# Highly diastereoselective preparation of chiral NHC-boranes stereogenic at boron atom.

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## **Supporting Information**

1.	G	eneral Experimental	2
2. Preliminary attempts to form the B-C bond			
8	a.	Hydroboration of aryne	3
ł	э.	B-H bond-rhodium carbene insertion	4
3.	P	rocedure and Analytical Data	6
8	a.	Synthetic procedures and spectroscopic data for the preparation of chlorinated NH	C-
ł	oora	ane 5	6
ł	Э.	Synthetic procedures and spectroscopic data for the preparation of NHC-borane 4	10
4.	N	MR Spectra	28
5.	Μ	lodeling approach for <i>trans-</i> 5a, <i>cis- &amp; trans-</i> 5a•-, IIa and IIIa	61
8	a.	<i>trans</i> -NHC-borane <b>5a</b>	61
ł	э.	NHC-borane radical anion <b>5a</b> •-	62
(	с.	NHC-boryl radical IIa	65
(	d.	NHC-boryl radical IIIa	66
6.	0	rigin of the diastereoselectivity in the formation of NHC-boranes 4a and 4d	69
8	a.	DFT calculations	69
ł	э.	EPR Studies	75
7.	Μ	lechanism studies	76
8	a.	Ionic pathway	76
ł	э.	Radical pathway	78
8.	С	atalysis	81
8	a.	Imine reduction with silane catalyzed by chiral NHC-borenium	81
ł	э.	Borenium IVa-Silane complex studies	82
9.	С	ristal structures	86

## 1. General Experimental

All reactions were performed using standard Schlenk techniques under inert atmosphere of dry argon or in a glovebox Jacomex GP (concept)-II-P. <sup>1</sup>H NMR spectra were measured on a Bruker AC 400 (400 MHz) or a Bruker AC 300 (300 MHz) spectrometer at 298 K (20 °C). Data were reported as follows: chemical shifts in ppm referenced to the internal solvent signal (peak at 7.26 ppm in the case of  $CDCl_3$ ; peak at 5.32 in the case of  $CD_2Cl_2$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, sep = septet, dd = doubletdoublet of doublets, m = multiplet, br = broad signal) and coupling constants (Hz).  ${}^{13}C$  { $^{1}H$ } NMR spectra were measured on a Bruker AC 400 (100 MHz) or a Bruker AC 300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the internal solvent signal (peak at 77.16 ppm in the case of CDCl<sub>3</sub>, peak at 53.84 in the case of  $CD_2Cl_2$ ). The resonance of the carbon carbon and any tetrasubstituted carbon  $\alpha$  to the boron center could not be observed. <sup>11</sup>B NMR spectra were measured on a Bruker AC 400 (128 MHz). <sup>11</sup>B chemical shifts are given relative to boron trifluoroetherate ( $^{11}B = 0$  ppm) used as external reference. High-resolution mass spectra (HRMS) were performed on a SYNAPT G2 HDMS (Waters) spectrometer equipped with atmospheric pression ionization source (API) pneumatically assisted. Samples were ionized by positive electrospray mode as follows: electrospray tension (ISV): 2800 V; opening tension (OR): 20 V; nebulization gas pression (nitrogen): 100 L/h. Infrared spectra were recorded on a Bruker TENSOR 27 Fourier Transform infrared spectrometer equipped with a single reflection diamond Attenuated Total Reflexion accessory (Bruker A222). The measurements were done for pure samples at room temperature. For each individual spectrum, about 20 scans were average at 4 cm<sup>-1</sup> resolution. The Fourier Transform (FT) of the interferograms have been done using the Blackaman-Harris 3-term apodization function, the Mertz phase correction mode and zerofilling factor of 2. The diamond crystal without sample served as reference. Wavenumbers are reported in cm<sup>-1</sup> with the corresponding intensities s (strong), m (medium), w (weak). The X-band EPR spectra were recorded on a Bruker EMX spectrometer with a continuous flow at 298 K. Unsaturating microwave power: 10-20 mW, modulation range: 0.1-1.5 G; scanning time range: 10-42 s; receptor gain:  $5.10^4$  to  $10^6$ ; number of scans: from 1 to 9. The probes were transferred into a sealed and deoxygenated NMR tube and the spectra were simulated with WinSim. Analytical thin layer chromatography (TLCs) were developed on silica Macherey-Nagel 818333 plates. Visualization was achieved under a UVP mineralight UVGL-58 lamp, and by developing the plates with vanillin reagent. The products were purified by flash column chromatography on silica gel 60 (Macherey-Nagel® Si 60, 0.040-0.063 mm). Anhydrous dichloromethane, toluene and tetrahydrofuran were obtained from the Solvent Purification System BRAUN MB-SPS800. Benzene was purchased anhydrous over 4 Å molecular sieves and stored in the glovebox. Unless otherwise noted, other analytical grade solvents were used without further purification. All reagents were obtained from commercial suppliers unless otherwise stated.

## 2. Preliminary attempts to form the B-C bond

a. Hydroboration of aryne



To a stirred solution of 2-(trimethylsilyl)phenyl trifuoromethanesulfonate (0.35 mmol, 2.0 equiv) and NHC-borane **3a** (0.17 mmol, 1.0 equiv) in THF (2.0 mL) at 0 °C, was added *n*-tetrabutylammonium fluoride (1.0 M in THF, 2.4 equiv, 0.42 mL). The mixture was stirred at 0 °C for 24 h. Then the reaction mixture was filtered through a short plug of silica gel using dichloromethane as eluent, then the solvent was evaporated under reduced pressure. The crude material was purified by silica gel chromatography using pentane:diethylether 95:5 as eluent to give the borane **4f** in mixture with the bisfunctionalized product **4f**'.







### b. B-H bond-rhodium carbene insertion



#### **Procedure:**

NHC-Borane **3a** (1.0 equiv, 0.62 mmol) and the  $Rh_2(esp)_2$  (0.02 equiv, 9.5 mg) were dissolved in dry DCM (1 mL) under argon. The solution was green. The reaction mixture was heated to reflux. A solution of the (trimethylsilyl)methyldiazo compound (2.0 M in THF, 2.0 equiv, 0.62 mL) in dry DCM (0.8 mL) was added via syringe pump over a period of 4 h. The color of the solution turned orange. After 4 h, the mixture was filtered through a short plug of silica gel using dichloromethane as eluent and the solvent was removed under reduced pressure. The compound **8a** was obtained in 96% yield as two diastereomers (4:1 *dr*) and as a pale-yellow oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.94 (bs, 3H), 6.72 (d, <sup>3</sup>*J* = 1.5 Hz, 1H), 4.18 (dd, <sup>2</sup>*J* = 10.6 Hz, <sup>3</sup>*J* = 7.9 Hz, 1H), 3.49 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 6.0 Hz, 1H), 2.33 (s, 3H), 2.03 (s, 6H), 1.52 - 1.39 (m, 1H), 1.08 (d, <sup>3</sup>*J* = 7.0 Hz, 1H), -0.24 (s, 9H), -0.99 (bs, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 138.9, 135.8, 134.7, 134.0, 129.2, 128.8, 123.0, 116.4, 58.1, 33.3 (HSQC), 21.2, 21.1, 18.0, 17.9, 3.2 (HSQC), 0.8, C<sub>9</sub> is not observed.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -16.2 (d, <sup>1</sup>*J*<sub>B-H</sub> = 85.6 Hz), -17.5 (d, <sup>1</sup>*J*<sub>B-H</sub> = 83.8 Hz).

<sup>29</sup>Si NMR (79.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 3.3

**HRMS** (ES, [M+Na]<sup>+</sup>) calcd for [C<sub>19</sub>H<sub>31</sub>N<sub>2</sub>BSiNa]<sup>+</sup>: 349.2246; found: 349.2240





## 3. Procedure and Analytical Data

a. Synthetic procedures and spectroscopic data for the preparation of chlorinated NHC-borane **5** 



The appropriate NHC-borane **3** (0.25 mmol, 1 equiv) was dissolved in dry dichloromethane (2.5 mL) in a 10 mL Schlenk flask under argon. Then, 0.125 mL of HCl (2.0 M in Et<sub>2</sub>O, 0.25 mmol, 1 equiv) was added and the mixture was stirred at room temperature under argon for 1 hour. The solution was then evaporated under vacuum to give a mixture of two diastereomers of monochlorinated NHC-borane **5**.

5a

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C<sub>15</sub>H<sub>20</sub>BCIN<sub>2</sub> Mw: 274.60 g.mol<sup>-1</sup>

## quantitative yield; dr = 1.1:1

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.11 - 7.09 (m, 1H), 6.98 - 6.94 (m, 2H), 6.90 (d, <sup>3</sup>*J* = 1.4 Hz, 1H), 4.44 (dd, <sup>2</sup>*J* = 11.2, <sup>3</sup>*J* = 7.3 Hz, 1H), 3.61 (dd, <sup>2</sup>*J* = 11.2, <sup>3</sup>*J* = 3.2 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H), 1.98 (s, 3H), 1.97 - 1.90 (m, 1H), 1.07 (d, <sup>3</sup>*J* = 7.4 Hz, 3H).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.11 - 7.09 (m, 1H), 6.98 - 6.94 (m, 2H), 6.86 (d, <sup>3</sup>*J* = 1.5 Hz, 1H), 4.14 (dd, <sup>2</sup>*J* = 10.8, <sup>3</sup>*J* = 8.0 Hz, 1H), 3.77 (dd, <sup>2</sup>*J* = 10.8, <sup>3</sup>*J* = 8.9 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H), 1.97 (s, 3H), 1.97 - 1.90 (m, 1H), 1.17 (d, <sup>3</sup>*J* = 7.0 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 139.7, 135.3, 134.7, 129.6, 129.5, 129.2, 124.7, 124.2, 117.5, 117.31, 57.8, 56.8, 32.6<sub>(HSQC)</sub>, 29.1<sub>(HSQC)</sub>, 21.2, 19.3, 18.1, 17.6, 17.5, 14.7.

<sup>11</sup>**B NMR** (128 MHz, CDCl<sub>3</sub>) δ (ppm) -7.5 (bs).

HRMS (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>ClBNa]<sup>+</sup>: 297.1303; found: 297.1302

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3136 (w), 2945 (m), 2924 (m), 2391 (m), 1606 (w), 1490 (s), 1037 (s), 746 (s), 566 (s)

5b

C<sub>21</sub>H<sub>24</sub>BCIN<sub>2</sub> Mw: 350.69 g.mol<sup>-1</sup>

quantitative yield; dr = 1.2:1

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.33 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 7.07 – 7.04 (m, 1H), 6.98 (s, 2H), 6.90 (d,  ${}^{3}J$  = 1.7 Hz, 1H), 4.19 (dd,  ${}^{2}J$  = 11.5 Hz,  ${}^{3}J$  = 7.2 Hz, 1H), 3.70 (dd,  ${}^{2}J$  = 11.6 Hz,  ${}^{3}J$  = 3.8 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.41 (dd,  ${}^{2}J$  = 13.9,  ${}^{3}J$  = 11.8 Hz, 1H), 2.34 (s, 3H), 2.31 – 2.17 (m, 1H), 2.14 (s, 3H), 2.03 (s, 3H).

