Electronic Supplementary Information

Synthesis of new asymmetric substituted boron amidines - Reactions with CO and transfer hydrogenations of phenylacetylene

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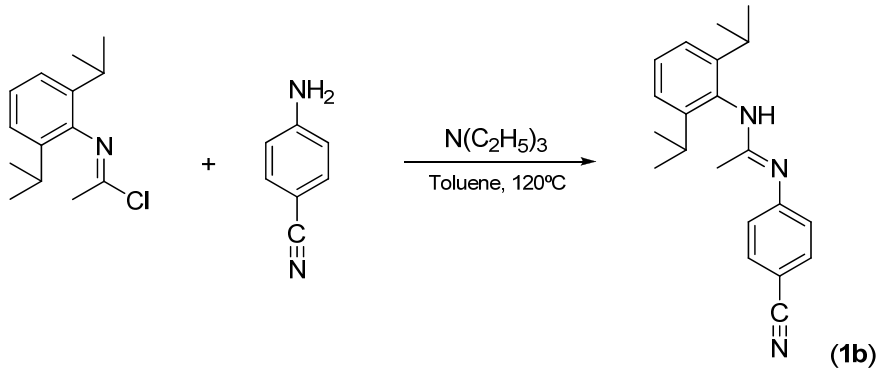
Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from *Aldrich* unless otherwise specified. Toluene and pentane were distilled from benzophenone ketyl. The following instruments were used for the physical characterization of the compounds. NMR: *Varian Inova* 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz), *Bruker Unity Plus* 600 (^{1}H: 600 MHz, ^{31}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 64 MHz) and *Bruker Advance 400*. Most NMR assignments were supported by additional 2D experiments. FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets. X-ray crystal structure analyses: Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. 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) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), 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) and SCHAKAL (E. Keller, 1997). *R*-values are given for the observed reflections, wR^2-values for all.

CCDC 1051038 - 1051040 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

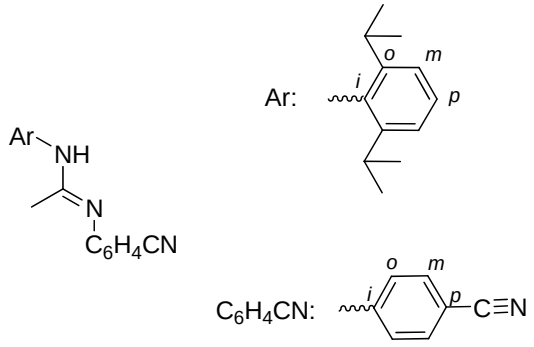
Synthesis and Characterization of Compounds.

N'-(2,6-diisopropylphenyl)-N-(4-cyanophenyl)acetimidamide. (1b)



(**1b**)

N-(2,6-diisopropylphenyl)acetimidoylchloride [1] (1.11 g; 4.7 mmol) and NEt_3 (0.7 ml) was added to a solution of 4-aminobenzonitrile (0.55 g; 4.7 mmol) in anhydrous toluene (40 ml). The mixture was refluxed for 3 h with vigorous stirring. The white precipitated (Et_3NHCl) formed was removed by filtration and the yellow solution was evaporated under vacuum to dryness. The crude product was washed with cold toluene and recrystallized from methanol. Compound **(1b)** was isolated as white solid in (70%) yield (1.04 g; 3.3 mmol).



^{1}H NMR (400 MHz, C_7D_8, 298 K): δ/ppm = 7.48 (d, *J* = 8.6Hz, 2H, *m*-C_6H_4CN), 7.12 (d, *J* = 6.9Hz , 2H, *m*-Ar), 7.09 (m, 1H, *p*-Ar), 7.05 (d, *J* = 8.6Hz, 2H, *o*-C_6H_4CN), 5.83 (br., 1H, *NH*), 2.95 (hept, *J* = 6.9Hz, 2H, HCiPr), 1.33 (s, 3H, MeC), 1.18 (d, *J* = 6.9 Hz, 6H, MeiPr), 1.15 (d, *J* = 6.9 Hz, 6H, MeiPr').

^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 298 K): δ/ppm = 151.7 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 145.1 (*i*-Ar), 144.8 (*i*-C_6H_4CN), 138.1 (*o*-Ar), 133.0 (*o*-C_6H_4CN), 123.8 (*p*-Ar), 123.4 (*m*-Ar), 119.3 (*p*-C_6H_4CN), 118.7 (*m*-C_6H_4CN), 105.3 (C≡N)), 28.6 (HCiPr), 23.8 (MeiPr'), 23.0 (MeiPr), 18.3 (MeC).

^{1}H, ^{13}C-GHMBC (400 MHz / 100 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.48 / 144.8, 105.3 (*m*-C_6H_4CN / *i*-C_6H_4CN, C≡N), 7.12/ 145.1, 28.6 (*m*-Ar / *i*-Ar, HCiPr), 7.05 / 144.8, 119.3 (*i*-C_6H_4CN / *p*-C_6H_4CN), 2.95 / 145.1, 138.1, 123.8, 23.8, 23.0 (HCiPr / *i*-Ar, *o*-Ar, *m*-Ar, MeiPr', MeiPr), 1.33 / 151.7 (MeC / $^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 1.18 / 138.1, 28.6, 23.8 (MeiPr / *o*-Ar, HCiPr, MeiPr'), 1.15 / 138.1, 28.6, 23.0 (MeiPr' / *o*-Ar, HCiPr, MeiPr).

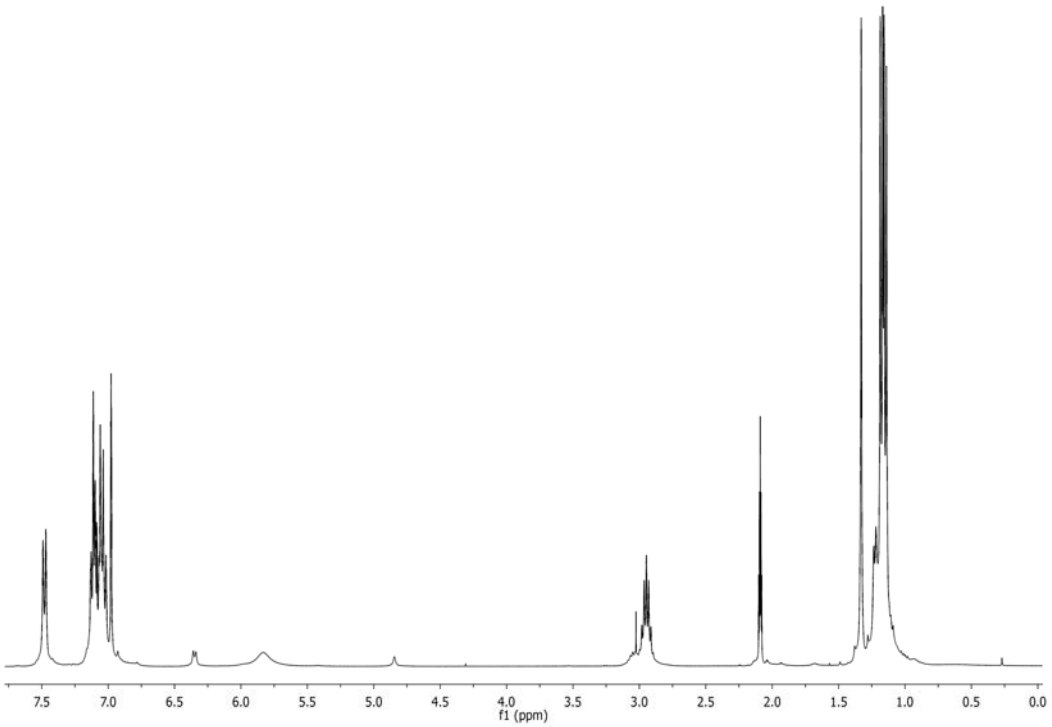
^{1}H, ^{13}C-GHSQC (400 MHz / 100 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.48 / 118.7 (*m*-C_6H_4CN / *m*-C_6H_4CN), 7.12 / 123.4 (*m*-Ar / *m*-Ar), 7.09 / 123.8 (*p*-Ar / *p*-Ar), 7.05 / 133.0 (*o*-C_6H_4CN / *o*-C_6H_4CN), 2.95 / 28.6 (HCiPr / HCiPr), 1.33 / 18.3 (MeC / MeC), 1.18 / 23.0 (MeiPr / MeiPr), 1.15 / 23.8 (MeiPr' / MeiPr').

GCOSY (400 MHz / 400 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{1}H) = 7.48 / 7.05 (*m*-C_6H_4CN / *o*-C_6H_4CN), 2.95 / 1.18 (HCiPr / MeiPr), 2.95 / 1.15 (HCiPr / MeiPr').

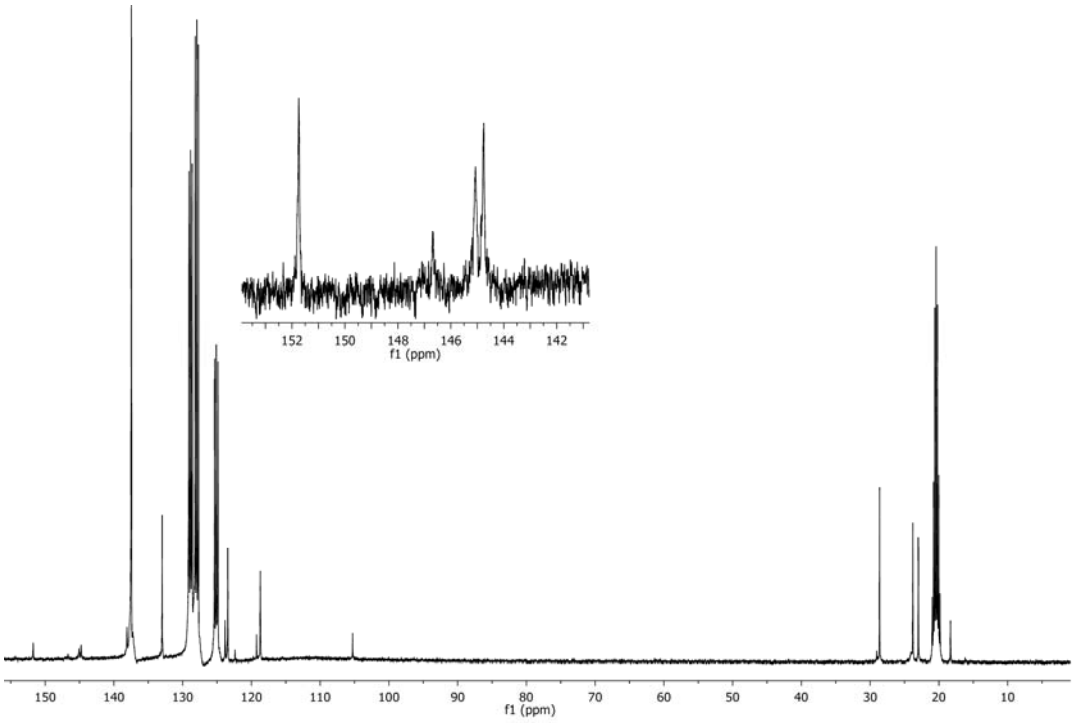
IR (KBr): ν/cm^{-1} = 3427, 3100, 3076, 2965, 2225 (ν(C≡N), s), 1676, 1586, 1536, 1378, 1338, 1195, 1174, 1105, 1058, 1007, 933, 845, 822, 785, 759, 651, 547.

Elemental analysis (%): $C_{21}H_{25}N_3$ (M = 319.44 g/mol): calculated C 78.96, H 7.89, N 13.15; found C 79.04, H 7.84, N 13.17.

MS (ESI, Exact mass**):** Calc: 342.195 ; Found: 342.194 [$C_{21}H_{25}N_3\ Na^+$]. Calc: 320.213 ; Found: 320.212 [$C_{21}H_{25}N_3\ H^+$].

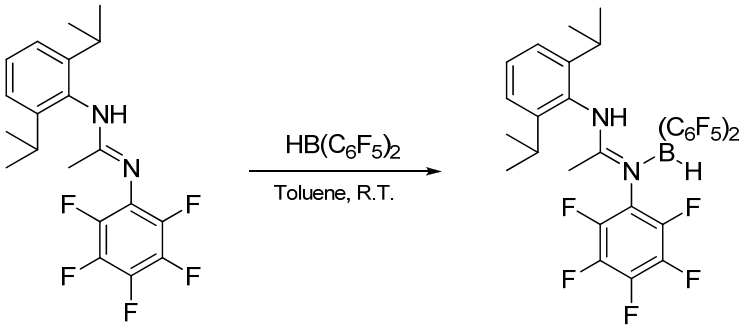


^{1}H NMR (400 MHz, C_7D_8, 298 K)

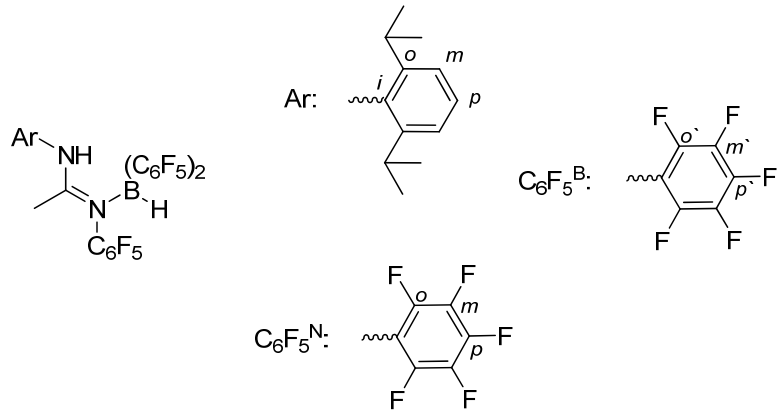


^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 298 K)

[N'-(2,6-diisopropylphenyl)-N-(pentafluorophenyl)acetimidamide]bis(pentafluoro phenyl)borate (2a)



Bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$] (180 mg, 0.52 mmol) in toluene (10 ml) was added to a solution of **1a** [2] (200 mg, 0.52 mmol) in toluene (10 ml). The reaction mixture was stirred for 2 hours at room temperature. Then, the volatiles were removed in vacuum, and the solid washed with pentane. Finally the white solid is recrystallized from cold toluene given **2a** as a white crystalline material in 87% yield (331 mg, 0.45 mmol).



^{1}H NMR (600 MHz, C_7D_8, 298 K): δ/ppm = 8.33 (s, 1H, NH), 7.05 (m, 1H, *p*-Ar), 6.88 (d, *J* = 6.9Hz, 2H, *m*-Ar), 4.57 (br, 1H, *BH*), 2.87 (hept, *J* = 6.9Hz, 2H, HCiPr), 1.27 (s, 3H, MeC), 1.06 (d, *J* = 6.9 Hz, 6H, MeiPr), 0.91 (d, *J* = 6.9 Hz, 6H, MeiPr').

