Supplementary Information for

Anthranilamide-substituted borane [H–B(aam)]: Its stability and application to iridium-catalyzed stereoselective hydroboration of alkynes

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Abbreviations

Å: Angstrom
aam: Anthranilamidato
Ac: Acetyl
COD: 1,5-Cyclooctadiene
CPME: Cyclopentyl methyl ether
DMF: N,N-Dimethylformamide
DMSO: Dimethyl sulfoxide
equiv: Equivalent
mp: Melting point
pin: Pinacolato
THF: Tetrahydrofuran
TIPS: Triisopropylsilyl
TMS: Trimethylsilyl
Ts: p-Toluenesulfonyl
1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (1H, 500 MHz; 13C, 125 MHz; 11B, 160 MHz; 31P, 202 MHz) spectrometer using a residual proton in DMSO-d6 (1H, δ = 2.50), DMSO-d6 (13C, δ = 39.52), residual chloroform (1H, δ = 7.26) or CDCl3 (13C, δ = 77.0) as an internal standard, and boron trifluoride diethyl etherate (11B, δ = 0.00) or 85% H3PO4 (31P, δ = 0.00) as an external standard. 1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GL Science), 30 m x 0.25 mm, film 0.25 µm; Flow rate: 1.89 mL/min; Injector temperature: 250 °C; Oven temperature: 100 °C to 250 ºC at 20 °C/min, hold at 250 °C for 10 min; FID temperature: 250 °C). High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Florisil or Merk Kieselgel 60. All microwave reactions (Biotage, Initiator+) were conducted in a sealed tube, and the reaction temperature was maintained by an external infrared sensor. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieves 3Å. 6-Ethynyl-1,1,4,4,7-pentamethyl-1,2,3,4-tetrahydronaphthalene (2n) was prepared according to a literature procedure.1

2. Synthesis of H–B(aam) (1)

A 200 mL two necked flask, equipped with a septum, was charged with anthranilamide (2.72 g, 20 mmol) and THF (60 mL). To the solution was added BH3•SMe2 (1.67 g, 22 mmol) dropwise via syringe, and the resulting solution was stirred at 0 ºC for 12 h. After the volatiles were removed in vacuo, the residue was purified by Florisil column chromatography (THF as an eluent) to afford 1 (2.89 g, 99% yield).

2,3-Dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (H–B(aam), 1)

Isolated in 99% yield as a white solid

S3
$^1$H NMR (400 MHz, Chloroform-$d$) δ 6.69 (brs, 1H), 7.03 (dd, $J$ = 8.1, 1.1, 0.5 Hz, 1H), 7.17 (dd, $J$ = 8.1, 7.2, 1.1 Hz, 1H), 7.30 (brs, 1H), 7.53 (dd, $J$ = 8.1, 7.2, 1.6 Hz, 1H), 8.22 (dd, $J$ = 8.0, 1.5, 0.7 Hz, 1H).

The $H$–$B$ peak could not be observed in $^1$H NMR spectrum, probably owing to quadrupolar coupling.

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 165.45, 145.08, 133.27, 127.94, 121.09, 119.44, 117.84.

$^{11}$B NMR (160 MHz, Chloroform-$d$) δ 27.0 (d, $^1$$J$$_{B-H}$ = 151.3 Hz).

HRMS Calcd for C$_7$H$_8$BN$_2$O: [M+H]$^+$, 147.0724. Found: m/z 147.0720.
3. Optimization of reaction conditions

Table S1. Effect of Ir catalyst and temperature$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>Ir catalyst</th>
<th>temp. ($^\circ$C)</th>
<th>NMR yield (%)$^b$</th>
<th>3a:3’a$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^d$</td>
<td>[IrCl(COD)]$_2$</td>
<td>rt</td>
<td>46</td>
<td>94:6</td>
</tr>
<tr>
<td>2</td>
<td>[IrCl(COD)]$_2$</td>
<td>rt</td>
<td>77</td>
<td>89:11</td>
</tr>
<tr>
<td>3$^e$</td>
<td>[IrCl(COD)]$_2$</td>
<td>50</td>
<td>96</td>
<td>89:11</td>
</tr>
<tr>
<td>4</td>
<td>[IrOMe(COD)]$_2$</td>
<td>50</td>
<td>84</td>
<td>93:7</td>
</tr>
</tbody>
</table>

