Pd-Catalyzed Stereoselective 1,2-Aryboration of Alkenylarenes

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1. General Considerations

All manipulations were conducted with Schlenk tube. $^1$H NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). HPLC data were collected on a Shimadzu LC-2030 spectrometer. Optical rotations were determined using an Autopol IV automatic polarimeter. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonic mior OTOF-QII. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
2. Synthesis of alkenes Substrates

These substrates were prepared according to the corresponding literature reports. Analytical data ($^1$H NMR, $^{13}$C NMR) matches with the literature. All aryldiazonium salts were synthesized according to the literature.$^{10}$

$^{1b}$: 6-fluoro-1,2-dihydronaphthalene$^1$

$^{1c}$: 6-chloro-1,2-dihydronaphthalene$^1$

$^{1d}$: 6-bromo-1,2-dihydronaphthalene$^1$

$^{1e}$: 6-nitro-1,2-dihydronaphthalene$^1$

$^{1f}$: 6,7-dihydro-5$H$-benzo[7]annulene$^1$

$^{1h}$: 2$H$-chromene$^2$

$^{1i}$: benzyl quinoline-1(2$H$)-carboxylate$^3$

$^{1j}$: (E)-2-(prop-1-en-1-yl)naphthalene$^4$

$^{1k}$: (E)-2-(pent-1-en-1-yl)naphthalene$^5$

$^{1l}$: (E)-2-(hept-1-en-1-yl)naphthalene$^6$

$^{1m}$: (E)-2-methoxy-6-(prop-1-en-1-yl)naphthalene$^7$

$^{1n}$: (E)-1-chloro-4-(prop-1-en-1-yl)benzene$^8$

$^{1o}$: methyl (E)-4-(prop-1-en-1-yl)benzoate$^9$
3. The effect of different reaction conditions

Table S1. The effect of different bases and additives:

<table>
<thead>
<tr>
<th>Entry</th>
<th>base</th>
<th>additive</th>
<th>T (°C)</th>
<th>Yield (%) (b)</th>
<th>d : r (c)</th>
<th>en (d)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Na$_2$PO$_4$</td>
<td>--</td>
<td>25</td>
<td>72</td>
<td>&gt;20:1</td>
<td>81.19</td>
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<tr>
<td>2</td>
<td>Na$_2$PO$_4$</td>
<td>--</td>
<td>10</td>
<td>20</td>
<td>&gt;20:1</td>
<td>84.16</td>
</tr>
<tr>
<td>3</td>
<td>Na$_2$PO$_4$</td>
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<td>10</td>
<td>&gt;20:1</td>
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<tr>
<td>4</td>
<td>Na$_2$PO$_4$</td>
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<td>75</td>
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<tr>
<td>5</td>
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<td>74</td>
<td>&gt;20:1</td>
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<tr>
<td>6(c)</td>
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<td>67</td>
<td>&gt;20:1</td>
<td>77.23</td>
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<td>8</td>
<td>Na$_2$CO$_3$</td>
<td>--</td>
<td>25</td>
<td>53</td>
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<td>79.21</td>
</tr>
<tr>
<td>9</td>
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<td>66</td>
<td>&gt;20:1</td>
<td>78.22</td>
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<tr>
<td>10</td>
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<td>11</td>
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<td>25</td>
<td>64</td>
<td>&gt;20:1</td>
<td>62.37</td>
</tr>
</tbody>
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\(b\) Yield determined by $^1$H NMR. \(c\) $d : r$ determined by $^1$H NMR. \(d\) determined by chiral HPLC analysis. \(e\) Pd[OAc]$_2$ instead of Pd$_2$dba$_3$

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Table S2. The effect of different solvent and temperature:

