Enamine/Butadienylborane Cycloaddition in the Frustrated Lewis Pair Regime

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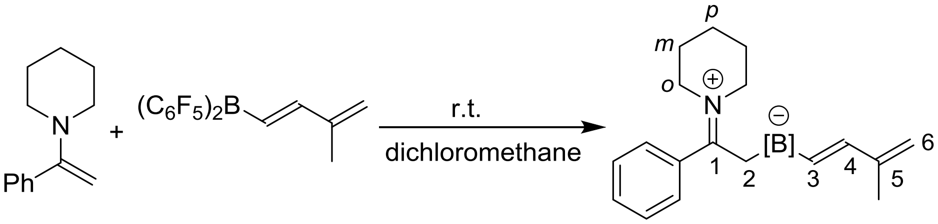
General Procedures

Standard Schlenk-type glassware (or glove box) was applied for the syntheses compounds involving air- and/or moisture-sensitive under an atmosphere of argon. Solvents were purified and stored under an argon atmosphere. NMR spectra were recorded on the following instruments: Agilent VNMRS 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz), Agilent DD2 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz). Bruker AV 300 (^{1}H: 300 MHz, ^{13}C: 126 MHz, ^{19}F: 282 MHz, ^{11}B: 96 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift δ is given relative to $CFCl_3$ (external reference); ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a Elementar Vario El III, while IR spectra Varian 3100 FT-IR (Excalibur Series) and melting points DSC Q20 (TA Instruments). X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). For compounds **8a, 7a** and **11b** data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **4a** one C6F5 group and one 2-propenyl group were found disordered over two positions. Compound **4b** present one 2-propenyl group disordered over two positions. In compound **11c** one morpholino group at boron atom is disordered over two positions. For all these tree compounds several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compound **7a** a disordered half dichloromethane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek A. L. *J. Appl. Cryst.,* **2003**, *36*, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. CCDC deposition no.: 1411182 to 1411189.

Materials

Bis(pentafluorophenyl)borane (*Piers'* borane) [Parks, D. J.; Spence, R. E. von H.; Piers, W. E. *Angew. Chem. Int. Ed.* **1995**, *34*, 809-811; Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492-5503], dimesitylethynylphosphane (**4**) [Zhao, X.; Lough, A. J.; Stephan, D. W. *Chem. Eur. J.* **2011**, *17*, 6731-6743], the dienylborane **2a** [Moquist, P.; Chen, G.-Q.; Mück-Lichtenfeld, C.; Bussmann, K.; Daniliuc, C. G.; Kehr, G.; Erker, G. *Chem. Sci.* **2015**, *6*, 816-825.] and the enamines **3a** and **3b** [White, W. A., Weingarten, H. *J. Org. Chem.* **1967**, *32*, 213-214; NMR data see: Reddy, C. R. V.; Urgaonkar, S.; Verkade, J. G. *Org. Lett.* **2005**, *7*, 4427-4430] were prepared according to a procedure described in the literature.

Synthesis of compound **4a**:



4a

[B]: $B(C_6F_5)_2$

Scheme S1

A solution of the enyne **1a** (21.0 mg, 0.32 mmol, 1 eq) in dichloromethane (1 mL) was added to a stirred suspension of bis(pentafluorophenyl)borane (110 mg, 0.32 mmol, 1 eq) and dichloromethane (1 mL). After stirring the reaction mixture for 3 h at room temperature, a solution of the enamine **3a** (59.0 mg, 0.32 mmol, 1 eq) in dichloromethane (1 mL) was added to the yellow suspension. Before removal of the volatiles *in vacuo*, the reaction mixture was stirred for 1 h at room temperature. The obtained residue was washed with *n*-pentane (2 × 1 mL) twice. Drying of the obtained solid *in vacuo* gave compound **4a** as a colorless powder (154 mg, 0.26 mmol, 81%).

[Comment: compound **4a** slowly decomposes at room temperature both in solution (CD_2Cl_2) and in solid state].

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **4a** in dichloromethane covered with *n*-pentane at room temperature.

X-ray crystal structure analysis of compound 4a: formula $C_{30}H_{24}BF_{10}N \cdot 0.5\ C_6H_6$, M = 638.37, colourless crystal, 0.20 x 0.20 x 0.10 mm, a = 8.3589(1), b = 20.9131(3), c = 17.1468(4) Å, β = 97.582(1) °, V = 2971.2(1) Å^3, ρ_{calc} = 1.427 gcm^{-3}, μ = 0.126 mm^{-1}, empirical absorption correction ($0.975 \leq T \leq 0.987$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 25543 reflections collected (±*h*, ±*k*, ±*l*), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 7262 independent (R_{int} = 0.048) and 5314 observed reflections [$I > 2\sigma(I)$], 536 refined parameters, R = 0.058, wR^2 = 0.119, max. (min.) residual electron density 0.25 (-0.18) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

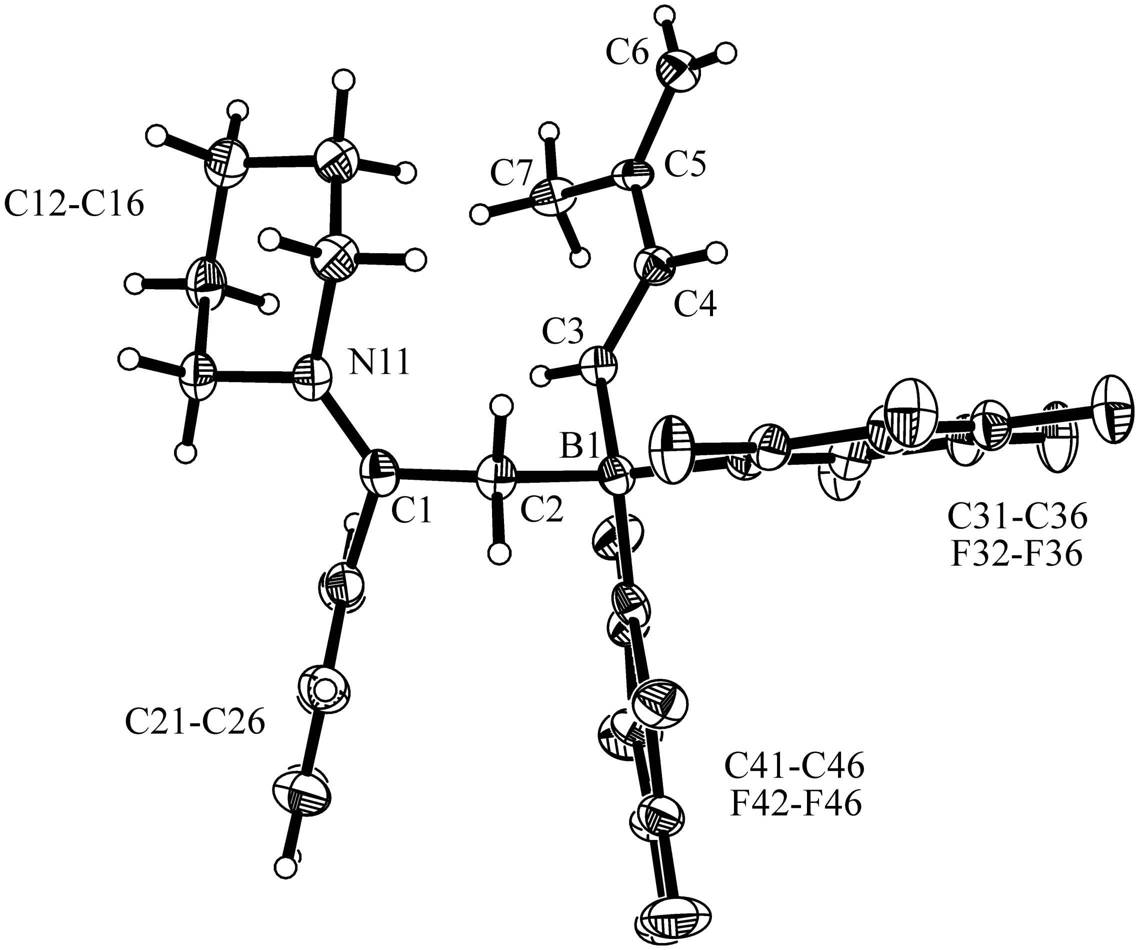


Figure S1

Melting point: 112 °C. **Anal. Calc.** for $C_{30}H_{24}BF_{10}N$: C, 60.12; H, 4.04, N, 2.34. Found: C, 60.35; H, 4.26; N, 2.23.

IR (KBr): ṽ/ cm^{-1} = 4479 (w), 4393 (w), 4058 (w), 3902 (w), 3854 (m), 3838 (m), 3803 (m), 3748 (s), 3771 (m), 3674 (s), 3650 (s), 3598 (s), 3568 (m), 3089 (s), 3060 (s), 3034 (s), 2970 (vs), 2932 (vs), 2865 (s), 2812 (m), 2538 (m), 2361 (s), 2340 (s), 2279 (m), 1891 (w), 1770 (m), 1643 (vs), 1600 (vs), 1558 (s), 1514 (vs), 1457 (vs), 1365 (vs), 1272 (vs), 1237 (vs), 1124 (vs), 1082 (vs), 965 (vs), 878 (vs), 768 (vs), 741 (vs), 697 (vs), 574 (m), 508 8s), 459(w).

[Comment: Pip: NC_5H_{10}]
^{1}**H NMR** (600 MHz, 273 K, dichloromethane-d$_2$): δ ^{1}H: 7.37 (m, 1H, *p*-Ph), 7.29 (m, 2H, *m*-Ph), 7.15 (m, 2H, *o*-Ph), 6.50 (d, $^3J_{HH}$ = 17.7 Hz, 1H, BCH), 5.73 (d, $^3J_{HH}$ = 17.7 Hz, 1H, =CH), 4.80, 4.66 (each br, each 1H, =CH$_2$), 3.96, 3.72 (each br, each 2H, *o*-Pip), 3.31 (br, 2H, BCH$_2$), 1.90 (m, 3H, CH$_3$), 1.85, 1.64 (each br, each 2H, *m*-Pip), 1.75(br, 2H, *p*-Pip).
^{13}**C{^{1}H} NMR** (151 MHz, 273 K, dichloromethane-d$_2$): δ ^{13}C: 194.9 (br, N=C), 147.9 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 144.5 (=C), 143.7 (br, BCH), 138.3 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 135.5 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 135.6 (br, =CH), 135.1 (*i*-Ph), 131.4 (*p*-Ph), 128.6 (*m*-Ph), 127.0 (*o*-Ph), 124.9 (br, *i*-C_6F_5), 112.7 (br, =CH$_2$), 55.5, 53.6 (each br, *o*-Pip), 41.8 (br, BCH$_2$), 27.5, 26.8 (each br, *m*-Pip), 23.3 (*p*-Pip), 19.2 (CH$_3$).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 273 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{1}H: 7.37 / 7.29, 7.15 (*p*-Ph / *m*-Ph, *o*-Ph), 5.73 / 6.50, 4.66, 1.90 (=CH / BCH, =CH$_2$, CH$_3$), 3.96 / 1.85 (*o*-Pip / *m*-Pip).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 273 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 7.37 / 131.4 (*p*-Ph), 7.29 / 128.6 (*m*-Ph), 7.15 / 127.0 (*o*-Ph), 6.50 / 143.7 (BCH), 5.73 / 135.6 (=CH), 4.80, 4.66 / 112.7 (=CH$_2$), 3.96, 3.72 / 55.5, 53.6 (*o*-Pip), 3.31 / 41.8 (BCH$_2$), 1.90 / 19.2 (CH$_3$), 1.85 / 27.5 (*m*-Pip), 1.75 / 23.3 (*p*-Pip), 1.64 / 26.8 (*m*-Pip).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 273 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{13}C: 7.29 / 135.1, 128.6, 127.0 (*m*-Ph */ i*-Ph, *m*-Ph, *o*-Ph), 7.15 / 194.9, 131.4, 128.6, 127.0 (*o*-Ph / N=C, *p*-Ph, *m*-Ph, *o*-Ph), 4.80 / 135.6, 19.2 (=CH$_2$ / =CH, CH$_3$), 3.96 / 194.9, 26.8 (*o*-Pip / N=C, *m*-Pip), 3.31 / 135.1 (BCH$_2$/ *i*-Ph), 1.90 / 144.5, 135.6, 112.7 (CH$_3$ / =C, =CH, =CH$_2$).

^{19}F NMR (564 MHz, 273 K, dichloromethane-d$_2$): δ ^{19}F: -132.6 (br, 2F, *o*-C$_6$F$_5$), -162.6 (br, 1F, *p*-C$_6$F$_5$), -166.3 (br, 2F, *m*-C$_6$F$_5$), [Δδ ^{19}F$_{m,p}$ = 3.7].

^{11}B{^{1}H} NMR (192 MHz, 273 K, dichloromethane-d$_2$): δ ^{11}B: -10.9 ($\nu_{1/2}$ ~ 200 Hz).

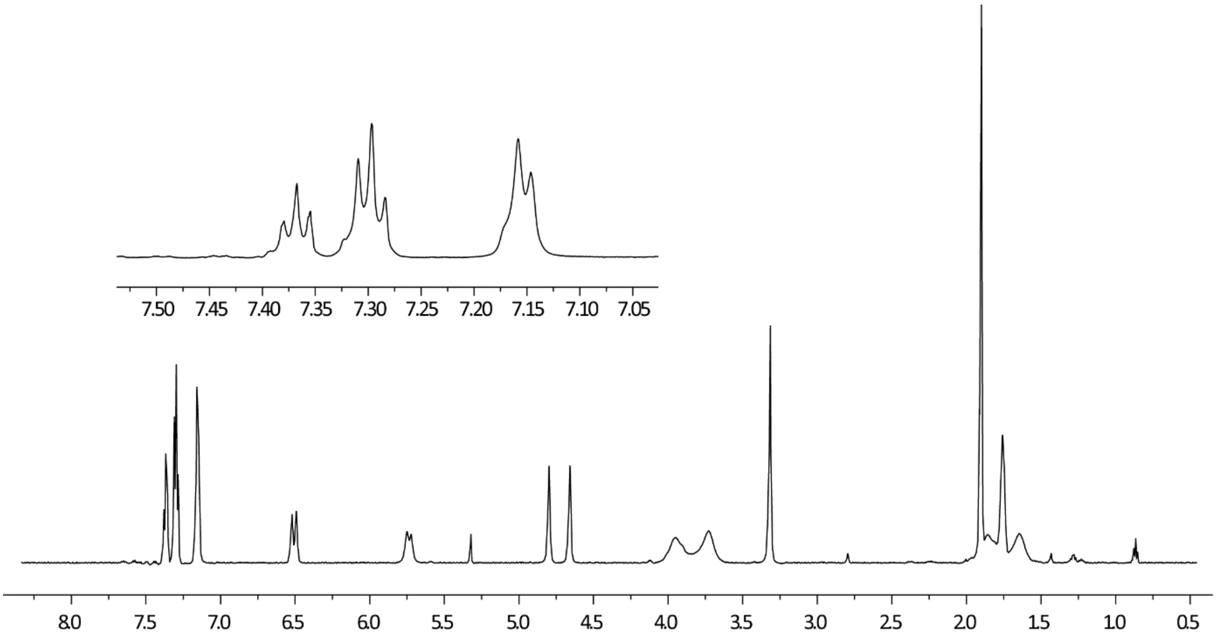


Figure S2 *^{1}H NMR (600 MHz, 273 K, dichloromethane-d$_2$) spectrum of compound* ***4a****.*

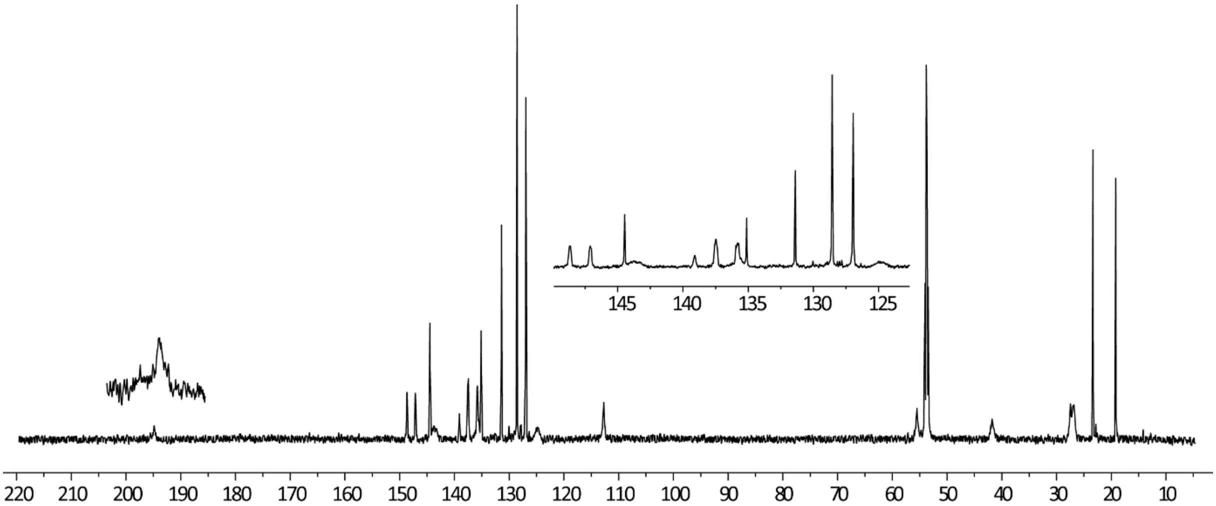


Figure S3 *^{13}C{^{1}H} NMR (151 MHz, 273 K, dichloromethane-d$_2$) spectrum of compound* ***4a****.*

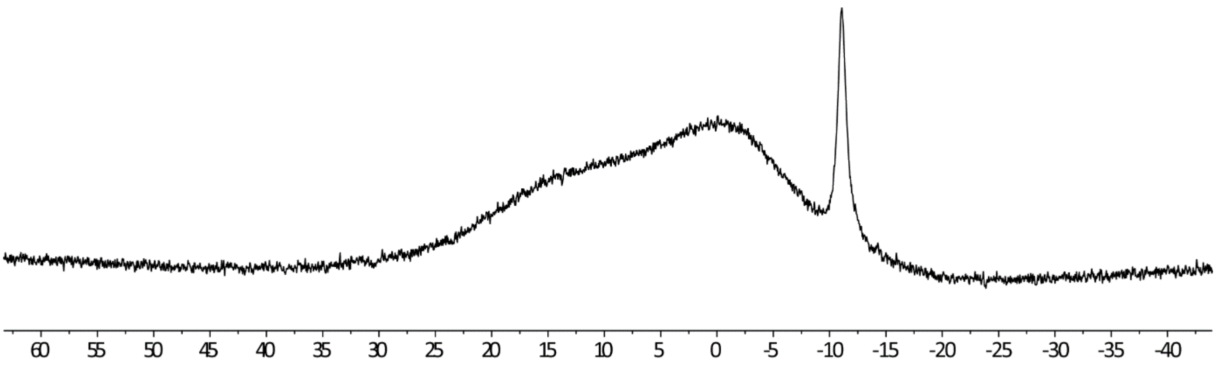


Figure S4 *^{11}B{^{1}H} NMR (192 MHz, 273 K, dichloromethane-d$_2$) spectra of compound* ***4a***.

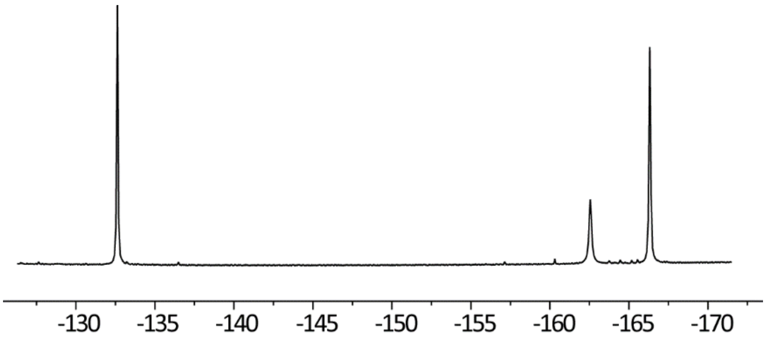
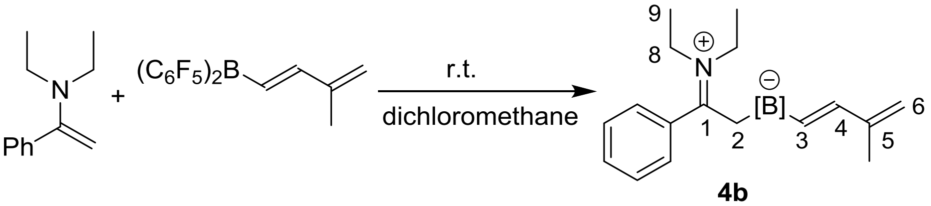


Figure S5 *^{19}F NMR (564 MHz, 273 K, dichloromethane-d$_2$) spectra of compound* ***4a***.

Synthesis of compound **4b**:



4b
[B]: $B(C_6F_5)_2$

Scheme S2

The enyne **1a** (29.0 mg, 0.44 mmol, 1 eq) in dichloromethane (1 mL) was added to a stirred suspension of bis(pentafluorophenyl)borane (153 mg, 0.44 mmol, 1 eq) in dichloromethane (1 mL). After stirring the yellow reaction mixture for 3 h at room temperature a solution of the enamine **3b** (78.0 mg, 0.44 mmol, 1 eq) in dichloromethane (1 mL) was added. The reaction mixture was stirred for 1 h at room temperature and after removal of the volatiles *in vacuo*, the resulting residue was washed four times with *n*-pentane (4 × 1 mL). Drying of the obtained solid *in vacuo* gave compound **4b** as a colorless powder (128 mg, 0.31 mmol, 70%).
[Comment: compound **4b** slowly decomposes at room temperature both in solution and in solid state].

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **4b** in dichloromethane at room temperature.

X-ray crystal structure analysis of compound 4b: formula $C_{29}H_{24}BF_{10}N$, M = 587.30, colourless crystal, 0.12 x 0.06 x 0.03 mm, a = 8.3829(2), b = 18.0928(5), c = 18.0057(6) Å, β = 95.814(1) °, V = 2716.9(1) Å^3, ρ_{calc} = 1.436 gcm^{-3}, μ = 0.131 mm^{-1}, empirical absorption correction (0.984 ≤ T ≤ 0.996), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 15978 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4665 independent (R_{int} = 0.063) and 3183 observed reflections [I>2σ(I)], 402 refined parameters, R = 0.070, wR^2 = 0.148, max. (min.) residual electron density 0.19 (-0.21) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

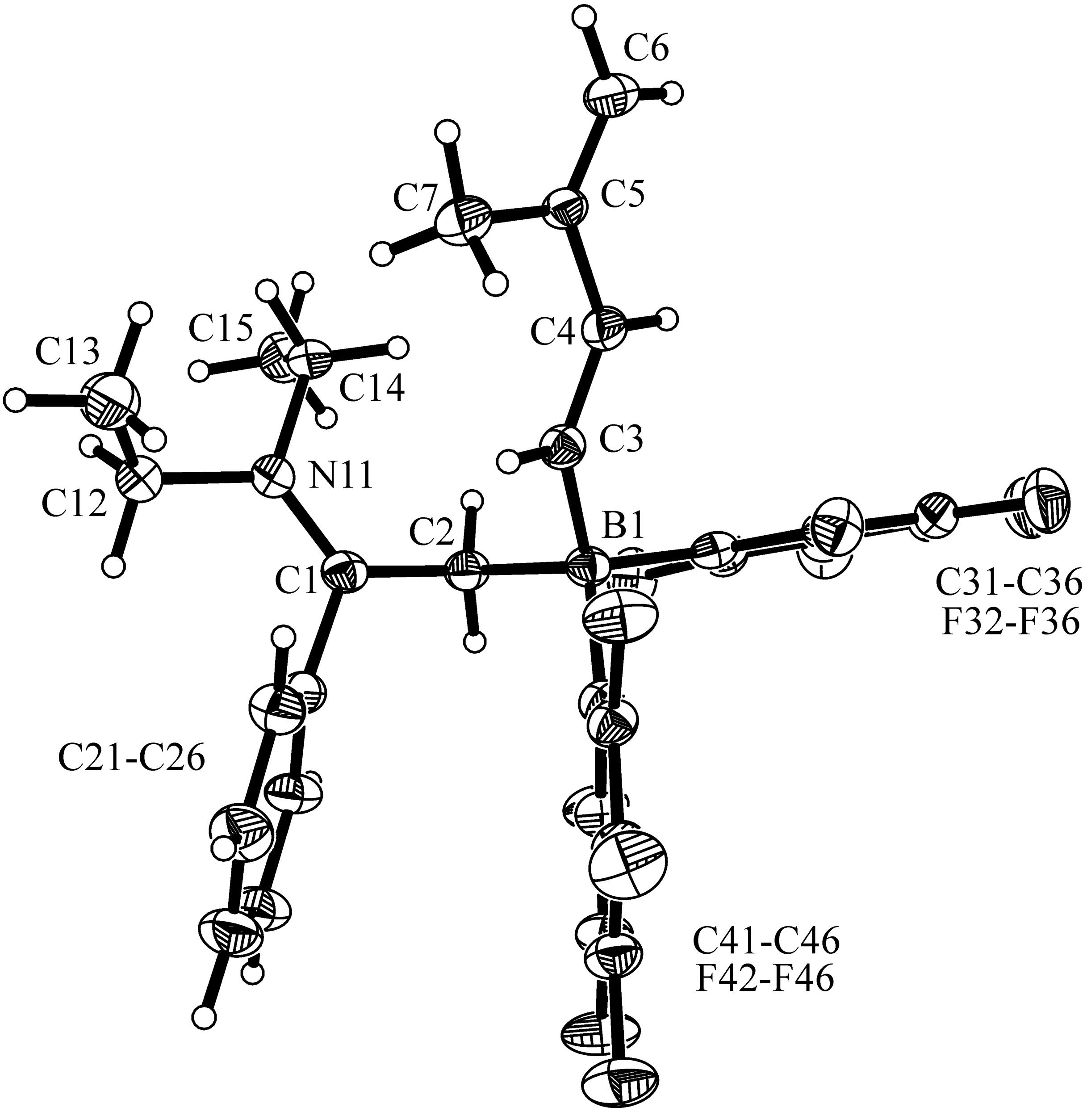


Figure S6

Melting point: 138 °C. **Anal. Calc.** for $C_{29}H_{24}BF_{10}N$: C, 59.31; H, 4.12; N, 2.38. Found: C, 58.92; H, 3.75; N; 2.33.

IR (KBr): ṽ/ cm^{-1} = 4444 (w), 4063 (w), 3752 (w), 3598 (m), 3079 (m), 2979 (vs), 2344 (m), 1642 (vs), 1602 (vs), 1513 (vs), 1458 (vs), 1390 (s), 1355 (vs), 1304 (s), 1271 (vs), 1239 (s), 1186 (s), 1124 (vs), 1082 (vs), 999 (vs), 964 (vs), 876 (vs), 798 (s), 766 (vs), 696 (vs), 600 (m), 574 (m), 539 (m).

^{1}H NMR (500 MHz, 263 K, dichloromethane-d$_2$): δ ^{1}H: 7.35 (m, 1H, *p*-Ph), 7.28 (m, 2H, *m*-Ph), 7.18 (m, 2H, *o*-Ph), 6.46 (br d, $^3J_{HH}$ = 17.6 Hz, 1H, BCH), 5.74 (br d, $^3J_{HH}$ = 17.6 Hz, 1H, =CH), 4.80, 4.66 (each br, each 1H, =CH$_2$), 3.87 (2H), 1.39 (3H) (each br m, NEt). 3.47 (2H), 1.44 (3H) (each br m, NEt), 3.30 (s, 2H, BCH$_2$), 1.90 (br, 3H, CH$_3$).

^{13}C{^{1}H} NMR (126 MHz, 263 K, dichloromethane-d$_2$): δ ^{13}C: 196.4 (br, N=C), 147.9 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 144.3 (=C), 142.8 (br, BCH), 138.0 (dm, $^1J_{FC}$ ~ 220 Hz, C_6F_5), 136.4 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 135.1

(br, =CH), 135.0 (br, *i*-Ph), 131.2 (*p*-Ph), 128.3 (*m*-Ph), 126.0 (*o*-Ph), 124.5 (br, *i*-C_6F_5), 112.6 (br, =CH_2), 48.8, 14.7 (each br, NEt), 46.4, 11.6 (each br, NEt), 41.3 (br, BCH_2), 19.0 (CH_3).

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 263 K, dichloromethane-d_2) [selected traces]: δ ^{1}H / δ ^{1}H: 7.35 / 7.28, 7.18 (*p*-Ph / *m*-Ph, *o*-Ph), 6.46 / 5.74 (BCH / =CH), 4.80 / 4.66, 1.90 (=CH_2 / =CH_2, CH_3), 3.87 / 1.39 (NEt / NEt).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, 263 K, dichloromethane-d_2): δ ^{1}H / δ ^{13}C: 7.35 / 131.2 (*p*-Ph), 7.28 / 128.3 (*m*-Ph), 7.18 / 126.0 (*o*-Ph), 6.46 / 142.8 (BCH), 5.74 / 135.1 (=CH), 4.80, 4.66 / 112.6 (=CH_2), 3.87 / 46.4 (NEt), 3.47 / 48.8 (NEt), 3.30 / 41.3 (BCH_2), 1.90 / 19.0 (CH_3), 1.44 / 14.7 (NEt), 1.39 / 11.6 (NEt).

^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, 263 K, dichloromethane-d_2) [selected traces]: δ ^{1}H / δ ^{13}C: 7.28 / 135.0, 128.3, 126.0 (*m*-Ph / *i*-Ph, *m*-Ph, *o*-Ph), 7.18 / 196.4, 131.2, 126.0 (*o*-Ph / N=C, *p*-Ph *o*-Ph), 5.74 / 144.3, 112.6, 19.0 (=CH / =C, =CH_2, CH_3), 3.87 / 196.4, 14.7 (NEt / N=C, NEt), 3.30 / 196.4, 135.0 (BCH_2 / N=C, *i*-Ph), 1.90 / 144.3, 135.1, 112.6 (CH_3 / =C, =CH, =CH_2).

^{1}H{^{1}H} TOCSY (500 MHz, 263 K, dichloromethane-d_2) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$: 6.46 / 5.74, 3.30, 1.91 (BCH / =CH, BCH_2, CH_3), 1.44 / 3.47, 1.39 (NEt / NEt, NEt).

^{19}F NMR (470 MHz, 263 K, dichloromethane-d_2): δ ^{19}F: -132.8 (m, 2F, *o*-C_6F_5), -162.4 (br t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-C_6F_5), -166.3 (m, 2F, *m*-C_6F_5), [Δδ $^{19}F_{m,p}$ = 3.9].

^{11}B{^{1}H} NMR (160 MHz, 263 K, dichloromethane-d_2): δ ^{11}B: -11.4 ($\nu_{1/2}$ ~ 100 Hz).