$^a$ Conditions: 1 (0.15 mmol), 2a (0.225 mmol), Ir catalyst (3.75 µmol), DPEPhos (9.00 µmol), THF (0.5 mL), 24 h. $^b$ Determined by $^1$H NMR using anisole as an internal standard. $^c$ Determined by $^1$H NMR spectra of the crude reaction mixture. $^d$ Reaction time = 2 h.
Table S2. Effect of ligand<sup>a</sup>

<table>
<thead>
<tr>
<th>entry</th>
<th>ligand</th>
<th>NMR yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ratio 3a:3’a&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DPEPhos</td>
<td>96</td>
<td>89:11</td>
</tr>
<tr>
<td>2</td>
<td>ligand A</td>
<td>73</td>
<td>89:11</td>
</tr>
<tr>
<td>3</td>
<td>PPh&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>77</td>
<td>95:5</td>
</tr>
<tr>
<td>4</td>
<td>DPPE</td>
<td>37</td>
<td>82:18</td>
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<tr>
<td>5</td>
<td>DPPP</td>
<td>9</td>
<td>81:19</td>
</tr>
<tr>
<td>6</td>
<td>DPPB</td>
<td>56</td>
<td>82:18</td>
</tr>
<tr>
<td>7</td>
<td>DPPF</td>
<td>88</td>
<td>89:11</td>
</tr>
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<td>8</td>
<td>BINAP</td>
<td>64</td>
<td>80:20</td>
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<tr>
<td>9</td>
<td>XantPhos</td>
<td>28</td>
<td>87:13</td>
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<td>10</td>
<td>–</td>
<td>59</td>
<td>80:20</td>
</tr>
<tr>
<td>11&lt;sup&gt;e&lt;/sup&gt;</td>
<td>–</td>
<td>0</td>
<td>–</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conditions: 1 (0.15 mmol), 2a (0.225 mmol), [IrCl(COD)]<sub>2</sub> (3.75 µmol), ligand (9.00 µmol), THF (0.5 mL), 50 °C, 24 h.  
<sup>b</sup> Determined by <sup>1</sup>H NMR using anisole as an internal standard.  
<sup>c</sup> Determined by <sup>1</sup>H NMR spectra of the crude reaction mixture.  
<sup>d</sup> PPh<sub>3</sub> (12 mol %, 0.018 mmol).  
<sup>e</sup> Without [IrCl(COD)]<sub>2</sub>. 

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![Chemical structures](image-url)
Table S3. Effect of solvent and molar ratio of substrates$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>NMR yield (%)$^b$</th>
<th>$3a$ : $3'a$ $^c$</th>
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<tr>
<td>1</td>
<td>THF</td>
<td>94</td>
<td>94:6</td>
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<td>2</td>
<td>CPME</td>
<td>94</td>
<td>94:6</td>
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<tr>
<td>3</td>
<td>toluene</td>
<td>83</td>
<td>90:10</td>
</tr>
<tr>
<td>4$^d$</td>
<td>CH$_2$Cl$_2$</td>
<td>84</td>
<td>91:9</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>78</td>
<td>93:7</td>
</tr>
<tr>
<td>6</td>
<td>MeCN</td>
<td>93</td>
<td>93:7</td>
</tr>
<tr>
<td>7$^e$</td>
<td>THF</td>
<td>93</td>
<td>94:6</td>
</tr>
</tbody>
</table>

$^a$ Conditions: 1 (0.225 mmol), 2a (0.15 mmol), [IrCl(COD)]$_2$ (3.75 µmol), DPEPhos (9.00 µmol), solvent (0.5 mL), 50 °C, 24 h. $^b$ Determined by $^1$H NMR using anisole as an internal standard. $^c$ Determined by $^1$H NMR spectra of the crude reaction mixture. $^d$ Reaction temp. = 40 °C. $^e$ 1 (1.2 equiv, 0.18 mmol).