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Yield (%)</th>
<th>d: r</th>
<th>e%</th>
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<tr>
<td>1</td>
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<tr>
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<td>76</td>
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<tr>
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<td>57</td>
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<tr>
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<td>63.37</td>
</tr>
<tr>
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<td>toluene:MTBE = 3:2</td>
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<td>32</td>
<td>&gt;20:1</td>
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</tr>
<tr>
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<td>toluene:Et₂O = 3:2</td>
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<td>46</td>
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<td>toluene:MTBE = 1:1</td>
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<td>&gt;20:1</td>
<td>83.17</td>
</tr>
<tr>
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<td>84.16</td>
</tr>
<tr>
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<td>Chlorobenzene:MTBE = 3:2</td>
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<td>73</td>
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<tr>
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<td>&gt;20:1</td>
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</tr>
<tr>
<td>15</td>
<td>dimethylbenzene:MTBE = 3:2</td>
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<td>&gt;20:1</td>
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<tr>
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<tr>
<td>17</td>
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<td>0</td>
<td>20</td>
<td>&gt;20:1</td>
<td>53.7</td>
</tr>
</tbody>
</table>

a Yield determined by ¹H NMR of the corresponding alcohol product. b d: r determined by ¹H NMR of the corresponding alcohol product. c e% determined by chiral HPLC analysis of the corresponding alcohol product. d (R)-L12 instead of (R)-L8.
4. General procedure for the reaction

General procedure A:

\[
\begin{align*}
R^1\text{R}^2 &+ \text{ArN}_2\text{BF}_4 + \text{B}_2\text{Pin}_2 &\xrightarrow{\text{Pd}_2(\text{dba})_3 (2.5 \text{ mol\%})} &\text{R}^1\text{R}^2 \text{Pin} \\
1 &+ 2 &\text{toluene, 25 °C, 24 h} &3
\end{align*}
\]

In an oven dried 25-ml Schlenk tube containing a stirring bar was charged with charged with \( \text{B}_2\text{Pin}_2 \) (0.3 mmol), \( \text{Pd}_2\text{dba}_3 \) (2.5 mol%), and \( \text{ArN}_2\text{BF}_4 \) (0.3 mmol). The tube was then evacuated and back-filled under a \( \text{N}_2 \) flow (this sequence was repeated three times). Anhydrous toluene (2.0 ml), alkene 1 (0.20 mmol) were added subsequently under \( \text{N}_2 \). The tube was stirred at 25 °C for 24 h. The reaction was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (EtOAc/petroleum ether) to afford the product 3.

General procedure B:

\[
\begin{align*}
\text{R}^1\text{R}^2 + \text{V}_2\text{BF}_4 + \text{B}_2\text{Pin}_2 &\xrightarrow{\text{Pd}_2\text{dba}_3 (5 \text{ mol\%}) \text{ Ligand (10 mol\%) \text{ Na}_3\text{PO}_4 2.0 \text{ eq}}} &\text{toluene MTBE = 3.2} \\
1 &+ 2 &\text{0°C, 24 h} &3 &\text{THF-H}_2\text{O (1:1)} \\
& & &\text{25°C, 3h} &3-\text{OH}
\end{align*}
\]

In an oven dried 10-ml Schlenk tube containing a stirring bar was charged with charged with \( \text{B}_2\text{Pin}_2 \) (0.20 mmol), \( \text{Pd}_2\text{dba}_3 \) (5 mol%), \( \text{Ligand (10 mol\%) \text{ Na}_3\text{PO}_4 2.0 \text{ eq}} \), alkene 1 (0.10 mmol) were added under \( \text{N}_2 \). The reaction mixture was stirred for 10 min at rt and then alkene 1 (0.10 mmol) was added, the tube was stirred at 0 °C for 24 h. the reaction was filtered through a plug of cotton and eluted with EtOAc (3 \times 2 mL). The filtrate was concentrated by rotary evaporation to provide yellow oil, and then dissolved in tetrahydrofuran (THF, 1.0 mL). \( \text{NaBO}_3\cdot\text{4H}_2\text{O (76.9 mg, 0.500 mmol,)} \) and \( \text{H}_2\text{O (1.0 mL)} \) were added. The resulting mixture was allowed to stir at 25 °C for three hours. The reaction mixture diluted with EtOAc (5.0 ml) and \( \text{H}_2\text{O (5.0 ml)} \). Then it was extracted with EtOAc (5.0 ml \times 3). The organic layer was combined and dried over \( \text{Na}_2\text{SO}_4 \). Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (EtOAc/petroleum ether) to afford the product 3-OH.
5. Analytical data for compounds