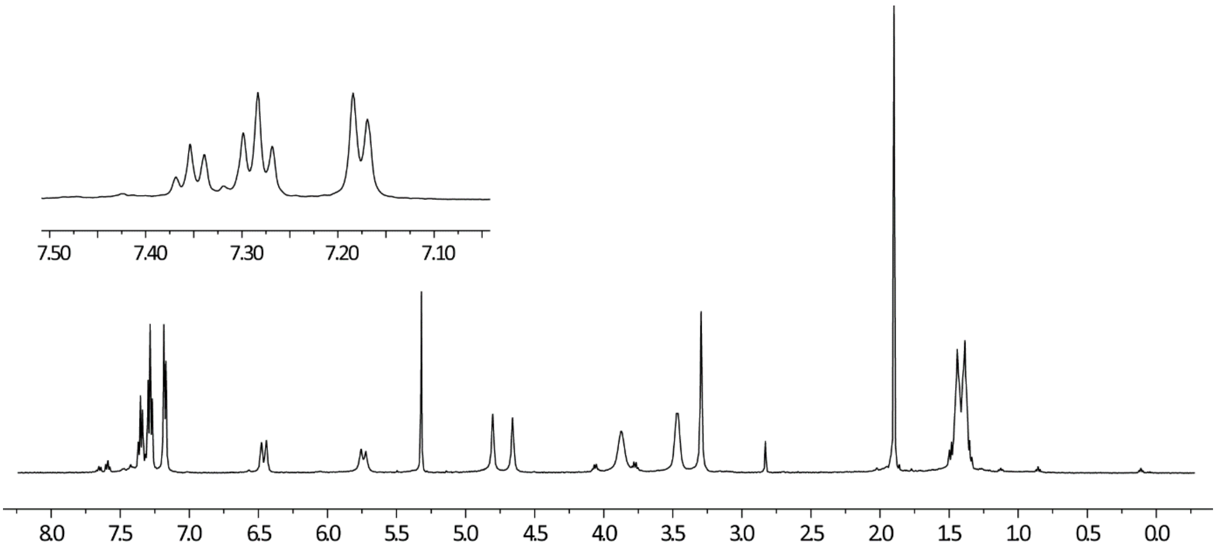


Figure S7 *^{1}H NMR (500 MHz, 263 K, dichloromethane-d_2) spectrum of compound* ***4b***

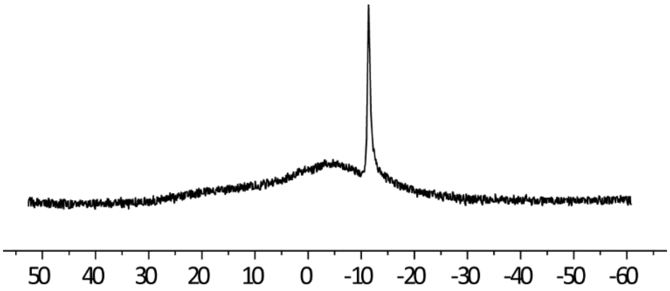


Figure S8 *^{11}B{^{1}H} NMR (160 MHz, 263 K, dichloromethane-d_2) spectra of compound* ***4b****.*

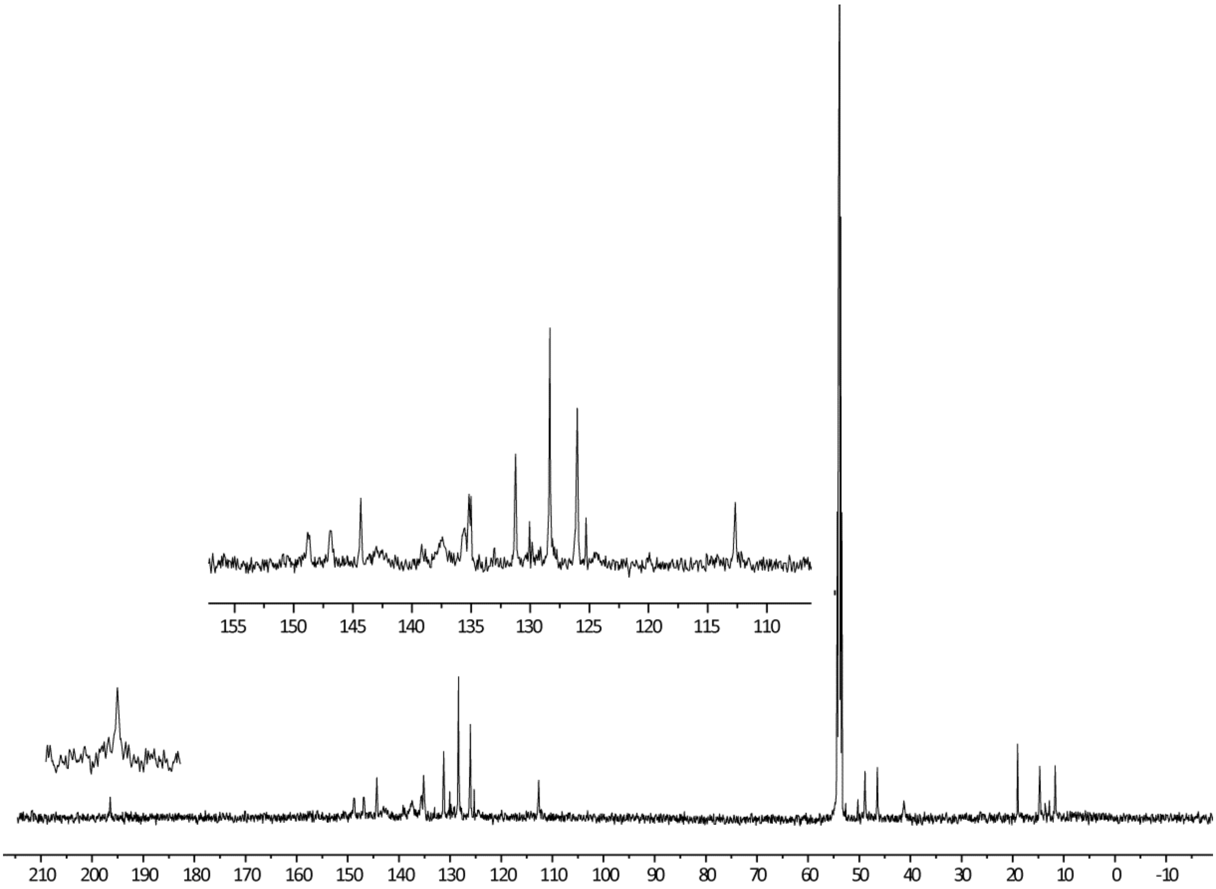


Figure S9 $^{13}C\{^{1}H\}$ *NMR (126 MHz, 263 K, dichloromethane-*d_2*) spectrum of compound* ***4b****.*

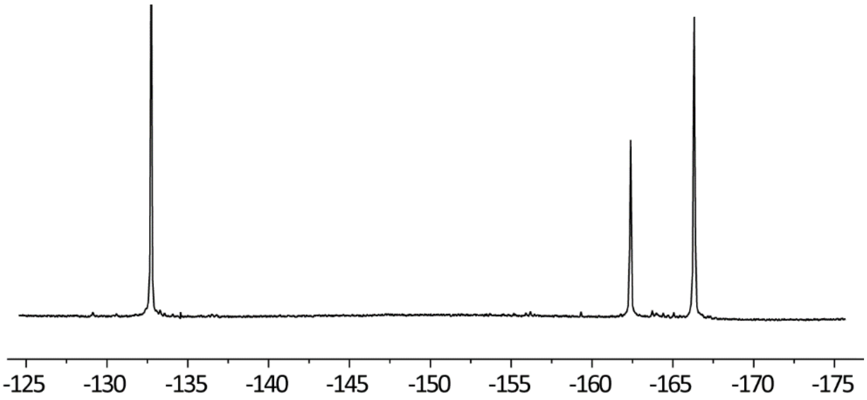
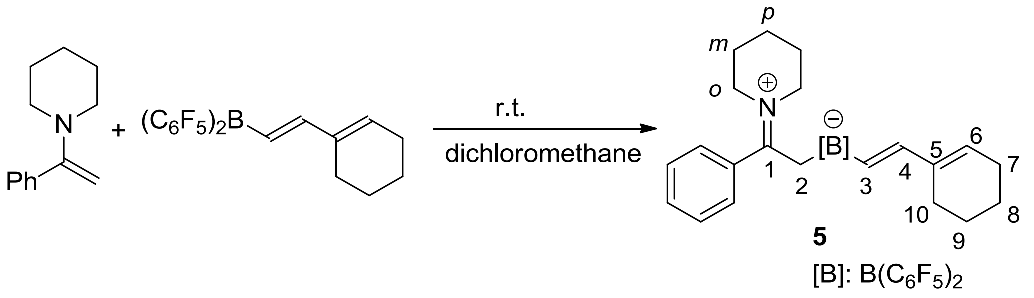


Figure S10 ^{19}F *NMR (470 MHz, 263 K, dichloromethane-*d_2*) spectra of compound* ***4b****.*

Synthesis of compound **5**:



5

[B]: $B(C_6F_5)_2$

Scheme S3

The enyne **1b** (31.0 mg, 0.29 mmol, 1 eq) in dichloromethane (1 mL) was added at room temperature to a stirred suspension of bis(pentafluorophenyl)borane (100 mg, 0.29 mmol, 1 eq) in dichloromethane (1 mL). The reaction mixture was stirred for 3 h at room temperature. Then a solution of the enamine **3a** (54.0 mg, 0.29 mmol, 1 eq) in dichloromethane (1 mL) was added to the reaction mixture. After stirring another 1 h at room temperature the volatiles were removed *in vacuo*. The resulting residue was washed four times with *n*-pentane (4 × 1 mL). Drying of the obtained solid *in vacuo* gave compound **5** as a colorless powder (116 mg, 0.28 mmol, 81%). [Comment: compound**5** slowly decomposes at room temperature both in solution and in solid state].

Melting point: 134 °C. **Anal. Calc.** for $C_{33}H_{28}BF_{10}N$: C, 61.99; H, 4.41; N, 1.69. Found: C, 60.6; H, 4.21; N, 1.69.

IR (KBr): $\tilde{\nu}$/ cm^{-1} = 4473 (w), 3748 (w), 3601 (m), 3421(m), 3032 (m), 2934 (vs), 2866 (s), 2834 (s), 2667 (w), 2599 (w), 2471 (w), 2367 (m), 2340 (m), 2227 (w), 1642 (vs), 1606 (vs), 1513(vs), 1458 (vs), 1350 (vs), 1270 (vs),1236 (vs),1179 (s), 1121 (vs), 1080 (vs), 999 (vs), 966 (vs), 919 (s), 883 (s), 858 (s), 792 (vs), 761 (vs), 741 (vs), 698 (vs), 642 (m), 595 (m).

[Comment: Pip: NC_5H_{10}, Cy: cyclohexenyl]
^{1}H NMR (600 MHz, 253 K, dichloromethane-d$_2$): δ ^{1}H: 7.34 (m, 1H, *p*-Ph), 7.27 (m, 2H, *m*-Ph), 7.13 (br, 2H, *o*-Ph), 6.32 (d, $^3J_{HH}$ = 17.4 Hz, 1H, BCH), 5.54 (d, $^3J_{HH}$ = 17.4 Hz, 1H, =CH), 5.40 (br, 1H, =CH^{Cy}), 3.96, 3.72 (each br, each 2H, *o*-Pip), 3.27 (br, 2H, BCH$_2$), 2.20, 2.04, 1.67, 1.57 (each br m, each 2H, Cy), 1.86, 1.61 (each br, each 2H, *m*-Pip), 1.74 (br m, 2H, *p*-Pip).
^{13}C{^{1}H} NMR (151 MHz, 253 K, dichloromethane-d$_2$): δ ^{13}C: 194.4 (br, N=C), 147.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 138.3 (br, BCH), 138.0 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.4 (=C), 136.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 135.8 (br, =CH), 134.9 (br, *i*-Ph), 131.1 (br, *p*-Ph), 128.3 (br, *m*-Ph), 126.8 (br, *o*-Ph), 125.9 (br, =CH^{Cy}), 125.0 (br, *i*-C_6F_5), 55.3, 53.4 (each br, *o*-Pip), 41.4 (br, BCH$_2$), 27.5, 26.5 (each br, *m*-Pip), 25.8, 25.1, 22.90, 22.85 (Cy), 23.2 (*p*-Pip).
^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 253 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{1}H: 7.34 / 7.27, 7.13 (*p*-Ph / *m*-Ph, *o*-Ph), 6.32 / 5.54 (BCH / =CH), 3.96 / 1.86 (*o*-Pip / *m*-Pip), 2.04 / 6.32, 5.40, 2.20, 1.57 (Cy / BCH, =CH^{Cy}, Cy, Cy).
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 253 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 7.34 / 131.1 (*p*-Ph), 7.27 / 128.3 (*m*-Ph), 7.13 / 126.8 (*o*-Ph), 6.32 / 137.4 (BCH), 5.54 / 135.8 (=CH), 5.40 / 125.9 (=CH^{Cy}), 3.96 / 55.3 (*o*-Pip), 3.72 / 53.4 (*o*-Pip), 3.27/ 41.4 (BCH$_2$), 2.20 / 25.1 (Cy), 2.04 / 25.8 (Cy), 1.86 / 27.5 (*m*-Pip), 1.74 / 23.2 (*p*-Pip), 1.67 / 22.90 (Cy), 1.61 / 26.5 (*m*-Pip), 1.57 / 22.85 (Cy).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 253 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{13}C: 7.27 / 134.9, 128.3 (*m*-Ph / *i*-Ph, *m*-Ph), 6.32 / 137.4, 125.9, 41.4 (BCH / =C, =CH^{Cy}, BCH$_2$), 5.54 / 137.4, 125.9 (=CH / =C, =CH^{Cy}), 3.27 / 194.4, 135.8 (BCH$_2$ / N=C, =CH), 1.67 / 137.4, 25.8, 22.90 (Cy / =C, Cy, Cy), 1.57 /125.9, 25.8, 22.90 (Cy / =CH^{Cy}, Cy, Cy).

^{1}H{^{1}H} TOCSY (600 MHz, 253 K, dichloromethane-d$_2$) [selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$: 5.40 / 2.20, 2.04, 1.67, 1.57 (=CH^{Cy} / Cy, Cy, Cy, Cy), 1.74 / 3.96, 3.72, 1.86, 1.74, 1.61 (*p*-Pip / *o*-Pip, *o*-Pip, *m*-Pip, *p*-Pip, *m*-Pip).

^{19}F NMR (564 MHz, 253 K, dichloromethane-d$_2$): δ ^{19}F: -132.8 (br, 2F, *o*-C$_6$F$_5$), -162.6 (br, 1F, *p*-C$_6$F$_5$), -166.3 (br, 2F, *m*-C$_6$F$_5$), [Δδ^{19}F$_{m,p}$ = 3.7].

^{11}B{^{1}H} NMR (192 MHz, 253 K, dichloromethane-d$_2$): δ ^{11}B: -11.1 (ν$_{1/2}$ ~ 200 Hz).

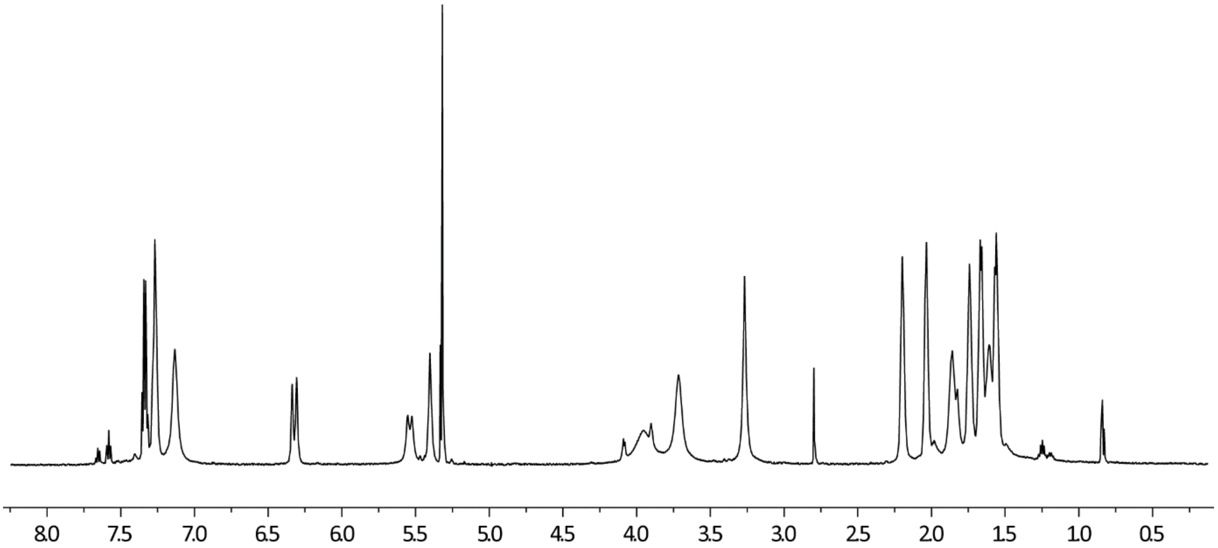


Figure S11 *^{1}H NMR (600 MHz, 253 K, dichloromethane-d$_2$) spectrum of compound **5**.*

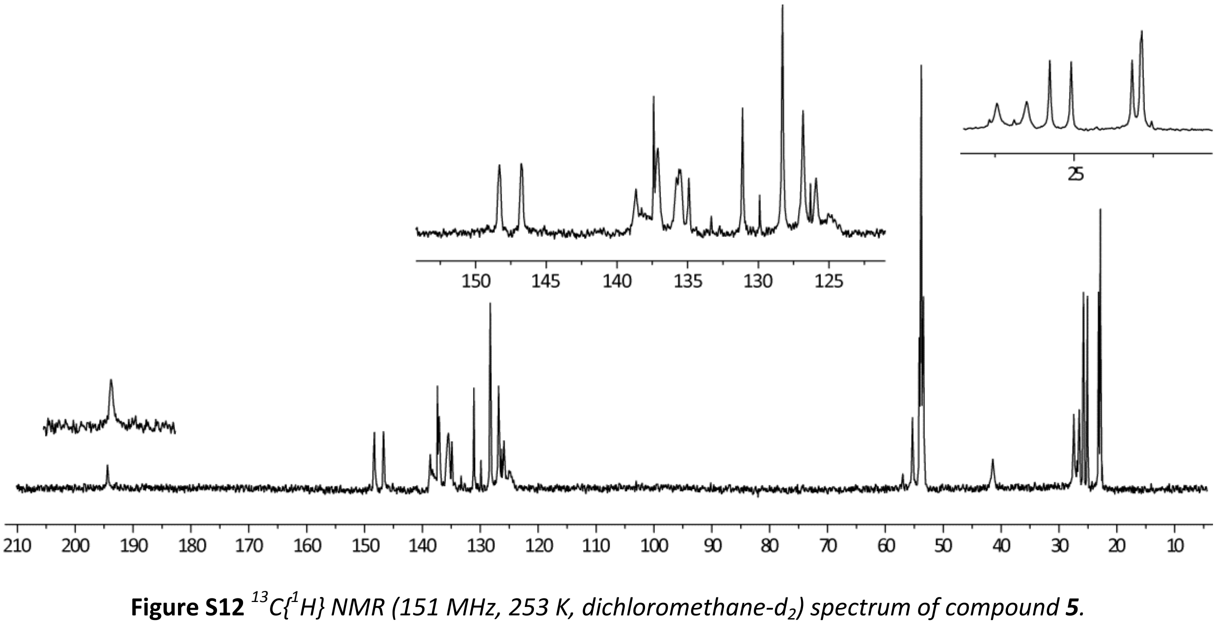


Figure S12 *^{13}C{^{1}H} NMR (151 MHz, 253 K, dichloromethane-d$_2$) spectrum of compound **5**.*

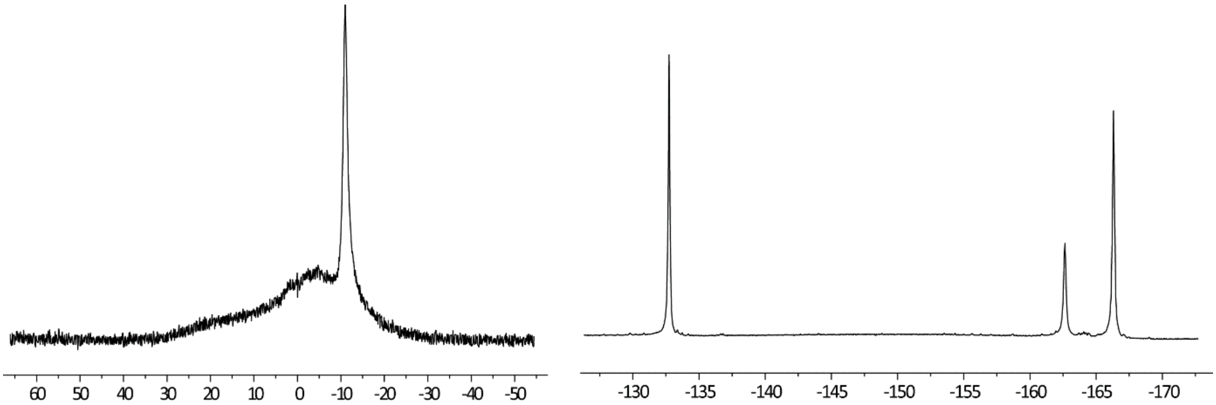
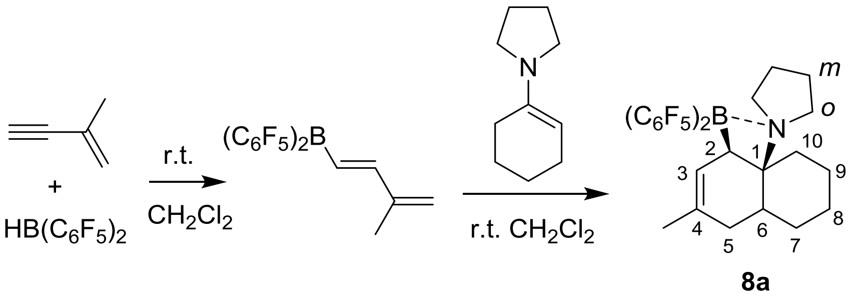


Figure S13 *$^{11}B\{^1H\}$ NMR (192 MHz, 253 K, dichloromethane-d_2), ^{19}F NMR (564 MHz, 253 K, dichloromethane-d_2) spectra of compound* ***5****.*

Synthesis of compound **8a**:



Scheme S4

The enyne **1a** (33.0 mg, 0.5 mmol) and bis(pentafluorophenyl)borane (173 mg, 0.5 mmol) were dissolved in CH_2Cl_2 (5 mL). The solution was stirred at r.t. for 3 h. Then pyrrolidino cyclohexene **6a** (75.6 mg, 0.5 mmol) was added and the reaction mixture was stirred at r.t. for 1 h. After removal of the volatiles in vacuo, pentane (2 mL) was added. The solid of the resulting suspension was collected and washed with pentane (2 x 1 mL) to give compound **8a** in 76% yield (214 mg, 0.38 mmol). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **8a** in dichloromethane at -35 ^{o}C.

X-ray crystal structure analysis of compound 8a: formula $C_{27}H_{24}BF_{10}N$, M = 563.28, pale yellow crystal, 0.22 x 0.20 x 0.18 mm, a = 10.0839(3), b = 10.3125(3), c = 11.7098(3) Å, α = 93.787(1), β = 92.769(1), γ = 102.949(1)°, V = 1181.6(1) Å^3, ρ_{calc} = 1.583 gcm^{-3}, μ = 1.293 mm^{-1}, empirical absorption correction (0.710 ≤ T ≤ 0.800), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 100(2) K, ω and ϕ scans, 13126 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4285 independent (R_{int} = 0.031) and 3710 observed reflections [I>2σ(I)], 353 refined parameters, R = 0.038, wR^2 = 0.103, max. (min.) residual electron density 0.30 (-0.22) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

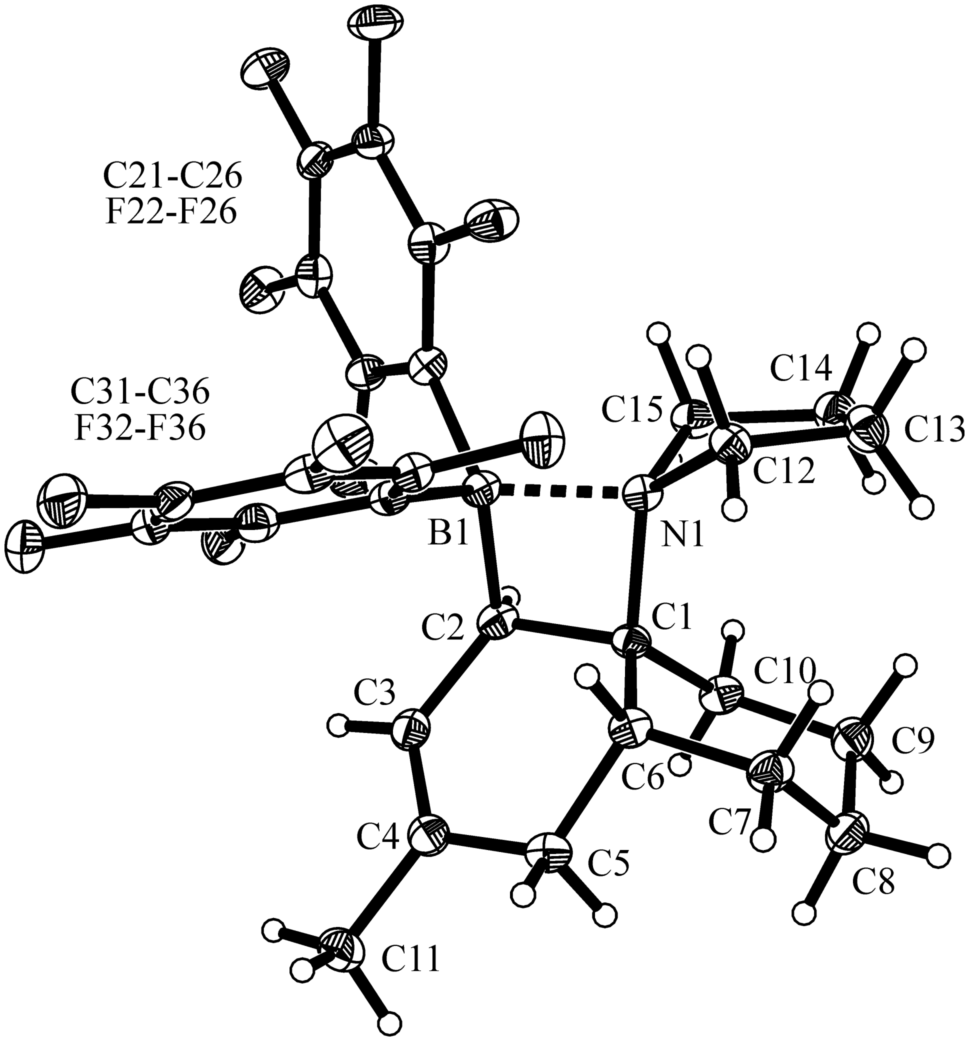


Figure S14

Decomp. (DSC): 146 °C. **Anal. Calc.** for $C_{27}H_{24}BF_{10}N$: C: 57.57; H: 4.29; N: 2.49. Found: C: 56.98; H: 3.93; N: 2.72.

IR (KBr): ΰ / cm^{-1} = 2964(s), 1648 (m), 1519(s), 1467(s), 1378(w), 1280(m), 1092(s), 971(s).

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 5.45 (m 1H, =CH), 3.83, 3.61 (each m, each 1H, *o*-NCH_2), 3.39, 2.76 (each m, each 1H, *o*'-NCH_2), 2.72 (m, 1H, BCH), 2.48 (m, 1H, CH), 2.12, 2.01 (each m, each 1H, *m*-NCH_2), 2.09, 1.62 (each m, each 1H, 5-CH_2), 1.87, 1.62 (each m, each 1H, 10-CH_2), 1.79, 1.48 (each m, each 1H, 7-CH_2), 1.77, 1.68 (each m, each 1H, *m*'-NCH_2), 1.61, 1.37 (each m, each 1H, 9-CH_2)^t, 1.59, 1.54 (each m, each 1H, 8-CH_2)^t, 1.51 (s, 3H, CH_3), [^{t} tentative assignment].
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 126.5 (=C), 122.1 (=CH), 75.5 (NC), 56.5 (*o*'-NCH_2), 54.8 (tm, *J* = 12.4 Hz, *o*-NCH_2), 36.8 (br, BCH), 34.1 (5-CH_2), 32.8 (CH), 31.5 (10-CH_2), 28.9 (7-CH_2), 23.7 (9-CH_2)^t, 23.1 (*m*-NCH_2), 22.8 (CH_3), 22.1 (*m*'-NCH_2), 20.2 (8-CH_2)^t, [C_6F_5 not listed, ^{t} tentative assignment].
^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected trace]: δ ^{1}H / δ ^{1}H = 5.45 / 2.72, 2.09, 1.62, 1.51 (=CH / BCH, 5-CH_2, 5-CH_2, CH_3), 3.83 / 3.61, 2.12, 2.01 (*o*-NCH_2 / *o*-NCH_2, *m*-NCH_2, *m*-NCH_2), 3.39 / 2.76, 1.77, 1.68 (*o*'-NCH_2 / *o*'-NCH_2, *m*'-NCH_2, *m*'-NCH_2), 2.48 / 2.09, 1.79, 1.62, 1.48 (CH / 5-CH_2, 7-CH_2, 5-CH_2, 7-CH_2), 1.87 / 1.62, 1.61, 1.37 (10-CH_2/ 10-CH_2, 9-CH_2, 9-CH_2).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 5.45 / 122.1 (=CH), 3.83, 3.61 / 54.8 (*o*-NCH_2), 3.39, 2.76 / 56.5 (*o*'-NCH_2), 2.72 / 36.8 (BCH), 2.48 / 32.8 (CH), 2.12, 2.01 / 23.1 (*m*-NCH_2), 2.09, 1.62 / 34.1 (5-CH_2), 1.87, 1.62 / 31.5 (9-CH_2), 1.79, 1.48 / 28.9 (7-CH_2), 1.77, 1.68 / 22.1 (*m*'-NCH_2), 1.61, 1.37 / 23.7 (9-CH_2), 1.59, 1.54 / 20.2 (8-CH_2), 1.51 / 22.8 (CH_3).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) [selected trace]: δ ^{1}H / δ ^{13}C = 5.45 / 75.5, 34.1, 22.8 (=CH / NC, 5-CH_2, CH_3), 2.72 / 126.4, 122.1, 75.5, 31.5 (BCH/ =C, =CH, NC, 9-CH_2).

^{1}H{^{1}H} TOCSY (600 MHz, 299 K, CD_2Cl_2)[selected experiment]**:** $^1H_{ir}$/$^1H_{res}$ = 5.45 / 2.72, 1.51 (=CH / BCH, CH_3), 3.83 / 3.61, 3.39, 2.76, 2.12, 2.01, 1.77, 1.68 (*o*-NCH_2 / *o*-NCH_2, *o*'-NCH_2, *o*'-NCH_2, *m*-NCH_2, *m*-NCH_2, *m*'-NCH_2, *m*'-NCH_2).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 3.2 ($\nu_{1/2}$ ~ 150 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -126.9 (br, 2F, *o*), -160.7 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*), -165.7 (br m, 2F, *m*)($BC_6F_5{}^a$)[$\Delta\delta\,^{19}F_{m,p}$ = 5.0], -129.4, -135.3 (each br, each 1F, *o*), -158.4 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*), -164.3 (br, 2F, *m*)($BC_6F_5{}^b$)[$\Delta\delta^{19}F_{m,p}$ = 5.9].