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.33 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 7.07 – 7.04 (m, 1H), 6.98 (s, 1H), 6.95 (s, 1H), 6.87 (d, <sup>3</sup>*J* = 1.7 Hz, 1H), 4.03 – 3.80 (m, 2H), 3.18 – 3.07 (m, 1H), 2.79 (dd, <sup>2</sup>*J* = 14.0, <sup>3</sup>*J* = 10.1 Hz, 1H), 2.33 (s, 3H), 2.31 – 2.17 (m, 1H), 2.16 (s, 3H), 1.95 (s, 3H).

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ (ppm) 144.1, 143.6, 139.8, 135.3, 134.7, 133.0<sub>(HSQC)</sub>, 129.6, 129.5, 129.2, 129.2, 128.9, 128.8, 128.3, 128.3, 125.6, 125.4, 124.8, 124.3, 117.5, 117.4, 54.9, 54.3, 39.9, 37.7<sub>(HSQC)</sub>, 36.7, 21.2, 18.1, 18.1, 17.7, 17.5.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -7.9 (bs). HRMS (ESI, [M+Na]<sup>+</sup>) not detected

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3240 (m), 3145 (m), 2927 (m), 2860 (w), 1606 (w), 1454 (m), 1373 (s), 1197 (s), 1074 (s), 742 (s). The BH vibration band is not observed.

5c



C<sub>18</sub>H<sub>26</sub>BCIN<sub>2</sub> Mw: 316.68 g.mol<sup>-1</sup>

quantitative yield; dr = 1:0.8

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.43 (t, <sup>3</sup>*J* = 7.7 Hz, 1H), 7.30 – 7.18 (m, 2H), 7.12 (brs, 1H), 6.90 (d, <sup>3</sup>*J* = 7.9 Hz, 1H), 4.45 (dd, <sup>2</sup>*J* = 11.1 Hz, <sup>3</sup>*J* = 6.7 Hz, 1H), 3.62 (dd, <sup>2</sup>*J* = 11.2 Hz, <sup>3</sup>*J* = 2.8 Hz, 1H), 2.63 (sex, <sup>3</sup>*J* = 6.7 Hz, 1H), 2.34 – 2.20 (m, 1H), 1.83 – 1.76 (m, 1H), 1.20–0.89 (m, 15H).

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.43 (t, <sup>3</sup>*J* = 7.7 Hz, 1H), 7.30 – 7.18 (m, 2H), 7.12 (brs, 1H), 6.90 (d, <sup>3</sup>*J* = 7.9 Hz, 1H), 4.15 (t, <sup>2</sup>*J* = 9.8 Hz, 1H), 3.76 (t, <sup>2</sup>*J* = 9.8 Hz, 1H), 2.63 (sex, 1H), 2.34 – 2.20 (m, 1H), 1.83 – 1.76 (m, 1H), 1.20 – 0.89 (m, 15H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 146.2, 146.1, 145.7, 145.6, 132.7, 132.6, 130.5, 126.1, 125.6, 124.3, 124.2, 123.9, 123.9, 117.3, 117.0, 57.7, 56.6, 33.0<sub>(HSQC)</sub>, 28.5<sub>(HSQC)</sub>, 28.5, 25.8, 25.7, 24.8, 24.8, 23.5, 23.4, 23.0, 22.9, 19.1, 14.5<sub>(HMBC)</sub>.

<sup>11</sup>**B NMR** (128 MHz, CDCl<sub>3</sub>) δ (ppm) -7.5 (brs).

**HRMS** (ESI,  $[M+Na]^+$ ) calcd for  $[C_{18}H_{26}N_2BCINa]^+$ : 339.1773; found: 339.1777

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3158 (w), 3136 (w), 2963 (s), 2922 (m), 2864 (m), 2386 (m), 2342 (m), 1593 (w), 1551 (w), 1490 (m), 1463 (s), 1387 (m), 1358 (m), 1271 (m), 1140 (s), 1057 (s), 1011 (s), 974 (s), 814 (s), 785 (s), 759 (s), 646 (m).

5d



C<sub>12</sub>H<sub>14</sub>BCIN<sub>2</sub> Mw: 232.52 g.mol<sup>-1</sup>

quantitative yield; dr = 1:1

<sup>1</sup>**H** NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 7.83 (m, 2H), 7.53 (m, 2H), 7.47-7.43 (m, 1H), 7.42-7.36 (m, 1H), 7.17 – 7.13 (m, 1H), 4.39 (dd, <sup>2</sup>*J* = 11.4 Hz, <sup>3</sup>*J* = 7.1 Hz, 1H), 3.62 (dd, <sup>2</sup>*J* = 11.4 Hz, <sup>3</sup>*J* = 3.1 Hz, 1H), 1.99 – 1.84 (m, 1H), 1.06 (d, <sup>3</sup>*J* = 7.5 Hz, 3H).

<sup>1</sup>**H** NMR (300 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) 7.79 (m, 2H), 7.53 (m, 2H), 7.47-7.43 (m, 1H), 7.42-7.36 (m, 1H), 7.17 - 7.13 (m, 1H), 4.13 (dd,  ${}^{2}J = 11.0$  Hz,  ${}^{3}J = 8.0$  Hz, 1H), 3.71 (dd,  ${}^{2}J = 11.0$  Hz,  ${}^{3}J = 9.4$  Hz, 1H), 1.99 - 1.84 (m, 1H), 1.18 (d,  ${}^{3}J = 7.0$  Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 137.6, 137.4, 129.6, 129.6, 128.3, 122.6, 122.4, 122.3, 122.0, 118.0, 117.9, 57.2, 56.1, 32.0<sub>(HSQC)</sub>, 29.1<sub>(HSQC)</sub>, 18.9, 14.2.

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -6.4 (br t, <sup>1</sup>*J* = 112.7 Hz).

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3116 (w), 2943 (w), 2428 (m), 2362 (m), 1597 (m), 1499 (s), 1447 (m), 1269 (m), 1142 (w), 972 (m), 918 (m), 760 (s), 690 (s), 592 (m).

HRMS (ESI, [M+Na]<sup>+</sup>) not detected

b. Synthetic procedures and spectroscopic data for the preparation of NHCborane **4** 



The appropriate chlorinated NHC-borane **5** (0.15 mmol, 1 equiv) was dissolved in dry benzene (1 mL) in a 10 mL Schlenk flask under argon. Then, 1 equivalent of Grignard reagent R"MgX (0.15 mmol) was added via a syringe at room temperature. The Schlenk was sealed and the reaction was stirred at 50 °C for 5 hours. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent to give the desired NHC-borane **4**.

4a



C<sub>24</sub>H<sub>31</sub>BN<sub>2</sub> Mw: 358.33 g.mol<sup>-1</sup>

2,4,6-trimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent to give **4a** in 93% yield as one diastereomer.

Aspect: white solid.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.01 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.83 (s, 1H), 6.81 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.67 (s, 1H), 6.55 (s, 2H), 4.48 (dd, <sup>2</sup>*J* = 11.2 Hz, <sup>3</sup>*J* = 9.2 Hz, 1H), 3.64 (dd, <sup>2</sup>*J* =

11.2 Hz,  ${}^{3}J = 6.2$  Hz, 1H), 2.64 (q,  ${}^{1}J = 83.6$  Hz, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 2.09 – 2.03 (m, 10H), 1.73 (s, 3H), 1.18 (d,  ${}^{3}J = 7.0$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 141.1, 138.7, 135.6, 134.5, 133.6, 132.8, 128.8, 127.4, 123.9, 116.4, 58.7, 29.5<sub>(HSQC)</sub>, 24.1<sub>(HSQC)</sub>, 23.1, 21.1, 20.9, 18.1, 17.3.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -15.2 (d, <sup>1</sup>*J* = 83.6 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>24</sub>H<sub>31</sub>N<sub>2</sub>BNa]<sup>+</sup>: 381.2477; found: 381.2480

 $[\alpha]^{25}_{D}$ : +66.4, c = 0.8, CHCl<sub>3</sub>

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3156 (w), 3125(m), 2951 (s), 2915 (s), 2853 (m), 2720 (w), 2353 (m), 1721 (w), 1670 (w), 1597 (m), 1543 (m), 1493 (s), 1449 (s), 1287 (m), 1217 (m), 1144 (m), 1032 (m), 1011 (m), 843 (s), 806 (m), 731 (s), 719 (s).

**X-Ray:** Crystals were obtained from slow evaporation of a product solution in DCM, layered with pentane.

#### 4b



C<sub>23</sub>H<sub>29</sub>BN<sub>2</sub> Mw: 344.30 g.mol<sup>-1</sup>

2,6-dimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent to give **4b** in 85% yield as one diastereomer.

Aspect: white solid.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.02 (d,  ${}^{3}J$  = 1.7 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.76 (dd,  ${}^{3}J$  = 8.3, 6.2 Hz, 1H), 6.72 – 6.68 (m, 2H), 6.65 (s, 1H), 4.48 (dd,  ${}^{2}J$  = 11.3 Hz,  ${}^{3}J$  = 9.7 Hz,

1H), 3.65 (dd,  ${}^{2}J$  = 11.3 Hz,  ${}^{3}J$  = 6.2 Hz, 1H), 2.22 (s, 3H), 2.17 – 2.01 (m, 10H), 1.69 (s, 3H), 1.18 (d,  ${}^{3}J$  = 6.9 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 144.6<sub>(HSQC)</sub>, 142.1<sub>(HSQC)</sub>, 138.8, 135.5, 134.5, 133.5, 132.8, 128.8, 128.7, 126.5, 124.0, 116.4, 58.7, 28.3<sub>(HSQC)</sub>, 24.2<sub>(HSQC)</sub>, 23.2, 21.0, 18.1, 17.1.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -15.3 (d, <sup>1</sup>*J* = 84.6 Hz)

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>BNa]<sup>+</sup>: 367.2320; found: 367.2317

 $[\alpha]^{25}$ <sub>D</sub>: +35.4, c = 0.14, CHCl<sub>3</sub>

**X-Ray:** Crystals were obtained from slow evaporation of a product solution in DCM, layered with pentane.

4c



C<sub>22</sub>H<sub>26</sub>BFN<sub>2</sub> Mw: 348.26 g.mol<sup>-1</sup>

2-Methyl-4-fluorophenylmagnesium bromide (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 9:1 as eluent to give 4c in 66% yield as two diastereomers (87:13 *dr*). Aspect: white solid.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.05 (d, <sup>3</sup>*J* = 1.5 Hz, 1H), 6.98 - 6.91 (m, 1H), 6.89 (s, 1H), 6.77 (d, <sup>3</sup>*J* = 1.5 Hz, 1H), 6.70 (s, 1H), 6.60 - 6.51 (m, 2H), 4.39 (dd, <sup>2</sup>*J* = 10.6 Hz, <sup>3</sup>*J* = 8.2 Hz, 1H), 3.66 (dd, <sup>2</sup>*J* = 10.8 Hz, <sup>3</sup>*J* = 5.6 Hz, 1H), 2.27 (s, 3H), 2.06 (s, 3H), 1.86 (s, 3H), 1.53 (s, 3H), 1.17 (d, <sup>3</sup>*J* = 6.9 Hz, 3H).