**4,4,5,5-tetramethyl-2-(2-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3a):** The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and 4-nitrophenyl diazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3a as a colorless solid (55 mg, 73% yield, >20:1 dr): \( R_f = 0.6 \) (EtOAc : petroleum ether = 1 : 10); \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \( \delta \): 8.16 (d, \( J = 8.0 \) Hz, 2H), 7.51 (d, \( J = 8.0 \) Hz, 2H), 7.15-7.08 (m, 4H), 3.32-3.28 (m, 1H), 3.05-2.91 (m, 3H), 2.59-2.49 (m, 1H), 2.16-2.13 (m, 1H), 0.96 (s, 6H), 0.92 (s, 6H); \(^{13}C\) NMR (CDCl\(_3\), 100 MHz) \( \delta \): 153.6, 146.3, 136.7, 135.6, 129.4, 128.6, 128.5, 125.5, 125.3, 123.3, 83.2, 41.3, 29.3, 25.2, 24.6, 24.1 ppm; HRMS (ESI-TOF) \( m/z \) calcd for C\(_{22}\)H\(_{27}\)BO\(_4\)N (M + H\(^+\)): 379.2069, found 379.2073.

**4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3b):** The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and phenyl diazonium tetrafluoroborate (2b, 58 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3b as a colorless solid (56 mg, 84% yield, >20:1 dr): \( R_f = 0.8 \) (EtOAc : petroleum ether = 1 : 10); \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \( \delta \): 7.35-7.33 (m, 2H), 7.29-7.23 (m, 2H), 7.19-7.07 (m, 5H), 3.21-3.19 (m, 1H), 3.06-2.89 (m, 3H), 2.55-2.45 (m, 1H), 2.14-2.11 (m, 1H), 0.97 (s, 6H), 0.88 (s, 6H); \(^{13}C\) NMR (CDCl\(_3\), 100 MHz) \( \delta \): 145.6, 137.7, 136.1, 129.4, 128.6, 128.0, 127.6, 125.9, 125.3, 124.9, 82.9, 41.0, 29.7, 25.3, 24.5, 24.2 ppm; HRMS (ESI-TOF) \( m/z \) calcd for C\(_{22}\)H\(_{28}\)BO\(_2\) (M + H\(^+\)): 334.2219, found 334.2220.

**4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3c):** The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and 4-(trifluoromethyl)phenyl diazonium tetrafluoroborate (2c, 78 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3c as a colorless solid (73 mg, 91% yield, >20:1 dr): \( R_f = 0.8 \) (EtOAc : petroleum ether = 1 : 10); \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \( \delta \): 7.55 (d, \( J = 8.0 \) Hz, 2H), 7.46 (d, \( J = 8.0 \) Hz, 2H), 7.14-7.07 (m, 4H), 3.29-3.24 (m, 1H), 3.05-2.90 (m, 3H), 2.56-2.46 (m, 1H), 2.15-2.12 (m, 1H), 0.96 (s, 6H), 0.89 (s, 6H); \(^{13}C\) NMR (CDCl\(_3\), 100 MHz) \( \delta \): 149.8, 137.1, 135.8,
Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalen-2-yl benzoate (3d): The general procedure A was followed using 1,2-dihydropnaphthalene (1a, 26 mg, 0.20 mmol) and the corresponding diazonium tetrafluoroborate (2d, 75 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3d as a yellow solid (66 mg, 85% yield, >20:1 dr); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.97 (d, \(J = 7.9\) Hz, 2H), 7.42 (d, \(J = 7.9\) Hz, 2H), 7.13-7.07 (m, 4H), 3.91 (s, 3H), 3.27-3.23 (m, 1H), 3.05-2.90 (m, 3H), 2.58-2.48 (m, 1H), 2.14-2.11 (m, 1H), 0.96 (s, 6H), 0.90 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 167.2, 151.2, 137.2, 135.8, 129.4, 128.6, 125.5, 125.0, 83.0, 52.0, 41.2, 29.5, 25.2, 24.5, 24.2 ppm; HRMS (ESI-TOF) \(m/z\) calcd for C\(_{23}\)H\(_{27}\)BO\(_2\)F\(_3\) (M + H)\(^{+}\): 403.2060, found 403.2061.