^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K): δ/ppm = 169.2 ($^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 146.3 (*o*-Ar), 131.0 (*p*-Ar), 130.6 (*i*-Ar), 124.8 (*m*-Ar), 28.8 (HCiPr), 23.9 (MeiPr'), 22.6 (MeiPr), 16.8 (MeC).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.05 / 146.3 (*p*-Ar / *o*-Ar), 6.88 / 146.3, 130.6, 28.8 (*m*-Ar / *o*-Ar, *i*-Ar, HCiPr), 2.87 / 146.3, 130.6, 124.8, 23.9, 22.6 (HCiPr

/ *o*-Ar, *i*-Ar, *m*-Ar, MeiPr', MeiPr), 1.27 / 169.2 (MeC / $^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 1.06 / 146.3, 28.8, 23.9 (MeiPr / *o*-Ar, HCiPr, MeiPr'), 0.91 / 146.3, 28.8, 22.6 (MeiPr' / *o*-Ar, HCiPr, MeiPr).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.05 / 131.0 (*p*-Ar / *p*-Ar), 6.88 / 124.8 (*m*-Ar / *m*-Ar), 2.87 / 28.8 (HCiPr / HCiPr), 1.27 / 16.8 (MeC / MeC), 1.06 / 22.6 (MeiPr / MeiPr), 0.91 / 23.9 (MeiPr' / MeiPr').

GCOSY (600 MHz / 600 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{1}H) = 7.05 / 6.88 (*p*-Ar / *m*-Ar), 2.87 / 1.06 (HCiPr / MeiPr), 2.87 / 0.91 (HCiPr / MeiPr').

^{1}H{NOE} NMR (600 MHz, C_7D_8, 298 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 7.05 / 6.88 (*p*-Ar / *m*-Ar), 6.88 / 7.05, 1.06, 0.91 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 2.87 / 1.06, 0.91 (HCiPr / MeiPr, MeiPr'), 1.27 / 1.06, 0.91 (MeC / MeiPr, MeiPr'), 1.06 / 6.88, 2.87, 0.91 (MeiPr / *m*-Ar, HCiPr, MeiPr'), 0.91 / 6.88, 2.87, 1.06 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

1D TOCSY (500 MHz, CD_2Cl_2, 298 K): δ ($^{1}H_{Irr}$) / δ ($^{1}H_{Res}$) [ppm] = 7.05 / 6.88 (*p*-Ar / *m*-Ar), 6.88 / 7.05 (*m*-Ar / *p*-Ar), 2.87 / 1.06, 0.91 (HCiPr / MeiPr, MeiPr'), 1.06 / 6.88, 2.87, 0.91 (MeiPr / *m*-Ar, HCiPr, MeiPr'), 0.91 / 6.88, 2.87, 1.06 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

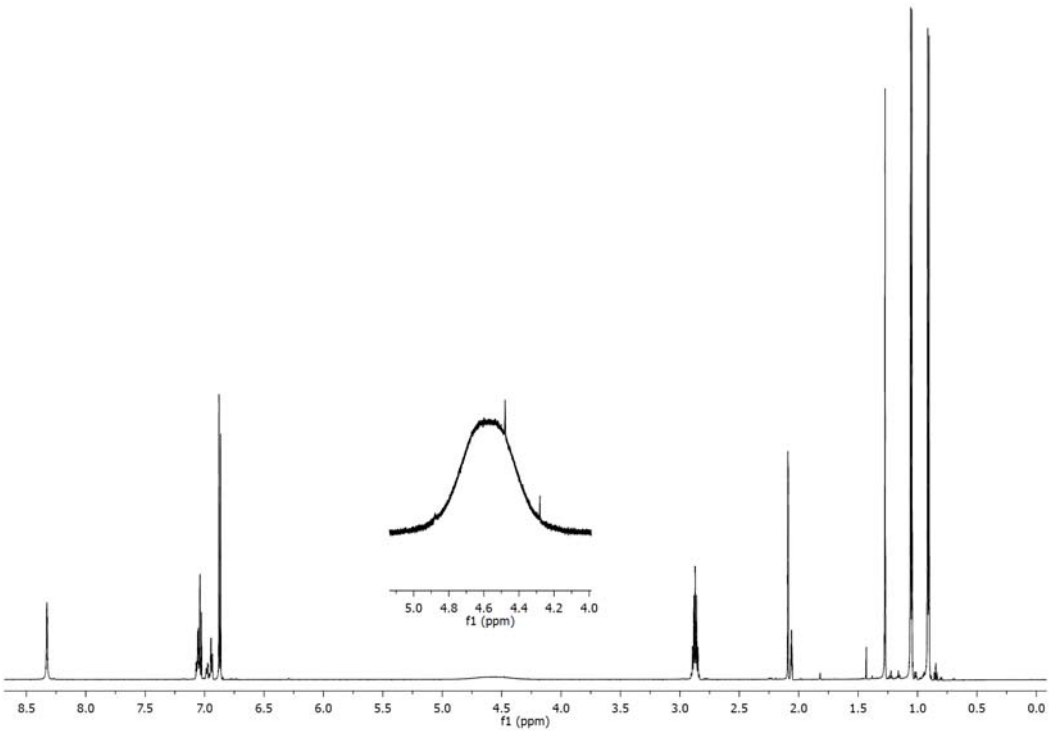
^{19}F NMR (564 MHz, C_7D_8, 298 K): δ/ppm = -132.9 (s, 4F, *o*-$C_6F_5^{B}$), -144.1 (d, *J* = 17.4Hz, 2F, *o*-$C_6F_5^{N}$), -153.3 (t, *J* = 21.9Hz, 1F, *p*-$C_6F_5^{N}$), -157.4 (t, *J* = 20.3Hz, 2F, *p*-$C_6F_5^{B}$), -161.4 (td, *J* = 22.7, 6.2 Hz, 2F, *m*-$C_6F_5^{N}$), -163.7 (td, *J* = 23.8, 9.5 Hz, 4F, *m*-$C_6F_5^{B}$).

^{19}F, ^{19}F GCOSY (564 MHz, C_7D_8, 298 K): δ (^{19}F) / δ (^{19}F) = -132.9 / -163.7 (*o*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$), -144.1 / -161.4 (*o*-$C_6F_5^{N}$ / *m*-$C_6F_5^{N}$), -153.3 / -161.4 (*p*-$C_6F_5^{N}$ / *m*-$C_6F_5^{N}$), -157.4 / -163.7 (*p*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$).

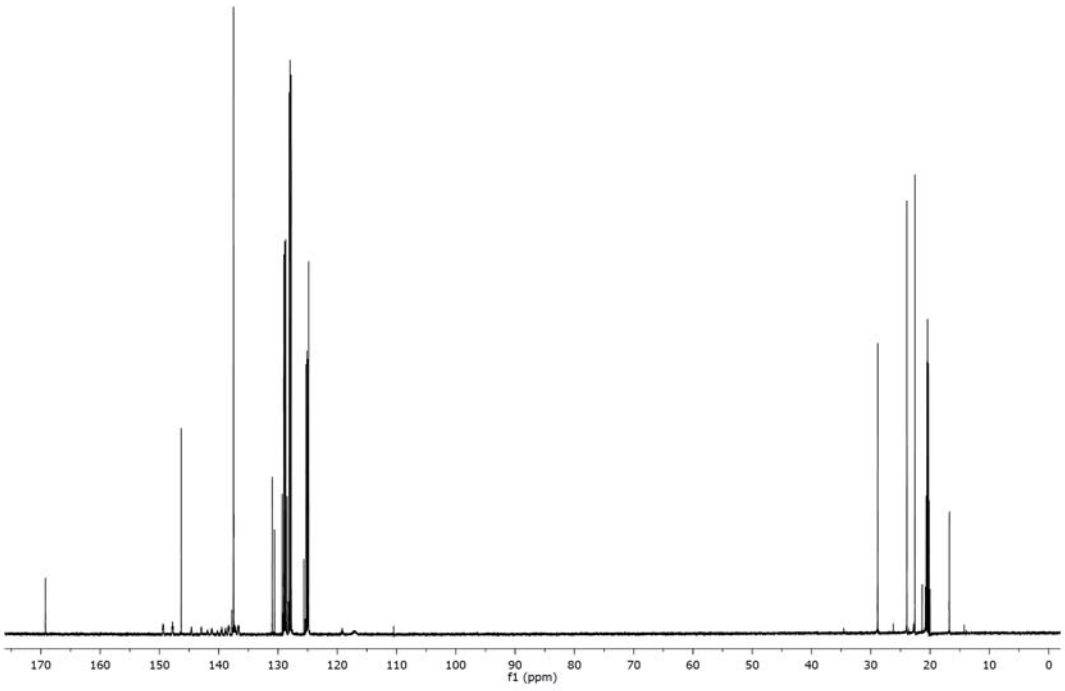
^{11}B{1H} NMR (192 MHz, C_7D_8, 298 K): δ/ppm = -13.3 (ν1/2 ~ 230 Hz).

IR (KBr): ν/cm^{-1} = 3345, 3071, 2973, 2934, 2876, 2388, 1644, 1606, 1529, 1458, 1389, 1331, 1287, 1109, 1043, 994, 972, 913, 878, 849, 818, 801, 766, 741, 701, 670, 565, 535.

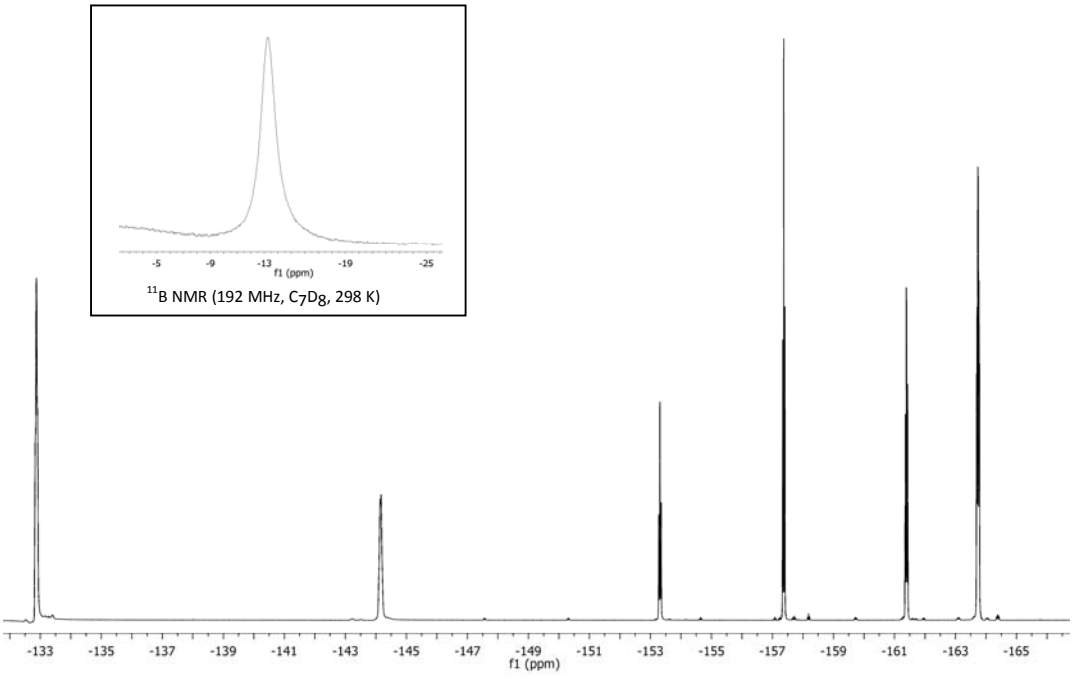
Elemental analysis (%) $C_{32}H_{22}BF_{15}N_2$ (M = 730.32 g/mol): calculated C 52.63, H 3.04, N 3.84; found C 54.30, H 3.27, N 3.80.



^{1}H NMR (600 MHz, C_7D_8, 298 K)



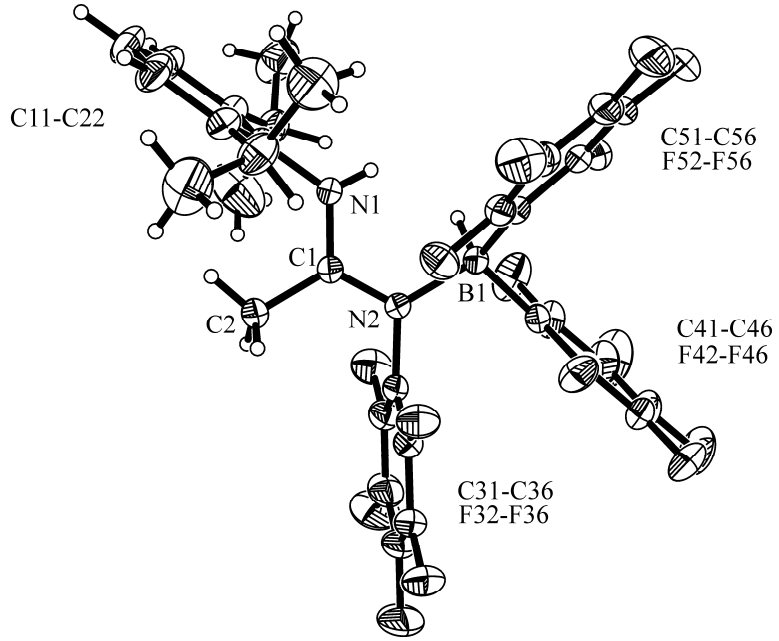
^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K)



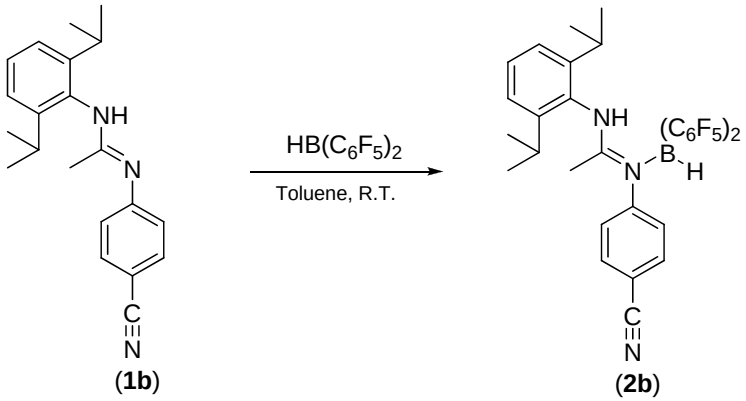
^{11}B NMR (192 MHz, C_7D_8, 298 K)

^{19}F NMR (564 MHz, C_7D_8, 298 K)

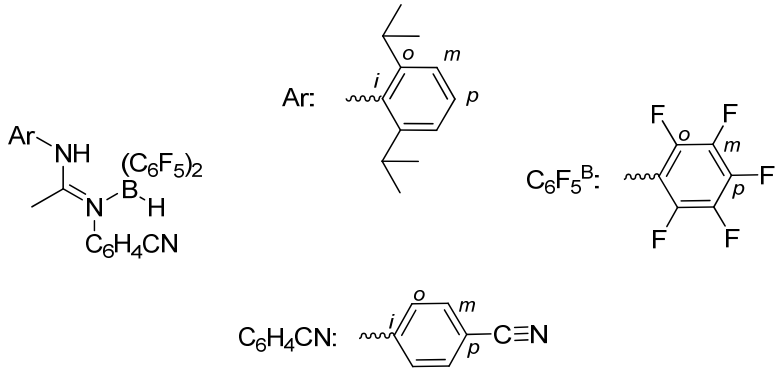
X-ray crystal structure analysis of **2a**:



[N'-(2,6-diisopropylphenyl)-N-(4-cyanophenyl)acetimidamide]bis(pentafluoro phenyl)borate (2b)



Bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$] (217 mg, 0.63 mmol) in toluene (10 ml) was added to a solution of **1b** (200 mg, 0.63 mmol) in toluene (10 ml). The reaction mixture was stirred for 2 hours at room temperature. Then, the volatiles were removed in vacuum and the solid washed with pentane. Finally the white solid is recrystallized from cold toluene given **2b** as white crystalline material in 90% yield (375 mg, 0.56 mmol).



