}), [2.44, 2.20, 1.74](each s, each 6H, CH₃^{Mes}), 2.20 (br, 1H, B-H-B), [0.72 (br t, ³*J*_{HH} \approx ²*J*_{HH} \approx 10 Hz), 0.08 (br d, ²*J*_{HH} \approx 10 Hz)](each 1H, CH₂)

¹³C{¹H} NMR (151 MHz, 299K, d_8 -thf): $\delta = 159.8$ (br, BC^{IMes}), [148.8 (dm, ${}^{1}J_{FC} \approx 243$ Hz), 140.4 (dm, ${}^{1}J_{FC} \approx 247$ Hz), 137.8 (dm, ${}^{1}J_{FC} \approx 251$ Hz), 119.3 (br, *i*-)](C₆F₅), [145.6 (br, BC), 136.9 (br, *o*-C), 135.4 (br, *o*-CH), 130.7 (q, ${}^{2}J_{FC} = 31.4$ Hz, *m*-C), 126.8 (br, *m*-CH), 126.2 (q, ${}^{1}J_{FC} = 274.3$ Hz, *o*-CF₃), 124.6 (q, ${}^{1}J_{FC} = 272.7$ Hz, *m*-CF₃), 123.4 (q, ${}^{3}J_{FC} = 3.7$ Hz, *p*-CH),](FpXyl), {[140.9, 136.2, 135.3, 134.8](C^{Mes}), [130.2, 129.2](CH^{Mes}), [20.7, 18.5, 17.8](CH₃^{Mes})}(Mes), 126.8 (=CH), 2.1 (br, CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, d_8 -thf): δ = -14.0 ($v_{1/2} \approx 400$ Hz), -19.3 ($v_{1/2} \approx 350$ Hz)

¹¹**B** NMR (192 MHz, 299K, d_8 -thf): δ = -14.0 ($v_{1/2} \approx 400$ Hz), -19.3 ($v_{1/2} \approx 350$ Hz)

¹⁹**F NMR** (564 MHz, 299K, *d*₈-thf): δ = [-55.6, -64.1](each s, each 3F, FpXyl), [-129.4 (br, 4F, *o*-), -161.8 (t, ³*J*_{FF} = 17.8 Hz, 2F, *p*-), -166.2 (m, 4F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 4.4]







Figure S109: ¹⁹**F NMR** (564 MHz, CD₂Cl₂, 299 K) spectrum of compound **17b**. [# NTf₂ based impurity originated from starting material].



Figure S110: ¹H NMR (599 MHz, *d*₈-thf, 299 K) spectrum of compound **17b**.



Figure S111: Excerpt from ¹**H NMR** and ¹**H 1D TOCSY** (599 MHz, d_8 -thf, 299 K) spectrum of compound **17b**. [# denotes TOCSY irradiation peak $\delta_H = 0.71$]



Figure S112: ¹¹B and ¹¹B ^{1}H NMR (192 MHz, d_8 -thf, 299K) spectra of compound 17b.





Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **17b** in tetrahydrofurane covered with heptane at -35°C.

X-ray crystal structure analysis of compound 17b (erk10141): A colorless prism-like specimen of $C_{42}H_{30}B_2F_{16}N_2$, approximate dimensions 0.081 mm x 0.121 mm x 0.154 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube CuKa (CuKa, $\lambda = 1.54178$ Å) and a MX mirror monochromator. A total of 1393 frames were collected. The total exposure time was 18.12 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 88498 reflections to a maximum θ angle of 68.28° (0.83 Å resolution), of which 6927 were independent (average

redundancy 12.776, completeness = 99.7%, $R_{int} = 7.26\%$, $R_{sig} = 2.61\%$) and 5759 (83.14%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 16.1044(3) Å, <u>b</u> = 17.0992(3) Å, <u>c</u> = 27.5040(4) Å, volume = 7573.8(2) Å³, are based upon the refinement of the XYZ-centroids of 9375 reflections above 20 $\sigma(I)$ with 6.427° < 20 < 136.4°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.915. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8260 and 0.9030. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pbca*, with Z = 8 for the formula unit, $C_{42}H_{30}B_2F_{16}N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 626 variables converged at R1 = 3.40%, for the observed data and wR2 = 8.41% for all data. The goodness-of-fit was 1.014. The largest peak in the final difference electron density synthesis was 0.230 e⁻ /Å³ and the largest hole was -0.224 e⁻/Å³ with an RMS deviation of 0.043 e⁻/Å³. On the basis of the final model, the calculated density was 1.558 g/cm³ and F(000), 3600 e⁻. The bridging hydrogen between B1 and B2 atoms was refined freely. CCDC Nr.: 2108153.