4. **Ir-catalyzed hydroboration of alkynes: a general procedure**

A Schlenk tube equipped with a magnetic stirring bar was charged with [IrCl(COD)]$_2$ (2.52 mg, 3.75 µmol), DPEPhos (4.85 mg, 9.00 µmol), and THF (0.5 mL). After the mixture was stirred at room temperature for 15 minutes, an alkyne (0.15 mmol) and 1 (26.3 mg, 0.18 mmol) were added. Then the resulting mixture was stirred at 50 °C for 24 h. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over MgSO$_4$, and evaporated. The product was isolated by Florisil column chromatography (hexane/ethyl acetate as an eluent).

**(E)-2-Styryl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3a)**

\[ \text{Ph} \equiv \text{B(aam)} \]

Isolated in 50% yield as a white solid: mp 130-133 °C

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 6.45 (d, $J = 18.7$ Hz, 1H), 7.02 – 7.07 (m, 1H), 7.26 (d, $J = 8.1$ Hz, 1H), 7.30 – 7.36 (m, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.49 – 7.55 (m, 3H), 7.61 (d, $J = 18.7$ Hz, 1H), 7.96
(dd, $J = 7.9, 1.5$ Hz, 1H), 9.18 (s, 1H), 9.45 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 165.97, 145.84, 145.42, 137.46, 133.32, 128.90, 128.84, 127.97, 126.65, 120.59, 118.86, 117.84.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 29.5.

HRMS Calcd for C$_{15}$H$_{14}$BN$_2$O: [M+H]$^+$, 249.1194. Found: $m/z$ 249.1192

$(E)$-2-(4-Butylstyryl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3b)

\[
\begin{array}{c}
\text{B(aam)} \\
\text{Bu} \\
\end{array}
\]

Isolated in 94% yield as a white solid: mp 171-175 °C

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 0.90 (t, $J = 7.3$ Hz, 3H), 1.26 – 1.37 (m, 2H), 1.51 – 1.60 (m, 2H), 2.59 (t, $J = 7.7$ Hz, 2H), 6.40 (d, $J = 18.7$ Hz, 1H), 7.06 (ddd, $J = 8.1$, 7.1, 1.1 Hz, 1H), 7.21 – 7.29 (m, 3H), 7.40 – 7.46 (m, 2H), 7.53 (ddd, $J = 8.5$, 7.1, 1.7 Hz, 1H), 7.60 (d, $J = 18.7$ Hz, 1H), 7.97 (dd, $J =$ 8.0, 1.6 Hz, 1H), 9.16 (s, 1H), 9.43 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 165.95, 145.45, 143.30, 133.28, 128.81, 127.95, 126.62, 120.51, 118.82, 117.80, 34.61, 32.98, 21.74, 13.79.

HRMS Calcd for C$_{19}$H$_{22}$BN$_2$O: [M+H]$^+$, 305.1820. Found: $m/z$ 305.1820

$(E)$-2-(4-Methoxystyryl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3c)

\[
\begin{array}{c}
\text{B(aam)} \\
\text{MeO} \\
\end{array}
\]

Isolated in 88% yield (linear:branch = 96:4) as a white solid: mp 202-205 °C

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 3.79 (s, 3H), 6.29 (d, $J = 18.6$ Hz, 1H), 6.99 (d, $J = 8.7$ Hz, 2H), 7.03 – 7.08 (m, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.7$ Hz, 2H), 7.50 – 7.55 (m, 1H), 7.57 (d, $J = 18.6$ Hz, 1H), 7.96 (dd, $J = 7.9$, 1.2 Hz, 1H), 9.12 (s, 1H), 9.40 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 165.98, 159.87, 145.50, 133.28, 130.21, 128.10, 127.96, 120.44, 118.78, 117.78, 114.31, 55.22.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 31.2

HRMS Calcd for C$_{16}$H$_{16}$BN$_2$O$_2$: [M+H]$^+$, 279.1299. Found: $m/z$ 279.1298