Remarkable signals of the minor diastereomer: 4.22 (dd,  ${}^{2}J = 10.5$  Hz,  ${}^{3}J = 8.0$  Hz, 1H), 3.77 (dd,  ${}^{2}J = 10.7$  Hz,  ${}^{3}J = 5.7$  Hz, 1H), 2.25 (s, 3H), 2.15 (s, 3H), 2.03 (s, 3H), 1.98 - 1.88 (m, 3H), 0.74 (d,  ${}^{3}J = 7.2$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.0 (d, <sup>1</sup>*J*<sub>CF</sub> = 239.4 Hz), 144.6 (d, <sup>3</sup>*J*<sub>CF</sub> = 6.1 Hz), 139.2, 139.0, 135.3, 135.0, 134.3, 133.7 (d, <sup>3</sup>*J*<sub>CF</sub> = 7.0 Hz), 129.3, 128.9, 128.8, 124.0, 123.6, 116.8, 114.8 (d, <sup>2</sup>*J*<sub>CF</sub> = 18.1 Hz), 110.1 (d, <sup>2</sup>*J*<sub>CF</sub> = 18.1 Hz), 109.3 (d, <sup>3</sup>*J*<sub>CF</sub> = 18.8 Hz), 58.5, 58.2, 32.1, 22.2, 21.6, 21.1, 18.1, 17.9, 17.3, 17.1.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -14.9 (d, <sup>1</sup>*J* = 88.5 Hz), -15.9 (d, <sup>1</sup>*J* = 88.5 Hz)

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -121.7 (q, <sup>1</sup>*J* = 9.5 Hz), -121.9 (q, <sup>1</sup>*J* = 9.5 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>FBNa]<sup>+</sup>: 371.2069; found: 371.2070



2-methyl-4-methoxyphenylmagnesium bromide (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 1:1 as eluent to give 4d in 61% yield as two diastereomers (87:13 dr). Unfortunately, traces of bis-functionalized compound were found in mixture.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.04 (d, <sup>3</sup>*J* = 1.5 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.77 (d, <sup>3</sup>*J* = 1.5 Hz, 1H), 6.71 (s, 1H), 6.50 – 6.45 (m, 2H), 4.39 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.65 (dd, <sup>2</sup>*J* = 10.9 Hz, <sup>3</sup>*J* = 5.1 Hz, 1H), 2.27 (s, 3H), 2.07 (s, 3H), 1.97 – 1.86 (m, 7H), 1.57 (s, 3H), 1.18 (d, <sup>3</sup>*J* = 7.0 Hz, 3H).

Remarkable signals of the minor diastereomer: 4.21 (dd,  ${}^{2}J = 10.3$  Hz,  ${}^{3}J = 8.2$  Hz, 1H), 2.25 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H), 1.90 (s, 3H), 1.01 (d,  ${}^{3}J = 7.7$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) (major diastereomer) 156.7, 139.0, 138.9, 135.6, 135.1, 134.3, 128.9, 123.6, 116.8, 115.0, 114.5, 109.3, 58.6, 58.2, 55.1, 32.0, 23.1, 22.4, 21.9, 21.1, 18.1, 17.9.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -14.7 (d, <sup>1</sup>*J* = 86.4 Hz), -15.9 (d, <sup>1</sup>*J* = 86.4 Hz).

HRMS (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>OBNa]<sup>+</sup>: 383.2269; found: 383.2267



C<sub>26</sub>H<sub>29</sub>BN<sub>2</sub><sup>+</sup> Mw: 380.33 g.mol<sup>-1</sup>

2-Methylnaphtylmagnesium bromide (0.25 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 9:1 as eluent to give **4e** in 35% yield as one diastereomer.

Aspect: white solid

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.86 (bs, 1H), 7.58 (d,  ${}^{3}J = 7.8$  Hz, 1H), 7.33 (d,  ${}^{3}J = 8.2$  Hz, 1H), 7.20 – 7.06 (m, 3H), 7.04 (d,  ${}^{3}J = 8.3$  Hz, 1H), 6.80 (d,  ${}^{3}J = 1.8$  Hz, 1H), 6.64 (s, 1H), 6.35 (s, 1H), 4.56 (dd,  ${}^{2}J = 10.6$  Hz,  ${}^{3}J = 9.4$  Hz, 1H), 3.72 (dd,  ${}^{2}J = 10.9$  Hz,  ${}^{3}J = 8.4$  Hz, 1H), 3.03 (q,  ${}^{1}J = 80.5$  Hz, 1H, BH), 2.41 – 2.24 (m, 4H), 2.07 (s, 3H), 2.06 (s, 3H), 1.43 (s, 3H), 1.17 (d,  ${}^{3}J = 6.7$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 139.6<sub>(HMBC)</sub>, 138.4, 138.2, 135.3, 134.2, 133.1, 133.0, 132.2, 129.0, 128.9, 128.6, 128.4, 128.2, 124.4, 123.9, 123.3, 122.5, 116.5, 58.3, 31.3<sub>(HSQC)</sub>, 21.4, 20.9, 18.2, 17.5.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -15.3 (d, <sup>1</sup>*J* = 84.3 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>BNa]<sup>+</sup>: 403.2321; found: 403.2321

 $[\alpha]^{25}_{D}$ : +107.4, c = 0.28, CHCl<sub>3</sub>



 $C_{21}H_{25}BN_2$ Mw: 316.25 g.mol<sup>-1</sup>

in mixture with



C<sub>27</sub>H<sub>29</sub>BN<sub>2</sub> Mw: 392.34 g.mol<sup>-1</sup>

Phenyl Grignard reagent (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using Pentane:DCM 9:1 as eluent to give **4f** as one diastereomer in mixture with the bis-functionalized product.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.74 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 4.37 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 8.1 Hz, 1H), 3.66 (dd, <sup>2</sup>*J* = 10.8 Hz, <sup>3</sup>*J* = 6.5 Hz, 1H), 2.30 (s, 3H), 2.10 (s, 3H), 1.44 (s, 3H), 0.84 (d, <sup>3</sup>*J* = 6.8 Hz, 3H). The signals of the aromatic part are overlapping with the signals of the bis-functionalized product.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.18 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 7.09 – 6.91 (m, 4H), 6.87 – 6.71 (m, 5H), 6.73 – 6.68 (m, 2H), 6.53 (s<sub>app</sub>, 1H), 4.27 – 4.12 (m, 1H,), 3.71 (t<sub>app</sub>, <sup>3</sup>*J* = 10.7 Hz, 1H), 2.60 – 2.44 (m, 1H), 2.25 (s, 3H), 1.97 (s, 3H), 1.09 (s, 3H), 0.70 (d, <sup>3</sup>*J* = 7.0 Hz, 3H).

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -8.9, -12.8 (d, <sup>1</sup>*J*<sub>BH</sub> = 85.0 Hz)

4g



C<sub>19</sub>H<sub>29</sub>BN<sub>2</sub> Mw: 296.26 g.mol<sup>-1</sup>

*tert*-Butylmagnesium bromide (0.75 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent to give 4g in 74% yield as two diastereomers (67:33 *dr*).

Aspect: white solid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.97 – 6.92 (m, 3H), 6.73 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 4.17 (dd, <sup>2</sup>*J* = 10.5 Hz, <sup>3</sup>*J* = 8.2 Hz, 1H), 3.47 (dd, <sup>2</sup>*J* = 10.5 Hz, <sup>3</sup>*J* = 7.6 Hz, 1H), 2.34 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.54 – 1.45 (m, 1H), 1.11 (d, <sup>3</sup>*J* = 6.9 Hz, 3H), 1.06 – 0.93 (m, 1H), 0.64 (s, 3H), 0.62 (s, 3H), 0.06 – 0.05 (m, 2H).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.97 – 6.92 (m, 3H), 6.71 (d, <sup>3</sup>*J* = 1.7 Hz, 1H), 4.08 (dd, <sup>2</sup>*J* = 10.4 Hz, <sup>3</sup>*J* = 6.6 Hz, 1H), 3.59 (dd, <sup>2</sup>*J* = 10.4 Hz, <sup>3</sup>*J* = 1.1 Hz, 1H), 2.33 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.84 – 1.75 (m, 1H), 1.06 – 0.93 (m, 1H), 0.89 (d, <sup>3</sup>*J* = 7.2 Hz, 3H), 0.69 (s, 3H), 0.68 (s, 3H), 0.63 (d, *J* = 6.5 Hz), - 0.14 – - 0.22 (m, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm) 139.9, 139.4, 136.2, 136.1, 135.8, 135.5, 135.3, 134.8, 134.7, 129.7, 129.6, 129.4, 129.2, 123.4, 123.3, 117.1, 116.9, 59.4, 58.5, 32.0<sub>(HSQC)</sub>, 28.8<sub>(HSQC)</sub>, 29.1, 28.9, 26.5, 26.4, 26.2, 25.8, 25.6, 21.6, 20.8, 18.4, 18.3, 18.3, 18.1, 17.9, 17.8.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -14.8 (d, <sup>1</sup>*J* = 82.9 Hz), -16.5 (d, <sup>1</sup>*J* = 82.0 Hz).

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3097 (w), 2951 (m), 2922 (m), 2353 (w), 1606 (w), 1496 (s), 1379 (s), 1064 (s), 817 (s), 665 (s)

### HRMS (ESI, [M+Na]<sup>+</sup>) not detected



C<sub>29</sub>H<sub>33</sub>BN<sub>2</sub> Mw: 420.40 g.mol<sup>-1</sup>

2,6-dimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 9:1 as eluent to give **4i** in 63% yield as one diastereomer. Aspect: white solid.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.28 – 7.17 (m, 4H), 7.16 – 7.11 (m, 1H), 6.97 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.83 (s, 1H), 6.81 (d, <sup>3</sup>*J* = 1.7 Hz, 1H), 6.78 (dd, <sup>3</sup>*J* = 8.1 Hz, <sup>3</sup>*J* = 6.4 Hz, 1H), 6.74 – 6.69 (m, 2H), 6.63 (s, 1H), 4.21 (dd, <sup>2</sup>*J* = 11.6 Hz, <sup>3</sup>*J* = 9.2 Hz, 1H), 3.77 (dd, <sup>2</sup>*J* = 11.7 Hz, <sup>3</sup>*J* = 5.9 Hz, 1H), 3.09 (dd, <sup>2</sup>*J* = 14.3 Hz, <sup>3</sup>*J* = 4.0 Hz, 1H), 2.66 (dd, <sup>2</sup>*J* = 14.1 Hz, <sup>3</sup>*J* = 11.9 Hz, 1H), 2.54 – 2.44 (m, 1H), 2.23 (s, 3H), 2.08 (s, 3H), 2.07 (s, 6H), 1.64 (s, 3H).

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ (ppm) 145.4, 138.9, 135.5, 134.6, 133.4, 128.8, 128.7, 128.1, 126.6, 125.1, 124.2, 124.0, 116.5, 55.9, 44.6, 36.6<sub>(HSOC)</sub>, 24.3<sub>(HSOC)</sub>, 21.1, 18.1, 17.0.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -16.1 (d, <sup>1</sup>*J* = 83.5 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>29</sub>H<sub>33</sub>N<sub>2</sub>BNa]<sup>+</sup>: 443.2634; found: 443.2634

 $[\alpha]^{25}_{D}$ : -14.5, c = 0.1, CHCl<sub>3</sub>



C<sub>30</sub>H<sub>35</sub>BN<sub>2</sub> Mw: 434.42 g.mol<sup>-1</sup>

2,4,6-trimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 9:1 as eluent to give **4j** in 56% yield as one diastereomer.

