Intramolecular Frustrated N/B Lewis Pairs by Enamine Hydroboration

Sina Schwendemann, Roland Fröhlich, Gerald Kehr and Gerhard Erker

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

Supporting Information

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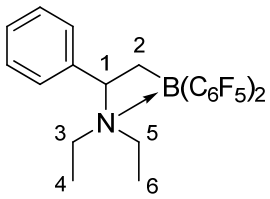
General Information. All reactions were carried out under argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Elemental analyses: Elementar Vario ELIII. NMR: Bruker AC 200 P (^{1}H, 200 MHz; ^{11}B, 64 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{11}B, 160 MHz; ^{19}F, 470 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{11}B, 192 MHz; ^{19}F, 564 MHz). Assignments of the resonances are supported by 2D experiments and chemical shift calculations. ^{11}B NMR spectra were referenced to an external $Et_2O{\cdot}BF_3$ (neat) sample ($\delta^{11}B = 0$); ^{19}F NMR spectra were referenced to an external $CFCl_3$ (neat) sample ($\delta^{19}F = 0$). X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids with 50 % probability, *R* values are given for the observed reflections, wR^2 values for all reflections.

Materials. $B(C_6F_5)_3$ [A. G. Massey, A. J. Park and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, 212; A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245], $HB(C_6F_5)_2$ [D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492], *N*-(1-phenylethen-1-yl)diethylamine, *N*-(1-phenylethen-1-yl)piperidine, *N*-(2-methyl-1-phenylpropen-1-yl)piperidine [Paleček, J.; Paleta, O. *Synthesis*, **2004**, *4*, 521-524] and *N*-(cyclohex-1-enyl)piperidine [Carlson, R.; Nilsson, A. *Acta Chem. Scand. B*, **1984**, *38*, 49-53] were prepared according to modified literature procedures.

Synthesis of 5a



N-(1-phenylethen-1-yl)diethylamine (**4a**) (109 mg, 0.622 mmol) was added to a suspension of bis(pentafluorophenyl)borane (215 mg, 0.622 mmol) in pentane (3 mL). The reaction mixture was stirred for 20 minutes at room temperature. Then the solvent was removed from the precipitate by a syringe. After washing the solid with pentane (3 mL) and drying in vacuo product **5a** was obtained as a white solid (224 mg, 70%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a pentane solution of **5a** at –30 °C. Anal. Calc. for $C_{24}H_{18}BF_{10}N$: C 55.31, H 3.48, N 2.69; found: C 55.24, H 3.58, N 2.84.

^{1}H NMR (500 MHz, 298 K, benzene-d_6) δ = 7.09 (m, 1H, *p*-Ph), 7.04 (m, 2H, *m*-Ph), 6.96 (m, 2H, *o*-Ph), 4.55 (dd, $^{3}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 7.1 Hz, 1H, 1-H), 2.93 (m, 1H, 5-H), 2.59 (m, 1H, 5′-H), 2.38 (m, 1H, 3-H), 2.20 (ddm, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 7.1 Hz, 1H, 2-H), 2.13 (m, 1H, 3'-H), 1.80 (t, $^{2}J_{HH}$ ~ $^{3}J_{HH}$ = 13.5 Hz, 1H, 2'-H), 0.74 (m, 3H, 4-H), -0.36 (m, 3H, 6-H).

^{13}C{^{1}H} NMR (126 MHz, 298 K, benzene-d_6) δ = 135.5 (*i*-Ph), 129.9 (*o*-Ph), 129.6 (*p*-Ph), 128.9 (*m*-Ph), 75.0 (C1), 50.2 (C3), 40.7 (C5), 17.9 (br, C2), 9.0 (C4), 8.3 (C6), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 7.04 / 7.09, 6.96 (*m*-Ph / *p*-Ph, *o*-Ph), 2.93 / 2.59, -0.36 (5-H / 5′-H, 6-H), 2.59 / 2.13, 2.93, -0.36 (5′-H / 3′-H, 5-H, 6-H), 2.38 / 2.13, 0.74 (3-H / 3′-H, 4-H), 2.20 / 4.55, 1.80 (2-H / 1-H, 2′-H), 2.13 / 2.38, 0.74 (3′-H / 3-H, 4-H), 1.80 / 4.55, 2.20 (2′-H / 1-H, 2-H), 0.74 / 2.38, 2.13 (4-H / 3-H, 3′-H), -0.36 / 2.93, 2.59 (6-H / 5-H, 5′-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.09 / 129.6 (*p*-Ph / *p*-Ph), 7.04 / 128.9 (*m*-Ph / *m*-Ph), 6.96 / 129.9 (*o*-Ph / *o*-Ph), 4.55 / 75.0 (1-H / C1), 2.93, 2.59 / 40.7 (5-H, 5′-H / C5), 2.38 / 50.2 (3-H / C3), 2.20 / 17.9 (2-H / C2), 2.13 / 50.2 (3′-H / C3), 1.80 / 17.9 (2′-H / C2), 0.74 / 9.0 (4-H / C4), -0.36 / 8.3 (6-H / C6).

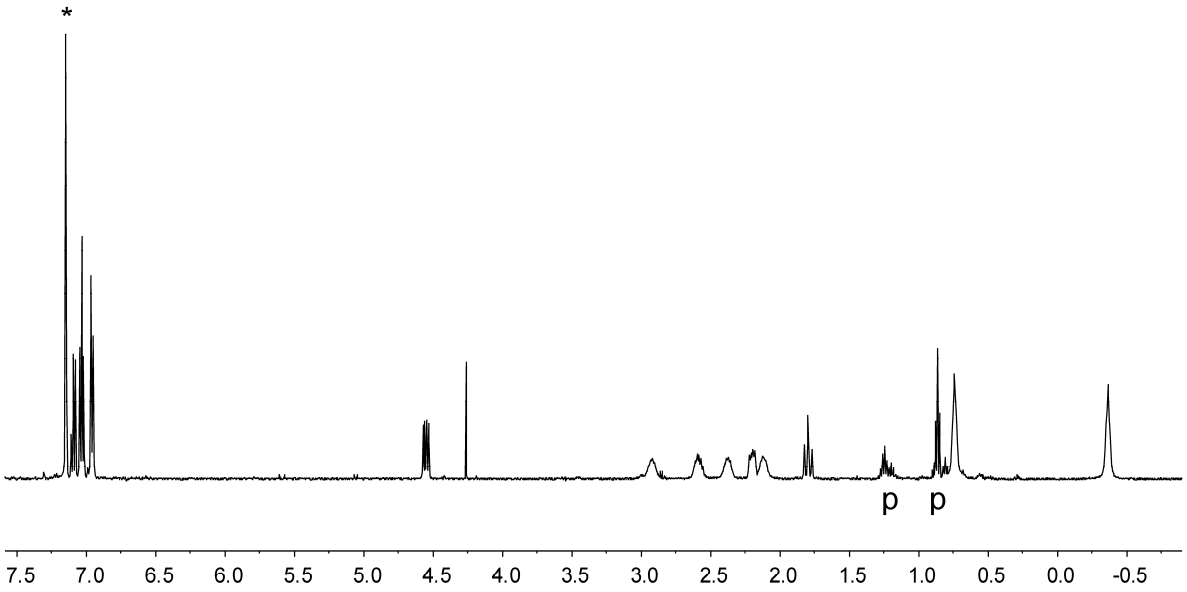
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.09 / 129.9 (*p*-Ph / *o*-Ph), 7.04 / 135.5, 129.6 (*m*-Ph / *i*-Ph, *p*-Ph), 4.55 / 135.5, 129.9, 129.6, 50.2, 40.7 (1-H / *i*-Ph, *o*-Ph, *p*-Ph, C3, C5), 1.80 / 135.5, 75.0 (2′-H / *i*-Ph, C1), 0.74 / 50.2 (4-H / C3).

^{1}H{^{1}H} TOCSY (500 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.96 / 7.09, 7.04 (*o*-Ph / *p*-Ph, *m*-Ph), -0.36 / 2.93, 2.59, 2.38, 2.13, 0.74 (6-H / 5-H, 5′-H, 3-H, 3′-H, 4-H), [selected experiments].

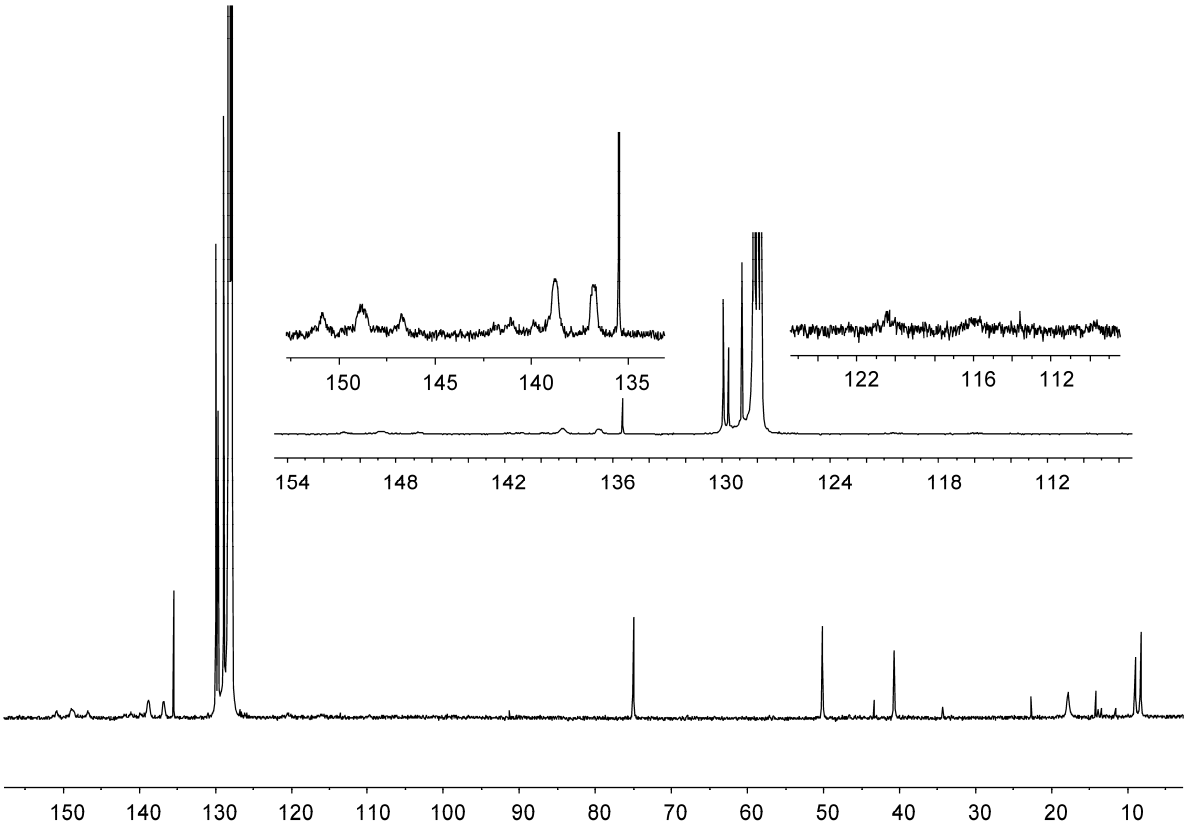
^{11}B{^{1}H} NMR (160 MHz, 298 K, benzene-d_6) δ = 2.1 ($\nu_{1/2}$ ~ 220 Hz).

^{19}F NMR (470 MHz, 298 K, benzene-d_6) δ = –127.6 (br, 2F, *o*-$C_6F_5^A$), –129.0 (br, 2F, *o*-$C_6F_5^B$), –154.9 (br, 1F, *p*-$C_6F_5^B$), –157.7 (br, 1F, *p*-$C_6F_5^A$), –162.6 (br, 2F, *m*-$C_6F_5^B$), –164.0 (br, 2F, *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{mp}$ = 6.3^A, 7.7^B].

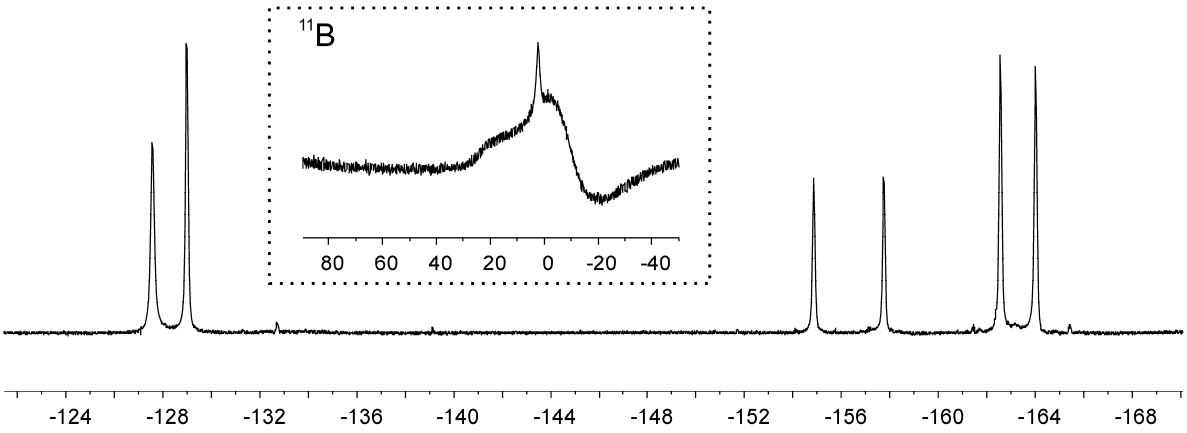
^{19}F,^{19}F GCOSY (564 MHz, 298 K, benzene-d_6) δ ^{19}F / δ ^{19}F = –162.6 / –129.0, –154.9 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$), –164.0 / –127.6, –157.7 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$).



^{1}H NMR (500 MHz, 298 K, benzene-d_6) of **5a**; [* C_6D_5H, p: pentane]

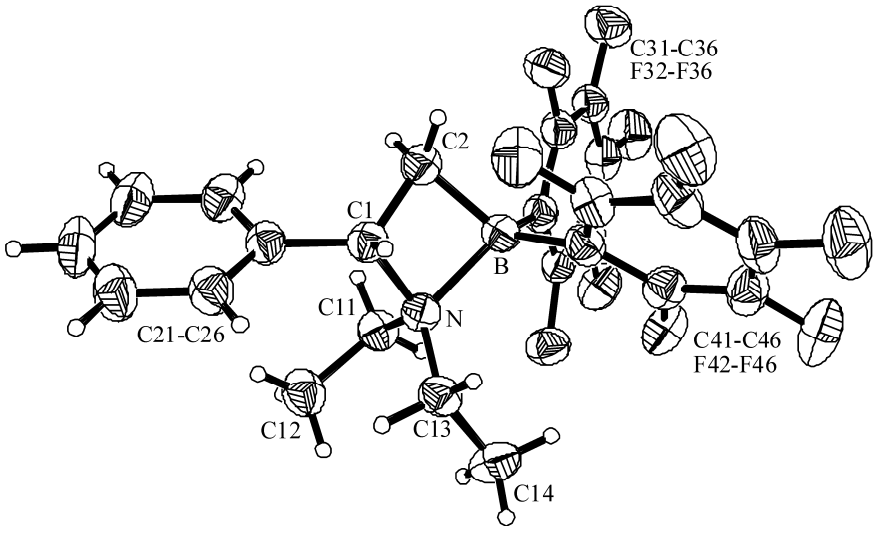


^{13}C{^{1}H} NMR (126 MHz, 298 K, benzene-d_6) of **5a**

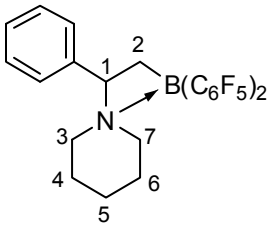


^{19}F NMR (470 MHz, 298 K, benzene-d_6) and ^{11}B{^{1}H} NMR (160 MHz) of **5a**

Crystal data for $C_{24}H_{18}BF_{10}N$ (**5a**), M = 521.20, tetragonal, P-42$_1$c (No. 114), a = 22.3613(6), c = 8.7343 (3) Å, V = 4367.4(2) Å^3, D_c = 1.585 g cm^{-3}, μ = 1.349 mm^{-1}, $F(000)$ = 2112, Z = 8, λ = 1,54178 Å, T = 223(2) K, 33954 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3881 independent (R_{int} = 0.066), and 3572 observed reflections [I ≥ 2σ(I)], 327 refined parameters, R = 0.038, wR^2 = 0.104, GoF = 1.029.



Synthesis of 5b



The reaction procedure was carried out as described for the preparation of **5a**: *N*-(1-phenylethen-1-yl)piperidine (**4b**) (100 mg, 0.535 mmol) reacted with bis(pentafluoro-phenyl)borane (185 mg, 0.535 mmol) in pentane (10 mL) to obtain **5b** as a white solid (160 mg, 57%). Anal. Calc. $C_{25}H_{18}BF_{10}N$: C 56.31, H 3.40, N 2.63; found: C 56.74, H 3.76, N 2.60.

^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.06 (m, 1H, *p*-Ph), 7.03 (m, 2H, *m*-Ph), 7.02 (m, 2H, *o*-Ph), 4.48 (dd, $^{3}J_{HH}$ = 13.2 Hz, $^{3}J_{HH}$ = 6.7 Hz, 1H, 1-H), 2.98 (m, 1H, 7-H), 2.85 (m, 1H, 3-H), 2.59 (m, 1H, 3′-H), 2.44 (m, 1H, 7′-H), 2.15 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 6.7 Hz, 1H, 2-H), 1.97 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 13.2 Hz, 1H, 2'-H), 1.19 (m, 1H, 6-H), 0.94 (m, 1H, 6′-H), 0.77 (m, 2H, 5-H), 0.47 (m, 1H, 4-H), 0.08 (m, 1H, 4′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 136.6 (*i*-Ph), 130.7 (*o*-Ph), 129.6 (*p*-Ph), 128.7 (*m*-Ph), 75.7 (C1), 57.4 (C7), 47.2 (C3), 22.3 (C5), 21.8 (C6), 21.3 (C4), 18.5 (C2) [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 7.06 / 7.03, 7.02 (*p*-Ph / *m*-Ph, *o*-Ph), 4.48 / 2.15, 1.97 (1-H / 2-H, 2′-H), 2.98 / 2.44, 1.19, 0.94 (7-H / 7′-H, 6-H, 6′-H), 2.85 / 2.59, 0.47, 0.08 (3-H / 3′-H, 4-H, 4′-H), 2.44 / 2.98, 1.19, 0.94 (7′-H / 7-H, 6-H, 6′-H), 2.15 / 4.48, 1.97 (2-H / 1-H, 2′-H), 1.19 / 2.98, 2.44, 0.94, 0.77 (6-H / 7-H, 7′-H, 6′-H, 5-H), 0.94 / 2.98, 2.44, 1.19, 0.77 (6′-H / 7-H, 7′-H, 6-H, 5-H), 0.77 / 1.19, 0.94, 0.47, 0.08 (5-H / 6-H, 6′-H, 4-H, 4′-H), 0.47 / 2.85, 2.59, 0.77, 0.08 (4-H / 3-H, 3′-H, 5-H, 4′-H), 0.08 / 2.85, 0.77, 0.47 (4′-H / 3-H, 5-H, 4-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.06 / 129.6 (*p*-Ph / *p*-Ph), 7.03 / 128.7 (*m*-Ph / *m*-Ph), 7.02 / 130.7 (*o*-Ph / *o*-Ph), 4.48 / 75.7 (1-H / C1), 2.98, 2.44 / 57.4 (7-H, 7′-H / C7), 2.85, 2.59 / 47.2 (3-H, 3′-H / C3), 2.15, 1.97 / 18.5 (2-H, 2′-H / C2), 1.19, 0.94 / 21.8 (6-H, 6′-H / C6), 0.77 / 22.3 (5-H / C5), 0.47, 0.08 / 21.3 (4-H, 4′-H / C4).

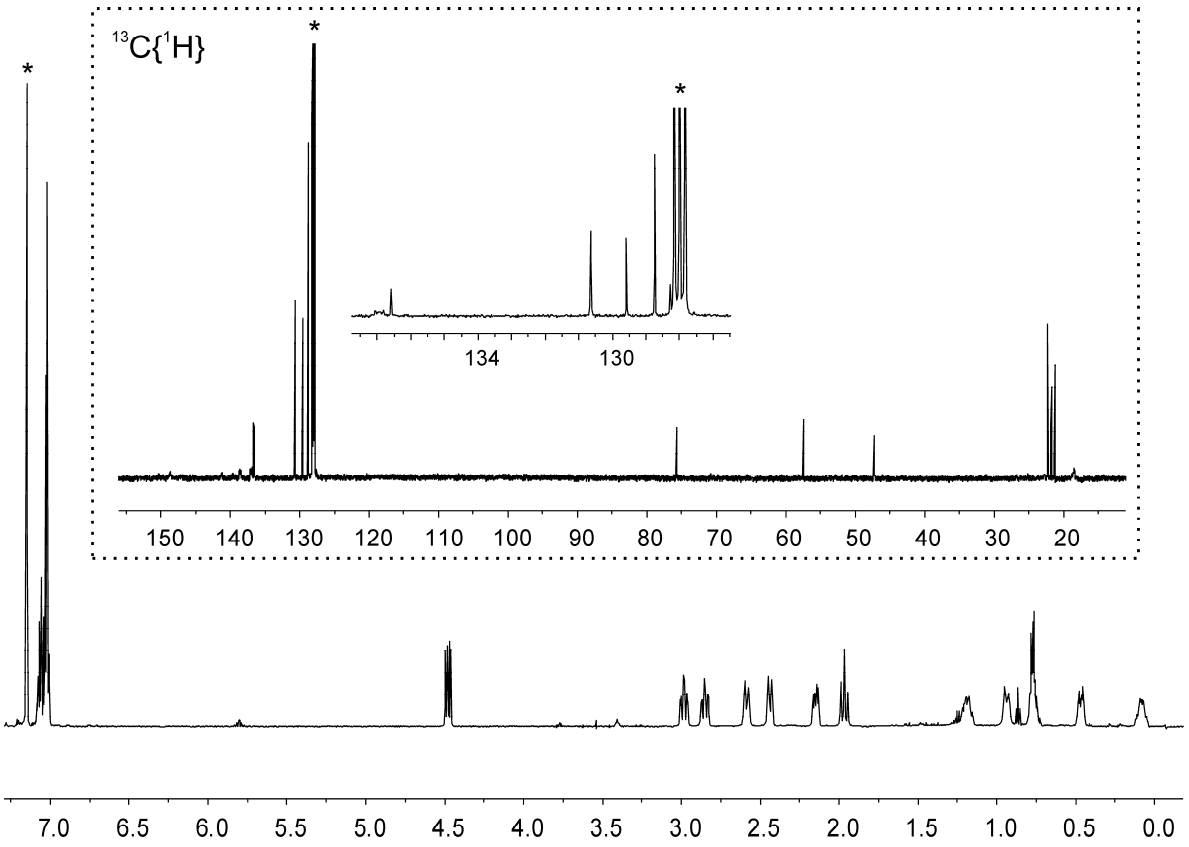
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.02 / 136.6, 129.6, 75.7 (*o*-Ph / *i*-Ph, *p*-Ph, C1), 4.48 / 57.4, 47.2 (1-H / C7, C3), 1.97 / 136.6, 75.7 (2′-H / *i*-Ph, C1), 0.08 / 47.2, 22.3 (4′-H / C3, C5).

^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.06 / 7.03, 7.02 (*p*-Ph / *m*-Ph, *o*-Ph), 1.97 / 4.48, 2.15 (2′-H / 1-H, 2-H), 0.08 / 2.98, 2.85, 2.59, 2.44, 1.19, 0.94, 0.77, 0.47 (4′-H / 7-H, 3-H, 3′-H, 7′-H, 6-H, 6′-H, 5-H, 4-H), [selected experiments].

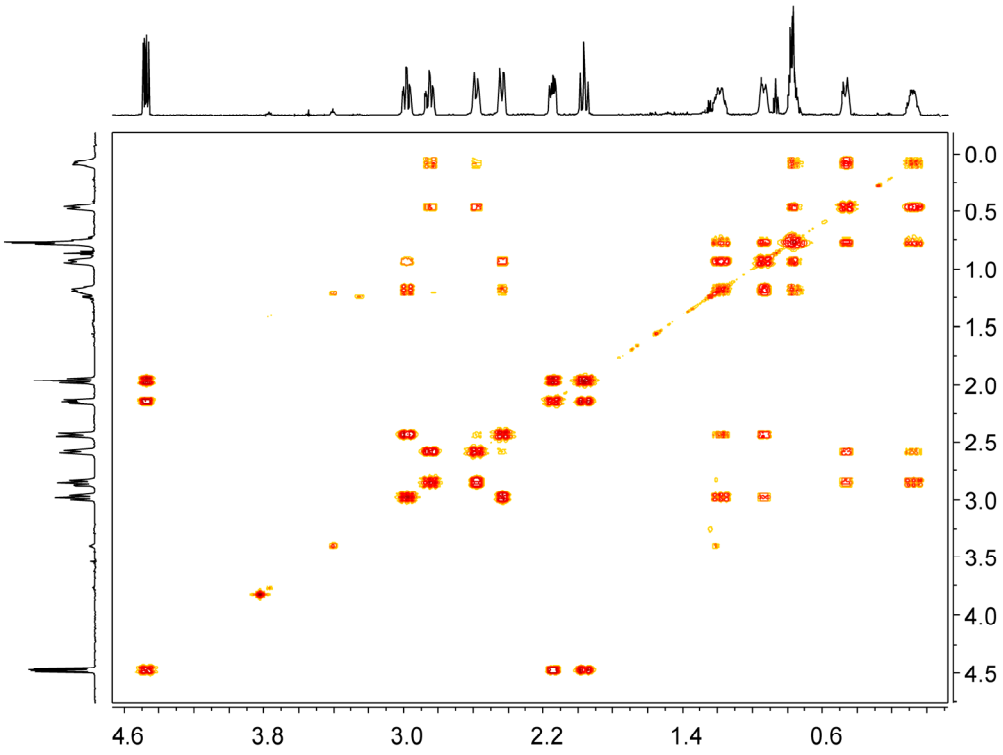
^{11}B{^{1}H} NMR (192 MHz, 298 K, toluene-d_8) δ = 2.1 ($\nu_{1/2}$ ~ 250 Hz).

^{19}F NMR (564 MHz, 298 K, toluene-d_8) δ = –127.9 (br, 2F, *o*-$C_6F_5^{A}$), –129.4 (br, 2F, *o*-$C_6F_5^{B}$), –156.0 (br, 1F, *p*-$C_6F_5^{B}$), –157.5 (br, 1F, *p*-$C_6F_5^{A}$), –163.1 (br, 2F, *m*-$C_6F_5^{B}$), –163.5 (br, 2F, *m*-$C_6F_5^{A}$), [$\Delta\delta^{19}F_{mp} = 6.0^{A}, 7.1^{B}$].

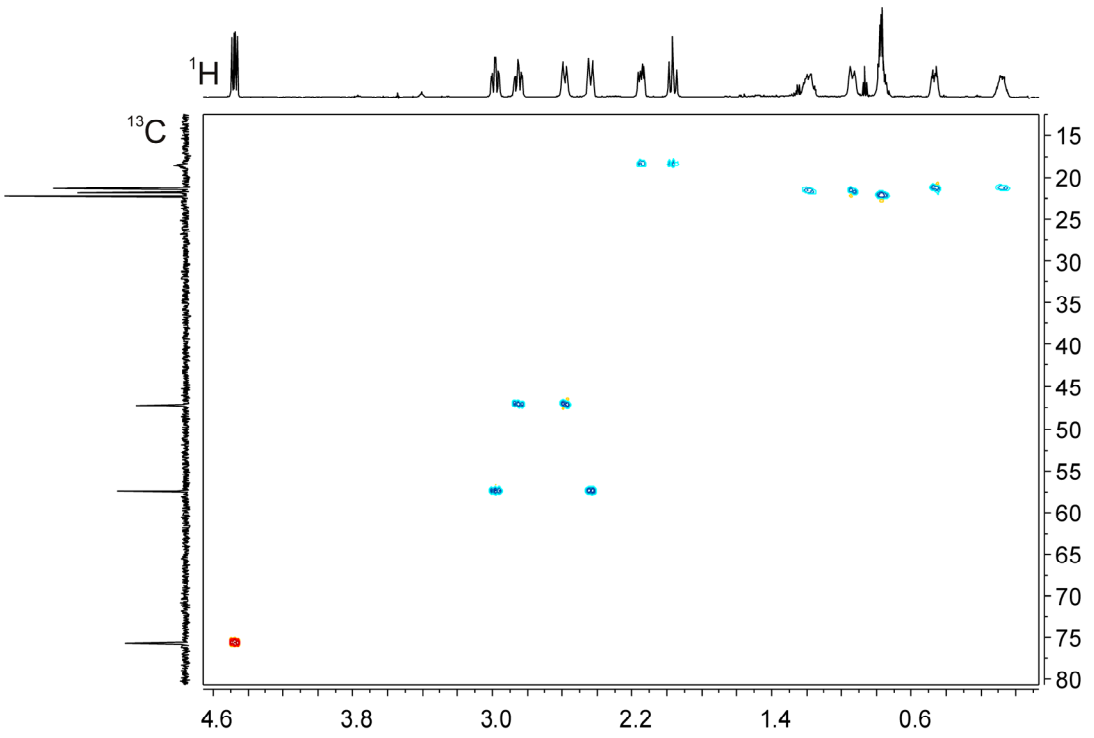
^{19}F,^{19}F GCOSY (564 MHz, 298K, toluene-d_8) δ ^{19}F / δ ^{19}F = –163.1 / –129.4, –156.0 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$), –163.1 / –127.9, –157.5 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$).



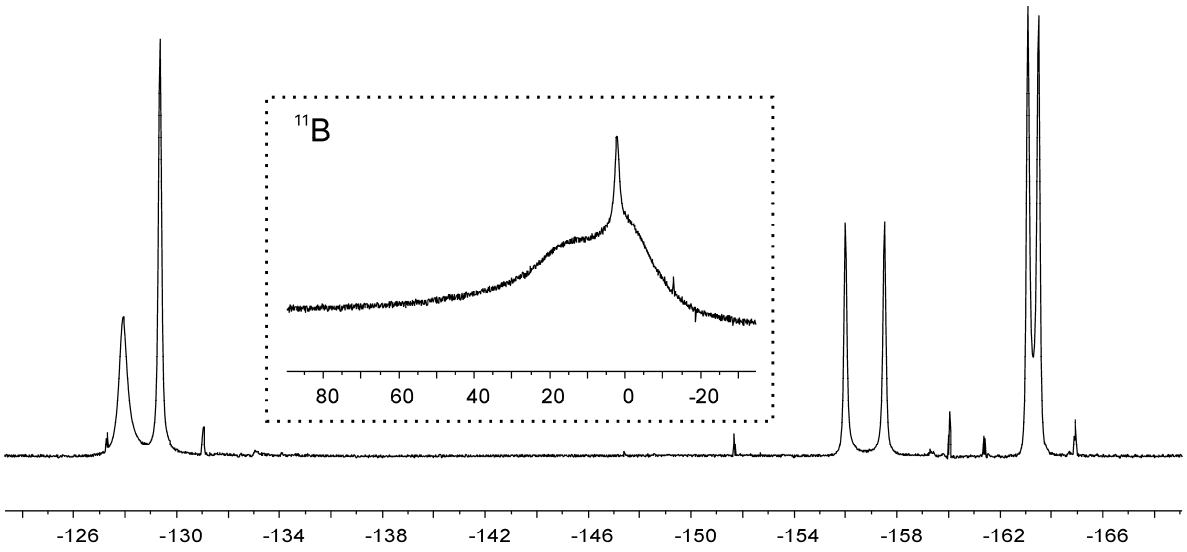
^{1}H NMR (600 MHz, 298 K, benzene-d_6(*)) and ^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of **5b**



^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) of **5b**



^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) of **5b**



^{19}F NMR (564 MHz, 298 K, toluene-d_8) and ^{11}B NMR (192 MHz, 298 K, toluene-d_8)of **5b**

Dynamic ^{19}F NMR:

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\delta\nu)$ [Jmol-1]

R = 8.314 J(mol K)$^{-1}$

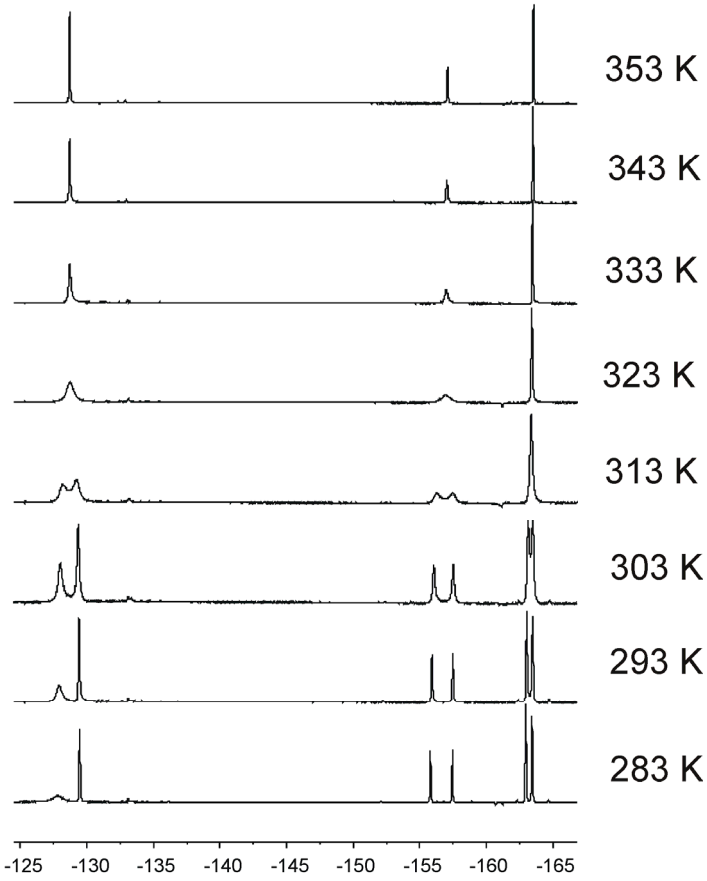
1 cal = 4.187 J

$\Delta G^{\neq}_{diss}$ (T_c = 323K; $\Delta\nu$(p-F, 283K) = 930 Hz) = 14.0 kcal/mol

$\Delta G^{\neq}_{diss}$ (T_c = 313K; $\Delta\nu$(p-F, 283K) = 930 Hz) = 13.6 kcal/mol

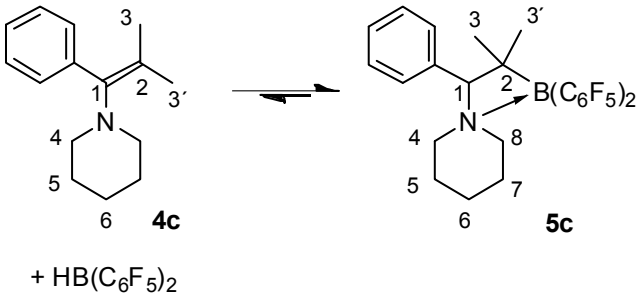
$\Delta G^{\neq}_{diss}$ (T_c = 308K; $\Delta\nu$(m-F, 283K) = 270 Hz) = 14.1 kcal/mol

average value: $\Delta G^{\neq}_{diss}$ = 13.9 ± 0.3 kcal/mol



^{19}F NMR (564 MHz, toluene-d_8) of **5b**.

Synthesis of 5c



The reaction procedure was carried out as described for the preparation of **5a**: *N*-(2-methyl-1-phenylpropen-1-yl)-piperidine (**4c**) (100 mg, 0.465 mmol) reacted with bis(pentafluorophenyl)borane (160 mg, 0.465 mmol) in pentane (10 mL). The obtained precipitate was washed with pentane (5 mL). A white solid (140 mg, 54%) was obtained, which gave a mixture of **5c** and **4c**/$HB(C_6F_5)_2$ (5:1; ^{1}H NMR) in benzene-d_6 solution.

Anal. Calc. for $C_{27}H_{22}BF_{10}N$ (white solid): C 57.78, H 3.95, N 2.50; found: C 58.20, H 4.00, N 2.43.

Crystals of **5c** suitable for the X-ray crystal structure analysis were obtained by slow evaporation from a pentane solution at -30 °C.

5c and **4c**/$HB(C_6F_5)_2$: no separate resonances of the compounds were observed in **^{11}B{^{1}H}** NMR (64 MHz, 298 K, benzene-d_6) δ = 9.3 ($\nu_{1/2}$ ~ 240 Hz) and **^{19}F** NMR (470 MHz, 298 K, toluene-d_8) δ = -125.3 (br, 2F, *o*-C_6F_5), -157.1 (t, ^3J = 21.7 Hz, 1F, *p*-C_6F_5), -163.0 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 5.9].

4c/$HB(C_6F_5)_2$: **^{1}H NMR** (600 MHz, 298 K, benzene-d_6) δ = 7.20 (m, 2H, *m*-Ph), 7.11 (m, 2H, *o*-Ph), 7.10 (m, 1H, *p*-Ph), 2.58 (m, 4H, 4/8-H), 1.97 (s, 3H, 3-H)^t, 1.56 (s, 3H, 3'-H)^t, 1.49 (m, 4H, 5/7-H), 1.28 (m, 2H, 6-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 145.4 (C1), 139.0 (*i*-Ph), 130.1 (*o*-Ph), 128.0 (*m*-Ph), 126.7 (*p*-Ph), 121.9 (C2), 53.1 (C4/8), 27.1 (C5/7), 24.8 (C6), 20.8 (C3'), 19.2 (C3) [^{t} tentative assignment].

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 7.20 / 7.11, 7.10 (*m*-Ph / *o*-Ph, *p*-Ph), 2.58 / 1.49 (4/8-H / 5/7-H), 1.97 / 1.56 (3-H / 3′-H), 1.49 / 2.58, 1.28 (5/7-H / 4/8-H, 6-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.20 / 128.0 (*m*-Ph / *m*-Ph), 7.11 / 130.1 (*o*-Ph / *o*-Ph), 7.10 / 126.7 (*p*-Ph / *p*-Ph), 2.58 / 53.1 (4/8-H / C4/8), 1.97 / 19.2 (3-H / C3), 1.56 / 20.8 (3′-H / C3′), 1.49 / 27.1 (5/7-H / C5/7), 1.28 / 24.8 (6-H / C6).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.20 / 139.0 (*m*-Ph / *i*-Ph), 7.11 / 145.4, 126.7 (*o*-Ph / C1, *p*-Ph), 2.58 / 27.1, 24.8 (4/8-H / C5/7, C6), 1.97 / 145.4, 121.9, 20.8 (3-H / C1, C2, C3′), 1.56 / 145.4, 121.9, 19.2 (3′-H / C1, C2, C3), 1.49 / 53.1, 24.8 (5/7-H / C4/8, C6), 1.28 / 53.1, 27.1 (6-H / C4/8, C5/7).

5c: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.01 (m, 5H, *o*-, *m*-, *p*-Ph), 4.23 (s, 1H, 1-H), 3.47 / 2.95 (each br, each 1H, 8-H), 2.94 / 2.67 (each br, each 1H, 4-H), 1.33 (br, 3H, 3-H), 1.25 / 0.96 (each br, each 1H, 5-H)^t, 0.95 (br, 3H, 3′-H), 0.83 / 0.65 (each br, each 1H, 6-H), 0.60 (br, 2H, 7-H)^t.

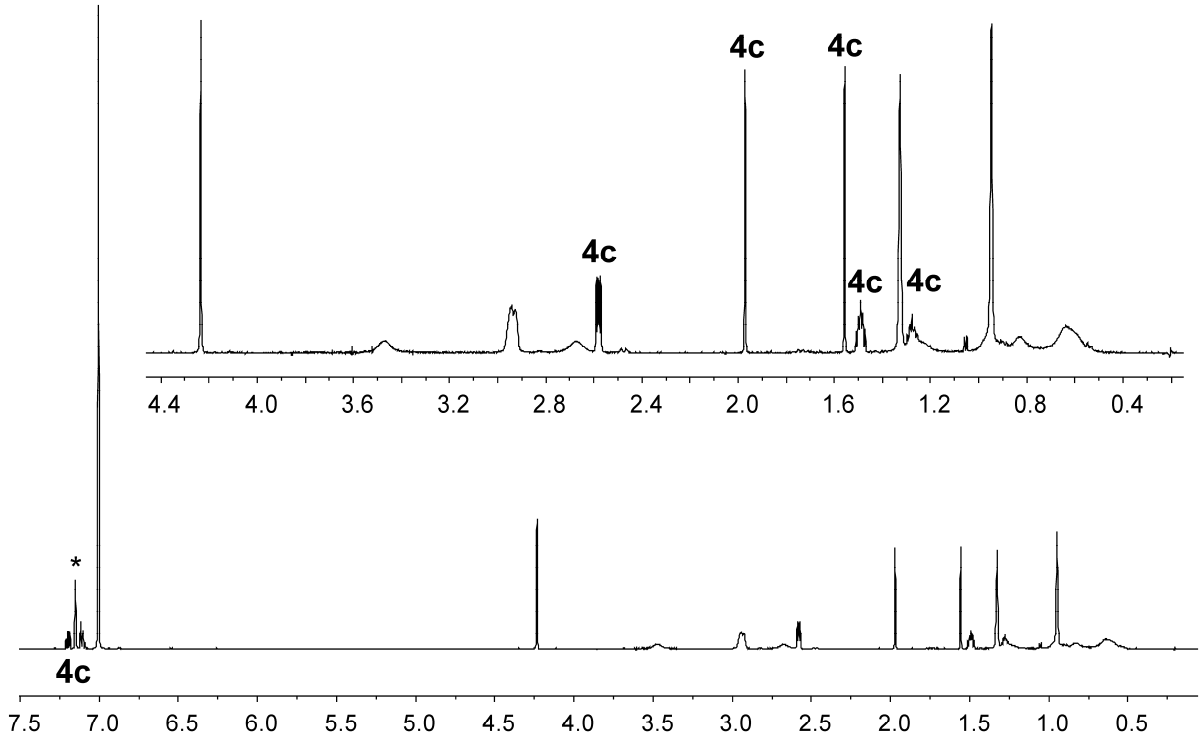
$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-d_6) δ = 133.9 (*i*-Ph), 132.0, 128.8 (*p*), 128.3 (Ph), 84.3 (C1), 61.2 (br, C4)^{t}, 52.8 (br, C8)^{t}, 33.2 (C3), 27.3 (C3′), 27.0 (C2), 22.1 (C5)^{t}, 21.9 (C6), 21.5 (C7)^{t}, [C_6F_5 not listed; ^{t} tentative assignment].

$^{1}H,^{1}H$ GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 3.47, 2.95 / 2.94, 2.67 (8-H / 4-H), 1.33 / 0.95 (3-H / 3′-H).