2-(2-(3,5-difluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e): The general procedure A was followed using 1,2-dihydropnaphthalene (1a, 26 mg, 0.20 mmol) and 3,5-difluorophenyl diazonium tetrafluoroborate (2e, 68 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3e as a yellow solid (61 mg, 83% yield, >20:1 dr); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.11-7.03 (m, 4H), 6.89-6.87 (m, 2H), 6.65-6.61 (m, 1H), 3.16-3.13 (m, 1H), 3.00-2.89 (m, 3H), 2.53-2.43 (m, 1H), 2.08-2.04 (m, 1H), 1.01 (s, 6H), 0.96 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 164.2, 164.0, 161.7, 161.6, 150.1, 150.0, 149.9, 136.9, 135.6, 129.4, 128.6, 125.5, 125.2, 110.63, 110.57, 110.45, 110.39, 101.5, 101.3, 101.0, 83.1, 41.2, 29.5, 25.5, 24.5, 24.2 ppm; HRMS (ESI-TOF) \(m/z\) calcd for C\(_{22}\)H\(_{26}\)BO\(_2\)F\(_2\) (M + H)\(^{+}\): 370.2030, found 370.2237.

2-(2-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f): The general procedure A was followed using 1,2-dihydropnaphthalene (1a, 26 mg, 0.20 mmol) and 3,5-difluorophenyl diazonium tetrafluoroborate (2f, 63 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3f as a colorless solid (63 mg, 90% yield, >20:1 dr); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.31-7.28 (m, 2H), 7.13-7.06 (m, 4H), 7.00-6.95 (m, 2H), 6.92-6.87 (m, 2H), 6.65-6.61 (m, 1H), 3.16-3.13 (m, 1H), 3.00-2.89 (m, 3H), 2.53-2.43 (m, 1H), 2.08-2.04 (m, 1H), 1.01 (s, 6H), 0.96 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 164.2, 164.0, 161.7, 161.6, 150.1, 150.0, 149.9, 136.9, 135.6, 129.4, 128.6, 125.5, 125.2, 110.63, 110.57, 110.45, 110.39, 101.5, 101.3, 101.0, 83.1, 41.2, 29.5, 25.5, 24.5, 24.2 ppm; HRMS (ESI-TOF) \(m/z\) calcd for C\(_{23}\)H\(_{30}\)BO\(_4\) (M + H)\(^{+}\): 393.2242, found 393.2237.
3.20-3.16 (m, 1H), 3.03-2.89 (m, 3H), 2.51-2.41 (m, 1H), 2.11-2.08 (m, 1H), 0.98 (s, 6H), 0.91 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 162.5, 160.1, 141.33, 141.30, 137.4, 135.9, 129.4, 129.0, 128.9, 128.6, 125.4, 125.0, 114.8, 114.4, 83.0, 40.3, 29.6, 25.5, 24.5, 24.2 ppm; HRMS (ESI-TOF) $m/z$ calcd for C$_{22}$H$_{27}$BO$_2$F (M + H)$^+$: 352.2124, found 352.2120.

2-(2-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and 4-chlorophenyl diazonium tetrafluoroborate (2g, 68 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3g as a colorless solid (69 mg, 94% yield, >20:1 dr): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.29-7.24 (m, 4H), 7.11-7.06 (m, 4H), 3.19-3.15 (m, 1H), 3.02-2.88 (m, 3H), 2.51-2.41 (m, 1H), 2.10-2.07 (m, 1H), 0.98 (s, 6H), 0.92 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 144.1, 137.3, 135.8, 131.6, 129.4, 129.0, 128.6, 125.4, 125.0, 83.0, 40.4, 29.5, 25.3, 24.5, 24.2 ppm; HRMS (ESI-TOF) $m/z$ calcd for C$_{22}$H$_{27}$BO$_2$Cl (M + H)$^+$: 369.1797, found 369.1798.

4,4,5,5-tetramethyl-2-(2-(o-tolyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3i): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and o-tolyldiazenium tetrafluoroborate (2i, 62 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3i as a colorless liquid (42 mg, 61% yield, >20:1 dr): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR.