Figure S115: Crystal structure of compound **17b** (thermal ellipsoids are set at 30% probability).

Preparation of 20b





Boraalkene **3b** (54.2 mg, 0.1 mmol) and HB(C₆F₅)₂ (34.6 mg, 0.1 mmol) were combined in dichloromethane (5 mL) and stirred for 15 minutes at room temperature. The initially homogenous colourless mixture became turbid and formation of a white precipitate was observed. Subsequently the mixture was degassed using freeze-thaw cycles and treated with CO (1.0 atm). The precipitate gradually dissolved, the mixture turned homogenous and after 60 minutes stirring at room temperature the volatiles were removed under reduced pressure. The solid residue was taken up in a small amount of dichloromethane (ca 1 mL) and carefully layered with pentane (5 mL). The mixture was placed in a freezer (-35°C). After three days, white crystals had formed. They were isolated by decantation, washed with pentane (3x 1 mL) and dried in vacuo to give compound **20b** as a white crystalline solid (69.1 mg, 0.075 mmol, 75% yield).

Melting point: 164.8 °C

Elemental analysis calculated for $C_{43}H_{30}N_2B_2F_{16}O$ (916.3): C 56.36, H 3.30, N 3.06; found: C 55.92, H 3.66, N 3.18

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.83 \text{ (s, } o), 7.81 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, m), 7.75 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), 6.99 \text{ (s, 2H, =CH)}, [7.11, 6.70](\text{each s, each 2H, CH}^{\text{Mes}}), 5.67 \text{ (s, 1H, CHO)}, [2.34, 2.33, 1.76](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), [1.93 \text{ (br d, } {}^{2}J_{\text{HH}} = 18.8 \text{ Hz}), 0.81 \text{ (br dd, } {}^{2}J_{\text{HH}} = 18.8 \text{ Hz}, J = 6.8 \text{ Hz})](\text{each 1H, CH}_{2})$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 169.7$ (br, BC^{IMes}), [140.6 (*p*-C), 135.9 (*o*-C), 134.6 (*o*-C), 134.3 (*i*-C), 129.7 (CH), 129.2 (CH), 20.9 (*p*-CH₃), 18.2 (*o*-CH₃), 17.8 (*o*-CH₃)](Mes), {137.9 (br, BC), 137.9 (q, ²J_{FC} = 30.8 Hz, *o*-C), 132.9 (q, ³J_{FC} = 3.6 Hz, *o*-CH), 132.4 (q, ²J_{FC} = 32.3 Hz, *m*-C), 126.7 (q, ³J_{FC} = 3.8 Hz, *p*-CH), 126.0 (q, ³J_{FC} = 5.9 Hz, *m*-CH), [124.5 (q, ¹J_{FC} = 274.4 Hz), 124.4 (q, ¹J_{FC} = 272.6 Hz)](CF₃)}(FpXyl), 124.1 (=CH), 77.4 (br m, BCHO), 16.2 (br, BCH₂), [C₆F₅ not listed].

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 52.6 (v_{1/2} \approx 1000 \text{ Hz}, R_2\text{B-O}), -11.0 (v_{1/2} \approx 60 \text{ Hz}, R_3\text{B-IMes})$

¹¹**B NMR** (192 MHz, 299K, CD₂Cl₂): δ = 52.6 (v_{1/2} \approx 1000 Hz, R₂B-O), -11.0 (v_{1/2} \approx 60 Hz, R₃B-IMes)

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-58.7 (d, *J* = 6.8 Hz), -68.0 (s)](each 3F, FpXyl), [-123.2 (m, *o*-), -131.2 (m, *o*-), -161.4 (t, ³*J*_{FF} = 20.0 Hz, *p*-), -164.8 (m, *m*-), -166.9 (m, *m*-)](each 1F, B-C₆F₅)[$\Delta\delta^{19}F_{m,p}$ = 3.4 and 5.5], [-138.0 (m, *o*-), -143.7 (m, *o*-), -159.8 (t, ³*J*_{FF} = 20.9 Hz, *p*-), -165.6 (m, *m*-), -165.6 (m, *m*-)](each 1F, C-C₆F₅)[$\Delta\delta^{19}F_{m,p}$ = 5.8 and 5.8]



Figure S116: ¹**H NMR** (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **20b** [*P* denotes residual pentane].