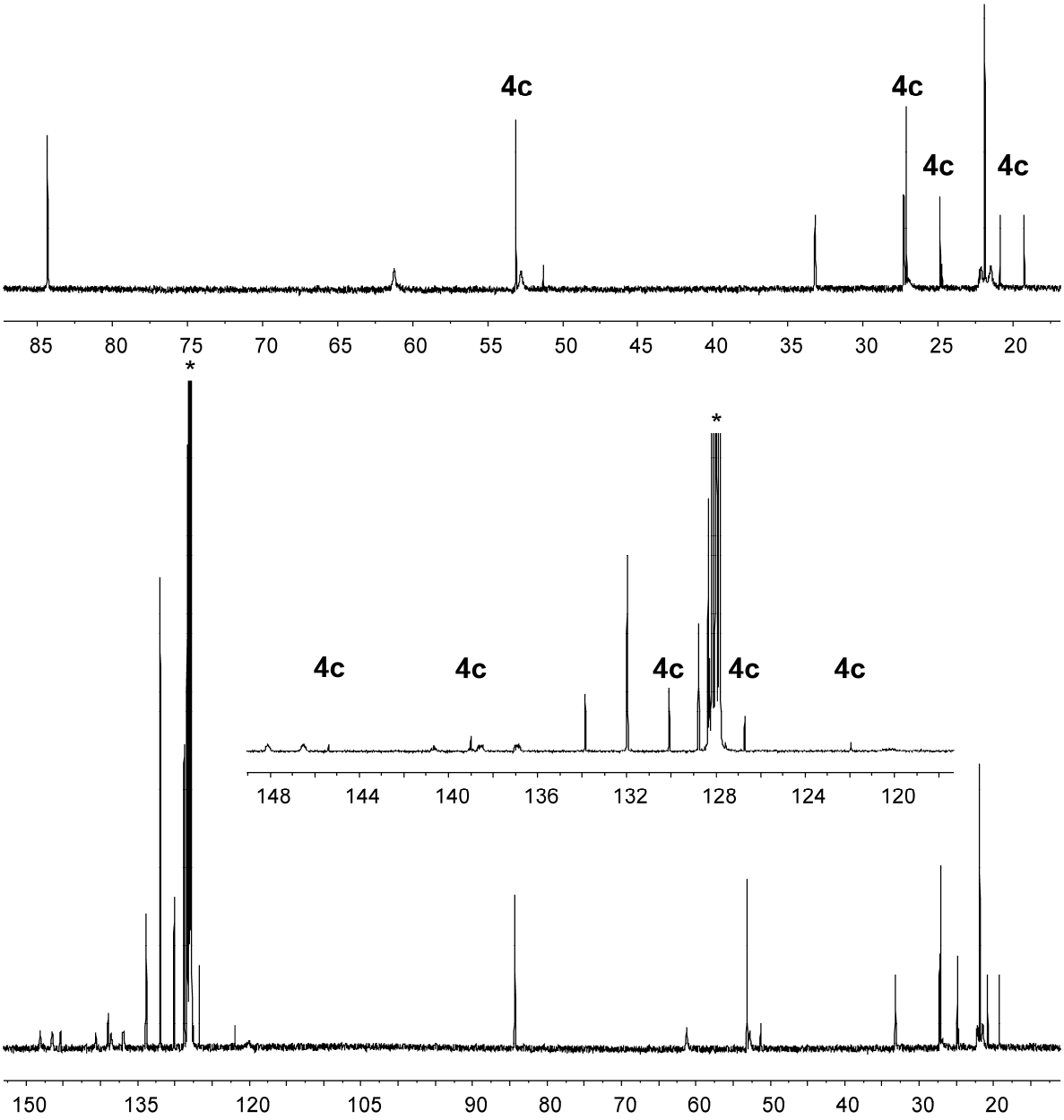
$^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.01 / 132.0, 128.8, 128.3 (*o*-, *m*-, *p*-Ph / *o*-, *m*-, *p*-Ph), 4.23 / 84.3 (1-H / C1), 3.47, 2.95 / 52.7 (8-H / C8), 2.94, 2.67 / 61.2 (4-H / C4), 1.33 / 33.2 (3-H / C3), 1.25, 0.96 / 22.1 (5-H / C5), 0.95 / 27.3 (3′-H / C3′), 0.83, 0.65 / 21.9 (6-H / C6), 0.60 / 21.5 (7-H / C7).

$^{1}H,^{13}C$ GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 4.23 / 133.9, 132.0, 128.3, 61.2, 52.8, 33.2, 27.3 (1-H / *i*-Ph, Ph, C4, C8, C3, C3′), 3.47, 2.95 / 84.3, 22.1 (8-H / C1, C5), 2.94, 2.67 / 84.3, 22.1 (4-H / C1, C5), 1.33 / 84.3, 27.3 (3-H / C1, C3′), 0.95 / 84.3, 33.2 (3′-H / C1, C3), 0.83, 0.65 / 27.0 (6-H / C2).

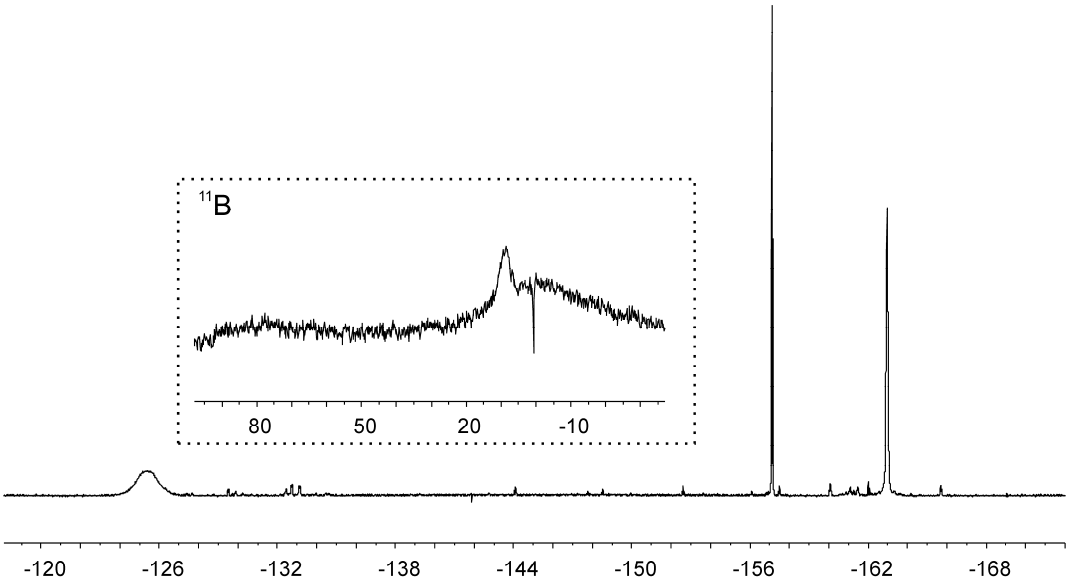
$^{1}H\{^{1}H\}$ TOCSY (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.94, 2.95 / 3.47, 2.67, 1.33, 0.95, 0.83, 0.65 (4-H, 8-H / 8-H, 4-H, 3-H, 3′-H, 6-H) [selected experiment].



^{1}H NMR (600 MHz, 298 K, benzene-d_6(*)) of **5c** and **4c**/$HB(C_6F_5)_2$

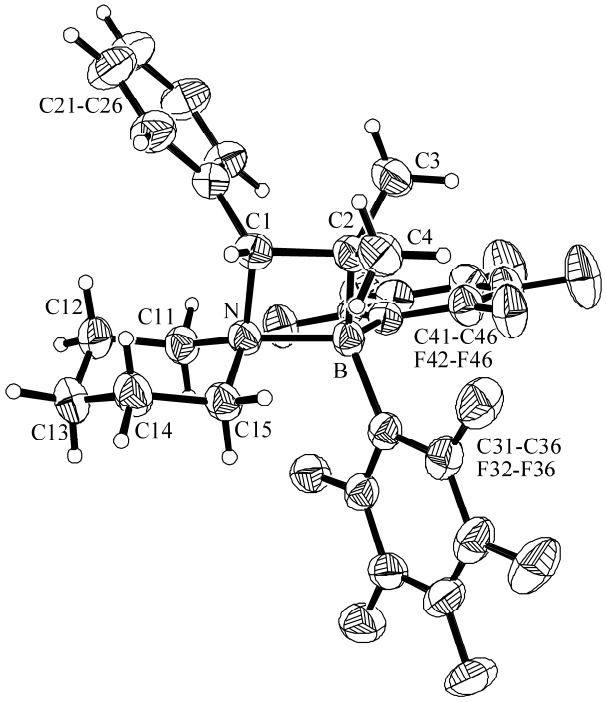


$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-d_6(*)) of **5c** and **4c**/$HB(C_6F_5)_2$

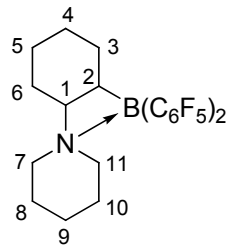


^{19}F NMR (470 MHz, 298 K, benzene-d_6) and ^{11}B{^{1}H} NMR (64 MHz, 298 K, benzene-d_6) of **5c** and **4c**/HB(C_6F_5)$_2$

Crystal data for $C_{27}H_{22}BF_{10}N$ (**5c**), M = 561.27, triclinic, $P\bar{1}$ (No. 2), a = 9.1677(1), b = 11.1135(4), c = 13.3821(2) Å, α = 68.696(1), β = 78.909(1), γ = 81.699(1)°, V = 1242.40(3) Å^3, D_c = 1.500 g cm^{-3}, μ = 1.229 mm^{-1}, F(000) = 572, Z = 4, λ = 1.54178 Å, T = 223(2) K, 15451 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4251 independent (R_{int} = 0.036), and 4053 observed reflections [I ≥ 2σ(I)], 354 refined parameters, R = 0.045, wR^2 = 0.118, GoF = 1.058.



Synthesis of 5d



The reaction procedure was carried out as described for the preparation of **5a**: *N*-(cyclohex-1-enyl)piperidine (**4d**) (152 mg, 0.921 mmol) and bis(pentafluorophenyl)-borane (319 mg, 0.921 mmol) were dissolved in pentane (10 ml). After stirring for 20 minutes at room temperature the solvent was removed and the product was isolated as a white solid (216 mg, 46%, 0.423 mmol). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation from a pentane solution of **5d** at -30 °C. Anal. Calc. for $C_{23}H_{20}BF_{10}N$: C 54.04 , H 3.94, N 2.74; found: C 54.55, H 4.41, N 2.67.

^{1}H NMR (600 MHz, 298 K, toluene-d_8) δ = 2.94 (br, 1H, 11-H), 2.55 (ddd, $^{3}J_{HH}$ = 13.3, 11.8, 3.0 Hz, 1H, 1-H), 2.51 (br, 1H, 11′-H), 2.30 (br, 1H, 7-H), 2.24 (br, 1H, 7′-H), 2.08 (m, 1H, 3-H), 1.55 (m, 1H, 5-H), 1.54 (m, 2H, 4-H), 1.49 (m, 1H, 2-H), 1.42 (m, 1H, 6-H), 1.21, 1.01, 0.98, 0.76 (each br, each 1H, 8-, 10-H), 1.09 (m, 1H, 4′-H), 1.09 (m, 1H, 6′-H), 1.04 (m, 1H, 3′-H), 0.99 (br, 1H, 9-H), 0.92 (m, 1H, 5′-H), 0.88 (br, 1H, 9′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, toluene-d_8) δ = 147.7 (dm, $^{1}J_{FC}$ ~ 242 Hz, C_6F_5), 140.1 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 137.5 (dm, $^{1}J_{FC}$ ~ 247 Hz, C_6F_5), 117.5 (*i*-C_6F_5), 75.3 (C1), 59.2 (br, C11), 49.9 (br, C7), 32.5 (C6), 32.2 (br, C2), 29.4 (br, C3), 27.5 (C4), 26.2 (C5), 23.3 (C8,10), 22.7 (C9).

^{1}H,^{1}H GCOSY (600 MHz, 298 K, toluene-d_8) δ ^{1}H / δ ^{1}H = 2.94 / 2.51, 0.98 (11-H / 11′-H, 10-H), 2.55 / 1.49, 1.42, 1.09 (1-H / 2-H, 6-H, 6′-H), 2.51 / 2.94 (11′-H / 11-H), 2.08 / 1.54, 1.49, 1.09, 1.04 (3-H / 4-H, 2-H, 4′-H, 3′-H), 1.55, 1.54 / 2.08, 1.42, 1.09, 0.92 (5-H, 4-H / 3-H, 6-H, 4′-H, 5′-H), 1.49 / 2.55, 2.08, 1.04 (2-H / 1-H, 3-H, 3′-H), 1.42 / 2.55, 1.55, 1.09, 0.92 (6-H / 1-H, 5-H, 6′-H, 5′-H), 1.21 / 0.76 (8-, 10-H / 8-, 10-H), 1.09 / 2.55, 2.08, 1.54, 1.42, 1.04, 0.92 (4′-H, 6′-H / 1-H, 3-H, 4-H, 6-H, 3′-H, 5′-H), 1.04 / 2.08, 1.54, 1.49, 1.09 (3′-H / 3-H, 4-H, 2-H, 4′-H), 0.92 / 1.54, 1.42, 1.09 (5′-H / 4-H, 6-H, 4′-H, 6′-H), 0.76 / 0.99 (8-, 10-H / 9-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, toluene-d_8) δ ^{1}H / δ ^{13}C = 2.94 / 59.2 (11-H / C11), 2.55 / 75.3 (1-H / C1), 2.51 / 59.2 (11′-H / C11), 2.30 / 49.9 (7-H / C7), 2.24 / 49.9 (7′-H / C7), 2.08 / 29.4 (3-H / C3), 1.55 / 26.2 (5-H / C5), 1.54 / 27.5 (4-H / C4), 1.49 / 32.2 (2-H / C2), 1.42 / 32.5 (6-H / C6), 1.21, 1.01, 0.98, 0.76 / 23.3 (8-, 10-H / C8, C10), 1.09 / 27.5 (4′-H / C4), 1.09 / 32.5 (6′-H / C6), 1.04 / 29.4 (3′-H / C3), 0.99 / 22.7 (9-H / C9), 0.92 / 26.2 (5′-H / C5), 0.88 / 22.7 (9′-H / C9).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, toluene-d_8) δ ^{1}H / δ ^{13}C = 1.09 / 75.3, 26.2 (6′-H / C1, C5).

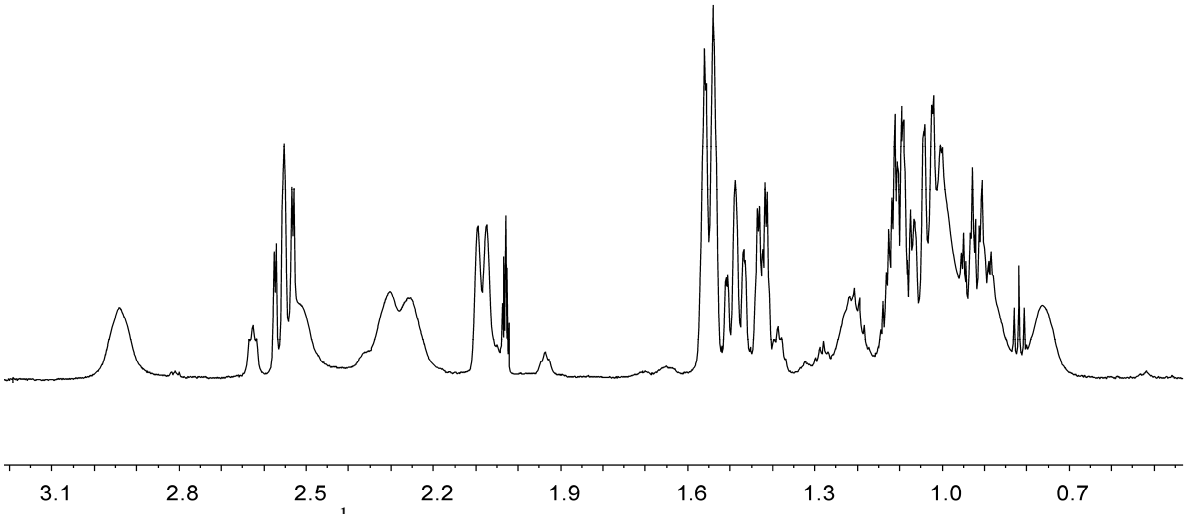
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, toluene-d_8) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.94 / 2.51, 2.30, 2.24, 1.21, 1.01, 0.98, 0.76, 0.99, 0.88 (11-H / 11′-H, 7-H, 7′-H, 8-H, 10-H, 9-H, 9′-H), 0.92 / 2.55, 2.08, 1.54, 1.49, 1.42, 1.09, 1.04 (5′-H / 1-H, 3-H, 4-H, 5-H, 2-H, 6-H, 4′-H, 6′-H, 3′-H) [selected experiments].

^{1}H{^{1}H} NOE (600 MHz, 298 K, toluene-d_8): δ $^{1}H_{irr}$ / δ$^{1}H_{res}$ = 2.55 / 1.42, 1.04, 0.92 (1-H / 6-H, 3′-H, 5′-H), 2.08 / 1.49, 1.09, 1.04 (3-H / 2-H, 4′-H, 6′-H, 3′-H), 1.55, 1.54 / 1.09, 0.92 (4-H, 5-H / 4′-H, 6′-H, 5′-H), 1.49 /

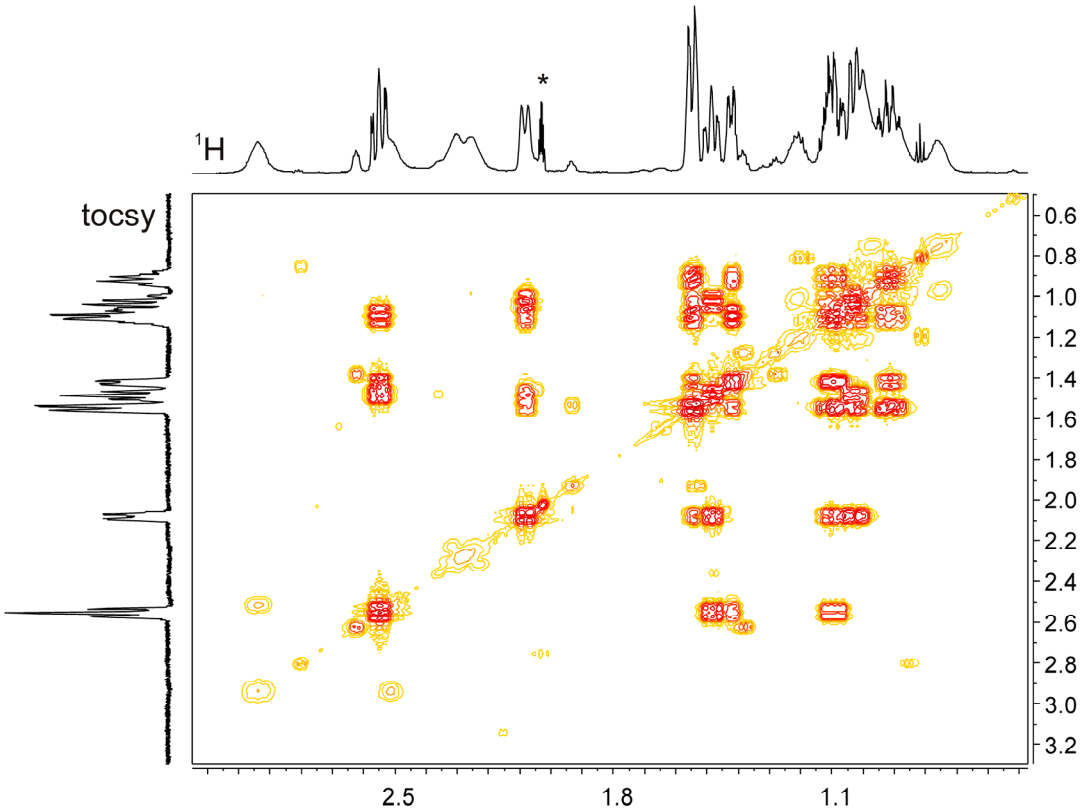
2.08, 1.09 (2-H / 3-H, 4′-H, 6′-H), 1.42 / 2.55, 1.09, 0.92 (6-H / 1-H, 4′-H, 6′-H, 5′-H), 1.09 / 2.08, 1.55, 1.54, 1.49, 1.42 (4′-H, 6′-H / 3-H, 5-H, 4-H, 2-H, 6-H), 1.04 / 2.55, 2.08, 1.55, 1.54 (3′-H / 1-H, 3-H, 5-H, 4-H), 0.92 / 2.55, 1.55, 1.54, 1.43 (5′-H / 1-H, 5-H, 4-H, 6-H).

^{11}B{^{1}H} NMR (192 MHz, 298 K, toluene-d_8): δ = 9.3 ($\nu_{1/2}$ ~ 250 Hz).

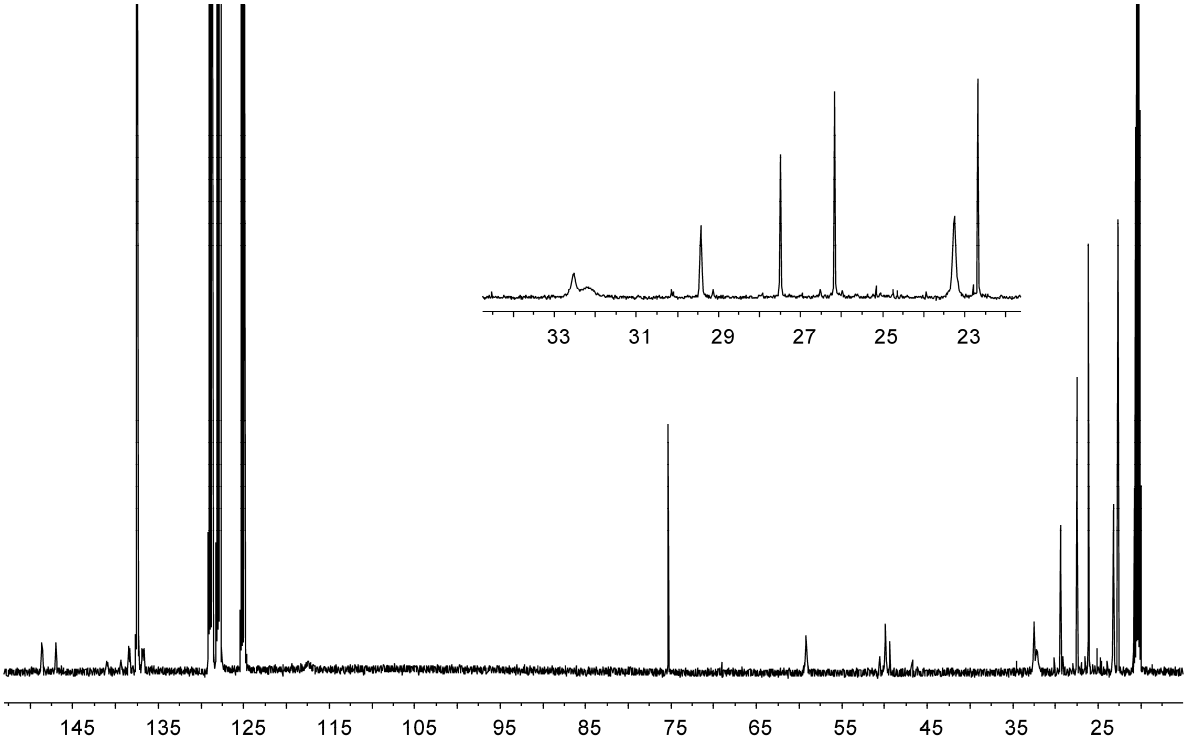
^{19}F NMR (564 MHz, 298 K, toluene-d_8): δ = –125.4, –131.7 (each br, each 1F, *o*-C_6F_5), –157.3 (br, 1F, *p*-C_6F_5), –163.5 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 6.2].



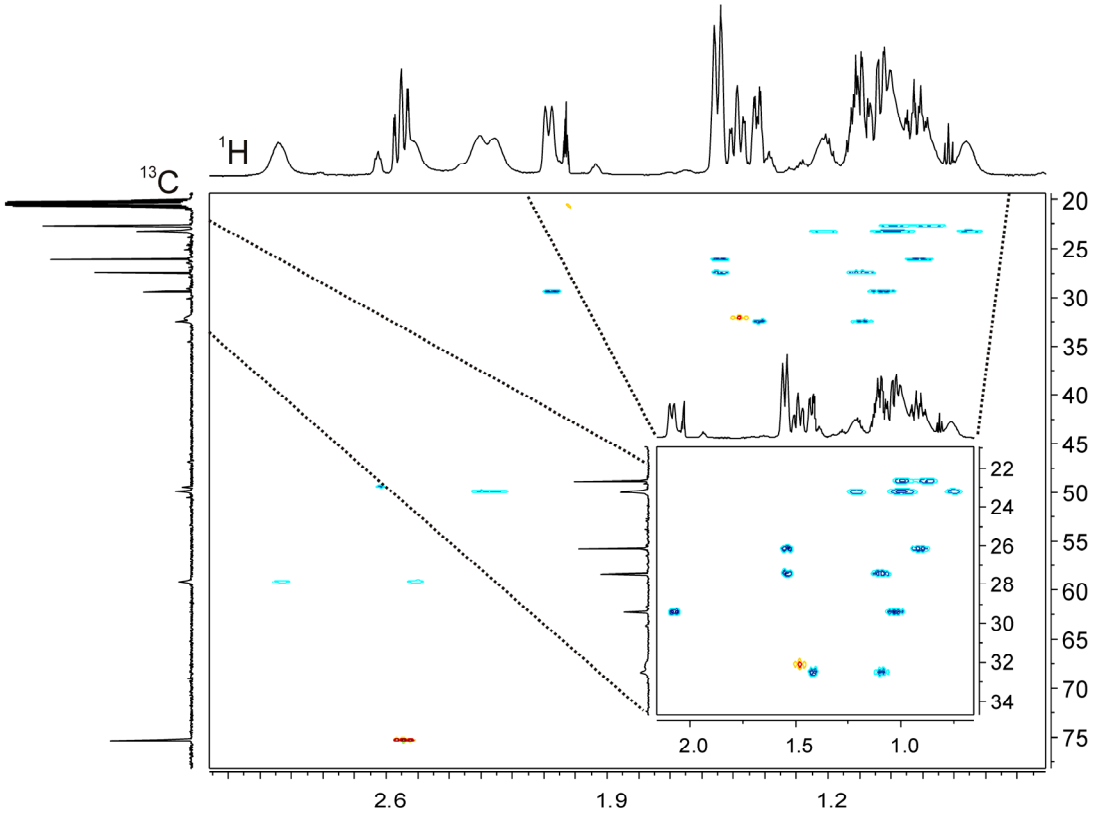
^{1}H NMR (600 MHz, 298 K, toluene-d_8)



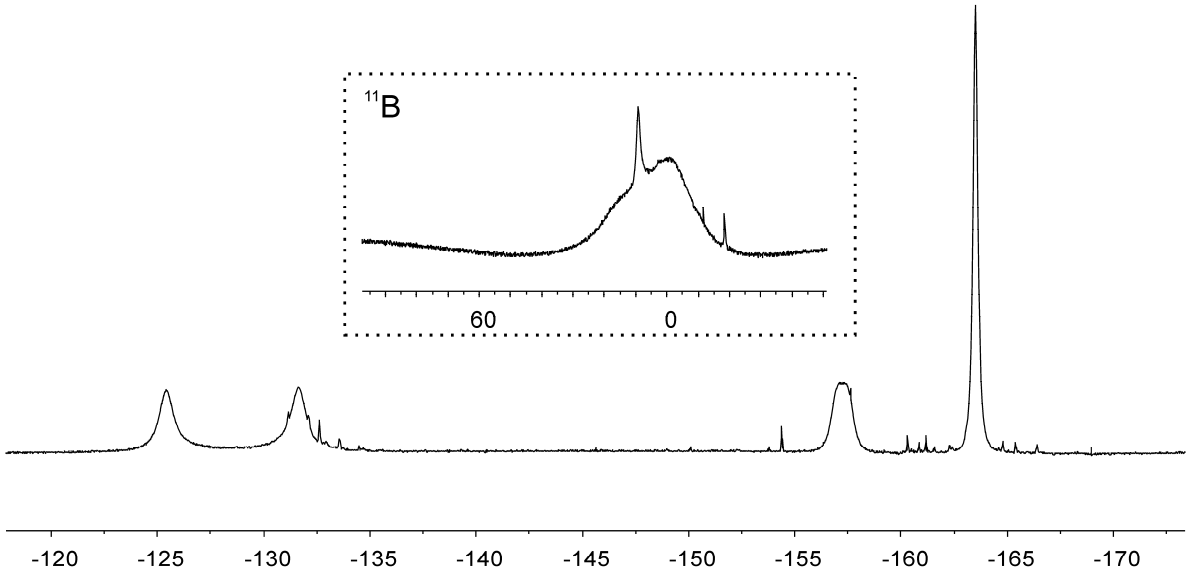
^{1}H,^{1}H GCOSY (600 MHz, 298 K, toluene-d_8(*); projections: ^{1}H spectrum and ^{1}H{1H} TOCSY [δ $^{1}H_{irr}$ = 2.55] spectrum) of **5d**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, toluene-d_8) of **5d**



$^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 298 K, toluene-d_8;
projections: ^{1}H spectrum and $^{13}C\{^{1}H\}$ spectrum) of **5d**



^{19}F NMR (564 MHz, 298 K, toluene-d_8) and ^{11}B{^{1}H} NMR (192 MHz, 298 K, toluene-d_8) of **5d**

Dynamic ^{19}F NMR:

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\delta\nu)$ [Jmol-1]

R = 8.314 J(mol K)$^{-1}$

1 cal = 4.187 J

$\Delta G^{\neq}_{diss}$ (T_c = 293K; $\Delta\nu$(p-F, 283K) = 580 Hz) = 13.0 kcal/mol

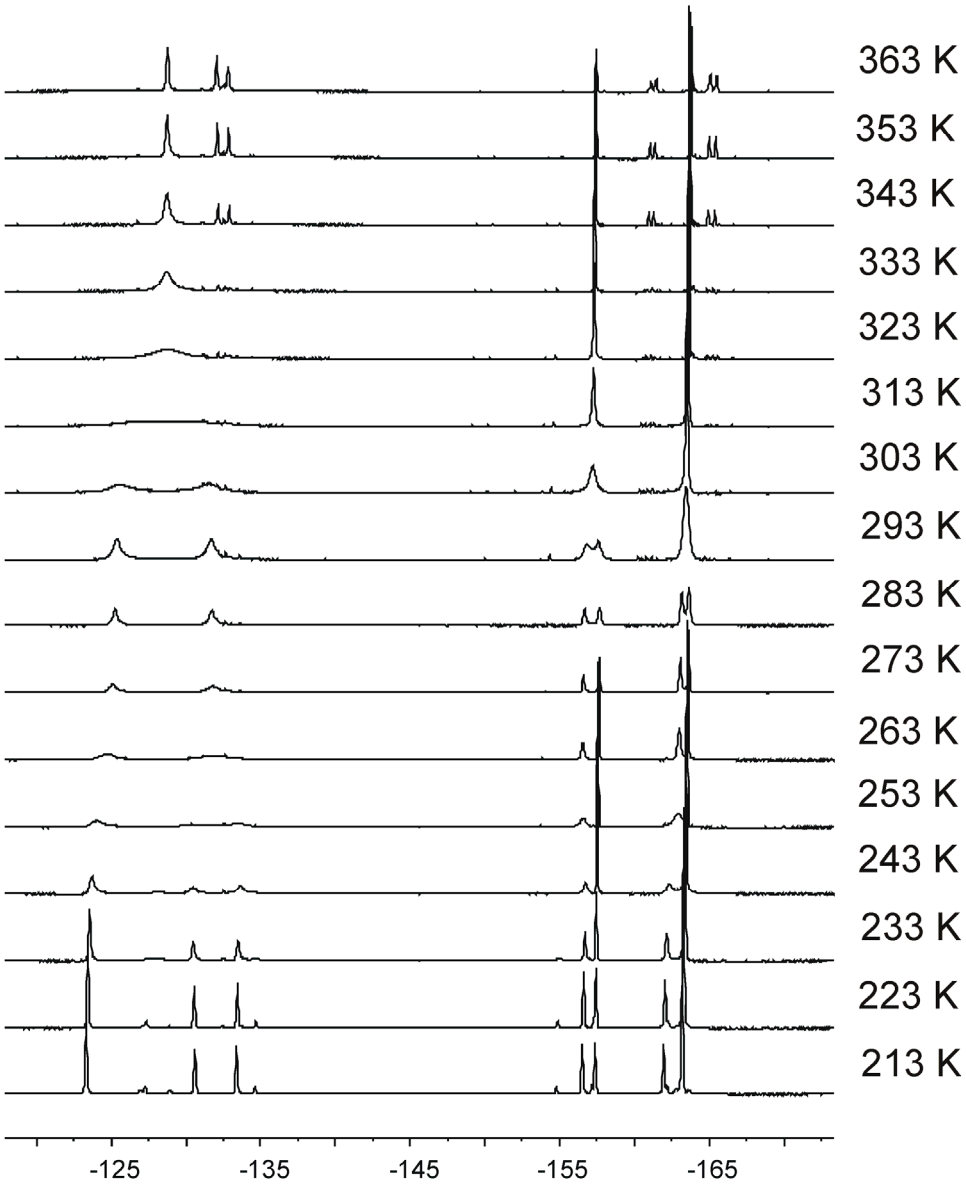
$\Delta G^{\neq}_{diss}$ (T_c = 303K; $\Delta\nu$(p-F, 283K) = 580 Hz) = 13.4 kcal/mol

$\Delta G^{\neq}_{diss}$(T_c= 313K; $\Delta\nu$(m-F, 293K) = 3570Hz) = 12.8 kcal/mol

$\Delta G^{\neq}_{diss}$(T_c= 318K; $\Delta\nu$(m-F, 293K) = 3570 Hz) = 13.0 kcal/mol

average value:

$\Delta G^{\neq}_{diss}$ = 13.1 ± 0.3 kcal/mol

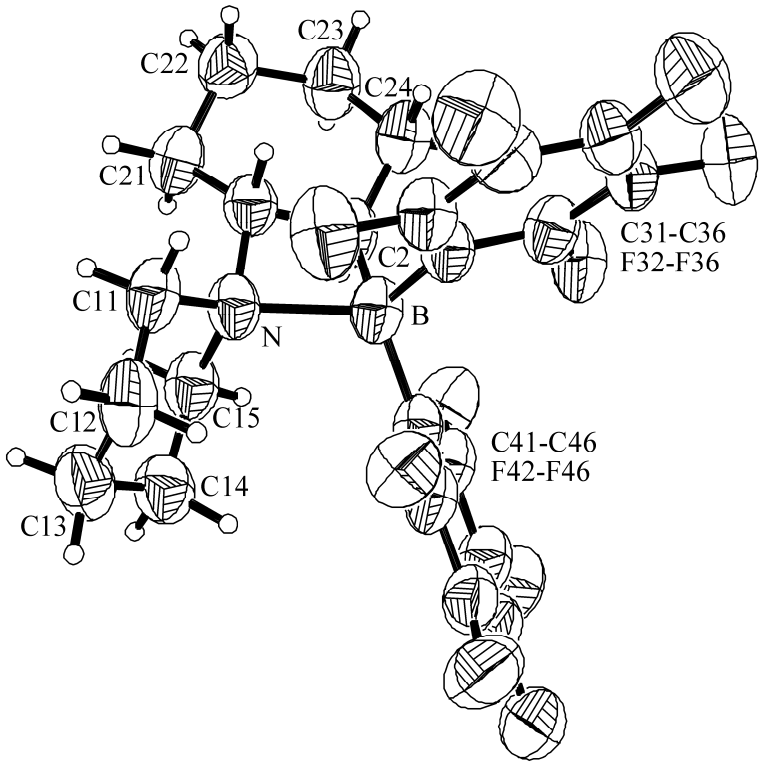


^{9}F NMR (564 MHz, toluene-d_8) of **5d** [T > 333 K: decomposition]

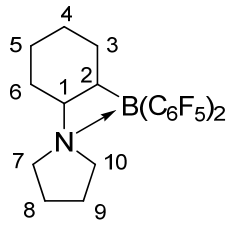
Dynamic of the rotation of one C_6F_5 goup around the B-C_{ipso} vector of the B(C_6F_5)$_2$ substituent:

$\Delta G^{\neq}_{rot}$ (T_c = 253K; $\Delta\nu$(m-F, 293K) = 1700Hz) = 10.6 kcal/mol; $\Delta G^{\neq}_{rot}$(T_c= 263K; $\Delta\nu$ (m-F, 293K) = 1700 Hz) = 11.0 kcal/mol; average value: $\Delta G^{\neq}_{rot}$ (258K) = 10.8 ± 0.2 kcal/mol

Crystal data for $C_{23}H_{20}BF_{10}N$ (**5d**), M = 511.21, monoclinic, $C2/c$ (No. 15), a = 18.5936(9), b = 9.2952(6), c = 26.1791(17) Å, β = 104.988(3)°, V = 4370.6(5) Å^3, D_c = 1.554 g cm^{-3}, μ = 1.332 mm^{-1}, $F(000)$ = 2080, Z = 8, λ = 1.54178 Å, T = 223(2) K, 18687 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3044 independent (R_{int} = 0.102), and 1876 observed reflections [I ≥ 2σ(I)], 316 refined parameters, R = 0.058, wR^2 = 0.143, GoF = 1.078.



Synthesis of 5e



The reaction procedure was carried out as described for the preparation of **5a**: *N*-(cyclohex-1-enyl)pyrrolidine (**4e**) (13 mg, 0.086 mmol) and bis(pentafluorophenyl)-borane (30 mg, 0.086 mmol) were dissolved in pentane (3 mL). After stirring for 20 minutes at room temperature the solvent was removed and the product **5e** was isolated as a white solid (30 mg, 70%).

^{1}H NMR (600 MHz, 298 K, toluene-d_8) δ = 3.06 (m, 1H, 10-H), 2.66 (m, 1H, 10′-H), 2.46 (m, 1H, 1-H), 2.45 (m, 1H, 7-H), 1.97 (m, 1H, 3-H), 1.76 (m, 1H, 7′-H), 1.48 (m, 1H, 4-H), 1.48 (m, 1H, 5-H), 1.26 (m, 1H, 2-H), 1.19 (m, 1H, 9-H), 1.09 (m, 1H, 6-H), 1.06 (m, 1H, 4′-H), 1.04 (m, 1H, 9′-H), 0.98 (m, 1H, 8-H), 0.91 (m, 1H, 8′-H), 0.86 (m, 1H, 6′-H), 0.84 (m, 1H, 5′-H), 0.80 (m, 1H, 3′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, toluene-d_8) δ = 147.7 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 147.4 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.3 (dm, $^{1}J_{FC}$ ~ 246 Hz, C_6F_5), 139.4 (dm, $^{1}J_{FC}$ ~ 249 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 117.7 (*i*-C_6F_5), 75.2 (C1), 59.6 (br m, C10), 51.6 (C7), 32.7 (br, C2), 30.1 (C6), 28.7 (br m, C3), 27.1 (C4), 25.6 (C5), 23.8 (C9), 22.4 (C8).

^{1}H,^{1}H GCOSY (600 MHz, 298 K, toluene-d_8) δ ^{1}H / δ ^{1}H = 3.06 / 2.66, 1.19 (10-H / 10′-H, 9-H), 2.66 / 3.06 (10′-H / 10-H), 2.46 / 1.26, 1.09, 0.86 (1-H / 2-H, 6-H, 6′-H), 2.45 / 1.76 (7-H / 7′-H) , 1.97 / 1.26, 1.06, 0.80 (3-H / 2-H, 4′-H, 3′-H), 1.76 / 2.45, 0.98 (7′-H / 7-H, 8-H), 1.48 / 1.97, 1.06, 0.86, 0.84, 0.80 (4-H, 5-H / 3-H, 4′-H, 6′-H, 5′-H, 3′-H), 1.26 / 2.46, 1.97, 0.80 (2-H / 1-H, 3-H, 3′-H), 1.19 / 3.06, 0.91 (9-H / 10-H, 8′-H), 1.09 / 2.46, 1.48, 0.84 (6-H / 1-H, 5-H, 5′-H), 1.06 / 1.97, 1.48 (4′-H / 3-H, 4-H, 5-H), 1.04 / 3.06, 2.66 (9′-H / 10-H, 10′-H), 0.98 / 2.45, 1.76, 0.91 (8-H / 7-H, 7′-H, 8′-H), 0.91 / 2.445, 1.76, 1.19 (8′-H / 7-H, 7′-H, 9-H), 0.86, 0.84 / 2.46, 1.48, 1.09 (6′-H, 5′-H / 1-H, 4-H, 5-H, 6-H), 0.80 / 1.97, 1.48, 1.26, 1.06, 0.84 (3′-H / 3-H, 4-H, 5-H, 2-H, 4′-H, 5′-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, toluene-d_8) δ ^{1}H / δ ^{13}C = 3.06 / 59.6 (10-H / C10), 2.66 / 59.6 (10′-H / C10), 2.46 / 75.2 (1-H / C1), 2.45 / 51.6 (7-H / C7), 1.97 / 28.7 (3-H / C3), 1.76 / 51.6 (7′-H / C7), 1.48 / 27.1 (4-H / C4), 1.48 / 25.6 (5-H / C5), 1.26 / 32.7 (2-H / C2), 1.19 / 23.8 (9-H / C9), 1.09 / 30.1 (6-H / C6), 1.06 / 27.1 (4′-H / C4), 1.04 / 23.8 (9′-H / C9), 0.98 / 22.4 (8-H / C8), 0.91 / 22.4 (8′-H / C8), 0.86 / 30.1 (6′-H / C6), 0.84 / 25.6 (5′-H / C5), 0.80 / 28.7 (3′-H / C3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, toluene-d_8) δ ^{1}H / δ ^{13}C = 3.06 / 75.2 (10-H / C1), 1.76 / 75.2, 22.4 (7′-H / C1, C8), 1.26 / 75.2, 30.1, 28.7, 27.1 (2-H / C1, C6, C3, C4), 1.09 / 75.2, 27.1 (6-H / C1, C4), 1.06 / 30.1, 28.7, 25.6 (4′-H / C6, C3, C5), 0.84 / 30.1 (5′-H / C6), 0.80 / 75.2, 27.1 (3′-H / C1, C4).

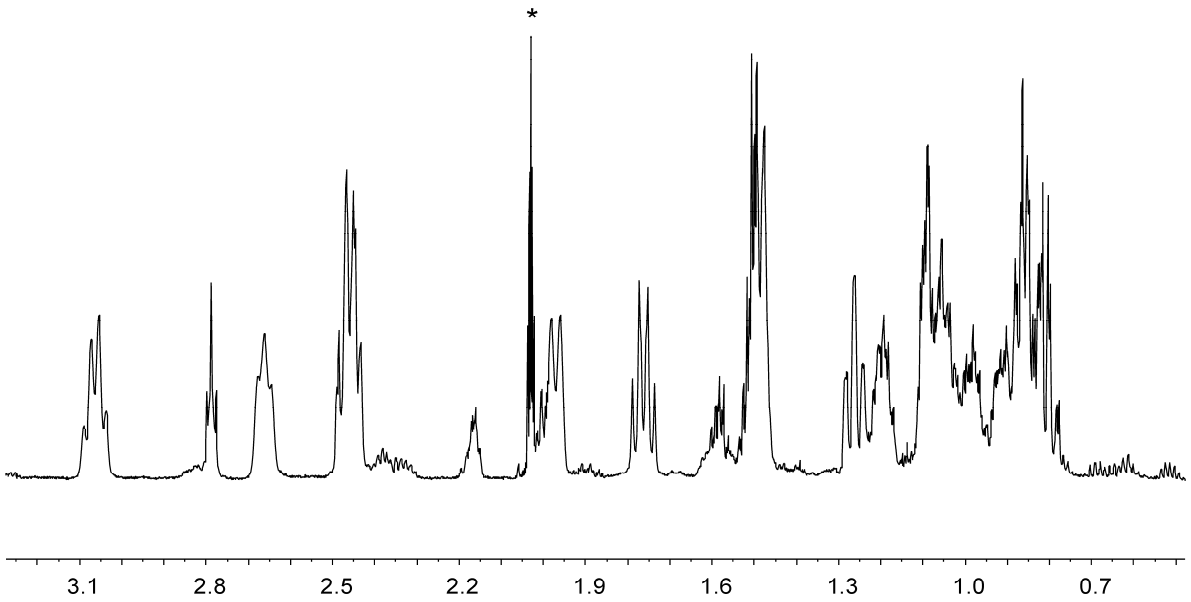
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, toluene-d_8) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 0.98 / 3.06, 2.66, 2.45, 1.76, 1.19, 0.91 (8-H / 10-H, 10′-H, 7-H, 7′-H, 9-H, 8′-H), 0.80 / 2.46, 1.97, 1.48, 1.26, 1.09, 1.06, 0.86, 0.84 (3′-H / 1-H, 3-H, 4-H, 2-H, 6-H, 4′-H, 6′-H, 5′-H), [selected experiments].