^{19}F NMR (564 MHz, 223 K, CD_2Cl_2): δ = -126.5 (m, *o*), -127.1 (m, *o*'), -160.4 (t, $^3J_{FF}$ = 21.2 Hz, *p*), -165.0 (m, *m*'), -166.0 (m, *m*)(each 1F, $BC_6F_5{}^a$)[$\Delta\delta^{19}F_{m,p}$ = 4.6, 5.6], -129.7 (m, *o*), -136.0 (m, *o*'), -158.2 (t, $^3J_{FF}$ = 20.8 Hz, *p*), -163.6 (m, *m*'), -164.5 (m, *m*)(each 1F, $BC_6F_5{}^b$)[$\Delta\delta^{19}F_{m,p}$ = 5.4, 6.3].

^{19}F, ^{19}F GCOSY (564 MHz / 564 MHz, 223 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -126.5 / -166.0 (*o*-$BC_6F_5{}^a$ / *m*-$BC_6F_5{}^a$), -127.1 / -165.0 (*o*'-$BC_6F_5{}^a$ / *m*'-$BC_6F_5{}^a$), -129.7 / -164.5 (*o*-$BC_6F_5{}^b$ / *m*-$BC_6F_5{}^b$), -136.0 / -163.6 (*o*'-$BC_6F_5{}^b$ / *m*'-$BC_6F_5{}^b$), -158.2 / -163.6, -164.5 (*p*-$BC_6F_5{}^b$ / *m*'-$BC_6F_5{}^b$, *m*-$BC_6F_5{}^b$), -160.4 / -165.0, -166.0 (*p*-$BC_6F_5{}^a$ / *m*'-$BC_6F_5{}^a$, *m*-$BC_6F_5{}^a$).

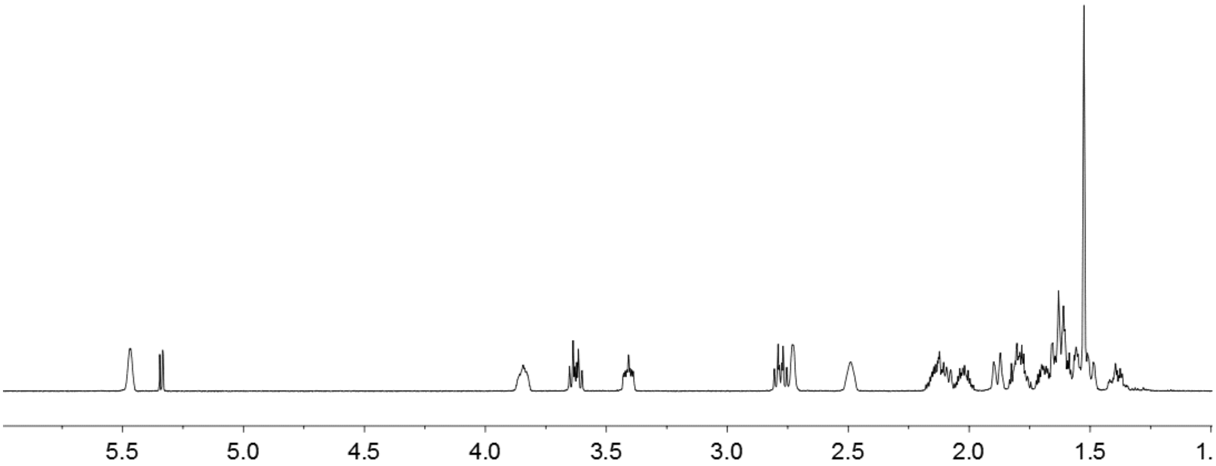


Figure S15 *^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) of compound **8a**.*

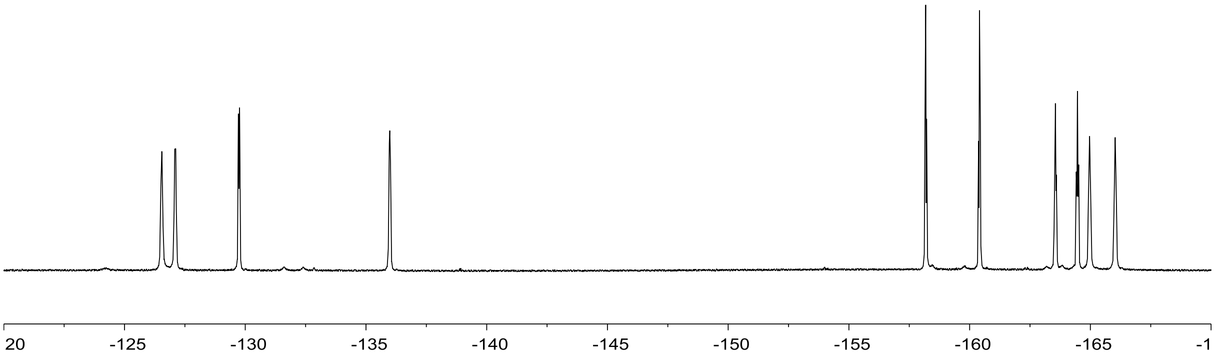


Figure S16 *^{19}F NMR (470 MHz, 223 K, CD_2Cl_2) of compound **8a**.*

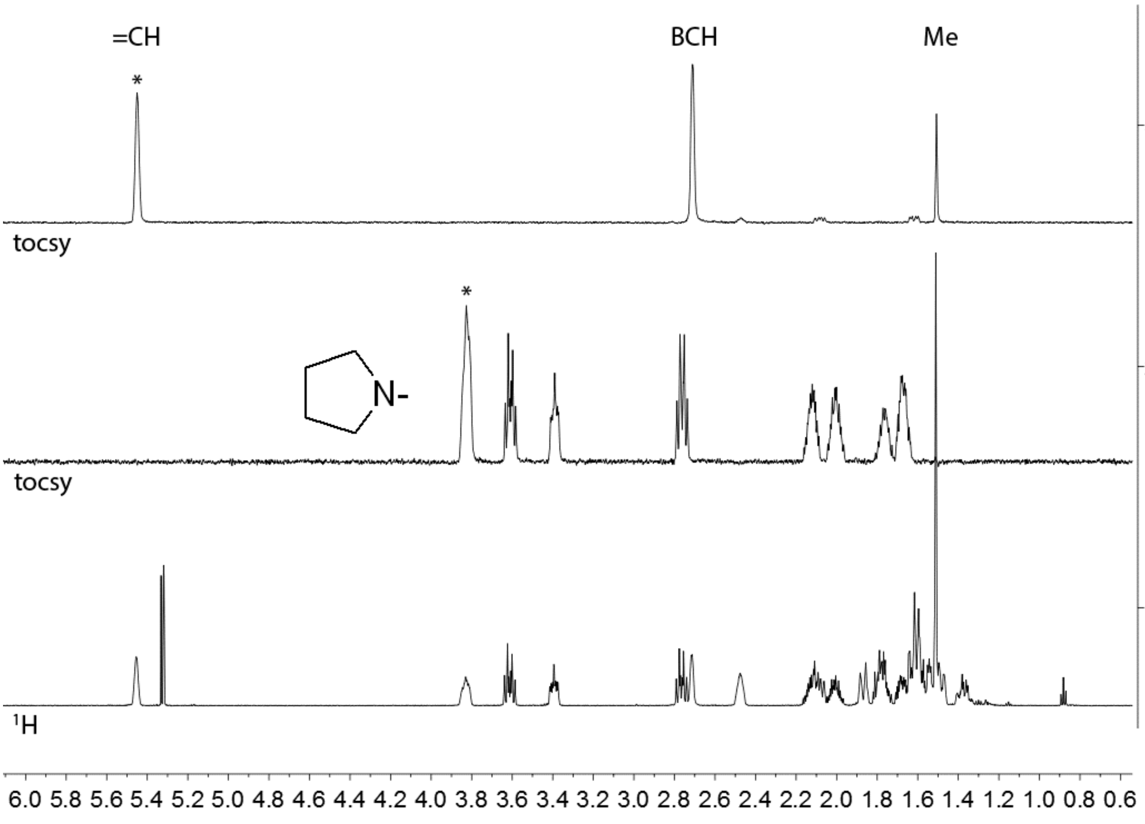


Figure S17 *^{1}H{^{1}H} tocsy (500 MHz, 299 K, CD_2Cl_2) of compound* ***8a****.*
** irradiation at (2): δ^1H = 3.83 (o-NCH_2), (3): δ^1H = 5.45 (=CH).*

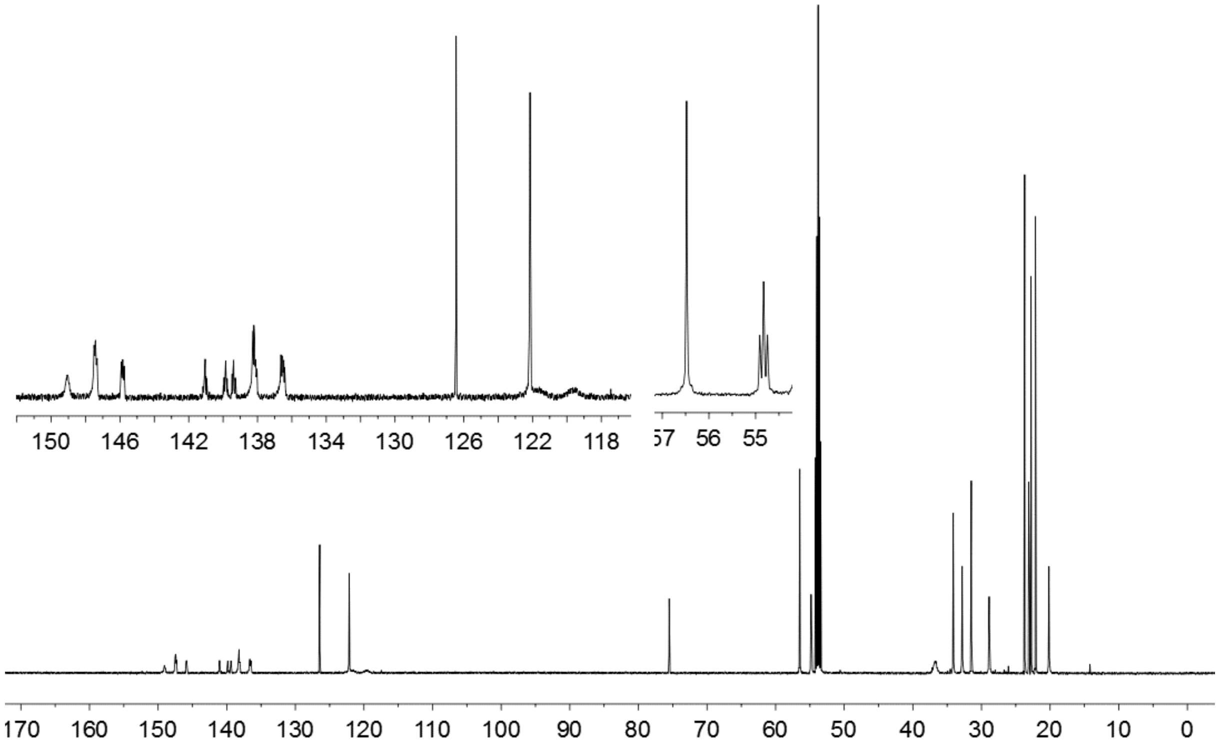


Figure S18 *^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) of compound* ***8a****.*

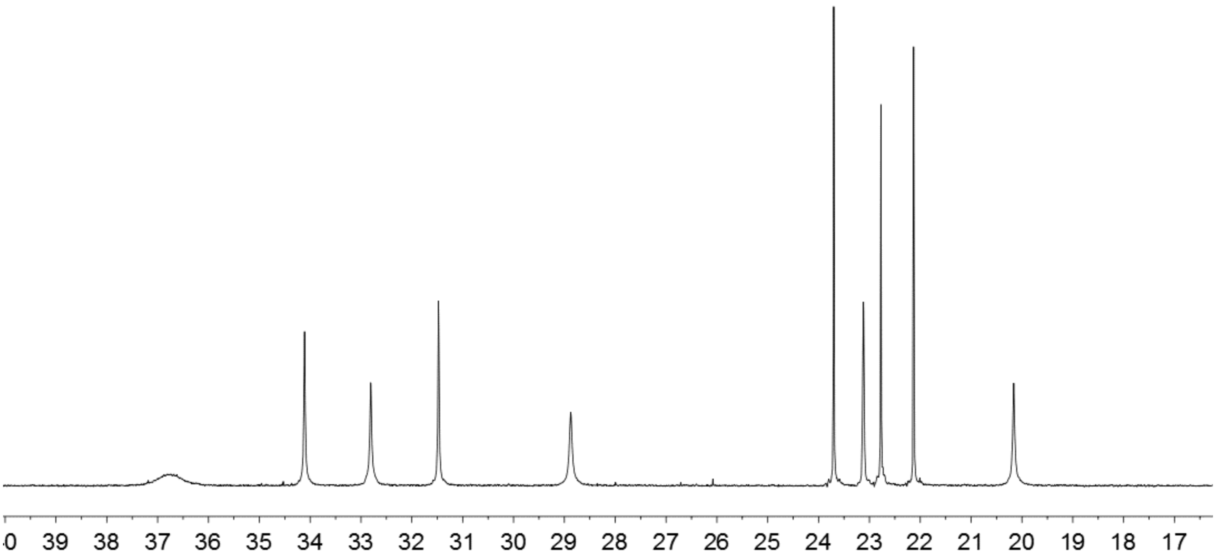


Figure S19 *$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound* ***8a****.*

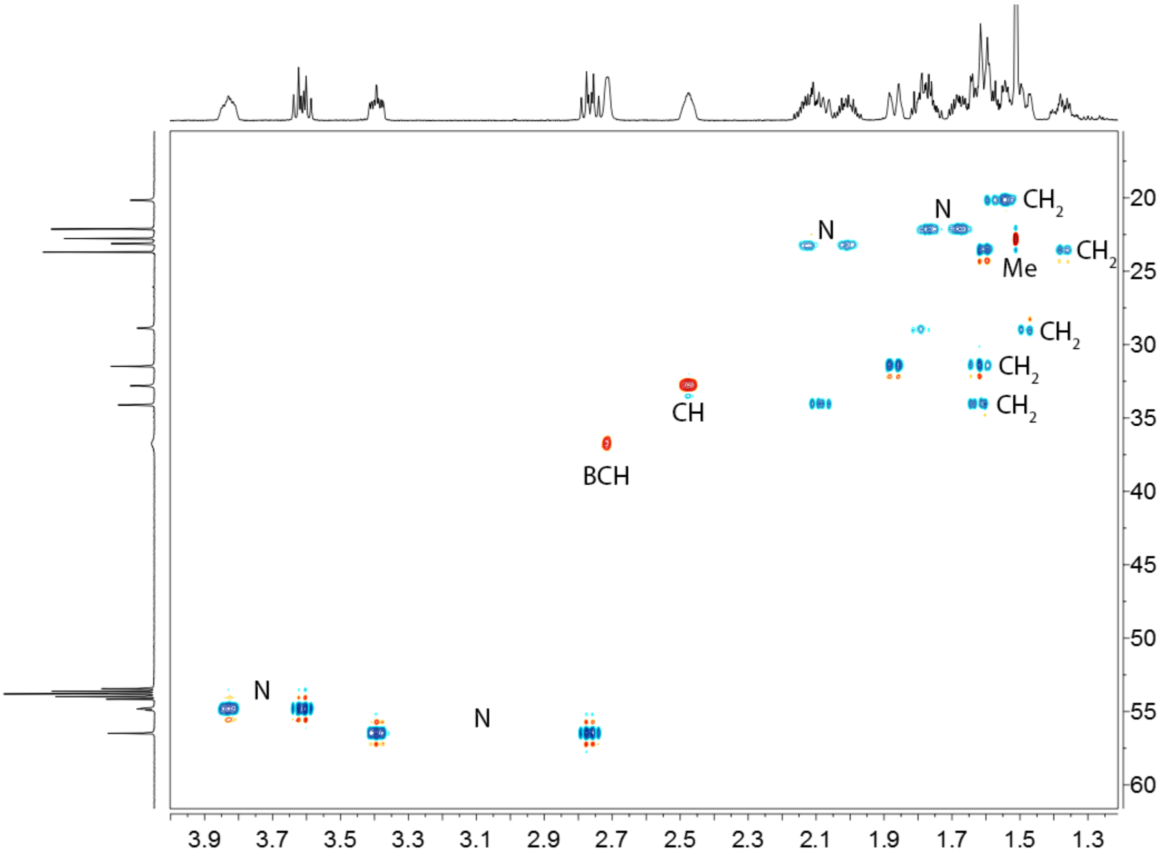


Figure S20 *^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2) of compound* ***8a****.*

N: pyrrolidino

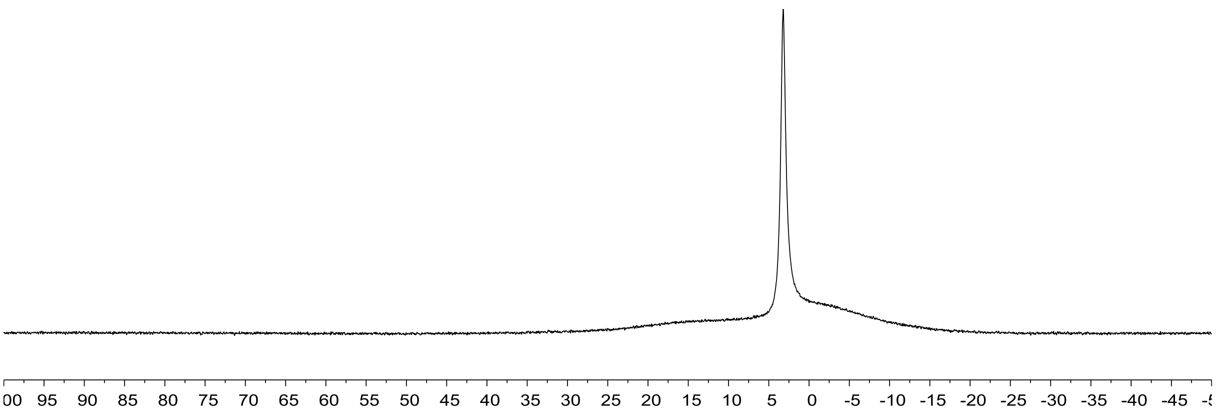


Figure S21 *$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) of compound* ***8a****.*

Dynamic ^{19}F NMR experiments:

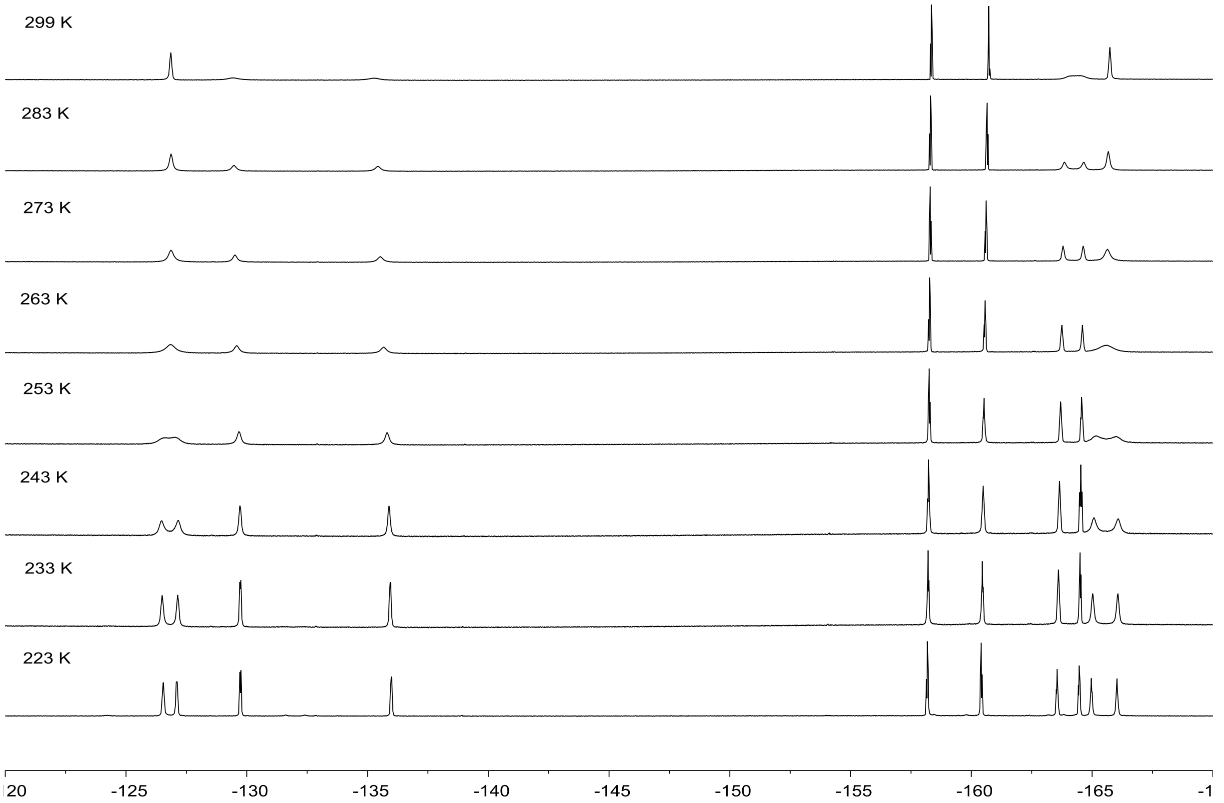


Figure S22 ^{19}F NMR (470 MHz, CD_2Cl_2) of compound **8a**.

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\Delta \nu)$ [J mol^{-1}]; R = 8.314 J (mol K)$^{-1}$; 1 cal = 4.187 J.

Rotation of the C_6F_5 substituents at B1:

^{19}F NMR (564 MHz, CD_2Cl_2): δ^{19}F(*o*-BC_6F_5^{a}, 299K): -126.9 (br, 2F); δ^{19}F(*o*-C_6F_5^{a}, 233K): -126.5, -127.1 (each m, each 1F).

^{19}F NMR (564 MHz, CD_2Cl_2): $\delta^{19}F(m\text{-}BC_6F_5{}^{a}$, 299K): -165.7 (br m, 2F); $\delta^{19}F(m\text{-}C_6F_5{}^{a}$, 233K): -165.0, -166.0 (each m, each 1F).

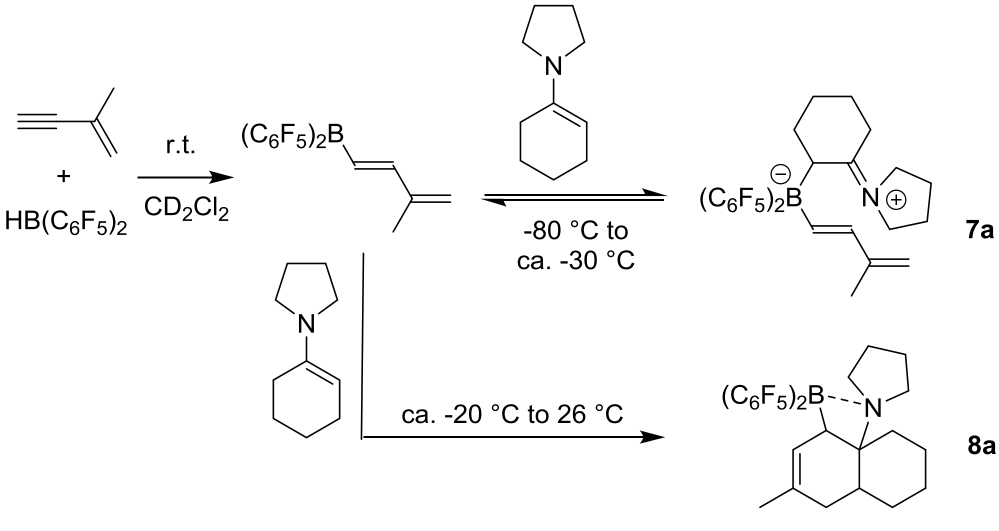
^{19}F NMR (564 MHz, CD_2Cl_2): $\delta^{19}F(m\text{-}BC_6F_5{}^{b}$, 299K): -164.3 (br, 2F); $\delta^{19}F(m\text{-}C_6F_5{}^{b}$, 233K): -163.6, -164.5 (each m, each 1F).

$\Delta G^{\neq}_{rot}(\text{ortho}^{a}$, T_c = 253 K; $\Delta\nu$(233K) = 315 Hz) = 11.4 kcal/mol

$\Delta G^{\neq}_{rot}(\text{meta}^{a}$, T_c = 258 K; $\Delta\nu$(233K) = 600 Hz) = 11.3 kcal/mol

$\Delta G^{\neq}_{rot}(\text{meta}^{b}$, T_c = 299 K; $\Delta\nu$(233K) = 516 Hz) = 13.3 kcal/mol

Reaction of borane **2a** with enamine **6a**: monitored by NMR experiments



Scheme S5

The enyne **1a** (3.3 mg, 0.05 mmol) and bis(pentafluorophenyl)borane (17.3 mg, 0.05 mmol) were dissolved in CD_2Cl_2 (0.5 mL). The solution was stirred at r.t. for 3 h. Then the solution was transfer to an NMR tube which was cooled to -80 °C. Pyrrolidino cyclohexene **6a** (7.6 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) was added at this temperature and the NMR tube was sealed immediately. Then the reaction mixture was monitored by NMR experiments starting at -80 °C.

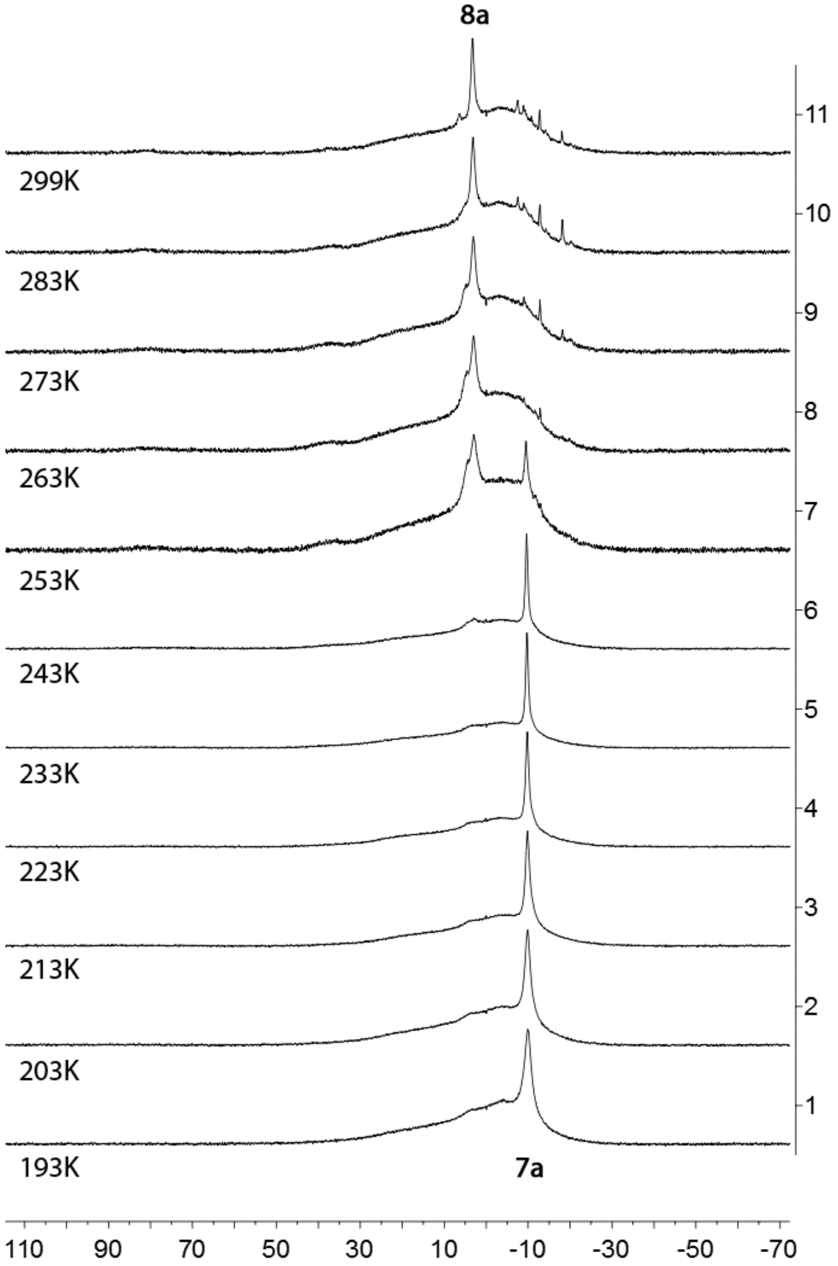
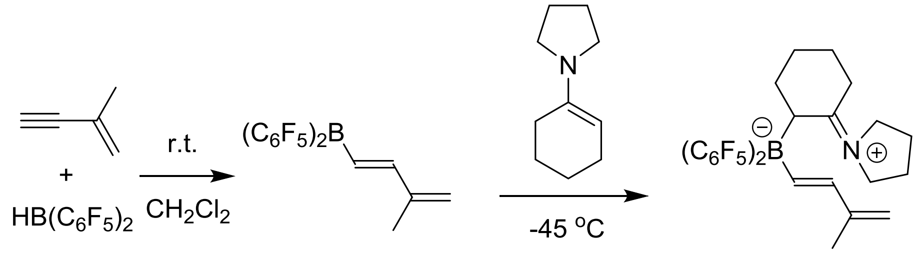


Figure S23 *$^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) spectra of the* reaction of borane **2a** with enamine **6a***.* δ^{11}B(193K): -10.0 ($\nu_{1/2}$~ 300 Hz; tentatively assigned as compound **7a**), δ^{11}B(299K): 3.2 ($\nu_{1/2}$~ 200 Hz; assigned as compound **8a**).

Characterization of compound **7a** by X-ray crystal structure analysis:



Scheme S6

The enyne **1a** (33 mg, 0.5 mmol) and bis(pentafluorophenyl)borane (173 mg, 0.5 mmol) were dissolved in CH_2Cl_2 (1 mL). After stirring at r.t. for 3 h and the solution was cooled down to -80 °C. Then pyrrolidino cyclohexene **6a** (76 mg, 0. 5 mmol) in CH_2Cl_2 (0.5 mL) was added and pentane (5 mL) was carefully layered above the reaction mixture. The schlenk tube was kept at -45 °C for several days to give single crystals which were suitable for the X-ray crystal structure analysis.