Figure S119: ¹⁹F,¹H HOESY (564 / 599 MHz, CD₂Cl₂, 299 K) spectrum of compound **20b**.



Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **20b** in dichloromethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 20b (erk10114): A colorless plate-like specimen of $C_{43}H_{30}B_2F_{16}N_2O$, approximate dimensions 0.050 mm x 0.110 mm x 0.140 mm, was used for the X-ray

crystallographic analysis. The X-ray intensity data were measured on a Kappa CCD APEXII Bruker APEXII Diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuK α , $\lambda = 1.54178$ Å) and a graphite monochromator. A total of 1532 frames were collected. The total exposure time was 21.51hours. 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 24541 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 7127 were independent (average redundancy 3.443, completeness = 99.7%, R_{int} = 9.36%, R_{sig} = 9.63%) and 4608 (64.66%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 10.0449(4) Å, <u>b</u> = 12.1685(4) Å, <u>c</u> = 16.6430(5) Å, $\alpha = 92.256(2)^{\circ}$, $\beta = 90.440(2)^{\circ}$, γ $= 95.170(2)^{\circ}$, volume $= 2024.32(12) \text{ Å}^3$, are based upon the refinement of the XYZ-centroids of 1796 reflections above 20 σ (I) with 7.300° < 2 θ < 131.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.843. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8450 and 0.9400. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, $C_{43}H_{30}B_2F_{16}N_2O$. The final anisotropic fullmatrix least-squares refinement on F^2 with 583 variables converged at R1 = 5.34%, for the observed data and wR2 = 14.53% for all data. The goodness-of-fit was 1.001. The largest peak in the final difference electron density synthesis was 0.254 e^{-}/A^3 and the largest hole was -0.304 e^{-}/A^3 with an RMS deviation of 0.060 e^{-/Å³}. On the basis of the final model, the calculated density was 1.503 g/cm³ and F(000), 928 e⁻. CCDC Nr.: 2108154.



Figure S121: Crystal structure of compound **20b** (thermal ellipsoids are set at 30% probability).

Preparation of compound **21b**



Scheme S21

Boraalkene **3b** (54.2 mg, 0.1 mmol) and Schwartz reagent ($[Cp_2Zr(H)Cl]_n$, 25.7 mg, 0.1 mmol) were combined in benzene (5 mL) and the obtained mixture was stirred at room temperature overnight. Subsequently all volatiles were removed under reduced pressure. The yellow solid residue was taken up in a small amount of toluene (1 mL) and then filtered through a Celite plug. The filtrate was carefully layered with heptane (5 mL) and placed into a freezer (-35 °C). After several days, a yellow crystalline solid and a small amount of a white precipitate has formed. The yellow crystalline solid was carefully separated, washed with pentane and dried in vacuo. Compound **21b** was obtained as a yellow solid (61.0 mg, 0.076 mmol, 76% yield).

Decomposition point: 165.8 °C

IR (KBr): v(BH) 2353 cm⁻¹

Elemental analysis calculated for $C_{40}H_{40}N_2BClF_6Zr \cdot 0.5$ toluene (846.2): C 61.73, H 5.24, N 3.31; found: C 61.89, H 5.37, N 3.28.

[Note: according to the ¹H NMR (CD_2Cl_2) the sample contains about 0.5 equivalents of toluene].