^{1}H{^{1}H} NOE (600 MHz, 298 K, toluene-d_8) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 3.06 / 2.66, 1.76, 1.26, 0.86 (10-H / 10′-H, 7′-H, 2-H, 6′-H), 2.66 / 3.06, 2.45, 1.04 (10′-H / 10-H, 7-H, 9′-H), 2.46, 2.45 / 2.66, 1.76, 1.26, 1.09, 0.86, 0.80 (1-H, 7-H / 10′-H, 7′-H, 2-H, 6-H, 6′-H, 3′-H), 1.97 / 1.48, 1.26, 1.06, 0.80 (3-H / 4-H, 2-H, 4′-H, 3′-H), 1.76 / 3.06, 2.45, 0.98 (7′-H / 10-H, 7-H, 8-H), 1.48 / 1.06, 0.86 (4-H, 5-H / 4′-H, 6′-H), 1.26 / 3.06, 2.46, 2.45, 1.97, 1.06, 0.84 (2-H / 10-H, 1-H, 7-H, 3-H, 4′-H, 5′-H), 1.19 / 3.06, 2.45, 1.76 (9-H / 10-H, 7-H, 7′-H), 1.09 / 2.46, 1.48, 0.84 (6-H / 1-H, 5-H, 5′-H), 0.98 / 2.66, 2.45, 1.48 (8-H / 10′-H, 7-H, 4-H, 5-H), 0.86 / 3.06, 2.46, 2.45, 1.97, 1.48, 1.09 (6′-H / 10-H, 1-H, 7-H, 3-H, 4-H, 5-H, 6-H), 0.80 / 2.46, 1.97, 1.48, 1.09 (3′-H / 1-H, 3-H, 4-H, 5-H, 6-H).

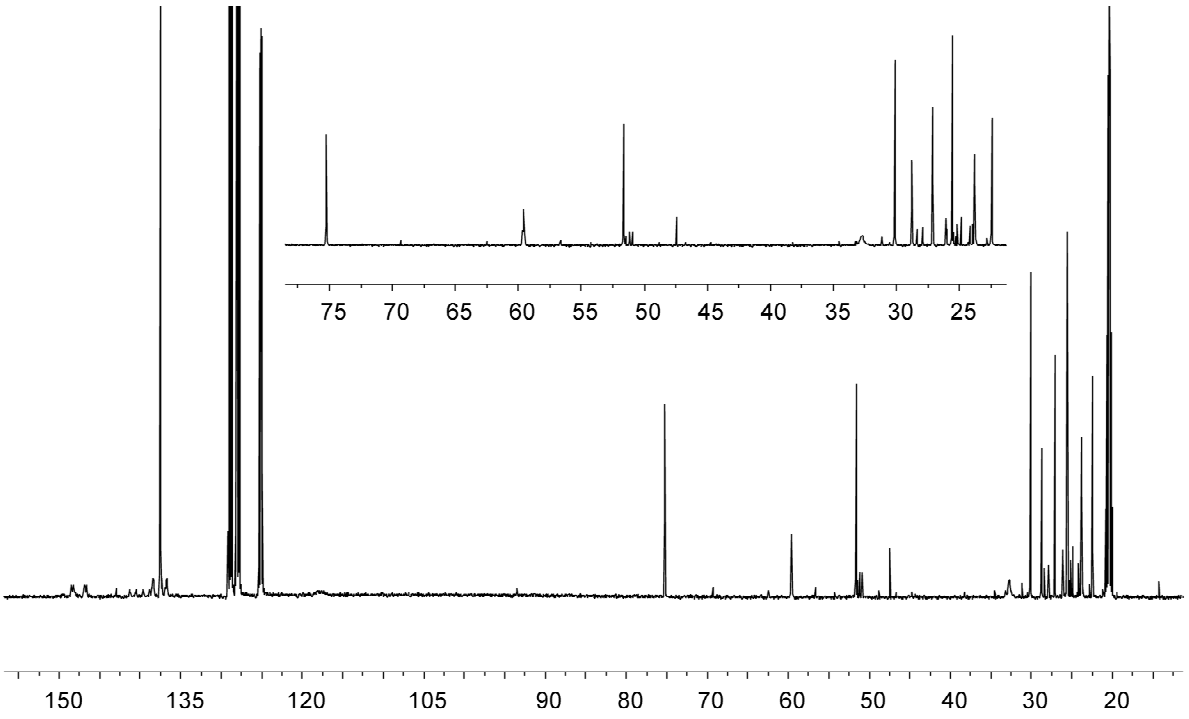
^{11}B{^{1}H} NMR (192 MHz, 298 K, toluene-d_8) δ = 6.4 ($\nu_{1/2}$ ~ 250 Hz).

^{19}F NMR (564 MHz, 298 K, toluene-d_8) δ = –127.9 (m, 2F, *o*-$C_6F_5^A$), –133.4 (m, 2F, *o*-$C_6F_5^B$), –157.0 (t, ^{3}J = 21.3 Hz, 1F, *p*-$C_6F_5^B$), –158.3 (t, ^{3}J = 21.3 Hz, 1F, *p*-$C_6F_5^A$), –163.2 (m, 2F, *m*-$C_6F_5^B$), –164.0 (m, 2F, *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{mp}$ = 5.7^A, 6.2^B].

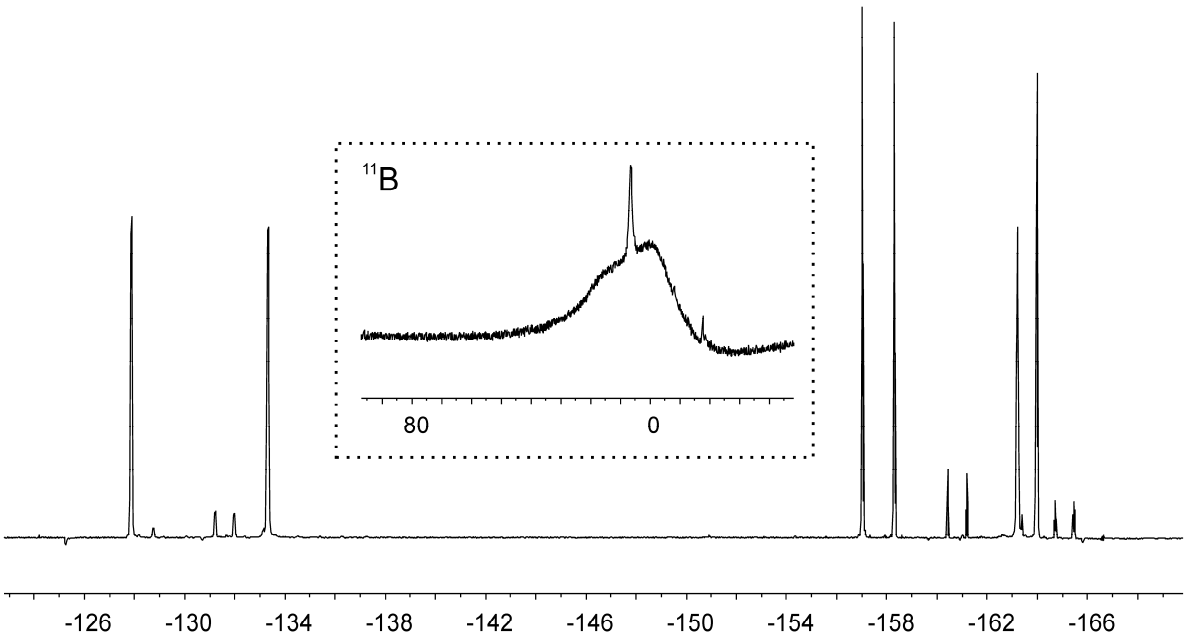
^{19}F,^{19}F GCOSY (564 MHz, 298 K, toluene-d_8) δ ^{19}F / δ ^{19}F = –163.2 / –133.4, –157.0 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$), –164.0 / –127.9, –158.3 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$).



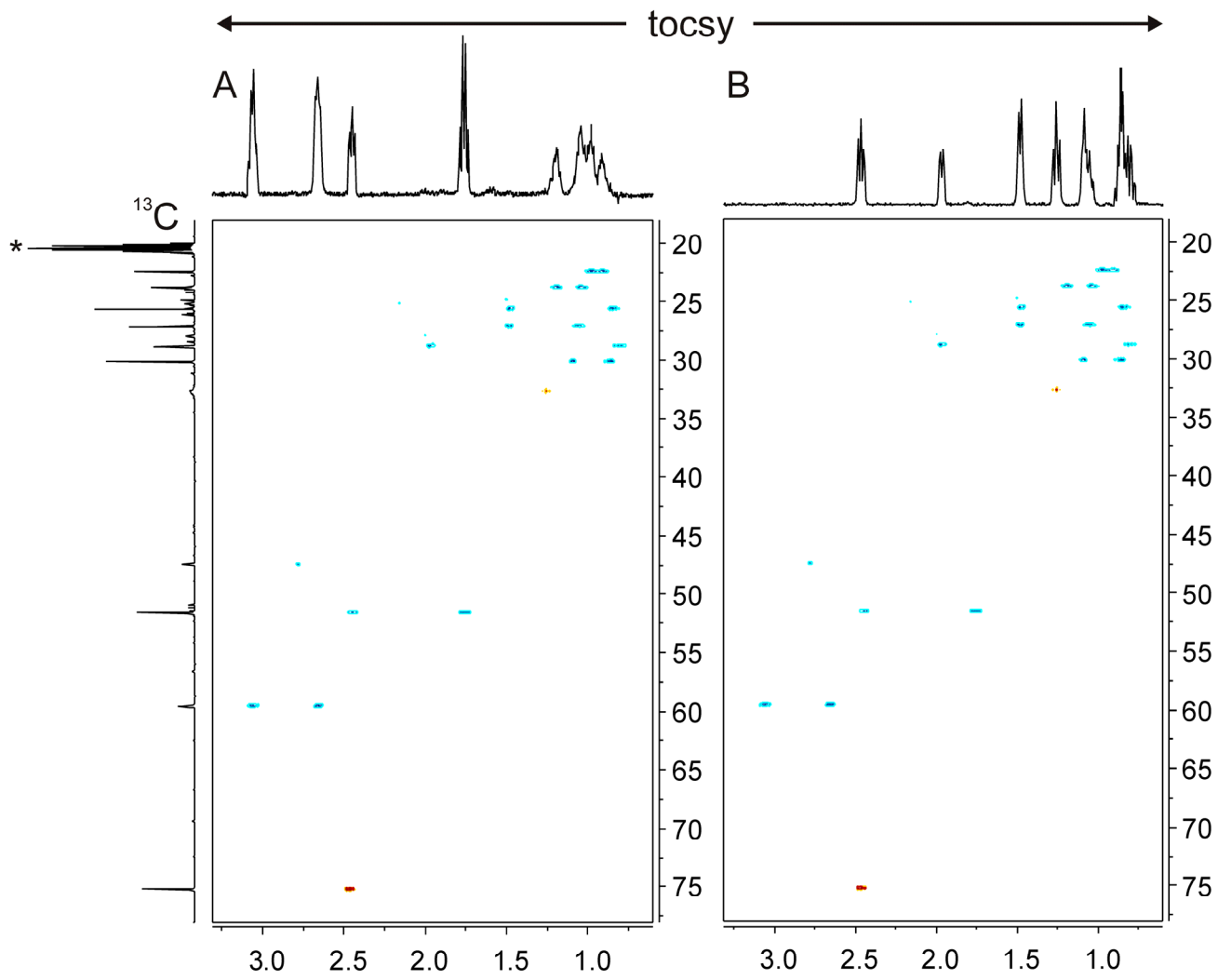
^{1}H NMR (600 MHz, 298 K, toluene-d_8(*)) of **5e**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, toluene-d_8) of **5e**

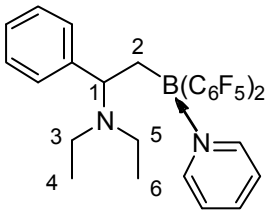


^{19}F NMR (564 MHz, 298 K, toluene-d_8) and $^{11}B\{^{1}H\}$ NMR (192 MHz, 298 K, toluene-d_8) of **5e**



$^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 298 K, toluene-d_8(*); projections: $^{1}H\{1H\}$ TOCSY [$\delta\ ^{1}H_{irr}$ = 3.06 (A) and 1.26 (B)] spectrum and $^{13}C\{^{1}H\}$ spectrum) of **5e**

Reaction of 5a with pyridine: generation of 6a



6a

Pyridine (20 µl, 20 mg, 0.25 mmol, 2eq.) was added to a solution of in situ generated **5a** [*N*-(1-phenylethen-1-yl)-diethylamine **4a** (22 mg, 0.13 mmol) and bis(pentafluoro-phenyl)borane (43.9 mg, 0.13 mmol)] in benzene-d_6 (0.8 mL). The resulting mixture of **6a** and pyrdidine was investigated spectroscopically [ratio **6a:** pyridine ~ 1: 1].

Pyridine: ^{1}H NMR (500 MHz, 298 K, benzene-d_6) δ = 8.51 (m, 2H, *o*-py), 6.98 (m, 1H, *p*-py), 6.67 (m, 2H, *m*-py).

^{13}C{^{1}H} NMR (126 MHz, 298 K, benzene-d_6) δ = 150.1 (*o*-py), 135.3 (*p*-py), 123.5 (*m*-py).

6a: ^{1}H NMR (500 MHz, 298 K, benzene-d_6) δ = 8.72 (m, 2H, *o*-py), 7.03 (m, 2H, *m*-Ph), 6.97 (m, 1H, *p*-Ph), 6.84 (m, 2H, *o*-Ph), 6.70 (m, 1H, *p*-py), 6.45 (m, 2H, *m*-py), 3.64 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, 1-H), 2.74 (dq, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 7.4 Hz, 2H, 3/5-H), 2.34 (d, $^{2}J_{HH}$ = 15.4 Hz, 1H, 2-H), 2.22 (dd, $^{2}J_{HH}$ = 15.4 Hz, $^{3}J_{HH}$ = 8.2 Hz, 1H, 2′-H), 1.86 (dq, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 6.8 Hz, 2H, 3/5-H), 1.03 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 6.8 Hz, 6H, 4/6-H).

^{13}C{^{1}H} NMR (126 MHz, 298 K, benzene-d_6) δ = 147.3 (*o*-py), 141.0 (*p*-py), 139.2 (*i*-Ph), 128.9 (*o*-Ph), 127.4 (*m*-Ph), 126.6 (*p*-Ph), 125.4 (*m*-py), 61.6 (C1), 43.5 (C3/5), 27.4 (br, C2), 14.7 (C4/6), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 8.72 / 6.70, 6.45 (*o*-py / *p*-py, *m*-py), 7.03 / 6.97, 6.84 (*m*-Ph / *p*-Ph, *o*-Ph), 6.97 / 7.03, 6.84 (*p*-Ph / *m*-Ph, *o*-Ph), 6.84 / 7.03 (*o*-Ph / *m*-Ph), 6.70 / 8.72, 6.45 (*p*-py / *o*-py, *m*-py), 6.45 / 8.72, 6.70 (*m*-py / *o*-py, *p*-py), 3.64 / 2.34, 2.22 (1-H / 2-H, 2′-H), 2.74 / 1.86, 1.03 (3/5-H / 3/5-H, 4/6-H), 2.34 / 3.64, 2.22 (2-H / 1-H, 2′-H), 2.22 / 3.64, 2.34 (2′-H / 1-H, 2-H), 1.86 / 2.74, 1.03 (3/5-H / 3/5-H, 4/6-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 8.72 / 147.3 (*o*-py / *o*-py), 7.03 / 127.4 (*m*-Ph / *m*-Ph), 6.97 / 126.6 (*p*-Ph / *p*-Ph), 6.84 / 128.9 (*o*-Ph / *o*-Ph), 6.70 / 141.0 (*p*-py / *p*-py), 6.45 / 125.4 (*m*-py / *m*-py), 3.64 / 61.6 (1-H / C1), 2.74 / 43.5 (3/5-H / C3/5), 2.34, 2.22 / 27.4 (2-H, 2′-H / C2), 1.86 / 43.5 (3/5-H / C3/5), 1.03 / 14.7 (4/6-H / C4/6).

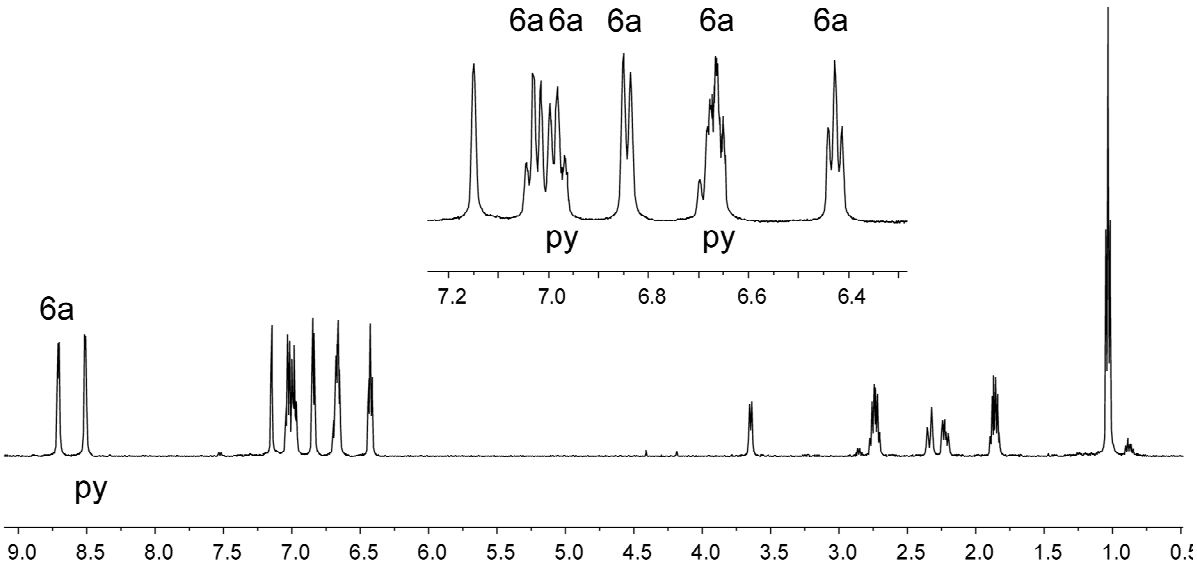
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 8.72 / 141.0, 125.4 (*o*-py / *p*-py, *m*-py), 7.03 / 139.2 (*m*-Ph / *i*-Ph), 6.97 / 128.9 (*p*-Ph / *o*-Ph), 6.84 / 126.6, 61.6 (*o*-Ph / *p*-Ph, C1), 6.45 / 147.3 (*m*-py / *o*-py), 3.64 / 139.2, 43.5 (1-H / *i*-Ph, C3/5), 2.74 / 61.6, 14.7 (3/5-H / C1, C4/6), 2.34 / 61.6 (2-H / C1), 2.22 / 139.2, 61.6 (2′-H / *i*-Ph, C1), 1.86 / 61.6, 14.7 (3/5-H / C1, C4/6), 1.03 / 43.5 (4/6-H / C3/5).

^{1}H{^{1}H} TOCSY (500 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 8.72 / 6.70, 6.45 (*o*-py / *p*-py, *m*-py), 2.22 / 3.64, 2.34 (2′-H / 1-H, 2-H).

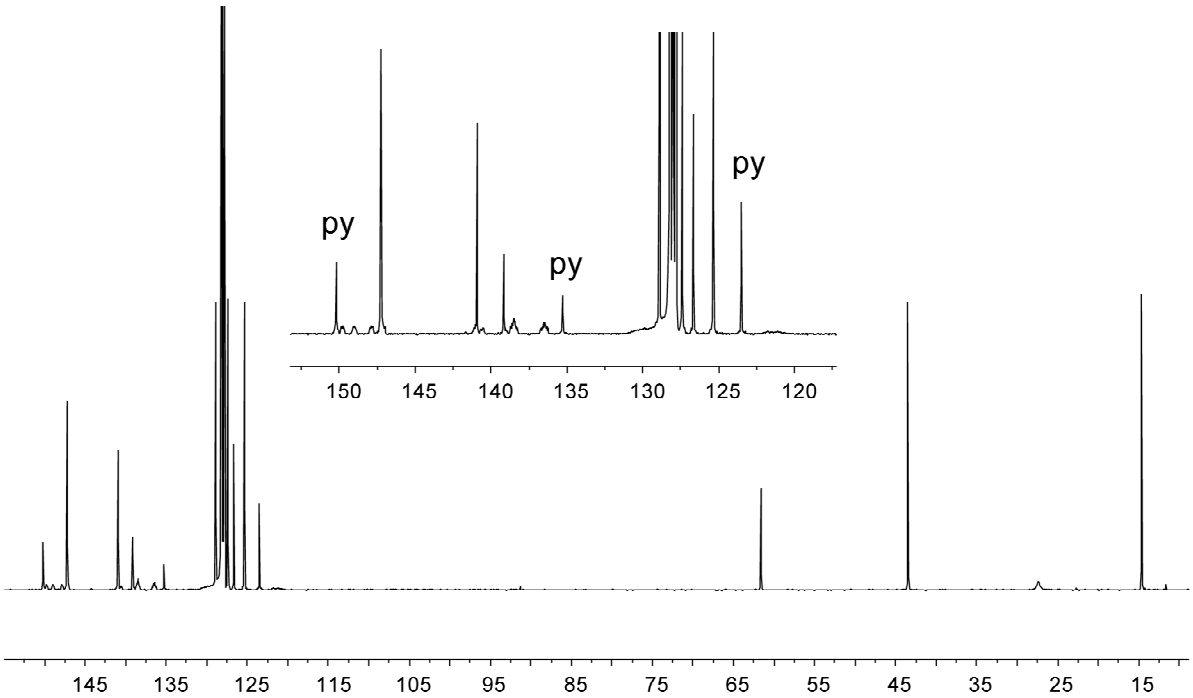
^{11}B{^{1}H} NMR (160 MHz, 298 K, benzene-d_6) δ = –0.6 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (470 MHz, 298 K, benzene-d_6) δ = –131.3 (m, 2F, *o*-$C_6F_5^A$), –134.2 (m, 2F, *o*-$C_6F_5^B$), –157.6 (t, ^{3}J = 21.1 Hz, 1F, *p*-$C_6F_5^A$), –160.0 (t, ^{3}J = 20.6 Hz, 1F, *p*-$C_6F_5^B$), –163.3 (m, 2F, *m*-$C_6F_5^A$), –165.0 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp}$ = 5.7^A, 5.0^B].

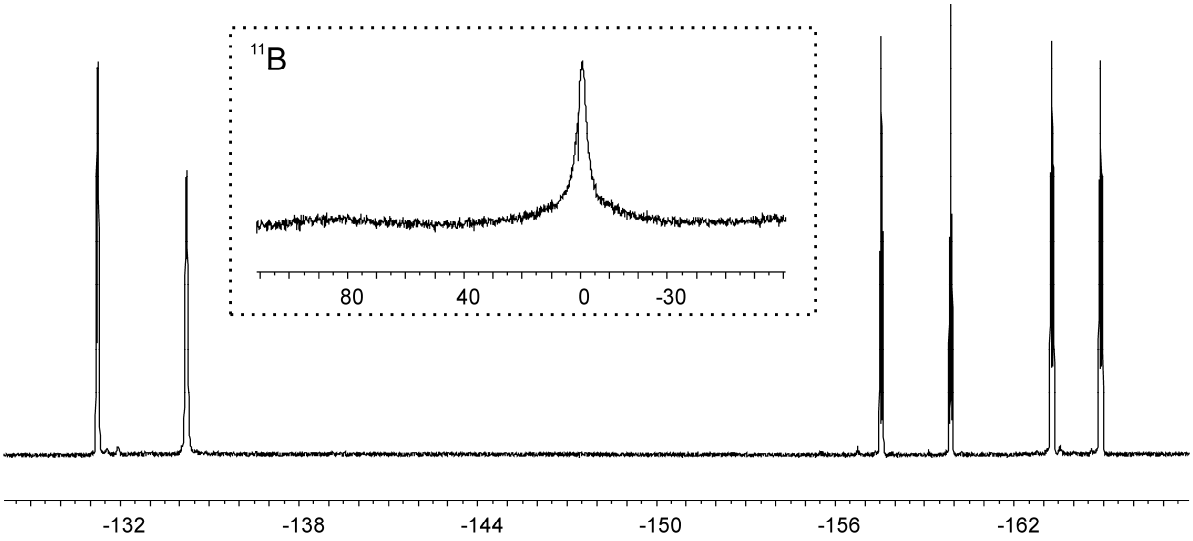
^{19}F,^{19}F GCOSY (470 MHz, 298 K, benzene-d_6) δ ^{19}F/ δ ^{19}F = –131.3 / –157.6, –163.3 (*o*-$C_6F_5^A$ / *p*-$C_6F_5^A$, *m*-$C_6F_5^A$), –134.2 / –160.0, –165.0 (*o*-$C_6F_5^B$ / *p*-$C_6F_5^B$, *m*-$C_6F_5^B$).



^{1}H NMR (500 MHz, 298K, benzene-d_6) of **6a**.

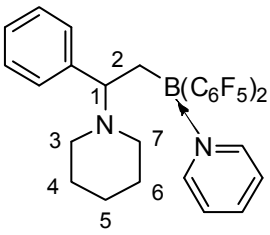


^{13}C{^{1}H} NMR (126 MHz, 298K, benzene-d_6) of **6a**.



^{11}F NMR (470 MHz, 298K, benzene-d_6) and ^{11}B{^{1}H} NMR (64 MHz, 298K, benzene-d_6) of **6a**.

Reaction of 5b with pyridine: generation of 6b



Pyridine (5.3 µl, 5.2 mg, 0.066 mmol, 2eq.) was added to a solution of **5b** (20 mg, 0.033 mmol) in benzene-d_6 (0.8 mL). The resulting mixture of **6b** and pyridine was investigated spectroscopically **[6b** : pyridine ~ 1 : 1.2].

Pyridine: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 8.48 (m, 2H, *o*-py), 6.95 (tt, $^3J_{HH}$= 7.6 Hz, $^4J_{HH}$= 1.9 Hz, 1H, *p*-py), 6.64 (m, 2H, *m*-py).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 149.9 (*o*-py), 135.4 (*p*-py), 123.5 (*m*-py).

6b: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 8.59 (m, 2H, *o*-py), 7.08 (m, 2H, *m*-Ph), 7.02 (m, 1H, *p*-Ph), 6.87 (m, 2H, *o*-Ph), 6.62 (m, 1H, *p*-py), 6.36 (m, 2H, *m*-py), 3.40 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 3.0 Hz, 1H, 1-H), 2.49 (1H), 2.39 (1H), 1.99 (2H) (each br, 3/7-H), 2.36 (dm, $^2J_{HH}$ = 15.3 Hz, 1H, 2-H), 2.14 (dd, $^2J_{HH}$ = 15.3 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, 2′-H), 1.50 (2H), 1.45 (2H) (each br, 4/6-H), 1.25 (1H), 1.15 (1H) (each br, 5-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 146.8 (*o*-py), 140.6 (*p*-py), 138.7 (*i*-Ph), 129.0 (*o*-Ph), 127.3 (*m*-Ph), 126.7 (*p*-Ph), 125.3 (*m*-py), 69.2 (C1), 50.9 (C3/7), 27.2 (C4/6), 26.6 (br, C2)[1], 25.0 (C5) [C_6F_5 not listed; [1] from the ^{1}H,^{13}C ghsqc experiment].

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 8.59 / 6.62, 6.36 (*o*-py / *p*-py, *m*-py). 7.08 / 7.02, 6.87 (*m*-Ph / *p*-Ph, *o*-Ph), 7.02 / 7.08, 6.87 (*p*-Ph / *m*-Ph, *o*-Ph), 6.87 / 7.08 (*o*-Ph / *m*-Ph), 6.62 / 8.59, 6.36 (*p*-py / *o*-py, *m*-py), 6.36 / 8.59, 6.62 (*m*-py / *o*-py, *p*-py), 3.40 / 2.36, 2.14 (1-H / 2-H, 2′-H), 2.36 / 3.40, 2.14 (2-H / 1-H, 2′-H), 1.25, 1.15 / 1.50, 1.45 (5-H / 4/6-H), 1.50, 1.45 / 1.99, 1.25, 1.15 (4/6-H / 3/7-H, 5-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 8.59 / 146.8 (*o*-py / *o*-py), 7.08 / 127.3 (*m*-Ph / *m*-Ph), 7.02 / 126.7 (*p*-Ph / *p*-Ph), 6.87 / 129.0 (*o*-Ph / *o*-Ph), 6.62 / 140.6 (*p*-py / *p*-py), 6.36 / 125.3 (*m*-py / *m*-py), 3.40 / 69.2 (1-H / C1), 2.49, 2.39, 1.99 / 50.9 (3/7-H / C3/7), 2.36, 2.14 / 26.6 (2-H, 2′-H / C2), 1.50, 1.45 / 27.2 (4/6-H / C4/6), 1.25, 1.15 / 25.0 (5-H / C5).

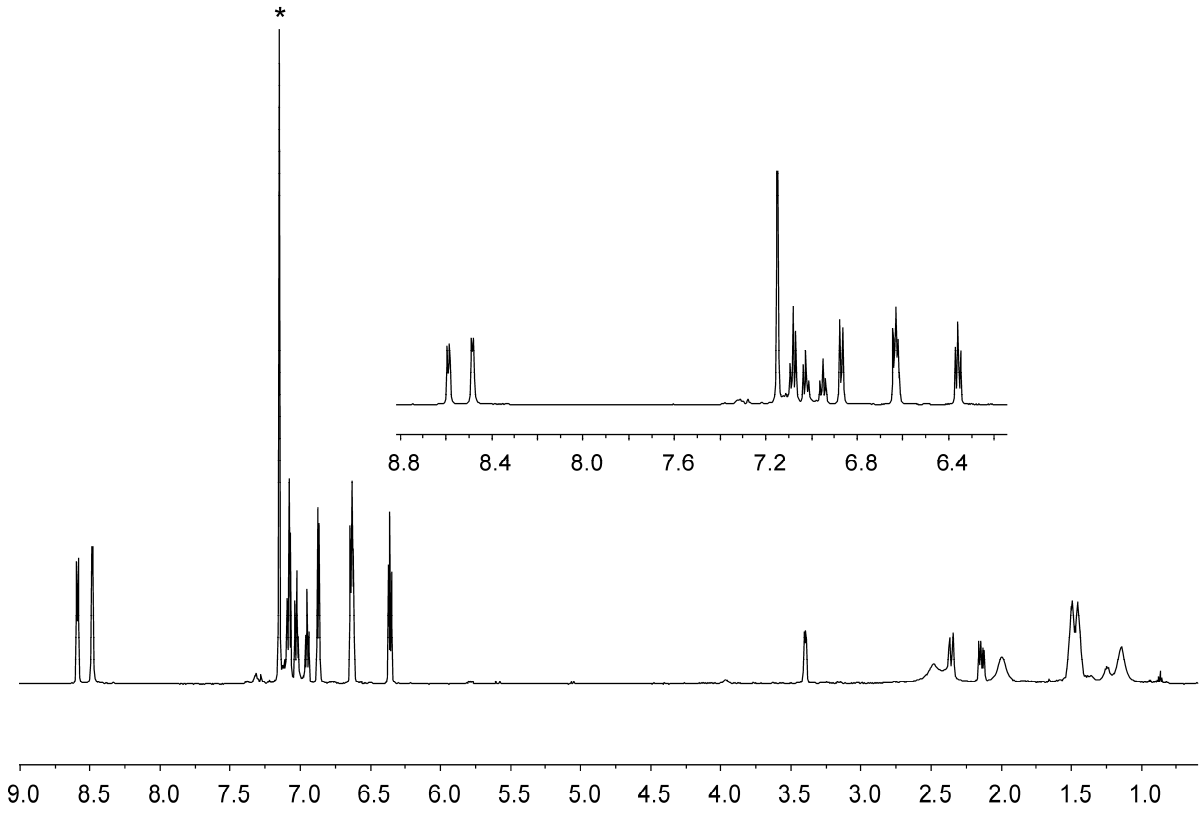
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 8.59 / 140.6, 125.3 (*o*-py / *p*-py, *m*-py), 7.08 / 138.7 (*m*-Ph / *i*-Ph), 7.02 / 129.0 (*p*-Ph / *o*-Ph), 6.87 / 126.7, 69.2 (*o*-Ph / *p*-Ph, C1), 6.62, 6.36 / 146.8 (*p*-py, *m*-py / *o*-py), 3.40 / 129.0 (1-H / *o*-Ph), 2.14 / 138.7, 69.2 (2′-H / *i*-Ph, C1).

^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^1H_{irr}$ / δ $^1H_{res}$ = 6.87 / 7.08, 7.02 (*o*-Ph / *m*-Ph, *p*-Ph). 6.62 / 8.59, 6.36 (*p*-py / *o*-py, *m*-py), 2.14 / 3.40, 2.36 (2′-H / 1-H, 2-H).

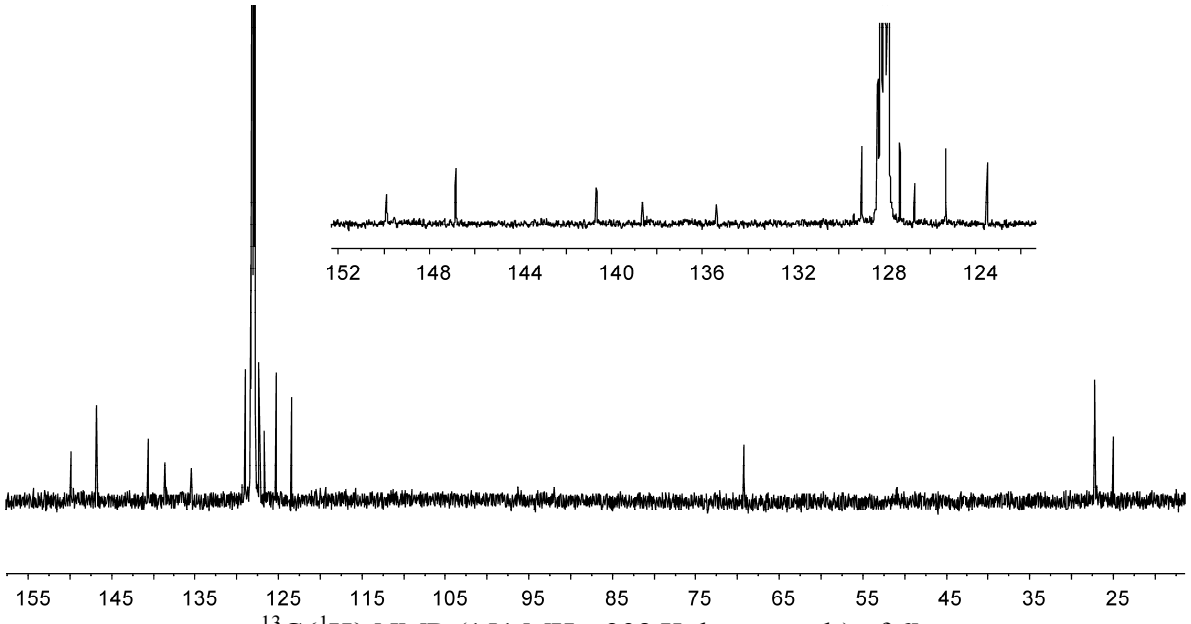
^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d_6) δ = –0.6 (br, $\nu_{1/2}$ ~ 250 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6) δ = –131.3 (m, 2F, *o*-$C_6F_5^A$), –133.5 (m, 2F, *o*-$C_6F_5^B$), –157.7 (t, ^{3}J = 20.6 Hz, 1F, *p*-$C_6F_5^A$), –159.4 (t, ^{3}J = 21.0 Hz, 1F, *p*-$C_6F_5^B$), –163.4 (m, 2F, *m*-$C_6F_5^A$), –164.6 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp} = 5.7^A, 5.2^B$].

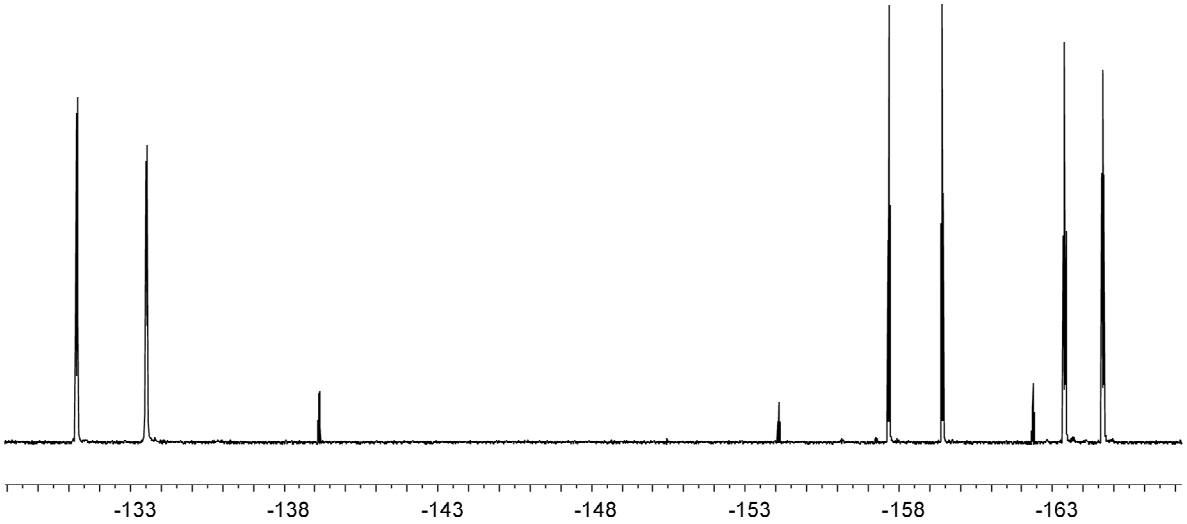
^{19}F,^{19}F GCOSY (564 MHz, 298 K, benzene-d_6) δ ^{19}F / δ ^{19}F = –163.4 / –131.3, –157.7 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), –164.6 / –133.5, –159.4 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **6b**

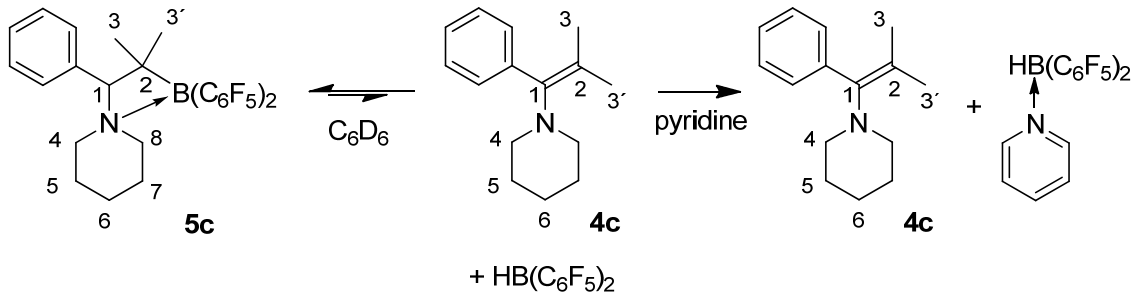


^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of **6b**



^{19}F NMR (564 MHz, 298 K, benzene-d_6) of **6b**

Reaction of 5c with pyridine



Pyridine (15 µl, 14.7 ml, 0.186 mmol, 2eq.) was added to a solution of **5c** (20 mg, 0.093 mmol, 1eq.) in benzene-d_6 (0.8 mL) [as a mixture of **5c** : **4c**/$HB(C_6F_5)_2$ ~ 5 : 1; see a above]. The resulting mixture of **4c**, pyridine-$HB(C_6F_5)_2$ and pyridine was investigated spectroscopically **[4c** : pyridine-$HB(C_6F_5)_2$: pyridine ~ 1 : 1.4 : 3 (^{1}H NMR)]

Pyridine: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 8.52 (m, 2H, *o*-py), 6.98 (tt, $^3J_{HH}$= 7.8 Hz, $^4J_{HH}$= 1.9 Hz, 1H, *p*-py), 6.66 (m, 2H, *m*-py).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 150.2 (*o*-py), 135.2 (*p*-py), 123.5 (*m*-py).

Pyridine-$HB(C_6F_5)_2$: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.76 (m, 2H, *o*-py), 6.59 (tt, $^3J_{HH}$= 7.8 Hz, $^4J_{HH}$= 1.6 Hz, 1H, *p*-py), 6.21 (m, 2H, *m*-py), 4.66 (br, 1H, BH).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 146.6 (*o*-py), 140.6 (*p*-py), 125.4 (*m*-py), [C_6F_5 not listed].

^{11}B NMR (192 MHz, 298 K, benzene-d_6) δ = –8.1 (d, $^1J_{BH}$ ~ 95 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6) δ = –133.5 (m, 2F, *o*-C_6F_5), –157.3 (t, ^{3}J = 20.9 Hz, 1F, *p*-C_6F_5), –163.7 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 6.4].

4c: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.20 (m, 2H, *m*-Ph), 7.11 (m, 2H, *o*-Ph), 7.10 (m, 1H, *p*-Ph), 2.58 (m, 4H, 4-H), 1.97 (s, 3H, 3-H), 1.56 (s, 3H, 3'-H), 1.49 (m, 4H, 5-H), 1.27 (m, 2H, 6-H).

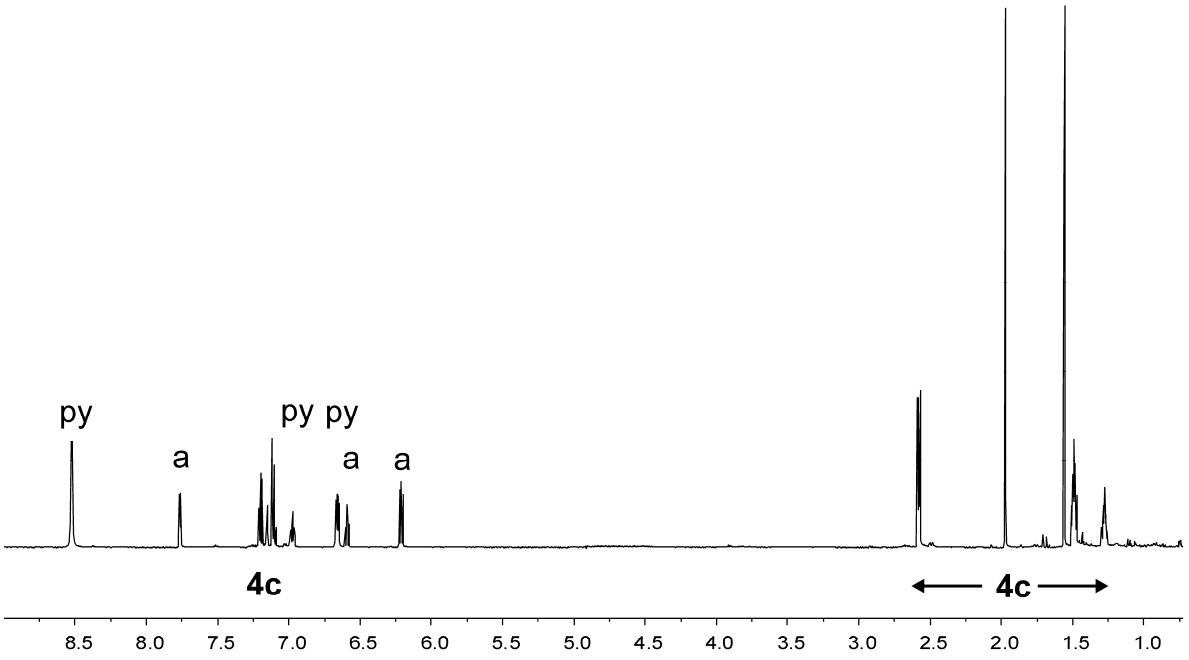
^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 145.4 (C1), 139.0 (*i*-Ph), 130.1 (*o*-Ph), 128.0 (*m*-Ph), 126.7 (*p*-Ph), 121.9 (C2), 53.1 (C4), 27.1 (C5), 24.8 (C6), 20.8 (C3′), 19.2 (C3).