^{1}H NMR (600 MHz, C_7D_8, 298 K): δ/ppm = 8.03 (s, 1H, NH), 7.06 (t, *J* = 7.7Hz, 1H, *p*-Ar), 6.89 (d, *J* = 7.7Hz, 2H, *m*-Ar), 6.81 (d, *J* = 8.5Hz, 2H, *m*-C_6H_4CN), 6.67 (d, *J* = 8.5Hz, 2H, *o*-C_6H_4CN), 4.55 (br, 1H, *BH*), 2.87 (hept, *J* = 6.9Hz, 2H, HCiPr), 1.15 (s, 3H, MeC), 1.08 (d, *J* = 6.9 Hz, 6H, MeiPr), 0.94 (d, *J* = 6.9 Hz, 6H, MeiPr').

^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K): δ/ppm = 165.5 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 147.1 (*i*-$C_6H_4CN$), 146.3 (*o*-Ar), 133.1 (*o*-C_6H_4CN), 131.0 (*i*-Ar), 130.6 (*p*-Ar), 127.2 (*m*-C_6H_4CN), 124.7 (*m*-Ar),117.4 (*p*-C_6H_4CN), 112.4 (C≡N), 29.1 (HCiPr), 23.8 (MeiPr'), 22.5 (MeiPr), 16.9 (MeC).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.06 / 146.3 (*p*-Ar / *o*-Ar), 6.89 / 131.0, 29.1 (*m*-Ar / *i*-Ar, HCiPr), 6.81 / 133.1, 112.4 (*m*-C_6H_4CN / *o*-C_6H_4CN, C≡N), 6.67 / 147.1, 127.2, 117.4 (*o*-C_6H_4CN / *i*-C_6H_4CN, *m*-C_6H_4CN, *p*-C_6H_4CN), 2.87 / 146.3, 131.0, 124.7, 23.8, 22.5 (HCiPr / *o*-Ar, *i*-Ar, *m*-Ar, MeiPr', MeiPr), 1.15 / 165.5 (MeC / $^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 1.08 / 146.3, 29.1, 23.8 (MeiPr / *o*-Ar, HCiPr, MeiPr'), 0.94 / 146.3, 29.1, 22.5 (MeiPr' / *o*-Ar, HCiPr, MeiPr).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.06 / 130.6 (*p*-Ar / *p*-Ar), 6.89 / 124.7 (*m*-Ar / *m*-Ar), 6.81 / 127.2 (*m*-C_6H_4CN / *m*-C_6H_4CN), 6.67 / 133.1 (*o*-C_6H_4CN / *o*-C_6H_4CN), 2.87 / 29.1 (HCiPr / HCiPr), 1.15 / 16.9 (MeC / MeC), 1.08 / 22.5 (MeiPr / MeiPr), 0.94 / 23.8 (MeiPr' / MeiPr').

GCOSY (600 MHz / 600 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{1}H) = 7.06 / 6.89 (*p*-Ar / *m*-Ar), 6.81 / 6.67 (*m*-C_6H_4CN / *o*-C_6H_4CN), 2.87 / 1.08 (HCiPr / MeiPr), 2.87 / 0.94 (HCiPr / MeiPr').

^{1}H{NOE} NMR (600 MHz, C_7D_8, 298 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 7.06 / 6.89 (*p*-Ar / *m*-Ar), 6.89 / 7.06, 1.08, 0.94 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 6.81 / 6.67, 1.15 (*m*-C_6H_4CN / *o*-C_6H_4CN, MeC), 6.67 / 6.81 (*o*-C_6H_4CN / *m*-C_6H_4CN), 2.87 / 8.03, 1.15, 1.08, 0.94 (HCiPr / NH, MeC, MeiPr, MeiPr'), 1.15 / 6.81, 6.67, 2.87 (MeC / *m*-C_6H_4CN, *o*-C_6H_4CN, HCiPr), 1.08 / 6.89, 2.87, 0.94 (MeiPr / *m*-Ar, HCiPr, MeiPr'), 0.94 / 6.89, 2.87, 1.08 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

1D TOCSY (500 MHz, CD_2Cl_2, 298 K): δ ($^{1}H_{Irr}$) / δ ($^{1}H_{Res}$) [ppm] = 7.06 / 6.89 (*p*-Ar / *m*-Ar), 6.89 / 7.06 (*m*-Ar / *p*-Ar), 6.81 / 6.67 (*m*-C_6H_4CN / *o*-C_6H_4CN), 6.67 / 6.81 (*o*-C_6H_4CN / *m*-C_6H_4CN), 2.87 / 1.08, 0.94 (HCiPr / MeiPr, MeiPr'), 1.08 / 6.89, 2.87, 0.94 (MeiPr / *m*-Ar, HCiPr, MeiPr'), 0.94 / 6.89, 2.87, 1.08 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

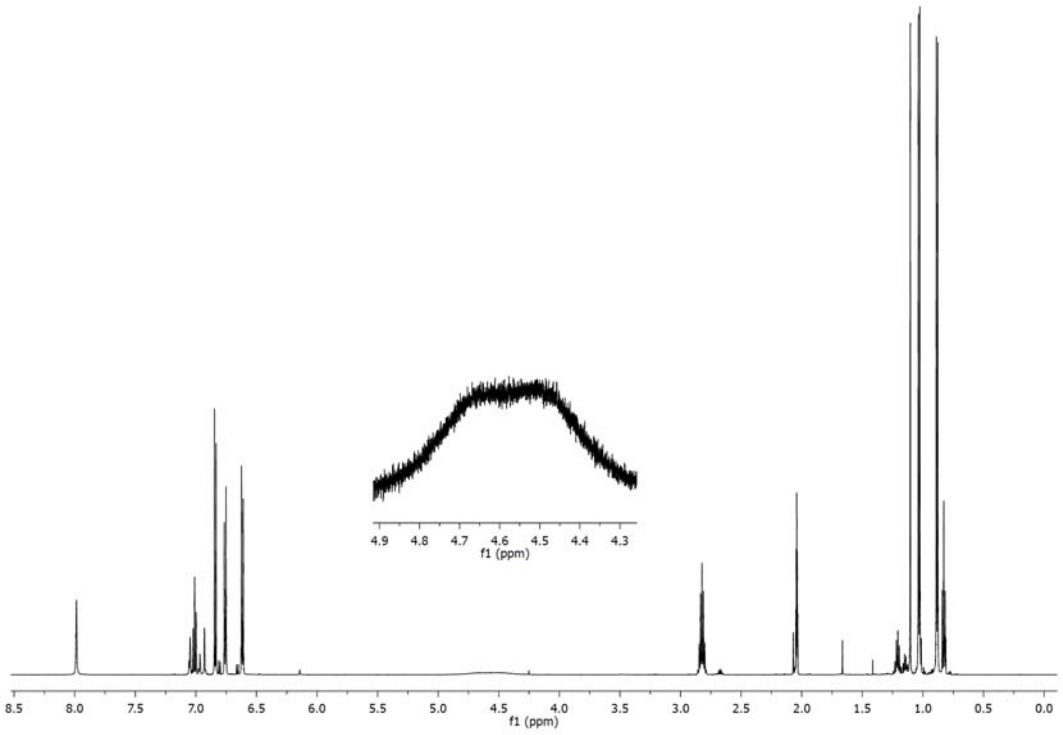
^{19}F NMR (564 MHz, C_7D_8, 298 K): δ/ppm = -133.3 (dd, *J* = 23.6, 7.9 Hz, 4F, *o*-$C_6F_5^{B}$), -157.6 (t, *J* = 20.4 Hz, 2F, *p*-$C_6F_5^{B}$), -163.7 (td, *J* = 23.9, 9.4 Hz, 4F, *m*-$C_6F_5^{B}$).

^{19}F, ^{19}F GCOSY (564 MHz, C_7D_8, 298 K): δ (^{19}F) / δ (^{19}F) = -133.3 / -163.7 (*o*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$), -157.6 / -163.7 (*p*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$).

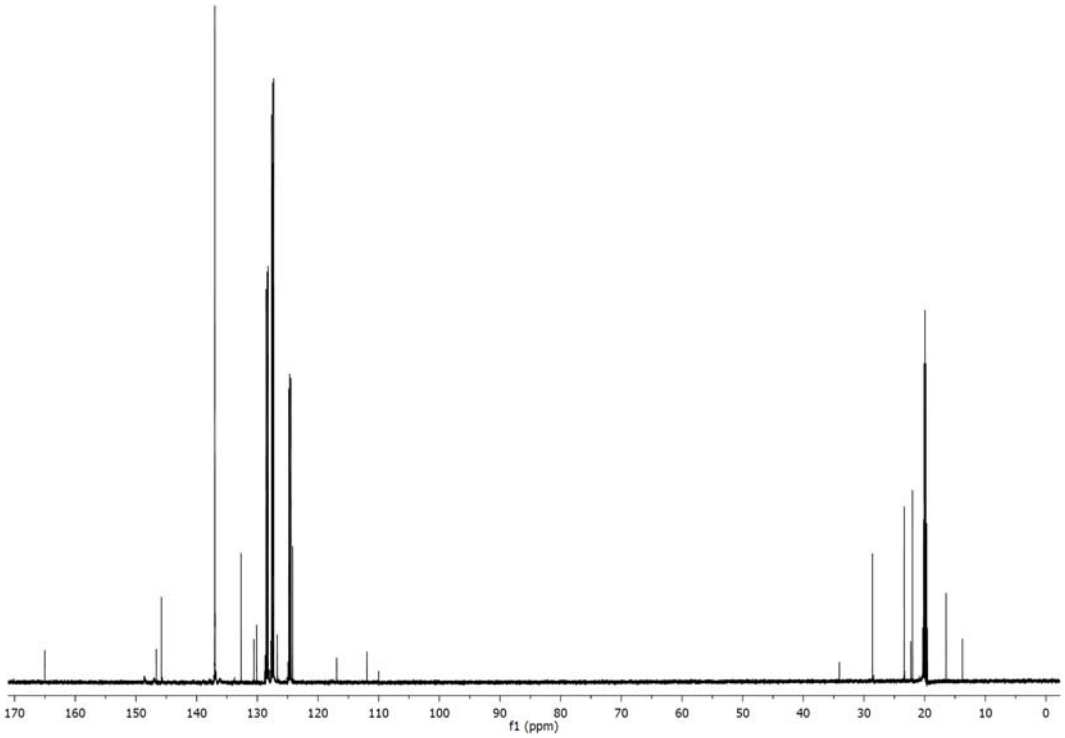
^{11}B{1H} NMR (192 MHz, C_7D_8, 298 K): δ/ppm = -14.6 (ν1/2 ~ 210 Hz).

IR (KBr): ν/cm^{-1} = 3314, 3072, 2969, 2932, 2873, 2366, 2233 (ν(C≡N), s), 1645, 1616, 1598, 1516, 1459, 1379, 1243, 1180, 1107, 921, 868, 845, 804, 762, 699, 669, 577, 547.

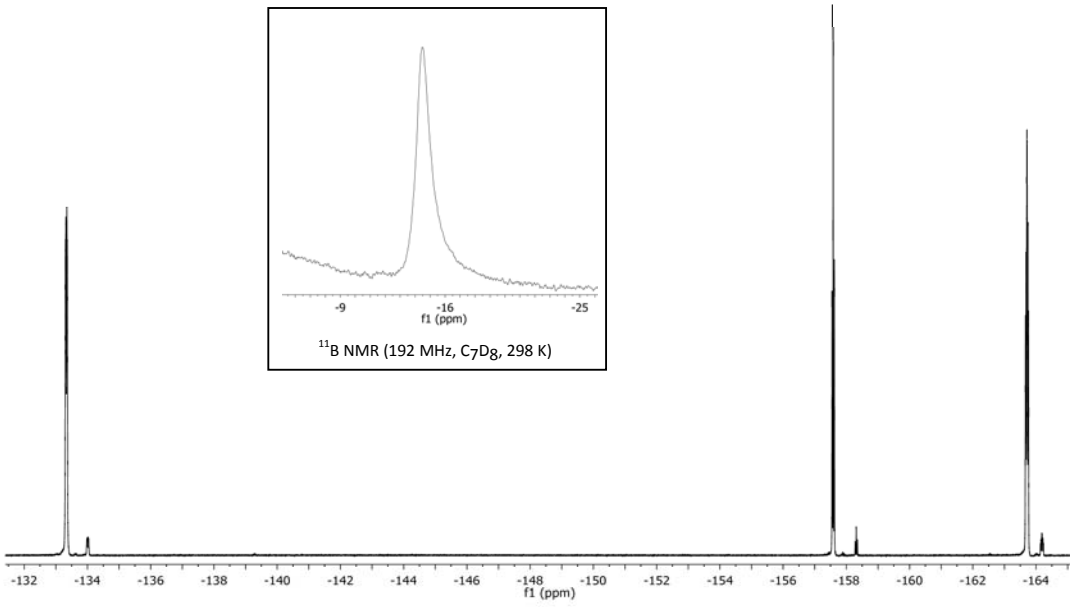
Elemental analysis (%) $C_{33}H_{26}BF_{10}N_3$ (M = 665.37 g/mol): calculated C 59.57, H 3.94, N 6.32; found C 60.50, H 4.12, N 6.29.