$(E)$-2-(2-(6-Methoxynaphthalen-2-yl)vinyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3d)

\[
\begin{array}{c}
\text{MeO} \\
\end{array}
\]
Isolated in 82% yield as a white solid: mp 230-233 °C

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 3.89 (s, 3H), 6.53 (d, \(J = 18.6\) Hz, 1H), 7.05 – 7.09 (m, 1H), 7.19 (dd, \(J = 8.9, 2.5\) Hz, 1H), 7.29 (d, \(J = 8.1\) Hz, 1H), 7.35 (d, \(J = 2.5\) Hz, 1H), 7.55 (ddd, \(J = 8.6, 7.2, 1.6\) Hz, 1H), 7.71 (dd, \(J = 8.6, 1.6\) Hz, 1H), 7.76 (d, \(J = 18.6\) Hz, 1H), 7.83 – 7.92 (m, 3H), 7.98 (dd, \(J = 7.9, 1.4\) Hz, 1H), 9.22 (s, 1H), 9.49 (s, 1H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 166.02, 157.84, 145.98, 145.49, 134.62, 133.31, 132.86, 129.89, 128.45, 128.00, 127.37, 127.13, 123.71, 120.54, 119.03, 118.87, 117.85, 106.12, 55.27.

\(^{11}\)B NMR (160 MHz, Chloroform-\(d\)) \(\delta\) 31.3.

HRMS Calcd for C\(_{20}\)H\(_{18}\)BN\(_2\)O\(_2\): [M+H]\(^+\), 329.1456. Found: m/z 329.1456

\((E)-2-(4-Acetylstyryl)-2,3-dihydrobenzo[\(d\)][1,3,2]diazaborinin-4(1H)-one (3e)\)

Isolated in 90% yield as a white solid: mp 232-235 °C

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 2.60 (s, 3H), 6.63 (d, \(J = 18.7\) Hz, 1H), 7.09 (t, \(J = 8.0\) Hz, 1H), 7.28 (d, \(J = 8.0\) Hz, 1H), 7.51 – 7.59 (m, 1H), 7.66 (d, \(J = 8.4\) Hz, 2H), 7.69 (d, \(J = 18.7\) Hz, 1H), 7.98 (d, \(J = 7.9\) Hz, 1H), 8.01 (d, \(J = 8.4\) Hz, 2H), 9.27 (s, 1H), 9.52 (s, 1H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 197.33, 165.95, 145.32, 144.56, 141.71, 136.56, 133.37, 128.91, 128.00, 126.78, 120.75, 118.95, 117.91, 26.77.

\(^{11}\)B NMR (160 MHz, Chloroform-\(d\)) \(\delta\) 31.2.

HRMS Calcd for C\(_{17}\)H\(_{16}\)BN\(_2\)O\(_2\): [M+H]\(^+\), 291.1299. Found: m/z 291.1298

\((E)-2-(4-Bromostyryl)-2,3-dihydrobenzo[\(d\)][1,3,2]diazaborinin-4(1H)-one (3f)\)

Isolated in 92% yield (linear:branch = 90:10) as a white solid: mp 240-244 °C

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 5.93 (d, \(J = 1.9\) Hz, 1H, minor), 6.02 (d, \(J = 2.0\) Hz, 1H, minor), 6.48 (d, \(J = 18.7\) Hz, 1H), 7.05 – 7.10 (m, 1H), 7.27 (d, \(J = 7.8\) Hz, 1H), 7.30 – 7.35 (m, 3H, minor), 7.47 (d, \(J = 8.5\) Hz, 2H), 7.51 – 7.58 (m, 1H), 7.60 – 7.64 (m, 3H), 7.97 (d, \(J = 9.3\) Hz, 1H), 8.88 (s, 1H, minor), 9.22 (s, 1H), 9.29 (s, 1H, minor), 9.48 (s, 1H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 165.95, 145.36, 144.45, 136.68, 133.36, 131.88, 128.60, 127.99, 121.90, 120.68, 118.89, 117.87.

\(^{11}\)B NMR (160 MHz, Chloroform-\(d\)) \(\delta\) 31.0.