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 7.20 / 7.11, 7.10 (*m*-Ph / *o*-Ph, *p*-Ph), 2.58 / 1.49 (4-H / 5-H), 1.56 / 1.97 (3′-H / 3-H), 1.49 / 2.58, 1.27 (5-H / 4-H, 6-H), 1.27 / 1.49 (6-H / 5-H).

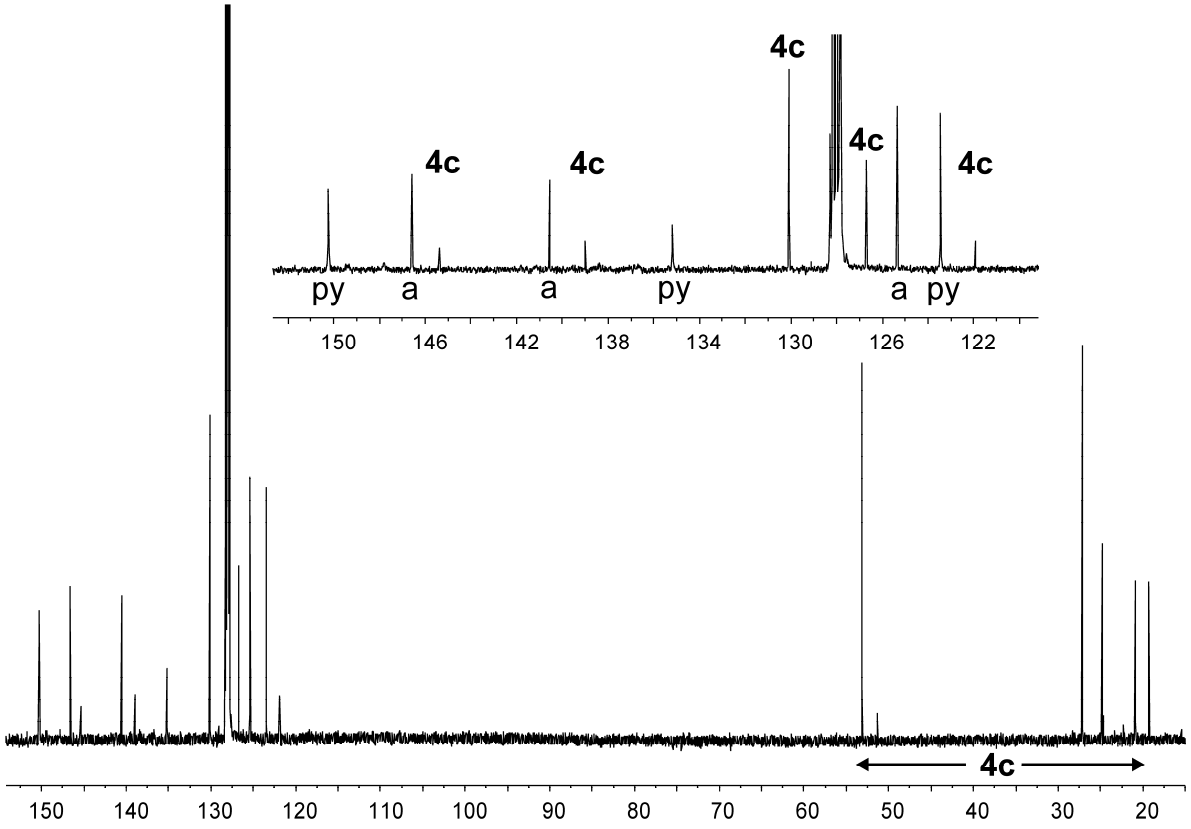
^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.20 / 128.0 (*m*-Ph / *m*-Ph), 7.11 / 130.1 (*o*-Ph / *o*-Ph), 7.10 / 126.7 (*p*-Ph / *p*-Ph), 2.58 / 53.1 (4-H/ C4), 1.97 / 19.2 (3-H / C3), 1.56 / 20.8 (3′-H / C3′), 1.49 / 27.1 (5-H / C5), 1.27 / 24.8 (6-H / C6).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.20 / 139.0 (*m*-Ph / *i*-Ph), 7.11 / 126.7 (*o*-Ph / *p*-Ph), 2.58 / 27.1, 24.8 (4-H / C5, C6), 1.97 / 145.4, 130.1, 121.9, 20.8 (3-H / C1, *o*-Ph, C2, C3′), 1.56 / 145.4, 121.9, 53.1, 19.2 (3′-H / C1, C2, C4, C3), 1.49 / 53.1, 27.1, 24.8 (5-H / C4, C5, C6), 1.27 / 53.1, 27.1 (6-H / C4, C5).

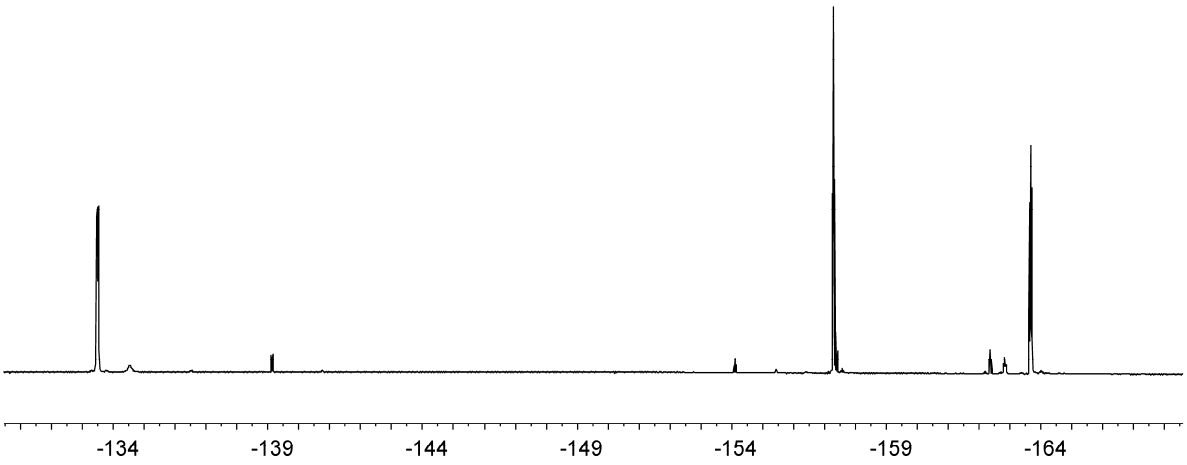
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^1H_{irr}$ / δ $^1H_{res}$ = 2.58 / 1.49, 1.27 (4-H / 5-H, 6-H), [selected experiment].



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of the reaction of **5c** with pyridine [py: pyridine, a: py-HB(C_6F_5)$_2$]

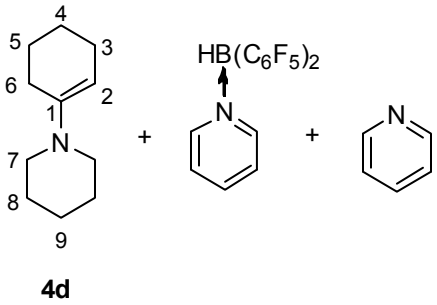


^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of the reaction of **5c** with pyridine [py: pyridine, a: py-HB(C_6F_5)$_2$]



^{19}F NMR (564 MHz, 298 K, benzene-d_6) of the reaction of **5c** with pyridine

Reaction of 5d with pyridine



4d

Pyridine (3.1 µl, 3.1 mg, 0.04 mmol, 2eq.) was added to a solution of **5d** (10 mg, 0.02 mmol mmol) in benzene-d_6 (0.8 mL). The resulting mixture of **4d**, pyridine-HB(C_6F_5)$_2$ and pyridine was investigated spectroscopically **[4d** : pyridine-HB(C_6F_5)$_2$ **:** pyridine : ~ 0.8 : 0.8: 1].

Pyridine: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 8.53 (m, 2H, *o*-py), 6.96 (tt, $^3J_{HH}$= 7.7 Hz, $^4J_{HH}$= 1.9 Hz, 1H, *p*-py), 6.65 (m, 2H, *m*-py).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 150.1 (*o*-py), 135.3 (*p*-py), 123.5 (*m*-py).

Pyridine-HB(C_6F_5)$_2$: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.74 (m, 2H, *o*-py), 6.57 (tt, $^3J_{HH}$= 7.8 Hz, $^4J_{HH}$= 1.5 Hz, 1H, *p*-py), 6.19 (m, 2H, *m*-py), 4.63 (br, 1H, BH).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 146.6 (*o*-py), 140.5 (*p*-py), 125.3 (*m*-py), n.o. (C_6F_5).

^{11}B NMR (192 MHz, 298 K, benzene-d_6) δ = –8.2 (d, $^1J_{BH}$ ~ 95 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6) δ = –133.5 (m, 2F, *o*-C_6F_5), –157.3 (t, ^{3}J = 20.6 Hz, 1F, *p*-C_6F_5), –163.7 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 6.4].

4d: ^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 4.72 (t, $^3J_{HH}$= 4.1 Hz, 1H, 2-H), 2.70 (m, 4H, 7-H), 2.15 (m, 2H, 3-H), 2.02 (m, 2H, 6-H), 1.60 (m, 2H, 5-H), 1.53 (m, 2H, 4-H), 1.46 (m, 4H, 8-H), 1.34 (m, 2H, 9-H).

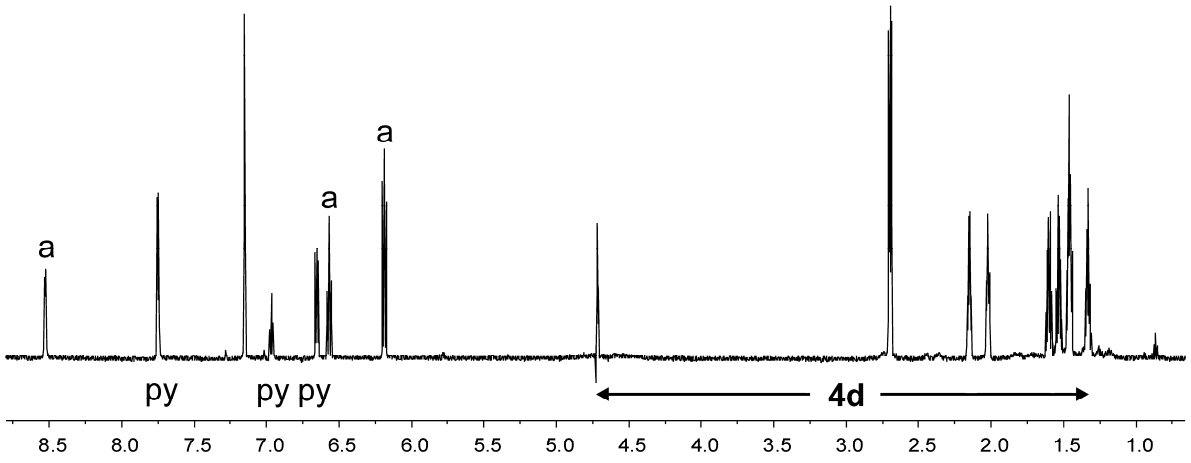
^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 146.7 (C1), 100.1 (C2), 49.4 (C7), 28.1 (C6), 26.4 (C8), 25.1 (C3, C9), 23.9 (C5), 23.5 (C4).

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 4.72 / 2.15 (2-H / 3-H), 2.70 / 1.46 (7-H / 8-H), 2.15 / 4.72, 1.53 (3-H / 2-H, 4-H), 2.02 / 1.60 (6-H / 5-H), 1.60 / 2.02, 1.53 (5-H / 6-H, 4-H), 1.53 / 2.15, 1.60 (4-H / 3-H, 5-H), 1.46 / 2.70, 1.34 (8-H / 7-H, 9-H), 1.34 / 1.46 (9-H / 8-H).

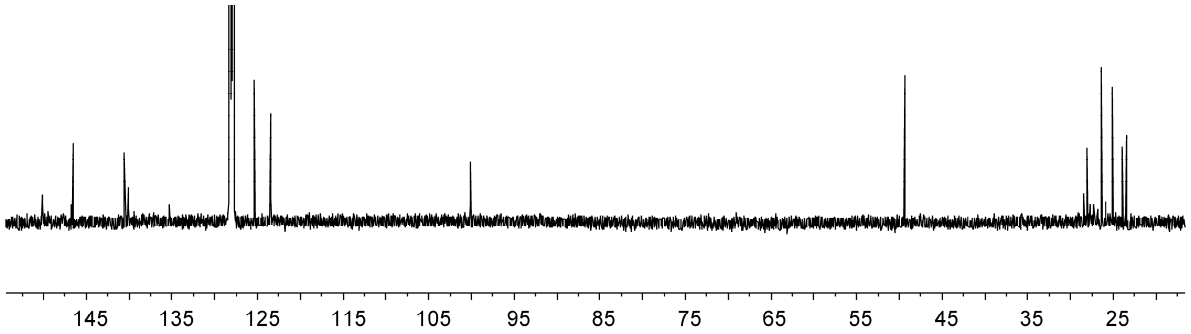
^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 4.72 / 100.1 (2-H / C2), 2.70 / 49.4 (7-H / C7), 2.15 / 25.1 (3-H / C3), 2.02 / 28.1 (6-H / C6), 1.60 / 23.9 (5-H / C5), 1.53 / 23.5 (4-H / C4), 1.46 / 26.4 (8-H / C8), 1.34 / 25.1 (9-H / C9).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 2.70 / 26.4, 25.1 (7-H / C8, C9), 1.34 / 49.4 (9-H / C7).

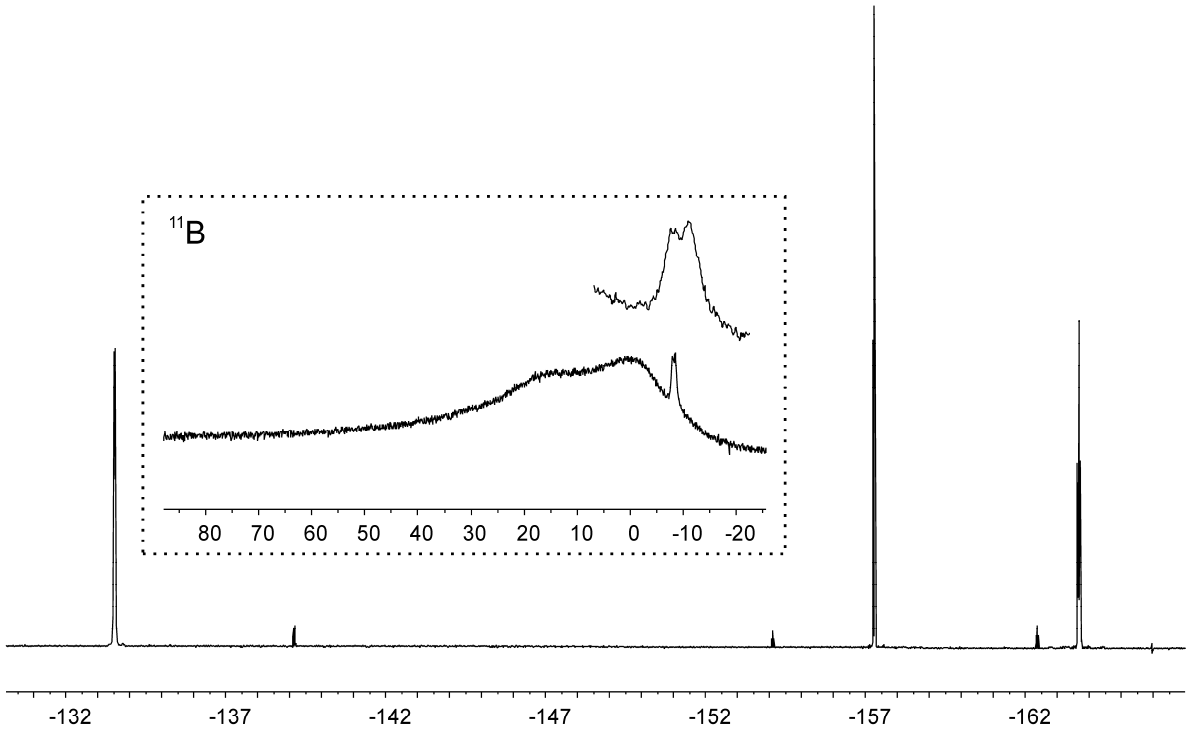
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^1H_{irr}$ / δ $^1H_{res}$ = 4.72 / 2.15, 2.02, 1.60, 1.53 (2-H / 3-H, 6-H, 5-H, 4-H), 1.34 / 2.70, 1.46 (9-H / 7-H, 8-H), [selected experiments].



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of the reaction of **5d** and pyridine (a: py-HB(C_6F_5)$_2$)

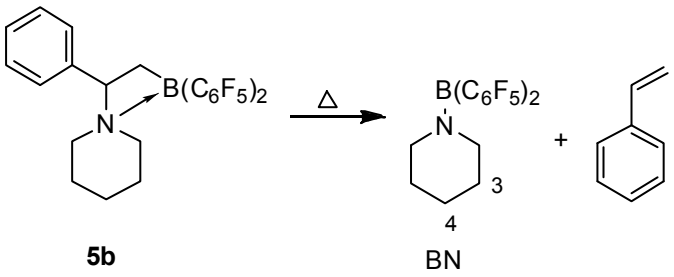


^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of the reaction of **5d** and pyridine



^{19}F NMR (564 MHz, 298 K, benzene-d_6) and ^{11}B NMR (192 MHz, 298 K, benzene-d_6) of the reaction of **5d** and pyridine

Heating of 5b



5b BN

20 mg (0.038 mmol) **5b** was dissolved in 1 ml toluene-d_8 in a sealed NMR-tube. The solution was heated for ca. 6 hours to 80 °C and then investigated by NMR spectroscopy [major products: styrene : $H_{10}C_5N$-$B(C_6F_5)_2$ ~ 1 : 1].

Styrene: **^{1}H NMR** (500 MHz, 298 K, toluene-d_8) δ = 7.14 – 6.91 (m, Ph; without assigment), 6.48 (ddm, $^3J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 10.9 Hz, 1H, $CH^{=}$), 5.51 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HH}$ = 1.0 Hz, 1H, $CH_2^{=}$), 5.00 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HH}$ = 1.0 Hz, 1H, $CH_2^{=}$).

^{13}C{^{1}H} NMR (126 MHz, 298 K, toluene-d_8) δ = 137.5 ($^{=}$CH), 113.4 ($C^{=}$), [Ph: not assigned].

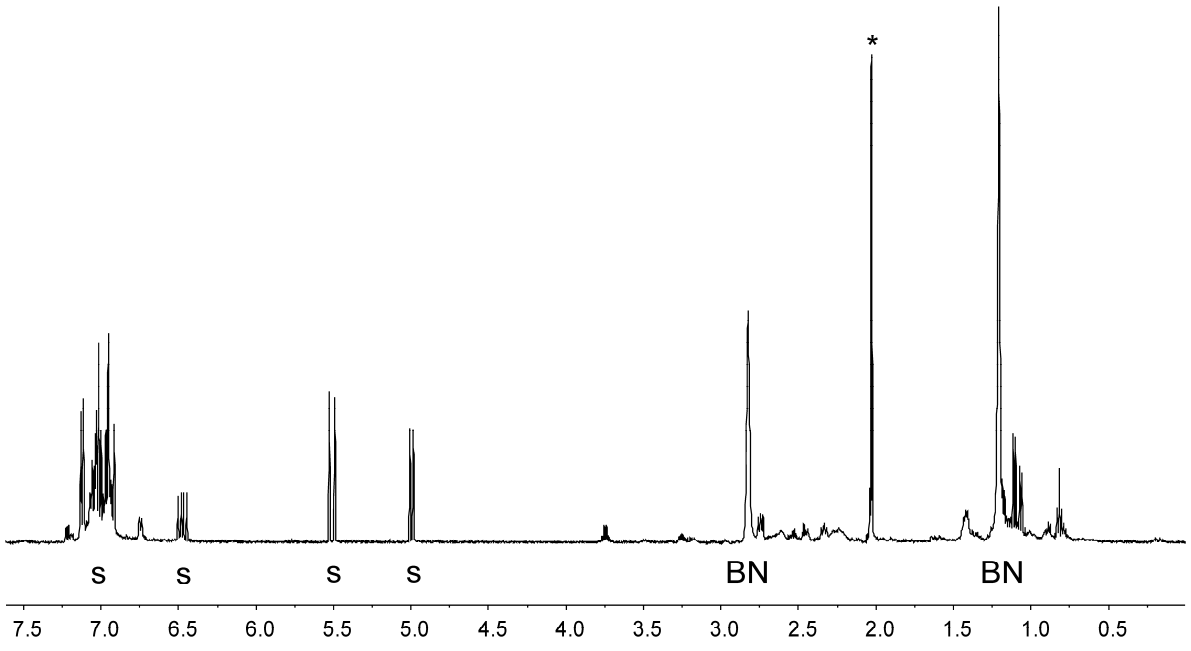
$H_{10}C_5N$-$B(C_6F_5)_2$: ^{1}H NMR (500 MHz, 298 K, toluene-d_8) δ = 2.83 (br, 4H, CH_2^N), 1.21 (br, 6H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, 298 K, toluene-d_8) δ = 51.0 (CH_2^N), 27.6 (C3), 24.6 (C4) [C_6F_5 not listed].

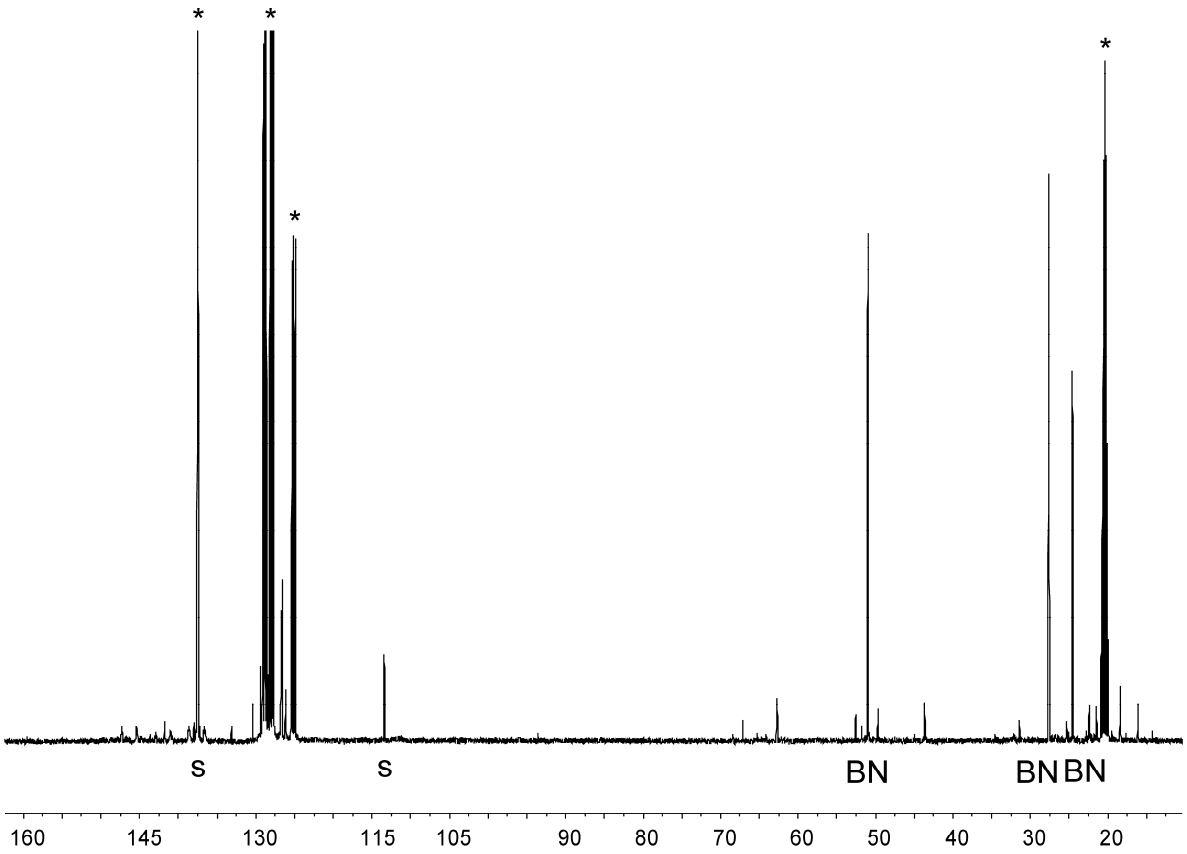
^{11}B NMR (160 MHz, 298 K, toluene-d_8) δ = 32.3 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (470 MHz, 298 K, toluene-d_8) δ = –132.5 (m, 2F, *o*-C_6F_5), –152.7 (t, ^{3}J = 21.0 Hz, 1F, *p*-C_6F_5), –161.6 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 8.9].

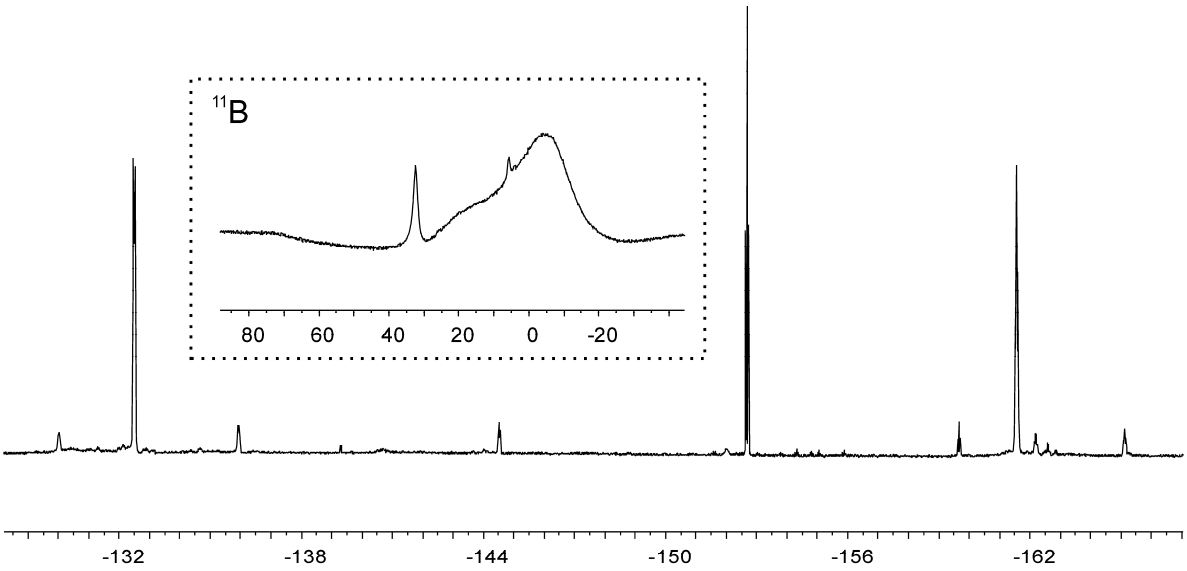
[$H_{10}C_5N$-$B(C_6F_5)_2$: See for comparison: U. Flierer, D. Leusser, H. Ott, G. Kehr, G. Erker, S. Grimme and D. Stalke, *Chem. Eur. J.,* 2009, **15**, 4595; G. Kehr, R. Fröhlich, B. Wibbeling and G. Erker, *Chem. Eur. J.,* 2000, **6**, 258.



^{1}H NMR (500 MHz, 298 K, toluene-d_8(*)) of the reaction mixture after heating of **5b** [s: styrene, BN: $H_{10}C_5N$-$B(C_6F_5)_2$]

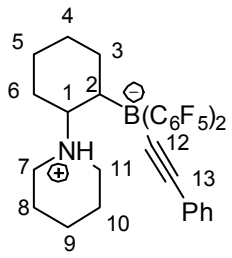


$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, toluene-d_8(*)) of the reaction mixture after heating of **5b** [s: styrene, BN: $H_{10}C_5N$-$B(C_6F_5)_2$]



^{19}F NMR (470 MHz, 298 K, toluene-d_8) and ^{11}B NMR (160 MHz, 298 K, toluene-d_8) of the reaction mixture after heating of **5b**

Synthesis of 7a



N-(cyclohex-1-enyl)piperidine (**4d**) (51 mg, 0.309 mmol) and bis(pentafluorophenyl)-borane (107 mg, 0.309 mmol) was dissolved in pentane (8 ml). Then phenylacetylene (32 mg, 0.309 mmol) was added to the solution. After a few hours of stirring a yellow solid precipitated, which was isolated by filtation and washing with pentane as a yellow solid (122 mg, 64%). Anal. Calc. for $C_{31}H_{26}BF_{10}N$: C 60.71, H 4.27, N 2.28; found: C 60.75, H 4.42, N 2.39.

Crystals suitable for X-ray crystal structure analysis were obtained by slow evapuration of a pentane solution of **7a** into toluene at -30 °C.

^{1}H NMR (600 MHz, 298 K, benzene-d_6): δ = 8.90 (br, 1H, N-H), 7.26 (m, 2H, *o*-Ph), 6.92 (m, 2H, *m*-Ph), 6.90 (m, 1H, *p*-Ph), 2.98 (m, 1H, 7-H), 2.36 (m, 1H, 1-H), 2.35 (m, 1H, 6-H)^t, 2.32 (m, 1H, 11-H), 1.85 (m, 1H, 2-H), 1.74 (m, 1H, 11′-H), 1.53 (m, 1H, 5-H)^t, 1.53 (m, 1H, 4-H)^t, 1.52 (m, 1H, 7′-H), 1.44 (m, 1H, 8-H), 1.24 (m, 1H, 10-H), 1.19 (m, 1H, 5′-H)^t, 0.97 (m, 1H, 3-H), 0.92 (m, 1H, 10′-H), 0.86 (m, 1H, 8′-H), 0.80 (m, 1H, 9-H), 0.78 (m, 1H, 4′-H)^t, 0.77 (m, 1H, 6′-H)^t, 0.75 (m, 1H, 3′-H), 0.28 (m, 1H, 9′-H), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6): δ = 131.7 (*o*-Ph), 128.6 (*m*-Ph), 127.7 (*p*-Ph), 125.7 (*i*-Ph), 109.4 (br, C12), 101.1 (br, C13), 72.7 (C1), 52.4 (C11), 46.9 (C7), 31.9 (br, C2), 31.2 (C6)^t, 27.0 (C5)^t, 26.5 (C3), 25.8 (C4)^t, 23.9 (C10), 22.2 (C8), 21.7 (C9), [C_6F_5 not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{1}H = 8.90 / 1.74, 1.52 (N-H / 11′-H, 7′-H), 7.26 / 6.92 (*o*-Ph / *m*-Ph), 2.98 / 2.32, 1.52, 1.44, 0.86 (7-H / 11-H, 7′-H, 8-H, 8′-H), 2.36 / 2.35, 1.85, 1.53, 1.19, 0.97, 0.78, 0.75 (1-H / 6-H, 2-H, 4-H, 5-H, 5′-H, 3′-H), 2.35 / 2.36, 1.85, 1.53, 1.19, 0.97, 0.77 (6-H / 1-H, 2-H, 4-H, 5-H, 5′-H, 3-H, 6′-H), 2.32 / 2.98, 1.74, 1.24, 0.92 (11-H / 7-H, 11′-H, 10-H, 10′-H), 1.85 / 2.36, 0.78, 0.75 (2-H / 1-H, 4′-H, 3′-H), 1.74 / 8.90, 2.32, 1.24, 0.92 (11′-H / N-H, 11-H, 10-H, 10′-H), 1.53 / 2.36, 2.35, 1.44, 1.19, 0.97, 0.86, 0.78, 0.77, 0.75 (4-H, 5-H / 1-H, 6-H, 8-H, 5′-H, 3-H, 8′-H, 4′-H, 6′-H, 3′-H), 1.52 / 8.90, 2.98, 1.44, 1.19, 0.97, 0.86, 0.80 (7′-H / N-H, 7-H, 8-H, 5′-H, 3-H, 8′-H, 9-H), 1.44 / 2.98, 1.52, 0.86, 0.80, 0.28 (8-H / 7-H, 7′-H, 8′-H, 9-H, 9′-H), 1.24 / 2.32, 1.74, 0.80, 0.28 (10-H / 11-H, 11′-H, 9-H, 9′-H), 1.19 / 2.35, 1.53, 0.78, 0.77, 0.75 (5′-H / 6-H, 4-H, 5-H, 4′-H, 6′-H, 3′-H), 0.97 / 2.36, 1.53, 0.78, 0.75 (3-H / 1-H, 4-H, 5-H, 4′-H, 3′-H), 0.92 / 2.32, 1.74, 1.24, 0.80, 0.28 (10′-H / 11-H, 11′-H, 10-H, 9-H, 9′-H), 0.86 / 2.98, 1.44, 0.92, 0.80, 0.28 (8′-H / 7-H, 8-H, 10′-H, 9-H, 9′-H), 0.80 / 1.52, 1.24, 0.92, 0.86, 0.28 (9-H / 7′-H, 10-H, 10′-H, 8′-H, 9′-H), 0.78 / 2.35, 1.85, 1.53, 1.19 (4′-H / 6-H, 2-H, 4-H, 5-H, 5′-H), 0.77 / 2.35, 1.85, 1.53, 1.19 (6′-H / 6-H, 2-H, 4-H, 5-H, 5′-H), 0.75 / 2.36, 1.85, 1.53, 1.19 (3′-H / 1-H, 2-H, 4-H, 5-H, 5′-H), 0.28 / 1.44, 1.24, 0.92, 0.86, 0.80 (9′-H / 8-H, 10-H, 10′-H, 8′-H, 9-H).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 7.26 / 131.7 (*o*-Ph / *o*-Ph), 6.92 / 128.6 (*m*-Ph / *m*-Ph), 6.90 / 127.7 (*p*-Ph / *p*-Ph), 2.98 / 46.9 (7-H / C7), 2.36 / 72.7 (1-H / C1), 2.35 / 31.2 (6-H /

C6), 2.32 / 52.4 (11-H / C11), 1.85 / 31.9 (2-H / C2), 1.74 / 52.4 (11′-H / C11), 1.53 / 27.0 (5-H / C5), 1.53 / 25.8 (4-H / C4), 1.52 / 46.9 (7′-H / C7), 1.44 / 22.2 (8-H / C8), 1.24 / 23.9 (10-H / C10), 1.19 / 27.0 (5′-H / C5), 0.97 / 26.5 (3-H / C3), 0.92 / 23.9 (10′-H / C10), 0.86 / 22.2 (8′-H / C8), 0.78 / 25.8 (4′-H / C4), 0.77 / 31.2 (6′-H / C6), 0.75 / 26.5 (3′-H / C3), 0.28 / 21.7 (9′-H / C9).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 7.26 / 127.7, 101.1 (*o*-Ph / *p*-Ph, C13), 6.92 / 131.7, 125.7 (*m*-Ph / *o*-Ph, *i*-Ph), 2.35 / 25.8 (6-H / C4), 1.24 / 52.4, 21.7 (10-H / C11, C9), 0.92 / 72.7 (10′-H / C1), 0.28 / 23.9 (9′-H / C10).

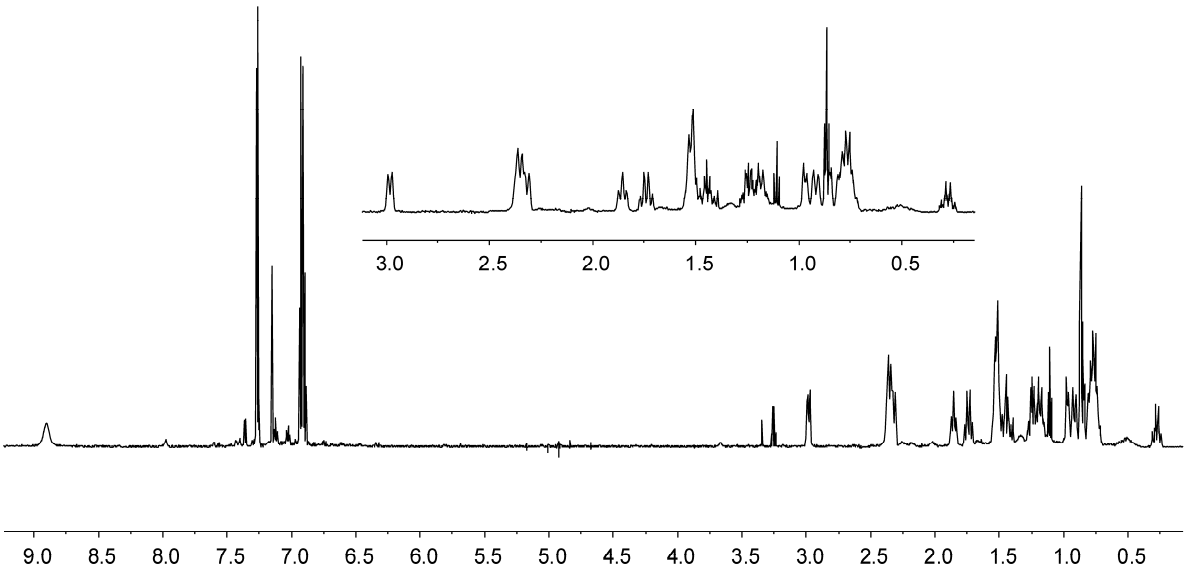
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 1.74 / 8.90, 2.98, 2.32, 1.52, 1.44, 1.24, 0.92, 0.86, 0.80, 0.28 (11′-H / N-H, 7-H, 11-H, 7′-H, 8-H, 10-H, 10′-H, 8′-H, 9-H, 9′-H), 1.19 / 2.36, 2.35, 1.85, 1.53, 0.97, 0.78, 0.77, 0.75 (5′-H / 1-H, 6-H, 2-H, 4-H, 5-H, 3-H, 4′-H, 6′-H, 3′-H) [selected experiments].

^{1}H{^{1}H} NOE (600 MHz, 298 K, benzene-d_6): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.26 / 6.92, 6.90 (*o*-Ph / *m*-Ph, *p*-Ph), 2.98 / 8.90, 1.85, 1.52, 1.44 (7-H / N-H, 2-H, 7′-H, 8-H), 2.36, 2.35 / 8.90, 1.85, 1.74, 0.80, 0.78, 0.77, 0.75 (1-H, 6-H / N-H, 2-H, 11′-H, 9-H, 4′-H, 6′-H, 3′-H), 1.85 / 8.90, 2.98, 2.36, 1.19, 0.78, 0.77, 0.75 (2-H / N-H, 7-H, 1-H, 6-H, 5′-H, 4′-H, 6′-H, 3′-H), 1.74 / 2.32, 0.97, 0.92, 0.28 (11′-H / 11-H, 3-H, 10′-H, 9′-H), 1.53, 1.52 / 2.98, 1.19, 0.97, 0.86, 0.78, 0.77, 0.75 (4-H, 5-H, 7′-H / 7-H, 5′-H, 3-H, 8′-H, 4′-H, 6′-H, 3′-H), 1.44 / 2.98, 0.86 (8-H / 7-H, 8′-H), 1.24 / 8.90, 0.92 (10-H / N-H, 10′-H), 1.19 / 2.36, 2.35, 1.85, 1.53 (5′-H / 1-H, 6-H, 2-H, 4-H, 5-H), 0.97 / 2.36, 2.35, 1.53, 0.78, 0.75 (3-H / 1-H, 6-H, 4-H, 5-H, 4′-H, 3′-H), 0.80 / 1.52 (9-H / 7′-H), 0.77 / 2.36, 2.35, 1.53, 0.97, 0.28 (6′-H / 1-H, 6-H, 4-H, 5-H, 3-H, 9′-H).

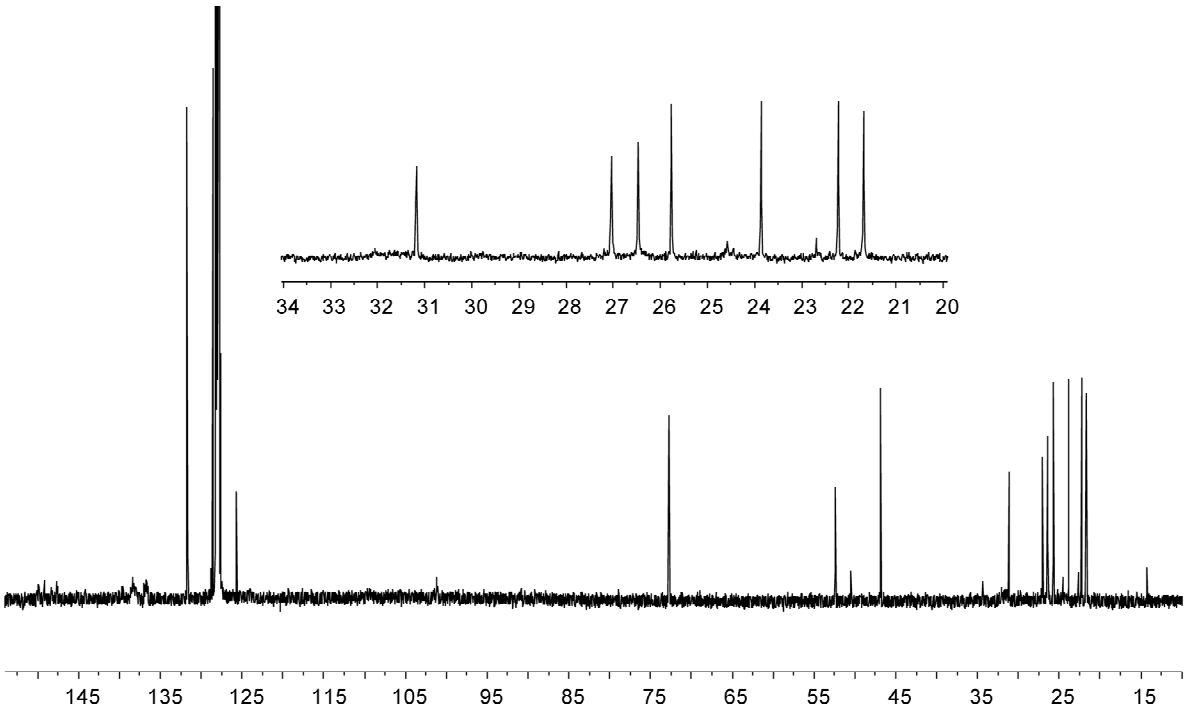
^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d_6): δ = -17.4 ($\nu_{1/2}$ ~ 50 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6): δ = -130.1 (m, 2F, *o*-$C_6F_5^A$), -133.1 (m, 2F, *o*-$C_6F_5^B$), -160.6 (t, ^{3}J = 20.9 Hz, 1F, *p*-$C_6F_5^A$), -161.9 (t, ^{3}J = 20.6 Hz, 1F, *p*-$C_6F_5^B$), -164.1 (m, 2F, *m*-$C_6F_5^A$), -165.0 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp}$ = 3.5^A, 3.1^B].