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.58 \text{ (s, } o), 7.45 \text{ (d, } {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, m), 7.13 \text{ (d, } {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), [7.02, 6.79](\text{each s, each 2H, CH}^{\text{Mes}}), 6.81 \text{ (s, 2H, =CH)}, [5.70, 5.59](\text{each s, each 5H, Cp}), 3.07 \text{ (br m, 1H, BH)}, [2.30 (p), 2.22 (o), 1.86 (o)](\text{each s, each 6H, CH}_{3}^{\text{Mes}}), [2.24 \text{ (ddmt, } {}^{2}J_{\text{HH}} = 7.1 \text{ Hz}, {}^{3}J_{\text{HH}} = 9.5 \text{ Hz}), -0.20 \text{ (d, } {}^{2}J_{\text{HH}} = 7.1 \text{ Hz})](\text{each 1H, CH}_{2}).$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 173.7$ (br, BC^{IMes}), [155.9 (br m, *i*-C), 135.8 (q, ²J_{FC} = 28.2 Hz, *o*-C), 134.7 (q, ³J_{FC} = 4.4 Hz, *o*-CH), 129.5 (q, ²J_{FC} = 30.3 Hz, m, *m*-C), 125.4 (q, ¹J_{FC} = 274.3 Hz, *o*-CF₃), 125.0 (q, ¹J_{FC} = 272.8 Hz, *m*-CF₃), 124.6 (q, ³J_{FC} = 6.4 Hz, *m*-CH), 120.8 (q, ³J_{FC} = 3.3 Hz, *p*-CH)](FpXyl), 139.8 (*p*-Mes), [135.6, 135.3](*o*-Mes), 135.0 (*i*-Mes), [129.6, 129.6](CH^{Mes}), 122.5 (=CH), [112.4, 111.1](Cp₂Zr), 91.0 (br m, CH₂), [21.0 (*p*), 18.1 (*o*), 17.6 (*o*)](CH₃^{Mes}).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): δ = -16.0 (v_{1/2} \approx 70 Hz)

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): δ = -16.0 (d, ¹*J*_{BH} ~ 90 Hz)

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): δ = -57.2 (d, J_{FH} = 8.1 Hz, 1F), -62.5 (s, 1F)



Figure S122: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **21b** [*T*: toluene].



Figure S123: ¹H, ¹H and ¹H, ¹H{¹⁹F} **1D-TOCSY** (599 MHz, CD₂Cl₂, 299 K) spectra of compound **21b** [% denotes TOCSY irradiation peak at δ^{1} H(CH₂)_{irr} = -0.19].





compound **21b** [selective decoupling was applied at δ^{1} H(BH)_{irr} = 3.11].

Preparation of compound 22a





Solutions of boraalkene **3a** (49.6 mg, 0.1 mmol) and [AuCl(SMe₂)] (29.4 mg, 0.1 mmol) in dichloromethane (both ca 2 mL) were combined and allowed to stir for 10 minutes at room temperature while the mixture was protected against sunlight by wrapping the vessel with aluminium foil. The mixture turned slightly turbid. It was filtered and all volatiles were removed in vacuo to give a grey solid of compound **22a** (68.1 mg, 0.093 mmol, 93% yield).

NOTE: Product seems to be slightly sensitive to light. Even in the solid state, samples slowly turned grey, satisfactory elemental analysis was not obtained.

HRMS for $C_{28}H_{26}N_2Au_2ClBF_5Na \ [M + Na]^+$: calculated 751.1360; found 751.1359

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): δ = 7.24 (s, 2H, =CH), [6.96, 6.94](each s, each 2H, CH^{Mes}), [2.99, 2.59](each d, ²J_{HH} = 6.5 Hz, each 1H, =CH₂), [2.33, 2.14, 2.13](each s, each 6H, CH₃^{Mes}).

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): δ = 155.0 (br, BC^{IMes}), [146.4 (dm, ¹*J*_{FC} ≈ 240 Hz), 139.9 (dm, ¹*J*_{FC} ≈ 254 Hz), 137.0 (dm, ¹*J*_{FC} ≈ 252 Hz), 115.9 (br, *i*-)](C₆F₅), [141.1 (*p*-C), 135.3 (*o*-C), 134.9 (*o*-C), 133.1 (*i*-), 130.2 (*m*-CH), 129.5 (*m*-CH), 21.1 (*p*-CH₃), 18.1 (*o*-CH₃), 17.8 (*o*-CH₃)](Mes), 124.6 (=CH), 58.9 (br, ¹*J*_{CH} ≈ 140 Hz, ¹*J*_{CH} ≈ 145 Hz, CH₂).

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 14.1 (v_{1/2} \approx 400 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 14.1 (v_{1/2} \approx 400 \text{ Hz})$

¹⁹**F NMR** (564 MHz, 299K, CD₂Cl₂): δ = [-126.7 (br, 2F, *o*-), -159.1 (t, ³*J*_{FF} = 20.0 Hz, 1F, *p*-), -164.8 (m, 2F, *m*-)](C₆F₅)[Δδ¹⁹F_{m,p} = 5.7]



Figure S127: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound 22a.