HRMS Calcd for C\(_{15}\)H\(_{14}\)BN\(_2\)OBr: [M+H]\(^+\), 327.0299. Found: m/z 327.0300

\((E)-2-(Oct-1-en-1-yl)-2,3-dihydrobenzo[\(d\)][1,3,2]diazaborinin-4(1H)-one (3g)\)
Isolated in 68% yield as a white solid: mp 142-145 °C
$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 0.83 – 0.90 (m, 3H), 1.21 – 1.35 (m, 6H), 1.41 (p, $J$ = 7.1 Hz, 2H), 2.17 (qd, $J$ = 7.2, 1.5 Hz, 2H), 5.67 (dt, $J$ = 18.1, 1.5 Hz, 1H), 6.78 (dt, $J$ = 18.1, 6.4 Hz, 1H), 6.98 – 7.08 (m, 1H), 7.22 (dd, $J$ = 8.2, 1.0 Hz, 1H), 7.50 (ddd, $J$ = 8.4, 7.1, 1.6 Hz, 1H), 7.93 (dd, $J$ = 7.9, 1.7 Hz, 1H), 8.93 (s, 1H), 9.26 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 166.02, 150.52, 145.49, 133.20, 127.91, 120.31, 118.67, 117.74, 39.69, 35.48, 31.20, 28.30, 28.04, 22.11, 14.01.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 29.7.

HRMS Calcd for C$_{16}$H$_{22}$BN$_2$O: [M+H]$^+$, 257.1820. Found: m/z 257.1819

(E)-2-(5-Chloropent-1-en-1-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3h)

Isolated in 92% yield as a white solid: mp 241-245 °C
$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 1.85 (p, $J$ = 6.7 Hz, 2H), 2.29 (q, $J$ = 7.1, 6.4 Hz, 2H), 3.67 (t, $J$ = 6.6 Hz, 2H), 5.70 (d, $J$ = 18.1 Hz, 1H), 6.75 (dt, $J$ = 18.1, 6.4 Hz, 1H), 7.02 (t, $J$ = 7.5 Hz, 1H), 7.20 (d, $J$ = 7.8 Hz, 1H), 7.46-7.50 (m, 1H), 7.92 (dd, $J$ = 7.9, 1.4 Hz, 1H), 8.95 (s, 1H), 9.28 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 165.98, 148.58, 145.42, 133.22, 127.92, 120.40, 118.70, 117.72, 44.73, 32.41, 31.02.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 29.2.

HRMS Calcd for C$_{16}$H$_{22}$BN$_2$OCl: [M+H]$^+$, 249.0960. Found: m/z 249.0959

(E)-5-(4-Oxo-3,4-dihydrobenzo[d][1,3,2]diazaborinin-2(1H)-yl)pent-4-enenitrile (3i)

Isolated in 84% yield (linear:branch = 93:7) as a white solid: mp 135-138 °C
$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 1.69 (q, $J$ = 7.3 Hz, 2H), 2.26 (q, $J$ = 7.0, 6.4 Hz, 2H), 2.52 (t, $J$ = 7.1 Hz, 2H), 5.71 (d, $J$ = 18.1 Hz, 1H), 6.67-6.74 (m, 1H), 7.00-7.04 (m, 1H), 7.20 (d, $J$ = 7.8 Hz, 1H), 7.47-7.51 (m, 1H), 7.92 (dd, $J$ = 7.9, 1.4 Hz, 1H), 8.96 (s, 1H), 9.27 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 165.99, 148.18, 145.42, 133.25, 127.93, 120.53, 120.44, 118.71, 117.74, 34.07, 23.87, 15.66.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 28.8, 20.6.