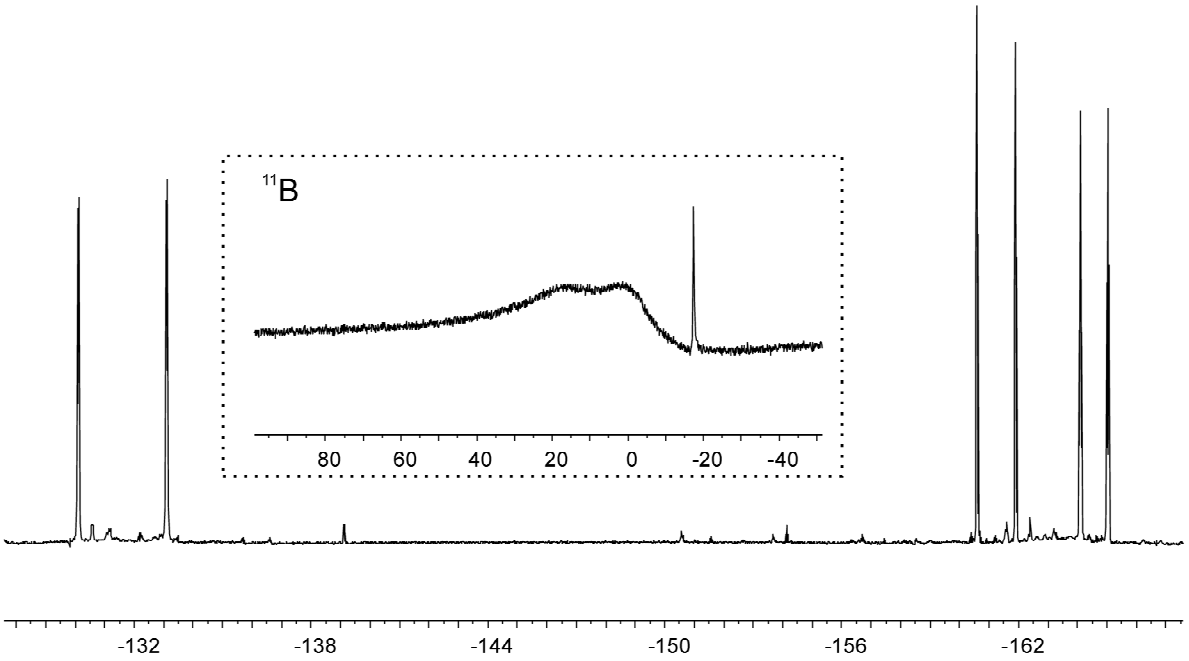
^{19}F,^{19}F GCOSY (564 MHz, 298 K, benzene-d_6): δ ^{19}F / δ ^{19}F = -164.1 / -130.1, -160.6 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), -165.0 / -133.1, -161.9 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **7a**.

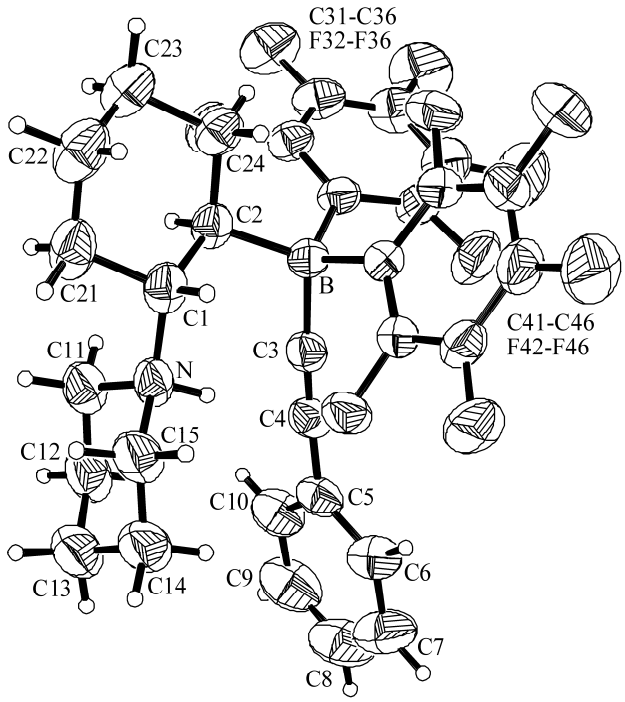


^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of **7a**.

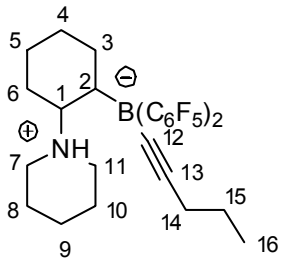


^{19}F NMR (564 MHz, 298 K, benzene-d$_6$) and ^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d$_6$) of **7a**.

Crystal data for $C_{31}H_{26}BF_{10}N$ * C_7H_8 (**7a**), M = 705.47, monoclinic, $P2_1/n$ (No. 14), a = 13.6638(3), b = 16.1258(5), c = 16.8550(6) Å, β = 111.633(1)°, V = 3452.2(2) Å^3, D_c = 1.357 g cm^{-3}, μ = 1.000 mm^{-1}, F(000) = 1456, Z = 4, λ = 1.54178 Å, T = 223(2) K, 46576 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6118 independent (R_{int} = 0.052), and 5222 observed reflections [I ≥ 2σ(I)], 440 refined parameters, R = 0.055, wR^2 = 0.159, GoF = 1.032.



Synthesis of 7b



N-(cyclohex-1-enyl)piperidine (**4d**) (58 mg, 0.353 mmol) and bis(pentafluorophenyl)-borane (122 mg, 0.355 mmol) were dissolved in pentane (5 ml). Then 1-pentyne (35 µl, 23.8 mg, 0.354 mmol) was added. After 5 minutes a yellow solid precipitated. After stirring for another 1.5 hours the supernatand liquid was removed and the product **7b** was isolated as a red solid (119 mg, 59%). Anal. Calc. for $C_{28}H_{28}BF_{10}N$: C 58.05, H 4.87, N 2.42; found: C 58.06, H 4.93, N 2.37. Crystal suitable for X-ray crystal structure analysis were obtained by slow evaporation of a pentane / dichloromethane solution of **7b** at -30 °C.

^{1}H NMR (600 MHz, 298 K, benzene-d_6): δ = 9.42 (br, 1H, N-H), 2.93 (m, 1H, 7-H), 2.34 (m, 1H, 11-H), 2.33 (m, 1H, 1-H), 2.32 (m, 1H, 3-H), 1.86 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H, 14-H), 1.76 (m, 1H, 11′-H), 1.71 (m, 1H, 2-H), 1.54 (m, 1H, 7′-H), 1.51 (m, 2H, 5-H, 6-H)^{t}, 1.45 (m, 1H, 8-H), 1.35 (m, 2H, 15-H), 1.29 (m, 1H, 10-H), 1.16 (m, 1H, 6′-H)^{t}, 1.09 (m, 1H, 9-H), 1.02 (m, 1H, 10′-H), 0.99 (m, 1H, 8′-H), 0.98 (m, 1H, 4-H)^{t}, 0.84 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, 16-H), 0.77 (m, 1H, 5′-H)^{t}, 0.74 (m, 1H, 4′-H)^{t}, 0.69 (m, 1H, 3′-H), 0.45 (m, 1H, 9′-H), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6): δ = 101.3 (br, C13), 72.6 (C1), 52.3 (C11), 46.7 (C7), 31.4 (br, C2), 31.0 (C3), 27.0 (C6)^{t}, 26.3 (C4)^{t}, 25.8 (C5)^{t}, 23.9 (C10), 23.1 (C14), 22.9 (C15), 22.3 (C8), 21.9 (C9), 13.3 (C16), n.o. (C12), [C_6F_5 not observed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{1}H = 2.93 / 2.34, 1.54, 1.45, 1.09, 0.99 (7-H / 11-H, 7′-H, 8-H, 9-H, 8′-H), 2.34 / 2.93, 1.76, 1.54, 1.29, 1.02, 0.99 (11-H / 7-H, 11′-H, 7′-H, 10-H, 10′-H, 8′-H), 2.33 / 1.71, 1.51, 1.16, 0.98, 0.77, 0.74, 0.69 (1-H / 2-H, 5-H, 6-H, 6′-H, 4-H, 5′-H, 4′-H, 3′-H), 2.32 / 1.71, 1.51, 1.16, 0.98, 0.77, 0.74, 0.69 (3-H / 2-H, 5-H, 6-H, 6′-H, 4-H, 5′-H, 4′-H, 3′-H), 1.86 / 1.35 (14-H / 15-H), 1.76 / 9.42, 2.34, 1.29, 1.02 (11′-H / N-H, 11-H, 10-H, 10′-H), 1.71 / 2.33, 2.32, 0.69 (2-H / 1-H, 3-H, 3′-H), 1.54 / 9.42, 2.93, 2.34, 1.45, 1.09, 0.99 (7′-H / N-H, 7-H, 11-H, 8-H, 9-H, 8′-H), 1.51 / 2.33, 2.32, 1.16, 0.98, 0.77, 0.74, 0.69 (5-H, 6-H / 1-H, 3-H, 6′-H, 4-H, 5′-H, 4′-H, 3′-H), 1.45 / 2.93, 1.54, 1.09, 1.02, 0.99, 0.45 (8-H / 7-H, 7′-H, 9-H, 10′-H, 8′-H, 9′-H), 1.35 / 1.86, 0.84 (15-H / 14-H, 16-H), 1.29 / 2.34, 1.76, 1.09, 1.02, 0.45 (10-H / 11-H, 11′-H, 9-H, 10′-H, 9′-H), 1.16 / 2.33, 1.51 (6′-H / 1-H, 5-H, 6-H), 1.09 / 1.45, 1.29, 1.02, 0.45 (9-H / 8-H, 10-H, 10′-H, 9′-H), 1.02 / 2.34, 1.76, 1.29, 1.09, 0.45 (10′-H / 11-H, 11′-H, 10-H, 9-H, 9′-H), 0.99 / 2.93, 1.54, 1.45 (8′-H / 7-H, 7′-H, 8-H), 0.98 / 1.51, 0.77, 0.74 (4-H / 5-H, 5′-H, 4′-H), 0.84 / 1.35 (16-H / 15-H), 0.77 / 1.51, 1.16 (5′-H / 5-H, 6-H, 6′-H), 0.74 / 1.51 (4′-H / 5-H), 0.69 / 2.32, 1.71, 0.98 (3′-H / 3-H, 2-H, 4-H), 0.45 / 1.45, 1.29, 1.09, 1.02 (9′-H / 8-H, 10-H, 9-H, 10′-H).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 2.93 / 46.7 (7-H / C7), 2.34 / 52.3 (11-H / C11), 2.33 / 72.6 (1-H / C1), 2.32 / 31.0 (3-H / C3), 1.86 / 23.1 (14-H / C14), 1.76 / 52.3 (11′-H / C11), 1.54 / 46.7 (7′-H / C7), 1.51 / 27.0 (6-H / C6), 1.51 / 25.8 (5-H / C5), 1.45 / 22.3 (8-H / C8), 1.35 / 22.9 (15-H /

C15), 1.29 / 23.9 (10-H / C10), 1.16 / 27.0 (6′-H / C6), 1.09 / 21.9 (9-H / C9), 1.02 / 23.9 (10′-H / C10), 0.99 / 22.3 (8′-H / C8), 0.98 / 26.3 (4-H / C4), 0.84 / 13.3 (16-H / C16), 0.77 / 25.8 (5′-H / C5), 0.74 / 26.3 (4′-H / C4), 0.69 / 31.0 (3′-H / C3), 0.45 / 21.9 (9′-H / C9).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 1.86 / 101.3, 22.9, 13.3 (14-H / C13, C15, C16), 0.69 / 25.8 (3′-H / C5).

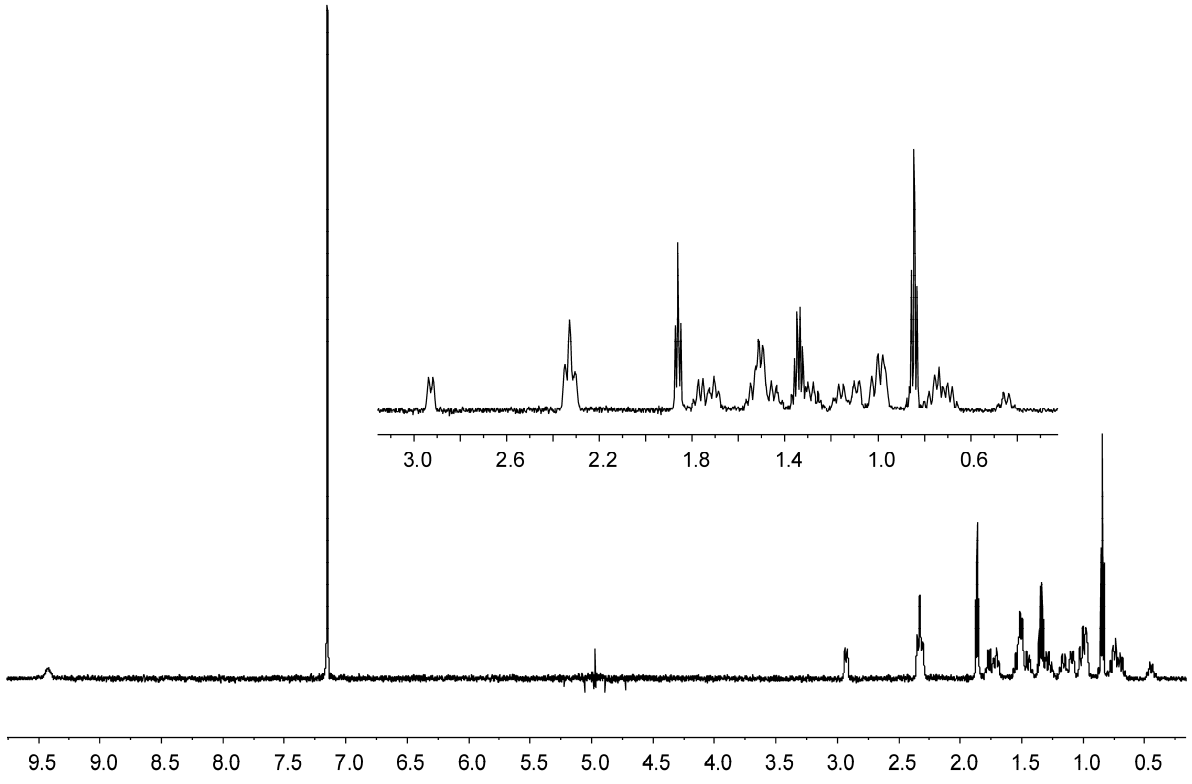
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.93 / 9.42, 2.34, 1.76, 1.45, 1.29, 1.09, 1.02, 0.99, 0.45 (7-H / N-H, 11-H, 11′-H, 8-H, 10-H, 9-H, 10′-H, 8′-H, 9′-H), 1.86 / 1.35, 0.84 (14-H / 15-H, 16-H), 0.77 / 2.33, 2.32, 1.71, 1.51, 1.16, 0.98, 0.74 (5′-H / 1-H, 3-H, 2-H, 5-H, 6-H, 6′-H, 4-H, 4′-H) [selected experiments].

^{1}H{^{1}H} NOE (600 MHz, 298 K, benzene-d_6): δ$^{1}H_{irr}$ / δ$^{1}H_{res}$ = 2.93 / 1.71, 1.54, 1.45 (7-H / 2-H, 7′-H, 8-H), 2.34, 2.32 / 1.76, 0.69 (11-H, 3-H / 11′-H, 3′-H), 1.71 / 2.93, 2.33, 2.32 (2-H / 7-H, 1-H, 3-H), 1.54, 1.51 / 1.16, 0.77, 0.74 (7′-H, 5-H, 6-H / 6′-H, 4′-H, 5′-H), 1.35 / 1.86, 0.84 (15-H / 14-H, 16-H), 0.99, 0.98 / 2.32, 1.76, 1.54, 1.51, 1.45, 1.29, 0.77, 0.45 (8′-H, 4-H / 1-H, 3-H, 11-H, 11′-H, 7′-H, 5-H, 6-H, 8-H, 10-H, 5′-H, 9′-H), 0.77, 0.74 / 2.33, 2.32 (5′-H, 4′-H / 1-H, 3-H).

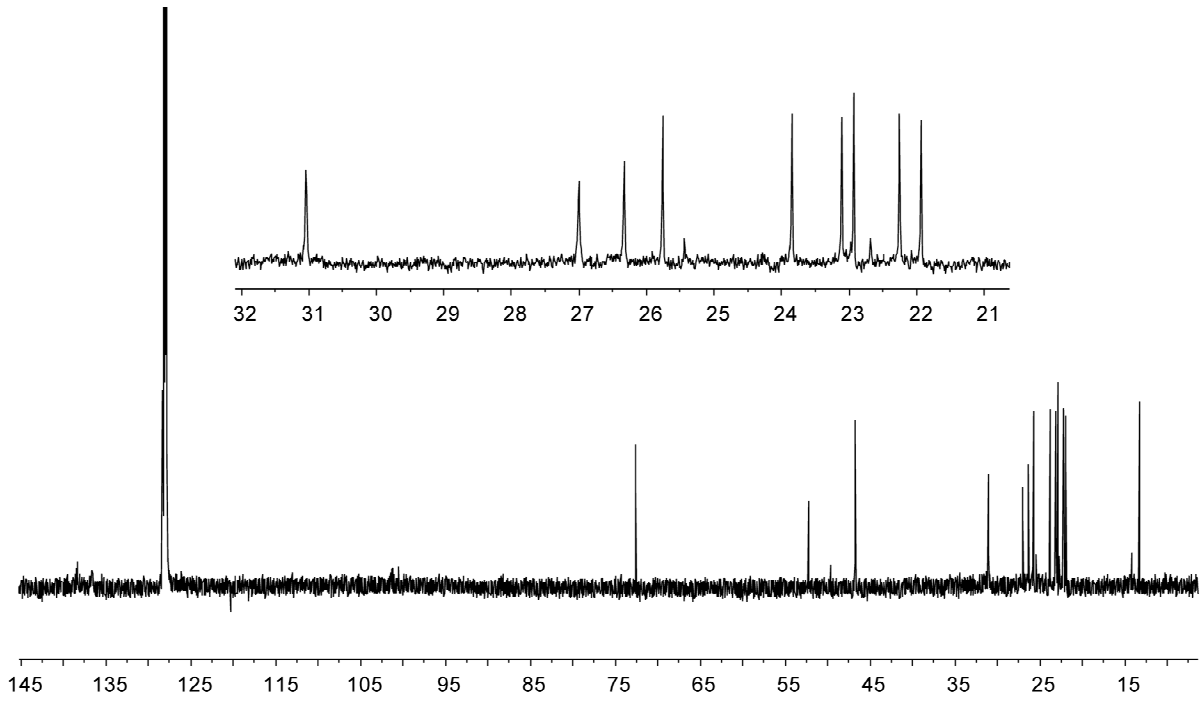
^{11}B{^{1}H} NMR (64 MHz, 298 K, benzene-d_6): δ = –17.8 ($\nu_{1/2}$ ~ 40 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6): δ = -130.0 (m, 2F, *o*-$C_6F_5^A$), -133.3 (m, 2F, *o*-$C_6F_5^B$), -161.0 (t, ^{3}J = 21.1 Hz, 1F, *p*-$C_6F_5^A$), -162.7 (t, ^{3}J = 20.6 Hz, 1F, *p*-$C_6F_5^B$), -164.6 (m, 2F, *m*-$C_6F_5^A$), -165.6 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp}$ = 3.6^A, 2.9^B].

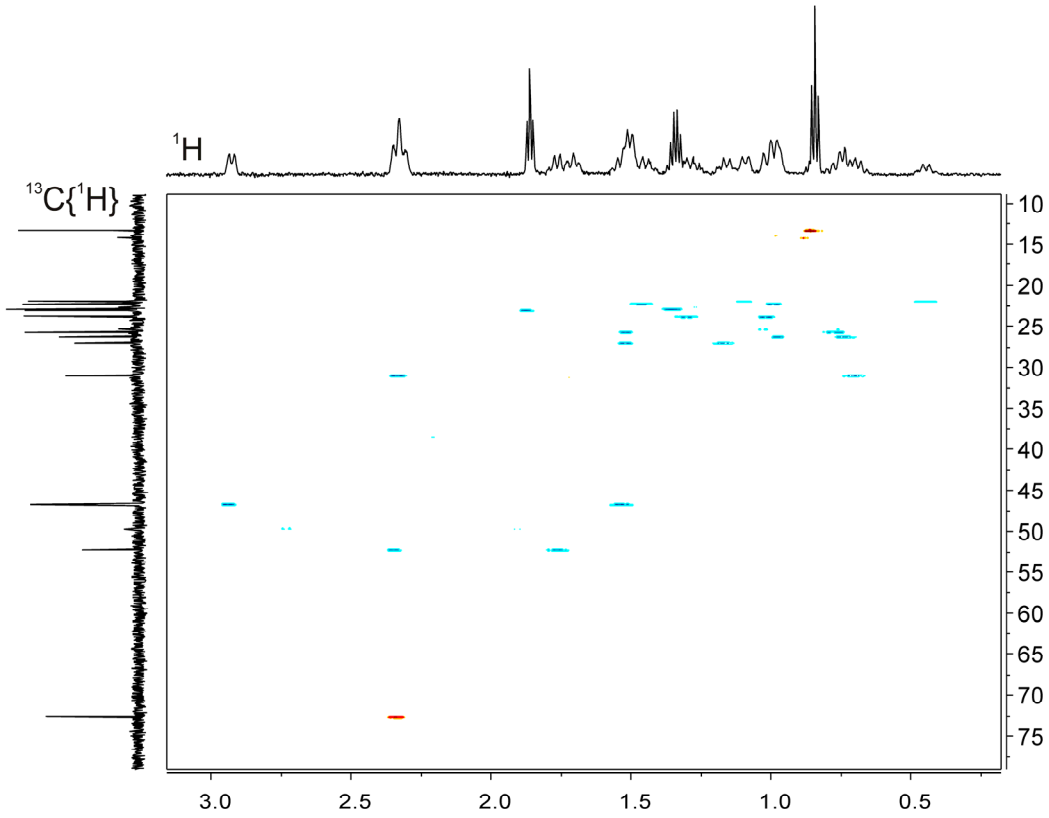
^{19}F,^{19}F GCOSY (470 MHz, 298 K, benzene-d_6): δ ^{19}F / δ ^{19}F = -164.6 / -130.0, -161.0 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), -165.6 / -133.3, -162.7 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



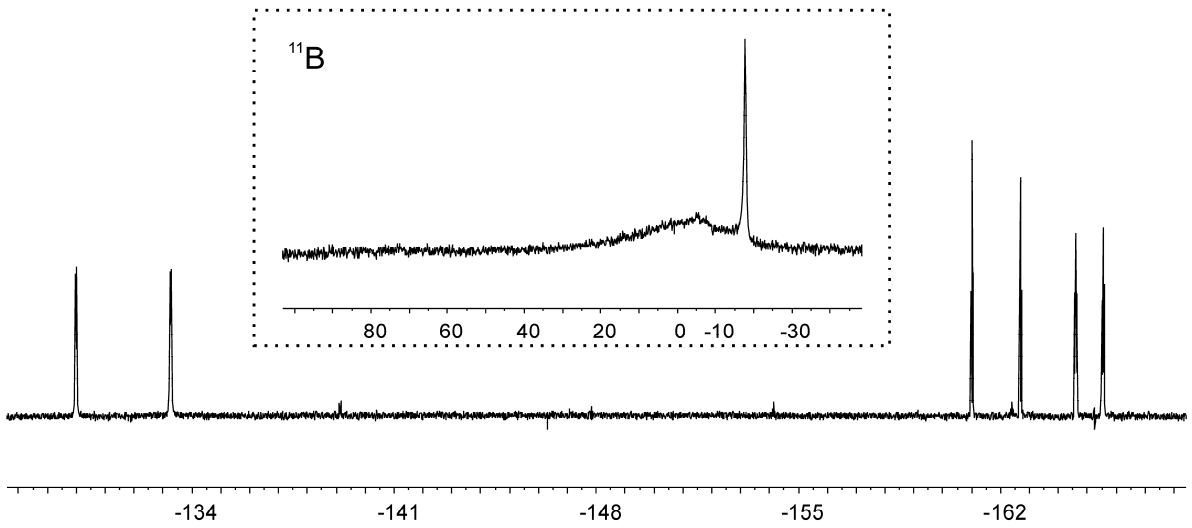
^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **7b**



^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of **7b**

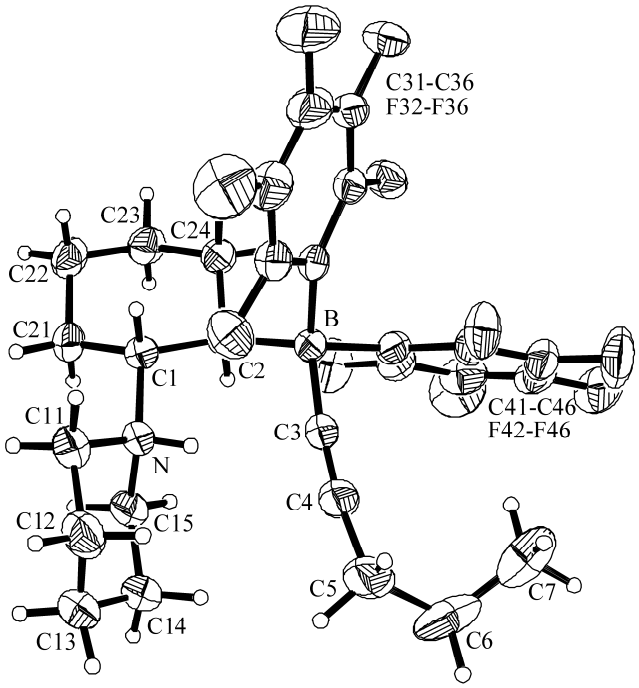


GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6; projections: ^{1}H and ^{13}C{^{1}H} NMR spectrum) of **7b**

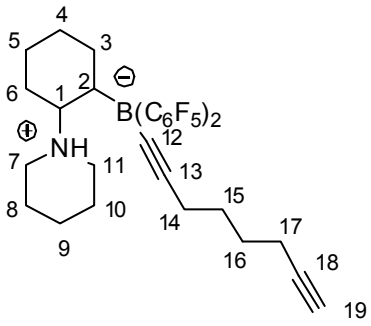


^{19}F NMR (470 MHz, 298 K, benzene-d_6) and ^{11}B{^{1}H} NMR (64 MHz, 298 K, benzene-d_6) of **7b**

Crystal data for $C_{28}H_{28}BF_{10}N$ (**7b**), M = 579.32, monoclinic, $C2/c$ (No. 15), a = 18.8907(6), b = 17.3259(6), c = 16.9954(6) Å, β = 105.094(3)°, V = 5370.7(3) Å^3, D_c = 1.433 g cm^{-3}, μ = 1.151 mm^{-1}, F(000) = 2384, Z = 8, λ = 1.54178 Å, T = 223(2) K, 35670 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4766 independent (R_{int} = 0.049), and 4231 observed reflections [I ≥ 2σ(I)], 373 refined parameters, R = 0.041, wR^2 = 0.114, GoF = 1.014.



Synthesis of 7c



N-(cyclohex-1-enyl)piperidine (**4d**) (32 mg, 0.197 mmol) and bis(pentafluorophenyl)borane (68 mg, 0.197 mmol) was dissolved in pentane (4 ml). Then 1,7-octadiyne (41 mg, 0.387 mmol, 2 eq) was added. After keeping it for 3 days at -30 °C white crystals were built. The solvent was removed and the product **7c** isolated as a yellow solid (62 mg, 49%). Anal. Calc. for $C_{31}H_{30}BF_{10}N$: C 60.31, H 4.90, N 2.27; found: C 60.26, H 5.05, N 2.30. Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a pentane / dichloromethane solution of **7c** at -30 °C.

^{1}H NMR (600 MHz, 298 K, benzene-d_6): δ = 9.32 (br, 1H, N-H), 2.91 (m, 1H, 7-H), 2.33 (m, 1H, 11-H), 2.32 (m, 1H, 1-H), 2.30 (m, 1H, 3-H), 1.91 (m, 2H, 17-H), 1.86 (m, 2H, 14-H), 1.76 (m, 1H, 11′-H), 1.75 (t, $^{4}J_{HH}$ = 2.6 Hz, 1H, 19-H), 1.69 (m, 1H, 2-H), 1.54 (m, 1H, 7′-H), 1.50 (m, 2H, 4-H, 5-H)^{t}, 1.43 (m, 1H, 8-H), 1.40 (m, 2H, 16-H), 1.39 (m, 2H, 15-H), 1.29 (m, 1H, 10-H), 1.16 (m, 1H, 5′-H)^{t}, 1.12 (m, 1H, 9-H), 1.03 (m, 1H, 10′-H), 1.00 (m, 1H, 8′-H), 0.97 (m, 1H, 6-H)^{t}, 0.77 (m, 1H, 4′-H)^{t}, 0.72 (m, 1H, 6′-H)^{t}, 0.69 (m, 1H, 3′-H), 0.45 (m, 1H, 9′-H), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6): δ = 100.8 (br, C13), 83.8 (C18), 72.6 (C1), 68.8 (C19), 52.3 (C11), 46.7 (C7), 31.4 (br, C2), 31.0 (C3), 28.2 (C16), 27.4 (C15), 27.0 (C5)^{t}, 26.3 (C6)^{t}, 25.8 (C4)^{t}, 23.9 (C10), 22.3 (C8), 21.9 (C9), 20.4 (C14), 17.9 (C17), n.o. (C12), [C_6F_5 not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{1}H = 9.32 / 1.76, 1.54 (N-H / 11′-H, 7′-H), 2.91 / 2.33, 1.54, 1.03, 1.00 (7-H / 11-H, 7′-H, 10′-H, 8′-H), 2.33 / 2.91, 1.76, 1.29, 1.03, 1.00 (11-H / 7-H, 11′-H, 10-H, 10′-H, 8′-H), 2.32 / 1.69, 0.97, 0.72 (1-H / 2-H, 6-H, 6′-H), 2.30 / 1.69, 1.50, 0.69 (3-H / 2-H, 4-H, 3′-H), 1.91 / 1.40, 1.39 (17-H / 16-H, 15-H), 1.86 / 1.40, 1.39 (14-H / 16-H, 15-H), 1.76 / 9.32, 2.32, 1.03 (11′-H / N-H, 1-H, 10′-H), 1.69 / 0.69 (2-H / 3′-H), 1.54 / 9.32, 2.91 (7′-H / N-H, 7-H), 1.50 / 2.30, 0.97, 0.77, 0.69 (4-H, 5-H / 3-H, 6-H, 4′-H, 3′-H), 1.43 / 2.91, 1.12, 1.03, 1.00, 0.45 (8-H / 7-H, 9-H, 10′-H, 8′-H, 9′-H), 1.29 / 2.33, 1.76, 1.12, 1.00, 0.45 (10-H / 11-H, 11′-H, 9-H, 8′-H, 9′-H), 1.16 / 2.32, 1.50, 0.77 (5′-H / 1-H, 4-H, 5-H, 4′-H), 1.12 / 1.43, 1.29, 1.03, 1.00, 0.45 (9-H / 8-H, 10-H, 10′-H, 8′-H, 9′-H), 1.03 / 2.33, 1.76, 1.29, 1.12, 0.45 (10′-H / 11-H, 11′-H, 10-H, 9-H, 9′-H), 1.00 / 2.91, 1.12, 0.45 (8′-H / 7-H, 9-H, 9′-H), 0.97 / 2.32, 1.50, 0.72 (6-H / 1-H, 4-H, 5-H, 6′-H), 0.77 / 2.30, 1.50, 1.16, 0.97 (4′-H / 3-H, 4-H, 5-H, 5′-H, 6-H), 0.72 / 2.32, 1.69, 1.50 (6′-H / 1-H, 2-H, 5-H), 0.69 / 2.30, 1.69, 1.50 (3′-H / 3-H, 2-H, 4-H), 0.45 / 1.43, 1.29, 1.12, 1.03, 1.00 (9′-H / 8-H, 10-H, 9-H, 10′-H, 8′-H).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 2.91 / 46.7 (7-H / C7), 2.33 / 52.3 (11-H / C11), 2.32 / 72.6 (1-H / C1), 2.30 / 31.0 (3-H / C3), 1.91 / 17.9 (17-H / C17), 1.86 / 20.4 (14-H / C14), 1.76 / 52.3 (11′-H / C11), 1.75 / 68.8 (19-H / C19), 1.69 / 31.4 (2H / C2), 1.54 / 46.9 (7′-H / C7), 1.50 / 27.0 (5-

H / C5), 1.50 / 25.8 (4-H / C4), 1.43 / 22.3 (8-H / C8), 1.40 / 28.2 (16-H / C16), 1.39 / 27.4 (15-H / C15), 1.29 / 23.9 (10-H / C10), 1.16 / 27.0 (5′-H / C5), 1.12 / 21.9 (9-H / C9), 1.03 / 23.9 (10′-H / C10), 1.00 / 22.3 (8′-H / C8), 0.97 / 26.3 (6-H / C6), 0.77 / 25.8 (4′-H / C4), 0.72 / 26.3 (6′-H / C6), 0.69 / 31.0 (3′-H / C3), 0.45 / 21.9 (9′-H / C9).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 1.91 / 83.8, 68.8 (17-H / C18, C19), 1.86 / 100.8, 28.2, 27.4 (14-H / C13, C16, C15), 1.54 / 68.8 (7′-H / C19), 1.40, 1.39 / 100.8, 83.8, 20.4, 17.9 (16-H, 15-H / C13, C18, C14, C17).

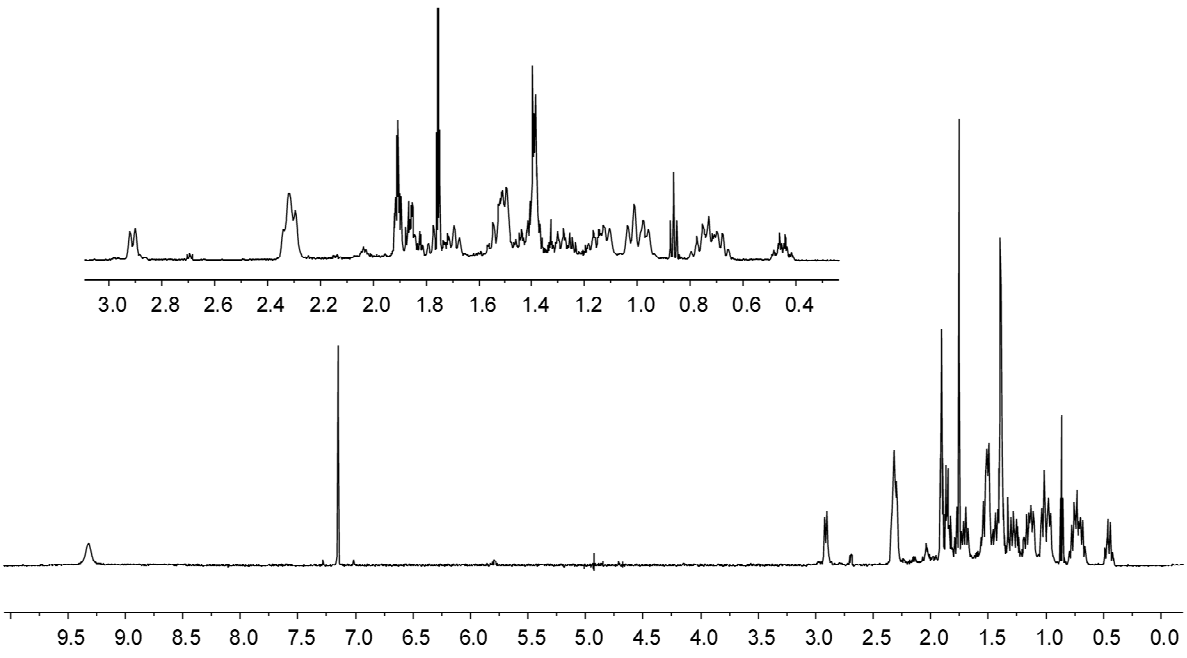
^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.91 / 9.32, 2.33, 1.76, 1.54, 1.43, 1.29, 1.12, 1.03, 1.00, 0.45 (7-H / N-H, 11-H, 11′-H, 7′-H, 8-H, 10-H, 9-H, 10′-H, 8′-H, 9′-H), 1.91 / 1.86, 1.75, 1.40, 1.39 (17-H / 14-H, 19-H, 16-H, 15-H), 1.69 / 2.32, 2.30, 1.50, 1.16, 0.97, 0.77, 0.72, 0.69 (2-H / 1-H, 3-H, 4-H, 5-H, 5′-H, 6-H, 4′-H, 6′-H, 3′-H), [selected experiments].

^{1}H{^{1}H} NOE (600 MHz, 298 K, benzene-d_6): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.91 / 9.32, 1.69, 1.54, 1.43 (7-H / N-H, 2-H, 7′-H, 8-H), 2.33 / 9.32, 1.76, 0.72 (11-H / N-H, 11′-H, 6′-H), 1.91 / 1.40, 1.39 (17-H / 16-H, 15-H), 1.85 / 1.40, 1.39, 1.91 (14-H / 16-H, 15-H, 17-H), 1.76 / 2.33, 0.97 (11′-H / 11-H, 6-H), 1.69 / 2.91, 2.32, 2.30, 1.16 (2-H / 7-H, 1-H, 3-H, 5′-H), 1.50 / 2.91, 1.16, 0.77 (4-H, 5-H / 7-H, 5′-H, 4′-H), 1.40, 1.39 / 1.91, 1.86 (16-H, 15-H / 17-H, 14-H), 0.97 / 2.32, 1.76, 1.54, 1.43, 1.29, 0.77, 0.45 (6-H / 1-H, 11′-H, 7′-H, 8-H, 10-H, 4′-H, 9′-H), 0.77 / 2.32, 2.30, 1.50, 0.97 (4′-H / 1-H, 3-H, 4-H, 5-H, 6-H), 0.45 / 1.76, 1.54, 1.12, 1.03, 1.00 (9′-H / 11′-H, 7′-H, 9-H, 10′-H, 8′-H).

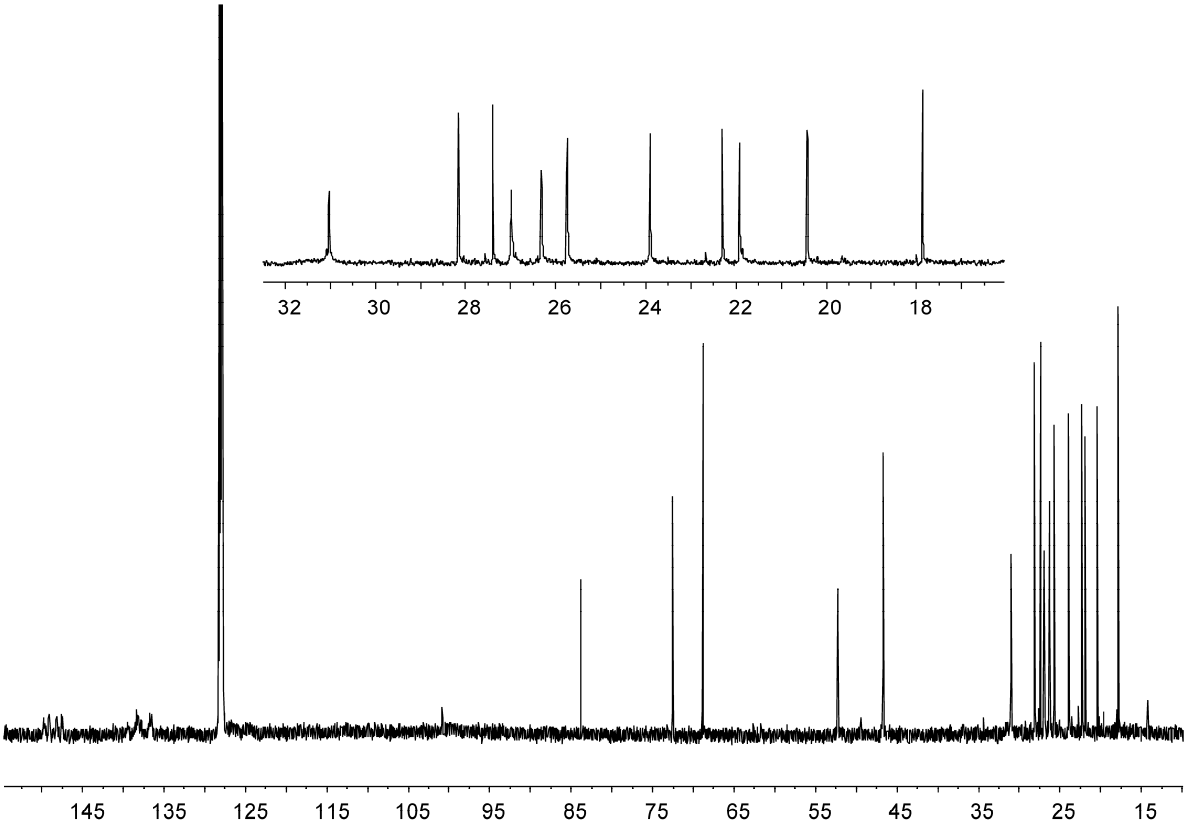
^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d_6): δ = -17.7 ($\nu_{1/2}$ ~ 50 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6): δ = -130.0 (m, 2F, *o*-$C_6F_5^A$), -133.4 (m, 2F, *o*-$C_6F_5^B$), -160.9 (t, ^{3}J = 20.9 Hz, 1F, *p*-$C_6F_5^A$), -162.4 (t, ^{3}J = 20.8 Hz, 1F, *p*-$C_6F_5^B$), -164.5 (m, 2F, *m*-$C_6F_5^A$), -165.4 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp}$ = 3.6^A, 3.0^B].

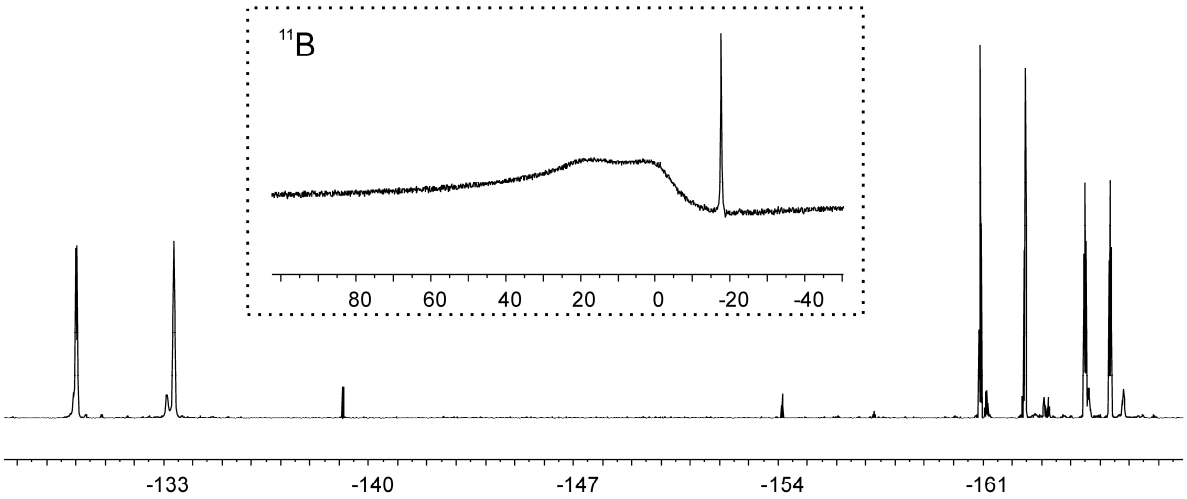
^{19}F,^{19}F GCOSY (564 MHz, 298 K, benzene-d_6): δ ^{19}F / δ ^{19}F = -164.5 / -130.0, -160.9 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), -165.4 / -133.4, -162.4 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **7c**

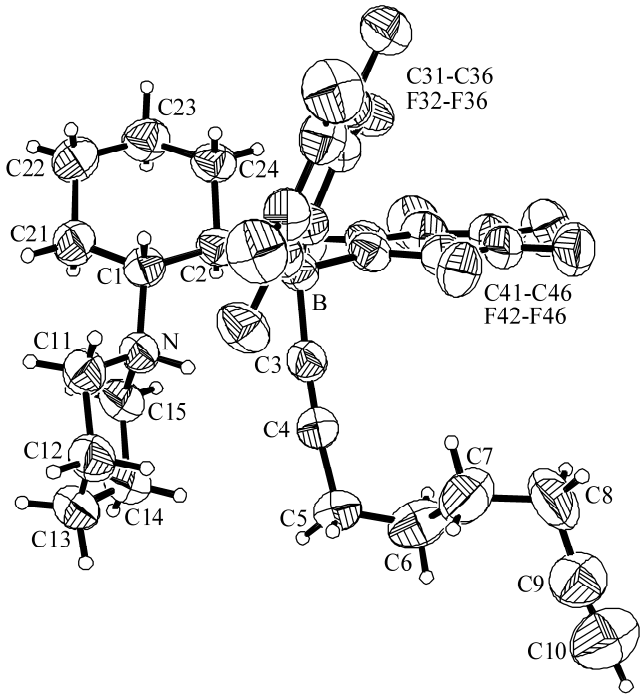


^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of **7c**

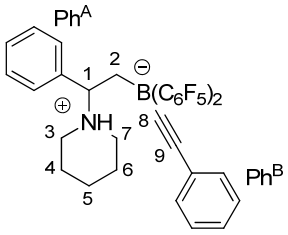


^{19}F NMR (564 MHz, 298 K, benzene-d$_6$) and ^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d$_6$) of **7c**.