X-ray crystal structure analysis of compound 7a: formula $C_{27}H_{24}BF_{10}N$, M = 563.28, colourless crystal, 0.269 x 0.141 x 0.083 mm, a = 8.0677(3), b = 9.7095(4), c = 18.3172(7) Å, α = 81.567(2), β = 85.147(1), γ = 70.608(1)°, V = 1337.8(1) Å^3, ρ_{calc} = 1.398 gcm^{-3}, μ = 1.142 mm^{-1}, empirical absorption correction (0.749 ≤ T ≤ 0.911), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 100(2) K, ω and ϕ scans, 14889 reflections collected (±h, ±k, ±l), 4869 independent (R_{int} = 0.026) and 4089 observed reflections [I>2σ(I)], 353 refined parameters, R = 0.042, wR^2 = 0.119, max. (min.) residual electron density 0.37 (-0.20) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

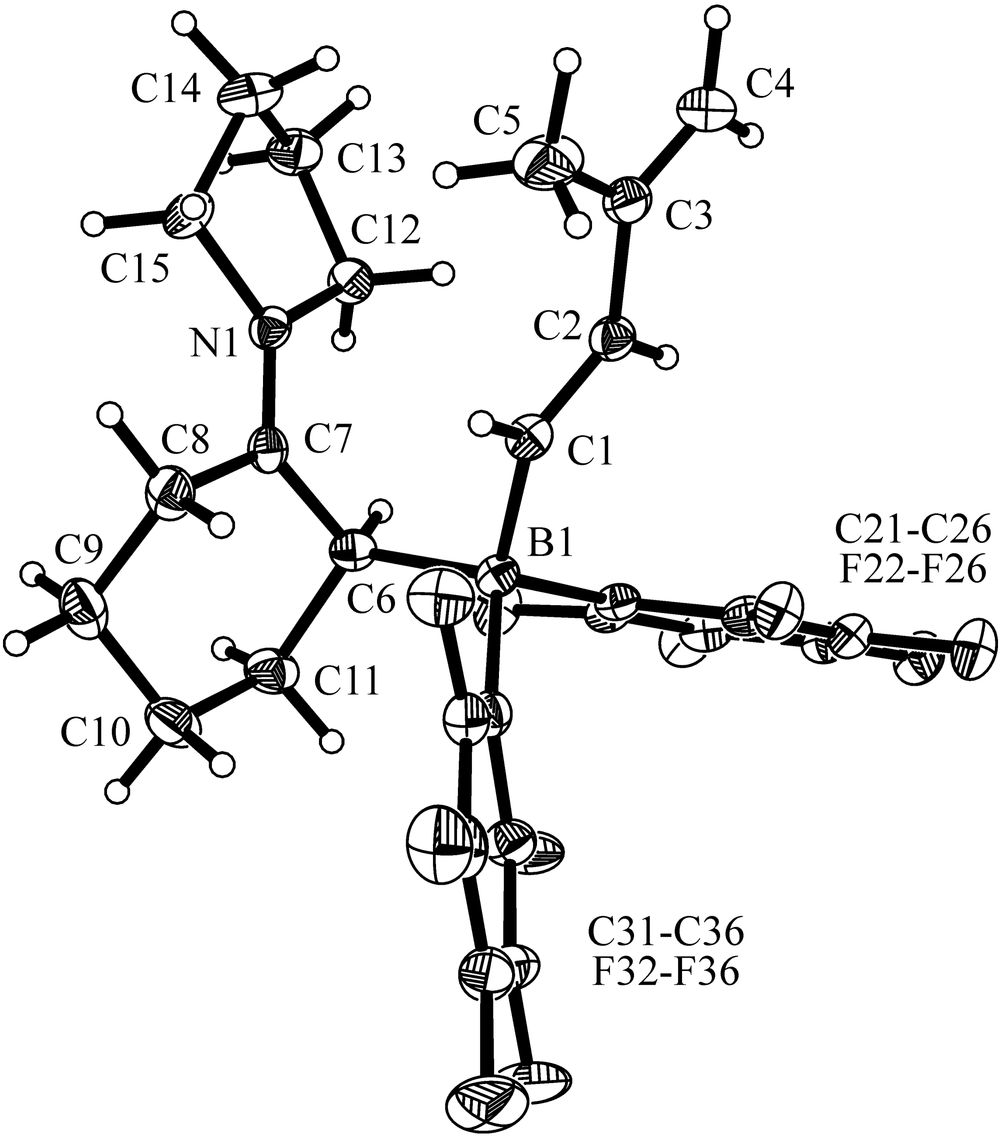
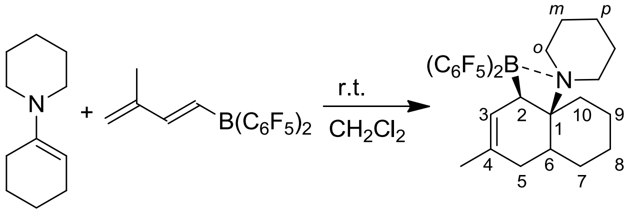


Figure S24

Synthesis of compound **8b**:



8b

Scheme S7

A solution of the enyne **1a** (58.0 mg, 0.88 mmol, 1 eq) in dichloromethane (1 mL) was added at room temperature to a stirred suspension of bis(pentafluorophenyl)borane (304 mg, 0.88 mmol, 1 eq) in dichloromethane (1 mL). After stirring the mixture for 3 h at room temperature, a solution of piperidino cyclohexene **6b** (146 mg, 0.88 mmol, 1 eq) in dichloromethane (1 mL) was added. Before removal of the volatiles *in vacuo*, the reaction mixture was stirred for 1 h at room temperature. The resulting yellow residue was suspended in dichloromethane (2 mL) and *n*-pentane (4 mL) and then stored at -35 °C for 2 h. Subsequently the supernatant solution was removed by decantation. Drying of the residue in vacuo gave a yellow powder, which was dissolved *n*-pentane (2 mL). After 30 min at room temperature crystalline material of compound **8b** was formed (325 mg, 0.56 mmol, 64%). [Comment: compound **8b** slowly decomposed at room temperature both in solution (CD_2Cl_2) and in solid state].

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

X-ray crystal structure of compound 8b: formula $C_{28}H_{26}BF_{10}N$, M = 577.31, yellow crystal, 0.20 x 0.10 x 0.04 mm, a = 9.0475(2), b = 10.2558(2), c = 14.7499(5) Å, α = 84.788(1), β = 79.791(1), γ = 76.629(2)°, V = 1308.7(1) Å^3, ρ_{calc} = 1.465 gcm^{-3}, μ = 0.134 mm^{-1}, empirical absorption correction (0.973 ≤ T ≤ 0.994), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 11743 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 4426 independent (R_{int} = 0.053) and 3246 observed reflections [$I>2\sigma(I)$], 362 refined parameters, R = 0.070, wR^2 = 0.156, max. (min.) residual electron density 0.26 (-0.20) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

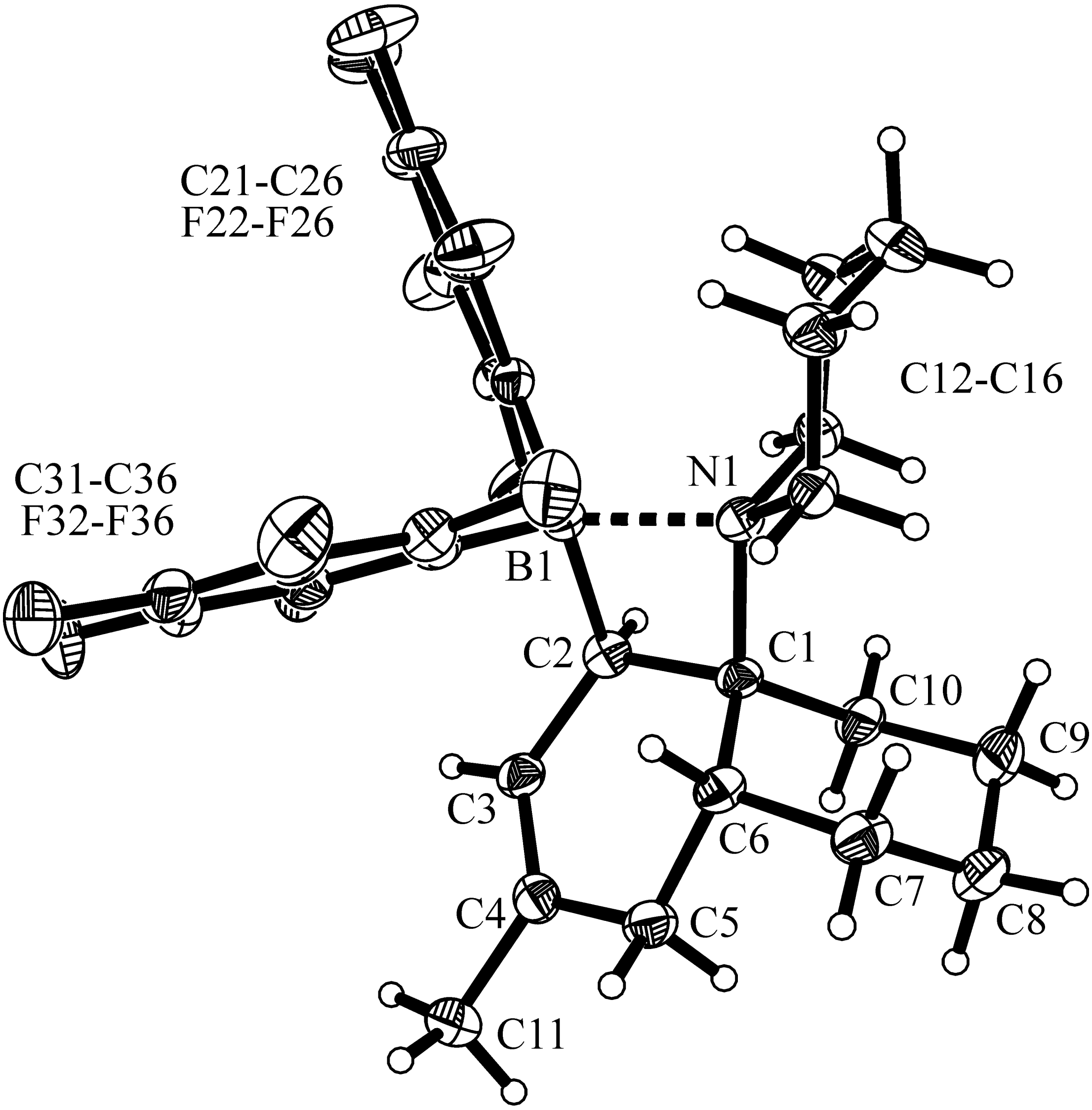


Figure S25

Decomposed: 118 °C. **Anal. Calc.** for $C_{28}H_{26}BF_{10}N$: C, 58.25; H, 4.54; N, 2.43. Found: C, 58.68; H, 4.47; N, 2.70.

IR (KBr): ṽ/ cm^{-1} = 4366 (w), 3433 (m), 2935 (s), 2871 (s), 2729 (w), 2559 (w), 2361 (m), 2340 (m), 1643 (s), 1596 (w), 1519 (vs), 1460 (vs), 1395 (m), 1373 (m), 1282 (s), 1246 (m), 1207 (m), 1145 (m), 1092 (vs), 1033 (w), 999 (s), 970 (vs), 882 (s), 835 (m), 773 (m), 742 (m), 718 (m), 670 (m), 599 (w), 575 (w), 477 (w).

The solution of the colorless crystals in dichloromethane-d_2 showed a mixture of two isomers and traces of a compound not identified yet (213K: ratio ca. 2 : 1 : 0.2 (^{19}F)]
^{11}B{^{1}H} NMR (192 MHz, 213 K, dichloromethane-d_2): δ ^{11}B: 2.7 ($\nu_{1/2}$~ 1200 Hz).

Major isomer:
^{1}H NMR (600 MHz, 213 K, dichloromethane-d_2): δ ^{1}H: 5.30 (m, 1H, =CH), 4.18, 2.89 (each m, each 1H, *o*-NCH_2), 3.52, 2.85 (each m, each 1H, *o'*-NCH_2), 2.89 (m, 1H, BCH), 2.31 (m, 1H, CH), 2.12, 1.45 (each m, each 1H, 10-CH_2)^t, 2.08, 1.50 (each m, each 1H, 5-CH_2), 1.99, 1.34 (each m, each 1H, 7-CH_2)^t, 1.86,

1.73 (each m, each 1H, *m*-NCH$_2$), 1.56, 1.20 (each m, each 1H, *p*-NCH$_2$), 1.55 (m, 2H, 8-CH$_2$)^t, 1.55, 1.45 (each m, each 1H, 9-CH$_2$)^t, 1.36, 0.78 (each m, each 1H, *m'*-NCH$_2$), 1.42 (m, 3H, CH$_3$), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 213 K, dichloromethane-d$_2$): δ ^{13}C: 126.1 (=C), 121.0 (d, *J* = 9.3 Hz, =CH), 75.9 (NC), 57.7 (d, *J* = 22.0 Hz, *o*-NCH$_2$), 54.1 (*o'*-NCH$_2$), 34.3 (br, BCH), 33.4 (5-CH$_2$), 31.0 (CH), 30.4 (10-CH$_2$)^t, 28.0 (7-CH$_2$)^t, 23.0 (*m'*-NCH$_2$), 22.7 (9-CH$_2$)^t, 22.6 (*m*-NCH$_2$), 22.5 (*p*-NCH$_2$), 22.4 (CH$_3$), 19.7 (8-CH$_2$)^t, [C$_6$F$_5$ not listed; ^{t} tentative assignment].

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 213 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{1}H: 5.30 / 2.89, 1.42 (=CH / BCH, CH$_3$), 3.52 / 2.85, 1.36, 0.78 (o'-NCH$_2$ / o'-NCH$_2$, m'-NCH$_2$, m'-NCH$_2$), 2.31 / 2.08, 1.42 (CH / 5-CH$_2$, CH$_3$), 2.12 / 2.31, 1.99, 1.55, 1.45 (10-CH$_2$ / CH, 10-CH$_2$, 9-CH$_2$, 9-CH$_2$).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 213 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 5.30 / 121.0 (=CH), 4.18, 2.89 / 57.7 (*o*-NCH$_2$), 3.52, 2.85 / 54.1 (*o'*-NCH$_2$), 2.89 / 34.3 (BCH), 2.31 / 31.0 (CH), 2.12, 1.45 / 30.4 (10-CH$_2$), 2.08, 1.50 / 33.4 (5-CH$_2$), 1.99, 1.34 / 28.0 (7-CH$_2$), 1.86, 1.73 / 22.6 (m-NCH$_2$), 1.56, 1.20/ 22.5 (*p*-NCH$_2$), 1.55, 1.45 / 22.7 (9-CH$_2$), 1.55 / 19.7 (8-CH$_2$), 1.42 / 22.4 (CH$_3$), 1.36, 0.78 / 23.0 (m'-NCH$_2$).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 213 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{13}C: 5.30 / 75.9, 33.4, 22.4 (=CH / NC, 5-CH$_2$, CH$_3$), 4.18 / 54.1, 22.5 (*o*-NCH$_2$ / o'-NCH$_2$, *p*-NCH$_2$), 2.89 / 126.1, 121.0, 75.9, 22.7 (BCH / =C, =CH, NC, 9-CH$_2$), 2.31 / 75.9, 33.4, 30.4, 28.0, 19.7 (CH / NC, 5-CH$_2$, 10-CH$_2$, 7-CH$_2$, 8-CH$_2$), 2.08 / 126.1, 121.0, 31.0, 28.0 (5-CH$_2$ / =C, =CH, CH, 7-CH$_2$), 1.55 / 75.9, 31.0, 30.4, 28.0, 22.7, 19.7 (9-CH$_2$ / NC, CH, 10-CH$_2$, 7-CH$_2$, 9-CH$_2$, 8-CH$_2$), 1.50 / 126.1, 121.0, 75.9, 31.1 (5-CH$_2$ / =C, =CH, NC, CH), 1.34 / 75.9, 33.4, 30.4, 22.7, 19.7 (7-CH$_2$ / NC, 5-CH$_2$, 10-CH$_2$, 9-CH$_2$, 8-CH$_2$).

^{1}H{^{1}H} TOCSY (600 MHz, 263 K, dichloromethane-d$_2$) [selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$: 5.30 / 2.89, 2.31, 2.08, 1.50, 1.42 (=CH / BCH, CH, 5-CH$_2$, 5-CH$_2$, CH$_3$), 4.18 / 3.52, 2.85, 1.86, 1.73, 1.56, 1.36, 1.20, 0.78 (*o*-NCH$_2$ / *o'*-NCH$_2$, *o'*-NCH$_2$, *m*-NCH$_2$, *m*-NCH$_2$, *p*-NCH$_2$, *m'*-NCH$_2$, *p*-NCH$_2$, *m'*-NCH$_2$) .

^{1}H{^{1}H} TOCSY (600 MHz, 263 K, dichloromethane-d$_2$) [selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$: 5.30 / 2.89, 2.31, 2.08, 1.50, 1.42 (=CH / BCH, CH, 5-CH$_2$, 5-CH$_2$, CH$_3$), 4.18 / 3.52, 2.85, 1.86, 1.73, 1.56, 1.36, 1.20, 0.78 (*o*-NCH$_2$ / *o'*-NCH$_2$, *o'*-NCH$_2$, *m*-NCH$_2$, *m*-NCH$_2$, *p*-NCH$_2$, *m'*-NCH$_2$, *p*-NCH$_2$, *m'*-NCH$_2$) .

^{19}F NMR (564 MHz, 213 K, dichloromethane-d$_2$): δ ^{19}F: -126.07 (m, o), -136.6 (m, o'), -157.0 (t, $^3J_{FF}$ = 20.9 Hz, p), -163.6 (m, m'), -164.1 (m, m) (each 1F, C$_6$F$_5$^{a}) ($\Delta\delta^{19}$F$_{m,p}$ = 6.6, 7.1], -126.11 (o), -128.5 (o'), -160.5 (t, $^3J_{FF}$ = 20.9 Hz, p), -165.2 (m'), -165.9 (m) (each 1F, C$_6$F$_5$^{b}) ($\Delta\delta^{19}$F$_{m,p}$ = 4.7, 5.4].

^{19}F, ^{19}F GCOSY (564 MHz, 213 K, dichloromethane-d$_2$) [selected traces]: δ ^{19}F: -163.6 / -164.1, -157.0, -136.6 (*m'*-C$_6$F$_5$^{a} / *m*-C$_6$F$_5$^{a}, *p*-C$_6$F$_5$^{a}, *o'*-C$_6$F$_5$^{a}), -164.1 / -157.0, -136.6, -126.07 (*m*-C$_6$F$_5$^{a} / *p*-C$_6$F$_5$^{a}, *o'*-C$_6$F$_5$^{a}, *o*-C$_6$F$_5$^{a}), -165.2 / -160.5, -128.5, -126.11 (*m'*-C$_6$F$_5$^{b} / *p*-C$_6$F$_5$^{b}, *o'*-C$_6$F$_5$^{b}, *o*-C$_6$F$_5$^{b}), -165.9 / -160.5, -128.5, -126.11 (*m*-C$_6$F$_5$^{b} / *p*-C$_6$F$_5$^{b}, *o'*-C$_6$F$_5$^{b}, *o*-C$_6$F$_5$^{b}).

Minor Isomer:

^{1}H NMR (600 MHz, 213 K, dichloromethane-d$_2$): δ ^{1}H: 5.38 (br, 1H, =CH), 3.69, 3.60 (each m, each 1H, *o*-NCH$_2$), 3.25, 2.88 (each m, each 1H, *o'*-NCH$_2$), 2.91 (m, 1H, BCH), 2.45, 1.61 (5-CH$_2$), 2.22 (m, 1H, CH), 2.12, 1.65 (each m, each 1H, 10-CH$_2$)^t, 1.84, 1.68 (each m, each 1H, *m*-NCH$_2$), 1.79, 1.46 (each m, each 1H, *p*-NCH$_2$), 1.64, 1.49 (each m, each 1H, 8-CH$_2$)^t, 1.59 (m, 2H, *m'*-NCH$_2$), 1.54, 1.16 (each m, each 1H, 9-CH$_2$)^t, 1.52, 1.37 (each m, each 1H, 7-CH$_2$)^t, 1.49 (m, 3H, CH$_3$), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 213 K, dichloromethane-d$_2$): δ ^{13}C: 125.7 (=C), 124.8 (br, =CH), 78.2 (NC), 53.4 (d, *J* = 14.5 Hz, *o*-NCH$_2$), 51.5 (d, *J* = 7.3 Hz, *o'*-NCH$_2$), 38.0 (CH), 36.9 (5-CH$_2$), 35.3 (7-CH$_2$)^t, 33.9 (10-CH$_2$)^t, 26.0 (*m*-NCH$_2$), 25.8 (br, BCH), 25.5 (9-CH$_2$)^t, 24.1 (CH$_3$), 23.8 (8-CH$_2$)^t, 23.6 (*m'*-NCH$_2$), 23.2 (*p*-NCH$_2$), [C$_6$F$_5$ not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 213 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{1}H: 5.38 / 2.91 (=CH / BCH), 2.22/ 2.45, 2.12, 1.54, 1.37 (CH / 5-CH$_2$, 10-CH, 9-CH$_2$, 7-CH$_2$).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 213 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 5.38 / 124.8 (=CH), 3.68, 3.60 / 53.4 (*o*-NCH$_2$), 3.25, 2.88 / 51.5 (*o*'-NCH$_2$), 2.91 / 25.8 (BCH), 2.45, 1.61 / 36.9 (5-CH$_2$), 2.22 / 38.0 (CH), 2.12, 1.65 / 33.9 (10-CH$_2$), 1.84, 1.68 / 26.0 (*m*-NCH$_2$), 1.79, 1.46 / 23.2 (*p*-NCH$_2$), 1.64, 1.49 / 23.8 (8-CH$_2$), 1.59 / 23.6 (*m*'-NCH$_2$), 1.54, 1.16 / 25.5 (9-CH$_2$), 1.52, 1.37 / 35.3 (7-CH$_2$), 1.49 / 24.1 (CH$_3$).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 213 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{13}C: 5.38 / 124.8, 78.2, 33.9, 24.1 (=CH / =CH, NC, 10-CH$_2$, CH$_3$), 3.69 / 78.2, 53.4, 51.5, 26.0 (*o*-NCH$_2$ / NC, *o*-NCH$_2$, *o*'-NCH$_2$, *m*-NCH$_2$), 2.91 / 125.7, 78.2 (BCH / =C, NC), 2.45 / 35.3, 33.9 (5-CH$_2$ / 7-CH$_2$, 10-CH$_2$), 2.22 / 125.7, 78.2, 35.3, 25.8 (CH/ =C, NC, 7-CH$_2$, BCH), 1.49 / 35.3, 25.5 (8-CH$_2$ / 7-CH$_2$, 9-CH$_2$).

^{1}H{^{1}H} TOCSY (600 MHz, 213 K, dichloromethane-d$_2$) [selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$: 5.38 / 2.91, 1.49 (=CH / BCH, CH$_3$), 3.69 / 3.60, 3.25, 1.84, 1.79, 1.59, 1.46 (*o*-NCH$_2$ / *o*-NCH$_2$, *o*'-NCH$_2$, *m*-NCH$_2$, *p*-NCH$_2$, *m*'-NCH$_2$, *p*-NCH$_2$), 2.22 / 5.38, 2.45, 2.12, 1.64, 1.54, 1.49, 1.37, 1.16 (CH / =CH, 5-CH$_2$, 10-CH$_2$, 8-CH$_2$, 9-CH$_2$, 8-CH$_2$, 7-CH$_2$, 9-CH$_2$).

^{19}F NMR (564 MHz, 213 K, dichloromethane-d$_2$): δ ^{19}F: -121.7 (o), -131.5 (o'), -159.8 (t, $^3J_{FF}$ = 20.9 Hz, p), -163.8 (m), -164.4 (m') (each 1F, C$_6$F$_5^a$) [$\Delta\delta^{19}$F$_{mp}$ = 4.0, 4.6], -124.5 (o), -132.5 (o'), -158.0, (t, $^3J_{FF}$ = 20.9 Hz, p), -162.9 (m'), -164.5 (m) (each 1F, C$_6$F$_5^b$) [$\Delta\delta^{19}$F$_{mp}$ = 4.9, 6.5].

^{19}F, ^{19}F GCOSY (564 MHz, 213 K, dichloromethane-d$_2$) [selected traces]: δ ^{19}F: -163.8 / -159.8, -131.5, -121.7 (*m*-C$_6$F$_5^a$ / *p*-C$_6$F$_5^a$, *o*'-C$_6$F$_5^a$, *o*-C$_6$F$_5^a$), -164.4 / -159.8, -131.5, (*m*'--C$_6$F$_5^a$ / p-C$_6$F$_5^a$, *o*-C$_6$F$_5^a$, *o*'-C$_6$F$_5^a$), -162.9 / -158.0, -132.5, -124.5 (*m*'-C$_6$F$_5^b$ / *p*-C$_6$F$_5^b$, *o*'-C$_6$F$_5^b$, *o*-C$_6$F$_5^b$), -164.5 /-158.0, -132.5, (*m*-C$_6$F$_5^b$ / p-C$_6$F$_5^b$, *o*'-C$_6$F$_5^b$, *o*-C$_6$F$_5^b$).

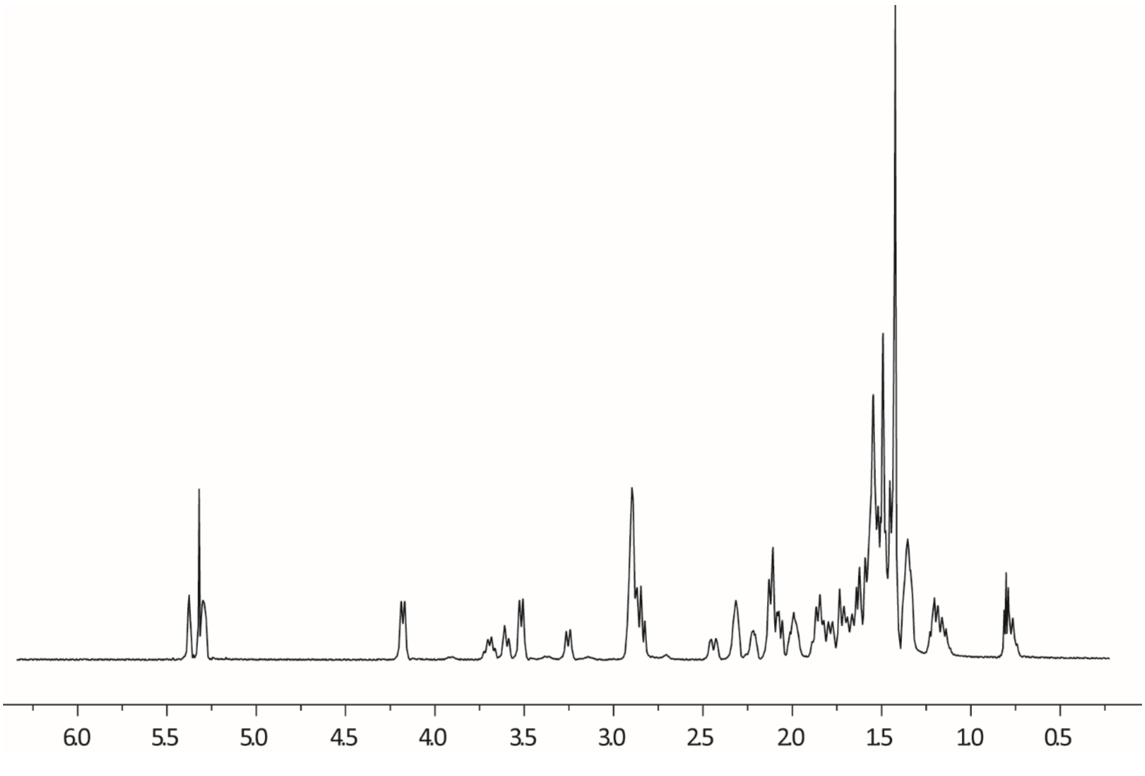


Figure S26 *^{1}H NMR (600 MHz, 213 K, dichloromethane-d$_2$) spectrum of **8b**.*

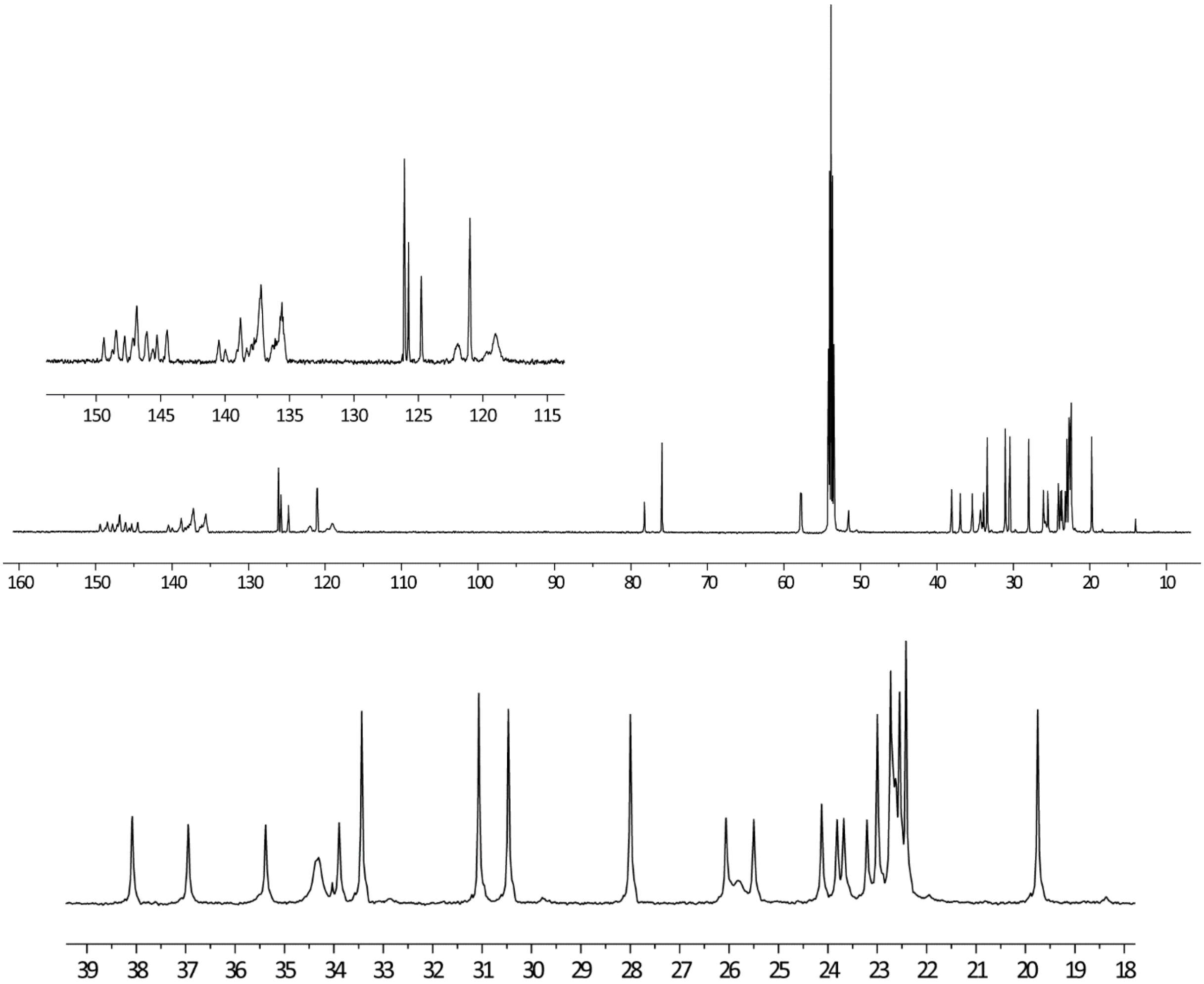


Figure S27 *$^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, dichloromethane-d_2) spectrum of compound **8b**.*