2-(2-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and 4-bromophenyl diazonium tetrafluoroborate (2h, 81 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3h as a yellow solid (72 mg, 87% yield, >20:1 dr): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.41 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 7.12-7.07 (m, 4H), 3.18-3.14 (m, 1H), 3.01-2.88 (m, 3H), 2.51-2.41 (m, 1H), 2.09-2.06 (m, 1H), 0.98 (s, 6H), 0.92 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 144.7, 137.3, 135.9, 131.0, 129.43, 129.37, 128.6, 125.4, 125.0, 83.0, 40.4, 29.5, 25.3, 24.5, 24.2 ppm; HRMS (ESI-TOF) $m/z$ calcd for C$_{22}$H$_{27}$BO$_2$Br (M + H)$^+$: 412.1324, found 412.1321.
(CDCl₃, 400 MHz) δ: 7.36-7.35 (m, 1H), 7.11-7.08 (m, 7H), 3.35-3.32 (m, 1H), 3.02-2.90 (m, 3H), 2.66-2.56 (m, 1H), 2.36 (s 3H), 2.00-1.97 (m, 1H), 1.03 (s, 6H), 0.90 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 143.7, 138.0, 136.2, 135.9, 130.1, 129.4, 128.7, 126.9, 125.8, 125.7, 125.3, 124.9, 82.9, 37.9, 30.0, 26.0, 24.5, 24.4, 19.4 ppm; HRMS (ESI-TOF) m/z calcd for C₂₃H₃₀BO₂ (M + H)⁺: 348.2375, found 348.2369.

4,4,5,5-tetramethyl-2-(2-(m-tolyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3j): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and m-tolyldiazonium tetrafluoroborate (2j, 62 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3j as a colorless liquid (54 mg, 78% yield, >20:1 dr): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); ¹H NMR (CDCl₃, 400 MHz) δ: 7.17-7.06 (m, 7H), 6.99-6.98 (m, 1H), 3.16-3.14 (m, 1H), 3.03-2.89 (m, 3H), 2.56-2.46 (m, 1H), 2.32 (s, 3H), 2.11-2.05 (m, 1H), 0.98 (s, 6H), 0.90 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 145.6, 137.8, 137.3, 136.1, 129.4, 128.6, 128.0, 126.6, 125.3, 124.9, 82.8, 41.1, 29.9, 25.4, 24.5, 24.2, 21.5 ppm; HRMS (ESI-TOF) m/z calcd for C₂₃H₃₀BO₂ (M + H)⁺: 348.2375, found 348.2380.

4,4,5,5-tetramethyl-2-(2-(p-tolyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3k): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and p-tolyldiazonium tetrafluoroborate (2k, 62 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3k as a colorless solid (53 mg, 76% yield, >20:1 dr): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); ¹H NMR (CDCl₃, 400 MHz) δ: 7.23-7.21 (m, 2H), 7.10-7.07 (m, 6H), 3.17-3.14 (m, 1H), 3.03-2.88 (m, 3H), 2.53-2.43 (m, 1H), 2.31 (s 3H), 2.11-2.08 (m, 1H), 0.99 (s, 6H), 0.90 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 142.6, 137.9, 136.2, 135.3, 129.3, 128.7, 128.6, 127.4, 125.3, 124.9, 82.9, 40.7, 29.8, 25.6, 24.5, 24.2, 21.0 ppm; HRMS (ESI-TOF) m/z calcd for C₂₃H₃₀BO₂ (M + H)⁺: 348.2375, found 348.2380.

2-(2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and 4-(tert-butyl)phenyl diazonium tetrafluoroborate (2l, 74 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40)
afforded product 3i as a yellow liquid (74 mg, 95% yield, >20:1 dr); Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); ¹H NMR (CDCl₃, 400 MHz) δ: 7.33-7.26 (m, 4H), 7.13-7.12 (m, 1H), 7.07-7.05 (m, 3H), 3.22-3.18 (m, 1H), 3.07-2.89 (m, 3H), 2.51-2.41 (m, 1H), 2.16-2.13 (m, 1H), 1.29 (s, 9H), 0.96 (s, 6H), 0.84 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 148.8, 142.5, 137.8, 136.1, 129.4, 128.6, 127.1, 125.3, 124.9, 124.8, 82.8, 40.3, 34.3, 31.4, 29.8, 25.2, 24.34, 24.30 ppm; HRMS (ESI-TOF) m/z calcd for C₂₆H₃₄BO₂ (M - H)⁻: 388.2688, found 388.2694.