Crystal data for $C_{31}H_{30}BF_{10}N$ (**7c**), M = 617.37, monoclinic, $P2_1/c$ (No. 14), a = 10.4501(9), b = 15.2692(9), c = 18.6614(7) Å, β = 105.576(3)°, V = 2868.3(3) Å^3, D_c = 1.430 g cm^{-3}, μ = 1.116 mm^{-1}, $F(000)$ = 1272, Z = 4, λ = 1.54178 Å, T = 223(2) K, 21958 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4751 independent (R_{int} = 0.061), and 3163 observed reflections [I ≥ 2σ(I)], 401 refined parameters, R = 0.054, wR^2 = 0.155, GoF = 1.031.



Synthesis of 8



Compound **5b** (53.3 mg, 0.100 mmol) was treated with 1-pentyne (10.3 mg, 0.100 mmol) in pentane (4 mL). After keeping it for 3 days at -30 °C white crystalls were formed. The solvent was removed and the product **8** isolated as a yellow solid (37 mg, 58%). Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a pentane / dichloromethane solution of **8** at -30 °C.

^{1}H NMR (500 MHz, 298 K, benzene-d_6): δ = 8.92 (br, 1H, N-H), 7.41 (m, 2H, *o*-Ph^B), 7.05 (m, 1H, *p*-Ph^A), 6.99 (m, 4H, *m*-$Ph^{A,B}$), 6.95 (m, 1H, *p*-Ph^B), 6.80 (m, 2H, *o*-Ph^A), 4.00 (m, 1H, 1-H), 2.99 (m, 1H, 7-H), 2.53 (m, 1H, 3-H), 2.06 (m, 1H, 2-H), 1.85 (m, 1H, 2′-H), 1.74 (m, 1H, 3′-H), 1.23 (m, 1H, 7′-H), 1.20 (m, 1H, 4-H)^t, 1.06 (m, 1H, 6-H)^t, 0.76 (m, 1H, 4′-H)^t, 0.73 (m, 1H, 6′-H)^t, 0.61 (m, 1H, 5-H), –0.19 (m, 1H, 5′-H), [^{t} tentative assignment].

^{13}C{^{1}H} NMR (126 MHz, 298 K, benzene-d_6): δ = 134.2 (*i*-Ph^A), 131.8 (*o*-Ph^B), 130.3 (*o*-Ph^A), 129.8 (*p*-Ph^A), 128.8 (*m*-Ph^A), 128.7 (*m*-Ph^B), 127.7 (*p*-Ph^B), 125.6 (*i*-Ph^B), 101.0 (br, C9), 75.1 (C1), 53.7 (C3), 46.5 (C7), 24.3 (br, C2), 23.7 (C6)^t, 22.8 (C4)^t, 21.2 (C5), n.o. (C8), [C_6F_5 not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{1}H = 6.99 / 6.80 (*m*-Ph^A / *o*-Ph^A), 6.80 / 7.05, 6.99 (*o*-Ph^A / *p*-Ph^A, *m*-Ph^A), 4.00 / 2.06 (1-H / 2-H), 2.99 / 1.23 (7-H / 7′-H), 2.53 / –0.19 (3-H / 5′-H), 2.06 / 4.00, 1.85, –0.19 (2-H / 1-H, 2′-H, 5′-H), 1.23 / 0.73 (7′-H / 6′-H), 0.73 / 6.80, 1.06 (6′-H / *o*-Ph^A, 6-H), –0.19 / 0.76, 0.73 (5′-H / 4′-H, 6′-H).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 7.41 / 131.8 (*o*-Ph^B / *o*-Ph^B), 7.05 / 129.8 (*p*-Ph^A/ *p*-Ph^A), 6.99 / 128.8, 128.7 (*m*-$Ph^{A,B}$ / *m*-$Ph^{A,B}$), 6.95 / 127.7 (*p*-Ph^B / *p*-Ph^B), 6.80 / 130.3 (*o*-Ph^A / *o*-Ph^A), 4.00 / 75.1 (1-H / C1), 2.99 / 46.5 (7-H / C7), 2.53 / 53.7 (3-H / C3), 2.06 / 24.3 (2-H / C2), 1.85 / 24.3 (2′-H / C2), 1.74 / 53.7 (3′-H / C3), 1.23 / 46.5 (7′-H / C7), 1.20 / 22.8 (4-H /C4), 1.06 / 23.7 (6-H / C6), 0.76 / 22.8 (4′-H / C4), 0.73 / 23.7 (6′-H / C6), 0.61 / 21.2 (5-H / C5), –0.19 / 21.2 (5′-H / C5).

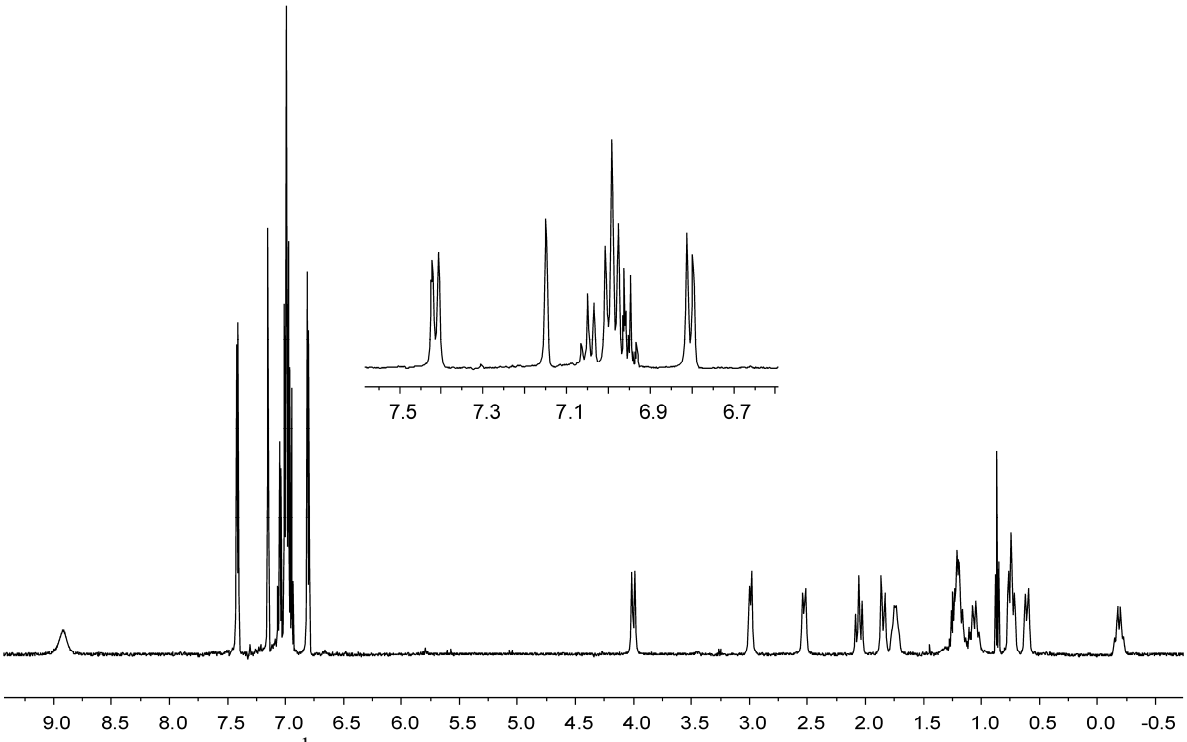
^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, 298 K, benzene-d_6): δ ^{1}H / δ ^{13}C = 7.41 / 127.7, 101.0 (*o*-Ph^B / *p*-Ph^B, C9), 7.05 / 130.3 (*p*-Ph^A / *o*-Ph^A), 6.99 / 134.2, 125.6 (*m*-$Ph^{A,B}$ / *i*-Ph^A, *i*-Ph^B), 6.95 / 131.8 (*p*-Ph^B / *o*-Ph^B), 6.80 / 128.8, 75.1 (*o*-Ph^A / *m*-Ph^A, C1), 4.00 / 134.2, 130.3 (1-H / *i*-Ph^A, *o*-Ph^A), 2.06 / 75.1 (2-H / C1).

^{1}H{^{1}H} TOCSY (500 MHz, 298 K, benzene-d_6): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.41 / 6.99, 6.95 (*o*-Ph^B / *m*-Ph^B, *p*-Ph^B), 6.80 / 7.05, 6.99 (*o*-Ph^A / *p*-Ph^A, *m*-Ph^A).

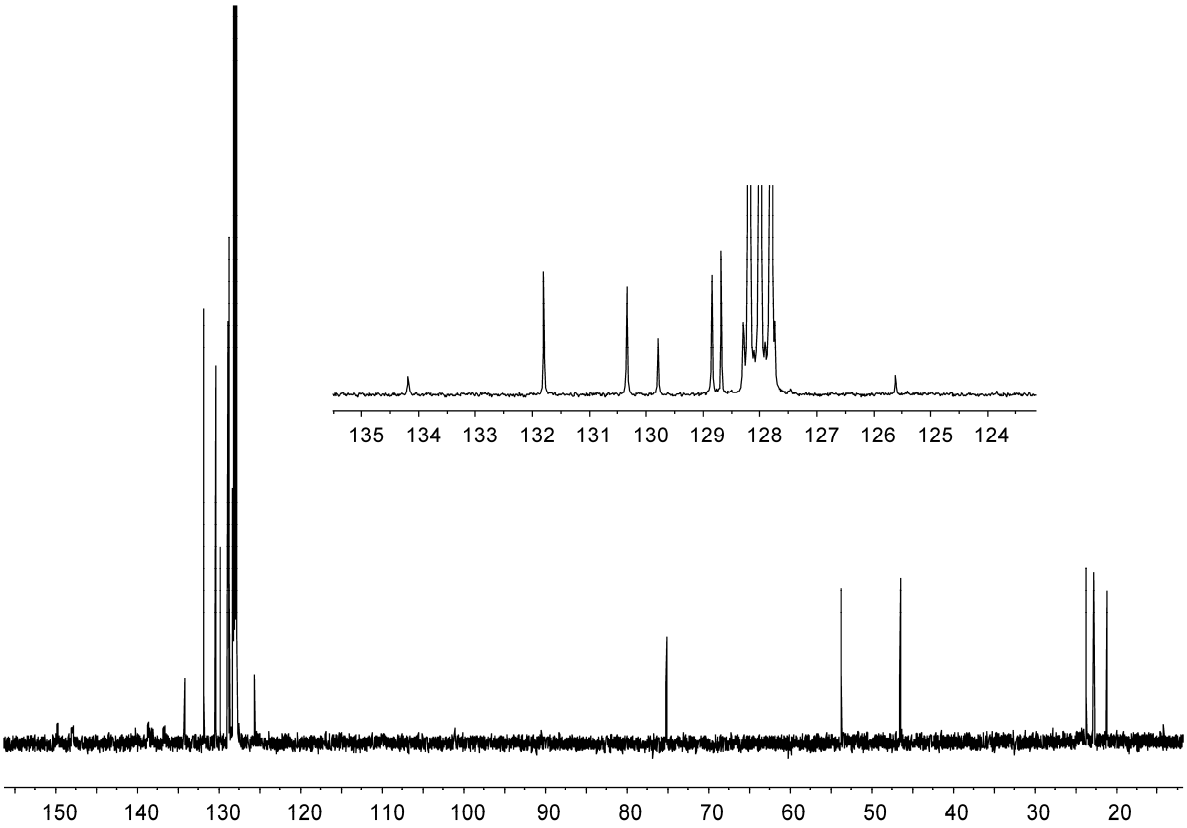
^{11}B{^{1}H} NMR (64 MHz, 298 K, benzene-d_6): δ = –19.2 ($\nu_{1/2}$ ~ 50 Hz).

^{19}F NMR (470 MHz, 298 K, benzene-d_6): δ = –132.5 (m, 2F, *o*-$C_6F_5{}^A$), –132.6 (m, 2F, *o*-$C_6F_5{}^B$), –160.4 (t, ^{3}J = 20.8 Hz, 1F, *p*-$C_6F_5{}^A$) , –161.5 (t, ^{3}J = 20.5 Hz, 1F, *p*-$C_6F_5{}^B$) , –164.2 (m, 2F, *m*-$C_6F_5{}^A$) , –165.2 (m, 2F, *m*-$C_6F_5{}^B$), [$\Delta\delta^{19}F_{mp}$ = 3.8^A, 3.7^B].

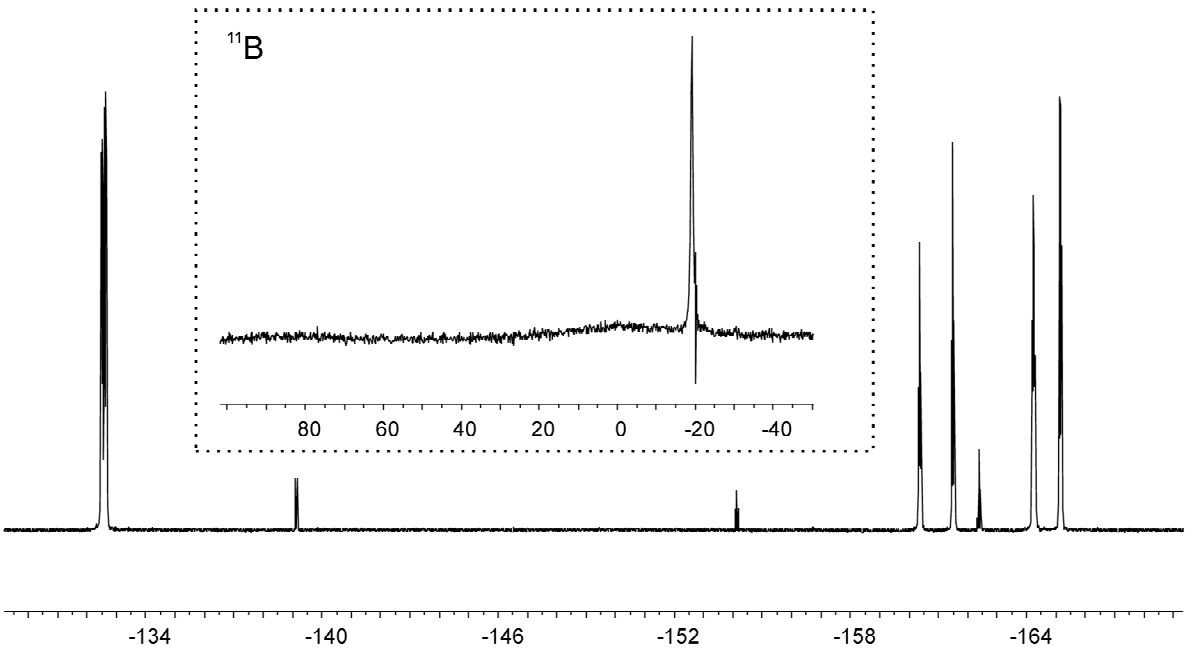
^{19}F,^{19}F GCOSY (470 MHz, 298 K, benzene-d$_6$): δ ^{19}F / δ ^{19}F = –164.2 / –132.5, –160.4 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), –165.2 / –132.6, –161.5 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



^{1}H NMR (500 MHz, 298 K, benzene-d$_6$) of **8**.

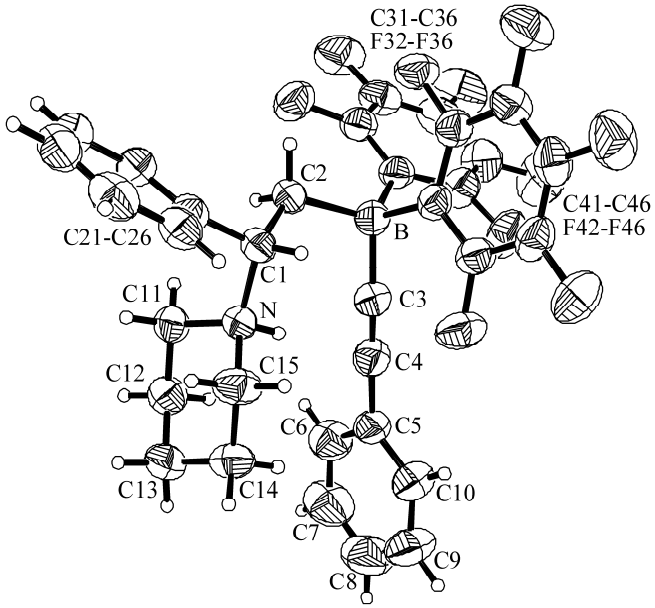


^{13}C{^{1}H} NMR (126 MHz, 298 K, benzene-d$_6$) of **8**

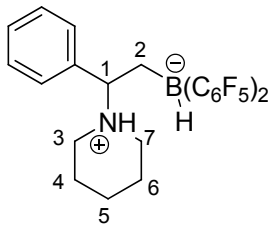


^{19}F NMR (470 MHz, 298 K, benzene-d$_6$) and ^{11}B{^{1}H} NMR (64 MHz, 298 K, benzene-d$_6$) of **8**.

Crystal data for $C_{33}H_{24}BF_{10}N$ (**8**), M = 705.47, monoclinic, $P2_1/n$ (No. 14), a = 8.9726(4), b = 13.4786(6), c = 24.6543(17) Å, β = 93.952(4)°, V = 2974.6(3) Å^3, D_c = 1.419 g cm^{-3}, μ = 1.100 mm^{-1}, $F(000)$ = 1296, Z = 4, λ = 1.54178 Å, T = 223(2) K, 23529 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5010 independent (R_{int} = 0.063), and 3379 observed reflections [I ≥ 2σ(I)], 406 refined parameters, R = 0.050, wR^2 = 0.156, GoF = 1.106.



Synthesis of 9b



N-(1-phenylethen-1-yl)piperidine (**4b**) (57 mg, 0.305 mmol) and bis(pentafluorophenyl)borane (105 mg, 0.305 mmol) were suspended in pentane (5 mL). After stirring for 20 minutes at room temperature the Schlenk flask was evacuated and then filled with 2.5 bar dihydrogen. The reaction mixture was stirred for 1h. Then the connection between the Schlenk flask and dihydrogen bottle was closed, and the reaction mixture was stirred at room temperature for another hour in dihydrogen-atmosphere. After removing the solvent with a syringe and washing with pentane (3 x 5 ml) the product **9b** was isolated as a white solid (93 mg, 58%).

Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation from a diethylether / pentane solution of **9b** at -35 °C.

^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.46 (br, 1H, N-H), 7.07 (m, 1H, *p*-Ph), 7.00 (m, 2H, *m*-Ph), 6.73 (m, 2H, *o*-Ph), 3.52 (d, $^{3}J_{HH}$ = 13.6 Hz, 1H, 1-H), 3.08 (br, 1:1:1:1 q, $^{1}J_{BH}$ ~ 80 Hz, 1H, B-H), 2.66 (m, 1H, 3-H), 2.21 (m, 1H, 7-H), 1.85 (m, 1H, 2-H), 1.75 (m, 1H, 2′-H), 1.66 (m, 1H, 7′-H), 1.13 (m, 1H, 3′-H), 1.03 (m, 1H, 6-H), 0.89 (m, 1H, 4-H), 0.80 (m, 1H, 6′-H), 0.77 (m, 1H, 5-H), 0.76 (m, 1H, 4′-H), -0.12 (m, 1H, 5′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 133.5 (*i*-Ph), 130.3 (*o*-Ph), 129.9 (*p*-Ph), 128.8 (*m*-Ph), 73.7 (C1), 53.3 (C7), 45.7 (C3), 23.6 (C6), 23.3 (C4), 22.4 (br, C2), 21.4 (C5), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 7.07 / 7.00, 6.73 (*p*-Ph / *m*-Ph, *o*-Ph), 7.00 / 7.07, 6.73, 3.52 (*m*-Ph / *p*-Ph, *o*-Ph, 1-H), 6.73 / 7.07, 7.00, 3.52 (o-Ph / *p*-Ph, *m*-Ph, 1-H), 3.52 / 6.73, 1.75 (1-H / *o*-Ph, 2′-H), 2.66 / 2.21, 1.13, 0.89, 0.76 (3-H / 7-H, 3′-H, 4-H, 4′-H), 2.21 / 2.66, 1.66, 1.03, 0.80, 0.76 (7-H / 3-H, 7′-H, 6-H, 6′-H, 4′-H), 1.85 / 3.52, 1.75 (2-H / 1-H, 2′-H), 1.66 / 7.46, 2.21, 1.03, 0.80 (7′-H / N-H, 7-H, 6-H, 6′-H), 1.13 / 7.46, 2.66, 0.89, 0.76 (3′-H / N-H, 3-H, 4-H, 4′-H), 1.03 / 2.21, 1.66, 0.80, 0.77, -0.12 (6-H / 7-H, 7′-H, 6′-H, 5-H, 5′-H), 0.89 / 2.66, 1.13, 0.77, 0.76, -0.12 (4-H / 3-H, 3′-H, 5-H, 4′-H, 5′-H), 0.80 /, 2.21, 1.66, 1.03, 0.77 (6′-H / 7-H, 7′-H, 6-H, 5-H), 0.77 / 2.21, 1.13, 1.03, 0.89, 0.80 (5-H / 7-H, 3′-H, 6-H, 4-H, 6′-H), 0.76 / 1.03, 0.89, 0.77 (4′-H / 6-H, 4-H, 5-H), -0.12 / 1.03, 0.89, 0.80, 0.77, 0.76 (5′-H / 6-H, 4-H, 6′-H, 5-H, 4′-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.07 / 129.9 (*p*-Ph / *p*-Ph), 7.00 / 128.8 (*m*-Ph / *m*-Ph), 6.73 / 130.3 (*o*-Ph / *o*-Ph), 3.52 / 73.7 (1-H / C1), 2.66 / 45.7 (3-H / C3), 2.21 / 53.3 (7-H / C7), 1.85, 1.75 / 22.4 (2-H, 2′-H / C2), 1.66 / 53.3 (7′-H / C7), 1.13 / 45.7 (3′-H / C3), 1.03 / 23.6 (6-H / C6), 0.89 / 23.3 (4-H / C4), 0.80 / 23.6 (6′-H / C6), 0.77 / 21.4 (5-H / C5), 0.76 / 23.3 (4′-H / C4), -0.12 / 21.4 (5′-H / C5)

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 7.07 / 130.3 (*p*-Ph /*o*-Ph), 7.00 / 133.5 (*m*-Ph / *i*-Ph), 6.73 / 73.7 (*o*-Ph / C1), 3.52 / 133.5, 130.3, 53.3, 45.7 (1-H / *i*-Ph, *o*-Ph, C7, C3), 1.75 / 73.7 (2′-H / C1), 1.03 / 53.3, 21.4 (6-H / C7, C5), 0.89 / 45.7, 21.4 (4-H / C3, C5), -0.12 / 23.3 (5′-H / C4).

^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.73 / 7.07, 7.00 (*o*-Ph / *p*-Ph, *m*-Ph), 1.75 / 3.52, 3.08, 1.85 (2′-H / 1-H, B-H, 2-H), -0.12 / 7.46, 2.66, 2.21, 1.66, 1.13, 1.03, 0.89, 0.80, 0.77, 0.76 (5′-H / N-H, 3-H, 7-H, 7′-H, 3′-H, 6-H, 4-H, 6′-H, 5-H, 4′-H) [selected experiments].

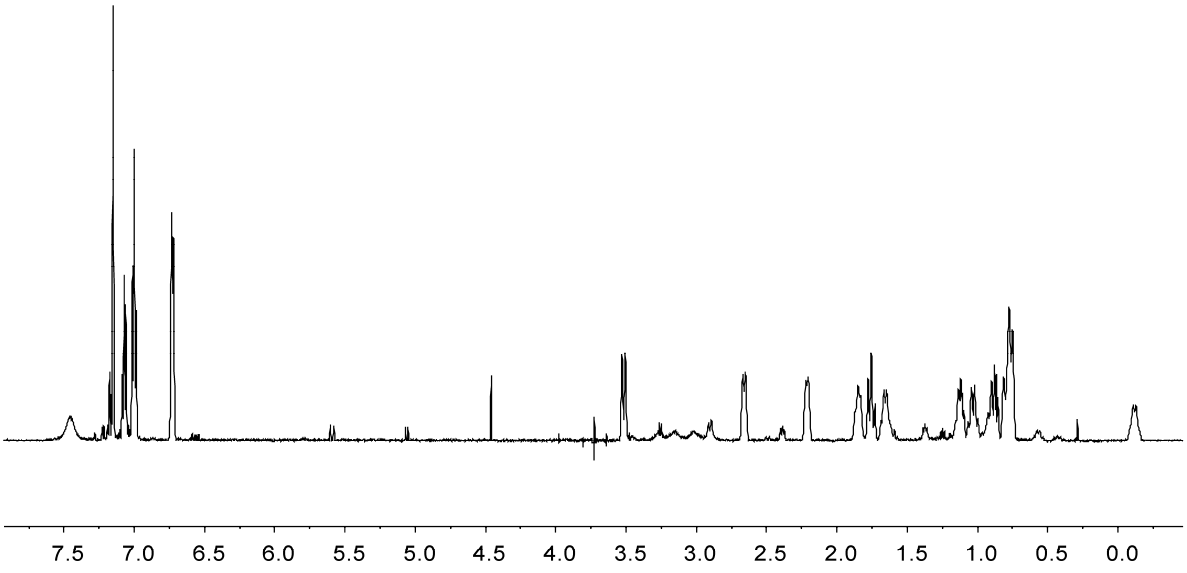
^{1}H{^{1}H} NOE (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.00 / 6.73 (*m*-Ph / *o*-Ph), 6.73 / 7.00, 3.52, 1.75 (*o*-Ph / *m*-Ph, 1-H, 2′-H), 3.52 / 7.46, 6.73, 2.21, 1.85 (1-H / N-H, *o*-Ph, 7-H, 2-H), 2.66 / 7.46, 6.73, 1.75, 1.13, 0.89, 0.80, 0.77, 0.76 (3-H / N-H, *o*-Ph, 2′-H, 3′-H, 4-H, 6′-H, 5-H, 4′-H), 2.21 / 6.73, 3.52, 1.03, 0.80, 0.77, 0.76 (7-H / *o*-Ph, 1-H, 6-H, 6′-H, 5-H, 4′-H), 1.85 / 3.52, 1.75 (2-H / 1-H, 2′-H), 1.75 / 6.73, 2.66, 1.85 (2′-H / *o*-Ph, 3-H, 2-H), 1.66 / 6.73, 2.21, 1.13, 0.80, 0.77, 0.76, -0.12 (7′-H / *o*-Ph, 7-H, 3′-H, 6′-H, 5-H, 4′-H, 5′-H), 1.13 / 6.73, 2.66, 1.66, 0.80, 0.77, 0.76, -0.12 (3′-H / *o*-Ph, 3-H, 7′-H, 6′-H, 5-H, 4′-H, 5′-H), 1.03 / 2.21, 0.80, 0.77, 0.76 (6-H / 7-H, 6′-H, 5-H, 4′-H), 0.89 / 0.80, 0.77, 0.76 (4-H / 6′-H, 5-H, 4′-H), 0.80, 0.77, 0.76 / 1.03, 0.89, -0.12 (6′-H, 5-H, 4′-H/ 6-H, 4-H, 5′-H), -0.12 / 0.80, 0.77, 0.76 (5′-H / 6′-H, 5-H, 4′-H).

^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d_6) δ = –22.8 ($\nu_{1/2}$ ~ 38 Hz).

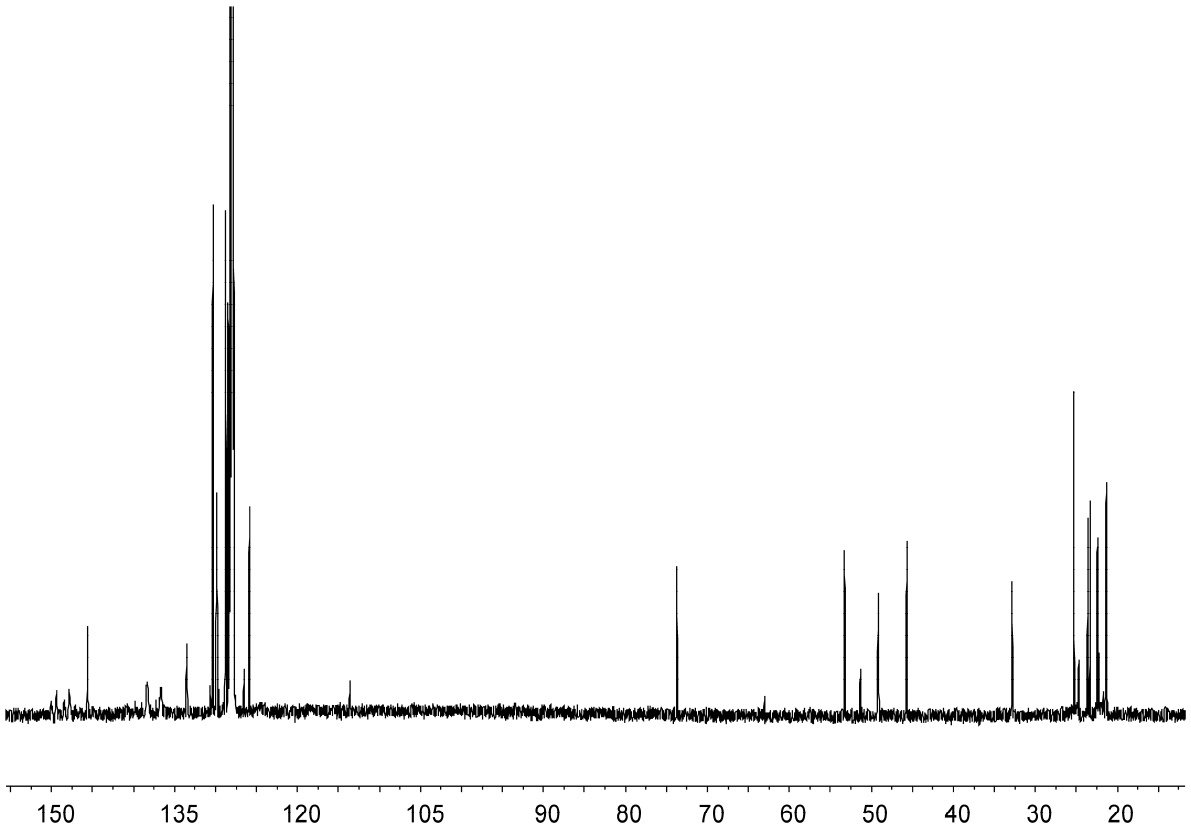
^{11}B NMR (192 MHz, 298 K, benzene-d_6) δ = –22.8 (d, $^{1}J_{BH}$ ~ 80 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6) δ = –132.6 (m, 2F, *o*-$C_6F_5^A$), –133.7 (m, 2F, *o*-$C_6F_5^B$), –160.6 (m, 1F, *p*-$C_6F_5^B$), –161.8 (m, 1F, *p*-$C_6F_5^A$), –164.1 (m, 2F, *m*-$C_6F_5^B$), –165.6 (m, 2F, *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{mp}$ = 3.8^A, 3.5^B].

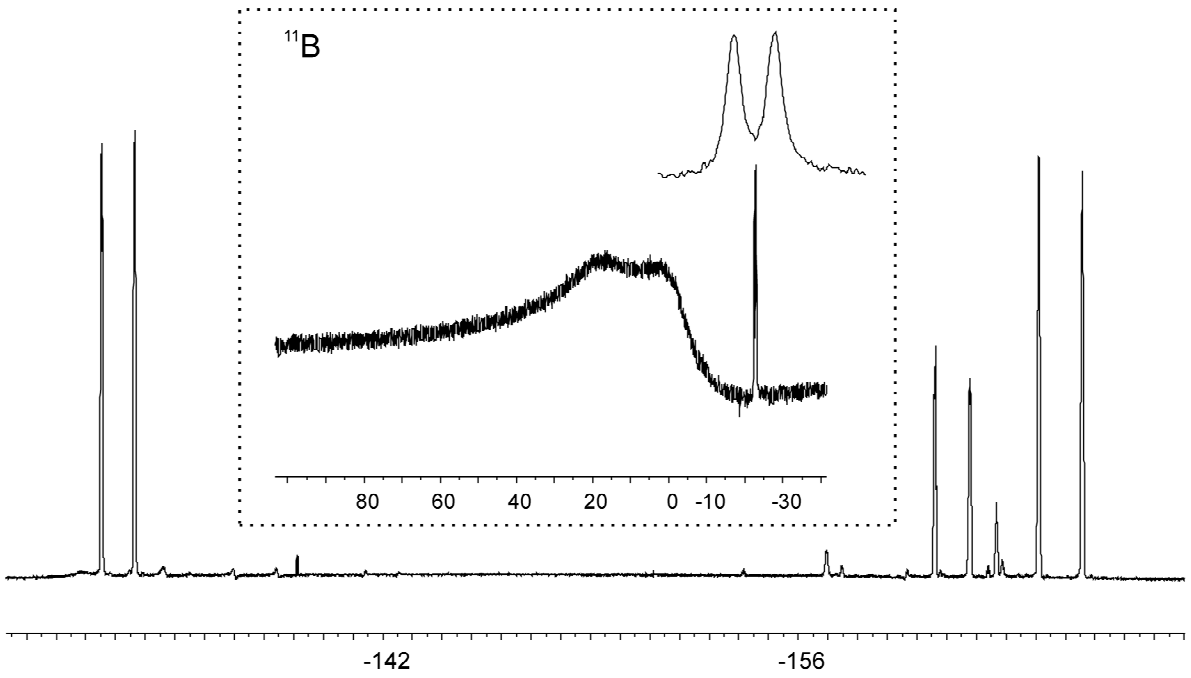
^{19}F,^{19}F GCOSY (564 MHz, 253 K, benzene-d_6) δ ^{19}F / δ ^{19}F = –164.1 / –133.7, –160.6 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$), –165.6 / –132.6, –161.8 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$).



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **9b**

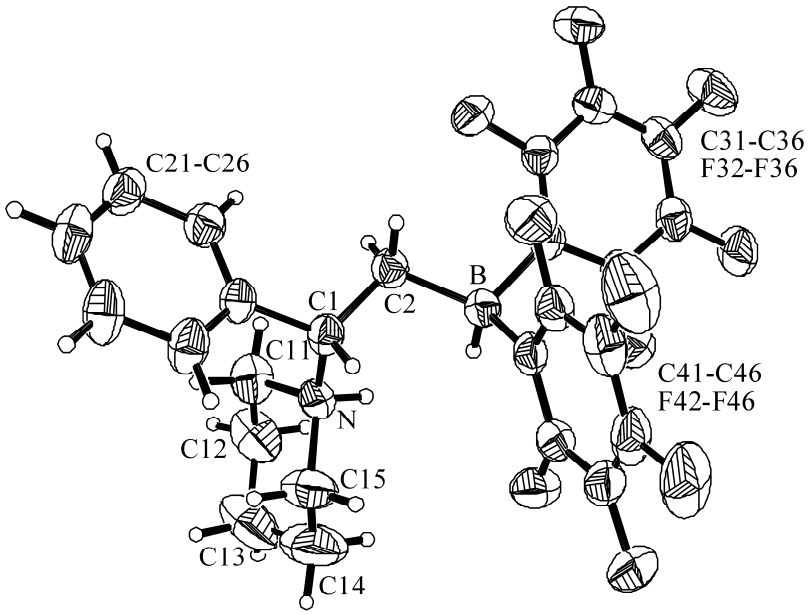


$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-d_6) of **9b**

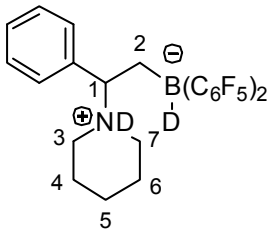


^{19}F NMR (564 MHz, 298 K, benzene-d_6) and ^{11}B NMR (192 MHz, 298 K, benzene-d_6) of **9b**

Crystal data for $C_{25}H_{20}BF_{10}N$ (**9b**), M = 535.23, orthorhombic, *A*ba2 (No. 41), a = 17.8309(7), b = 21.5961(10), c = 12.2832(3) Å, V = 4730.0(3) Å^3, D_c = 1.503 g cm^{-3}, μ = 1.261 mm^{-1}, F(000) = 2176, Z = 8, λ = 1.54178 Å, T = 223(2) K, 11202 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3838 independent (R_{int} = 0.037), and 3591 observed reflections [I ≥ 2σ(I)], 334 refined parameters, R = 0.038, wR^2 = 0.102, GoF = 1.021.



Synthesis of 9b-D



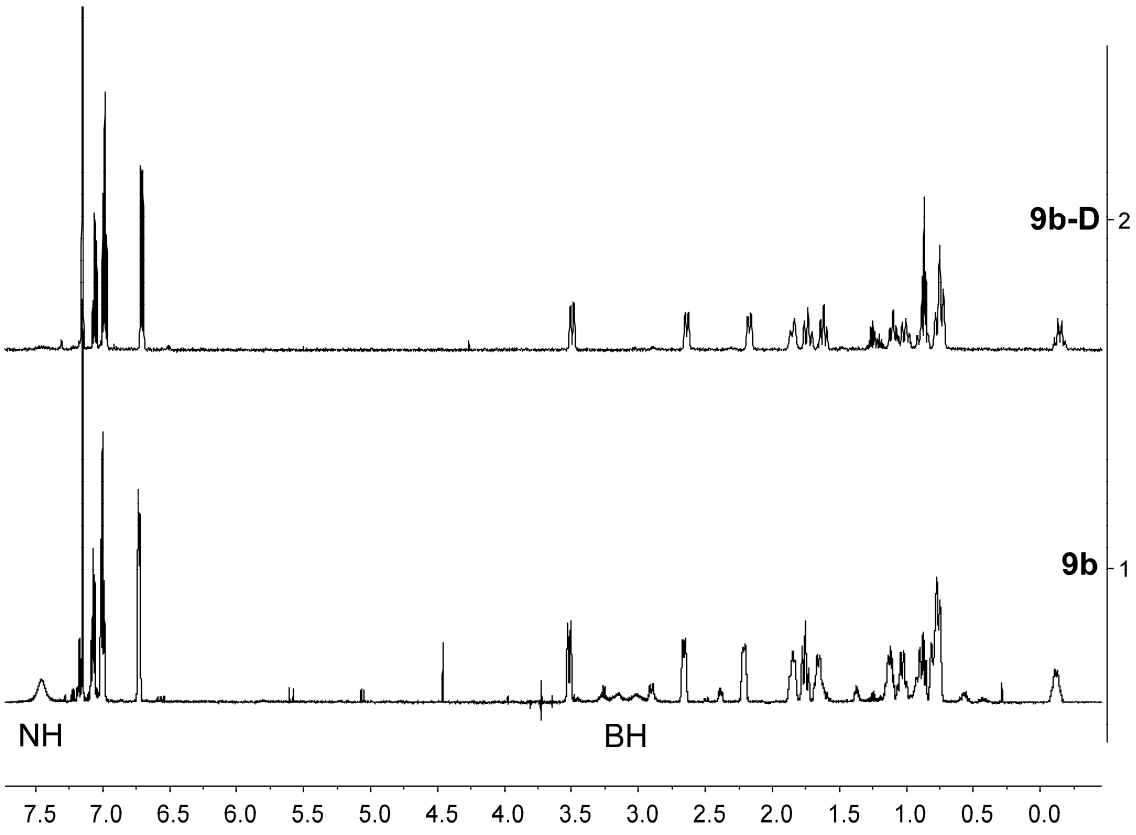
N-(1-phenylethen-1-yl)piperidine (**4b**) (14 mg, 0.076 mmol) and bis(pentafluorophenyl)borane (26 mg, 0.076 mmol) were suspended in pentane (4 mL). After stirring for 20 minutes at room temperature the Schlenk flask was filled with 2.0 bar deuterium gas and stirred for 10 minutes. Then the connection between the Schlenk flask and deuterium bottle was closed, and the reaction mixture was stirred at room temperature for another hour in the deuterium-atmosphere. After removing the solvent with a syringe and washing with pentane (5 mL) the product **9b-D** was isolated as a white solid (16 mg, 38%).

^{1}H NMR (500 MHz, 298 K, benzene-d_6) δ = 7.06 (m, 1H, *p*-Ph), 7.00 (m, 2H, *m*-Ph), 6.70 (m, 2H, *o*-Ph), 3.49 (d, $^{3}J_{HH}$ = 13.6 Hz, 1H, 1-H), 2.64 (m, 1H, 3-H), 2.17 (m, 1H, 7-H), 1.85 (m, 1H, 2-H), 1.74 (m, 1H, 2′-H), 1.62 (m, 1H, 7′-H), 1.10 (m, 1H, 3′-H), 1.00 (m, 1H, 6-H), 0.87 (m, 1H, 4-H), 0.77 (m, 1H, 6′-H), 0.75 (m, 1H, 5-H), 0.73 (m, 1H, 4′-H), -0.15 (m, 1H, 5′-H).

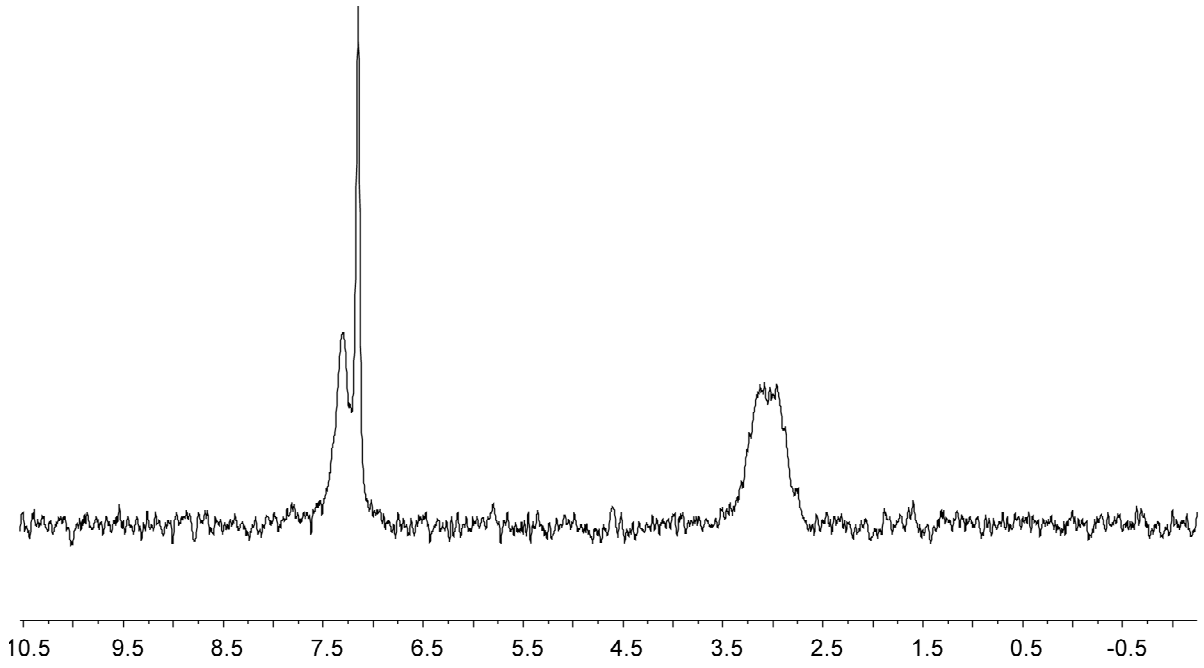
^{2}H NMR (77 MHz, 298 K, benzene-h_6) δ = 7.30 (br, 1D, N-D), 3.03 (br, 1D, B-D).