Aspect: white solid.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.32 – 7.23 (m, 4H), 7.20 – 7.14 (m, 1H), 7.00 (d, <sup>3</sup>*J* = 1.7 Hz, 1H), 6.88 (s, 1H), 6.84 (d, <sup>3</sup>*J* = 1.6 Hz, 1H), 6.70 (s, 1H), 6.60 (s, 2H), 4.24 (dd, <sup>2</sup>*J* = 11.5 Hz, <sup>3</sup>*J* = 9.1 Hz, 1H), 3.80 (dd, <sup>2</sup>*J* = 11.7 Hz, <sup>3</sup>*J* = 5.9 Hz, 1H), 3.14 (dd, <sup>2</sup>*J* = 14.3 Hz, <sup>3</sup>*J* = 3.9 Hz, 1H), 2.69 (dd, <sup>2</sup>*J* = 13.8 Hz, <sup>3</sup>*J* = 11.9 Hz, 1H), 2.56 – 2.44 (s, 1H), 2.28 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H), 2.08 (s, 6H), 1.71 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 145.5, 142,3, 138.8, 135.5, 134.6, 133.5, 133.0, 128.8, 128.8, 128.1, 127.5, 125.1, 124.0, 116.5, 55.8, 44.5, 36.9<sub>(HSQC)</sub>, 24.0<sub>(HSQC)</sub>, 21.1, 21.0, 18.1, 17.1.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -16.1 (d, <sup>1</sup>*J* = 81.7 Hz).

HRMS (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>30</sub>H<sub>35</sub>N<sub>2</sub>BNa]<sup>+</sup>: 457.2791; found: 457.2791

 $[\alpha]^{25}_{D}$ : +19.4, c = 0.27, CHCl<sub>3</sub>



C<sub>26</sub>H<sub>35</sub>BN<sub>2</sub> Mw: 386.38 g.mol<sup>-1</sup>

2,6-dimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 9:1 as eluent to give **4k** in 38% yield as one diastereomer. Aspect: Colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 7.32 (t, <sup>3</sup>*J* = 7.8 Hz, 1H), 7.20 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H), 7.08 (d, <sup>3</sup>*J* = 1.9 Hz, 1H), 6.98 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H), 6.90 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.69 – 6.65 (m, 3H), 4.55 (dd, <sup>2</sup>*J* = 11.7 Hz, <sup>3</sup>*J* = 9.3 Hz, 1H), 3.69 (dd, <sup>2</sup>*J* = 11.6 Hz, <sup>3</sup>*J* = 5.0 Hz, 1H), 2.49 (sept, <sup>3</sup>*J* = 6.8 Hz, 1H), 2.35 (sept, <sup>3</sup>*J* = 6.8 Hz, 1H), 2.02 – 1.93 (m, 7H), 1.35 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 1.14 (d, <sup>3</sup>*J* = 7.1 Hz, 3H), 1.03 (d, <sup>3</sup>*J* = 6.9 Hz, 3H), 0.99 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 0.52 (d, <sup>3</sup>*J* = 6.8 Hz, 3H).

<sup>13</sup>**C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 146.8, 146.0, 134.0, 130.1, 127.4, 126.2, 124.2, 124.1, 123.7, 116.7, 59.2, 29.0<sub>(HSQC)</sub>, 28.7, 26.0, 25.7, 24.3, 22.8, 21.9.

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -15.5 (d, <sup>1</sup>*J* = 88.2 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>26</sub>H<sub>35</sub>N<sub>2</sub>BNa]<sup>+</sup>: 409.2790; found: 409.2795

 $[\alpha]^{25}_{D}$ : +18.87, c = 0.53, CHCl<sub>3</sub>



C<sub>27</sub>H<sub>37</sub>BN<sub>2</sub> Mw: 400.41 g.mol<sup>-1</sup>

2,4,6-trimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 8:2 as eluent to give **4I** in 38% yield as one diastereomer.

Aspect: Colorless oil.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.31 (t, <sup>3</sup>*J* = 7.8 Hz, 1H), 7.18 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.4 Hz, 1H), 7.02 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.95 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.4 Hz, 1H), 6.86 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.54 (brs, 2H), 4.55 (dd, <sup>2</sup>*J* = 11.7 Hz, <sup>3</sup>*J* = 9.3 Hz, 1H), 3.69 (dd, <sup>2</sup>*J* = 11.6 Hz, <sup>3</sup>*J* = 4.4 Hz, 1H), 2.42 (sep, <sup>3</sup>*J* = 6.8 Hz, 1H), 2.28 (sep, <sup>3</sup>*J* = 6.8 Hz, 1H), 2.10 (s, 3H), 2.03 – 1.93 (m, 7H), 1.35 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 1.15 (d, <sup>3</sup>*J* = 7.1 Hz, 3H), 1.04 (d, <sup>3</sup>*J* = 6.9 Hz, 3H), 0.96 (d, <sup>3</sup>*J* = 6.9 Hz, 3H), 0.46 (d, <sup>3</sup>*J* = 6.7 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 146.4, 145.7, 133.6, 132.9, 129.9, 127.7, 125.7, 123.8, 123.4, 116.1, 59.2, 28.7<sub>(HSQC)</sub>, 28.4, 26.1, 25.6, 24.7, 24.5<sub>(HSQC)</sub>, 23.0<sub>(HSQC)</sub>, 22.9, 21.5, 20.9.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -15.61 (d, <sup>1</sup>*J* = 88.5 Hz).

**HRMS** (ESI,  $[M+Na]^+$ ) calcd for  $[C_{27}H_{37}N_2BNa]^+$ : 423.2947; found: 423.2947

 $[\alpha]^{25}_{D}$ : +18.29, c = 0.35, CHCl<sub>3</sub>



C<sub>32</sub>H<sub>35</sub>BN<sub>2</sub> Mw: 458.44 g.mol<sup>-1</sup>

9-Phenanthrylmagnesium bromide (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 7:3 as eluent to give **4m** in 57% yield as one diastereomer.

Aspect: Colorless oil.

<sup>1</sup>**H** NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 8.59 – 8.50 (m, 2H), 8.17 (dd, <sup>3</sup>*J* = 8.3 Hz, <sup>4</sup>*J* = 1.4 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.49 – 7.37 (m, 3H), 7.35 (s, 1H), 7.24 (d, <sup>3</sup>*J* = 1.2 Hz, 1H), 7.24 – 7.21 (m, 3H), 6.95 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.82 – 6.62 (m, 1H), 4.51 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 7.2 Hz, 1H), 3.75 (dd, <sup>2</sup>*J* = 11.0, <sup>3</sup>*J* = 4.1 Hz, 1H), 2.64 (sep, <sup>3</sup>*J* = 6.8 Hz, 1H), 2.44 (p, <sup>3</sup>*J* = 6.8 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.46 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 1.23 (d, <sup>3</sup>*J* = 7.2 Hz, 3H), 1.09 (d, <sup>3</sup>*J* = 6.9 Hz, 3H), 0.95 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 0.14 (d, <sup>3</sup>*J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 146.5, 145.8, 137.6, 134.1, 133.0, 130.3, 130.0, 129.9, 129.8, 127.9, 126.0, 125.9, 125.5, 124.9, 124.6, 124.3, 123.9, 122.4, 122.3, 117.5, 58.8, 32.3<sub>(HSOC)</sub>, 28.8, 28.6, 26.0, 25.7, 23.1, 21.8.

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -14.29 (d, <sup>1</sup>*J* = 91.5 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>32</sub>H<sub>35</sub>BN<sub>2</sub>Na]<sup>+</sup>: 481.2791; found: 481.2790

 $[\alpha]^{25}_{D}$ : +4.64, c = 0.14, CHCl<sub>3</sub>



C<sub>25</sub>H<sub>32</sub>BFN<sub>2</sub> Mw: 229.08 g.mol<sup>-1</sup>

2-Methyl-4-fluorophenylmagnesium bromide (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 8 :2 as eluent to give 4n in 43% yield as two diastereomers (95:5 *dr*). Aspect: Colorless oil.

<sup>1</sup>**H NMR** (400 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) 7.37 (t,  ${}^{3}J = 7.8$  Hz, 1H), 7.23 (dd,  ${}^{3}J = 7.8$  Hz,  ${}^{4}J = 1.5$  Hz, 1H), 7.12 (d,  ${}^{3}J = 1.8$  Hz, 1H), 7.06 (dd,  ${}^{3}J = 7.8$  Hz,  ${}^{4}J = 1.5$  Hz, 1H), 6.95 – 6.89 (m, 1H), 6.89 (d,  ${}^{3}J = 1.8$  Hz, 1H), 6.57 – 6.50 (m, 2H), 4.41 (dd,  ${}^{2}J = 11.1$  Hz,  ${}^{3}J = 7.7$  Hz, 1H), 3.66 (dd,  ${}^{2}J = 11.1$  Hz,  ${}^{3}J = 5.1$  Hz, 1H), 2.54 (sep,  ${}^{3}J = 6.8$  Hz, 1H), 2.27 (sep,  ${}^{3}J = 6.8$  Hz, 1H), 1.85 (brs, 3H), 1.81 – 1.77 (m, 1H), 1.31 (d,  ${}^{3}J = 6.8$  Hz, 3H), 1.12 (d,  ${}^{3}J = 6.4$  Hz, 3H), 1.05 (d,  ${}^{3}J = 6.9$  Hz, 3H), 0.99 (d,  ${}^{3}J = 6.8$  Hz, 3H), 0.62 (d,  ${}^{3}J = 6.8$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 162.4, 160.0, 146.6, 146.0, 144.8, 134.0, 130.3, 125.8, 124.3, 123.9, 117.1, 115.0, 110.6, 58.6,  $32.8_{(HSQC)}$ , 28.7, 26.1, 25.5, 22.9, 22.5, 21.9, 21.7. <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) -14.85 (d, <sup>1</sup>*J* = 90.4 Hz).

<sup>19</sup>**F NMR** (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) -122.37.

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>25</sub>H<sub>32</sub>N<sub>2</sub>BFNa]<sup>+</sup>: 413.2539; found: 413.2546

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3132 (w), 2961 (s), 2928 (s), 2870 (m), 2851 (m), 2359 (m), 2338 (m), 1578 (m), 1483 (s), 1360 (w), 1269 (m), 1223 (s), 1038 (m), 947 (m), 853 (m), 733 (s)



C<sub>26</sub>H<sub>29</sub>BF<sub>6</sub>N<sub>2</sub> Mw: 493.32 g.mol<sup>-1</sup>

3,5-Bis(trifluoromethyl)phenylmagnesium bromide (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using Pentane:DCM 8:2 as eluent to give **40** in 14% yield as one diastereomer.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.40 – 7.34 (m, 2H), 7.33 – 7.29 (m, 3H), 7.07 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 6.91 (dd, <sup>3</sup>*J* = 7.7 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H), 6.81 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 4.38 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 8.8 Hz, 1H), 3.70 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 8.8 Hz, 1H), 2.61 (sep, <sup>3</sup>*J* = 6.9 Hz, 1H), 2.25 – 2.14 (m, 1H), 1.92 (sep, <sup>3</sup>*J* = 6.8 Hz, 1H), 1.42 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 1.19 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 1.10 (d, <sup>3</sup>*J* = 6.9 Hz, 3H), 0.90 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 0.23 (d, <sup>3</sup>*J* = 6.8 Hz, 3H).