4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)benzoic acid (3m): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and the corresponding diazonium tetrafluoroborate (2m, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 4) afforded product 3m as a white solid (47 mg, 62% yield, >20:1 dr); Rf = 0.4 (EtOAc : petroleum ether = 1 : 1); ¹H NMR (CDCl₃, 400 MHz) δ: 8.05 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.13-7.09 (m, 4H), 3.28-3.26 (m, 1H), 3.06-2.91 (m, 3H), 2.59-2.49 (m, 1H), 2.16-2.13 (m, 1H), 0.97 (s, 6H), 0.91 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 171.8, 152.3, 137.2, 135.8, 130.1, 129.4, 128.7, 127.9, 127.0, 125.5, 125, 1, 83.1, 41.4, 29.5, 25.2, 24.5, 24.2 ppm; HRMS (ESI-TOF) m/z calcd for C₂₃H₂₈BO₄ (M + H)⁺: 379.2085, found 379.2088.

4,4,5,5-tetramethyl-2-(1,2,3,4-tetrahydro-[2,2'-binaphthalen]-1-yl)-1,3,2-dioxaborolane (3n): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and 2,2'-binaphthalen-1-yl diazonium tetrafluoroborate (2n, 73 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3n as a colorless solid (32 mg, 42% yield, >20:1 dr); Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); ¹H NMR (CDCl₃, 400 MHz) δ: 7.80-7.76 (m, 4H), 7.49 (d, J = 8.4 Hz, 1H), 7.14-7.09 (m, 4H), 3.36-3.33 (m, 1H), 3.15-3.14 (m, 1H), 3.06-2.95 (m, 2H), 2.71-2.60 (m, 1H), 2.24-2.21 (m, 1H), 0.90 (s, 6H), 0.80 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 143.3, 137.8, 136.1, 133.5, 132.2, 129.4, 128.6, 127.7, 127.5, 127.5, 127.0, 125.7, 125.4, 125.3, 125.0, 124.95, 82.9, 41.3, 29.8, 25.5, 24.6, 24.1 ppm; HRMS (ESI-TOF) m/z calcd for C₂₆H₃₀BO₂ (M + H)⁺: 385.2343, found 385.2339.

2-(2-(benzo[da][1,3]dioxol-5-yl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26
mg, 0.20 mmol) and the corresponding diazonium tetrafluoroborate (2o, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3o as a yellow solid (24 mg, 32% yield, >20:1 dr): Rf = 0.4 (EtOAc : petroleum ether = 1 : 10); ^1H NMR (CDCl₃, 400 MHz) δ: 7.12-7.06 (m, 4H), 6.87 (s, 1H), 6.80-6.73 (m, 2H), 5.91 (s, 2H), 3.14-3.10 (m, 1H), 2.98-2.88 (m, 3H), 2.50-2.40 (m, 1H), 2.06-2.03 (m, 1H), 1.02 (s, 6H), 0.95 (s, 6H); ^13C NMR (CDCl₃, 100 MHz) δ: 147.2, 145.5, 139.9, 137.6, 136.0, 129.4, 128.6, 125.4, 125.0, 120.4, 108.3, 107.9, 100.6, 82.9, 40.9, 29.8, 25.7, 24.6, 24.2 ppm; HRMS (ESI-TOF) m/z calcd for C₁₂H₁₈BO₄ (M + H)+: 378.2117, found 378.2107.

Methyl 3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalen-2-y1)thiophene-2-carboxylate (3p): The general procedure A was followed using 1,2-dihydronaphthalene (1a, 26 mg, 0.20 mmol) and the corresponding diazonium tetrafluoroborate (2p, 77 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3p as a yellow solid (46 mg, 58% yield, >20:1 dr): Rf = 0.3 (EtOAc : petroleum ether = 1 : 10); ^1H NMR (CDCl₃, 400 MHz) δ: 7.37 (d, J = 5.1 Hz, 1H), 7.20 (d, J = 5.1 Hz, 1H), 7.09-7.04 (m, 4H), 4.10-4.06 (m, 1H), 3.83 (s, 3H), 3.17 (d, J = 5.8 Hz, 1H), 2.95-2.91 (m, 2H), 2.60-2.50 (m, 1H), 1.04 (s, 6H), 0.94 (s, 6H); ^13C NMR (CDCl₃, 100 MHz) δ: 162.7, 154.4, 137.5, 135.8, 129.62, 129.56, 129.2, 128.8, 126.7, 125.3, 124.8, 83.0, 51.8, 35.9, 29.6, 26.6, 24.5, 24.4 ppm; HRMS (ESI-TOF) m/z calcd for C₂₂H₂₈BO₄S (M + H)+: 399.1805, found 399.1818.