Figure S128: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD_2Cl_2 , 299K) spectra of compound 22a.



Figure S130: ¹³C{¹H} NMR (151 MHz, $CD_2Cl_2^*$, 299 K) spectrum of compound 22a.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 22a in dichloromethane covered with pentane at -35°C.

X-ray crystal structure analysis of compound 22a (erk10147): A colorless needle-like specimen of C₂₈H₂₆AuBClF₅N₂, approximate dimensions 0.046 mm x 0.055 mm x 0.174 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 1.54178$ Å). A total of 1938 frames were collected. The total exposure time was 16.99 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 55159 reflections to a maximum θ angle of 68.33° (0.83 Å resolution), of which 4925 were independent (average redundancy 11.200, completeness = 99.1%, $R_{int} = 5.25\%$, and 4613 (93.66%) were $R_{sig} = 2.35\%$) greater than $2\sigma(F^2)$. The final cell constants of a = 23.8839(7) Å, b = 8.1547(2) Å, c = 14.4589(4) Å, β = 105.8530(10)°, volume = 2708.99(13) Å³, are based upon the refinement of the XYZ-centroids of 1198 reflections above 20 $\sigma(I)$ with 15.47° < 2 θ < 116.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.682. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2370 and 0.6170. 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, $C_{28}H_{26}AuBClF_5N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 455 variables converged at R1 = 1.99%, for the observed data and wR2 = 4.81% for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was 0.625 e⁻ $/Å^3$ and the largest hole was -0.857 e⁻/Å³ with an RMS deviation of 0.087 e⁻/Å³. On the basis of the final model, the calculated density was 1.787 g/cm³ and F(000), 1416 e⁻. The hydrogens at C4 atom were refined freely, but with C-H distance restraints (U-fixed value). CCDC Nr.: 2108155.



Figure S131: Crystal structure of compound 22a (thermal ellipsoids are set at 30% probability).

Preparation of compound 22b



Scheme S23

Solutions of boraalkene **3b** (54.2 mg, 0.1 mmol) and [AuCl(SMe₂)] (29.4 mg, 0.1 mmol) in dichloromethane (both ca 2 mL) were combined and allowed to stir for one hour at room temperature while the mixture was protected against sunlight by wrapping the vessel with aluminium foil. Subsequently all volatiles were removed in vacuo. The residue was dissolved in dichloromethane (ca 1 mL). The obtained suspension was filtered and the resulting solution was carefully layered with heptane (ca 5 mL). The mixture was stored in a freezer at -35°C and after several days, white crystals were formed. These were isolated by decantation, washed with pentane (3x 1 mL) and dried in vacuo to give an off-white powder of compound **22b** (56.3 mg, 0.072 mmol, 72% yield).

NOTE: Redissolving the isolated off-white powder in dichloromethane resulted in slightly turbid solution, possibly indicating the formation of elemental gold during the crystallization process. A satisfactory elemental analysis was not obtained.

HRMS for C₃₀H₂₉N₂AuClBF₆Na [M+Na⁺]: calculated 797.1580; found 797.1585

¹**H** NMR (599 MHz, 299K, CD₂Cl₂): $\delta = [7.71 \text{ (s, }o), 7.42 \text{ (d, }{}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, m), 7.26 \text{ (d, }{}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, p)](\text{each 1H, CH}^{\text{FpXyl}}), 7.19 \text{ (s, 2H, =CH)}, [7.00, 7.76](\text{each s, each 2H, CH}^{\text{Mes}}), [2.37, 2.18](\text{each d, }{}^{2}J_{\text{HH}} = 6.1 \text{ Hz}, \text{ each 1H, CH}_{2}), [2.27 (p-), 2.27 (o-), 2.07 (o-)](\text{each s, each 6H, CH}_{3}^{\text{Mes}})$