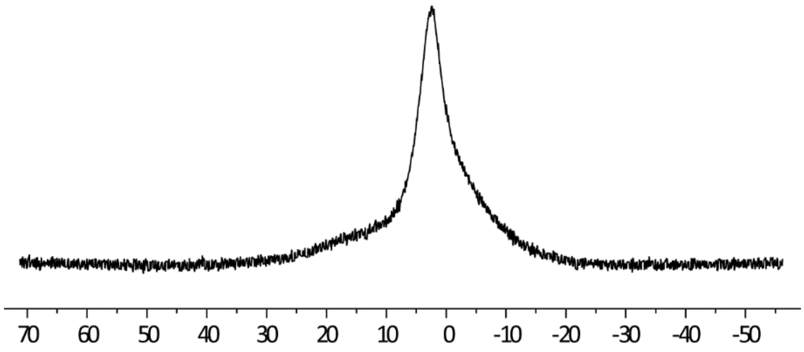


Figure S28 *$^{11}B\{^{1}H\}$ NMR (192 MHz, 213 K, dichloromethane-d_2) spectrum of compound **8b**.*

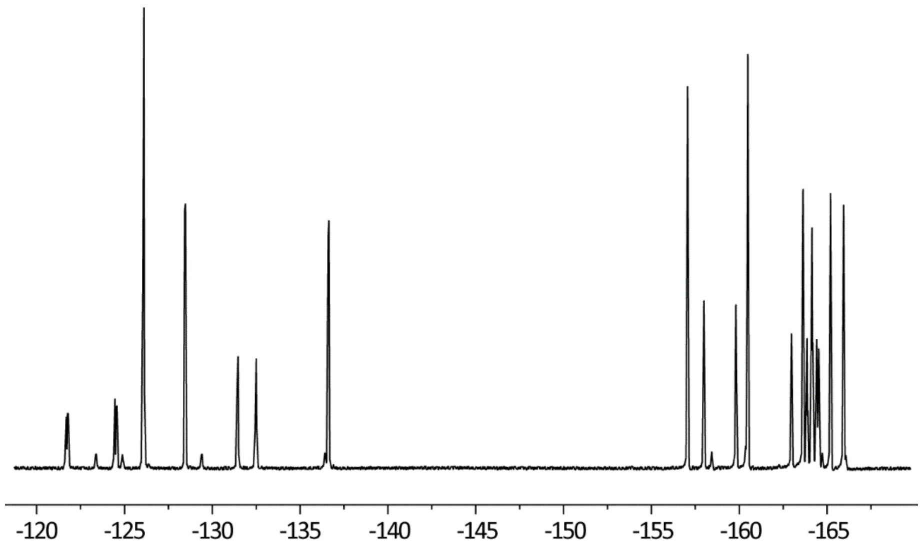


Figure S29 *^{19}F NMR (564 MHz, 213 K, dichloromethane-d$_2$) spectrum of compound* ***8b****.*

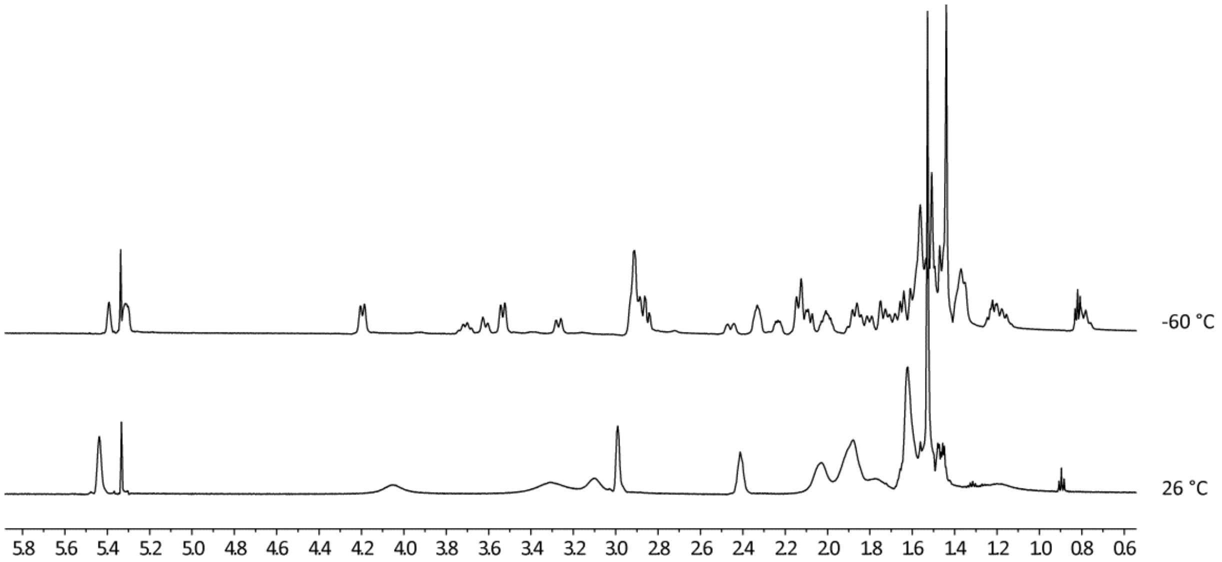


Figure S30 *^{1}H NMR (600 MHz, dichloromethane-d$_2$) spectrum of compound* ***8b*** *at variable temperatures.*

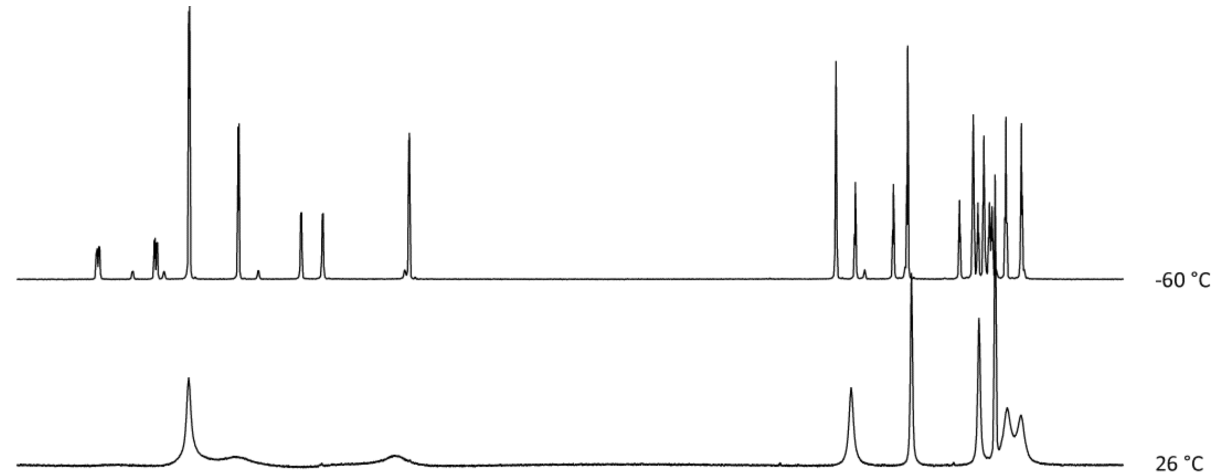
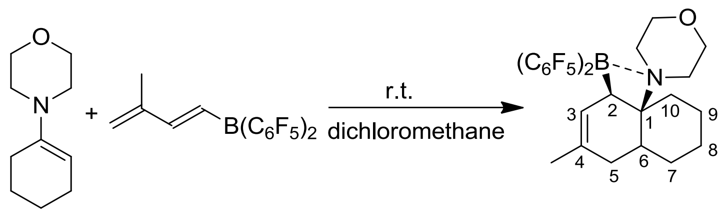


Figure S31 *^{19}F NMR (564 MHz, dichloromethane-d$_2$) spectra of compound* ***8b*** *at variable temperatures.*

Synthesis of compound **8c**:



8c

Scheme S8

A solution of The enyne **1a** (24.0 mg, 0.36 mmol, 1 eq) in dichloromethane (1 mL) was added to a solution of bis(pentafluorophenyl)borane (123 mg, 0.36 mmol, 1 eq) in dichloromethane (1 mL). After stirring the mixture for 3 h at room temperature, a solution of morpholino cyclohexene **6c** (59.0 mg, 0.36 mmol, 1 eq) in dichloromethane (1 mL) was added. Before removal of the volatiles *in vacuo*, the reaction mixture was stirred for 1 h at room temperature. The resulting precipitate was suspended in a mixture of dichloromethane (2 mL) and *n*-pentane (4 mL). Then the suspension was stored at -35 °C for 2 h. The supernatant was collected and then dried *in vacuo* to give a yellow powder. The powder was dissolved *n*-pentane (2 mL). After 1 h at room temperature colorless crystals (171 mg, 0.30 mmol, 83%) of compound **8c** were isolated which were suitable for the X-ray crystal structure analysis.
[Comment: compound **8c** slowly decomposed at room temperature both in solution (CD_2Cl_2) and in solid state].

X-ray crystal structure of compound 8c: formula $C_{27}H_{24}BF_{10}NO$, M = 579.28, colourless crystal, 0.20 x 0.18 x 0.12 mm, a = 8.9201(2), b = 10.7594(3), c = 25.6057(7) Å, β = 90.619(1) °, V = 2457.4(1) Å^3, ρ_{calc} = 1.566 gcm^{-3}, μ = 0.146 mm^{-1}, empirical absorption correction (0.971 ≤ T ≤ 0.982), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 13001 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4976 independent (R_{int} = 0.049) and 3891 observed reflections [I>2σ(I)], 362 refined parameters, R = 0.051, wR^2 = 0.121, max. (min.) residual electron density 0.30 (-0.20) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

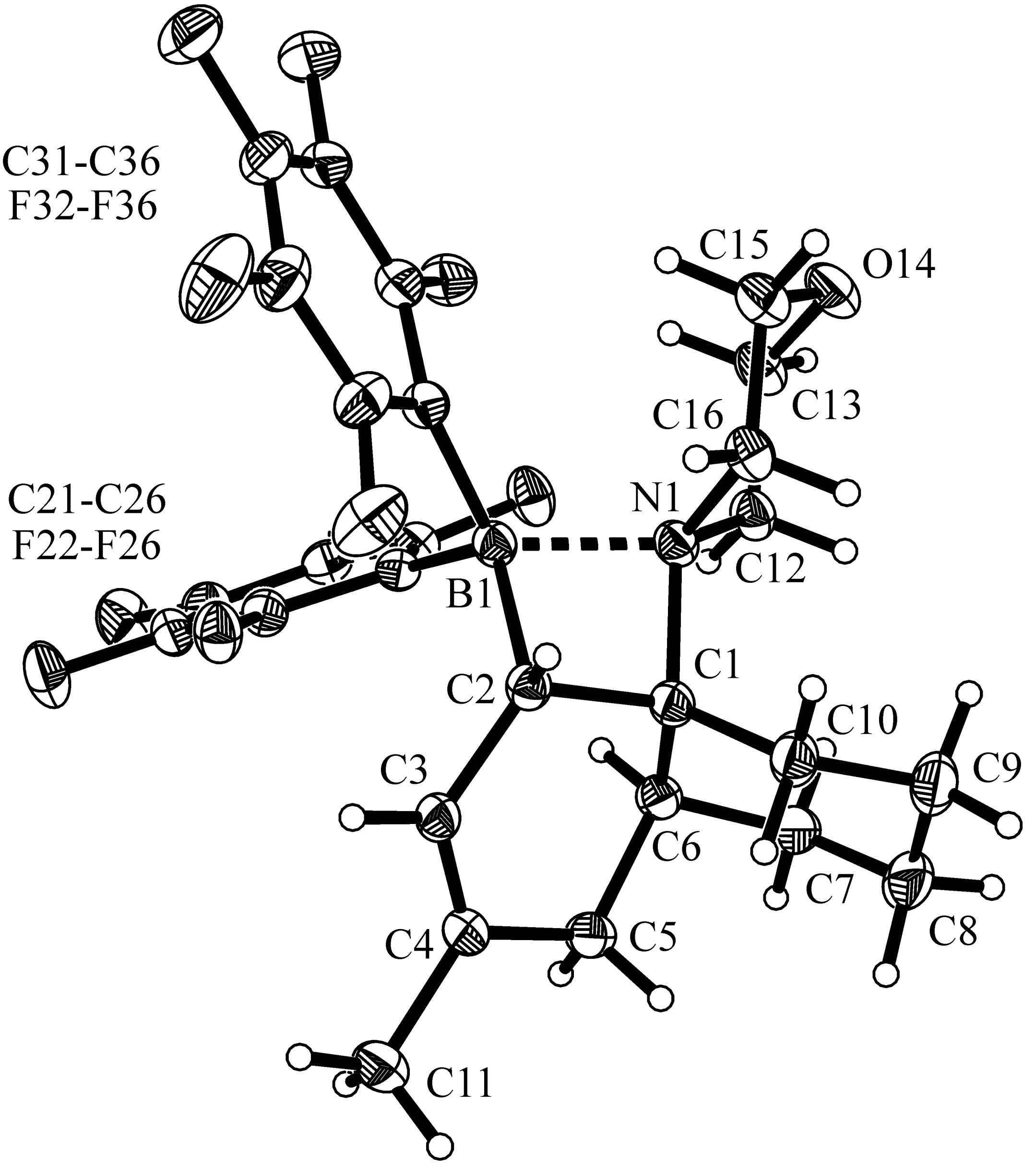


Figure S32

Decomposed: 108 °C. **Anal. Calc.** for $C_{27}H_{24}BF_{10}NO$: C, 55.98; H, 4.18; N, 2.24. Found: C, 55.28; H, 4.01; N, 2.35.

IR (KBr): ṽ/ cm^{-1} = 5342 (w), 3902 (w), 3854 (w), 3803 (w), 3748 (m), 3674 (w), 3650 (m), 3589 (w), 2955 (s), 2936 (s), 2873 (s), 2361 (s), 2340 (s), 1735 (m), 1699 (m), 1647 (v s), 1519 (v s), 1461 (v s), 1395 (s),1373 (s), 1282 (s), 1246 (s),1092 (v s), 971 (v s), 900 (s), 840 (w), 772 (m), 744 (m), 693 (m), 671 (m), 604 (m) 516 (w).

The solution of the crystals in dichloromethane-d_2 showed a mixture of two isomers
[193K: ratio ca. 5 : 1 (^{1}H)]

^{11}B{^{1}H} NMR (192 MHz, 193 K, dichloromethane-d_2): δ ^{11}B: 2.2 ($\nu_{1/2}$~ 1500 Hz).
^{11}B{^{1}H} NMR (192 MHz, 273 K, dichloromethane-d_2): δ ^{11}B: 4.3 ($\nu_{1/2}$~ 400 Hz).

Major Isomer:

^{1}H NMR (600 MHz, 193 K, dichloromethane-d$_2$): δ ^{1}H: 5.28 (br, 1H, =CH), 4.07, 3.30 (each m, each 1H, NCH$_2$), 3.87 (m, 2H, OCH$_2$), 3.54, 2.95 (each m, each 1H, OCH$_2$'), 3.33, 3.18 (each m, each 1H, NCH$_2$'), 2.88 (br, 1H, BCH), 2.27 (br, 1H, CH), 2.07, 1.46 (each m, each 1H, 10-CH$_2$)^t, 2.06, 1.51 (each m, each 1H, 5-CH$_2$), 1.93, 1.34 (each m, each 1H, 7-CH$_2$)^t, 1.56, 1.51 (each m, each 1H, 8-CH$_2$)^t, 1.54, 1.47 (each m, each 1H, 9-CH$_2$)^t, 1.42 (br, 3H, CH$_3$), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 193 K, dichloromethane-d$_2$): δ ^{13}C: 126.1 (=C), 120.2 (d, *J* = 9.5 Hz, =CH), 75.8 (NC), 63.5 (br d, *J* = 8.5 Hz OCH$_2$), 63.2 (OCH$_2$'), 56.8 (d, *J* = 21.4 Hz NCH$_2$), 52.5 (NCH$_2$'), 33.7 (br m, BCH), 32.9 (5-CH$_2$), 30.4 (CH), 30.1 (10-CH$_2$)^t, 27.5 (7-CH$_2$)^t, 22.2 (CH$_3$), 22.1 (9-CH$_2$)^t, 19.3 (8-CH$_2$)^t, [C$_6$F$_5$ not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 193 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{1}H: 5.28 / 2.06, 2.88, 1.42 (=CH / 5-CH$_2$, BCH, CH$_3$), 3.33 / 4.07, 3.87, 3.54, 3.18, 2.95 (NCH$_2$' / NCH$_2$, OCH$_2$, OCH$_2$', NCH$_2$', OCH$_2$'), 2.27 / 2.06, 1.51, 1.92, 1.34 (CH / 5-CH$_2$, 5-CH$_2$, 7-CH$_2$, 7-CH$_2$).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 193 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 5.28 / 120.3 (=CH), 4.07, 3.30 / 56.8 (NCH$_2$), 3.87 / 63.5 (OCH$_2$), 3.54, 2.95 / 63.2 (OCH$_2$'), 3.33, 3.18 / 52.5 (NCH$_2$'), 2.88 / 33.7 (BCH), 2.27 / 30.4 (CH), 2.07, 1.46 / 30.1 (10-CH$_2$), 2.06, 1.51 / 32.9 (5-CH$_2$), 1.93, 1.34 / 27.5 (7-CH$_2$), 1.56, 1.51 / 19.3 (8-CH$_2$), 1.54, 1.47 / 22.1 (9-CH$_2$), 1.42 / 22.2 (CH$_3$).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 193 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{13}C: 5.28 / 75.8, 32.9, 22.2 (=CH / NC, 5-CH$_2$, CH$_3$), 3.30 / 75.8, 63.5, 52.5 (NCH$_2$ / NC, OCH$_2$, NCH$_2$'), 3.18 / 75.9, 63.2 (NCH$_2$'/ NC, OCH$_2$'), 2.88 / 126.1, 120.2, 75.8, 30.1 (BCH / =C, =CH, NC, 10-CH$_2$), 2.27 / 75.8, 32.9, 30.4, 27.5, 19.3 (CH / NC, 5-CH$_2$, CH, 7-CH$_2$, 8-CH$_2$), 2.06 / 126.1, 120.2, 75.8, 30.1, 27.5, 19.3 (5-CH$_2$/ =C , =CH, NC, 10-CH$_2$, 7-CH$_2$, 8-CH$_2$), 1.51 / 126.1, 120.2, 75.8, 30.4, 22.2 (H-5 / =C, =CH, NC, CH, CH$_3$), 1.34 / 75.8, 22.1, 19.3 (7-CH$_2$ / NC, 9-CH$_2$, 8-CH$_2$).

^{1}H{^{1}H} TOCSY (600 MHz, 193 K, dichloromethane-d$_2$) [selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$: 5.28 / 2.88, 1.42 (=CH / BCH, CH$_3$), 3.33 / 4.07, 3.87, 3.54, 3.33, 2.95 (NCH$_2$' / NCH$_2$, OCH$_2$, OCH$_2$', NCH$_2$', OCH$_2$'), 2.27 / 5.28, 2.06, 1.93, 1.56, 1.46 (CH / =CH, 5-CH$_2$, 7-CH$_2$, 8-CH$_2$, 10-CH$_2$).

^{19}F NMR (564 MHz, 193 K, dichloromethane-d$_2$): δ ^{19}F: -124.9 (o), -136.2 (o'), -155.8 (p), -162.8 (m'), 163.2 (m) (each m, each 1F, C$_6$F$_5$^{a}) [Δδ ^{19}F$_{m,p}$ = 7.1, 7.5], -126.2 (o), -127.4 (o'), -159.7 (p), -164.8 (m'), -165.4 (m) (each m, each 1F, C$_6$F$_5$^{b}) [Δδ ^{19}F$_{m,p}$ = 5.0, 5.7].

^{19}F, ^{19}F GCOSY (564 MHz, 193 K, dichloromethane-d$_2$) [selected traces]: δ ^{19}F:
-162.8 / -155.8, -136.2, -124.9 (*m'*-C$_6$F$_5$^{a} / *p*-C$_6$F$_5$^{a}, *o'*-C$_6$F$_5$^{a}, *o*-C$_6$F$_5$^{a}), -163.2 / -155.8, -136.2, -124.9 (*m*-C$_6$F$_5$^{a} / *p*-C$_6$F$_5$^{a}, *o'*-C$_6$F$_5$^{a}, *o*-C$_6$F$_5$^{a}), -164.8 / -159.7, -127.4 (*m'*-C$_6$F$_5$^{b} / *p*-C$_6$F$_5$^{b}, *o'*-C$_6$F$_5$^{b}), -165.4 / -136.2, -159.7 (*m*-C$_6$F$_5$^{b} / *p*-C$_6$F$_5$^{b}, *o*-C$_6$F$_5$^{b}).

Minor Isomer:

^{1}H NMR (600 MHz, 193 K, dichloromethane-d$_2$): δ ^{1}H: 5.39 (br, 1H, =CH), 4.05, 3.57 (each m, each 1H, NCH$_2$), 3.89, 3.81 (each m, each 1H, OCH$_2$), 3.75 (m, 2H, OCH$_2$'), 3.28, 3.17 (each m, each 1H, NCH$_2$'), 2.94 (br, 1H, BCH), 2.33 (br, 1H, CH), 2.08, 1.66 (each m, each 1H, 5-CH$_2$), 2.08, 1.50 (each m, each 1H, 7-CH$_2$)^t, 1.64, 1.50 (each m, each 1H, 8-CH$_2$)^t, 1.53, 1.15 (each m, each 1H, 9-CH$_2$)^t, 1.52, 1.39 (each m, each 1H, 10-CH$_2$)^t, 1.46 (br, 3H, CH$_3$), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 193 K, dichloromethane-d$_2$): δ ^{13}C: 125.1 (=C), 125.0 (=CH), 79.1 (NC), 65.8 (OCH$_2$), 64.1 (OCH$_2$'), 52.9 (br d, *J* = 24 Hz, NCH$_2$), 50.6 (m, NCH$_2$'), 38.7 (CH), 36.5 (5-CH$_2$), 25.4 (br m, BCH), 35.1 (10-CH$_2$)^t, 34.4 (7-CH$_2$)^t, 23.8 (CH$_3$), 25.1 (9-CH$_2$)^t, 23.5 (8-CH$_2$)^t, [C$_6$F$_5$ not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 193 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{1}H: 5.39 / 2.94, 2.08, 1.66, 1.46 (=CH / BCH, 5-CH$_2$, 5-CH$_2$, CH$_3$), 4.05 / 3.89, 3.81, 3.75, 3.57 (NCH$_2$ / OCH$_2$, OCH$_2$, OCH$_2$’, NCH$_2$), 2.33 / 2.08, 1.52, 1.39 (CH / 5-CH$_2$, 8-CH$_2$, 10-CH$_2$, 10-CH$_2$).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 193 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 5.39 / 125.0 (=CH), 4.05, 3.57 / 52.9 (NCH$_2$), 3.89, 3.81 / 65.8 (OCH$_2$), 3.75 / 64.1 (OCH$_2$’), 3.28, 3.17 / 50.6 (NCH$_2$’), 2.94 / 25.4 (BCH), 2.33 / 38.7 (CH), 2.08, 1.66 / 36.5 (5-CH$_2$), 2.08, 1.50 / 34.4 (7-CH$_2$), 1.64, 1.50 / 23.5 (8-CH$_2$), 1.53, 1.15 / 25.1 (9-CH$_2$), 1.52, 1.39 / 35.1 (10-CH$_2$), 1.46 / 23.8 (CH$_3$).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 193 K, dichloromethane-d$_2$) [selected traces]: δ ^{1}H / δ ^{13}C: 5.39 / 79.1, 36.5, 23.9 (=CH / NC, 5-CH$_2$, CH$_3$), 3.28 / 79.1, 52.9 (NCH$_2$’ / NC, NCH$_2$), 2.94 / 35.1 (BCH / 10-CH$_2$), 2.33 / 79.1 , 35.1, 25.4 (CH / NC, 10-CH$_2$, BCH), 2.08 / 125.1, 38.7, 25.1, 23.5 (5-CH$_2$, 7-CH$_2$ / =C, CH, 9-CH$_2$, 8-CH$_2$), 1.66 / 125.1, 79.1, 35.1, 23.8 (5-CH$_2$ / =C, NC, 10-CH$_2$,CH$_3$), 1.52 / 79.1, 25.4, 23.5 (10-CH$_2$ / NC, BCH, 8-CH$_2$).

^{1}H{^{1}H} TOCSY (600 MHz, 193 K, dichloromethane-d$_2$) [selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$: 2.08 / 5.39, 2.94, 2.33, 1.66, 1.52, 1.50, 1.39 (5-CH$_2$, 7-CH$_2$ / =CH, BCH, CH, 5-CH$_2$, 10-CH$_2$, 8-CH$_2$, 10-CH$_2$)

^{19}F NMR (564 MHz, 193 K, dichloromethane-d$_2$): δ ^{19}F: -122.1 (o), -124.8 (o‘), -159.2 (p), -163.4 (m‘), -163.9 (m), (each m, each 1F, $C_6F_5^a$) [Δδ ^{19}F$_{m,p}$ = 4.2, 4.7], -131.8 (o), -132.4 (o‘), -157.2 (p), -162.5 (m‘), -163.9 (m) (each m, each 1F, $C_6F_5^b$) [Δδ ^{19}F$_{m,p}$ = 5.3, 6.7].

^{19}F, ^{19}F GCOSY (564 MHz, 193 K, dichloromethane-d$_2$) [selected traces]: δ ^{19}F: -163.4 / -159.2, -124.8 (*m*‘-$C_6F_5^a$ / *p*-$C_6F_5^a$, *o*‘-$C_6F_5^a$), -163.9 / -159.2, -124.8 (*m*-$C_6F_5^a$ / *p*-$C_6F_5^a$, *o*-$C_6F_5^a$), -162.5 / -157.2, -132.4 (*m*‘-$C_6F_5^b$ / *p*-$C_6F_5^b$, *o*‘-$C_6F_5^b$), -163.9 / -157.2, -131.8, (*m*-$C_6F_5^b$ / *p*-$C_6F_5^b$, *o*-$C_6F_5^b$, *o*-$C_6F_5^b$).

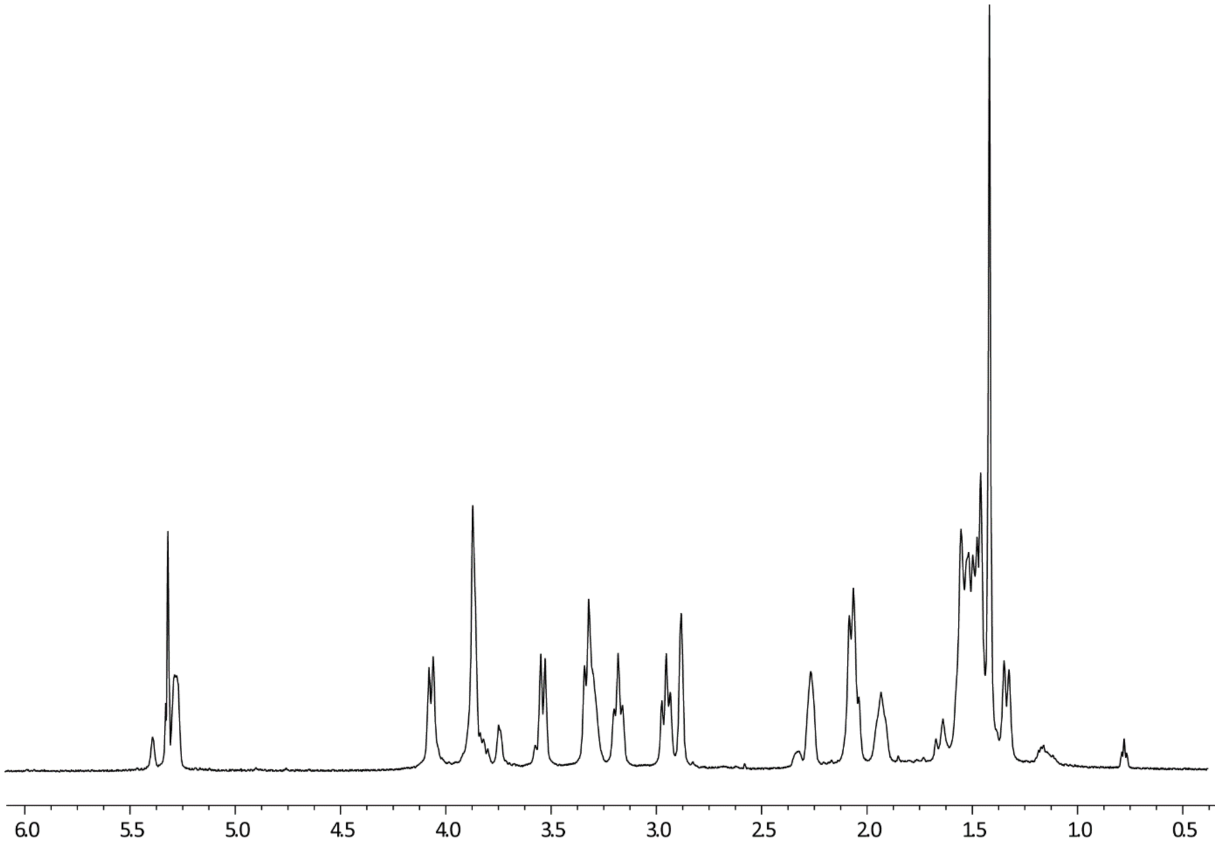


Figure S33 *^{1}H NMR (600 MHz, 193 K, dichloromethane-d$_2$) spectrum of compound* ***8c***.