2-(7-fluoro-2-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q): The general procedure A was followed using 6-fluoro-1,2-dihydronaphthalene (1b, 30 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3q as a colorless solid (68 mg, 85% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); ^1H NMR (CDCl₃, 400 MHz) δ: 8.16 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.10-7.06 (m, 1H), 6.87-6.78 (m, 2H) 3.29-3.27 (m, 1H), 3.01-2.84 (m, 3H), 2.55-2.45 (m, 1H), 2.15-2.13 (m, 1H), 0.98 (s, 6H), 0.93 (s, 6H); ^13C NMR (CDCl₃, 100 MHz) δ: 162.1, 159.7, 153.2, 146.5, 138.8, 138.7, 131.1, 130.63, 130.55, 128.6, 123.3, 114.8, 114.6, 112.6, 112.4, 83.4, 41.0, 28.6, 25.5, 24.5, 24.2 ppm; HRMS (ESI-TOF) m/z calcd for C₂₂H₂₆BNO₄F (M + H)+: 397.1975, found 397.1983.
2-(7-chloro-2-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaaborolane (3r): The general procedure A was followed using 6-chloro-1,2-dihydronaphthalene (1c, 33 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3r as a colorless solid (68 mg, 82% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 8.16 (d, $J$ = 7.8 Hz, 2H), 7.49 (d, $J$ = 7.8 Hz, 2H), 7.14 (s, 1H), 7.06 (s, 2H), 3.28-3.25 (m, 1H), 2.99-2.84 (m, 3H), 2.56-2.46 (m, 1H), 2.15-2.12 (m, 1H), 0.98 (s, 6H), 0.94 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 153.1, 146.5, 138.7, 134.0, 131.1, 130.6, 128.5, 128.3, 125.5, 123.3, 83.5, 41.0, 28.7, 25.2, 24.6, 24.1 ppm; HRMS (ESI-TOF) m/z calcd for C$_{22}$H$_{26}$BNO$_4$Cl (M + H)$^+$: 413.1680, found 413.1664.

2-(7-bromo-2-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaaborolane (3s): The general procedure A was followed using 6-bromo-1,2-dihydronaphthalene (1d, 42 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3s as a colorless solid (46 mg, 50% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 8.16 (d, $J$ = 7.8 Hz, 2H), 7.49 (d, $J$ = 7.8 Hz, 2H), 7.30 (s, 1H), 7.21 (d, $J$ = 8.0 Hz, 1H), 7.00 (d, $J$ = 8.0 Hz, 1H), 2.99-2.82 (m, 3H), 2.56-2.45 (m, 1H), 2.15-2.12 (m, 1H), 0.98 (s, 6H), 0.94 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 153.1, 146.5, 139.2, 134.6, 131.3, 131.0, 128.5, 128.4, 123.3, 119.1, 83.5, 41.0, 28.8, 25.2, 24.6, 24.1 ppm; HRMS (ESI-TOF) m/z calcd for C$_{22}$H$_{24}$BNO$_4$Br (M - H)$^-$: 455.1018, found 455.1018.

4,4,5,5-tetramethyl-2-(7-nitro-2-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaaborolane (3t): The general procedure A was followed using 6-nitro-1,2-dihydronaphthalene (1e, 35 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3t as a yellow solid (80 mg, 94% yield, >20:1 dr): Rf = 0.4 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 8.18 (d, $J$ = 7.9 Hz, 2H), 8.06 (s, 1H), 7.95 (d, $J$ = 8.4 Hz, 1H), 7.50 (d, $J$ = 7.9 Hz, 2H), 7.28 (d, $J$ = 10.1 Hz, 1H), 3.35-3.33 (m, 1H), 3.13-2.96 (m, 3H), 2.59-2.49 (m, 1H), 2.22-2.19 (m, 1H), 0.97 (s, 6H), 0.94 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100
MHz) δ: 152.4, 146.6, 146.1, 138.7, 130.2, 128.5, 123.7, 123.4, 120.3, 83.7, 40.7, 29.4, 25.0, 24.5, 24.1 ppm; HRMS (ESI-TOF) m/z calculated for $C_{22}H_{24}BN_2O_6$ (M - H)$^-$: 423.1732, found 423.1752.