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ (ppm) 145.8, 145.3, 133.6, 132.8, 130.7, 129.2, 125.1, 124.1, 123.7, 118.1, 116.5, 57.5, 30.2<sub>(HSOC)</sub>, 28.4, 28.2, 25.6, 25.4, 23.1, 21.3, 19.1.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -13.47 (d, <sup>1</sup>*J* = 88.1 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ (ppm) -62.39.

**HRMS** (ESI,  $[M+Na]^+$ ) calcd for  $[C_{26}H_{29}N_2BF_6Na]^+$ : 517.2225; found: 517.2218

 $[\alpha]^{25}_{D}$ : -39.68, c = 0.15, CHCl<sub>3</sub>



C<sub>20</sub>H<sub>29</sub>BN<sub>2</sub> Mw: 308.27 g.mol<sup>-1</sup>

Vinylmagnesium bromide (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent to afford the product **4p** as two diastereomers (81:19 dr) in mixture with the bis-functionalized product. Unfortunately, the product decomposed during column chromatography.

<sup>1</sup>**H** NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 7.45 (t, <sup>3</sup>*J* = 7.6 Hz, 1H), 7.25 (t<sub>app</sub>, *J* = 7.8 Hz, 2H), 7.04 (d, <sup>3</sup>*J* = 1.9 Hz, 1H), 6.83 (d, <sup>3</sup>*J* = 1.9 Hz, 1H), 5.89 – 5.71 (m, 1H), 4.99 – 4.78 (m, 2H), 4.23 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 8.1 Hz, 1H), 3.54 (dd, <sup>2</sup>*J* = 10.7 Hz, <sup>3</sup>*J* = 7.7 Hz, 1H), 2.53 (sep, <sup>3</sup>*J* = 6.9 Hz, 1H), 2.44 (sep, <sup>3</sup>*J* = 6.8 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.25 (d, <sup>3</sup>*J* = 6.8, 4.1 Hz, 3H), 1.17 (d, <sup>3</sup>*J* = 6.8 Hz, 3H), 1.13 – 1.03 (m, 9H).

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -14.8 (d, <sup>1</sup>*J* = 88.2 Hz).





 $C_{21}H_{25}BN_2$ Mw: 316.25 g.mol<sup>-1</sup>

2,4,6-trimethylphenylmagnesium bromide (1.0 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 8:2 as eluent to give 4r in 89% yield as two diastereomers (92:8 dr). Aspect: Colorless oil.

<sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 7.51-7.45 (m, 2H), 7.33 (d, <sup>3</sup>*J* = 1.98 Hz, 1H), 7.28-7.17 (m, 3H), 7.08 (d, <sup>3</sup>*J* = 2.0 Hz, 1H), 6.82 (brs, 1H), 6.66 – 6.54 (m, 1H), 4.35 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 8.8 Hz, 1H), 3.62 (dd, <sup>2</sup>*J* = 10.8 Hz, <sup>3</sup>*J* = 8.2 Hz, 1H), 3.00 (q, <sup>1</sup>*J* = 86.4 Hz, 1H), 2.29 (brs, 6H), 2.15 (brs, 3H), 1.88 – 1.84 (m, 1H), 1.21 (d, <sup>3</sup>*J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 138.1, 138.0, 133.2, 129.6, 129.5, 129.4, 129.4, 128.6, 128.0, 127.6, 121.6, 121.5, 120.8, 117.8, 58.1, 31.8<sub>(HSQC)</sub>, 21.4, 21.0, 20.9, 19.9.

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -14.9 (d, <sup>1</sup>*J* = 86.2 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>21</sub>H<sub>25</sub>BN<sub>2</sub>Na]<sup>+</sup>: 339.2007; found: 339.2003.

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3132 (w), 2918 (m), 2853 (m), 2313 (w), 2280 (w), 1597 (m), 1501 (s), 1435 (m), 1267 (m), 1198 (m), 1061 (m), 962 (m), 760 (s), 691 (s).

**4s** 



C<sub>22</sub>H<sub>21</sub>BN<sub>2</sub> Mw: 324.23 g.mol<sup>-1</sup>

1-Naphtylmagnesium bromide (0.25 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 8:2 as eluent to give **4s** in 74% yield as two diastereomers (87:13 dr). Aspect: Colorless oil.

<sup>1</sup>**H** NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 8.38 – 8.30 (m, 1H), 7.74 – 7.68 (m, 1H), 7.61 – 7.55 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.25 – 7.18 (m, 4H), 7.08 (dd, <sup>2</sup>*J* = 8.1 Hz, <sup>3</sup>*J* = 6.7 Hz, 1H), 6.77 (d, <sup>3</sup>*J* = 6.7 Hz, 1H), 4.25 (dd, <sup>2</sup>*J* = 10.9 Hz, <sup>3</sup>*J* = 7.5 Hz, 1H), 3.65 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 4.6 Hz, 1H), 3.15 (q, <sup>1</sup>*J* = 92.1 Hz, 1H), 1.84 – 1.72 (m, 1H), 1.27 (d, <sup>3</sup>*J* = 8.2 Hz, 3H).

<sup>1</sup>**H** NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 8.60-8.50 (m, 1H), 7.74 – 7.68 (m, 1H), 7.61 – 7.55 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.25 – 7.18 (m, 4H), 6.97 (dd, <sup>2</sup>*J* = 8.1 Hz, <sup>3</sup>*J* = 6.7 Hz, 1H), 6.57 (d, <sup>3</sup>*J* = 6.7 Hz, 1H), 4.31-4.24(m, 1H), 3.72 (dd, <sup>2</sup>*J* = 10.9 Hz, <sup>3</sup>*J* = 5.1 Hz, 1H), 3.15 (q, <sup>1</sup>*J* = 92.1 Hz, 1H), 2.39 – 2.25 (m, 1H), 0.51 (d, <sup>3</sup>*J* = 7.3 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 138.2, 134.1, 130.8, 129.9, 129.8, 129.6, 128.4, 128.3, 128.0, 127.9, 125.6, 124.8, 124.6, 124.6, 124.2, 124.1, 122.5, 122.3, 122.1, 121.8, 118.2, 58.3, 32.8<sub>(HSQC)</sub>, 27.9<sub>(HSQC)</sub>, 21.7, 18.3.

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -12.6 (d, <sup>1</sup>*J* = 90.6 Hz), -14.9 (d, <sup>1</sup>*J* = 89.0 Hz).

**HRMS** (ESI, [M+Ag]<sup>+</sup>) calcd for [C<sub>22</sub>H<sub>21</sub>BN<sub>2</sub>Ag]<sup>+</sup>: 431.0847; found: 431.0846.

**FT-IR** (ATR) v (cm<sup>-1</sup>) 3163 (w), 2928 (m), 2851 (m), 2324 (m), 1599 (m), 1502 (s), 1445 (m), 1186 (w), 1065 (w), 956 (w), 783 (s), 679 (s).





C<sub>26</sub>H<sub>23</sub>BN<sub>2</sub> Mw: 374.28 g.mol<sup>-1</sup>

9-Phenanthryl Grignard reagent (0.5 M in THF) was used in the process. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent. After evaporation the product was purified by flash chromatography using pentane:DCM 8:2 as eluent to give 4t in 52% yield as two diastereomers (85:15 dr).

<sup>1</sup>**H** NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 8.73 – 8.65 (m, 1H), 8.64 – 8.57 (m, 1H), 8.53 – 8.46 (m, 1H), 7.70 – 7.10 (m, 12H), 7.00 (brs, 1H), 4.25 (dd, <sup>2</sup>*J* = 11.2 Hz, <sup>3</sup>*J* = 7.5 Hz, 1H), 3.65 (dd, <sup>2</sup>*J* = 11.2 Hz, <sup>3</sup>*J* = 3.9 Hz, 1H), 3.06 (q, <sup>1</sup>*J* = 100.0 Hz, 1H), 1.80 – 1.62 (m, 1H), 1.18 (d, <sup>3</sup>*J* = 7.1 Hz, 3H).

<sup>1</sup>**H** NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 8.73 – 8.65 (m, 1H), 8.64 – 8.57 (m, 1H), 8.53 – 8.46 (m, 1H), 7.70 – 7.10 (m, 12H), 6.83 (bs, 1H), 4.31 (dd, <sup>2</sup>*J* = 10.4 Hz, <sup>3</sup>*J* = 7.5 Hz, 1H), 3.60 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 4.3 Hz, 1H), 3.06 (q, <sup>1</sup>*J* = 100.0 Hz, 1H), 1.78 – 1.65 (m, 1H), 0.42 (d, <sup>3</sup>*J* = 7.3 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 138.3, 137.6, 132.9, 131.0,130.4, 130.3, 129.7, 129.7, 129.6, 129.6, 128.1, 128.0, 127.7, 127.5, 126.1, 126.0, 125.8, 125.7, 125.4, 125.3, 124.8, 124.6, 122.8, 122.7, 122.6, 122.5, 122.5, 122.0, 121.9, 118.3, 118.2, 58.4, 58.3, 32.2<sub>(HSQC)</sub>, 27.7<sub>(HSQC)</sub>, 22.0, 18.5.

<sup>11</sup>**B** NMR (128 MHz,  $CD_2Cl_2$ )  $\delta$  (ppm) -12.4 (d, <sup>1</sup>*J* = 91.1 Hz), -14.5 (d, <sup>1</sup>*J* = 90.3 Hz).

**HRMS** (ESI, [M+Na]<sup>+</sup>) calcd for [C<sub>26</sub>H<sub>23</sub>BN<sub>2</sub>Na]<sup>+</sup>: 397.1851; found: 397.1852.

**FT-IR** (ATR) ν (cm<sup>-1</sup>) 3067 (w), 2918 (m), 2853 (m), 2309 (w), 1591 (w), 1497 (m), 1441 (m), 1134 (w), 1069 (w), 731 (s), 687 (s).

## 4. NMR Spectra







S29



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S30















S35








-1205 -1206 -1207 -1208 -1209 -1210 -1211 -1212 -1213 -1214 -1215 -1218 -1217 -1218 1219 -1220 -1221 -1222 -1223 -1224 -1225 -1225 -1225 -1225 -1229 -1230 -1231 -1232 -12









-19 -2 -13 -14 -15 -16 -17 -18 1 -2 -3 -4 -6 -7 f1 (ppm) -9 -10 -11 -12 -5





80 70 f1 (ppm) 





# 10 8 6 4 2 0 -2 4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -11 (10)











145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 f1 (ppm)







S52







5 0 -5 -10 -15 -20 -25 f1 (ppm) -60 -65 -7( 45 40 35 30 25 20 15 10 -35 -45 -50 -55 -30 -40

















## 5. Modeling approach for trans-5a, cis- & trans-5a•-, Ila and Illa

Geometry optimizations and frequency calculations for reactants, intermediates and products were performed at the DFT level of theory by using the M06-2X functional<sup>1</sup> as implemented in the Gaussian 09 or  $16.^2$  For all the atoms, all-electron standard 6-311g(d,p) basis set was, employed. For each optimized stationary point vibrational analysis was performed to establish its nature as a minimum or saddle point, and zero-point vibrational energy (ZPE) corrections were included in all relative energies ( $\Delta E$ ). NBO 6 program,<sup>3</sup> which is included in Gaussian 09 suite of programs, was used to obtain natural bond orbitals (NBOs), atomic net charges, and densities of spin at the M06-2X/6.311g(d,p) optimized geometries.