^{11}B{^{1}H} NMR (160 MHz, 298 K, benzene-d_6) δ = –23.0 (s, $\nu_{1/2}$ ~ 40 Hz).

^{11}B NMR (160 MHz, 298 K, benzene-d_6) δ = –23.0 (s, $\nu_{1/2}$ ~ 40 Hz).

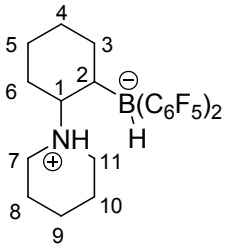


(1) ^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **9b**; (2) ^{1}H NMR (500 MHz, 298 K, benzene-d_6) of **9b-D**.



^{2}H NMR (77 MHz, 298 K, benzene-h_6) of **9b-D**.

Synthesis of 9d



N-(cyclohex-1-enyl)piperidine (**4d**) (58 mg, 0.351 mmol) and bis(pentafluorophenyl)-borane (122 mg, 0.351 mmol) were dissolved in pentane (5 mL). After stirring for 20 minutes at 0 °C the Schlenk flask was filled with 2.5 bar dihydrogen and stirred for 1h. During this time a white solid precipitated. Then the connection between the Schlenk flask and dihydrogen bottle was closed, and the reaction mixture was stirred at 0 °C for another hour in the dihydrogen-atmosphere. After removing the solvent with a syringe and washing with pentane (3 × 5 mL) the product **9d** was isolated as a white solid (90 mg, 50%).

Anal. Calc. for $C_{23}H_{22}BF_{10}N$: C 53.83, H 4.32, N 2.73; found: C 53.71, H 4.39, N 2.72. Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation from a benzene solution of **9d** at 25 °C.

^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 7.58 (br, 1H, N-H), 2.99 (br, 1:1:1:1 q, $^{1}J_{BH}$ ~ 78 Hz, 1H, B-H), 2.59 (m, 1H, 3-H), 2.50 (m, 1H, 7-H), 2.02 (t, $^{3}J_{HH}$ = 11.6 Hz, 1H, 1-H), 1.97 (m, 1H, 11-H), 1.64 (m, 1H, 11′-H), 1.59 (m, 1H, 4-H), 1.59 (m, 1H, 5-H), 1.37 (t, $^{3}J_{HH}$ = 11.6 Hz, 1H, 2-H), 1.26 (m, 1H, 7′-H), 1.23 (m, 1H, 4′-H), 0.97 (m, 1H, 6-H), 0.97 (m, 1H, 10-H), 0.89 (m, 1H, 9-H), 0.89 (m, 1H, 5′-H), 0.88 (m, 1H, 10′-H), 0.81 (m, 2H, 8-H), 0.76 (m, 1H, 3′-H), 0.65 (m, 1H, 6′-H), 0.28 (m, 1H, 9′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 71.7 (C1), 52.0 (C11), 45.5 (C7), 31.9 (br, C2), 31.1 (C3), 27.3 (C4), 26.0 (C5), 25.8 (C6), 23.8 (C10), 23.6 (C8), 21.8 (C9), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 2.59 / 1.59, 1.23, 0.76 (3-H / 4-H, 4′-H, 3′-H), 2.50 / 1.26, 0.81 (7-H / 7′-H, 8-H), 2.02 / 1.37, 0.97, 0.65 (1-H / 2-H, 6-H, 6′-H), 1.97 / 1.64, 0.97 (11-H / 11′-H, 10-H), 1.64 / 1.97, 0.88 (11′-H / 11-H, 10′-H), 1.59 / 2.59, 1.23, 0.97, 0.89, 0.76, 0.65 (4-H, 5-H / 3-H, 4′-H, 6-H, 5′-H, 3′-H, 6′-H), 1.37 / 2.59, 2.02, 0.76 (2-H / 3-H, 1-H, 3′-H), 1.26 / 2.50, 0.81 (7′-H / 7-H, 8-H), 1.23 / 2.59, 1.59 (4′-H / 3-H, 4-H, 5-H), 0.97 / 1.97, 0.89, 0.88, 0.65 (6-H, 10-H / 11-H, 5′-H, 9-H, 10′-H, 6′-H), 0.89 / 1.59, 0.97, 0.81, 0.28 (5′-H, 9-H / 4-H, 5-H, 6-H, 10-H, 8-H, 9′-H), 0.88 / 1.64, 0.97, 0.28 (10′-H / 11′-H, 10-H, 9′-H), 0.81 / 2.50, 0.89 (8-H / 7-H, 9-H), 0.76 / 2.59, 1.59, 1.37 (3′-H / 3-H, 4-H, 2-H), 0.65 / 2.02, 1.59, 0.97 (6′-H / 1-H, 5-H, 6-H), 0.28 / 0.89, 0.88, 0.81 (9′-H / 9-H, 10′-H, 8-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 2.59 / 31.1 (3-H / C3), 2.50 / 45.5 (7-H / C7), 2.02 / 71.7 (1-H / C1), 1.97 / 52.0 (11-H / C11), 1.64 / 52.0 (11′-H / C11), 1.59 / 27.3 (4-H / C4), 1.59 / 26.0 (5-H / C5), 1.26 / 45.5 (7′-H / C7), 1.23 / 27.3 (4′-H / C4), 0.97 / 25.8 (6-H / C6), 0.97 / 23.8 (10-H / C10), 0.89 / 26.0 (5′-H / C5), 0.89 / 21.8 (9-H / C9), 0.88 / 23.8 (10′-H / C10), 0.81 / 23.6 (8-H / C8), 0.76 / 31.1 (3′-H / C3), 0.65 / 25.8 (6′-H / C6), 0.28 / 21.8 (9′-H / C9).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 1.23 / 31.1, 26.0 (4′-H / C3, C5) 0.97 / 52.0 (10-H / C11), 0.89 / 27.3, 25.8 (5′-H / C4, C6), 0.65 / 71.7, 26.0 (6′-H / C1, C5).

^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 1.37 / 2.59, 2.02, 1.59, 1.23, 0.97, 0.89, 0.76, 0.65 (2-H / 3-H, 1-H, 4-H, 5-H, 4′-H, 6-H, 5′-H, 3′-H, 6′-H), 0.28 / 7.58, 2.50, 1.97, 1.64, 1.26, 0.97, 0.89, 0.88 (9′-H / N-H, 7-H, 11-H, 11′-H, 7′-H, 10-H, 9-H, 10′-H).

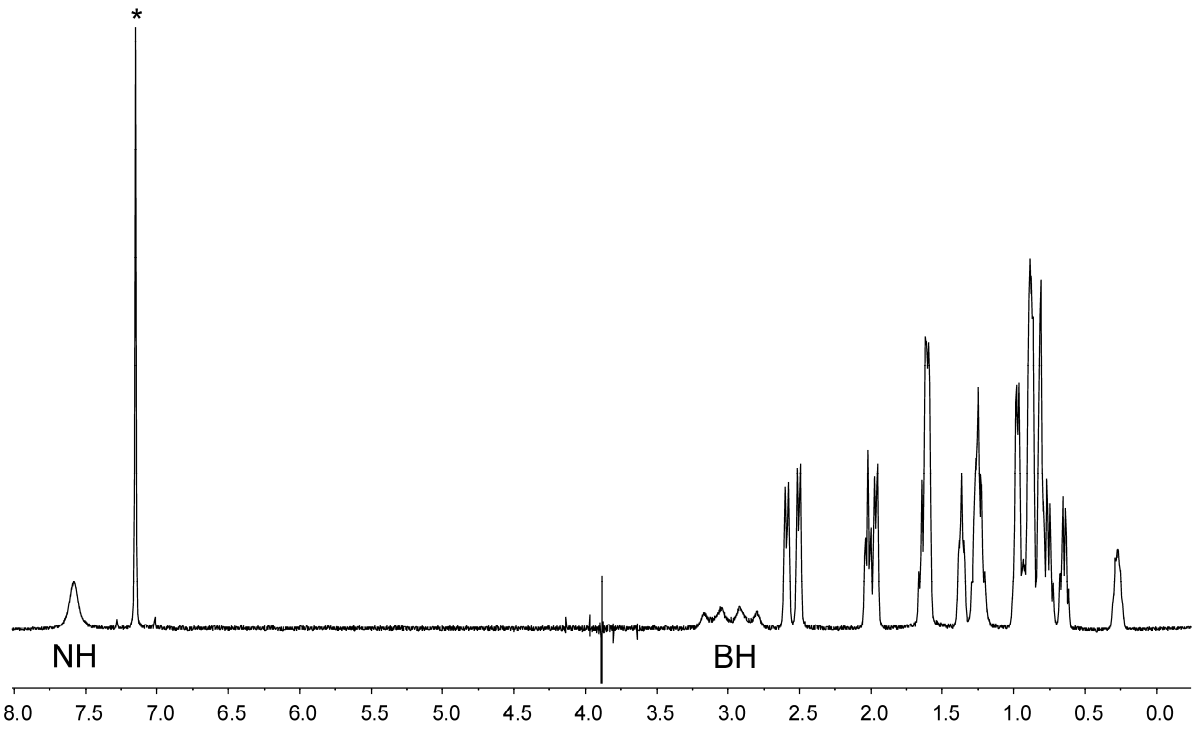
^{1}H{^{1}H} NOE (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ$^{1}H_{res}$ = 2.59 / 0.76 (3-H / 3′-H), 2.50 / 1.23, 0.97, 0.76 (7-H / 4′-H, 6-H, 10-H, 3′-H), 1.97 / 1.59 (11-H / 4-H, 5-H), 1.59 / 1.97, 0.97, 0.81 (4-H, 5-H / 11-H, 6-H, 10-H, 8-H), 1.37 / 1.59 (2-H / 4-H, 5-H), 1.23 / 2.59, 2.50 (4′-H / 3-H, 7-H), 0.97 / 2.50, 1.59 (6-H, 10-H / 7-H, 4-H, 5-H), 0.89 / 1.59, 0.65 (5′-H, 9-H / 4-H, 5-H, 6′-H), 0.81 / 0.28 (8-H / 9′-H), 0.76 / 2.59 (3′-H / 3-H), 0.65 / 0.89 (6′-H / 5′-H), 0.28 / 0.81 (9′-H / 8-H).

^{11}B{^{1}H} NMR (160 MHz, 298 K, dichloromethane-d_2) δ = –21.7 ($\nu_{1/2}$ ~ 20 Hz).

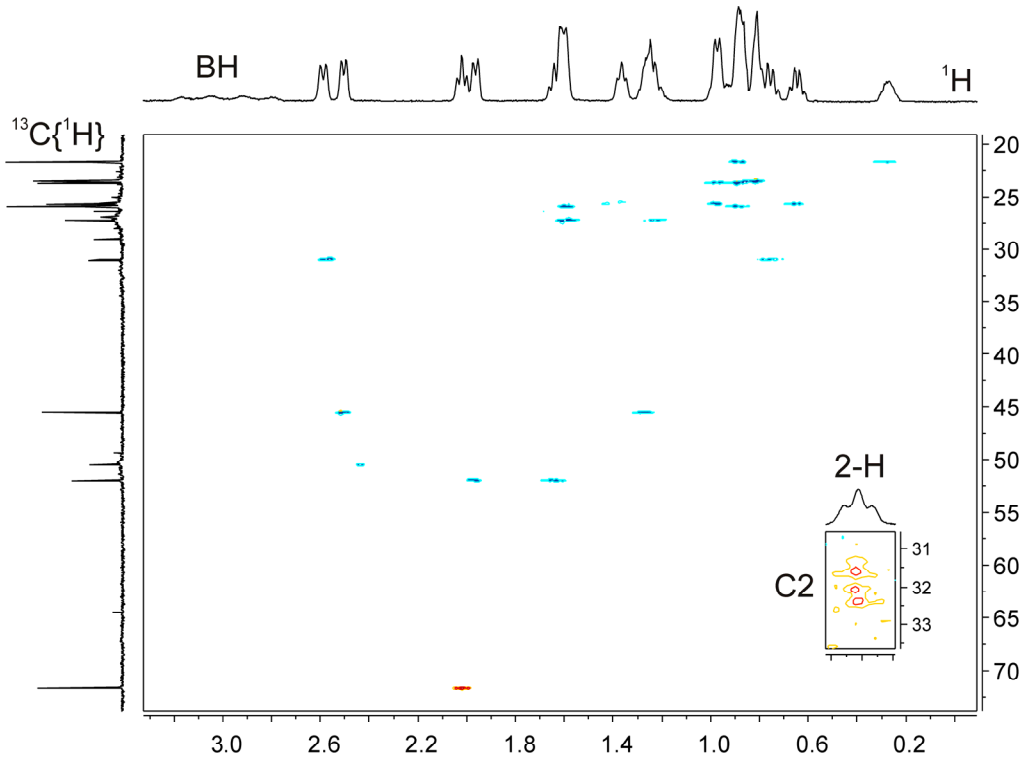
^{11}B NMR (160 MHz, 298 K, dichloromethane-d_2) δ = –21.7 (d, $^{1}J_{BH}$ = 78.3 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6) δ = –132.3 (m, 2F, *o*-$C_6F_5^A$), –133.1 (m, 2F, *o*-$C_6F_5^B$), –160.9 (t, ^{3}J = 23.5 Hz, 1F, *p*-$C_6F_5^A$), –162.3 (t, ^{3}J = 21.0 Hz, 1F, *p*-$C_6F_5^B$), –164.3 (m, 2F, *m*-$C_6F_5^A$), –165.6 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp}$ = 3.4^A, 3.3^B].

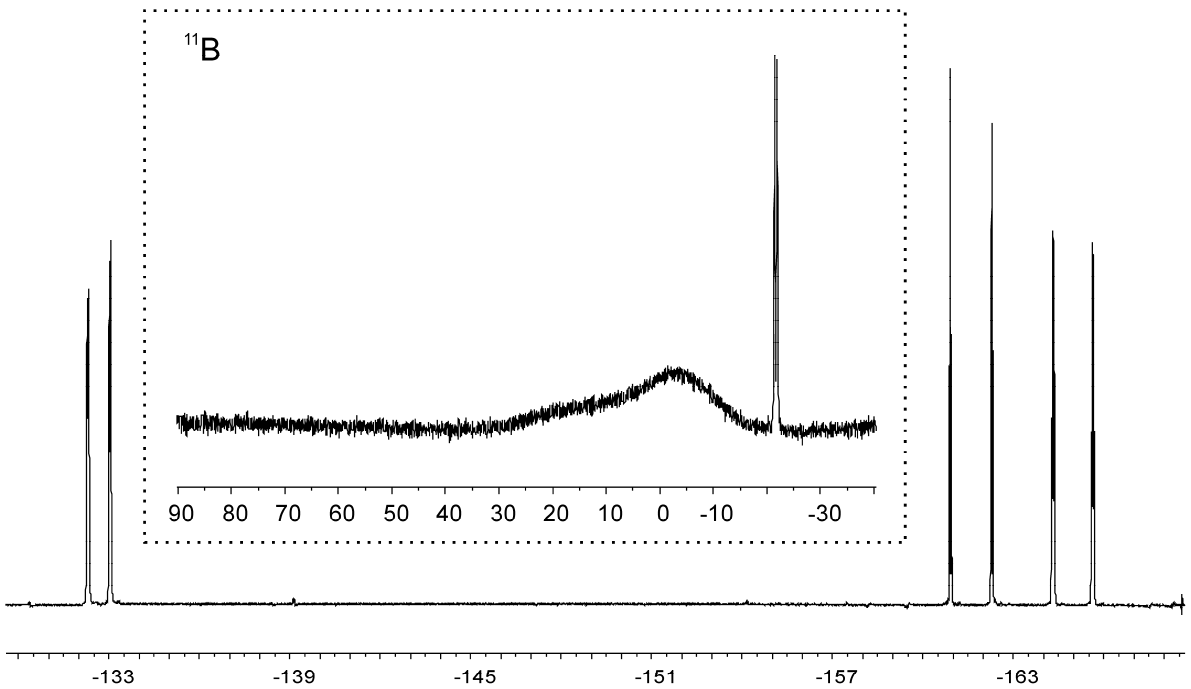
^{19}F,^{19}F GCOSY (564 MHz, 253 K, benzene-d_6) δ ^{19}F / δ ^{19}F = -164.3 / -132.3, -160.9 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), –165.6 / –133.1, –162.3 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



^{1}H NMR (600 MHz, 298 K, benzene-d_6(*)) of **9d**

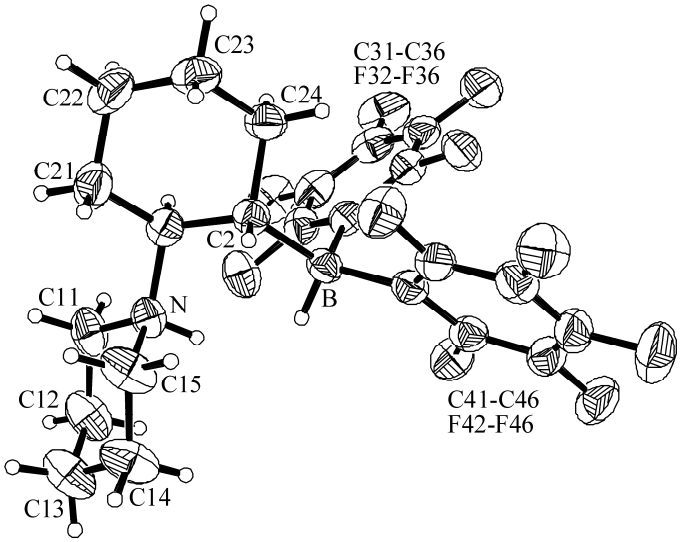


^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d$_6$; projections: ^{1}H and ^{13}C{^{1}H} spectrum) of **9d**

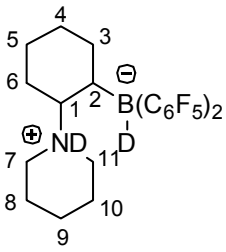


^{19}F NMR (564 MHz, 298 K, benzene-d$_6$) and ^{11}B NMR (160 MHz, 298 K, dichloromethane-d$_2$) of **9d**

Crystal data for $C_{23}H_{22}BF_{10}N$ (**9d**), M = 513.23, monoclinic, $P2_1/n$ (No. 14), a = 12.1379(4), b = 14.0463(5), c = 13.5423(5) Å, β = 105.934(2)°, V = 2220.15(14) Å^3, D_c = 1.535 g cm^{-3}, μ = 1.311 mm^{-1}, F(000) = 1048, Z = 4, λ = 1.54178 Å, T = 223(2) K, 32849 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3968 independent (R_{int} = 0.045), and 3647 observed reflections [I ≥ 2σ(I)], 316 refined parameters, R = 0.037, wR^2 = 0.100, GoF = 1.062.



Synthesis of 9d-D

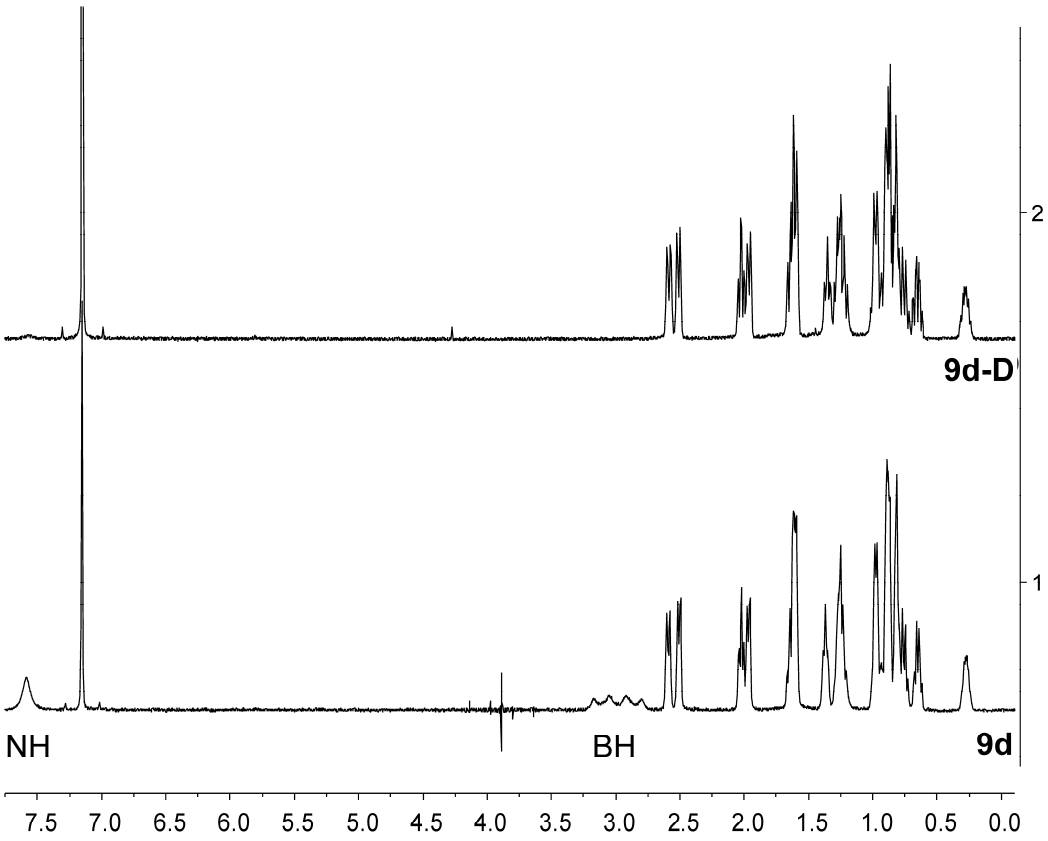


N-(cyclohex-1-enyl)piperidine (**4d**) (24 mg, 0.145 mmol) and bis(pentafluorophenyl)-borane (50 mg, 0.145 mmol) were dissolved in pentane (5 mL). After stirring for 20 minutes at 0 °C the Schlenk flask was filled with 2.0 bar deuterium gas and stirred for 5 minutes. During this time a white solid precipitated. Then the connection between the Schlenk flask and deuterium bottle was closed, and the reaction mixture was stirred at 0 °C for another hour in the deuterium-atmosphere. After removing the solvent with a syringe and washing with pentane (5 mL) the product **9d-D** was isolated as a yellow solid (30 mg, 40%).

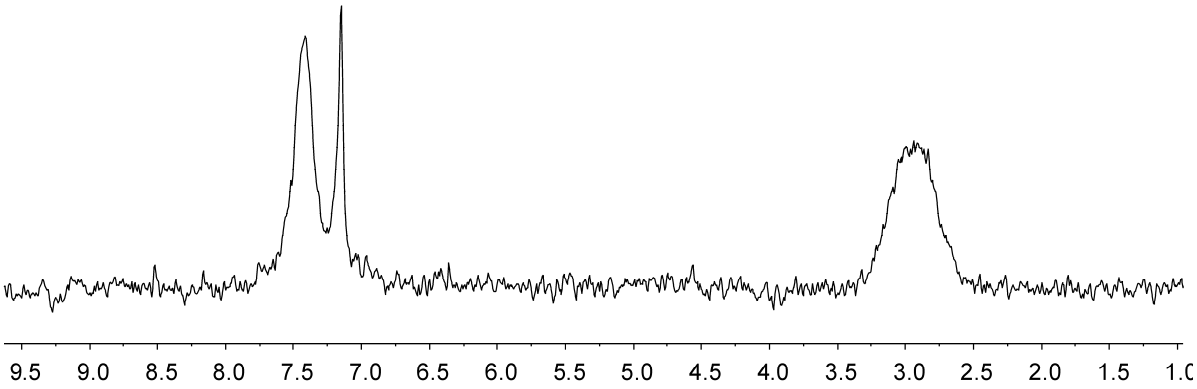
^{1}H NMR (500 MHz, 298 K, benzene-d_6) δ = 2.59 (m, 1H, 3-H), 2.51 (m, 1H, 7-H), 2.02 (t, $^{3}J_{HH}$ = 11.8 Hz, 1H, 1-H), 1.96 (m, 1H, 11-H), 1.64 (m, 1H, 11′-H), 1.61 (m, 1H, 4-H), 1.61 (m, 1H, 5-H), 1.35 (t, $^{3}J_{HH}$ = 11.6 Hz, 1H, 2-H), 1.26 (m, 1H, 7′-H), 1.23 (m, 1H, 4′-H), 0.98 (m, 1H, 6-H), 0.98 (m, 1H, 10-H), 0.90 (m, 1H, 9-H), 0.90 (m, 1H, 5′-H), 0.88 (m, 1H, 10′-H), 0.82 (m, 2H, 8-H), 0.76 (m, 1H, 3′-H), 0.65 (m, 1H, 6′-H), 0.28 (m, 1H, 9′-H).

^{2}H NMR (77 MHz, 298 K, benzene-h_6) δ = 7.41 (br, 1D, N-D), 2.94 (br, 1D, B-D).

^{11}B NMR (160 MHz, 298 K, benzene-d_6) δ = -21.7 ($\nu_{1/2}$ ~ 50 Hz).

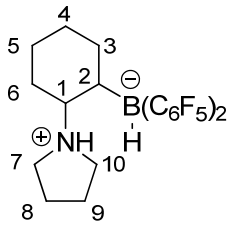


(1) ^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **9d**; (2) ^{1}H NMR (500 MHz, 298 K, benzene-d_6) of **9d-D**.



^{2}H NMR (77 MHz, 298 K, benzene-h_6) of **9d-D**.

Synthesis of 9e



N-(Cyclohex-1-enyl)pyrrolidine (**4e**) (23 mg, 0.151 mmol) and bis(pentafluorophenyl)-borane (52 mg, 0.151 mmol) were dissolved in pentane (10 mL). After stirring for 20 minutes at room temperature the Schlenk flask was filled with 2.5 bar dihydrogen and stirred for 1h. During this time a white solid precipitated. Then the connection between the Schlenk flask and dihydrogen bottle was closed, and the reaction mixture was stirred at room temperature for 20 hours in the dihydrogen-atmosphere. After removing the solvent with a syringe and washing with pentane (3 x 5 ml) the product **9e** was isolated as a white solid (21 mg, 28%). Anal. Calc. for $C_{22}H_{20}BF_{10}N$: C 52.93, H 4.04, N 2.81; found: C 52.80, H 4.04, N 2.77.

Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation from a pentane/dichloromethane solution of **9e** at -30 °C.

^{1}H NMR (600 MHz, 298 K, benzene-d_6) δ = 8.31 (br, 1H, N-H), 3.00 (br, 1:1:1:1 q, $^{1}J_{HH}$ ~ 77 Hz, 1H, B-H), 2.55 (m, 1H, 3-H), 2.24 (m, 1H, 10-H), 2.22 (m, 1H, 1-H), 2.15 (m, 1H, 7-H), 1.73 (m, 1H, 7′-H), 1.66 (m, 1H, 10′-H), 1.58 (m, 1H, 4-H), 1.53 (m, 1H, 5-H), 1.19 (m, 1H, 4′-H), 1.19 (m, 1H, 2-H), 0.83 (m, 1H, 6-H), 0.83 (m, 1H, 5′-H), 0.72 (m, 1H, 3′-H), 0.68 (m, 2H, 9-H), 0.65 (m, 2H, 8-H), 0.51 (m, 1H, 6′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 67.1 (C1), 50.1 (C10), 44.6 (C7), 33.4 (br, C2), 30.8 (C3), 27.2 (C4), 25.6 (C5), 24.5 (C6), 23.1 (C8), 22.9 (C9), [C_6F_5 not observed].

^{1}H,^{1}H GCOSY (600 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{1}H = 2.55 / 1.58, 1.19, 0.72 (3-H / 4-H, 2-H, 4′-H, 3′-H), 2.24 / 1.66, 0.83, 0.51 (10-H / 10′-H, 6-H, 6′-H), 2.22 / 1.19 (1-H / 2-H), 2.15 / 1.66, 0.65 (7-H / 10′-H, 8-H), 1.73 / 2.15, 0.65 (7′-H / 7-H, 8-H), 1.66 / 2.24, 0.68 (10′-H / 10-H, 9-H), 1.58 / 2.55, 1.19, 0.83, 0.72 (4-H / 3-H, 4′-H, 5′-H, 3′-H), 1.53 / 1.19, 0.83, 0.51 (5-H / 4′-H, 5′-H, 6-H, 6′-H), 1.19 / 2.22, 1.58, 1.53, 0.72 (2-H, 4′-H / 1-H, 4-H, 5-H, 3′-H), 0.83 / 1.58, 0.51 (5′-H, 6-H / 4-H, 6′-H), 0.72 / 2.55, 1.58, 1.19 (3′-H / 3-H, 4-H, 2-H, 4′-H), 0.51 / 2.22, 1.53, 0.83 (6′-H / 1-H, 5-H, 5′-H, 6-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 2.55 / 30.8 (3-H / C3), 2.24 / 50.1 (10-H / C10), 2.22 / 67.1 (1-H / C1), 2.15, 1.73 / 44.6 (7-H, 7′-H / C7), 1.66 / 50.1 (10′-H / C10), 1.58 / 27.2 (4-H / C4), 1.53 / 25.6 (5-H / C5), 1.19 / 33.4 (2-H / C2), 1.19 / 27.2 (4′-H / C4), 0.83 / 25.6 (5′-H / C5), 0.83 / 24.5 (6-H / C6), 0.72 / 30.8, (3′-H / C3), 0.68 / 22.9 (9′-H / C9), 0.65 / 23.1 (8-H / C8), 0.51 / 24.5 (6′-H / C6).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, benzene-d_6) δ ^{1}H / δ ^{13}C = 2.24 / 44.6, 22.9 (10-H / C7, C9), 2.15 / 50.1, 23.1 (7-H / C10, C8), 1.73 / 67.1, 23.1 (7′-H / C1, C8), 1.66 / 67.1, 23.1 (10′-H / C1, C8), 1.19 / 25.6 (2-H, 4′-H / C5), 0.83 / 27.2 (5′-H, 6-H / C4), 0.68 / 50.1, 44.6, 23.1 (9-H / C10, C7, C8), 0.51 / 67.1, 25.6 (6′-H / C1, C5).

^{1}H{^{1}H} TOCSY (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 1.66 / 8.31, 2.24, 2.15, 1.73, 0.68, 0.65 (10′-H / N-H, 10-H, 7-H, 7′-H, 9-H, 8-H), 0.51 / 2.55, 2.22, 1.58, 1.53, 1.19, 0.83, 0.72 (6′-H / 3-H, 1-H, 4-H, 5-H, 2-H, 4′-H, 5′-H, 6-H, 3′-H), [selected experiments].

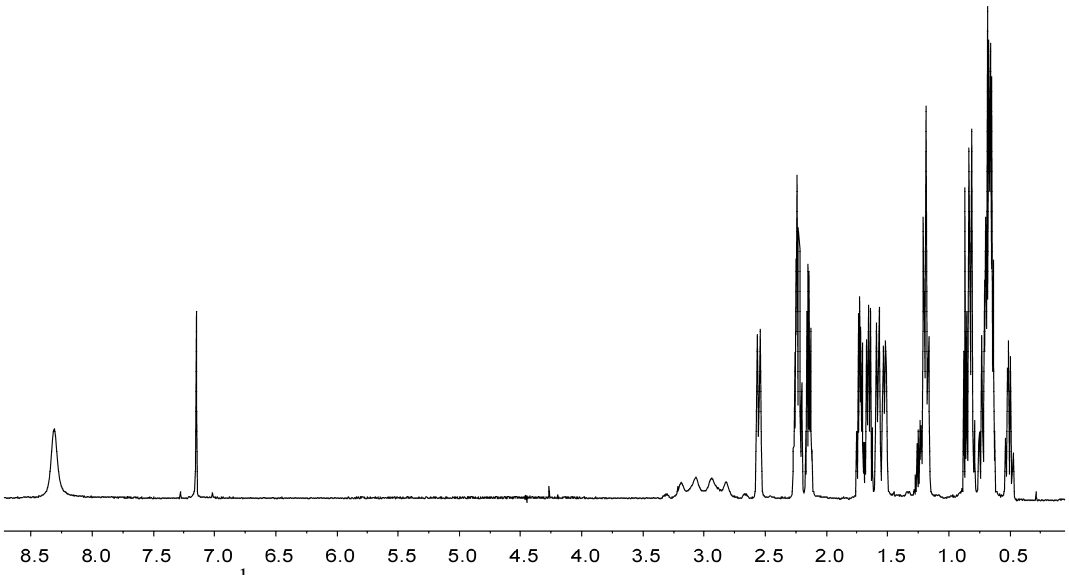
^{1}H{^{1}H} NOE (600 MHz, 298 K, benzene-d_6) δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.55 / 0.72 (3-H / 3′-H), 2.24 / 1.66 (10-H / 10′-H), 2.15 / 1.73 (7-H / 7′-H), 1.66 / 2.24 (10′-H / 10-H), 1.58 / 1.19 (4-H / 2-H, 4′-H), 1.53 / 0.83 (5-H / 5′-H, 6-H), 1.19 / 1.58 (2-H, 4′-H / 4-H), 0.83 / 2.24, 2.22, 1.66, 1.53, 0.51 (5′-H, 6-H / 10-H, 1-H, 10′-H, 5-H, 6′-H), 0.72 / 2.55 (3′-H / 3-H), 0.51 / 1.73, 1.19, 0.83 (6′-H / 7′-H, 2-H, 4′-H, 5′-H, 6-H).

^{11}B{^{1}H} NMR (192 MHz, 298 K, benzene-d_6) δ = -21.5 ($\nu_{1/2}$ ~ 30 Hz).

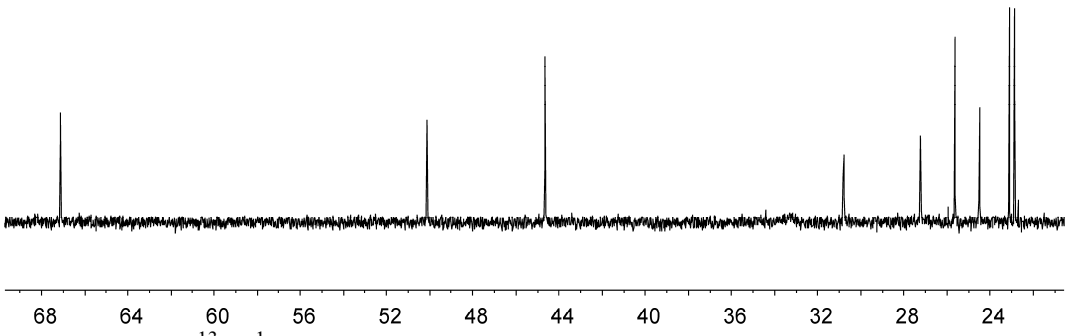
^{11}B NMR (192 MHz, 298 K, benzene-d_6) δ = -21.5 (d, $^{1}J_{BH}$ ~ 75 Hz).

^{19}F NMR (564 MHz, 298 K, benzene-d_6) δ = -132.2 (m, 2F, *o*-$C_6F_5^A$), -133.2 (m, 2F, *o*-$C_6F_5^B$), -161.0 (t, ^{3}J = 19.8 Hz, 1F, *p*-$C_6F_5^A$), -162.3 (t, ^{3}J = 19.6 Hz, 1F, *p*-$C_6F_5^B$), -164.4 (m, 2F, *m*-$C_6F_5^A$), -165.6 (m, 2F, *m*-$C_6F_5^B$), [$\Delta\delta^{19}F_{mp}$ = 3.4^A, 3.3^B].

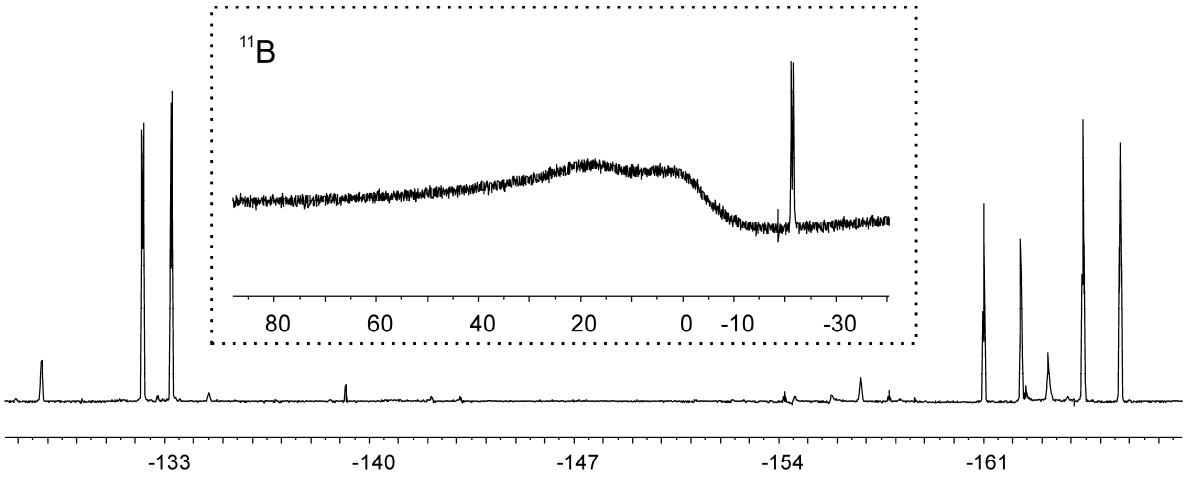
^{19}F,^{19}F GCOSY (564 MHz, 298 K, benzene-d_6) δ ^{19}F / δ ^{19}F = -164.4 / -132.2, -161.0 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), -165.6 / -133.2, -162.3 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$).



^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **9e**

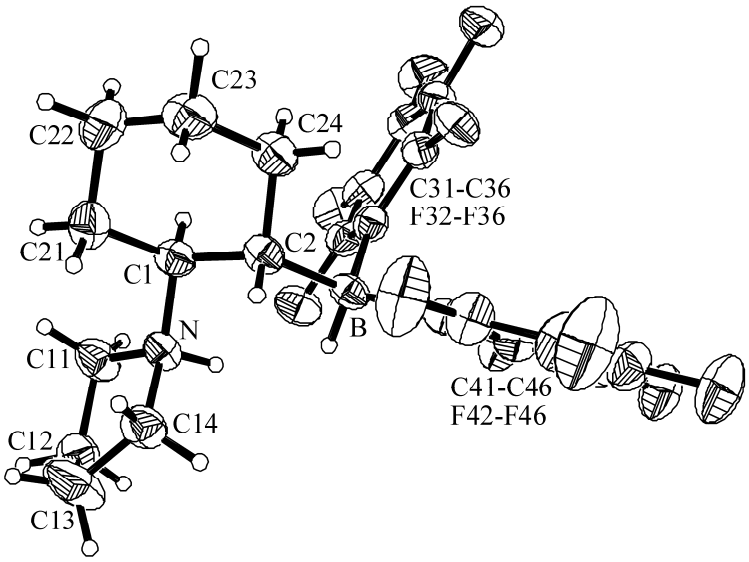


^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) of **9e**.

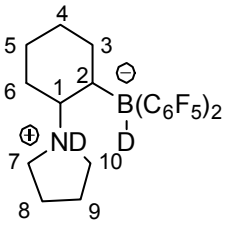


^{19}F NMR (564 MHz, 298 K, benzene-d_6) of **9e**.

Crystal data for $C_{22}H_{20}BF_{10}N$ (**9e**), M = 499.20, orthorhombic, $P2_12_12_1$ (No. 19), a = 10.9724(4), b = 11.3362(5), c = 16.9960(7) Å, V = 2114.05(15) Å^3, D_c = 1.568 g cm^{-3}, μ = 1.360 mm^{-1}, F(000) = 1016, Z = 4, λ = 1.54178 Å, T = 223(2) K, 10207 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3563 independent (R_{int} = 0.038), and 3354 observed reflections [I ≥ 2σ(I)], 307 refined parameters, R = 0.037, wR^2 = 0.092, GoF = 1.038, Flack parameter 0.12(12).



Synthesis of 9e-D

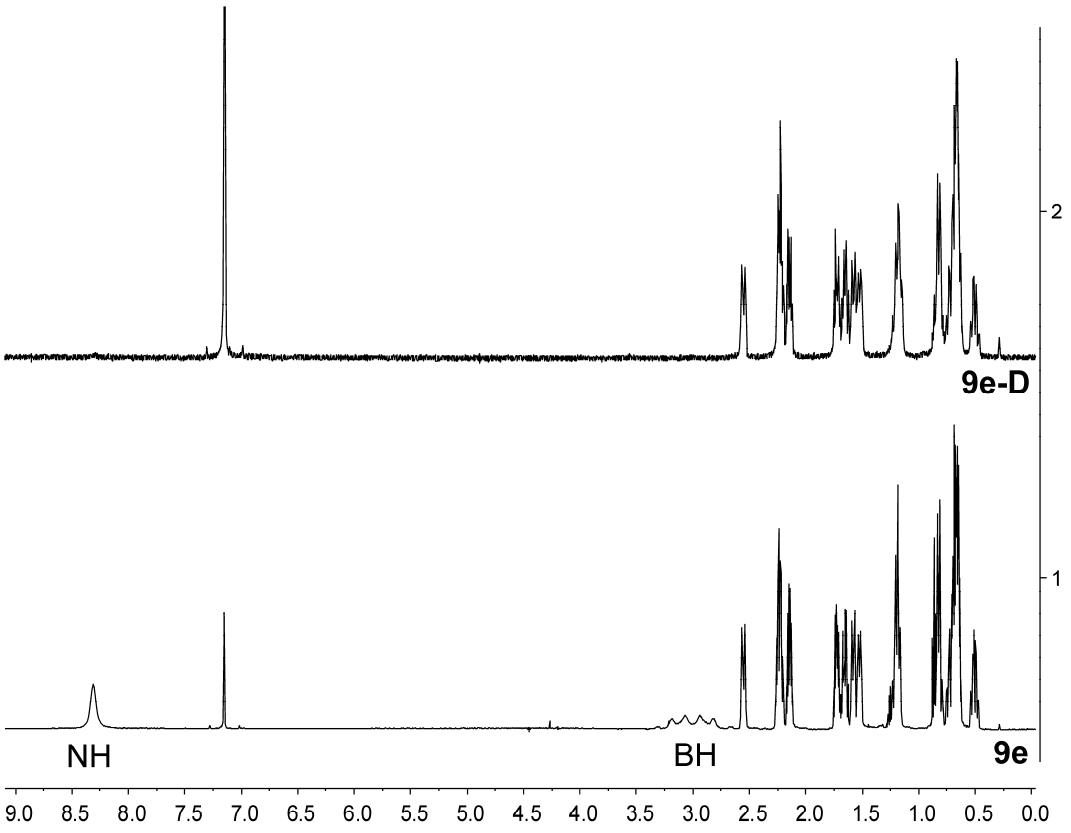


N-(Cyclohex-1-enyl)pyrrolidine (**4e**) (18 mg, 0.116 mmol) and bis(pentafluorophenyl)borane (40 mg, 0.116 mmol) were dissolved in pentane (4 mL). After stirring for 20 minutes at room temperature the Schlenk flask was filled with 2.0 bar deuterium and stirred for 5 minutes. During this time a yellow solid precipitated. Then the connection between the Schlenk flask and deuterium bottle was closed, and the reaction mixture was stirred at room temperature for 20 hours in the deuterium-atmosphere. After removing the solvent with a syringe and washing with pentane (5 mL) the product **9e-D** was isolated as a yellow solid (18 mg, 30%).