^{1}H NMR (600 MHz, C_7D_8, 298 K)



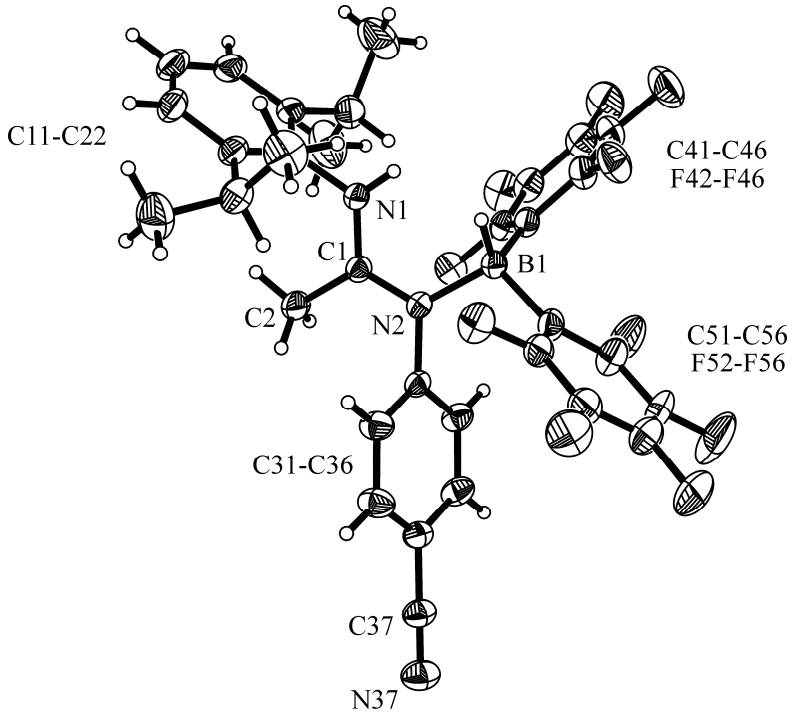
$^{13}C\{^{1}H\}$ NMR (151 MHz, C_7D_8, 298 K)



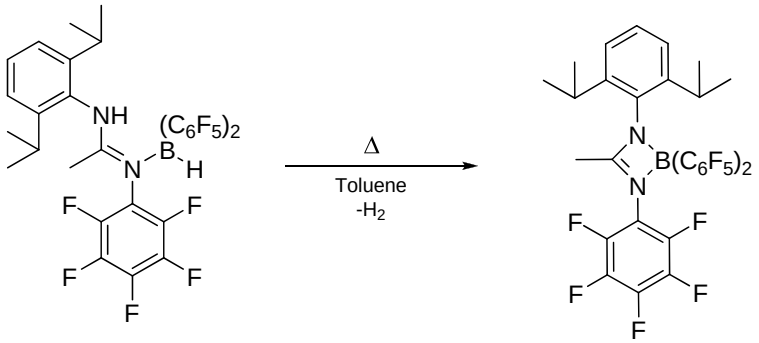
^{11}B NMR (192 MHz, C_7D_8, 298 K)

^{19}F NMR (564 MHz, C_7D_8, 298 K)

X-ray crystal structure analysis of **2b**:

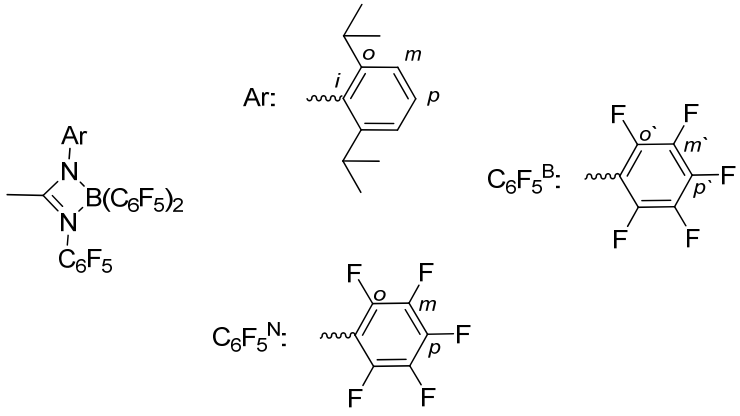


[N'-(2,6-diisopropylphenyl)-N-(pentafluorophenyl)acetimidamide]bis(pentafluoro phenyl)dehydroborane (3a)



(**2a**) (**3a**)

A solution of **2a** (200 mg; 0.27mmol) in toluene (20 ml) was heated to 100°C for 4 hours. Then, the volatiles were removed in vacuum, and the solid washed with pentane. Finally the white solid is recrystallized from cold toluene given **3a** as a white crystalline material in 95% yield (189 mg; 0.26 mmol).



^{1}H NMR (600 MHz, C_7D_8, 298 K): δ/ppm = 7.02 (m, 1H, *p*-Ar), 6.89 (d, *J* = 6.9Hz, 2H, *m*-Ar), 2.69 (hept, *J* = 6.9Hz, 2H, HCiPr), 1.47 (s, 3H, MeC), 1.00 (d, *J* = 6.9 Hz, 6H, MeiPr), 0.72 (d, *J* = 6.9 Hz, 6H, MeiPr').

^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K): δ/ppm = 177.3 ($^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 146.1 (*o*-Ar), 133.4 (*i*-Ar), 129.1 (*p*-Ar), 124.7 (*m*-Ar), 28.9 (HCiPr), 24.5 (MeiPr), 23.6 (MeiPr'), 13.9 (MeC).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.02 / 146.1, 124.7 (*p*-Ar / *o*-Ar, *m*-Ar), 6.89 / 146.1, 133.4, 129.1, 28.9 (*m*-Ar / *o*-Ar, *i*-Ar, *p*-Ar, HCiPr), 2.69 / 146.1, 133.4, 124.7, 24.5, 23.6 (HCiPr / *o*-Ar, *i*-Ar, *m*-Ar, MeiPr', MeiPr), 1.47 / 177.3 (MeC / $^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 1.00

/ 146.1, 28.9, 23.6 (MeiPr / *o*-Ar, HCiPr, MeiPr'), 0.72 / 146.1, 28.9, 24.5 (MeiPr' / *o*-Ar, HCiPr, MeiPr).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.02 / 129.1 (*p*-Ar / *p*-Ar), 6.89 / 124.7 (*m*-Ar / *m*-Ar), 2.69 / 28.9 (HCiPr / HCiPr), 1.47 / 13.9 (MeC / MeC), 1.00 / 24.5 (MeiPr / MeiPr), 0.72 / 23.6 (MeiPr' / MeiPr').

GCOSY (600 MHz / 600 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{1}H) = 7.02 / 6.89 (*p*-Ar / *m*-Ar), 2.69 / 1.00 (HCiPr / MeiPr), 2.69 / 0.72 (HCiPr / MeiPr').

^{1}H{NOE} NMR (600 MHz, C_7D_8, 298 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 7.02 / 6.89 (*p*-Ar / *m*-Ar), 6.89 / 7.02, 1.00, 0.72 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 2.69 / 1.47, 1.00, 0.72 (HCiPr / MeC, MeiPr, MeiPr'), 1.47 / 2.69, 1.00 (MeC / HCiPr, MeiPr), 1.00 / 6.89, 2.69, 1.47, 0.72 (MeiPr / *m*-Ar, HCiPr, MeC, MeiPr'), 0.72 / 6.89, 2.69, 1.00 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

1D TOCSY (500 MHz, CD_2Cl_2, 298 K): δ ($^{1}H_{Irr}$) / δ ($^{1}H_{Res}$) [ppm] = 7.02 / 6.89 (*p*-Ar / *m*-Ar), 6.89 / 7.02, 1.00, 0.72 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 2.69 / 1.00, 0.72 (HCiPr / MeiPr, MeiPr'), 1.00 / 6.89, 2.69, 0.72 (MeiPr / *m*-Ar, HCiPr, MeiPr'), 0.72 / 6.89, 2.69, 1.00 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

^{19}F NMR (564 MHz, C_7D_8, 298 K): δ/ppm = -132.8 (d, *J* = 18.7Hz , 4F, *o*-$C_6F_5^B$), -147.6 (d, *J* = 21.0Hz, 2F, *o*-$C_6F_5^N$), -154.5 (t, *J* = 20.5Hz, 2F, *p*-$C_6F_5^B$), -157.2 (t, *J* = 22.1Hz, 1F, *p*-$C_6F_5^N$), -161.9 (td, *J* = 22.7, 5.0 Hz, 2F, *m*-$C_6F_5^N$), -163.0 (td, *J* = 24.0, 8.9 Hz, 4F, *m*-$C_6F_5^B$).

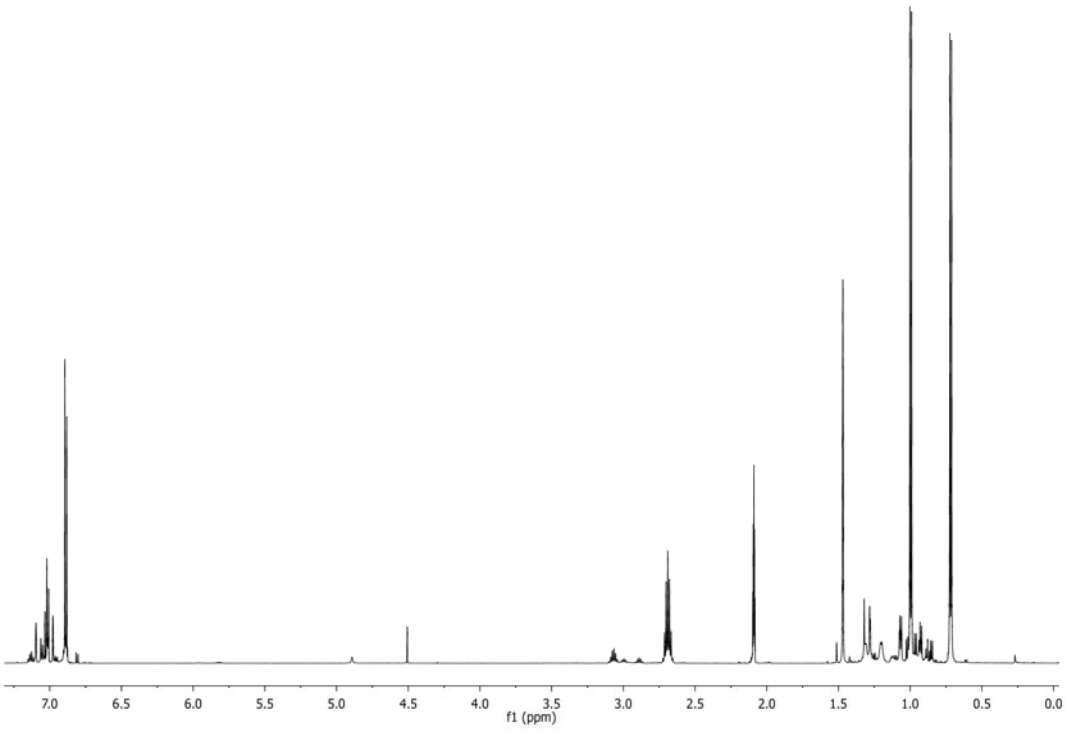
^{19}F, ^{19}F GCOSY (564 MHz, C_7D_8, 298 K): δ (^{19}F) / δ (^{19}F) = -132.8 / -163.0 (*o*-$C_6F_5^B$ / *m*-$C_6F_5^B$), -147.6 / -161.9 (*o*-$C_6F_5^N$ / *m*-$C_6F_5^N$), -154.5 / -163.0 (*p*-$C_6F_5^B$ / *m*-$C_6F_5^B$), -157.2 / -161.9 (*p*-$C_6F_5^N$ / *m*-$C_6F_5^N$).

^{11}B{1H} NMR (192 MHz, C_7D_8, 298 K): δ/ppm = 7.52 (ν1/2 ~ 210 Hz).

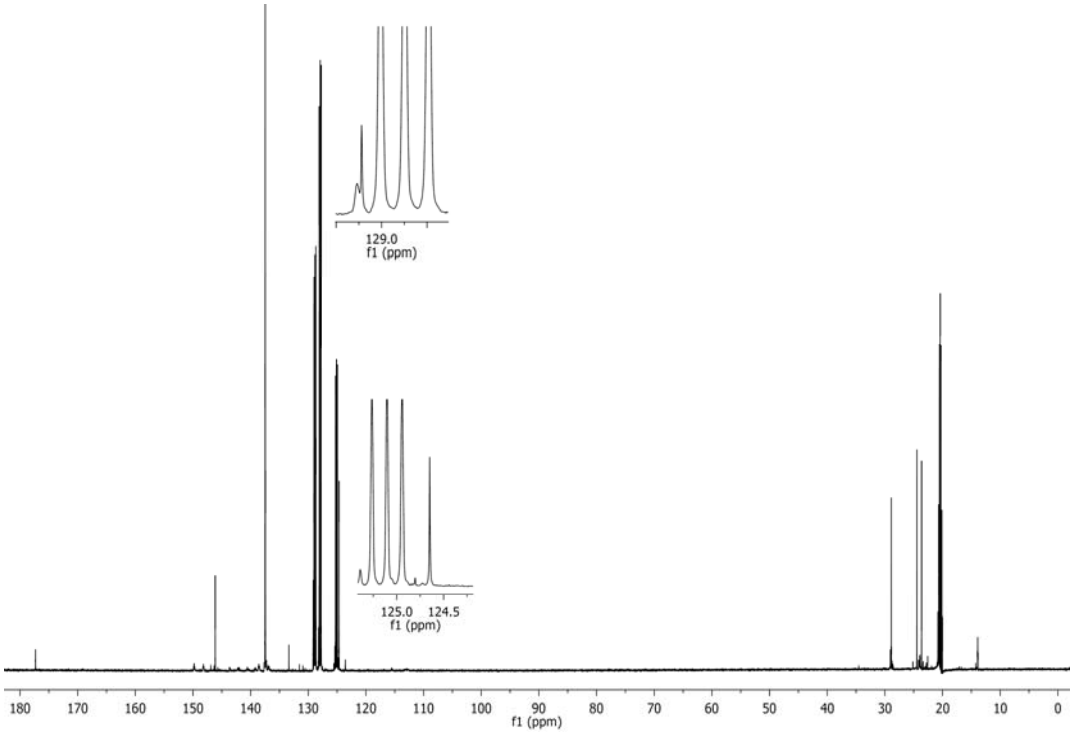
IR (KBr): ν/cm^{-1} = 2970, 2932, 2870, 1658, 1522, 1381, 1330, 1283, 1226, 1157, 1105, 1043, 972, 894, 804, 764, 701, 627, 592, 573, 534.

Elemental analysis (%) $C_{32}H_{20}BF_{15}N_2$ (M = 730.32 g/mol): calculated C 52.77, H 2.77, N 3.85; found C 51.14, H 2.47, N 4.32.

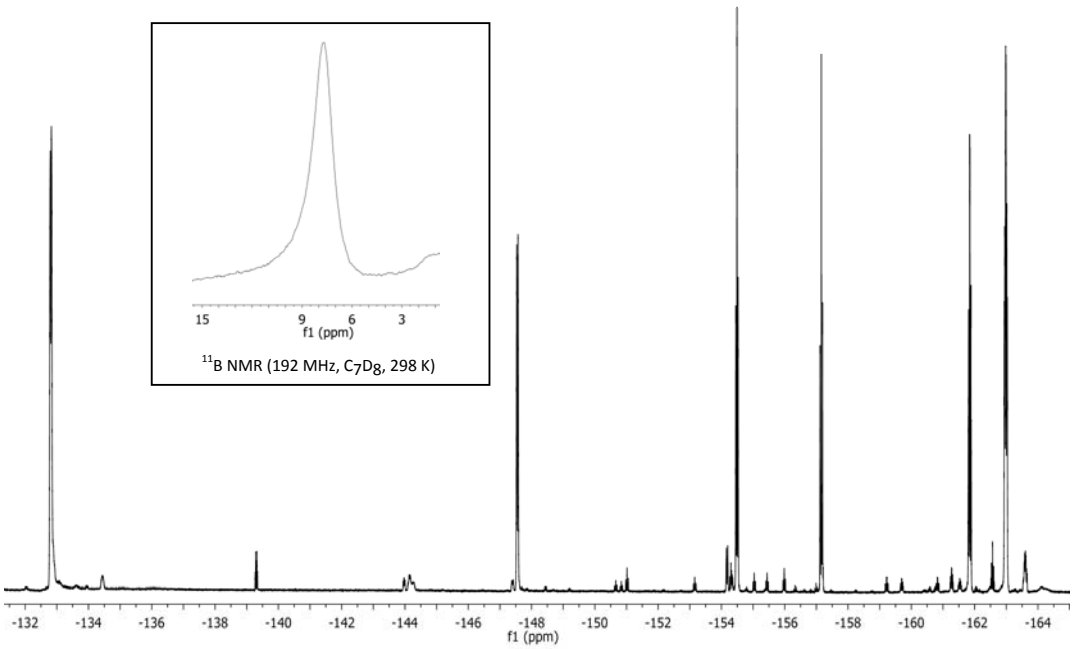
MS (ESI, Exact mass**):** Calc: 727.1 ; Found: 727.1 [$C_{32}H_{19}BF_{15}N_2^+$]. Calc: 709.145 ; Found: 709.149 [$C_{32}H_{20}BF_{14}N_2^+$].