#### a. trans-NHC-borane 5a

(M06-2x/6-311g(d,p))

<u> </u>			
C	-2.89433388	0.49770290	0.00000000
С	-1.53572188	0.52503490	0.03805400
С	-2.16468088	0.62678690	-2.10229800
Ν	-3.26368088	0.56418590	-1.33550500
Н	-3.62825288	0.42275790	0.78427000
Н	-0.85569388	0.49152490	0.87128000
Ν	-1.11937588	0.59468790	-1.27089300
С	0.18613012	0.74080990	-1.94835900
Н	0.91336412	0.08030590	-1.46948300
Н	0.50523812	1.77946090	-1.83963300
С	-0.13136988	0.38132890	-3.41350500
С	0.03365612	-1.12539510	-3.63510700
Н	-0.64039388	-1.69212310	-2.98155400
Н	-0.21707988	-1.39030610	-4.66372500
В	-1.69422588	0.83390890	-3.63278900
Н	1.05425812	-1.46656810	-3.43341500
Н	0.54187212	0.93306090	-4.07241700
С	-4.61069288	0.54583390	-1.83807500

<sup>&</sup>lt;sup>1</sup> Zhao, Y.; Truhlar, D. G. Theor. Chem. Acc., 2008, 120, 215-241.

<sup>&</sup>lt;sup>2</sup> Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

<sup>&</sup>lt;sup>3</sup> NBO 6.0. Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); <u>http://nbo6.chem.wisc.edu/</u>

С	-5.35448888	1.72569690	-1.80162200
С	-5.10514888	-0.64751610	-2.36331200
С	-6.65491588	1.67737990	-2.29479700
С	-6.41061288	-0.64430210	-2.84642900
С	-7.19873288	0.50406190	-2.81449800
Н	-7.25186388	2.58389690	-2.28742500
Н	-6.81742688	-1.55964010	-3.26450700
С	-4.23994288	-1.87718610	-2.43761000
Н	-3.45308988	-1.74165810	-3.18547300
Н	-3.75303088	-2.08135110	-1.48077500
Н	-4.83359888	-2.74738110	-2.71632700
С	-4.74734488	3.00373590	-1.28889500
Н	-5.45494988	3.82646790	-1.38482700
Н	-4.46159288	2.91904690	-0.23725500
Н	-3.84758688	3.24987590	-1.85952900
С	-8.61795488	0.47742690	-3.31886800
Н	-8.75529688	-0.30312710	-4.06810200
Н	-9.31345488	0.28027390	-2.49839300
Н	-8.89359488	1.43408690	-3.76495000
Cl	-1.83277388	2.72199290	-3.91553200
Н	-2.31914288	0.24460990	-4.46731200

## b. NHC-borane radical anion 5a--

# - *trans*-NHC-boron radical anion 5a•- (uM06-2x/6-311g(d,p))

Sum of electronic = -1178.1099 (Hartree/Particule)

С	-3.87957335	2.97256093 0.00000000	
С	-2.54486335	2.98949493 0.20847500	1
С	-3.05449135	4.87806793 -0.96114900	
Ν	-4.22846135	4.14854193 -0.69217600	
Н	-4.63282335	2.29763993 0.36762200	
Н	-1.93179235	2.27308093 0.73235300	
Ν	-2.03607135	4.16693193 -0.29172500	
С	-0.72914335	4.42281893 -0.90926700	
Н	-0.09469235	3.53588493 -0.79331500	
Н	-0.25701735	5.26901693 -0.40055300	
С	-1.05108435	4.78426193 -2.37120700	
С	-1.27256135	3.50001393 -3.17659300	
Н	-2.09078535	2.91627493 -2.73647100	
Н	-1.55604535	3.73018393 -4.20687800	
В	-2.46927235	5.61037493 -2.24213100	
Н	-0.38070335	2.85923793 -3.19898900	

-0.23608335	5.37092293	-2.80516300
-5.52891035	4.51270493	-1.04275900
-6.02011935	5.80554593	-0.73267600
-6.36833635	3.58014293	-1.69588000
-7.33228135	6.11108193	-1.05471800
-7.68652535	3.93705193	-1.97375800
-8.19518135	5.19278693	-1.66757500
-7.70811135	7.09897193	-0.79855900
-8.32162335	3.21730493	-2.48562900
-5.82906235	2.26160093	-2.19086900
-4.81775835	2.39244093	-2.58386300
-5.76754035	1.49499993	-1.41094300
-6.46774035	1.87385593	-2.98696700
-5.16550435	6.80777993	-0.00747300
-5.78568735	7.63034493	0.35608700
-4.66153535	6.33861893	0.84139700
-4.37446135	7.20849693	-0.64671400
-9.61646335	5.57437993	-1.99221300
-10.13756435	4.75445493	-2.49153100
-10.18113735	5.82826493	-1.08878700
-9.65437935	6.44647893	-2.65270000
-1.98897135	7.52514993	-1.85127600
-3.17803135	5.64696293	-3.21441000
	-0.23608335 -5.52891035 -6.02011935 -6.36833635 -7.33228135 -7.68652535 -8.19518135 -7.70811135 -8.32162335 -5.82906235 -4.81775835 -5.76754035 -6.46774035 -5.76550435 -5.78568735 -4.37446135 -9.61646335 -10.13756435 -10.13756435 -10.18113735 -9.65437935 -1.98897135 -3.17803135	-0.236083355.37092293-5.528910354.51270493-6.020119355.80554593-6.368336353.58014293-7.332281356.11108193-7.686525353.93705193-8.195181355.19278693-7.708111357.09897193-8.321623353.21730493-5.829062352.26160093-4.817758352.39244093-5.767540351.49499993-6.467740351.87385593-5.165504356.80777993-5.785687357.63034493-4.661535356.33861893-4.374461357.20849693-9.616463355.57437993-10.181137355.82826493-9.654379356.44647893-1.988971357.52514993-3.178031355.64696293



Somo (isoval 0.05)



Spin density (0.004)

# - *cis*-NHC-boron radical anion 5a•- (uM06-2x/6-311g(d,p))

Sum of electronic = -1178.1046082 (Hartree/Particule)

С	-3.08689038	2.42378045	0.00000000	
С	-4.40047038	2.46290745	0.30702200	
С	-3.64989438	0.37736745	0.86283000	
Ν	-2.58914838	1.15511645	0.35516100	
Н	-2.43005038	3.20483445	-0.34104000	
Н	-5.09750138	3.28014645	0.20607200	
Ν	-4.74768838	1.26741945	0.90181600	
С	-6.01145138	0.53419645	0.82346800	
Н	-6.77848738	1.17870145	0.37804000	
Н	-6.32676738	0.26949045	1.83962000	
С	-5.70054938	-0.72956155	-0.00220400	
С	-5.75637038	-0.37204455	-1.48970300	
Н	-5.01201838	0.39976945	-1.71984300	
Н	-5.51656438	-1.23556555	-2.11216700	
В	-4.16725638	-1.11127455	0.51568800	
Н	-6.74428238	0.00971645	-1.78151200	
Н	-6.44121738	-1.50654255	0.21875200	
С	-1.25870238	0.75891945	0.21994600	
С	-0.58094738	0.12263845	1.28830600	
С	-0.57729538	1.00022145	-0.99522900	
С	0.76174862	-0.18333255	1.13667400	
С	0.77804462	0.69379145	-1.08096300	
С	1.47673762	0.11065645	-0.03021300	
Н	1.27823862	-0.65986355	1.96717700	
Н	1.29018362	0.87201345	-2.02395500	
С	-1.33194938	1.42631145	-2.22888700	
Н	-2.28275938	0.88714245	-2.27272900	
Н	-1.56107638	2.49633145	-2.26249800	
Н	-0.75085538	1.18112445	-3.12010900	
С	-1.28123738	-0.18483355	2.58442500	
Н	-0.55415838	-0.51084555	3.33230900	
Н	-1.80851938	0.69597945	2.95880900	
Н	-2.03870338	-0.96109655	2.44811700	
С	2.94325462	-0.21904055	-0.13897600	
Н	3.30505862	-0.05824055	-1.15710600	
Н	3.54873562	0.40269745	0.53009200	
Н	3.13790662	-1.26313655	0.12433100	
Cl	-3.06378938	-1.89572555	-0.88703600	
Н	-4.14043338	-1.91285255	1.42467600	



Somo (isoval 0.05)

Spin density (0.004)

#### c. NHC-boryl radical IIa

(uM06-2x/6-311g(d,p))

Sum of electronic and zero-point Energies= -717.811978 (Hartree/Particle) Sum of electronic and thermal Energies= -717.793643 (Hartree/Particle) Sum of electronic and thermal Enthalpies= -717.792698 (Hartree/Particle) Sum of electronic and thermal Free Energies= -717.860882 (Hartree/Particle)

C       -1.06418801       0.95430798       0.02849300         C       -0.40038001       0.51938898       -2.10516500         N       0.71462999       0.74637098       -1.30828300         H       1.00765999       1.21755698       0.78631400         H       -1.74715201       1.09796398       0.85228600         N       -1.48170701       0.66101398       -1.24833200         C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
C       -0.40038001       0.51938898       -2.10516500         N       0.71462999       0.74637098       -1.30828300         H       1.00765999       1.21755698       0.78631400         H       -1.74715201       1.09796398       0.85228600         N       -1.48170701       0.66101398       -1.24833200         C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
N       0.71462999       0.74637098       -1.30828300         H       1.00765999       1.21755698       0.78631400         H       -1.74715201       1.09796398       0.85228600         N       -1.48170701       0.66101398       -1.24833200         C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
H       1.00765999       1.21755698       0.78631400         H       -1.74715201       1.09796398       0.85228600         N       -1.48170701       0.66101398       -1.24833200         C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
H       -1.74715201       1.09796398       0.85228600         N       -1.48170701       0.66101398       -1.24833200         C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
N       -1.48170701       0.66101398       -1.24833200         C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
C       -2.77514401       0.38886098       -1.88320000         H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
H       -3.46208501       1.22288798       -1.69158900         H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
H       -3.21233101       -0.51311002       -1.43568100         C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
C       -2.45548601       0.20242998       -3.40348300         C       -3.10181101       1.30764598       -4.26367900         H       -2.73135201       2.29979198       -3.97525700
C -3.10181101 1.30764598 -4.26367900 H -2.73135201 2.29979198 -3.97525700
Н -2.73135201 2.29979198 -3.97525700
H -2.85728801 1.16508798 -5.32225100
B -0.83555201 0.18728198 -3.49668500
Н -4.19787501 1.32086798 -4.17254800
Н -2.88237601 -0.75712302 -3.72936800
C 2.07453599 0.72150198 -1.75684300
C 2.71896199 -0.51531102 -1.92619200
C 2.72810499 1.93654498 -2.02670100
C 4.04753799 -0.51048802 -2.36269800
C 4.05773299 1.88890998 -2.45393800
C 4.73610799 0.67746298 -2.62468300
Н 4.55588899 -1.46248702 -2.50073400