HRMS Calcd for C$_{15}$H$_{18}$BN$_3$O: [M+H]$^+$, 240.1303. Found: m/z 240.1302

(E)-4-(4-Oxo-3,4-dihydrobenzo[d][1,3,2]diazaborinin-2(1H)-yl)but-3-en-1-yl methylbenzenesulfonate (3j)
Isolated in 72% yield as a colorless oil

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 2.34 (s, 3H), 2.43-2.47 (m, 2H), 4.09 (t, $J = 6.2$ Hz, 2H), 5.69 (d, $J = 18.2$ Hz, 1H), 6.59 (dt, $J = 18.2, 6.4$ Hz, 1H), 7.03 (ddd, $J = 8.1, 7.1, 1.1$ Hz, 1H), 7.22 (dd, $J = 8.2, 0.9$ Hz, 1H), 7.42 (d, $J = 8.2$ Hz, 2H), 7.50 (ddd, $J = 8.5, 7.1, 1.7$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.93 (d, $J = 7.9$ Hz, 1H), 8.95 (s, 1H), 9.26 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 165.96, 145.37, 144.94, 144.40, 133.26, 132.31, 130.15, 127.66, 125.49, 120.50, 118.73, 117.78, 69.72, 34.72, 21.07.

$^1$B NMR (160 MHz, Chloroform-d) $\delta$ 29.1.

HRMS Calcd for C$_{18}$H$_{20}$BN$_2$O$_4$: [M+H]$^+$, 371.1231. Found: m/z 371.1234

(E)-2-(4-((Triisopropylsilyl)oxy)but-1-en-1-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3k)

Isolated in 65% yield as a white solid: mp 60-64 °C

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 0.89-1.08 (m, 21H), 2.39 (q, $J = 6.4$ Hz, 2H), 3.75 (t, $J = 6.8$ Hz, 2H), 5.72 (d, $J = 18.1$ Hz, 1H), 6.74 (dt, $J = 18.1, 6.5$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 7.21 (d, $J = 8.1$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 1H), 8.94 (s, 1H), 9.26 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 165.99, 146.88, 145.45, 133.21, 127.91, 120.43, 118.70, 117.72, 62.24, 17.92, 11.44.

$^1$B NMR (160 MHz, Chloroform-d) $\delta$ 29.3.

HRMS Calcd for C$_{20}$H$_{33}$BN$_2$O$_2$: [M+H]$^+$, 373.2477. Found: m/z 373.2480

(E)-2-(3,3-Dimethylbut-1-en-1-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3l)

Isolated in 88% yield as a white solid: mp 150-153 °C

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 1.03 (s, 9H), 5.58 (d, $J = 18.5$ Hz, 1H), 6.81 (d, $J = 18.5$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 8.2$ Hz, 1H), 7.48 (t, $J = 7.3$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 8.93 (s, 1H), 9.22 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 165.95, 160.27, 145.50, 133.17, 127.89, 120.29, 118.64, 117.69, 34.70, 28.80.

$^1$B NMR (160 MHz, Chloroform-d) $\delta$ 29.7.

HRMS Calcd for C$_{13}$H$_{18}$BN$_2$: [M+H]$^+$, 229.1507. Found: m/z 229.1505

(E)-2-(2-(Trimethylsilyl)vinyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3m)
Isolated in 84% yield as a white solid: mp 150-154 °C

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 0.14 (s, 9H), 6.48 (d, $J = 21.9$ Hz, 1H), 6.94-7.05 (m, 3H), 7.13 (t, $J = 7.7$ Hz, 1H), 7.22 (s, 1H), 7.51 (t, $J = 7.7$ Hz, 1H), 8.20 (d, $J = 7.9$ Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 166.42, 153.88, 144.16, 133.73, 129.18, 121.70, 119.12, 117.41, -1.80.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 28.5.

HRMS Calcd for C$_{12}$H$_{18}$BN$_{2}$O$_{2}$Si: [M+H]$^+$, 245.1276. Found: m/z 245.1276

$(E)$-2-(2-(3,5,5,8,8-Pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)-1,4-dihydrobenzo[e][1,4,2]diazaborinin-3(2H)-one (3n)

Isolated in 84% yield as a white solid: mp 213-215 °C

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 1.29 (s, 6H), 1.32 (s, 6H), 1.69 (s, 4H), 2.40 (s, 3H), 6.30 (d, $J = 18.4$ Hz, 1H), 6.61 (s, 2H), 7.05 (d, $J = 8.0$ Hz, 1H), 7.10-7.17 (m, 2H), 7.46-7.56 (m, 3H), 8.23 (d, $J = 7.9$ Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 19.68, 31.90, 32.10, 34.20, 34.32, 35.19, 35.25, 117.54, 119.23, 121.79, 123.95, 128.80, 129.34, 133.44, 133.82, 133.93, 143.09, 144.10, 144.54, 146.38, 166.77.