^{1}H NMR (600 MHz, C_7D_8, 298 K)



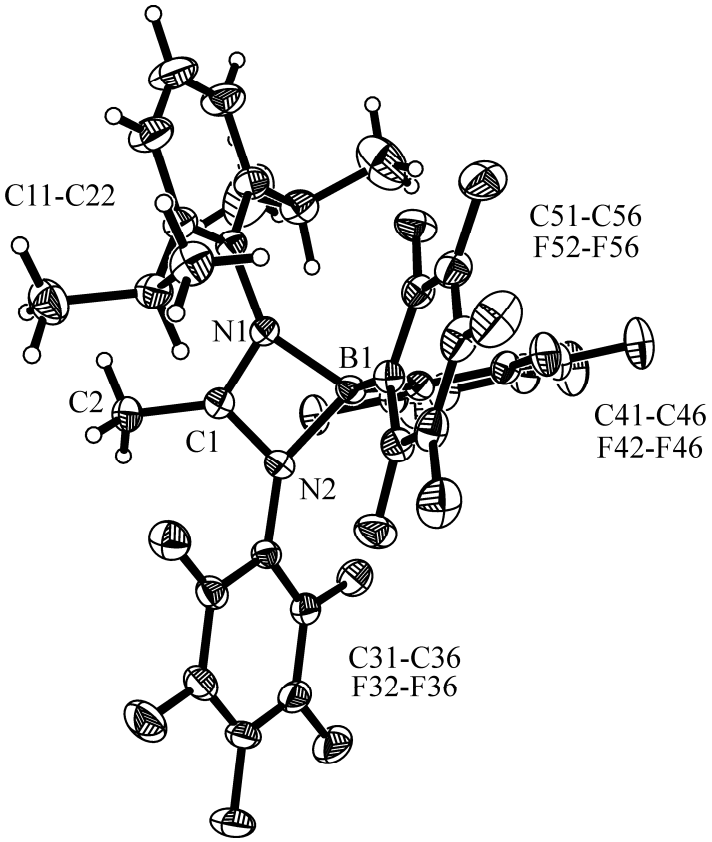
$^{13}C\{^{1}H\}$ NMR (151 MHz, C_7D_8, 298 K)



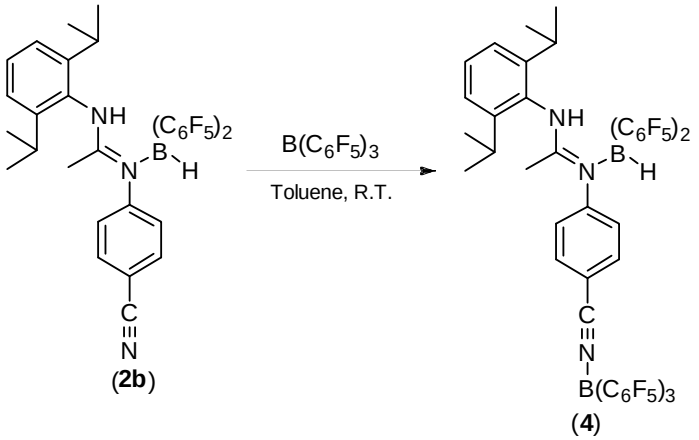
^{11}B NMR (192 MHz, C_7D_8, 298 K)

^{19}F NMR (564 MHz, C_7D_8, 298 K)

X-ray crystal structure analysis of **3a**:



[N'-(2,6-diisopropylphenyl)-N-(4-cyano(tris(pentafluorophenyl)borane)phenyl acetimidamide]bis(pentafluoro phenyl)borate (4)



To a stirred solution of **2b** (5.0 mg, 0.009 mmol) in toluene-d_8 (0.6 ml) was added $B(C_6F_5)_3$ (4.7 mg, 0.08 mmol). After 15 min the solution was subjected to NMR spectroscopy showing virtually quantitative spectroscopic yield of **4** based on the ^{19}F NMR spectrum. The volatiles were removed in vacuo and the residue was recrystallized from toluene to afford compound **4** as a colourless solid (7.4 mg, 83.6 %).

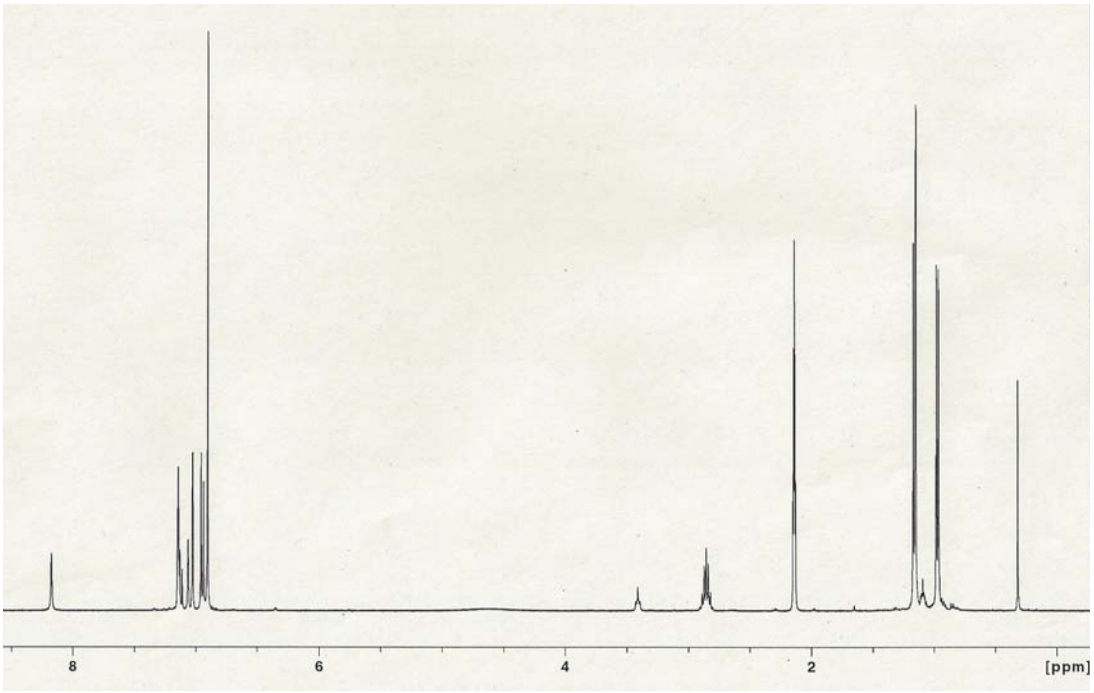
^{1}H NMR (400 MHz, C_7D_8, 295 K): δ/ppm = 8.17 (s, 1H, NH), 6.96 – 6.86 (m, 8H, Ar), 4.60 (br, 1H, *BH*), 2.86 (m, 2H, HC(iPr)), 1.18 (d, *J* = 10.2 Hz, 12H, Me(iPr)), 0.95 (d, *J* = 10.7 Hz, 6H, Me(iPr')).

^{13}C{^{1}H} NMR (125 MHz, C_7D_8, 298 K): δ/ppm = 165.5 ($^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 146.0 (*o*-Ar), 134.8 (*i*-Ar), 130.6 (*p*-Ar), 124.7 (*m*-Ar), 29.2 (HCiPr), 23.8 (MeiPr), 22.5 (MeiPr'), 17.0 (MeC).

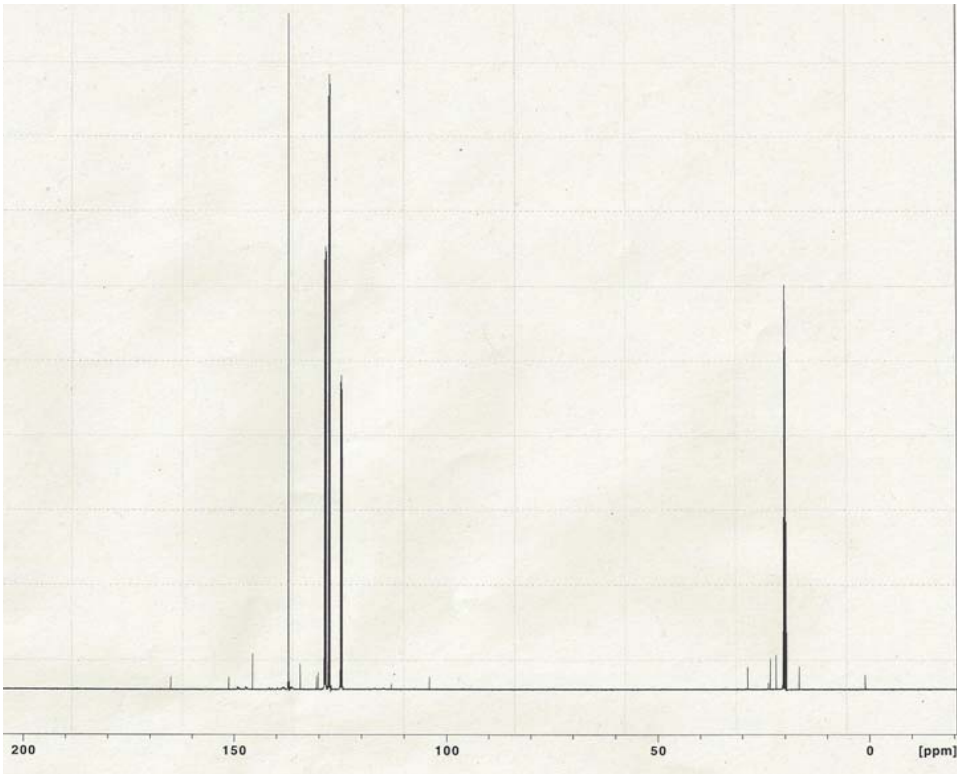
^{19}F NMR (282 MHz, C_7D_8, 295 K): δ/ppm = -134.77 (dd, *J* = 14.9, 9.0 Hz, 4F, *o*-$C_6F_5^B$, -$B(C_6F_5)_2$), -136.07 (m, 6F, *o*-$C_6F_5^B$, $B(C_6F_5)_3$), -156.37 (t, *J* = 20.6, 2F, *p*-$C_6F_5^B$, -$B(C_6F_5)_2$), -157.70 (t, *J* = 19.7 Hz, 3F, *p*-$C_6F_5^B$, $B(C_6F_5)_3$), -164.08 - -164.47 (m, 10F, *m*-$C_6F_5^B$, -$B(C_6F_5)_2$, $B(C_6F_5)_3$).

^{11}B{1H} NMR (128 MHz, C_7D_8, 295 K): δ/ppm = -14.09 (v1/2 ~ 256 Hz).

Elemental analysis (%) $C_{51}H_{26}B_2F_{25}N_3$ (M = 1177.35 g/mol): calculated C 52.03, H 2.23, N 3.57; found C 52.34, H 2.40, N 3.50.

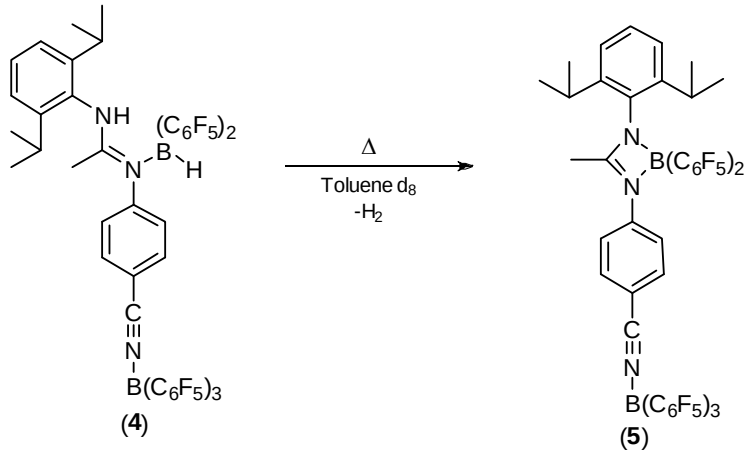


^{1}H NMR (400 MHz, C_7D_8, 295 K)



$^{13}C\{^{1}H\}$ NMR (125 MHz, C_7D_8, 310 K)

[N'-(2,6-diisopropylphenyl)-N-(4-cyano(tris(pentafluorophenyl)borane)phenyl acetimidamide]bis(pentafluorophenyl)dehydroborane (5)



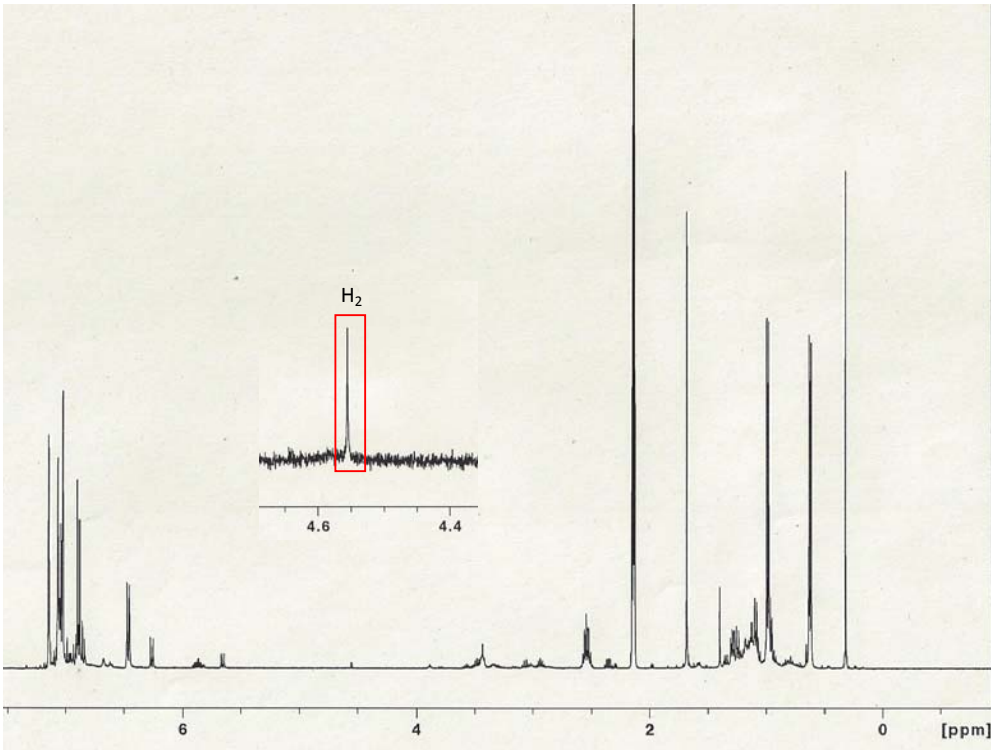
To a solution of **2b** (5.0 mg, 0.008 mmol) in toluene-d_8 (0.6 ml) was added $B(C_6F_5)_3$ (4.7 mg, 0.009 mmol) and the mixture was heated to 120 °C for 22 h. The resulting mixture was subjected to ^{1}H, ^{19}F, ^{13}C and ^{11}B NMR spectroscopy.