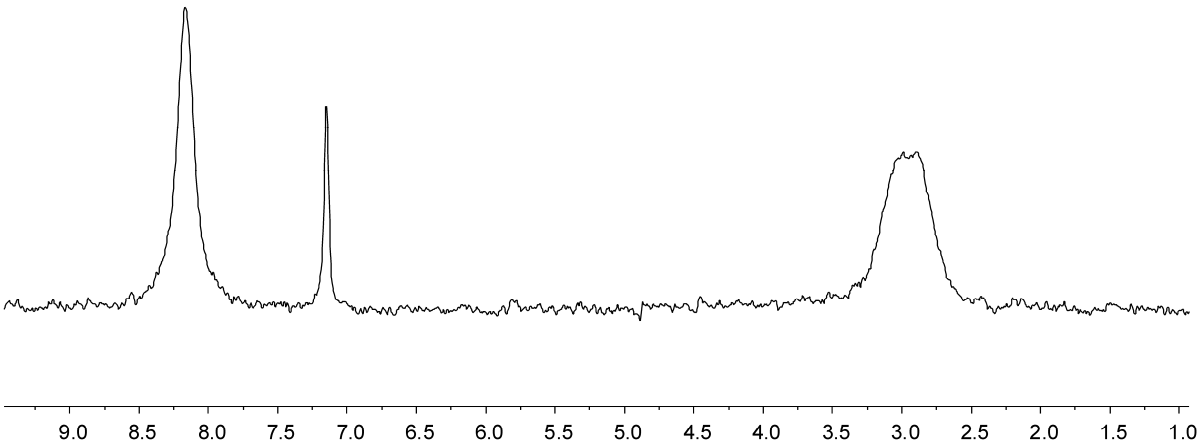
^{1}H NMR (500 MHz, 298 K, benzene-d_6) δ = 2.56 (m, 1H, 3-H), 2.23 (m, 1H, 10-H), 2.21 (m, 1H, 1-H), 2.13 (m, 1H, 7-H), 1.71 (m, 1H, 7′-H), 1.65 (m, 1H, 10′-H), 1.58 (m, 1H, 4-H), 1.52 (m, 1H, 5-H), 1.17 (m, 1H, 4′-H), 1.17 (m, 1H, 2-H), 0.82 (m, 1H, 6-H), 0.82 (m, 1H, 5′-H), 0.72 (m, 1H, 3′-H), 0.67 (m, 2H, 9-H), 0.64 (m, 2H, 8-H), 0.49 (m, 1H, 6′-H).

^{2}H NMR (77 MHz, 298 K, benzene-h_6) δ = 8.19 (br, 1D, N-D), 2.99 (br, 1D, B-D).

^{11}B NMR (160 MHz, 298 K, benzene-d_6) δ = -21.7 ($\nu_{1/2}$ ~ 50 Hz).

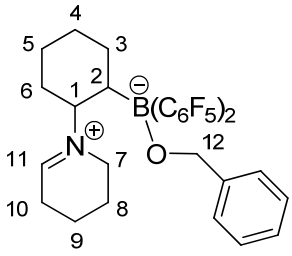


(1) ^{1}H NMR (600 MHz, 298 K, benzene-d_6) of **9e**; (2) ^{1}H NMR (500 MHz, 298 K, benzene-d_6) of **9e-D**.



^{2}H NMR (77 MHz, 298 K, benzene-h_6) of **9e-D**.

Synthesis of 12a



Compound **5d** (97 mg, 0.182 mmol) and benzaldehyde (20 mg, 0.182 mmol) were dissolved in benzene (2 mL). After a while solid precipitated, which was filtered off the solution. It was dissolved in dichloromethane (2 mL), layered with pentane (8 mL) and stored at -30 °C over night. After removing the sovent with a syringe, the product was obtained as a white solid (41 mg, 37%). Anal. Calc. for $C_{30}H_{26}BF_{10}NO$: C 58.37, H 4.25, N 2.27; found: C 57.63, H 4.09, N 2.20.

Crystals suitable for X-ray crytstal structure analysis were obtained by slow evaporation from a pentane/dichloromethane solution of **12a** at -30 °C.

^{1}H NMR (500 MHz, 298 K, dichloromethane-d_2) δ = 8.45 (s, 1H, 11-H), 7.23 (m, 2H, *m*-Ph), 7.18 (m, 2H, *o*-Ph), 7.17 (m, 1H, *p*-Ph), 4.14 (d, $^2J_{HH}$ = 10.8 Hz, 1H, 12-H), 3.83 (d, $^2J_{HH}$ = 10.8 Hz, 1H, 12′-H), 3.80 (m, 1H, 7-H), 3.42 (m, 1H, 7′-H), 3.03 (m, 1H, 1-H), 2.14 (m, 1H, 10-H), 2.03 (m, 1H, 2-H), 1.92 (m, 1H, 6-H), 1.85 (m, 1H, 3-H), 1.80 (m, 1H, 10′-H), 1.77 (m, 1H, 5-H), 1.76 (m, 1H, 8-H), 1.62 (m, 1H, 4-H), 1.60 (m, 1H, 8′-H), 1.35 (m, 1H, 6′-H), 1.29 (m, 1H, 9-H), 1.24 (m, 1H, 9′-H), 1.20 (m, 1H, 4′-H), 1.15 (m, 1H, 5′-H), 0.81 (m, 1H, 3′-H) [kb_sin236_080310_298k_1h.fid].

^{13}C{^{1}H} NMR (126 MHz, 298 K, dichloromethane-d_2): δ = 173.9 (br, C11), 144.0 (*i*-Ph), 128.8 (*o*-Ph), 128.3 (*m*-Ph), 126.9 (*p*-Ph), 76.6 (C1), 67.8 (C12), 50.1 (C7), 36.5 (C6), 36.0 (br, C2), 29.5 (C3), 27.4 (C4), 27.2 (C10), 26.5 (C5), 21.2 (C8), 16.0 (C9), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 298 K, dichloromethane-d_2): δ ^{1}H / δ ^{1}H = 8.45 / 2.14, 1.80 (11-H / 10-H, 10′-H), 7.23 / 7.18 (*m*-Ph / *o*-Ph), 4.14 / 3.83 (12-H / 12′-H), 3.80 / 3.42 (7-H / 7′-H), 3.42 / 3.80, 1.60 (7′-H / 7-H, 8′-H), 3.03 / 2.03, 1.92, 1.35 (1-H / 2-H, 6-H, 6′-H), 2.14 / 8.45 (10-H / 11-H), 2.03 / 3.03, 1.85, 0.81 (2-H / 1-H, 3-H, 3′-H), 1.92 / 3.03, 1.77, 1.35, 1.15 (6-H / 1-H, 5-H, 6′-H, 5′-H), 1.85 / 2.03, 1.62, 1.20, 0.81 (3-H / 2-H, 4-H, 4′-H, 3′-H), 1.77 / 1.92, 1.15 (5-H / 6-H, 5′-H), 1.76 / 3.80, 3.42, 1.60, 1.29 (8-H / 7-H, 7′-H, 8′-H, 9-H), 1.62 / 1.85, 1.20, 1.15, 0.81 (4-H / 3-H, 4′-H, 5′-H, 3′-H), 1.60 / 3.42 (8′-H / 7′-H), 1.35 / 1.92, 1.15 (6′-H / 6-H, 5′-H), 1.29 / 2.14, 1.76, 1.60 (9-H / 10-H, 8-H, 8′-H), 1.24 / 2.14 (9′-H / 10-H), 1.20 / 1.85, 1.77, 1.62, 0.81 (4′-H / 3-H, 5-H, 4-H, 3′-H), 1.15 / 1.92 (5′-H / 6-H), 0.81 / 2.03, 1.85, 1.62, 1.20, 1.15 (3′-H / 2-H, 3-H, 4-H, 4′-H, 5′-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, dichloromethane-d_2): δ ^{1}H / δ ^{13}C = 8.45 / 173.9 (11-H / C11), 7.23 / 128.3 (*m*-Ph / *m*-Ph), 7.18 / 128.8 (*o*-Ph/ *o*-Ph), 7.17 / 126.9 (*p*-Ph / *p*-Ph), 4.14, 3.83 / 67.8 (12-H, 12′-H / C12), 3.80 / 50.1 (7-H / C7), 3.42 / 50.1 (7′-H / C7), 3.03 / 76.6 (1-H /C1), 2.14 / 27.2 (10-H / C10), 2.03 / 36.0 (2-H / C2), 1.92 / 36.5 (6-H / C6), 1.85 / 29.5 (3-H / C3), 1.80 / 27.2 (10′-H / C10), 1.77 / 26.5 (5-H / C5), 1.76 / 21.2 (8-H / C8), 1.62 / 27.4 (4-H / C4), 1.60 / 21.2 (8′-H / C8), 1.35 / 36.5 (6′-H / C6), 1.29 / 16.0 (9-H / C9), 1.24 / 16.0 (9′-H / C9), 1.20 / 27.4 (4′-H / C4), 1.15 / 26.5 (5′-H / C5), 0.81 / 29.5 (3′-H / C3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, dichloromethane-d_2): δ ^{1}H / δ ^{13}C = 7.23 / 144.0 (*m*-Ph / *i*-Ph), 7.18 / 67.8 (*o*-Ph / C12), 4.14, 3.83 / 144.0, 128.8 (12-H, 12′-H / *i*-Ph, *o*-Ph), 1.15 / 27.2 (5′-H / C10).

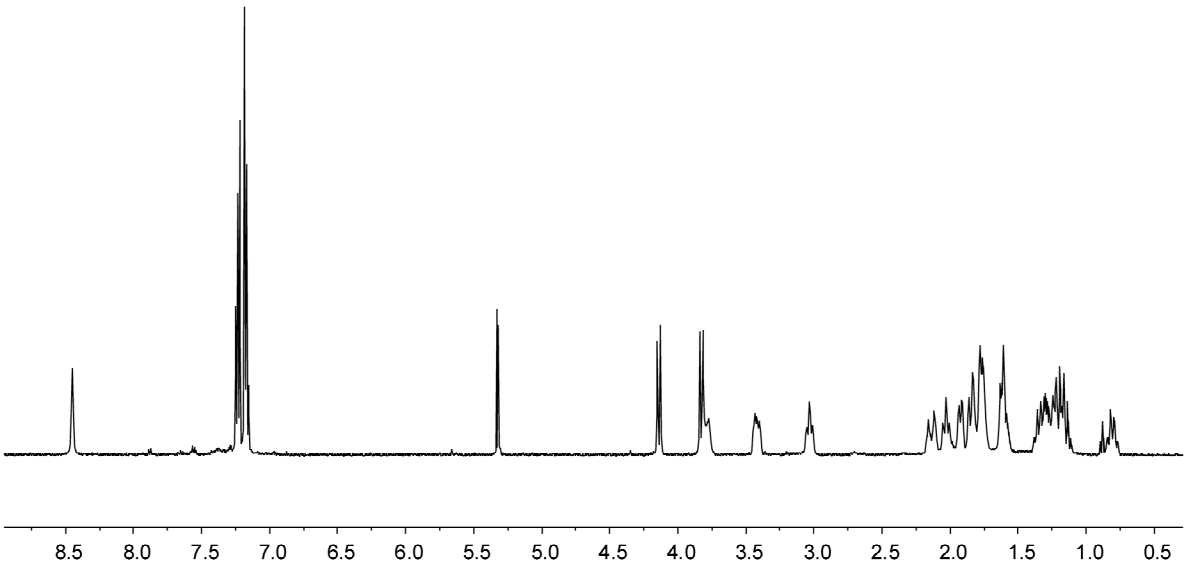
^{1}H{^{1}H} TOCSY (500 MHz, 298 K, dichloromethane-d_2): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.14 / 8.45, 3.80, 3.42, 1.76, 1.60, 1.29, 1.24 (10-H / 11-H, 7-H, 7′-H, 8-H, 8′-H, 9-H, 9′-H), 0.81 / 2.03, 1.92, 1.85, 1.77, 1.62, 1.35, 1.15 (3′-H / 2-H, 6-H, 3-H, 5-H, 4-H, 6′-H, 5′-H), [selected experiments].

^{1}H{^{1}H} NOE (500 MHz, 298 K, dichloromethane-d_2): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 8.45 / 3.03, 2.03 (11-H / 1-H, 2-H), 7.23 / 7.17 (*m*-Ph / *p*-Ph), 4.14 / 7.17, 3.83 (12-H / *p*-Ph, 12′-H), 3.80 / 4.14, 3.42 (7-H / 12-H, 7′-H), 3.42 / 3.80, 3.03, 1.76, 1.35 (7′-H / 7-H, 1-H, 8-H, 6′-H), 3.03 / 8.45, 3.42, 1.92, 0.81 (1-H / 11-H, 7′-H, 6-H, 3′-H), 2.14 / 8.45, 1.80 (10-H / 11-H, 10′-H), 2.03 / 8.45 (2-H / 11-H), 1.92 / 3.80, 3.03, 1.35, 1.20 (6-H / 7-H, 1-H, 6′-H, 4′-H), 1.85 / 1.60, 1.20, 0.81 (3-H / 8′-H, 4′-H, 3′-H), 1.80 / 1.60 (10′-H / 8′-H), 1.77 / 1.35, 1.20 (5-H / 6′-H, 4′-H), 1.60 / 1.20 (8′-H / 4′-H), 1.29 / 1.92, 1.80 (9-H / 6-H, 10′-H), 1.15 / 1.77, 1.62 (5′-H / 5-H, 4-H), 0.81 / 3.03, 1.85, 1.62 (3′-H / 1-H, 3-H, 4-H).

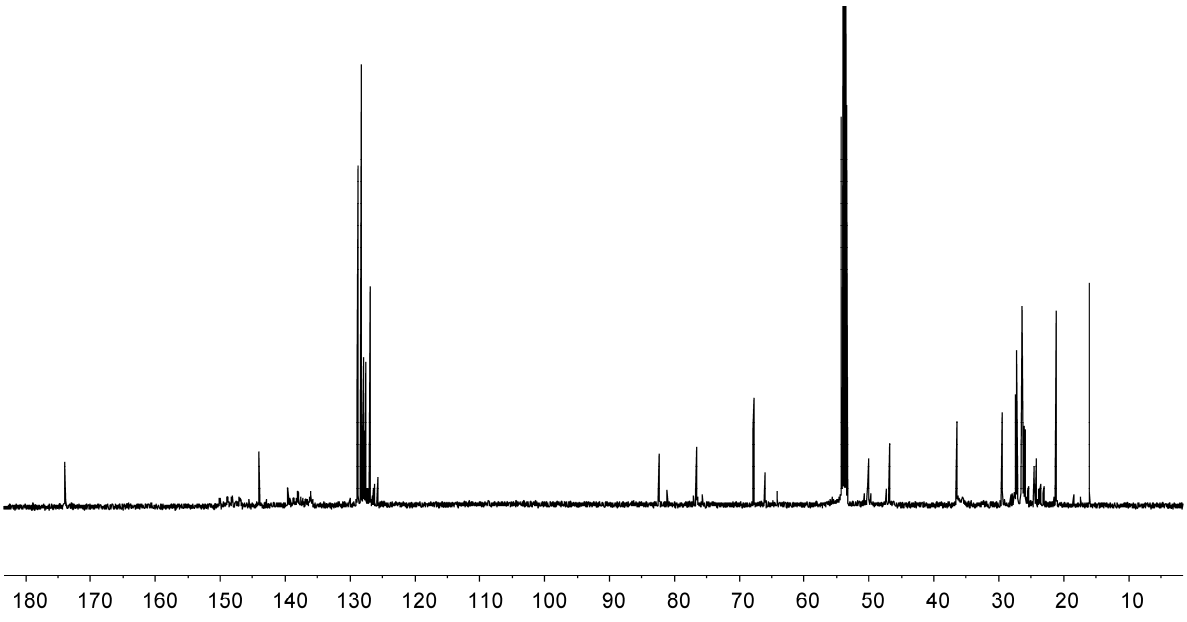
^{11}B{^{1}H} NMR (160 MHz, 298 K, dichloromethane-d_2): δ = 1.6 ($\nu_{1/2}$ ~ 55 Hz).

^{19}F NMR (470 MHz, 298 K, dichloromethane-d_2): δ = -131.7 (m, 2F, *o*-$C_6F_5^A$), -132.0 (br, 2F, *o*-$C_6F_5^B$), -162.5 (t, ^{3}J = 20.5 Hz, 1F, *p*-$C_6F_5^B$), -162.6 (t, ^{3}J = 20.5 Hz, 1F, *p*-$C_6F_5^A$), -165.7 (m, 2F, *m*-$C_6F_5^B$), -166.3 (m, 2F, *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{mp}$ = 3.7^A, 3.2^B].

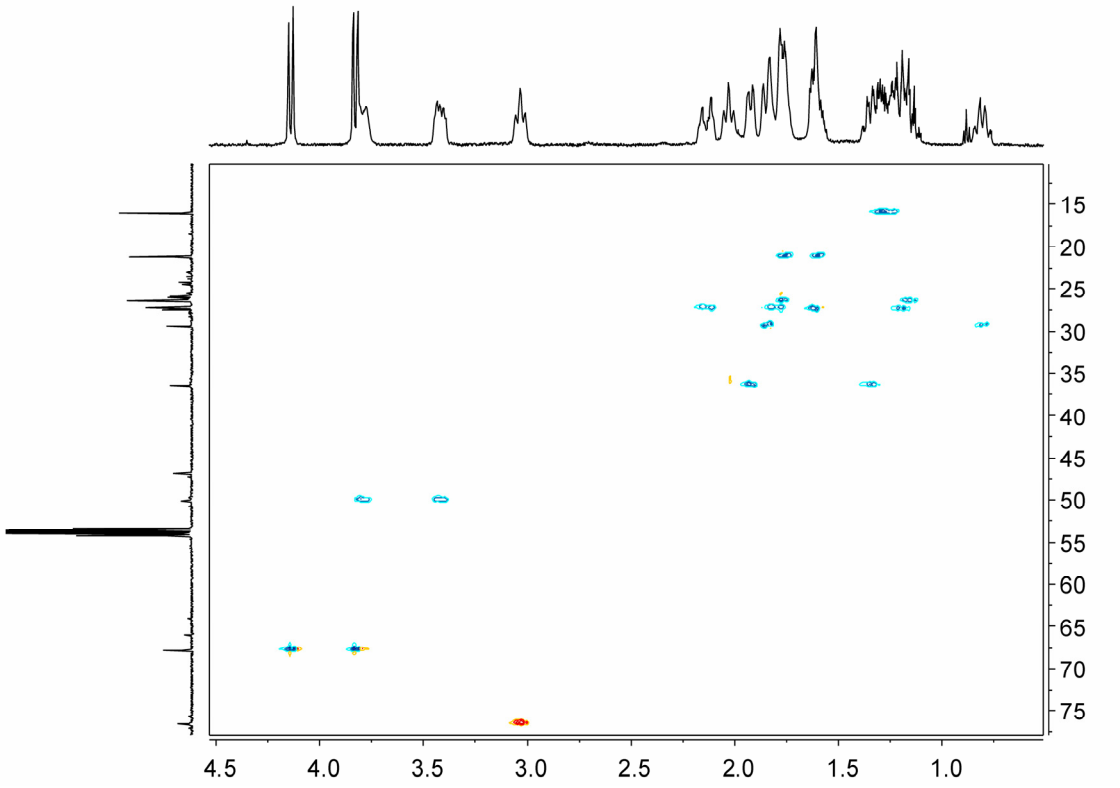
^{19}F,^{19}F GCOSY (564 MHz, 298 K, benzene-d_6) δ ^{19}F / δ ^{19}F = -165.7 / -132.0, -162.5 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$), -166.3 / -131.7, -162.6 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$).



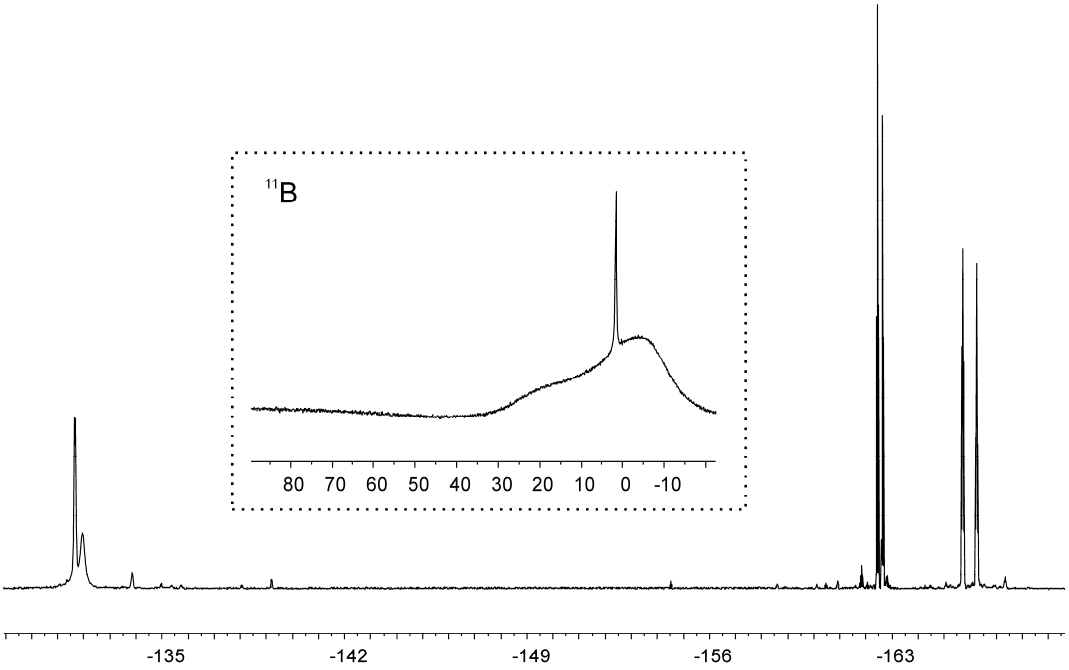
^{1}H NMR (600 MHz, 298 K, dichloromethane-d_2) of **12a**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, dichloromethane-d_2) of **12a**

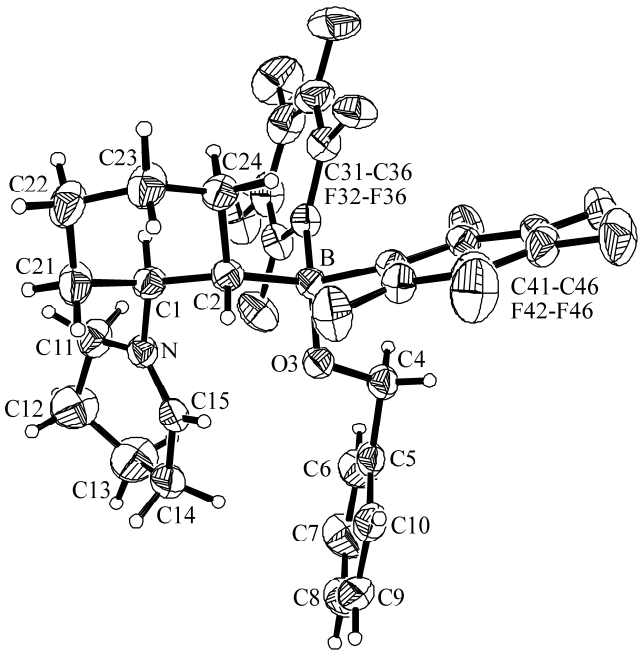


$^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 298 K, dichloromethane-d_2) of **12a**

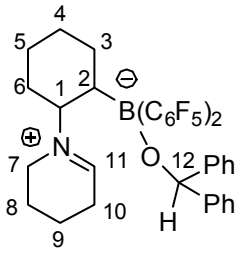


^{19}F NMR (470 MHz, 298 K, dichloromethane-d_2) and ^{11}B{^{1}H} NMR (160 MHz, 298 K, dichloromethane-d_2) of **12a**.

Crystal data for $C_{30}H_{26}BF_{10}NO$ (**12a**), M = 617.33, triclinic, P1bar (No. 2), a = 9.4180(4), b = 11.0909(6), c = 14.6744(8) Å, α = 108.637(3), β = 96.263(3), γ = 105.831(2)°, V = 1366.01(12) Å^3, D_c = 1.501 g cm^{-3}, μ = 1.202 mm^{-1}, F(000) = 632, Z = 4, λ = 1.54178 Å, T = 223(2) K, 22561 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4675 independent (R_{int} = 0.044), and 4030 observed reflections [I ≥ 2σ(I)], 388 refined parameters, R = 0.044, wR^2 = 0.114, GoF = 1.033.



Synthesis of 12b



N-(Cyclohex-1-enyl)piperidine (**4d**) (40 mg, 0.244 mmol) and bis(pentafluorophenyl)borane (85 mg, 0.244 mmol) were dissolved in pentane (2 ml). Then benzophenone (45 mg ,0.244 mmol) was added. While storing at -30 °C after a few days a white solid precipitated, which was filtered off the solution. The product **12b** was isolated as a white solid (23 mg, 14%) [mixture of benzophenone and **12b** (+ traces of **4d**, diphenylmethanol and compounds not identified yet) ~ 1 : 1 (94%)]. Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation from a pentane/dichloromethane solution of **5d** at -30 °C.

Benzophenone: **^{1}H NMR** (600 MHz, 298 K, dichloromethane-d_2) δ = 7.79 (m, 2H, *o*-Ph), 7.61 (m, 1H, *p*-Ph), 7.50 (m, 2H, *m*-Ph^{A}).

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-d_2): δ = 196.7 (C=O), 138.0 (*i*-Ph), 132.7 (*p*-Ph), 130.3 (*o*-Ph), 128.6 (*m*-Ph).

Diphenylmethanol (traces): **^{1}H NMR** (600 MHz, 298 K, dichloromethane-d_2) δ = 7.27 (m, 2H, *o*-Ph), 7.17 (m, 2H, *m*-Ph), 7.08 (m, 2H, *p*-Ph), 5.33 (s, 1H, 12-H), n.o. (OH).

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-d_2): δ = 146.1 (*i*-Ph), 128.3 (*m*-Ph), 126.8 (*i*-Ph), 125.9 (*o*-Ph), 78.5 (C12).

4d (traces; key resonances): 4.62 / 100.0 (2-H / C2), 2.72 / 49.4 (7-H / C7).

12b: ^{1}H NMR (600 MHz, 298 K, dichloromethane-d_2) δ = 8.56 (m, 1H, 11-H), 7.26 (m, 2H, *o*-Ph^{A}), 7.20 (m, 2H, *m*-Ph^{A}), 7.11 (m, 1H, *p*-Ph^{A}), 7.08 (m, 2H, *o*-Ph^{B}), 7.01 (m, 2H, *m*-Ph^{B}), 6.91 (m, 1H, *p*-Ph^{B}), 5.26 (s, 1H, 12-H), 3.99 (m, 1H, 7-H), 3.40 (m, 1H, 7′-H), 3.00 (m, 1H, 1-H), 2.12 (m, 1H, 10-H), 2.09 (m, 1H, 10′-H), 2.06 (m, 1H, 2-H), 1.88 (m, 1H, 6-H), 1.85 (m, 1H, 3-H), 1.79 (m, 1H, 5-H), 1.75 (m, 1H, 8-H), 1.61 (m, 1H, 4-H), 1.57 (m, 1H, 8′-H), 1.47 (m, 1H, 6′-H), 1.29 (m, 2H, 9-H), 1.23 (m, 1H, 4′-H), 1.18 (m, 1H, 5′-H), 0.76 (m, 1H, 3′-H).

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-d_2): δ = 174.3 (C11), 147.5 (*i*-Ph^{A}), 147.5 (*i*-Ph^{B}), 128.3 (*o*-Ph^{A}), 128.2 (*m*-Ph^{A}), 127.3 (*m*-Ph^{B}), 126.6 (*p*-Ph^{A}), 125.8 (*o*-Ph^{B}), 125.6 (*p*-Ph^{B}), 80.6 (C12), 78.1 (C1), 50.0 (C7), 37.0 (C6), 36.7 (br, C2), 29.8 (C3), 27.7 (C10), 27.5 (C4), 26.6 (C5), 21.1 (C8), 15.9 (C9), [C_6F_5 not listed].

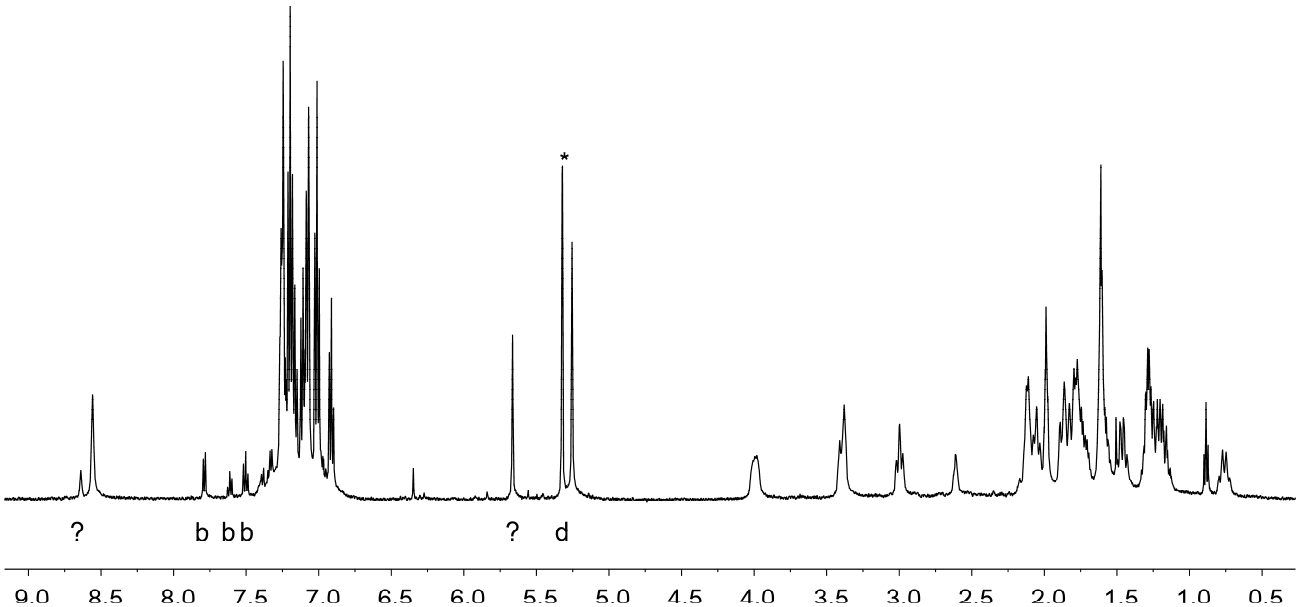
^{1}H,^{1}H GCOSY (600 MHz, 298 K, dichloromethane-d_2): δ ^{1}H / δ ^{1}H = 8.56 / 3.99, 3.40, 2.12, 2.09 (11-H / 7-H, 7′-H, 10-H, 10′-H), 7.26 / 7.20 (*o*-Ph^{A} / *m*-Ph^{A}), 7.20 / 7.26, 7.11 (*m*-Ph^{A} / *o*-Ph^{A}, *p*-Ph^{A}), 7.11 / 7.20 (*p*-Ph^{A} / *m*-Ph^{A}), 7.08 / 7.01 (*o*-Ph^{B} / *m*-Ph^{B}), 7.01 / 7.09, 6.91 (*m*-Ph^{B} / *o*-Ph^{B}, *p*-Ph^{B}), 6.91 / 7.01 (*p*-Ph^{B} / *m*-Ph^{B}), 5.26 / 7.26, 7.08 (12-H / *o*-Ph^{A}, *o*-Ph^{B}), 3.99 / 3.40 (7-H / 7′-H), 3.40 / 3.99, 1.75 (7′-H / 7-H, 8-H), 3.00 / 2.06, 1.88, 1.47 (1-H / 2-H, 6-H, 6′-H), 2.12, 2.09 / 8.56, 1.29 (10-H, 10′-H / 11-H, 9-H), 2.06 / 3.00, 1.85, 0.76 (2-H / 1-H, 3-H, 3′-H), 1.86 / 3.00, 1.79, 1.47 (6-H / 1-H, 5-H, 6′-H), 1.85 / 1.61, 1.22, 0.76 (3-H / 4-H, 4′-H, 3′-H), 1.79 /

1.88, 1.61, 1.22 (5-H / 6-H, 4-H, 4′-H), 1.75 / 3.40, 1.57, 1.29 (8-H / 7′-H, 8′-H, 9-H), 1.61 / 1.85, 1.22, 0.76 (4-H / 3-H, 4′-H, 3′-H), 1.57 / 3.99, 3.40, 1.75 (8′-H / 7-H, 7′-H, 8-H), 1.46 / 3.00, 1.88, 1.75, 1.22 (6′-H / 1-H, 6-H, 8-H, 4′-H), 1.29 / 2.12, 2.09 (9-H / 10-H, 10′-H), 1.22 / 1.83, 1.61, 0.76 (4′-H / 3-H, 4-H, 3′-H), 1.18 / 1.88, 1.76, 1.61, 1.47 (5′-H / 6-H, 5-H, 4-H, 6′-H), 0.76 / 2.06, 1.85, 1.61, 1.22 (3′-H / 2-H, 3-H, 4-H, 4′-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, dichloromethane-d_2): δ ^{1}H / δ ^{13}C = 8.56 / 174.3 (11-H / C11), 7.26 / 128.3 (*o*-Ph^{A} / *o*-Ph^{A}), 7.20 / 128.2 (*m*-Ph^{A}/ *m*-Ph^{A}), 7.11 / 126.6 (*p*-Ph^{A}/ *p*-Ph^{A}), 7.08 / 125.8 (*o*-Ph^{B} / *o*-Ph^{B}), 7.01 / 127.3 (*m*-Ph^{B}/ *m*-Ph^{B}), 6.91 / 125.6 (*p*-Ph^{B}/ *p*-Ph^{B}), 5.26 / 80.6 (12-H / C12), 3.99 / 50.0 (7-H / C7), 3.40 / 50.0 (7′-H / C7), 3.00 / 78.1 (1-H /C1), 2.12, 2.09 / 27.7 (10-H, 10′-H / C10), 2.06 / 36.7 (2-H / C2), 1.88 / 37.0 (6-H / C6), 1.85 / 29.8 (3-H / C3), 1.79 / 26.6 (5-H / C5), 1.75 / 21.1 (8-H / C8), 1.61 / 27.5 (4-H / C4), 1.57 / 21.1 (8′-H / C8), 1.47 / 37.0 (6′-H / C6), 1.29 / 15.9 (9-H / C9), 1.22 / 27.5 (4′-H / C4), 1.18 / 26.6 (5′-H / C5), 0.76 / 29.6 (3′-H / C3).

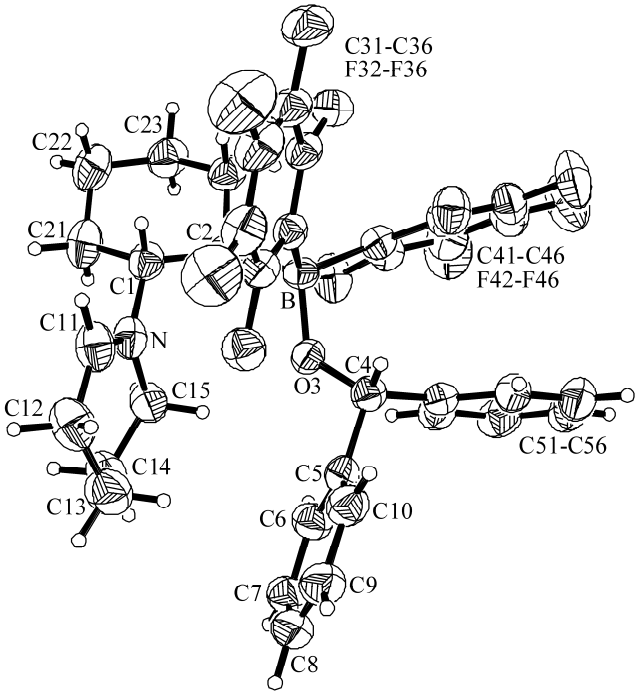
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, dichloromethane-d_2): δ ^{1}H / δ ^{13}C = 7.26 / 126.6, 80.6 (*o*-Ph^{A} / *p*-Ph^{A}, C12), 7.11 / 128.3 (*p*-Ph^{A} / *o*-Ph^{A}), 7.08 / 125.6, 80.6 (*o*-Ph^{B} / *p*-Ph^{B}, C12), 5.26 / 128.3, 125.8 (12-H / *o*-Ph^{A}, *o*-Ph^{B}), 1.29 / 50.0, 27.7, 21.1 (9-H / C7, C10, C8).

^{1}H{^{1}H} TOCSY (600 MHz, 298 K, dichloromethane-d_2): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 8.56 / 3.99, 3.40, 2.12, 2.09, 1.75, 1.57, 1.29 (11-H / 7-H, 7′-H, 10-H, 10′-H, 8-H, 8′-H, 9-H), 7.20 / 7.26, 7.11 (*m*-Ph^{A} / *o*-Ph^{A}, *p*-Ph^{A}), 7.08 / 7.01, 6.91 (*o*-Ph^{B} / *m*-Ph^{B}, *p*-Ph^{B}), 3.00 / 2.06, 1.88, 1.85, 1.79, 1.61, 1.47, 1.22, 1.18, 0.76 (1-H / 2-H, 6-H, 3-H, 5-H, 5′-H, 4-H, 6′-H, 4′-H, 3′-H) [selected experiments].



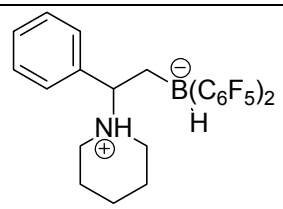
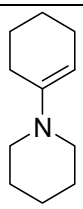
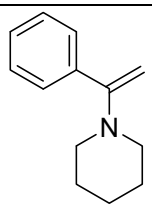
^{1}H NMR (600 MHz, 298 K, dichloromethane-d_2) of **12d** (b: benzophenone; d: diphenylmethanol; ?: compounds not identified yet).

Crystal data for $C_{36}H_{30}BF_{10}NO$ * C_7H_8(**12b**), M = 785.55, monoclinic, $P2_1/c$ (No. 14), a = 20.3695(8), b = 9.2993(7), c = 21.5910(10) Å, β = 114.314(2)°, V = 3727.1(4) Å^3, D_c = 1.400 g cm^{-3}, μ = 1.008 mm^{-1}, F(000) = 1624, Z = 4, λ = 1.54178 Å, T = 223(2) K, 26897 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6389 independent (R_{int} = 0.072), and 4471 observed reflections [I ≥ 2σ(I)], 507 refined parameters, R = 0.054, wR^2 = 0.157, GoF = 1.036.



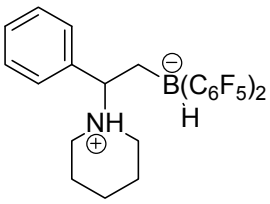
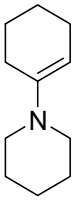
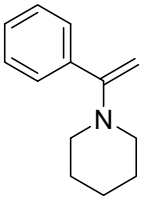
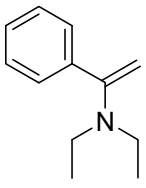
9b in catalytic hydrogenation:

Procedure A: Enamine and catalyst **9b** were dissolved in toluene (5 ml) and the colourless solution was stirred 20 hours under a hydrogen atmosphere of 2.5 bar. During this time the reaction mixture stayed colourless. Then 1 M HCl (20 ml) was added, the aquarous layer was separated, neutralized with 1M sodiumydroxide-solution (23 ml) and extracted with diethylether (3 x 20 ml). The combined organic layers were dried over magnesium sulfate. After evaporation in both cases a yellow oil was obtained.

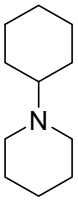
 **9b**	 **4d**	 **4b**
Catalyst [mol %] (**9b**)	20	20
Isolated yield [%] of **10**	53	83

Procedure B: Enamine and catalyst **9b** were dissolved in benzene-d_6 (1 ml) and placed in an autoclave. The autoclave was filled with 60 bar hydrogen and the mixture stirred for 3 hours. After releasing the pressure, the mixture was investigated by NMR spectroscopy subsequently.

Then HCl (1 M, 9 ml) was added to the benzene solution and stirred for 20 minutes. The aquarous layer was separated, neutralized with 1M sodiumydroxide solution (10 ml) and extracted with diethylether (3 × 10 ml). The combined organic layers were dried over magnesium sulfate. After evaporation in all cases the products were obtained as oils.

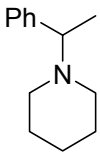
	 **4d**		 **4b**		 **4a**	
Catalyst [mol %] (**9b**)	5	3	5	3	5	3
Conversion from NMR [%]	100	33	83	56	80	55
Isolated yield [%] of **10**	56	~30	~64*,[a]	~37*,[b]	~53*,[c]	~26*,[d]

* Product contaminated with the respective ketone caused by hydrolysis. [a] Overall yield 75%, with ca. 15% acetophenone. [b] Overall yield 46%, with ca. 20% acetophenone. [c] Overall yield 61%, with ca. 13% acetophenone. [d] Overall yield 27%, with ca. 4% acetophenone.



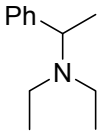
^{1}H NMR (200 MHz, 298 K, benzene-d_6) δ = 2.44 (m, 4H, ^{N}CH$_2$), 2.21 (m, 1H, ^{N}CH), 1.74 (m, 4H, CH$_2$), 1.56 (m, 4H, CH$_2$), 1.37 (m, 2H, CH$_2$), 1.17 (m, 4H, CH$_2$).

MS (ESI, exact Mass): calculated: 168.1747, found: 168.1747 $[C_{11}H_{21}NH]^+$.



^{1}H NMR (200 MHz, 298 K, benzene-d_6) δ = 7.32 (m, 2H, *o*-Ph), 7.20 (m, 2H, *m*-Ph), 7.10 (m, 1H, *p*-Ph), 3.26 (q, $^3J_{HH}$ = 6.4 Hz, 1H, ^{N}CH), 2.31 (m, 4H, ^{N}CH$_2$), 1.48 (m, 4H, CH$_2$), 1.28 (m, 2H, CH$_2$), 1.25 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH$_3$).

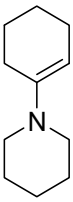
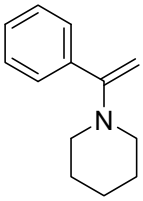
MS (ESI, exact Mass): calculated: 190.1590, found: 190.1607 $[C_{13}H_{19}NH]^+$.



^{1}H NMR (200 MHz, 298 K, benzene-d_6) δ = 7.38 (m, 2H, *o*-Ph), 7.21 (m, 2H, *m*-Ph), 7.12 (m, 1H, *p*-Ph), 3.69 (q, $^3J_{HH}$ = 6.8 Hz, 1H, ^{N}CH), 2.45 (q, $^3J_{HH}$ = 7.2 Hz, 4H, ^{N}CH$_2$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_3$), 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 6H, ^{N}CH$_2$C*H*$_3$).

MS (ESI, exact Mass): calculated: 178.1590, found: 178.1610 $[C_{12}H_{19}NH]^+$.

Control experiments:

Cat: 				
Catalyst [mol %]	20	5	20	5
Conditions	5 mL toluene 20h 2.5 bar H_2 rt	1 mL C_6D_6 3h 60 bar H_2 rt	5 mL Toluene 20h 2.5 bar H_2 rt	1 mL C_6D_6 3h 60 bar H_2 rt
Conversion by NMR	0	0	0	0