$^{11}$B NMR (160 MHz, Chloroform-$d$) $\delta$ 28.4.

HRMS Calcd for C$_{24}$H$_{29}$BN$_{2}$NaO: [M+H]$^+$, 395.2265. Found: m/z 395.2267

5. Synthesis of oxidative adduct 4

A 50 mL two necked flask was charged with [IrCl(COD)]$_2$ (67.2 mg, 0.1 mmol) and THF (3 mL). To this mixture was added DPEPhos (107.7 mg, 0.2 mmol), and the resulting mixture was stirred at room temperature for 15 min. After the solvent and 1,5-cyclooctadiene were removed in vacuo, THF (2 mL) and 1 (29.2 mg, 0.2 mmol) were added, and the resulting mixture was stirred at room temperature for 2 h. After the solvent was removed in vacuo, the residue was purified by recrystallization to afford oxidative adduct 4 (124.1 mg, 68% yield).

(DPEPhos)Ir(H)(Cl)[B(aam)] (4)
Isolated in 68% yield as a white solid

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ -18.59 (t, $^2J_{H-P} = 16.0$ Hz, 1H), 6.38 (d, $J = 8.3$ Hz, 1H), 6.47 (s, 1H), 6.68 (s, 1H), 6.84 (t, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 7.5$ Hz, 3H), 7.20-7.23 (m, 2H), 7.35-7.45 (m, 14H), 7.61-7.66 (m, 8H), 7.92-7.98 (m, 1H).

$^{31}$P NMR (0 °C, 202 MHz, Chloroform-$d$) $\delta$ 23.06.

HRMS Calcd for C$_{43}$H$_{35}$BN$_2$O$_2$ClIrP$_2$Na: [M+Na]$^+$ 935.1477. Found: m/z 935.1472

We could not obtain $^{13}$C NMR spectrum of 4, because this complex was unstable in solution, which led to gradual decomposition during the measurement.

6. Cross-coupling of 3n

A reaction tube equipped with a magnetic stirring bar was charged with tripotassium phosphate (239.9 mg, 1.13 mmol), 3n (83.8 mg, 0.225 mmol), palladium(II) acetate (1.68 mg, 7.50 µmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (6.16 mg, 0.0150 mmol), 1,4-dioxane (1.9 mL), H$_2$O (375 µl) and methyl 4-iodobenzoate (39.3 mg, 0.150 mmol). After the mixture was stirred at 140 °C for 0.5 h under microwave irradiation, the mixture was diluted with ethyl acetate. The organic solution was washed with brine, dried over MgSO$_4$, and evaporated. The residue was purified by silica gel column chromatography (hexane/ethyl acetate as an eluent) to afford 6 (37.5 mg, 69% yield).

Methyl (E)-4-(2-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (6)

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 1.29 (s, 6H), 1.34 (s, 6H), 1.70 (s, 4H), 2.40 (s, 3H), 3.93 (s, 3H), 6.97 (d, $J = 16.1$ Hz, 1H), 7.12 (s, 1H), 7.41 (d, $J = 16.1$ Hz, 1H), 7.53 (s, 1H), 7.57 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H).

7. Action of H–B(pin) upon exposure to air

Pinacolborane [H–B(pin)] (a colorless liquid) decomposed swiftly into a white solid, which was determined to be HO–B(pin) by $^{11}$B NMR, upon exposure to air at ambient temperature. Its video (MOV) of the action was provided as another ESI (title: Decomposition of H–B(pin)).
8. References


B(aam)

3a
MeO

3d

[Chemical structure image of 3d]

[Graph showing NMR spectra for 3d]
3e

$\text{Ac} - \text{B(aam)}$
$^{13}C$ NMR Spectra of 3j
TIPS\textsuperscript{O} \xrightarrow{\text{B(aam)}} 3k
TMS → B(aam)

3m
$3n$
expanded $^1H$ NMR