^{1}H NMR (400 MHz, C_7D_8, 295 K): δ/ppm = 7.18 – 6.90 (m, 8H, Ar), 2.54 (m, 2H, HC(iPr)), 0.99 (d, *J* = 6.8 Hz, 6H, Me(iPr)), 0.63 (d, *J* = 4.4 Hz, 6H, Me(iPr')).

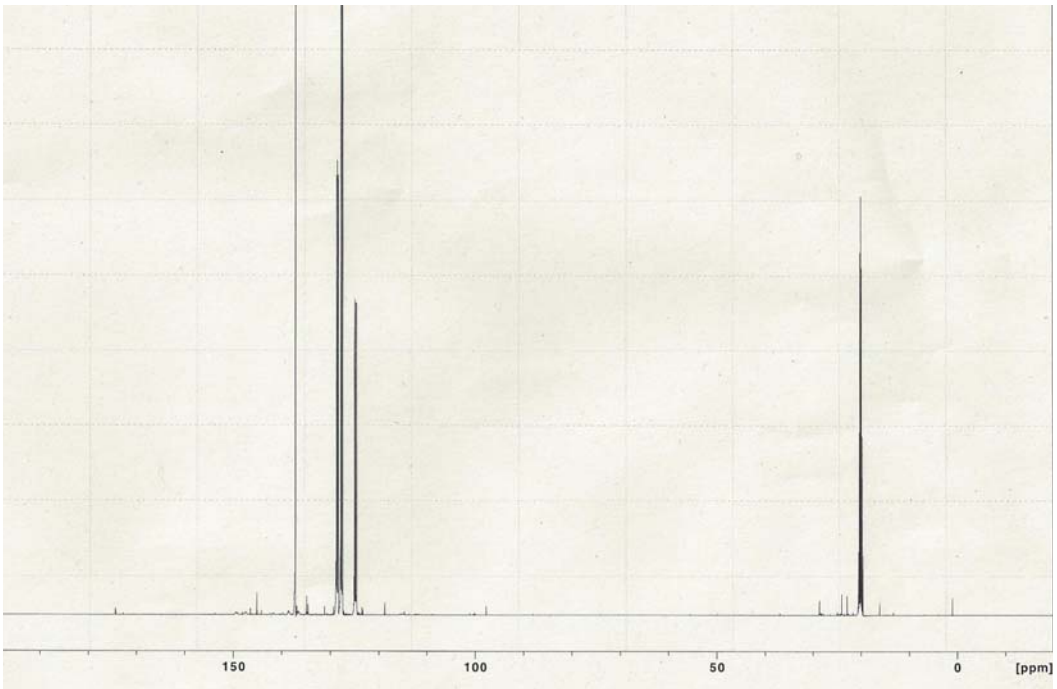
^{13}C{^{1}H} NMR (125 MHz, C_7D_8, 310 K): δ/ppm = 174.7 ($^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 145.5 (*o*-Ar), 135.2 (*i*-Ar), 129.7 (*p*-Ar), 124.0 (*m*-Ar), 29.3 (HCiPr), 24.6 (Me(iPr)), 23.3 (Me(iPr')), 16.5 (MeC).

^{19}F NMR (282 MHz, C_7D_8, 295 K): δ/ppm = -134.55 (m, 4F, *o*-$C_6F_5^{B}$, -$B(C_6F_5)_2$), -135.86 (m, 6F,*o*-$C_6F_5^{B}$, $B(C_6F_5)_3$), -154.12 (t, *J* = 20.6 Hz, 2F, *p*-$C_6F_5^{B}$, -$B(C_6F_5)_2$), -156.73 (t, *J* = 19.7 Hz, 3F, *p*-$C_6F_5^{B}$, $B(C_6F_5)_3$), -163.14 (m, 4F, *m*-$C_6F_5^{B}$, -$B(C_6F_5)_2$), -164.27 (m, 6F, *m*-$C_6F_5^{B}$, $B(C_6F_5)_3$).

^{11}B{1H} NMR (128 MHz, C_7D_8, 295 K): δ/ppm = -5.64 (v1/2 ~ 128 Hz, -$B(C_6F_5)_2$), -0.88 (v1/2 ~ 128 Hz, $B(C_6F_5)_3$).

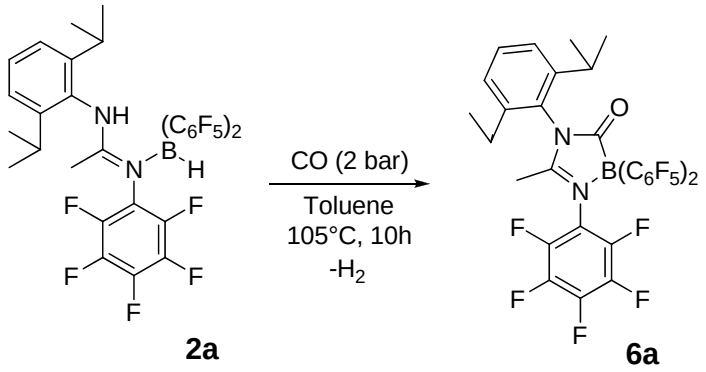


^{1}H NMR (400 MHz, C_7D_8, 295 K)



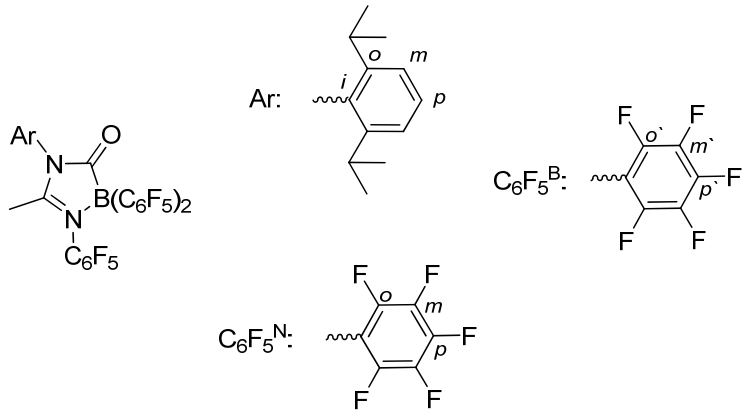
$^{13}C\{^{1}H\}$ NMR (125 MHz, C_7D_8, 310 K)

[N'-(2,6-diisopropylphenyl)-N-(pentafluorophenyl)acetimidamide](CO)bis(pentafluoro phenyl)dehydroborane (6a)



2a **6a**

A solution of **2a** (100 mg; 0.14mmol) in toluene (10 ml) was pressurized with 2 bar of CO and heated to 105°C for 10 hours. Then, the volatiles were removed in vacuum. Finally the white solid is recrystallized from cold toluene / pentane, given **6a** as a white crystalline material in 95% yield (98 mg; 0.13 mmol).



^{1}H NMR (600 MHz, C_7D_8, 298 K): δ/ppm = 7.16 (t, *J* = 7.8 Hz, 1H, *p*-Ar), 7.00 (d, *J* = 7.8Hz, 2H, *m*-Ar), 2.80 (hept, *J* = 6.8Hz, 2H, HCiPr), 1.53 (s, 3H, MeC), 1.11 (d, *J* = 6.9 Hz, 6H, MeiPr), 1.07 (d, *J* = 6.8 Hz, 6H, MeiPr').

^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K): δ/ppm = 193 (br., C=O), 176.5 ($^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 147.1 (*o*-Ar), 131.5 (*p*-Ar), 127.6 (*i*-Ar), 125.0 (*m*-Ar), 28.9 (HCiPr), 24.6 (MeiPr'), 23.4 (MeiPr), 15.7 (MeC).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.16 / 147.1, 125.0 (*p*-Ar / *o*-Ar, *m*-Ar), 7.00 / 127.6, 28.9 (*m*-Ar / *i*-Ar, HCiPr), 2.80 / 147.1, 127.6, 125.0, 24.6, 23.4 (HCiPr

/ *o*-Ar, *i*-Ar, *m*-Ar, MeiPr', MeiPr), 1.53 / 176.5 (MeC / $^{Ar\text{-}N}C^{N\text{-}C6F5N}$), 1.11 / 147.1, 28.9, 24.6 (MeiPr / *o*-Ar, HCiPr, MeiPr'), 1.07 / 147.1, 28.9, 23.4 (MeiPr' / *o*-Ar, HCiPr, MeiPr).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.16 / 131.5 (*p*-Ar / *p*-Ar), 7.00 / 125.0 (*m*-Ar / *m*-Ar), 2.80 / 28.9 (HCiPr / HCiPr), 1.53 / 15.7 (MeC / MeC), 1.11 / 23.4 (MeiPr / MeiPr), 1.07 / 24.6 (MeiPr' / MeiPr').

GCOSY (600 MHz / 600 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{1}H) = 7.16 / 7.00 (*p*-Ar / *m*-Ar), 2.80 / 1.11 (HCiPr / MeiPr), 2.80 / 1.07 (HCiPr / MeiPr').

^{1}H{NOE} NMR (600 MHz, C_7D_8, 298 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 7.16 / 7.00 (*p*-Ar / *m*-Ar), 7.00 / 7.16, 1.11, 1.07 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 2.80 / 1.53, 1.11, 1.07 (HCiPr / MeC, MeiPr, MeiPr'), 1.53 / 2.80, 1.11 (MeC / HCiPr, MeiPr), 1.11 / 7.00, 2.80, 1.53, 1.07 (MeiPr / *m*-Ar, HCiPr, MeC, MeiPr'), 1.07 / 7.00, 2.80, 1.11 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

1D TOCSY (500 MHz, CD_2Cl_2, 298 K): δ ($^{1}H_{Irr}$) / δ ($^{1}H_{Res}$) [ppm] = 7.16 / 7.00 (*p*-Ar / *m*-Ar), 7.00 / 7.16, 1.11, 1.07 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 2.80 / 1.11, 1.07 (HCiPr / MeiPr, MeiPr'), 1.11 / 2.80, 1.07 (MeiPr / HCiPr, MeiPr'), 1.07 / 2.80, 1.11 (MeiPr' / HCiPr, MeiPr).

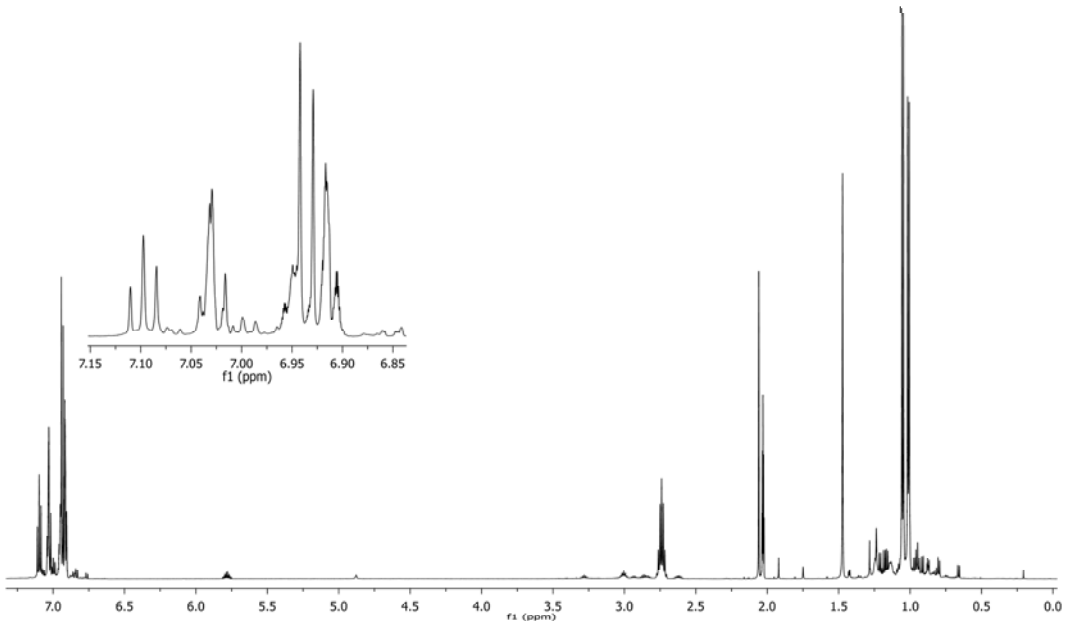
^{19}F NMR (564 MHz, C_7D_8, 298 K): δ/ppm = -132.4 (m, 4F, *o*-$C_6F_5^{B}$), -145.4 (m, 2F, *o*-$C_6F_5^{N}$), -151.3 (t, *J* = 21.9Hz, 1F, *p*-$C_6F_5^{N}$), -155.0 (t, *J* = 20.5Hz, 2F, *p*-$C_6F_5^{B}$), -159.8 (td, *J* = 22.3, 5.5 Hz, 2F, *m*-$C_6F_5^{N}$), -163.0 (td, *J* = 22.5, 8.4 Hz, 4F, *m*-$C_6F_5^{B}$).

^{19}F, ^{19}F GCOSY (564 MHz, C_7D_8, 298 K): δ (^{19}F) / δ (^{19}F) = -132.4 / -163.0 (*o*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$), -145.4 / -159.8 (*o*-$C_6F_5^{N}$ / *m*-$C_6F_5^{N}$), -151.3 / -159.8 (*p*-$C_6F_5^{N}$ / *m*-$C_6F_5^{N}$), -155.0 / -163.0 (*p*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$).