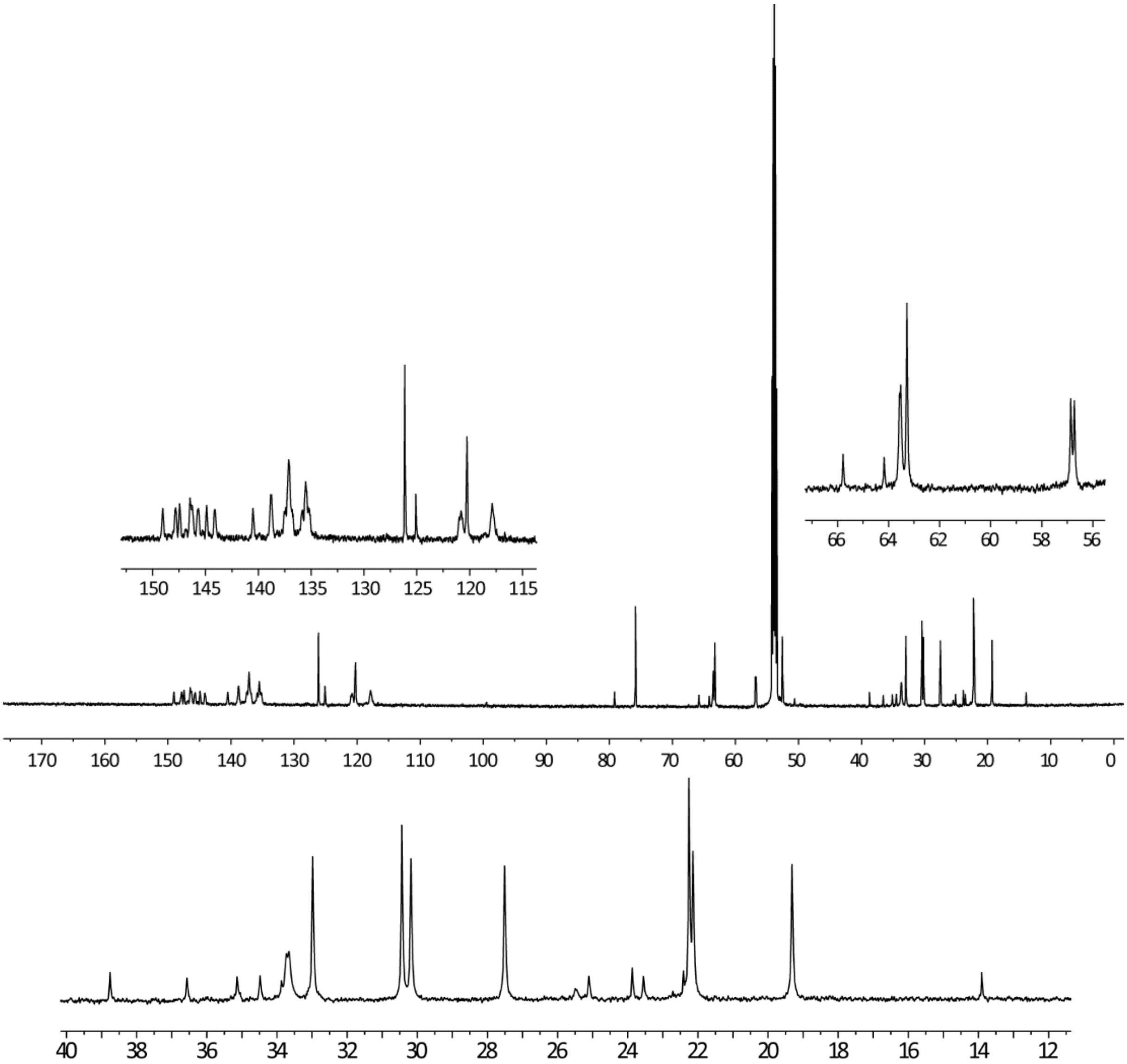


Figure S34 $^{13}C\{^{1}H\}$ *NMR (600 MHz, 193 K, dichloromethane-d_2) spectrum of compound* ***8c****.*

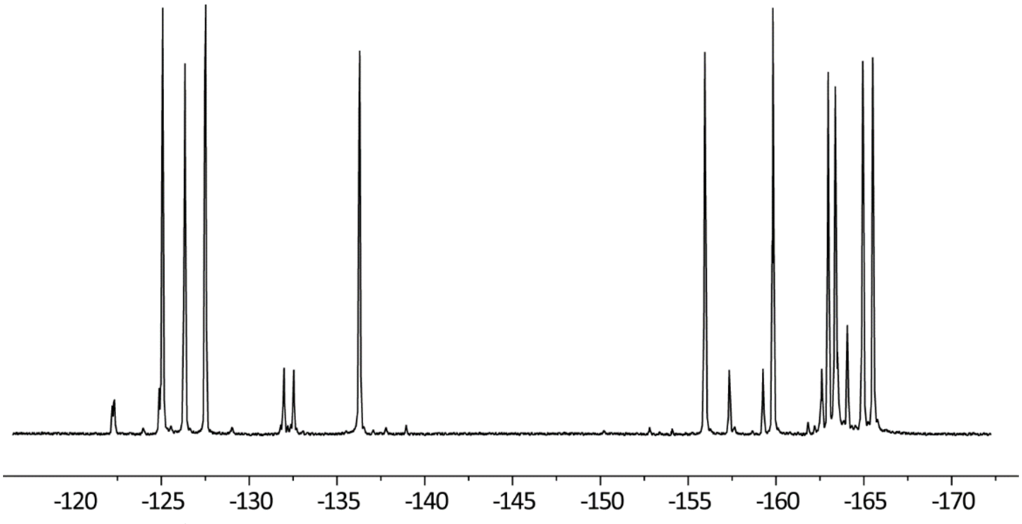


Figure S35 ^{19}F *NMR (564 MHz, 193 K, dichloromethane-d_2) spectrum of compound* ***8c****.*

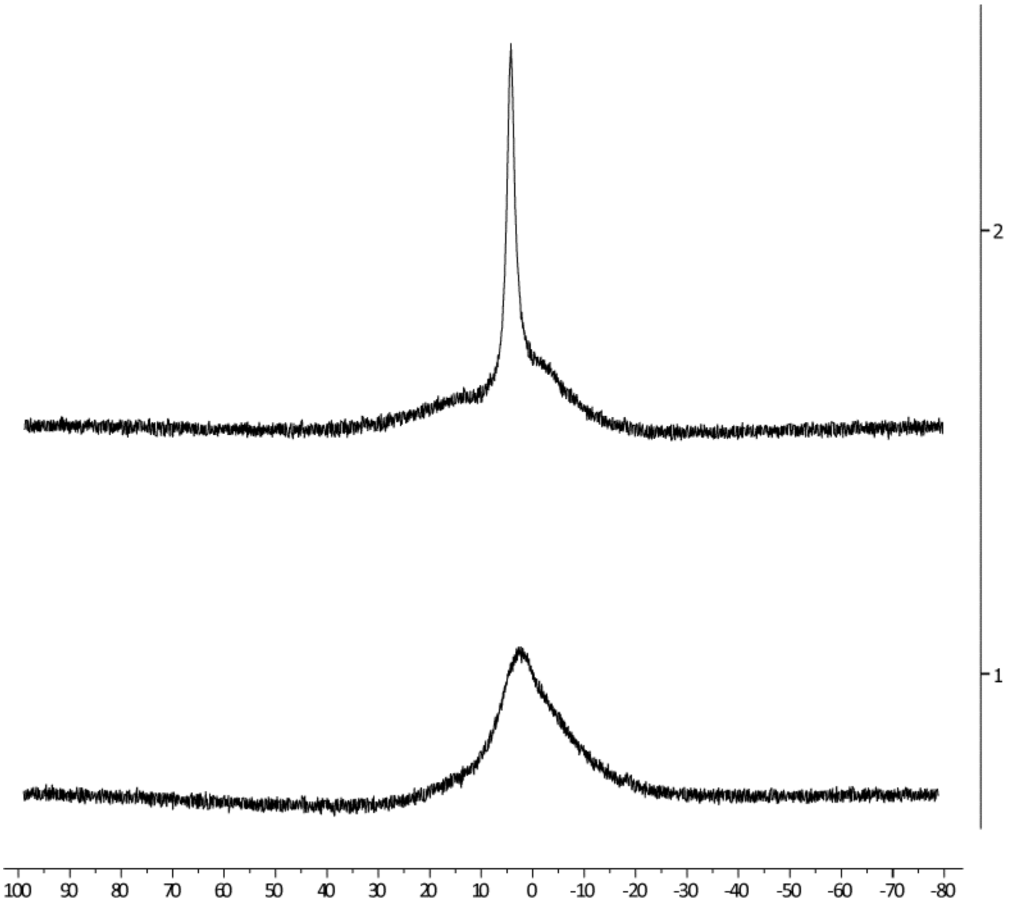
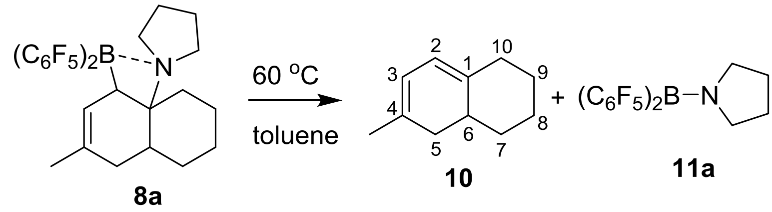


Figure S36 *^{11}B{^{1}H} NMR (192 MHz, dichloromethane-d_2) spectrum of compound* ***8c*** *at 193 K (1), and at 273 K (2).*

Generation of compound **10** by heating of compound **8**

1) Heating of compound **8a**: generation of compounds **10** and **11a** (NMR scale)



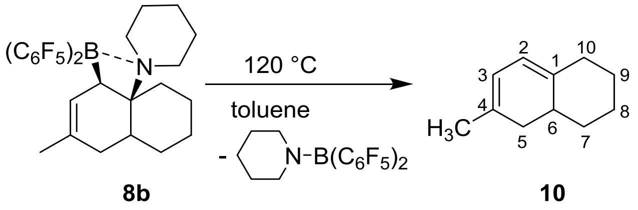
The compound **8a** (168.9 mg, 0.3 mmol) was dissolved in toluene (3 mL) and the solution was heated at 60 °C for 3 d. After removal of all volatiles, the obtained residue was washed with pentane (3 x 1 mL) to give compound **11a** (88%, 109.6 mg, 0.26 mmol) as a solid. The combined pentane solutions were filtered by a short column (SiO_2) and dried to give compound **10** (54%, 24.0 mg, 0.16 mmol) a colorless liquid.

Compound **10**: [Dauben, W. G.; Hart, D. J.; Ipaktschi, J.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, *44*, 4425-4428.]
^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 5.59 (m, 1H, H-3), 5.58 (m, 1H, H-2), 2.26, 1.95 (each m, each 1H, H-10), 2.22 (m, 1H, H-6), 2.10, 1.82 (each m, each 1H, H-5), 1.67, 1.16 (each m, each 1H, H-7), 1.65 (m, 3H, CH_3), 1.64, 1.24 (each m, each 1H, H-9), 1.63, 1.20 (each m, each 1H, H-8).
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 138.1 (C-1), 131.9 (C-4), 119.2 (3-C), 118.0 (2-C), 37.2 (5-C), 36.7 (C-6), 36.5 (C-7), 34.4 (C-10), 27.9 (C-9), 26.7 (C-8), 23.1 (CH_3).

Compound **11a**: [the NMR data are consistent to those reported in the literature: Kehr, G; Fröhlich, R.; Wibbeling, B.; Erker, G. *Chem. Eur. J.* **2000**, *6*, 258-266].

^{1}H NMR (500 MHz, 299 K, benzene-d$_6$): δ = 2.83 (m, 2H, NCH_2), 1.24 (m, 2H, CH_2).
^{11}B{^{1}H} NMR (160 MHz, 299 K, benzene-d$_6$): δ = 32.4 ($\nu_{1/2}$ ~ 200 Hz).
^{19}F NMR (470 MHz, 299 K, benzene-d$_6$): δ = -132.8 (m, 2F, *o*), -152.8 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*), -161.6 (m, 2F, *m*)[$\Delta\delta^{19}F_{mp}$ = 8.8].

2a) Heating of compound **8b**: isolation of compound **10**
[Dauben, W. G.; Hart, D. J.; Ipaktschi, J.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, *44*,4425-4428.]

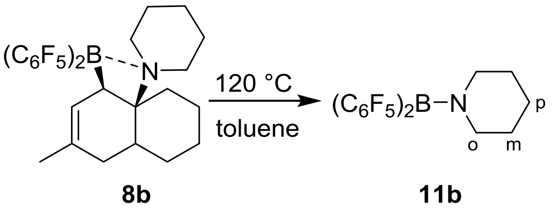


Scheme S9

After heating a solution of compound **8b** (320 mg, 0.55 mmol, 1 eq) in toluene (2 mL) at 120 °C for 3 h, the reaction mixture was filtrated twice through a short column (SiO_2). Removing of the volatiles of the filtrate *in vacuo* gave compound **10** as a colourless oil (65 mg, 0.44 mmol, 79%).

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2): δ ^{1}H: 5.47 (m, 1H, H-3), 5.46 (m, 1H, H-2), 2.29 (m, 2H, H-6), 2.27, 2.00 (each m, each 1H, H-10), 2.25, 1.88 (each m, each 1H, H-5), 1.85, 1.21 (each m, each 1H, H-7), 1.77, 1.27 (each m, each 1H, H-9), 1.75, 1.35 (each m, each 1H, H-8), 1.71 (m, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, 299 K, dichloromethane-d_2): δ ^{13}C: 138.9 (C-1), 132.7 (C-4), 118.6 (C-3), 117.4 (C-2), 37.2 (C-5), 36.7 (C-6), 36.6 (C-7), 34.4 (C-10), 28.0 (C-9), 26.7 (C-8), 23.1 (CH_3).

2b) Heating of compound **8b**: isolation of compound **11b**
[Schwendemann, S.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Sci.* **2011**, *2*, 1842-1849.]



Scheme S10

Compound **8b** (358 mg, 0.62 mmol, 1 eq) was dissolved in toluene and the solution was heated at 120 °C for 3 h. After removal of all volatiles in vacuo, the resulting residue was washed with pentane (3 x 1 mL) to give compound **11b** (152 mg, 0.35 mmol, 57%). Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **11b** in *n*-pentane at room temperature.

X-ray crystal structure of compound 11b: formula $C_{17}H_{10}BF_{10}N$, M = 429.07, colourless crystal, 0.214 x 0.207 x 0.173 mm, a = 9.0935(5), b = 9.5304(5), c = 11.4509(7) Å, α = 70.278(2), β = 74.540(2), γ = 65.394(2)°, V = 840.1(1) Å^3, ρ_{calc} = 1.696 gcm^{-3}, μ = 0.177 mm^{-1}, empirical absorption correction (0.963 ≤ T ≤ 0.970), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 100(2) K, ω and ϕ scans, 14380 reflections collected (±h, ±k, ±l), 3450 independent (R_{int} = 0.029) and 2806 observed reflections [I>2σ(I)], 262 refined parameters, R = 0.036, wR^2 = 0.092, max. (min.) residual electron density 0.26 (-0.25) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

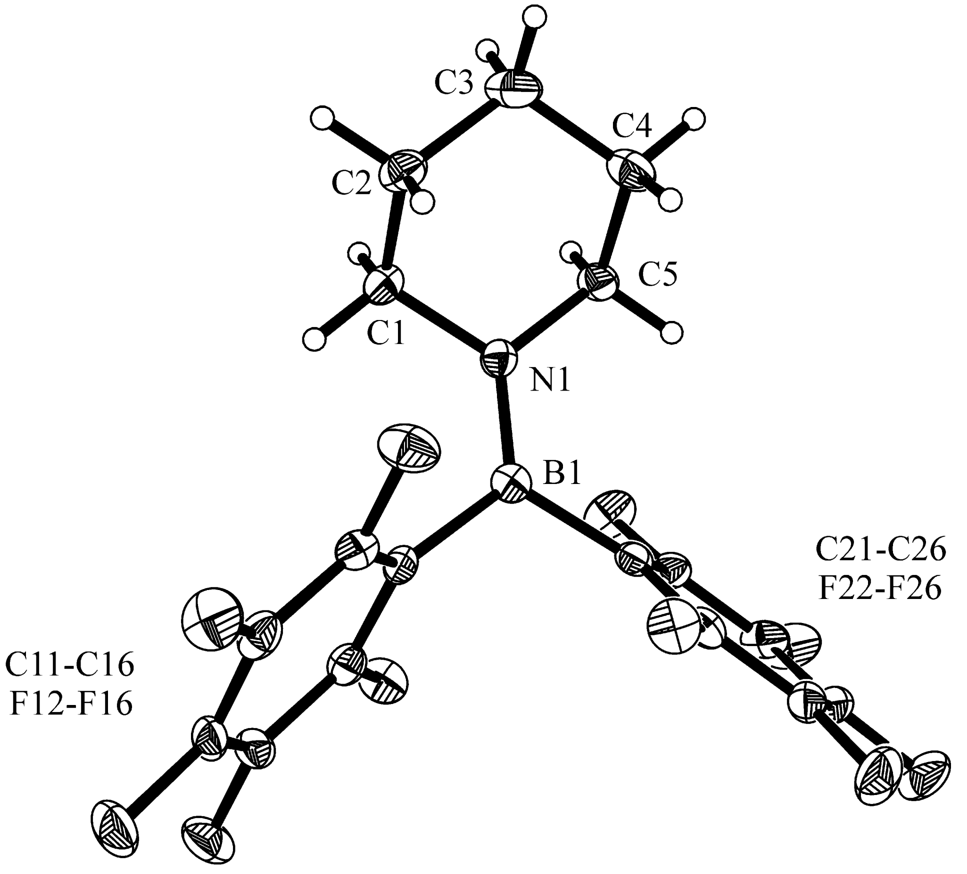


Figure S37

Decomposed: 125 °C. **Anal. Calc.** for $C_{17}H_{10}BF_{10}N$: C, 47.59; H, 2.35; N, 3.26. Found: C, 47.69; H, 2.32; N, 3.24.

IR (KBr): $\tilde{\nu}$/ cm^{-1} = 3345 (w), 3222 (w), 2945 (m), 2864 (m), 2363 (w), 1648 (m), 1517 (s), 1517 (vs), 1467 (vs), 1396 (m), 1355 (s), 1299 (s), 1239 (s), 1143 (s), 1094 (vs), 1035 (m), 973 (vs), 902 (m), 862 (m), 790 (m), 737 (m), 694 (m), 628 (w), 458 (w).

^{1}H NMR (600 MHz, 299 K, dichloromethane-d$_2$): δ ^{1}H: 3.30 (m, 2H, *o*-CH$_2$), 1.70 (m, 1H, *p*-CH$_2$), 1.64 (m, 2H, *m*-CH$_2$).
^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d$_2$): δ ^{13}C: 146.5 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 141.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 111.8 (br, *i*-C_6F_5), 51.5 (*o*-CH$_2$), 28.0 (*m*-CH$_2$), 24.9 (*p*-CH$_2$).
^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299K, dichloromethane-d$_2$)[selected trace]: δ ^{1}H / δ ^{1}H: 1.64 / 3.30, 1.70 (*m*-CH$_2$ / *o*-CH$_2$, *p*-CH$_2$).
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, dichloromethane-d$_2$): δ ^{1}H / δ ^{13}C: 3.30 / 51.6 (*o*-CH$_2$), 1.70 / 24.9 (*p*-CH$_2$). 1.64 / 28.0 (*m*-CH$_2$).
^{19}F NMR (564 MHz, 299 K, dichloromethane-d$_2$): δ ^{19}F: -132.5 (m, 2F, *o*-C_6F_5), -154.4 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -162.7 (m, 2F, *m* -C_6F_5) [$\Delta\delta$ $^{19}F_{m,p}$ = 8.3].
^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d$_2$): δ ^{11}B: 32.1 ($\nu_{1/2}$~250 Hz).
^{11}B NMR (192 MHz, 299 K, dichloromethane-d$_2$): δ ^{11}B: 32.1 ($\nu_{1/2}$ ~250 Hz).

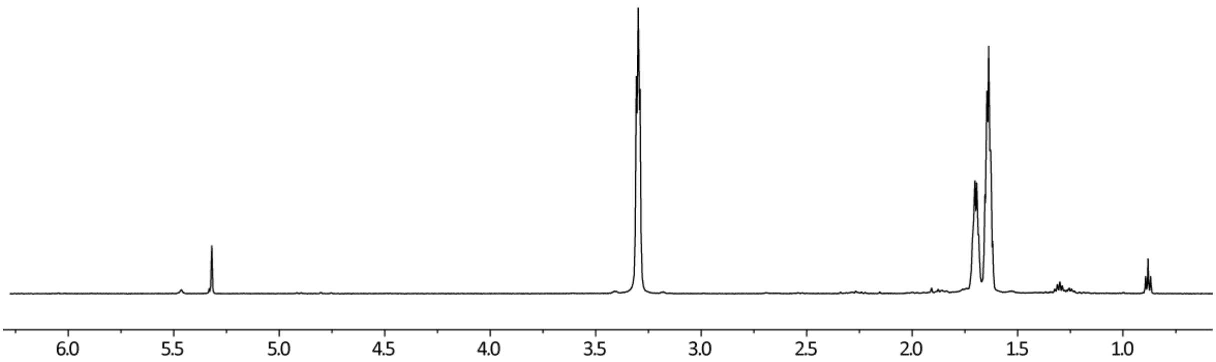


Figure S38 ^1H *NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of* ***11b***.

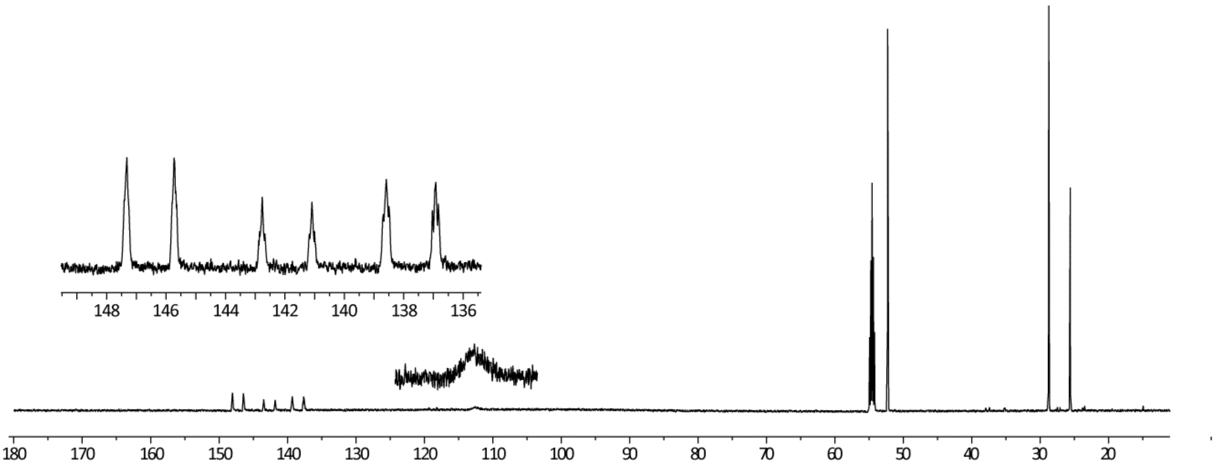


Figure S39 $^{13}C\{^1H\}$ *NMR (151 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound* ***11b***.

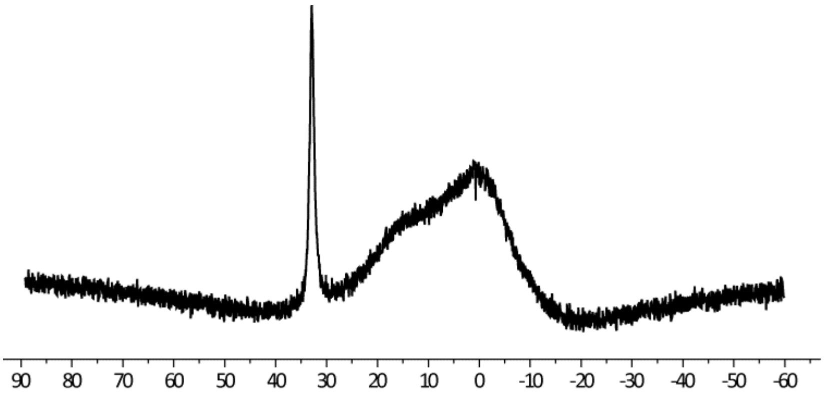


Figure S40 $^{11}B\{^1H\}$ *NMR (192 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound* ***11b***.

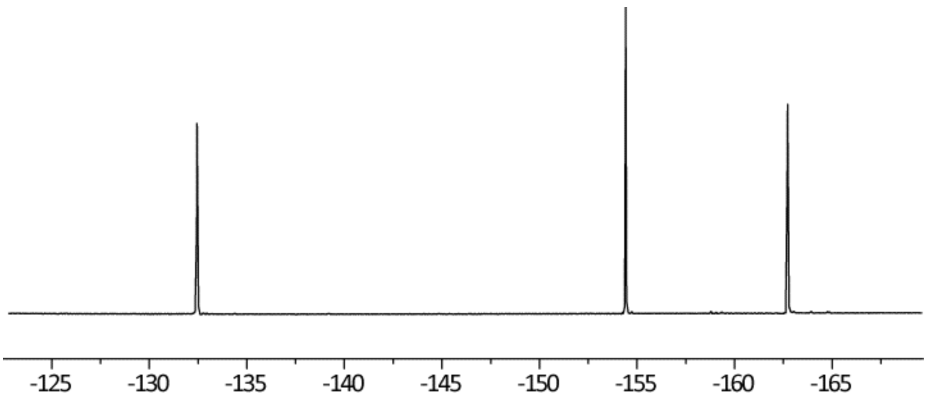
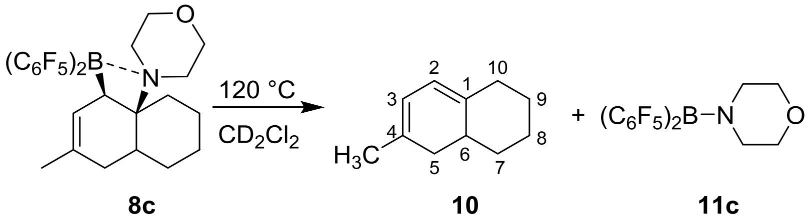


Figure S41 ^{19}F *NMR (564 MHz, 299 K, dichloromethane-d$_2$) spectra of compound* ***11b***.

3a) Heating of compound **8c**: generation of compound **10** and **11c** (NMR scale)



Scheme S11

A solution of compound **8c** (70.0 mg, 0.12 mmol, 1 eq) in dichloromethane-d$_2$ (1 mL) was heated in an autoclave at 120 °C for 3 h. Then the obtained mixture of compounds **10** and **11c** was characterized by NMR experiments.

N-[Bis(pentafluorophenyl)boryl]morpholine (11c)

^{1}H NMR (600 MHz, 299 K, dichloromethane-d$_2$): δ ^{1}H: 3.72 (m, 1H, OCH$_2$), 3.36 (m, 1H, NCH$_2$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d$_2$): δ ^{13}C: 146.5 (dm, $^1J_{FC}$ ~ 245 Hz, C$_6$F$_5$), 141.2 (dm, $^1J_{FC}$ ~ 255 Hz, C$_6$F$_5$), 137.8 (dm, $^1J_{FC}$ ~ 250 Hz, C$_6$F$_5$), 111.0 (br, *i*-C$_6$F$_5$), 68.4 (OCH$_2$), 50.9 (NCH$_2$).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d$_2$): δ ^{19}F: -132.3 (m, 2F, *o*-C$_6$F$_5$), -153.3 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C$_6$F$_5$), -162.2 (m, 2F, *m* -C$_6$F$_5$) [Δδ ^{19}F$_{m,p}$ = 8.9].

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d$_2$): δ ^{11}B: 32.9 ($\nu_{1/2}$~200 Hz).

6-Methyl-1,2,3,4,5,6-hexahydronaphthalene (10):

the NMR data are consistent to those given above (heating of compound **8a** and **8b**, respectively)

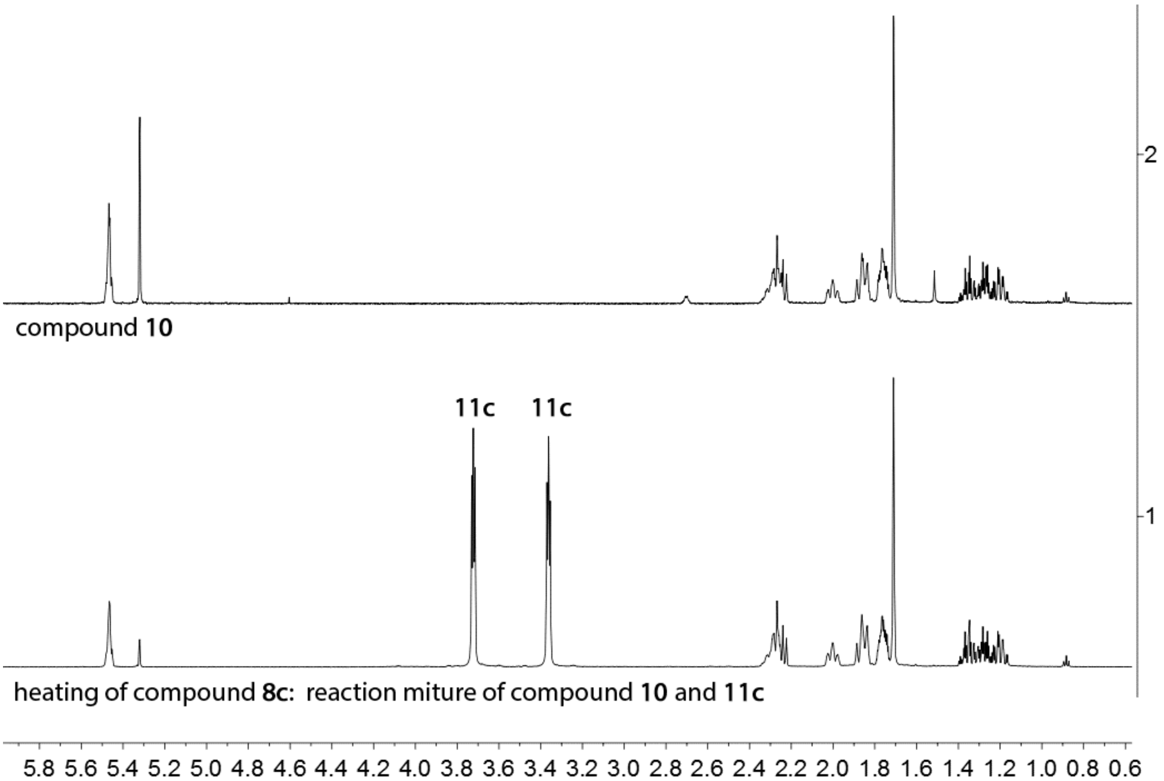


Figure S42 *^{1}H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectra (1) after heating of compound **8c**, (2) isolated compound **10**.*

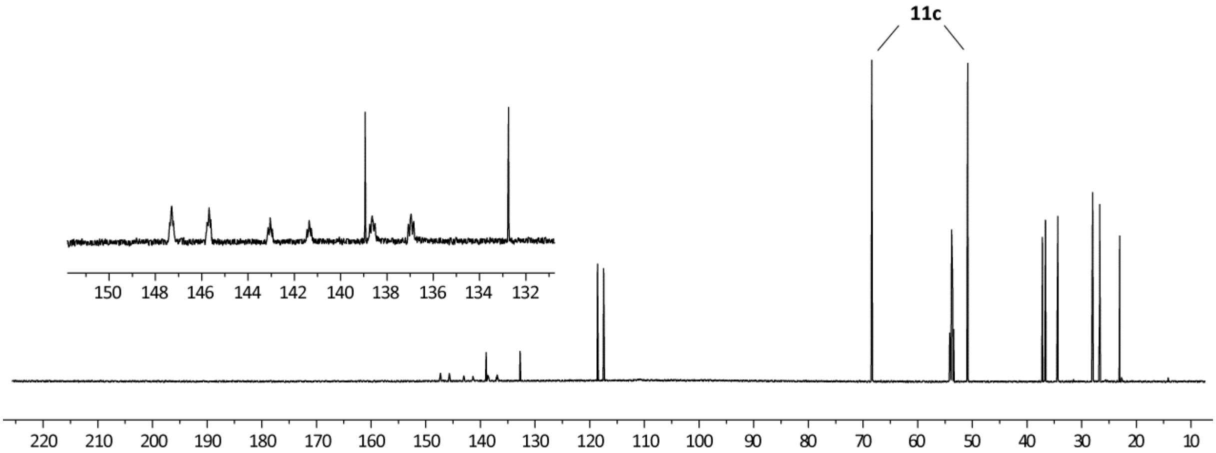


Figure S43 $^{13}C\{^{1}H\}$ *NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectra of the reaction mixture after heating compound* ***8c****.*