Н	4.57208299	2.82298298	-2.67125300
С	2.00709799	3.25632098	-1.88654200
Н	1.07764199	3.26034798	-2.46694500
Н	1.73181499	3.46593498	-0.84566300
Н	2.63548399	4.07956398	-2.23901000
С	1.99737199	-1.81294502	-1.65436200
Н	2.66486999	-2.66694602	-1.80266300
Н	1.61562399	-1.85295102	-0.62717800
Н	1.13303099	-1.92958402	-2.31884700
С	6.18174599	0.65746098	-3.06433000
Н	6.39343199	1.45798698	-3.78161800
Н	6.85889999	0.80012498	-2.21142800
Н	6.44492499	-0.29604302	-3.53359700
Н	-0.17273901	-0.00001102	-4.47126900



Somo (isoval 0.05) NBO charges: B (0.378); C<sub>NHC</sub> (0.118)

Spin density (0.004)

#### d. NHC-boryl radical IIIa

(uM06-2x/6-311g(d,p))

Sum of electronic and zero-point Energies= -1066.295511 (Hartree/Particle) Sum of electronic and thermal Energies= -1066.268229 (Hartree/Particle) Sum of electronic and thermal Enthalpies= -1066.267284 (Hartree/Particle) Sum of electronic and thermal Free Energies= -1066.353356 (Hartree/Particle)

С	-2.14176839	1.37195120	0.00000000
С	-0.83641239	1.02226220	-0.10488600
С	-0.96277139	3.27219420	-0.33232300
Ν	-2.22610039	2.75745220	-0.13480700
Н	-3.01555539	0.77600020	0.20009600
Н	-0.37227339	0.05300820	-0.03955200
Ν	-0.12371039	2.18283720	-0.27842500
С	1.24249961	2.50209920	-0.68983400
Н	1.36531561	2.22144620	-1.74383000
Н	1.95998361	1.93841620	-0.09027500
С	1.34312761	4.03821820	-0.52982200
С	2.25191261	4.66953020	-1.58468100
Н	1.85144461	4.49125120	-2.58756700
Н	2.30168261	5.75259220	-1.44731200
В	-0.19734239	4.55410920	-0.55314500
Н	3.27327161	4.27608020	-1.54999800
Н	1.77478961	4.23415820	0.46067500
С	-3.43593839	3.51258720	-0.11384300
С	-3.63654839	4.47084220	0.88464400
С	-4.38945539	3.28308020	-1.11538900
С	-4.81360639	5.21679620	0.84552500
С	-5.55729339	4.03765120	-1.09756000
С	-5.78393939	5.01535620	-0.12964700
Н	-4.97105139	5.97580520	1.60585000
Н	-6.29688539	3.87825920	-1.87678100
С	-4.13501839	2.29474120	-2.22414500
Н	-3.10539839	2.36621320	-2.58162100
Н	-4.29288039	1.26385420	-1.89630800
Н	-4.80807239	2.48610020	-3.06014400
С	-2.62722639	4.71874620	1.97288600
Н	-3.13061139	5.06135020	2.87796100
Н	-2.05767839	3.81815620	2.20582700
Н	-1.91958639	5.49186420	1.66011000
С	-7.06049139	5.81541020	-0.12940700
Н	-7.42439139	5.97467820	-1.14576900
Н	-7.84442039	5.29182620	0.42500700
Н	-6.91345239	6.78953320	0.33875200
С	-0.71213039	6.03310220	-0.69007200
C	-0.21656739	7.03966120	0.17680600
С	-1.67605739	6.41573020	-1.64255900
C	-0.68607439	8.34474520	0.09171900
C	-2.12617939	7.73736620	-1.70413200
С	-1.64691739	8.71756020	-0.84835300
Н	-0.29933639	9.09306420	0.77894900
Н	-2.87275639	8.00153820	-2.44948100



С	0.80991961	6.71223420	1.23607800
Н	1.78843961	6.50787320	0.79168600
Н	0.92764961	7.54352620	1.93270200
Н	0.52448861	5.82339320	1.80664600
С	-2.12036639	10.14504320	-0.94373400
Н	-1.39024139	10.76202820	-1.47545900
Н	-3.06711939	10.21094520	-1.48220300
Н	-2.25892739	10.58182620	0.04765900
С	-2.25339239	5.45004120	-2.65253000
Н	-3.32575839	5.31517720	-2.48580500
Н	-2.12239839	5.84175020	-3.66514500
Н	-1.77292639	4.47247820	-2.60324000



Somo (isoval 0.05) NBO charges: B (0.521); C<sub>NHC</sub> (0.093)

Spin density (0.004)

# 6. Origin of the diastereoselectivity in the formation of NHCboranes 4a and 4d

#### a. DFT calculations

To determine the origin of the diastereoselectivity in the formation of the boron stereogenic NHC-boranes **4**, we hypothesized that (i) the boron stereocenter could isomerize through a thermal equilibration *via* the intermediate radical and (ii) a preferential addition *anti* to the methyl substituent could occur. To acquire more insights, DFT calculations (M06-2X/6-311G(d,p), continuum solvent model PCM for diethylether) on *trans* and *cis*-**4a/d** were performed and clearly indicated a large preference for the *trans*-diastereomer in agreement with the experimental diastereomeric ratio.

NHC-borane *trans*-4a (M062X/6-311g(d,p)) //pcm (ether)
Sum of electronic and zero-point Energies= -1066.911673 (Hartree/Particle)
Sum of electronic and thermal Energies= -1066.884639 (Hartree/Particle)
Sum of electronic and thermal Enthalpies= -1066.883695 (Hartree/Particle)
Sum of electronic and thermal Free Energies= -1066.967892 (Hartree/Particle)

С	0.14062499	2.64062496	0.00000000
С	-1.19068001	2.86303296	0.16046400
С	-0.10862501	4.04233796	1.72125200
Ν	0.79220399	3.38166396	0.97549600
Н	0.68139199	2.03307196	-0.70535100
Н	-2.03616901	2.48625896	-0.38839200
Ν	-1.30993801	3.72529996	1.23072200
С	-2.43905501	4.40038696	1.89913900
Н	-3.18562001	3.64713596	2.16560900
Н	-2.88750701	5.09754196	1.18835100
С	-1.81024101	5.09133496	3.13833800
С	-2.20378401	4.31759696	4.40165200
Н	-1.82051001	3.29218196	4.35349700
Н	-1.76277101	4.78150496	5.28570700
В	-0.13820701	5.07787496	2.94963600
Н	-3.28942501	4.26771296	4.54512400
Н	-2.21435101	6.10308196	3.21707500
С	2.20002099	3.40210996	1.26619300
С	3.00093099	4.41266296	0.74449400
С	2.68667899	2.43387396	2.15524400
С	4.34465399	4.42812996	1.13003000

С	4.03136699	2.48106196	2.49233700
С	4.87489499	3.47587896	1.98944100
Н	4.98164199	5.22111196	0.75031500
Н	4.42859999	1.74373196	3.18342400
С	0.69567099	6.42954496	2.56314300
С	1.95601299	6.68099296	3.15250100
С	0.25908299	7.35345196	1.58830600
С	2.69740399	7.81280496	2.80345600
С	1.01190599	8.48465396	1.27025600
С	2.23726399	8.73993796	1.87493600
Н	3.66362499	7.97479496	3.27474100
Н	0.63820799	9.17594596	0.51891100
С	1.75399299	1.42254896	2.76624200
Н	1.00192799	1.92942496	3.37881400
Н	1.22283999	0.84947796	2.00232200
Н	2.30422899	0.72718896	3.39926500
С	2.47991799	5.48101096	-0.17759000
Н	3.01681099	5.44941396	-1.12909100
Н	1.41388199	5.37389096	-0.37580900
Н	2.63624999	6.46404896	0.27378000
C	6 32868099	3 50323696	2 38265200
н	6 44090599	3 40474796	3 46436500
н	6 86894099	2 67456696	1 91723000
н	6 80/21600	<i>1 1 3</i> 361 <i>1</i> 96	2.07166000
II C	2 57215800	5 72910406	4 16118200
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- NHC-borane *cis*-4a (M062X/6-311g(d,p))//pcm (ether)

Sum of electronic and zero-point Energies= -1066.906909 (Hartree/Particle) Sum of electronic and thermal Energies= -1066.880374 (Hartree/Particle) Sum of electronic and thermal Enthalpies= -1066.879430 (Hartree/Particle) Sum of electronic and thermal Free Energies= -1066.961136 (Hartree/Particle)

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 $\Delta E$  trans-4a vs cis-4a =-2.989 Kcal.mol<sup>-1</sup>

NHC-borane *trans*-4d (M062X/6-311g(d,p)) //pcm (ether)
Sum of electronic and zero-point Energies= -1102.844485 (Hartree/Particle)
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ч	-10 11065485 - 2 04027509	1 //087200
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н ц	-7.50570405 -1.00755598 0.02572185 0.62721100	1 61755700
П	-9.035/2185 -0.05/31198	1.01/33/00

- NHC-borane *cis*-4d (M062X/6-311g(d,p)) //pcm (ether)

Sum of electronic and zero-point Energies= -1102.841889 (Hartree/Particle)

Sum of electronic and thermal Energies= -1102.815460 (Hartree/Particle)

Sum of electronic and thermal Enthalpies= -1102.814515 (Hartree/Particle)

# Sum of electronic and thermal Free Energies= -1102.898764 (Hartree/Particle)

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Н	6.04744577	-3.54951500	-2.30884000
Н	6.36920377	-2.24235200	-1.13756500

 $\Delta E$  trans-4d vs cis-4d = -1,629 Kcal.mol<sup>-1</sup>

### b. EPR Studies

EPR assays were carried out on a Bruker EMX spectrometer operating at X-band with 100 kHz modulation frequency and equipped with an NMR gaussmeter for magnetic field calibration. The following conditions were used: non-saturating microwave power, 15 mW; modulation amplitude, from 0.1 G to 1 G; receiver gain,  $5x10^5$ ; 1-4 scans. The media were prepared under argon in the appropriate deoxygenated solvent and then transferred into sealed NMR tubes. The samples were heated directly into the EPR cavity with the aid of a Bruker Eurotherm B-VT 2000 variable temperature unit using a N<sub>2</sub> stream cooling system. For all the paramagnetic species detected, the hyperfine coupling constant values were determined after standard simulations of the experimental EPR signals using the WinSim software.

- Origin of the diastereoselectivity under thermal equilibrium by EPR study and possible explanation of by-product **3a**.



#### **Procedure:**

The spin trapping experiments were performed as follows. A 0.17 mol.L<sup>-1</sup> **4a** solution was prepared under argon in deoxygenated toluene in the presence of the spin trap  $\alpha$ -phenyl-N-terbutylnitrone (PBN, 0.15 mol.L<sup>-1</sup>). The medium was transferred into the EPR cavity before

being heated to 323K. The signal observed is given below and its simulation (superimposed red dotted lines) revealed the presence of two radical spin adducts. The major species (~ 60%,  $a_N = 14.6$  G and  $a_H = 8.5$  G) was assigned to the spin adduct formed after addition of the mesityl radical on PBN (Mes/PBN spin adduct).