¹³C{¹H} NMR (151 MHz, 299K, CD₂Cl₂): $\delta = 154.3$ (br, BC^{IMes}), [143.1 (br, BC), 135.3 (q, ${}^{3}J_{FC} \approx 3$ Hz, *o*-CH), 134.4 (q, ${}^{2}J_{FC} = 30.0$ Hz, *o*-C), 130.8 (q, ${}^{2}J_{FC} = 30.0$ Hz, *m*-C), 125.3 (q, ${}^{3}J_{FC} = 5.0$ Hz, *m*-CH), 125.2 (q, ${}^{1}J_{FC} = 274.4$ Hz, *o*-CF₃), 124.0 (q, ${}^{1}J_{FC} = 273.0$ Hz, *m*-CF₃), 123.0 (q, ${}^{3}J_{FC} = 3.5$ Hz, *p*-CH)](FpXyl), [141.1 (*p*-C), 135.3 (*o*-C), 134.6 (*o*-C), 133.6 (*i*-C), 130.0 (*m*-CH), 129.9 (*m*-CH), 21.0 (*p*-CH₃), 18.3 (*o*-CH₃), 18.2 (q, *J* = 1.9 Hz, *o*-CH₃)](Mes), 125.1 (=CH), 54.7 (br, CH₂),

¹¹B{¹H} NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 21.4 (v_{1/2} \approx 400 \text{ Hz})$

¹¹**B** NMR (192 MHz, 299K, CD₂Cl₂): $\delta = 21.4 (v_{1/2} \approx 400 \text{ Hz})$

¹⁹**F** NMR (564 MHz, 299K, CD₂Cl₂): δ = -56.6 (s, 1F), -63.3 (s, 1F)



Figure S132: ¹H NMR (599 MHz, CD₂Cl₂, 299 K) spectrum of compound **22b**, [#:impurity]



Figure S133: ¹¹B and ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299K) spectra of compound **22b**.






Figure S136: ${}^{1}H, {}^{13}C{}^{1}H$ gHSQC (599 / 151 MHz, CD₂Cl₂, 299 K) of compound 22b.

Generation of compound 23a



Scheme S24

Solutions of boraalkene **3a** (50.0 mg, 0.1 mmol) and $[RhCl(CO)_2]_2$ (19.4 mg, 0.05 mmol) in dichloromethane (both ca 1 mL) were combined and allowed to stir for one hour at room temperature while the mixture was protected against sunlight by wrapping the vessel with aluminium foil. Subsequently the brown/orange mixture was filtered, carefully layered with pentane (ca 5 mL) and placed into freezer at -35°C. The next day, some orange crystals had formed with a deep brown suspension. X-ray crystal structure analysis of the obtained orange crystals revealed specie **23a**.

Several attempts to perform the experiment on a preparative scale in ratio $[B=CH_2]:[Rh]$ 1:1 or 1:2 did not result in the isolation of any defined product. Similarly, replacing the Rh^I source with $[RhCl(cod)]_2$ or $[RhCl(nbd)]_2$ did not lead to any result.

X-ray crystal structure analysis of compound 23a (erk10056): A orange prism-like specimen of $C_{31}H_{26}BCl_2F_5N_2O_3Rh_2$, approximate dimensions 0.062 mm x 0.125 mm x 0.138 mm, was used for the Xray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK α (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 608 frames were collected. The total exposure time was 2.53 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 73765 reflections to a maximum θ angle of 26.74° (0.79 Å resolution), of which 8225 were independent (average redundancy 8.968, completeness = 99.7%, Rint = 5.70%, Rsig = 2.68%) and 7072 (85.98%) were greater than $2\sigma(F^2)$. The final cell constants of a = 15.1290(3) Å, b = 15.4702(4) Å, c = 17.7987(4) Å, $\beta = 111.5710(10)^{\circ}$, volume = 3874.00(16) Å3, are based upon the refinement of the XYZ-centroids of 9852 reflections above 20 $\sigma(I)$ with $5.391^{\circ} < 2\theta < 53.44^{\circ}$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.941. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8690 and 0.9380. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P_{21/c}$, with Z = 4for the formula unit, C₃₁H₂₆BCl₂F₅N₂O₃Rh₂. The final anisotropic full-matrix least-squares refinement on F^2 with 421 variables converged at R1 = 2.53%, for the observed data and wR2 = 6.39% for all data. The goodness-of-fit was 1.045. The largest peak in the final difference electron density synthesis was 0.412 e⁻ $/\text{Å}^3$ and the largest hole was -0.538 e/ Å^3 with an RMS deviation of 0.071 e/ Å^3 . On the basis of the final model, the calculated density was 1.469 g/cm³ and F(000), 1696 e⁻. CCDC Nr.: 2156435.



Figure S137: Crystal structure of compound 23a (thermal ellipsoids are set at 30% probability).

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