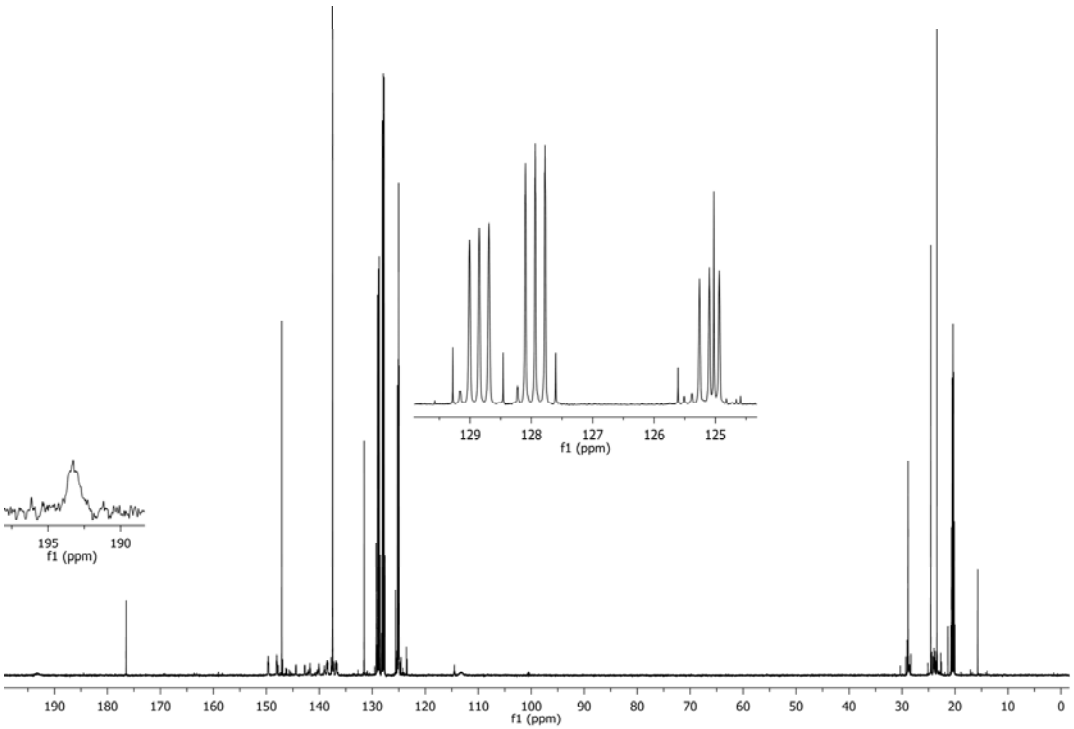
^{11}B{1H} NMR (192 MHz, C_7D_8, 298 K): δ/ppm = -10.01 (ν1/2 ~ 210 Hz).

IR (KBr): ν/cm^{-1} = 3073, 2871, 2933, 2874, 1752 (ν(C=O), s), 1646, 1560, 1478, 1388, 1338, 1287, 1233, 1094, 1072, 1037, 965, 882, 831, 804, 778, 763, 691, 667, 652, 604, 574, 555.

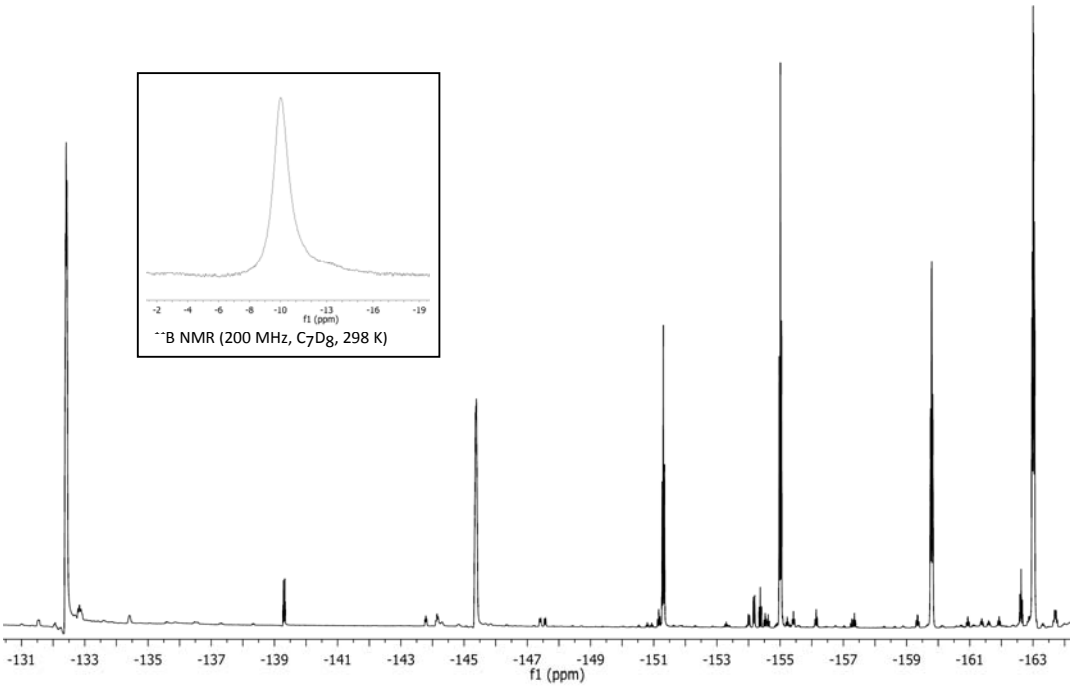
Elemental analysis (%) $C_{33}H_{20}BF_{15}N_2O$ (M = 756.31 g/mol): calculated C 52.41, H 2.67, N 3.70; found C 53.04, H 3.01, N 3.33.



^{1}H NMR (600 MHz, C_7D_8, 298 K)



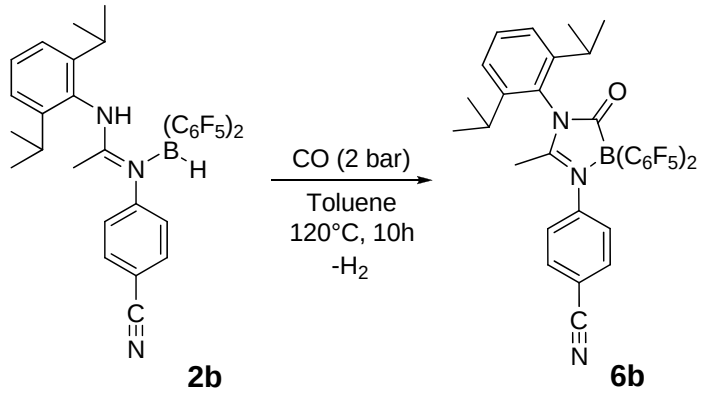
^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K)



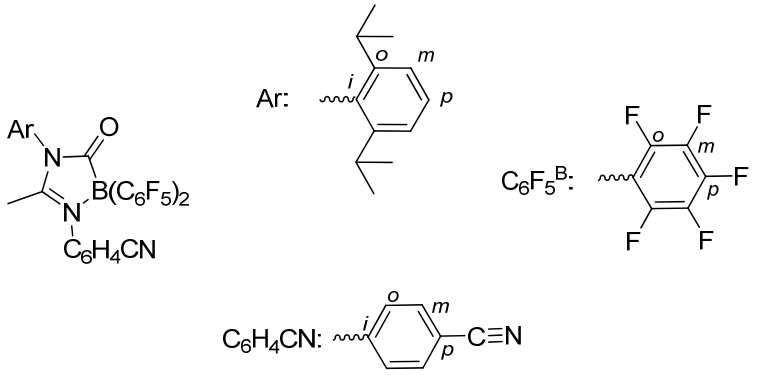
``B NMR (200 MHz, C_7D_8, 298 K)

^{19}F NMR (564 MHz, C_7D_8, 298 K)

[N'-(2,6-diisopropylphenyl)-N-(4-cyanophenyl)acetimidamide](CO)bis(pentafluoro phenyl)dehydroborate (6b)



A solution of **2b** (180 mg; 0.27 mmol) in toluene (10 ml) was pressurized with 2 bar of CO and heated to 120°C for 10 hours. Then, the volatiles were removed in vacuum. Finally the greenyellow solid is recrystallized from cold toluene / pentane, given **6b** as a greenyellow crystalline material in 87% yield (163 mg, 0.24 mmol).



^{1}H NMR (600 MHz, C_7D_8, 298 K): δ/ppm = 7.15 (t, *J* = 7.9Hz, 1H, *p*-Ar), 6.98 (d, *J* = 7.8Hz, 2H, *m*-Ar), 6.74 (d, *J* = 8.6Hz, 2H, *o*-C_6H_4CN), 6.71 (d, *J* = 8.7Hz, 2H, *m*-C_6H_4CN), 2.72 (hept, *J* = 6.73Hz, 2H, HCiPr), 1.48 (s, 3H, MeC), 1.11 (d, *J* = 6.9 Hz, 6H, MeiPr), 1.01 (d, *J* = 6.7 Hz, 6H, MeiPr').

^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K): δ/ppm = 193.9 (br., C=O), 172.2 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 146.9 (*o*-Ar), 142.2 (*i*-C_6H_4CN), 133.5 (*o*-C_6H_4CN), 131.4 (*p*-Ar), 125.7 (*m*-C_6H_4CN), 124.9 (*m*-Ar), 124.8 (*i*-Ar), 117.2 (*p*-C_6H_4CN), 112.8 (C≡N), 29.0 (HCiPr), 24.5 (MeiPr'), 23.3 (MeiPr), 15.3 (MeC).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.15 / 146.9 (*p*-Ar / *o*-Ar), 6.98 / 124.8, 29.0 (*m*-Ar / *i*-Ar, HCiPr), 6.74 / 142.2, 117.2 (*o*-C_6H_4CN / *i*-C_6H_4CN, *p*-C_6H_4CN),

6.71 / 112.8 (*m*-C_6H_4CN / C≡N), 1.48 / 172.2 (MeC / $^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 1.11 / 146.9, 29.0, 24.5 (MeiPr / *o*-Ar, HCiPr, MeiPr'), 1.01 / 146.9, 29.0, 23.3 (MeiPr' / *o*-Ar, HCiPr, MeiPr).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{13}C) = 7.15 / 131.4 (*p*-Ar / *p*-Ar), 6.98 / 124.9 (*m*-Ar / *m*-Ar), 6.74 / 133.5 (*o*-C_6H_4CN / *o*-C_6H_4CN), 6.71 / 125.7 (*m*-C_6H_4CN / *m*-C_6H_4CN), 2.72 / 29.0 (HCiPr / HCiPr), 1.48 / 15.3 (MeC / MeC), 1.11 / 23.3 (MeiPr / MeiPr), 1.01 / 24.5 (MeiPr' / MeiPr').

GCOSY (600 MHz / 600 MHz, C_7D_8, 298 K): δ (^{1}H) / δ (^{1}H) = 7.15 / 6.98 (*p*-Ar / *m*-Ar), 6.74 / 6.71 (*o*-C_6H_4CN / *m*-C_6H_4CN), 2.72 / 1.11 (HCiPr / MeiPr), 2.72 / 1.01 (HCiPr / MeiPr').

^{1}H{NOE} NMR (600 MHz, C_7D_8, 298 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 7.15 / 6.98 (*p*-Ar / *m*-Ar), 6.98 / 7.15, 1.11, 1.01 (*m*-Ar / *p*-Ar, MeiPr, MeiPr'), 6.74 / 6.71, 1.48 (*o*-C_6H_4CN / *m*-C_6H_4CN, MeC), 6.71 / 6.74, 1.48 (*m*-C_6H_4CN / *o*-C_6H_4CN, MeC), 1.48 / 6.71, 2.72, 1.11 (MeC / *m*-C_6H_4CN, HCiPr, MeiPr), 1.11 / 6.98, 2.72, 1.48, 1.01 (MeiPr / *m*-Ar, HCiPr, MeC, MeiPr'), 1.01 / 6.98, 2.72, 1.11 (MeiPr' / *m*-Ar, HCiPr, MeiPr).

1D TOCSY (500 MHz, CD_2Cl_2, 298 K): δ ($^{1}H_{Irr}$) / δ ($^{1}H_{Res}$) [ppm] = 7.15 / 6.98, 1.48, 1.11, 1.01 (*p*-Ar / *m*-Ar, MeC, MeiPr, MeiPr'), 6.98 / 7.15, 1.48, 1.11, 1.01 (*m*-Ar / *p*-Ar, MeC, MeiPr, MeiPr'), 6.74 / 6.71 (*o*-C_6H_4CN / *m*-C_6H_4CN), 6.71 / 6.74 (*m*-C_6H_4CN / *o*-C_6H_4CN), 2.72 / 1.11, 1.01 (HCiPr / MeiPr, MeiPr'), 1.11 / 6.98, 1.01 (MeiPr / *m*-Ar, MeiPr'), 1.01 / 1.01 (MeiPr' / MeiPr).

^{19}F NMR (564 MHz, C_7D_8, 298 K): δ/ppm = -133.0 (d, *J* = 17.64Hz, 4F, *o*-$C_6F_5^{B}$), -155.3 (t, *J* = 20.5Hz, 2F, *p*-$C_6F_5^{B}$), -162.6 (m, 4F, *m*-$C_6F_5^{B}$).

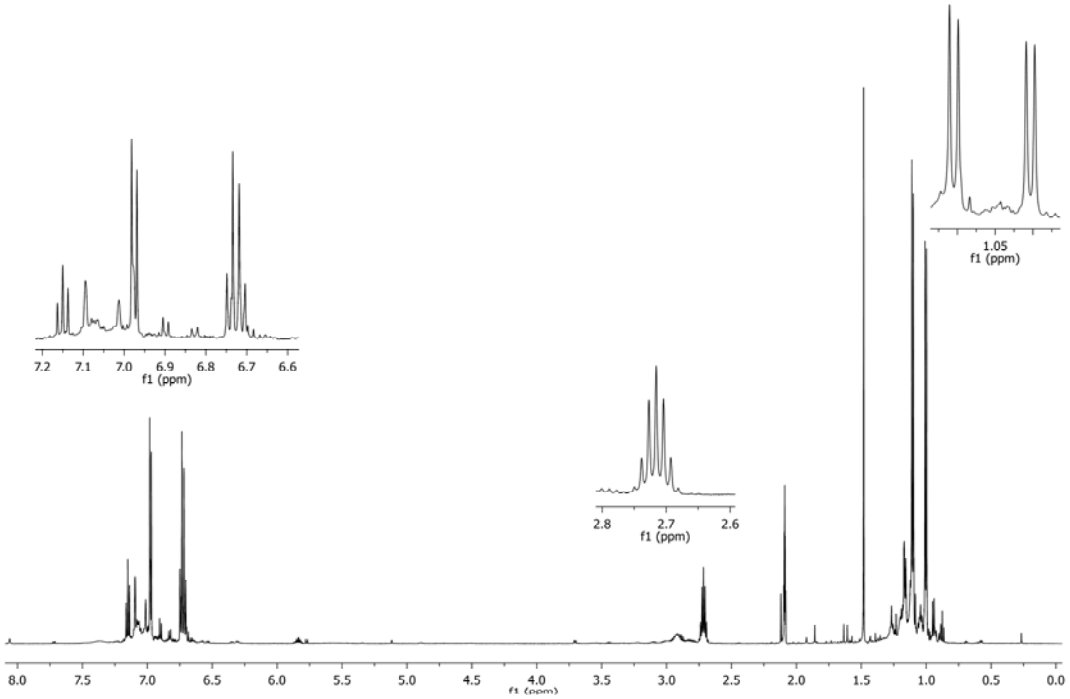
^{19}F, ^{19}F GCOSY (564 MHz, C_7D_8, 298 K): δ (^{19}F) / δ (^{19}F) = -133.0 / -162.6(*o*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$), -155.3 / -162.6 (*p*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$).

^{11}B{1H} NMR (192 MHz, C_7D_8, 298 K): δ/ppm = -10.2 (ν1/2 ~ 180 Hz).