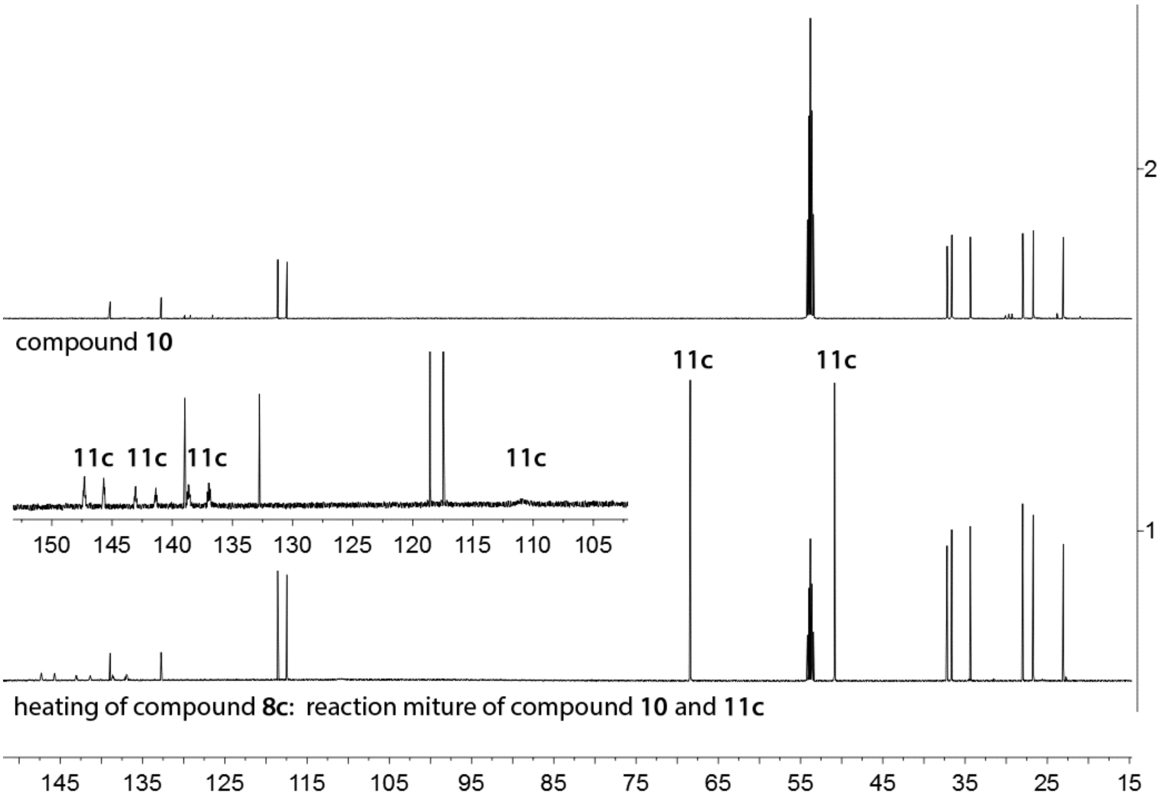


Figure S44 $^{13}C\{^{1}H\}$ *NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectra (1) after heating of compound* ***8c****, (2) isolated compound* ***10****.*

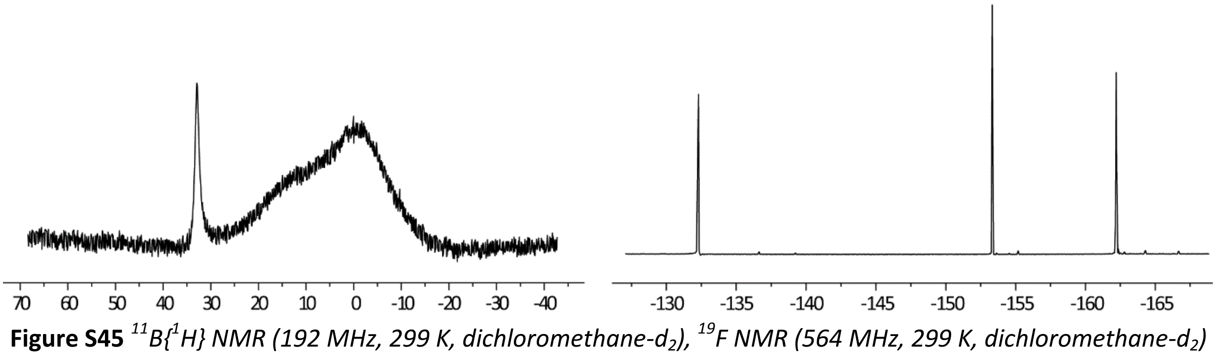
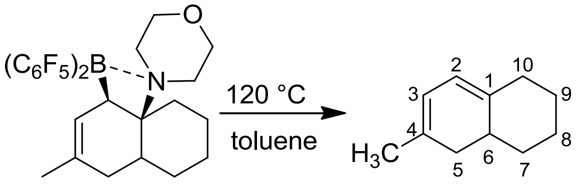


Figure S45 $^{11}B\{^{1}H\}$ *NMR (192 MHz, 299 K, dichloromethane-d$_2$),* ^{19}F *NMR (564 MHz, 299 K, dichloromethane-d$_2$) spectra of the reaction mixture after heating compound* ***8c****.*

3b) Heating of compound **8c**: isolation of compound **10**
[Dauben, W. G.; Hart, D. J.; Ipaktschi, J.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, *44*,4425-4428.]

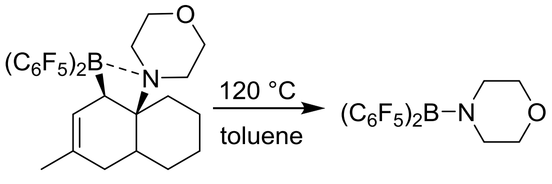


8c **10**

Scheme S12

A solution of compound **8c** (340 mg, 0.59 mmol, 1 eq) in toluene (2 mL) was heated at 120 °C for 3 h. After filtration (three times) through a short column (SiO_2) all volatiles of the filtrate were removed *in vacuo* to give compound **10** as a colourless oil (72 mg, 0.48 mmol, 82%).
The NMR data are consistent to those given above (heating of compound **8a** and **8b**, respectively)

3c) Heating of compound **8c**: isolation of compound **11c**



8c **11c**

Scheme S13

A solution of compound **8c** (376 mg, 0.65 mmol, 1 eq) in toluene (2 mL) was heated at 120 °C for 3 h. After removal all volatiles *in vacuo*, the resulting residue was washed with pentane (3 x 1 mL) to give compound **11c** as a red powder (161 mg, 0.37 mmol, 58 %).

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **11c** in deuterated dichloromethane covered with *n*-pentane at room temperature.

X-ray crystal structure of compound 11c: formula $C_{16}H_8BF_{10}NO$, M = 431.04, colourless crystal, 0.18 x 0.06 x 0.02 mm, a = 8.6260(5), b = 18.2872(12), c = 21.3911(14) Å, β = 91.102(2) °, V = 3373.7(4) Å^3, ρ_{calc} = 1.697 gcm^{-3}, μ = 0.181 mm^{-1}, empirical absorption correction (0.968 ≤ T ≤ 0.996), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 17034 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 5714 independent (R_{int} = 0.128) and 2608 observed reflections [$I > 2\sigma(I)$], 578 refined parameters, R = 0.190, wR^2 = 0.326, max. (min.) residual electron density 0.30 (-0.31) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

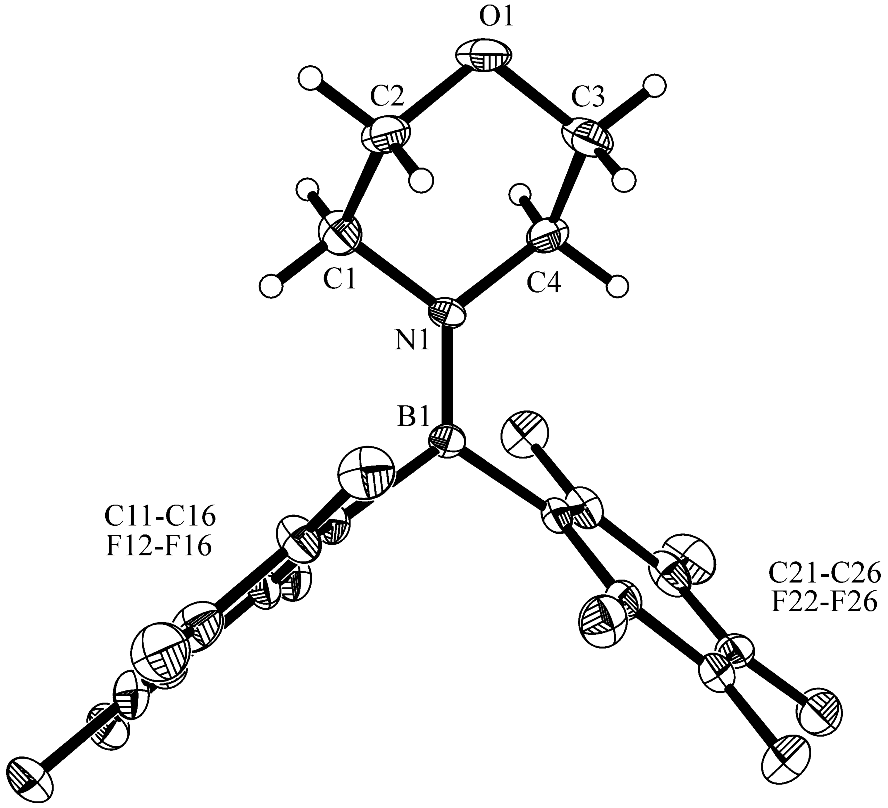


Figure S46

Decomposed: 100 °C. **Anal. Calc.** for $C_{16}H_8BF_{10}N$: C, 44.58; H, 1.87; N, 3.25. Found: C, 44.62; H, 2.45; N, 3.51.

IR (KBr): ṽ/ cm^{-1} = 3677 (w), 2985 (m), 2932 (m), 2867 (m), 2360 (m), 1651 (s), 1514 (vs), 1473 (vs), 1397 (s), 1306 (s), 1250 (s), 1174 (s), 1118 (vs), 1089 (vs), 1005 (s), 974 (vs), 910 (s), 795 (m), 737 (m), 694 (s), 652 (w), 634 (w), 506 (w), 466 (w), 447 (w).

^{1}H NMR (600 MHz, 299 K, benzene-d$_6$): δ ^{1}H: 3.29 (m, 1H, OCH_2), 2.74 (m, 1H, NCH_2).
^{13}C{^{1}H} NMR (151 MHz, 299 K, benzene-d$_6$): δ ^{13}C: 145.9 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 141.7 (dm, $^1J_{FC}$ ~ 255 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 110.2 (br, *i*-C_6F_5), 67.8 (OCH_2), 50.3 (NCH_2).
^{19}F NMR (564 MHz, 299 K, benzene-d$_6$): δ ^{19}F: -132.4 (m, 2F, *o*-C_6F_5), -151.8 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -161.1 (m, 2F, *m* -C_6F_5) [Δδ $^{19}F_{m,p}$ = 9.3].
^{11}B{^{1}H} NMR (192 MHz, 299 K, benzene-d$_6$): δ ^{11}B: 32.8 ($ν_{1/2}$ ~ 300 Hz).

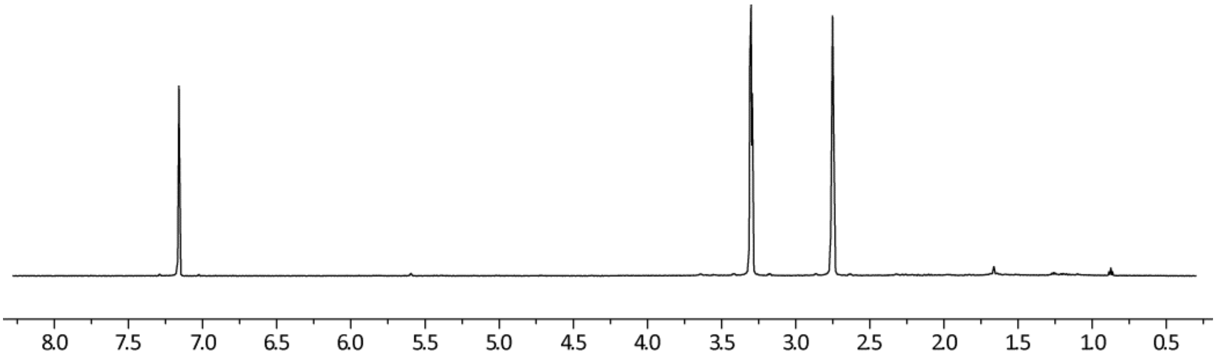


Figure S47 *^{1}H NMR (600 MHz, 299 K, d_6-benzene) spectrum of compound **11c**.*

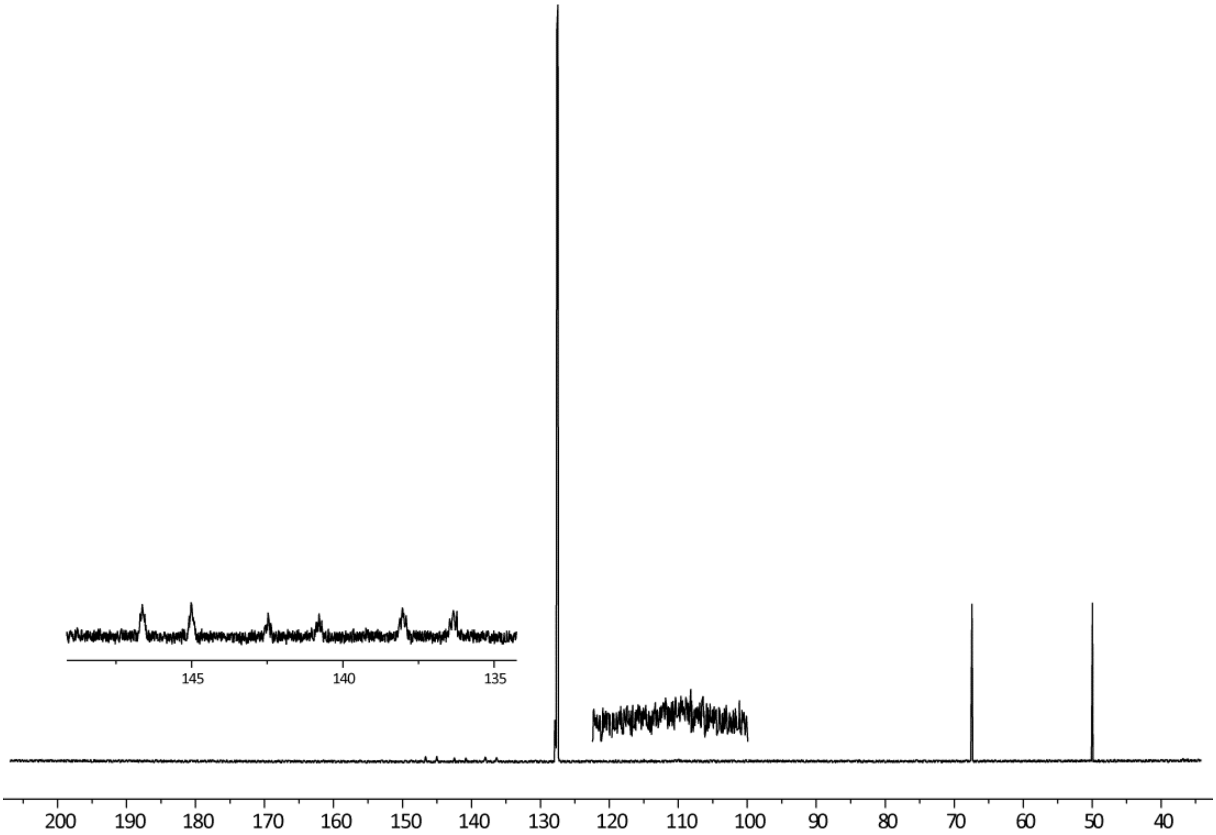


Figure S48 *$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, d_6-benzene) spectrum of compound* ***11c****.*

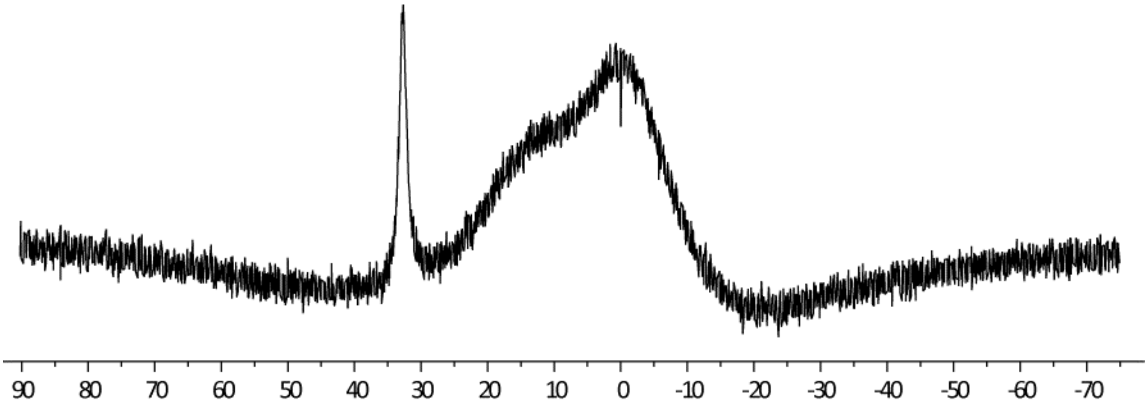


Figure S49 *^{11}B NMR (192 MHz, 299 K, d_6-benzene) spectrum of compound* ***11c****.*

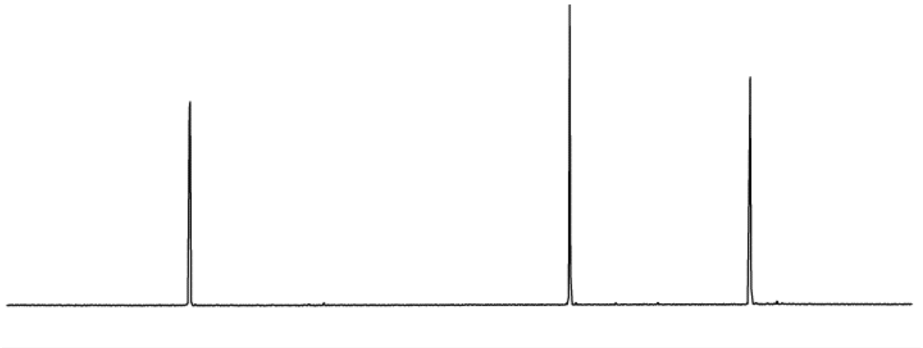
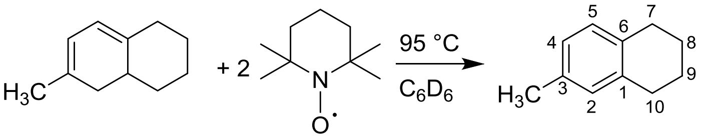


Figure S50 *^{19}F NMR (564 MHz, 299 K, d_6-benzene) spectrum of compound* ***11c****.*

Synthesis of compound **12**

[(a) Lawens, T.; Schmit-Quih, F.; Nicole, D. *Magn. Reson. Chem.* **1995**, *33*, 523-528; (b) Kostermans, G. B. M.; Dansik, P. v.; Wolf; W. H. d.; Bickelhaupt, F. *J. Org. Chem.* **1988**, *53*, 4531-4534.]



10 **12**

Scheme S14

A solution of compound **10** (205 mg, 1.38 mmol, 1 eq) in benzene-d$_6$ (0.5 mL) was added to a solution of TEMPO (432 mg, 2.77 mmol, 2 eq) in benzene-d$_6$ (1 mL). The reaction-mixture was stirred for 4 days at 95 °C. After filtration (four times) through a short column (SiO_2) all volatiles were removed *in vacuo* to give compound **12** as a yellow oil (103 mg, 0.70 mmol, 51%). The NMR data are consistent to those reported in the literature.

^{1}H NMR (600 MHz, 299 K, benzene-d$_6$): δ ^{1}H: 6.91 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-5), 6.88 (dm, $^3J_{HH}$ = 7.8 Hz, 1H, H-4), 6.79 (m, 1H, H-2), 2.58 (m, 4H, H-7,10), 2.16 (s, 3H, CH_3), 1.57 (m, 4H, H-8,9).

^{13}C{^{1}H} NMR (151 MHz, 299 K, benzene-d$_6$): δ ^{13}C: 136.8 (C-1), 134.7 (C-3), 134.0 (C-6), 130.0 (C-2), 129.3 (C-5), 126.6 (C-4), 29.7 (C-10), 29.3 (C-7), 23.74, 23.67 (C-8,9), 21.1 (CH_3).

Theoretical Methods and Technical Details of the Computations

The quantum chemical calculations were carried out with the TURBOMOLE suite of programs.[1] All structures (minima and transition states) were optimized at the efficient HF-3c level,[2] i.e., a minimal basis set Hartree-Fock with three geometry-based corrections. One of these corrections is the atom pairwise D3 correction with Becke-Johnson-damping to account for London dispersion interactions.[3] Basis set superposition errors are accounted by means of the geometrical counterpoise correction.[4] The third correction reduces the errors in bond lengths arising from the minimal basis set.[2]

For compound **8c**, we used the X-ray structure (ERK7821) as the starting geometry. For the dienylborane **2a**, we used the *E*-isomer (w.r.t. the C1-C2 double bond).

Harmonic frequencies were calculated on these geometries (by HF-3c) in order to verify these either as transition states or as minima.

The electronic energies presented in this work were obtained by applying the PW6B95 meta-hybrid density functional[5] (numerical integration grid *m5*) along with the D3(BJ) correction[3] and the large polarized quadruple-zeta (def2-QZVP) sets by Ahlrichs *et al.*[6,7] to the HF-3c geometries. The level of theory for the singlepoint calculations will be dubbed as PW6B95-D3(BJ)/def2-QZVP in the following. Using HF-3c instead of e.g., our standard procedure TPSS-D3(BJ)/def2-TZVP[3,7,8,9] leads only to minor deviations (< 1.5 kcal/mol) in relative energies (this was tested for minimum structures) but we may exploit the efficiency of HF-3c at finding and optimizing transition states.

In all density functional theory (DFT) calculations, the resolution-of-the-identity approximation has been used[10] to speed up the computations of the Coulomb integrals. In the following, we report free energies at 298.15 K and 1 atm (termed ΔG). The ro-vibrational corrections (including zero-point vibrational energies) to the free energy are obtained from a modified rigid rotor, harmonic oscillator statistical treatment[11] based on the scaled (by 0.86)[2] harmonic frequencies obtained at the HF-3c level (see above). In the entropy calculation, frequencies with wavenumbers below 100 $\mathrm{cm^{-1}}$ were treated partially as rigid rotors and harmonic oscillators (see Ref. [11] for details).

Solvent effects on the thermochemical properties have been obtained by the COSMO-RS method[12] (COSMOtherm software package[13]) based on BP86/TZVP[9,14] calculations (parametrization from 2012). Solvation contributions to free energies at 298.15 K in CH_2Cl_2 solution are computed from the gas phase structures obtained at the above mentioned levels of theory.

The computed free energies are then obtained by

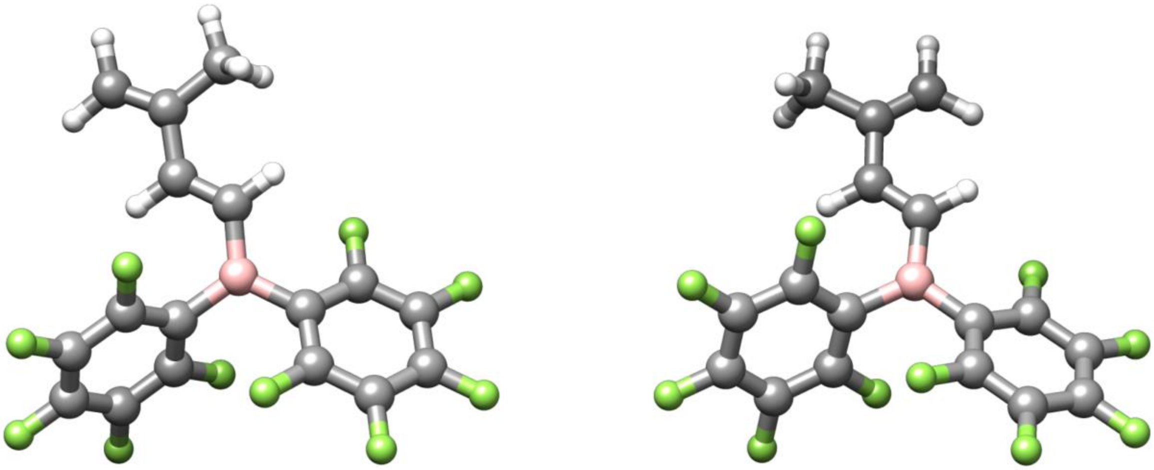
$$\Delta G = \Delta E + \Delta G_{\mathrm{RRHO}} + \Delta\delta G_{\mathrm{COSMO\text{-}RS}}\,.$$

The last two terms refer to the above mentioned ro-vibrational and solvation contributions to the free energy, respectively.

In the following, we will discuss free energies but will also give the differences in pure electronic energies (including dispersion and nuclear repulsion) ΔE in parentheses.

Discussion of the Computational Results

A concerted cycloaddition of **2a** to **6c** requires the presence of the *E-s-cis*-conformer ("*cis"* w.r.t. to the C2-C3 single bond) of **2a**. In Figure S51, both forms are depicted for clarity. The *E-s-cis*-conformer is only slightly higher in free energy by 3.1 kcal/mol than the *E-s-trans*-conformer. Thus, it can be expected that sufficient amounts the *E-s-cis*-conformer are present which can then react with **6c** to form the product **8c**. Nevertheless, whenever we present (free) energy differences w.r.t. the reactands, we will use the more stable *E-s-trans*-conformer as reference point.



E-*s*-*trans*-**2a**

E-*s*-*cis*-**2a**

$\Delta G = +3.1$ ($\Delta E = +3.5$)

Figure S51: Ball-and-stick depiction of the *E-s-trans* and *E-s-cis*-conformer of dienylborane **2a**. The numbers for ΔG and ΔE are given in kcal/mol. The colors in the ball-and-stick representation refer to: B = pink, C = grey, F = green, H = white.

According to our computational analysis, the formation of the cycloaddition product **8c** via a concerted, Diels-Alder-like transition state is unlikely. A reaction barrier of 53.3 (33.9) kcal/mol is obtained with our methodology (w.r.t. the reactands *E-s-trans*-**2a** and **6c**).

Another possible route is a two-step procedure in which the terminal carbon C4 of the dienylborane **2a** adds to double bond in enamine **6c** forming the intermediate **9**.

The reaction barrier for this addition is computed to be 15.3 (3.3) kcal/mol while the intermediate **9** is slightly less stable than the separate species **2a** and **6c** by 5.8 (–5.6) kcal/mol. Subsequently, the borata-alkene group in intermediate **9** adds to the iminum group. In this step, a single bond is formed between C1 and C10.

This step is predicted to occur with a very small barrier (relative to intermediate **9**) of 3.7 (–0.1) kcal/mol (the slightly negative ΔE results from the different potential energy surfaces of HF-3c and PW6B95-D3(BJ)/def2-QZVP).

In Figure S52, the reaction profile is depicted for both pathways.

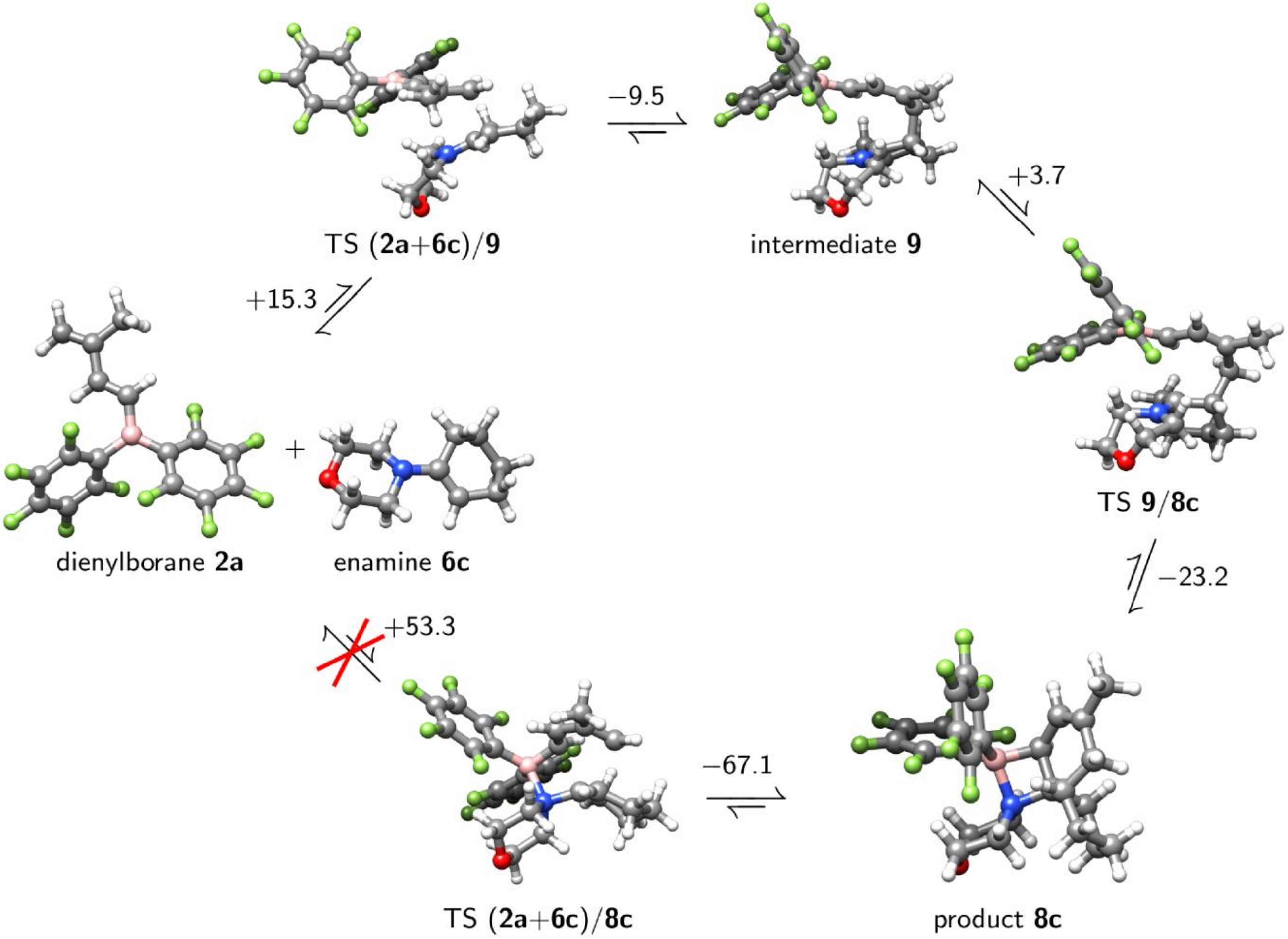


Figure S52: Reaction profile for the formation of **8c** starting from the dienylborane **2a** and the enamine **6c**. The formation via a concerted transition state is unfeasible (bottom) while a two-step process is reasonable (top). The colors in the ball-and-stick representation refer to: B = pink, C = grey, F = green, H = white, N = blue, O = red.