- Since nitroxides can be synthesized via Grignard reagents, the Mes/PBN nitroxide was also prepared by nucleophilic addition of MesMgBr to PBN: the same six-line spectrum was observed (100 %,  $a_N = 14.6$  G and  $a_H = 8.5$  G). (see for examples: (a) K. Hideg and L. Lex, *Perkin Trans 1*, 1986, **8**, 1431; (b) C. Sar, T. Kalai, J. Jeho K. Hideg, *Arkivoc*, 2012, 47).

- The second species (~ 40%,  $a_N = 14.5$  G and  $a_H = 3.2$  G) correspond to the adduct of an unidentified carbon-centered radical on PBN. It should be mentioned that this latter species was also observed before heating, or when the

same experiment was performed with **5a** Mes instead of **4a**. On the other hand, the Mes/PBN spin adduct was never formed before heating the medium or starting from **5a**.



## 7. Mechanism studies

a. Ionic pathway

Borane **5a** was submitted to MgBr<sub>2</sub> (1.0 equiv) in benzene-d<sub>6</sub>, the intermediate borenium was never observed by <sup>11</sup>B NMR, even in the presence of triethylphosphine oxide as borenium trap, and only the MgBr<sub>2</sub>•OP(Et)<sub>3</sub> complex (<sup>31</sup>P NMR;  $\delta = 64.4$  ppm) was observed. So, if the borenium was formed during our reaction, we should be able to see the phosphine oxide complex, which is not the case.

#### **Procedures:**



 $MgBr_2$  (0.07 mmol, 1 equiv) and triethylphosphine oxide (0.07 mmol, 1 equiv) were dissolved in dry benzene-d<sub>6</sub> (0.4 mL) in a 10 mL Schlenk flask in glove box. The Schlenk was sealed and the reaction was stirred at 50 °C for 5 h.



MesNHC-B(H)Cl **5a** (0.05 mmol, 1 equiv) and MgBr<sub>2</sub> (0.05 mmol, 1 equiv) were dissolved in dry benzene-d<sub>6</sub> (0.33 mL) in a 10 mL Schlenk flask in glove box. The reaction was heated at 50 °C then triethylphosphine oxide (0.05 mmol, 1 equiv) was added and the mixture was stirred at 50 °C for 5 h.

# <sup>11</sup>B NMR





#### b. Radical pathway

#### - Reaction of **5a** with TEMPO:

Attempts to stop the reaction or trap the boryl radical with TEMPO failed. The reaction of **5a** with mesityl Grignard reagent was conducted with 1 to 5 equivalents of TEMPO, sole the rate of the reaction was affected (62% yield after 5 h instead of 93%) and no side-product was ever observed. It is in fact possible that the TEMPO-boryl adduct is unstable and the reaction is reversible and in fine goes unnoticed in the reaction.

- Synthesis of 6a:



### **Procedure:**

The NHC-borane **3a** (1.0 equiv) and the phenyldisulfide (0.75 equiv) were introduced in a Schlenk flask. Then deoxygenated benzene was introduced, the Schlenk was sealed and the solution was stirred at 50 °C for 72 hours under an aluminum foil. After evaporation of the solvent, the compound was purified by flash chromatography using pentane:DCM 1:1 then 100% DCM as eluent to afford **6a** in 67% yield as two diastereomers (88:12 *dr*).

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.05 (d, <sup>3</sup>*J* = 1.8 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.89 (s, 1H), 6.85-6.77 (m, 4H), 6.63 (s, 1H), 4.31 (dd, <sup>2</sup>*J* = 11.1 Hz, <sup>3</sup>*J* = 7.4 Hz, 1H), 3.60 (dd, <sup>2</sup>*J* = 11.1 Hz, <sup>3</sup>*J* = 3.3 Hz, 1H), 2.27 (s, 3H), 2.04 (s, 3H), 1.91 - 1.80 (m, 4H), 1.18 (d, <sup>3</sup>*J* = 7.3 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 142.3, 139.5, 135.4, 134.7, 133.7, 129.5, 129.3, 128.9, 127.6, 124.5, 121.9, 117.3, 58.1, 30.0 (HSQC), 21.1, 21.1, 17.9, 17.7, C<sub>9</sub> is not observed.

<sup>11</sup>**B** NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -12.8 (d, <sup>1</sup>*J*<sub>BH</sub> = 103.8 Hz).

HRMS (ES, [M+Na]<sup>+</sup>) calcd for [C<sub>21</sub>H<sub>25</sub>N<sub>2</sub>SBNa]<sup>+</sup>: 371.1728; found: 371.1728



- Spin trapping experiment with **3a** with phenyldisulfide and α-phenyl-*N*-tertiary-butyl nitrone



## **Procedure:**

In a glovebox, NHC-borane **3a** (0.17 mmol, 1.0 equiv), PhSSPh (0.12 mmol, 0.75 equiv) and N-*tert*-Butyl- $\alpha$ -phenylnitrone (0.15 M) were dissolved in dry benzene (3 mL) in a 10 mL Schlenk flask.

- Indirect trap of IIa from 5a:



### **Procedure:**

NHC-borane **5a** (0.07 mmol, 1 equiv) and PhSSPh (0.03 mmol, 0.4 equiv) were dissolved in dry benzene (0.44 mL) in a 10 mL Schlenk flask under argon. Then, 0.6 equivalent of Grignard reagent MesMgBr (0.04 mmol, 0.6 equiv) was added via a syringe at room temperature. The Schlenk was sealed and the reaction was stirred at 50 °C for 6 h. The crude product was filtered through a short plug of silica gel using dichloromethane (10 mL) as eluent to give **4a** and **6a** in 58:42 ratio.



## <sup>11</sup>**B** NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



- Stability of final product **4a** under reductive conditions and possible explanation for bisfunctionalized adducts:

The stability of the final product **4a** was tested in presence of an excess of MesMgBr to see if it was able to abstract the last hydride.



#### **Procedure:**

A medium containing NHC-borane **4a** (1.0 equiv) and MesMgBr (0.3 equiv) was prepared in toluene (0.2 M) and submitted to EPR analysis. No signal was observed before heating. Raising the temperature to 323 K yielded an intense and wide signal.

# 8. Catalysis

### a. Imine reduction with silane catalyzed by chiral NHC-borenium

## **Procedure:**

In a glovebox, a solution of trityl borate (0.017 mmol, 1 equiv) in  $CH_2Cl_2$  (0.15 mL) was added to a solution of NHC-borane **4j** (0.017 mmol, 1 equiv) in  $CH_2Cl_2$  (0.15 mL) at room temperature to afford the corresponding NHC-borenium. To a solution of NHC-borenium (20 mol%, 0.017 mmol) in  $CH_2Cl_2$  (0.7 mL) was added phenylsilane (0.085 mmol, 1 equiv). After 10 minutes stirring at room temperature the imine (0.085 mmol, 1 equiv) was added in one portion. The reaction was monitored by TLC using pentane:DCM 7:3 as eluent. After 20 hours, 2 mL of a 1:1 MeOH/ KOH (2.0 M) was added dropwise and the solution was left to stir for 1 h. The solution was then diluted with  $H_2O$  (5 mL) then extracted with  $CH_2Cl_2$  (3 x 10 ml). The organic layer was concentrated *in vacuo* and purified by silica gel column chromatography using pentane:DCM 7:3 as eluent to afford the pure amine.



#### b. Borenium IVa-Silane complex studies

#### General procedure:

In a glovebox, NHC-borane **4a** (0.03 mmol, 1.0 equiv) and trityl tetrakis (pentafluorophenyl)borate (0.03 mmol, 1.0 equiv) were mixed in  $CD_2Cl_2$  (0.2 mL). The mixture was stirred at rt for 1 h, then silane (0.015 mmol, 0.5 equiv) was added, then the reaction was followed by <sup>1</sup>H and <sup>11</sup>B NMR.

- with PhSiH<sub>3</sub>:

The expected complex of phenylsilane and borenium species **IVa** was not detected and only the characteristic signals of the borenium precursor **IVa**, were confirmed by <sup>1</sup>H and <sup>11</sup>B NMR.



# <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



# <sup>1</sup>H NMR (400 MHz, $CD_2Cl_2$ )



# <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



- with Et<sub>3</sub>SiH:

After 2 h at rt, a second species appeared, corresponding to a hydrido complex where the hydride atom is partitioned between the silicon and the boron atom. This was revealed by the <sup>1</sup>H NMR chemical shifts of the characteristic diastereotopic CH<sub>2</sub> protons of the boracyclic moiety values which were found as intermediary values between borane **4a** and borenium **IVa** species. The same tendency was observed in <sup>11</sup>B NMR, where the borenium **IVa** and the complex borenium-silane co-exist ( $\delta = 71$  and 44 ppm respectively). Finally, only one diastereomer of the hydrido complex was detected by <sup>1</sup>H NMR after 20 h, confirming the results previously obtained with borenium **4a** and LiBH<sub>4</sub>.







# 9. Cristal structures



Compounds	4a	4d	4b
Identification code	ca493d	ca582d	ca609d
Empirical formula	$C_{24}H_{31}BN_2$	$C_{23}H_{29}BN_2$	$C_{23}H_{29}BN_2O$
Formula weight	358.32	344.29	360.29
Crystal system	orthorombic	orthorombic	orthorombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	7.55860 (10)	8.56120 (10)	7.76550(10)
b (Å)	9.20850 (10)	15.4461(2)	12.17080(10)
<i>c</i> (Å)	30.8403 (5)	15.9652(3)	22.3907(2)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å) <sup>3</sup>	2146.59 (5)	2111.19(5)	2116.20(4)
Z	4	4	4
T (K)	293	293	293
Density	1.109	1.083	1.131
F (000)	776.0	744.0	776.0
Crystal size	0.34x0.24x0.22	0.32x0.28x0.2	0.4x0.18x0.18
Theta range for data collection	10.024 to 141.852	7.964 to 142.106	7.898 to 148.88
Index reneas	$-9 \le h \le 9, -11 \le k \le 9, -23 \le$	$-10 \le h \le 9, -18 \le k \le 14, -$	$-9 \le h \le 9, -14 \le k \le 14, -27 \le l \le$
Index ranges	$1 \le 37$	$17 \le l \le 19$	27
Reflections collected	7385	7375	24338
Independent reflections	$4047 [R_{int} = 0.0112, R_{sigma} = 0.0157]$	$3980 [R_{int} = 0.0128, R_{sigma} = 0.0170]$	4258 [ $R_{int} = 0.0276$ , $R_{sigma} = 0.0140$ ]
Completeness to theta = $28.7^{\circ}$	1.68/0.97	1.70/0.97	1.77/0.99
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Data / restraints / parameters	4047/0/251	3980/0/241	4258/0/251
Goodness-of-fit on F2	1.146	1.083	1.040
Final R indexes [I>=2σ (I)]	$R_1 = 0.0420, wR_2 = 0.1196$	$R_1 = 0.0455, wR_2 = 0.1090$	$R_1 = 0.0364, wR_2 = 0.1027$
Final R indexes (all data)	$R_1 = 0.0429, wR_2 = 0.1205$	$R_1 = 0.0465, wR_2 = 0.1107$	$R_1 = 0.0371, wR_2 = 0.1040$
Largest diff. peak and hole	0.13/-0.15	0.18/-0.33	0.15/-0.21
CCDC	1856403	1857909	1857908