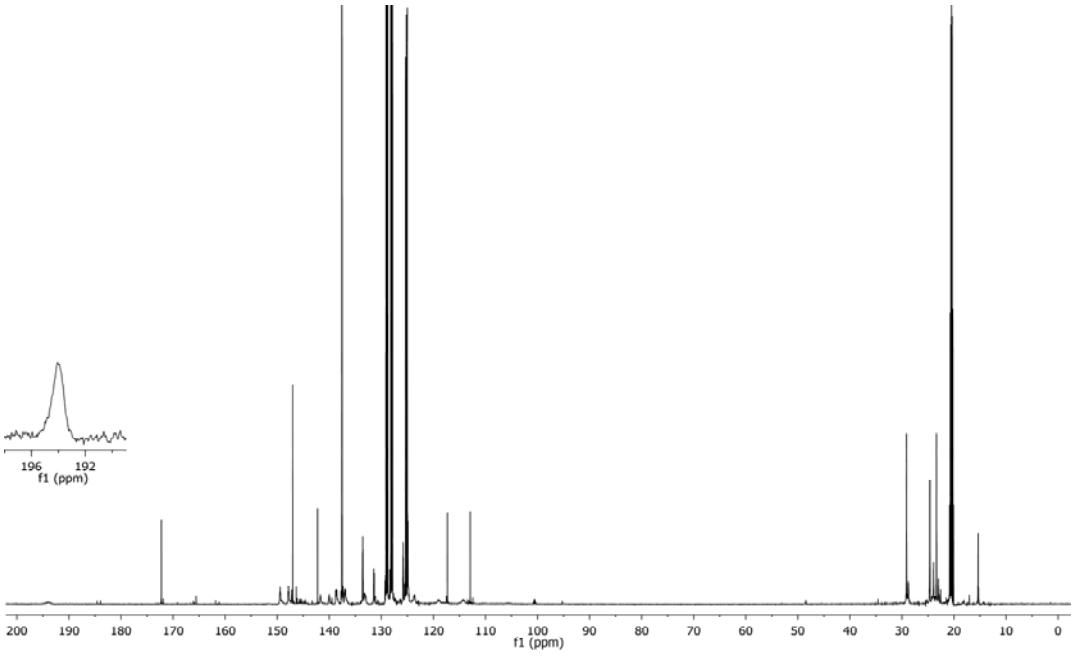
IR (KBr): ν/cm^{-1} = 3068, 2969, 2932, 2871, 2232 (ν(C≡N), s), 1758 (ν(C=O), s), 1669, 1646, 1567, 1518, 1467, 1411, 1387, 1320, 1288, 1232, 1194, 1175, 1098,1069, 972, 841, 805, 777, 762, 711, 665, 577, 545.

Elemental analysis (%) $C_{34}H_{24}BF_{10}N_3O$ (M = 691.37 g/mol): calculated C 59.07, H 3.50, N 6.08; found C 62.02, H 4.29, N 6.37.

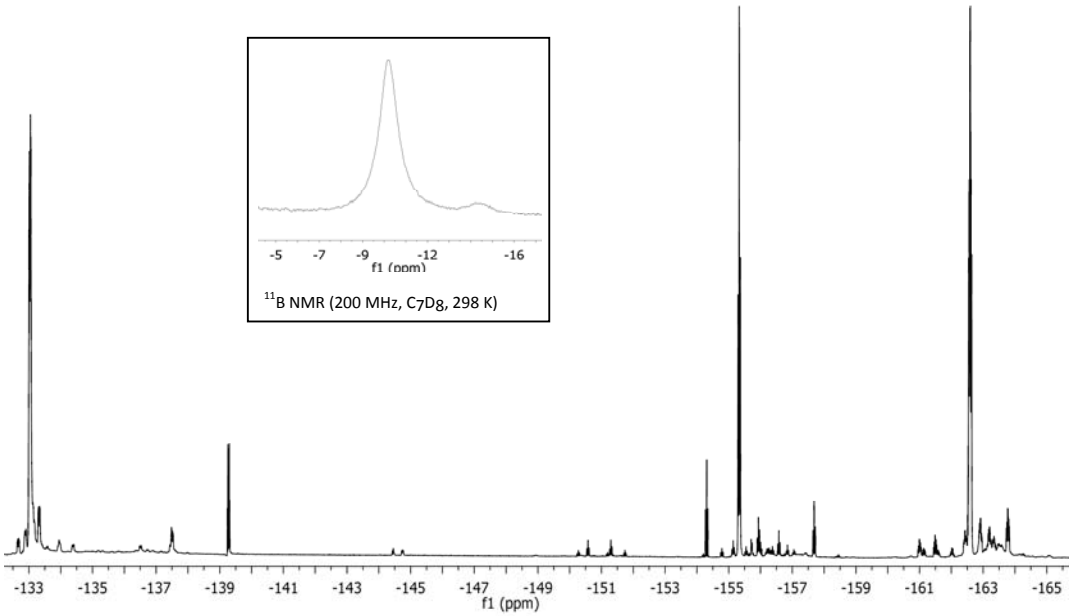
MS (ESI, Exact mass**):** Calc: 714.175 ; Found: 714.172 [$C_{34}H_{24}BF_{10}N_3ONa^+$]. Calc: 692.193 ; Found: 692.191 [$C_{34}H_{24}BF_{10}N_3OH^+$].



^{1}H NMR (600 MHz, C_7D_8, 298 K)

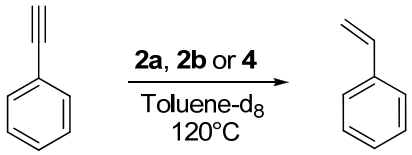


^{13}C{^{1}H} NMR (151 MHz, C_7D_8, 298 K)



^{19}F NMR (564 MHz, C_7D_8, 298 K)

Phenylacetylene hydrogenation.



A solution of **2a**, **2b** or **4** (0.08 mmol) in toluene-d_8 (0.6 ml) was mixed with stoichiometric amounts of phenylacetylene inside a NMR Young tube under argon atmosphere. Then, the reaction mixture was heated to 120°C and the conversion to styrene was pursued in time intervals of 1 hour using ^{1}H NMR.

Table S-1. Hydrogenation of phenylacetylene by compounds **2a**, **2b** and **4**.[a]

	Time (h)	Styrene yield (mg)	Conversion (%)
2a	10	7.4	100
2b	8	9.7	100
4 (**2b-B(C_6F_5)$_3$**)	1	6.0	100

[a] C_7D_8 as solvent, 120°C.

Monitoring by ^{1}H NMR revealed the production of styrene via appearance of a doublet doublet between 5.0 and 5.5 ppm along with the gradual decrease of the signal corresponding to the alkyne proton at 2.65 ppm (Figure S-1, S-2 and S-3). Also the production of the dehydrogenated cyclic compounds was observed showing the same pattern as seen in the synthesis of compounds **3** and **5**. Production of ethylbenzene (double hydrogenation of the triple bond) could not be observed, nor a resonance for molecular hydrogen.

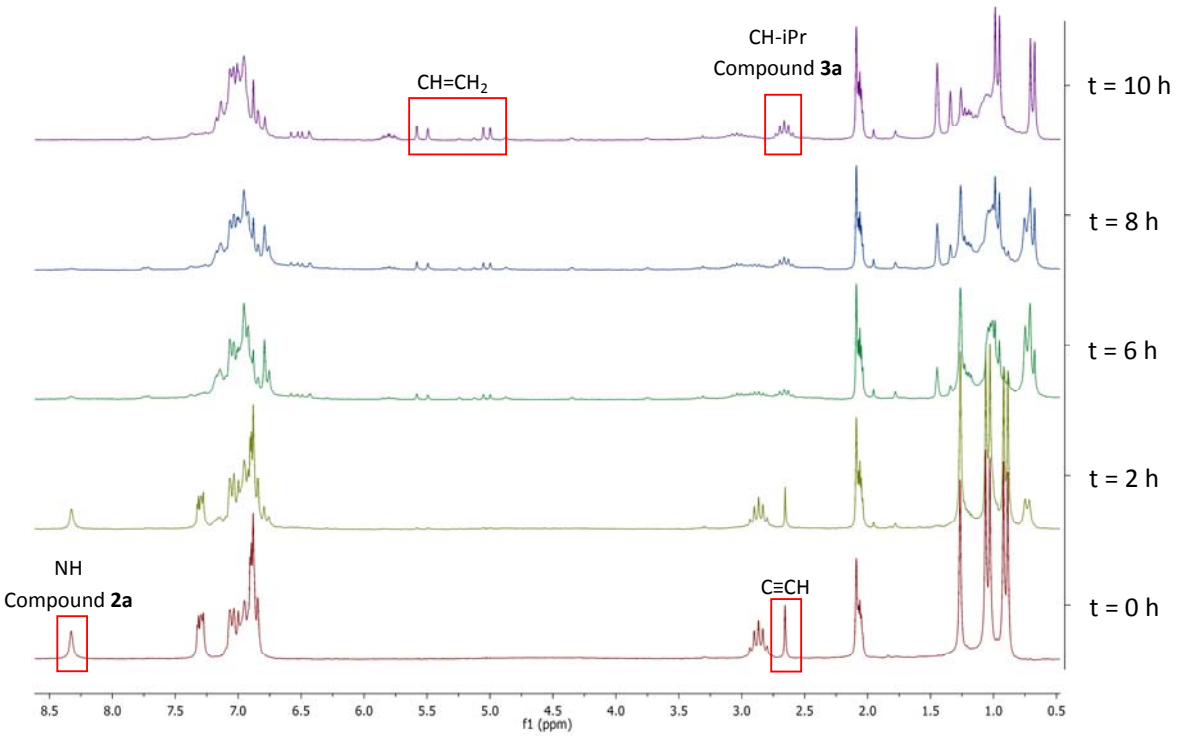


Figure S-1. Phenylacetylene hydrogenation using compound **2a**.

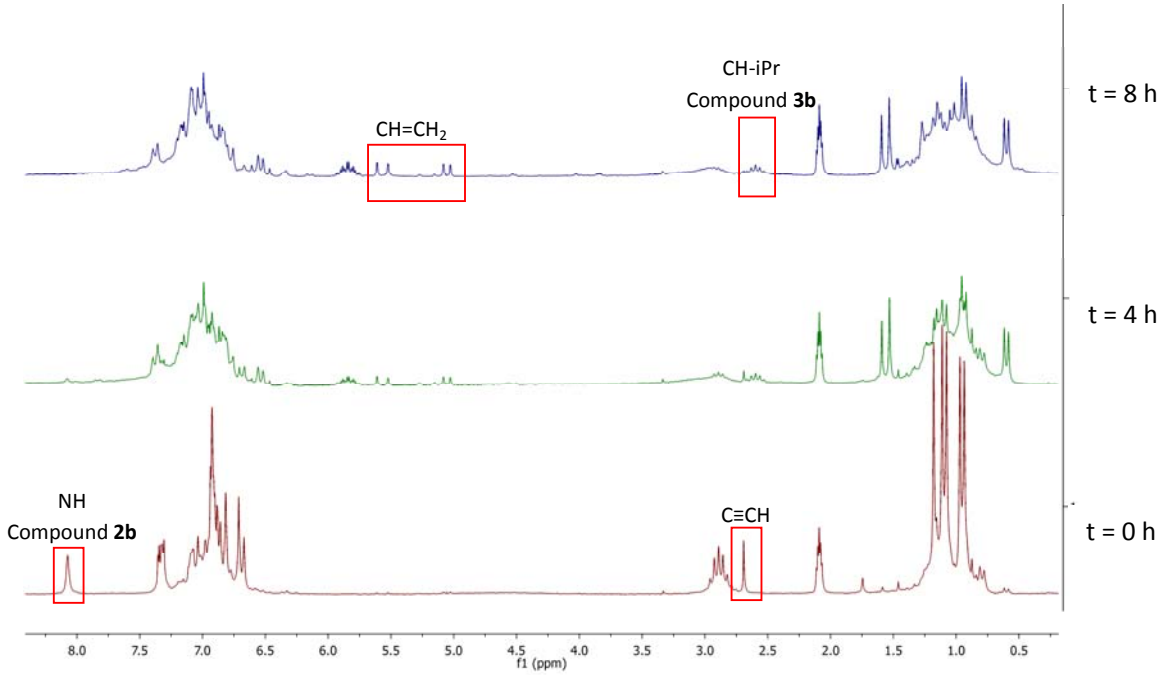


Figure S-2. Phenylacetylene hydrogenation using compound **2b**.

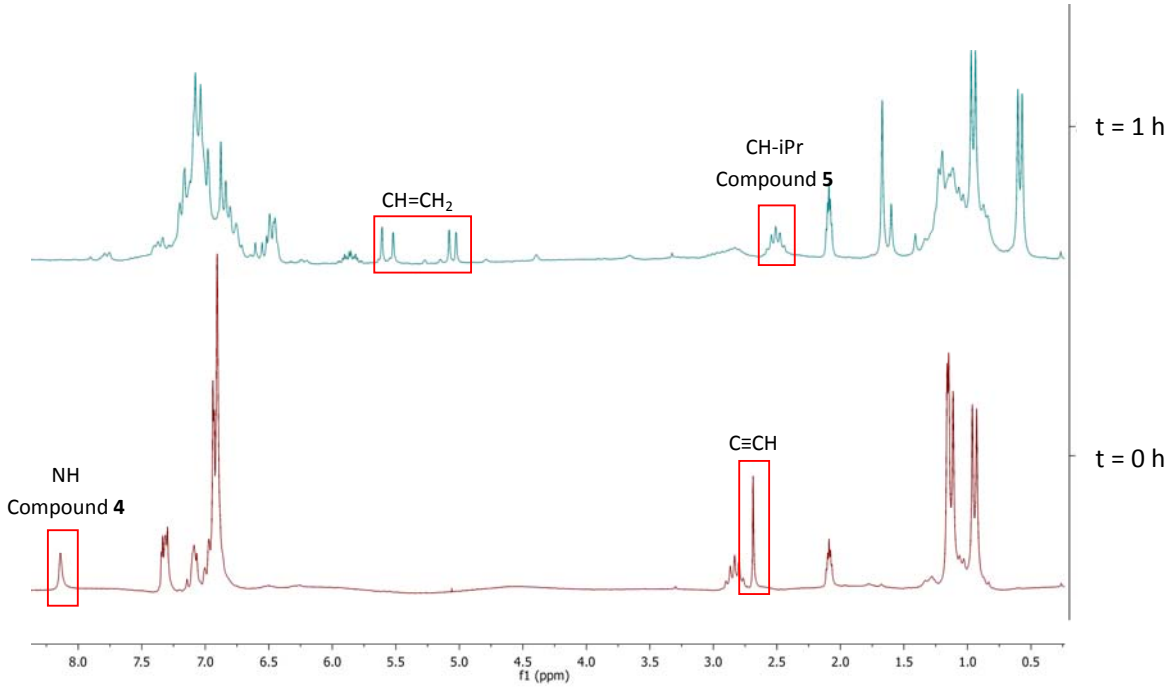


Figure S-3. Phenylacetylene hydrogenation using compound **4**.

[1] R.T. Boeré, V. Klassen, G. Wolmershäuser, *J. Chem. Soc., Dalton Trans*. **1998**, 4147.

[2] B.C. Peoples, G. De la Vega, C. Valdebenito, R. Quijada, A. Ibañez, M. Valderrama, R. Rojas, *J. Organomet. Chem.* **2012**, *700*, 147.