Therefore, the two-step process is predicted to be feasible while the concerted procedure is not. This requires a closer look at the transition state structure of the concerted mechanism. Given that an electron withdrawing substituent was present in diene **2a**, a Diels-Alder-like reaction with inverse electron demands seemed realistic. However, in the respective transition state geometry, B1 and N1 have already formed a Lewis adduct which weakens the anticipated substituent effects. In Figure S53, a plot of the electrostatic potential in TS (**2a**+**6c**)/**8c** is shown. It can be seen that the facing carbon atoms (i.e., C1/C10 and C4/C5, respectively) each show similar electrostatic potentials (depicted as partial charges in the Lewis scheme), thus the prerequisite for a Diels-Alder-type reaction is not given and the reaction barrier is too high.

In contrast to this, the two-step process occurs without the formation of the Lewis adduct. Therefore, the formation of the borata-alkene as well as an iminium in the intermediate **9** is possible which leads to a stabilization of this intermediate. The rate-determining step of the overall reaction is the first step with a barrier of 15.3 kcal/mol.

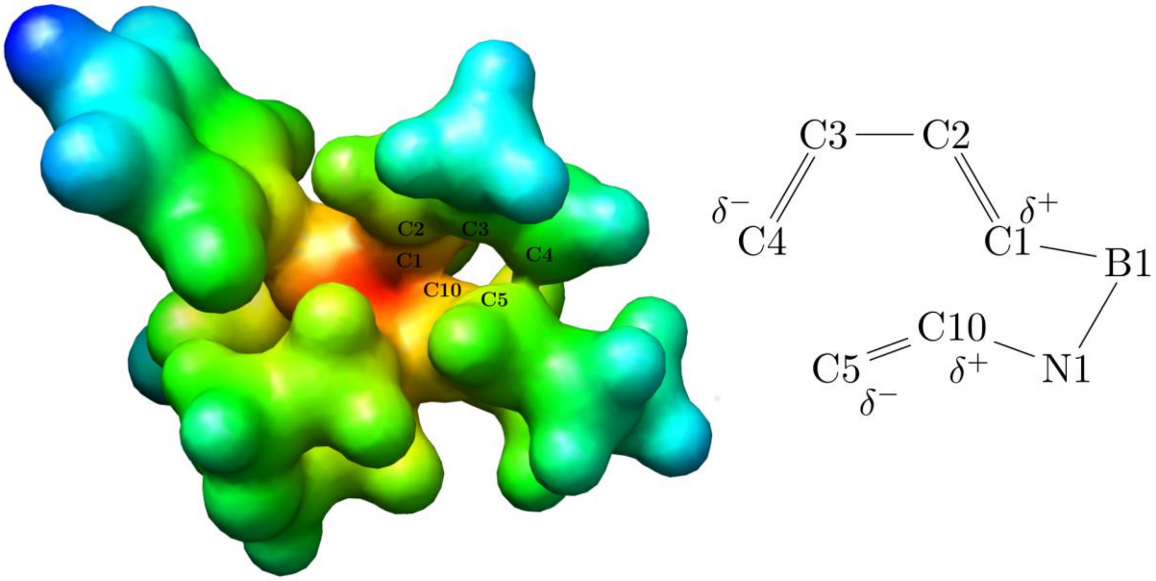


Figure S53: Electrostatic potential plotted for TS (**2a**+**6c**)/**8c** (left). Schematic Lewis depiction of the partial charge distribution in the transition state structure is given on the right.

References

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Thermodynamic data

PW6B95-D3(BJ)/def2-QZVP//HF-3c, CH_2Cl_2 , 298.15 K, HF-3c frequencies, total energies in Hartree, relative energies in kcal/mol:

dienylborane **2a** (E-s-trans)	→	dienylborane **2a** (E-s-cis)		
-1677.94673		-1677.94112	3.52	E_gas(tot)
-0.01258		-0.01261	-0.01	G_solv
0.14852		0.14782	-0.44	G_rovib
-1677.81080		-1677.80591	3.07	G_tot_solution

dienylborane **2a**	+	enamine **6c**	→	product **8c**		
-1677.94673		-522.13321		-2200.14065	-38.10	E_gas(tot)
-0.01258		-0.01090		-0.02631	-1.77	G_solv
0.14852		0.22498		0.41512	26.12	G_rovib
-1677.81080		-521.91913		-2199.75183	-13.75	G_tot_solution

dienylborane **2a**	+	enamine **6c**	→	concerted TS (**2a**+**6c**)/**8c**		
-1677.94673		-522.13321		-2200.02593	33.89	E_gas(tot)
-0.01258		-0.01090		-0.02648	-1.88	G_solv
0.14852		0.22498		0.40744	21.29	G_rovib
-1677.81080		-521.91913		-2199.64498	53.30	G_tot_solution

dienylborane **2a**	+	enamine **6c**	→	TS (**2a**+**6c**)/**9**		
-1677.94673		-522.13321		-2200.07468	3.30	E_gas(tot)
-0.01258		-0.01090		-0.03030	-4.28	G_solv
0.14852		0.22498		0.39941	16.26	G_rovib
-1677.81080		-521.91913		-2199.70557	15.28	G_tot_solution

dienylborane **2a**	+	enamine **6c**	→	intermediate **9**		
-1677.94673		-522.13321		-2200.08894	-5.64	E_gas(tot)
-0.01258		-0.01090		-0.03567	-7.64	G_solv
0.14852		0.22498		0.40393	19.09	G_rovib
-1677.81080		-521.91913		-2199.72068	5.80	G_tot_solution

dienylborane **2a**	+	enamine **6c**	→	TS **9**/**8c**		
-1677.94673		-522.13321		-2200.08901	-5.69	E_gas(tot)
-0.01258		-0.01090		-0.03173	-5.17	G_solv
0.14852		0.22498		0.40589	20.32	G_rovib
-1677.81080		-521.91913		-2199.71485	9.46	G_tot_solution

dienylborane **2a**	+	enamine **6c**	→	compound **7c**		
-1677.94673		-522.13321		-2200.10036	-12.81	E_gas(tot)
-0.01258		-0.01090		-0.03232	-5.54	G_solv
0.14852		0.22498		0.40376	18.99	G_rovib
-1677.81080		-521.91913		-2199.72891	0.64	G_tot_solution

Cartesian coordinates of structures

In Ångström at HF-3c level:

dienylborane **2a** (E-s-trans)

C	1.5313600	-1.9842800	0.1332657
C	0.2584579	-1.4167224	0.2294365
C	-0.8451709	-2.2717891	0.2348957
C	-0.6985167	-3.6740825	0.1542736
C	0.5947866	-4.2280588	0.0496703
C	1.7223122	-3.3783853	0.0344165
B	0.0947925	0.1618696	0.3157262
C	0.8637217	0.9319481	1.4639116
C	1.3682709	2.2225709	1.2528530
C	2.0570517	2.9319986	2.2603184
C	2.2307385	2.3375361	3.5280471
C	1.7223498	1.0432148	3.7686467
C	1.0557612	0.3602201	2.7293113
F	1.2355998	2.8105548	0.0754286
F	2.5331247	4.1458483	2.0239649
F	2.8643945	2.9906711	4.4865248
F	1.8723951	0.4801559	4.9586440
F	0.5794256	-0.8453050	2.9967153
F	-2.0692698	-1.7749649	0.3400450
F	-1.7608409	-4.4658485	0.1689721
F	0.7505336	-5.5389417	-0.0376999
F	2.9392288	-3.8908779	-0.0729490
F	2.5964563	-1.1946469	0.1049714
C	-0.7721942	0.9130532	-0.7055970
C	-1.2313175	0.3015338	-1.8021822
C	-2.0423191	0.9488790	-2.8670828
C	-2.3937178	2.4210604	-2.6965144

C	-2.4291668	0.2351387	-3.9115781
H	-0.9919293	1.9575427	-0.5679164
H	-1.0059805	-0.7435887	-1.9742630
H	-3.0228974	0.6634301	-4.7088763
H	-2.1693129	-0.8106325	-4.0131428
H	-2.9853364	2.7661680	-3.5362275
H	-1.4908735	3.0226921	-2.6332589
H	-2.9619180	2.5720379	-1.7827502

dienylborane **2a** (E-s-cis)

C	1.0406354	0.4358110	2.7999140
C	0.8535827	1.0262052	1.5422676
C	1.3458944	2.3255094	1.3570929
C	2.0199143	3.0248129	2.3814625
C	2.1881666	2.4117663	3.6410754
C	1.6900474	1.1089667	3.8563914
B	0.1038803	0.2672389	0.3744421
C	-0.7618038	1.0271757	-0.6423323
C	-1.2035926	0.4294391	-1.7533806
C	-2.0145354	1.0732810	-2.8297444
C	-2.1209253	2.3857100	-2.9322652
F	1.2147864	2.9325593	0.1892064
F	2.4874641	4.2462185	2.1682386
F	2.8071065	3.0553155	4.6154497
F	1.8332899	0.5290343	5.0390832
F	0.5762384	-0.7793690	3.0432614
C	0.2839087	-1.3080577	0.2640984
C	1.5634288	-1.8608786	0.1696434
C	1.7699061	-3.2513523	0.0527837
C	0.6513661	-4.1130028	0.0471435
C	-0.6485501	-3.5739131	0.1473333
C	-0.8105973	-2.1745508	0.2470639
F	2.6201950	-1.0596963	0.1602642
F	-2.0409795	-1.6921833	0.3471897
F	-1.7028249	-4.3764571	0.1397315
F	0.8217913	-5.4209463	-0.0551079
F	2.9929635	-3.7494176	-0.0523005
C	-2.6913419	0.1137957	-3.8056915
H	-1.0007097	2.0648701	-0.4829231
H	-0.9706055	-0.6143858	-1.9251078

H	-2.7076262	2.8451099	-3.7170419
H	-1.6198768	3.0596974	-2.2506044
H	-3.2584497	0.6619166	-4.5488721
H	-3.3646473	-0.5548377	-3.2751101
H	-1.9474998	-0.4953848	-4.3126549

enamine **6c**

C	-0.4873908	-1.3409374	-0.9708088
H	-0.9046511	-2.1141343	-0.3544481
C	-0.5957757	-1.4749879	-2.4823042
H	0.3794215	-1.6866084	-2.9106369
H	-1.2461436	-2.2994113	-2.7473958
C	-1.1421681	-0.1577124	-3.1057125
H	-1.0131013	-0.1871635	-4.1809544
H	-2.2061775	-0.1014068	-2.9127886
C	-0.4425743	1.1050708	-2.5142411
H	-1.1762164	1.7274686	-2.0169244
H	-0.0045835	1.6988065	-3.3076392
C	0.6617108	0.7279526	-1.4903483
H	1.4872459	0.2616283	-2.0189212
H	1.0505380	1.6145822	-1.0117542
C	0.1160647	-0.2780862	-0.4767603
N	0.3614903	-0.0437865	0.8934212
C	0.0277417	1.2707626	1.4424929
H	-1.0508170	1.3859320	1.5748481
H	0.3651451	2.0544323	0.7718297
C	0.7296301	1.4502070	2.8242614
H	1.8142396	1.4867772	2.6716986
H	0.4123815	2.3907101	3.2816862
O	0.3807085	0.4003106	3.7146042
C	0.7423209	-0.8682434	3.1875398
H	0.4298754	-1.6267072	3.9096833
H	1.8285384	-0.9384925	3.0604699
C	0.0559865	-1.1355608	1.8114172
H	0.4459254	-2.0632308	1.3995029
H	-1.0193652	-1.2581716	1.9581826

compound **7c**

C	-1.5732457	1.1148681	2.2331021
N	-1.1211130	2.0332544	1.1618483

C	-0.8156045	3.3738442	1.7119074
C	0.2352982	3.2382334	2.8630416
O	-0.2544815	2.3792116	3.8765237
C	-0.5052969	1.0764075	3.3751026
C	-1.0295930	1.6967250	-0.0910307
C	-1.3854849	0.3405631	-0.6317988
C	-1.9060267	0.5025660	-2.0851239
C	-2.8086263	1.7532906	-2.2221398
C	-1.9913181	3.0490069	-1.9422341
C	-0.6757446	2.7090450	-1.1752421
H	-2.1686094	-0.0814629	-0.0242252
H	-1.0843577	0.5686863	-2.7831659
H	-2.4678349	-0.3855499	-2.3413488
H	-3.2403794	1.7998027	-3.2152500
H	-3.6283538	1.6731861	-1.5178518
H	-2.5775824	3.7605057	-1.3712989
H	-1.7084558	3.5306977	-2.8723757
H	0.0003795	2.2117115	-1.8601924
H	-0.1875613	3.6001323	-0.8106545
H	-1.7450094	3.7859660	2.1117903
H	-0.4421635	4.0365700	0.9400801
H	1.1832435	2.8724985	2.4452831
H	0.4028680	4.2259525	3.3047035
H	-0.8946138	0.4679845	4.1971194
H	0.4090441	0.6054631	2.9890742
H	-1.7226828	0.1183108	1.8323541
H	-2.5198668	1.4989318	2.6196578
B	-0.0663064	-0.7326060	-0.5723359
C	1.1512043	-0.0608142	-1.4469348
C	0.3689336	-1.1263200	0.9393553
C	-0.5113842	-2.2175024	-1.1436736
C	1.9628630	0.9283488	-0.8840631
C	3.0350939	1.5408519	-1.5653826
C	3.3121971	1.1724758	-2.8942479
C	2.4828512	0.2169078	-3.5126866
C	1.4215200	-0.3687436	-2.7871632
F	1.7028116	1.4016420	0.3339035
F	3.7594983	2.4771617	-0.9625703
F	4.3105081	1.7366188	-3.5600988
F	2.6896012	-0.1182030	-4.7795052

F	0.6587292	-1.2192446	-3.4641172
C	0.5140978	-3.1371182	-1.4393494
C	0.2753587	-4.4718460	-1.8114301
C	-1.0506647	-4.9532800	-1.8767572
C	-2.0926116	-4.0784001	-1.5418079
C	-1.8045734	-2.7413514	-1.1708844
F	1.7867958	-2.7704603	-1.3530565
F	1.2881202	-5.2839021	-2.0882615
F	-1.2980967	-6.2089351	-2.2260306
F	-3.3532943	-4.4963618	-1.5576782
F	-2.8695686	-2.0204270	-0.8200310
C	1.5901251	-1.2469102	1.4177675
H	-0.4305589	-1.4824690	1.5653949
C	1.9348825	-1.8063952	2.7598186
H	2.4462892	-0.9495983	0.8363046
C	3.1745830	-1.7618820	3.2093203
C	0.8142261	-2.4504157	3.5715332
H	3.4523610	-2.1671009	4.1700943
H	3.9684453	-1.3190093	2.6270292
H	0.3666867	-3.2652084	3.0099038
H	1.2005138	-2.8412163	4.5048552
H	0.0319351	-1.7346881	3.7951302

product **8c**

B	0.6704628	0.1594629	0.5876063
C	0.7074334	0.7414244	-0.9514377
H	0.9734421	1.7849050	-0.9783216
C	1.4731969	0.0414059	-2.0398991
H	2.5389008	0.2087950	-2.0438562
C	0.9262771	-0.7059955	-2.9644469
C	-0.5734197	-0.9449474	-3.0128147
H	-0.7645989	-1.9651811	-3.3243090
H	-1.0145758	-0.3072529	-3.7698090
C	-1.2789389	-0.7288462	-1.6528708
H	-0.9529379	-1.5256404	-1.0044047
C	-2.8101686	-0.8605486	-1.8745835
H	-2.9820031	-1.7558529	-2.4600041
H	-3.3274756	-0.9989249	-0.9385823
C	-3.4175139	0.3563494	-2.6078386
H	-3.0593141	0.3907786	-3.6287083

H	-4.4956058	0.2514646	-2.6484157
C	-3.0371636	1.6729672	-1.8960867
H	-3.4941597	1.7068838	-0.9159895
H	-3.4185313	2.5192125	-2.4565153
C	-1.5010139	1.7864616	-1.7869424
H	-1.0780247	1.7536072	-2.7845926
H	-1.2083771	2.7368611	-1.3665158
C	-0.8316080	0.6197811	-1.0315817
C	1.7333430	-1.3687560	-4.0734925
H	2.7833353	-1.1147925	-3.9881457
H	1.3760957	-1.0491723	-5.0485306
H	1.6321751	-2.4495264	-4.0246437
N	-0.9717335	0.6224123	0.5151939
C	-1.1342005	2.0318476	1.0191594
H	-2.0405360	2.4367887	0.5797122
H	-0.2900594	2.6287355	0.6904868
C	-1.2786456	2.1209736	2.5726052
H	-0.3292494	1.8921673	3.0592609
H	-1.5436569	3.1540825	2.8186243
O	-2.3105830	1.2812002	3.0586157
C	-2.1115640	-0.0620547	2.6448985
H	-2.9431303	-0.6589665	3.0310328
H	-1.1772376	-0.4781754	3.0412137
C	-2.1161364	-0.1455170	1.0933865
H	-2.0646376	-1.1786239	0.7789405
H	-3.0388543	0.2976718	0.7283828
C	1.5023106	0.9096618	1.7832606
F	1.9960795	2.8941566	0.5524347
C	2.1271964	2.1564976	1.6492368
F	3.4749320	3.9222708	2.4770888
C	2.9154253	2.7356205	2.6696763
F	3.8284783	2.5868762	4.8557890
C	3.0967150	2.0569039	3.8883360
F	2.6040044	0.1455660	5.2029872
C	2.4713063	0.8067328	4.0616112
F	1.1129368	-0.8995184	3.2665208
C	1.6953887	0.2671326	3.0151944
C	1.1181269	-1.4262212	0.6064841
F	-0.8502291	-2.6879697	1.1164231
C	0.4437236	-2.6314415	0.8134638

F	0.3468378	-4.9933544	0.9187827
C	1.0703209	-3.8989866	0.7215312
F	3.0365053	-5.1715897	0.3302040
C	2.4369666	-3.9941283	0.4246834
F	4.4564998	-2.8354822	-0.0352473
C	3.1588652	-2.7970142	0.2353604
F	3.2444201	-0.4805888	0.1664772
C	2.4941826	-1.5625888	0.3339209

intermediate **9**

C	-0.8436316	-1.5728674	0.9308660
N	-1.5249819	-1.0650642	-0.2845053
C	-1.3279428	-1.9712268	-1.4572551
C	-1.0446702	-3.4221606	-0.9396828
O	-1.8676267	-3.6845643	0.1842822
C	-1.4675701	-2.9515683	1.3347887
C	-2.1267309	0.0728607	-0.3721438
C	-2.5725703	0.6404508	-1.7202330
C	-3.9997771	1.2407955	-1.6493970
C	-4.1567760	2.2320066	-0.4803134
C	-3.8512149	1.5081451	0.8460615
C	-2.4033025	0.9507767	0.8544300
C	-1.4985987	1.7059311	-2.1631583
C	-0.2066779	1.0527861	-2.6298588
C	-0.1718767	0.6841535	-4.1071850
C	0.8036003	0.7955851	-1.8068954
C	0.8664381	1.0594981	-0.3720999
B	1.8759865	0.6001966	0.5069783
C	1.7889163	0.8932482	2.0820692
C	1.3638032	2.1280845	2.5899908
C	1.2456636	2.3790463	3.9744116
C	1.5547092	1.3619331	4.8989504
C	1.9747187	0.1072559	4.4168616
C	2.0820314	-0.0983345	3.0254878
F	1.0475964	3.1284903	1.7769706
F	0.8339245	3.5646631	4.4092170
F	1.4370192	1.5783929	6.2030602
F	2.2490497	-0.8749985	5.2678326
F	2.4439987	-1.3138341	2.6217254
C	3.1521271	-0.2501728	0.0368715

C	3.0689862	-1.4317338	-0.6989145
C	4.2068988	-2.1417587	-1.1406750
C	5.4892007	-1.6506581	-0.8354054
C	5.6068361	-0.4591091	-0.0882287
C	4.4410581	0.2125718	0.3332304
F	1.8814107	-1.9572589	-1.0005645
F	4.5928510	1.3343531	1.0264596
F	6.8095736	0.0186597	0.2056280
F	6.5732961	-2.2984681	-1.2430857
F	4.0681467	-3.2650397	-1.8371893
H	0.0720631	1.6637768	-0.0011943
H	1.6712339	0.3158050	-2.2346345
H	-1.3206078	2.4023611	-1.3550261
H	-1.9501663	2.2592716	-2.9786727
H	-2.5653828	-0.1365068	-2.4688097
H	-4.1952371	1.7337514	-2.5953179
H	-4.7254507	0.4416685	-1.5411362
H	-3.4839948	3.0723924	-0.6077004
H	-5.1697789	2.6195795	-0.4621292
H	-4.5575322	0.6981435	0.9940598
H	-3.9480313	2.1878305	1.6871564
H	-2.2268692	0.4095177	1.7731355
H	-1.6998655	1.7824488	0.8209175
H	0.7548484	0.1788548	-4.3506787
H	-0.2486754	1.5682347	-4.7340543
H	-0.9958175	0.0288662	-4.3741475
H	-0.8995524	-0.8553974	1.7416465
H	0.2128419	-1.6688347	0.6582768
H	-0.7238465	-3.5033383	1.9262909
H	-2.3567595	-2.8002258	1.9556197
H	-1.3120551	-4.1294755	-1.7311833
H	0.0215292	-3.5498074	-0.7158410
H	-0.5021480	-1.5840490	-2.0640431
H	-2.2446385	-1.9759346	-2.0419169

TS (**2a**+ **6c**)/**8c** (concerted)

C	-1.6884439	-1.1888253	0.6584288
N	-0.8739668	0.0648663	0.5004988
C	-1.4839722	1.0790801	1.4529985
C	-1.8026364	0.5575520	2.8901350

O	-2.5417486	-0.6484972	2.8615086
C	-1.8046722	-1.6279110	2.1461067
C	-1.0822801	0.6167771	-0.9323565
C	-1.9308671	0.0305908	-1.8645345
C	-2.9878165	0.8384630	-2.6442091
C	-2.6032035	2.3171795	-2.8540846
C	-2.0874823	2.9061631	-1.5251656
C	-0.8217589	2.1237066	-1.0997405
C	0.8706303	-0.2108784	-1.1650142
C	0.6760768	-1.4233330	-1.7922927
C	-0.0067588	-1.5202722	-3.0121661
C	-0.3439984	-2.8966987	-3.5824226
B	0.8669199	-0.1557667	0.4504150
C	1.4975517	1.1417500	1.2299782
C	2.0254374	2.2830073	0.6115892
C	2.5674071	3.3643500	1.3438200
C	2.6125958	3.3127414	2.7495078
C	2.1298947	2.1591828	3.3971722
C	1.5988224	1.1058339	2.6256937
F	2.0699872	2.4118061	-0.7071399
F	3.0332329	4.4274786	0.7024346
F	3.1080522	4.3230810	3.4477264
F	2.1721809	2.0654316	4.7194651
F	1.1905063	0.0313640	3.2953591
C	1.6578497	-1.5130301	1.0189686
C	3.0600297	-1.3319150	1.0990741
C	3.9710256	-2.3293862	1.4907513
C	3.5102486	-3.6242376	1.8013119
C	2.1395722	-3.8692283	1.6602597
C	1.2577202	-2.8350542	1.2572876
F	3.6250515	-0.1816324	0.7548313
F	0.0110616	-3.2650208	1.0890990
F	1.6419014	-5.0782470	1.8851326
F	4.3476619	-4.5779474	2.1783386
F	5.2652795	-2.0476046	1.5511234
C	-0.6108727	-0.3877646	-3.5252127
H	1.1091909	0.6421765	-1.7722761
H	0.8198802	-2.3369204	-1.2450488
H	-1.2483422	-0.4729877	-4.3932396
H	-0.1753539	0.5862846	-3.3787239

H	-2.2426942	-0.9874596	-1.7070519
H	-3.2022340	0.3633857	-3.5937038
H	-3.9060625	0.8004515	-2.0616082
H	-1.8264074	2.3956310	-3.6050974
H	-3.4648422	2.8689266	-3.2121152
H	-2.8570034	2.8371015	-0.7666416
H	-1.8355518	3.9534676	-1.6481209
H	-0.0884843	2.2604574	-1.8855943
H	-0.3965734	2.5592086	-0.2134803
H	-0.3836616	-3.6429096	-2.7966002
H	0.4191273	-3.2035550	-4.2947162
H	-1.2959916	-2.8784230	-4.1008745
H	-2.4144245	1.4038897	0.9923596
H	-0.8260914	1.9338382	1.5372968
H	-0.8806684	0.4316633	3.4651399
H	-2.4110461	1.3218334	3.3834327
H	-2.3534094	-2.5731735	2.1891842
H	-0.8193670	-1.7736167	2.5978290
H	-1.2603298	-1.9648262	0.0331617
H	-2.6958784	-0.9715984	0.3118121

TS (**2a**+**6c**)/**9**

C	-0.7927592	-2.3999787	-1.6750584
N	-1.3737133	-1.3064149	-0.8801680
C	-1.1613336	-1.4313092	0.5590718
C	-1.8225386	-2.7552933	1.0748373
O	-1.7378014	-3.7858729	0.0970088
C	-0.6112730	-3.6522802	-0.7527122
C	-2.0494739	-0.3037912	-1.4597556
C	-1.9519780	-0.0483684	-2.8309250
C	-3.0125979	0.7898258	-3.5495375
C	-3.5779906	1.9073537	-2.6479392
C	-4.0523737	1.2899536	-1.3177007
C	-2.8790868	0.6241211	-0.5618782
C	-0.3165353	1.2077752	-2.7629541
C	0.8888766	0.5199582	-2.5026052
C	1.5822331	-0.1847652	-3.6639251
C	1.4235755	0.4600547	-1.2221986
C	0.8880557	0.9701341	-0.0336483
B	1.5369560	0.8145586	1.2605436

C	0.8502780	1.3755935	2.5896085
C	0.1740582	2.6015090	2.6052654
C	-0.4594022	3.0985886	3.7651330
C	-0.4306568	2.3405269	4.9528638
C	0.2345907	1.0980995	4.9609871
C	0.8643709	0.6442817	3.7826275
F	0.1116481	3.3564834	1.5173262
F	-1.0869869	4.2675413	3.7393539
F	-1.0301842	2.7870135	6.0469108
F	0.2582660	0.3629754	6.0654598
F	1.4580204	-0.5423519	3.8288753
C	2.9449533	0.0790897	1.4567948
C	4.0014889	0.7779839	2.0495495
C	5.2766600	0.2055180	2.2384934
C	5.5034333	-1.1246129	1.8257714
C	4.4527070	-1.8511792	1.2323868
C	3.1948213	-1.2339886	1.0572009
F	3.8170410	2.0331767	2.4387453
F	2.2319701	-1.9643454	0.5017950
F	4.6467403	-3.1038534	0.8393863
F	6.6933929	-1.6837265	1.9928888
F	6.2579603	0.9030628	2.7941703
H	-0.0487753	1.4786903	-0.1066070
H	2.3781694	-0.0443859	-1.1420926
H	-0.6839508	1.9085621	-2.0225454
H	-0.5187115	1.5063065	-3.7866509
H	-1.4939369	-0.8059287	-3.4414753
H	-2.5857019	1.2155362	-4.4506333
H	-3.8293455	0.1454288	-3.8647989
H	-2.8199538	2.6570723	-2.4575780
H	-4.4069571	2.3975238	-3.1457672
H	-4.8161398	0.5475307	-1.5199519
H	-4.4911680	2.0474792	-0.6772286
H	-3.2717344	0.0537677	0.2711029
H	-2.2236052	1.3901579	-0.1518090
H	2.5418435	-0.5771282	-3.3497816
H	1.7510636	0.4921667	-4.4958485
H	0.9886446	-1.0151493	-4.0373298
H	-1.5587846	-0.5730219	1.0870379
H	-0.0845377	-1.4397730	0.7427539

H	-1.3324822	-3.0568381	2.0094957
H	-2.8839043	-2.5909377	1.2840194
H	-0.5537339	-4.5479500	-1.3774359
H	0.3236593	-3.5755338	-0.1854693
H	0.1612129	-2.1090386	-2.1168194
H	-1.4865825	-2.6475840	-2.4766366

TS **9/8c**

C	4.0120161	-0.2755981	1.3970544
C	2.8609042	-0.4318529	0.6099896
C	2.8601106	-1.5080189	-0.2762490
C	3.9337184	-2.4192976	-0.3827322
C	5.0703394	-2.2452751	0.4255837
C	5.1102728	-1.1559218	1.3230915
B	1.6449385	0.6036879	0.7390055
C	1.1646548	0.9032992	2.2425218
C	0.7408576	2.1768664	2.6499064
C	0.2826738	2.4446195	3.9587459
C	0.2388670	1.4087616	4.9120393
C	0.6590103	0.1193013	4.5331154
C	1.1119478	-0.1025553	3.2163967
F	0.7513766	3.2049802	1.8113456
F	-0.1175972	3.6662708	4.2906768
F	-0.2026531	1.6407628	6.1411133
F	0.6097090	-0.8811990	5.4049246
F	1.4604396	-1.3502829	2.9098308
F	1.8032344	-1.7462359	-1.0489321
F	3.8622138	-3.4380616	-1.2328823
F	6.0890490	-3.0914367	0.3486538
F	6.1785123	-0.9731993	2.0888210
F	4.0972110	0.7389803	2.2485404
C	1.0079122	1.2341912	-0.3676119
C	1.3688932	1.1228079	-1.7856871
C	0.5856082	1.5067577	-2.7828168
C	0.9876800	1.4162122	-4.2475439
C	-0.8419429	1.9681784	-2.5100678
C	-1.7117455	0.7249420	-2.1327941
C	-1.4867376	0.2472035	-0.6945261
C	-1.9860731	1.2249175	0.3731478
C	-3.5310286	1.3271869	0.2031043

C	-3.8452775	1.8735845	-1.2088066
C	-3.2481341	0.9534933	-2.2969630
N	-1.2789461	-1.0166917	-0.4524034
C	-1.0271260	-1.5601508	0.8932917
C	-1.8998225	-2.8338396	1.1464623
O	-2.0011368	-3.6599377	-0.0066377
C	-0.9682482	-3.4399606	-0.9498708
C	-1.1068201	-2.0072719	-1.5511152
H	0.2853004	1.9918914	-0.1856731
H	2.3387674	0.7110880	-2.0226693
H	-0.8906182	2.7190892	-1.7325440
H	-1.2766953	2.3960309	-3.4049718
H	-1.4195733	-0.0548286	-2.8181284
H	-3.4157721	1.3768339	-3.2814571
H	-3.7506612	-0.0078481	-2.2646730
H	-3.4350119	2.8725640	-1.3054322
H	-4.9191298	1.9430144	-1.3479440
H	-3.9917816	0.3554094	0.3460839
H	-3.9163885	1.9956348	0.9669591
H	-1.7031471	0.9367014	1.3751004
H	-1.5614070	2.2021192	0.1807153
H	1.9887098	1.0124346	-4.3413568
H	0.9714564	2.3965917	-4.7162760
H	0.3074398	0.7791232	-4.8055498
H	-1.2396307	-0.8162105	1.6514504
H	0.0413777	-1.7904657	0.9509609
H	-1.4557441	-3.3833470	1.9876684
H	-2.9138883	-2.5358785	1.4339759
H	-1.0917377	-4.1663327	-1.7595788
H	0.0309738	-3.5802249	-0.5206653
H	-0.2258415	-1.7487675	-2.1450169
H	-1.9958584	-1.9748400	-2.1807003