$4,4',5,5'$-tetramethyl-2-(6-(4-nitrophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)-1,3,2-dioxaborolane (3u): The general procedure A was followed using 6,7-dihydro-5H-benzo[7]annulene (1f, 29 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3u as a colorless solid (57 mg, 72% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) δ: 8.14 (d, $J$ = 7.9 Hz, 2H), 7.53 (d, $J$ = 8.4 Hz, 2H), 7.14-7.11 (m, 4H), 3.16-3.10 (m, 1H), 3.00-2.97 (m, 1H), 2.79-2.62 (m, 3H), 2.10 (m, 1H), 1.99-1.96 (m, 1H), 1.51-1.45 (m, 1H), 1.18 (s, 6H), 1.13 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 156.3, 146.2, 142.8, 142.4, 140.2, 129.8, 128.5, 126.0, 123.4, 83.4, 47.5, 35.7, 34.0, 28.0, 24.8, 24.5 ppm; HRMS (ESI-TOF) m/z calculated for $C_{23}H_{27}BNO_4$ (M - H)$^-$: 391.2069, found 391.2085.

$4,4',5,5'$-tetramethyl-2-(2-(4-nitrophenyl)-2,3-dihydro-1H-inden-1-yl)-1,3,2-dioxaborolane (3v): The general procedure A was followed using 1H-indene (1g, 23 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3v as a colorless solid (49 mg, 67% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) δ: 8.08 (d, $J$ = 8.2 Hz, 2H), 7.36 (d, $J$ = 8.2 Hz, 2H), 7.34-7.32 (m, 1H), 7.28-7.26(m, 1H), 7.22-7.15 (m, 2H), 4.00-3.95 (m, 1H), 3.43-3.38 (m, 1H), 3.32-3.25 (m, 1H), 0.92 (s, 12H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 153.3, 146.4, 142.8, 142.4, 130.2, 129.8, 128.5, 126.3, 126.0, 123.4, 83.4, 47.5, 35.7, 34.0, 28.0, 24.8, 24.5 ppm; HRMS (ESI-TOF) m/z calculated for $C_{21}H_{23}BNO_4$ (M - H)$^-$: 363.1757, found 363.1757.

$4,4',5,5'$-tetramethyl-2-(3-(4-nitrophenyl)chroman-4-yl)-1,3,2-dioxaborolane (3w): The general procedure A was followed using 2H-chromene (1h, 26 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3w as a colorless solid (36 mg, 47% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); $^1$H
NMR (CDCl₃, 400 MHz) δ: 7.55 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.15-7.08 (m, 2H), 6.89-6.85 (m, 2H), 4.65 (d, J = 10.2 Hz, 1H), 3.47 (m, 1H), 3.04 (d, J = 8.4 Hz, 1H), 0.98 (s, 6H), 0.96 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 154.0, 145.9, 129.5, 128.0, 126.9, 125.3, 125.2, 122.5, 120.5, 116.9, 83.6, 67.7, 39.0, 24.5, 24.2 ppm; HRMS (ESI-TOF) m/z calcd for C₂₁H₂₅BNO₅ (M + H)⁺: 381.1862, found 381.1853.

Benzyl3-(4-nitrophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (3x): The general procedure A was followed using benzyl quinoline-1(2H)-carboxylate (1i, 53 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 15) afforded product 3x as a yellow solid (47 mg, 46% yield, >20:1 dr): Rf = 0.3 (EtOAc : petroleum ether = 1 : 10); ¹H NMR (CDCl₃, 400 MHz) δ: 8.05 (d, J = 8.0 Hz, 2H), 7.70 (m, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.29-7.16 (m, 7H), 7.09-7.05 (m, 1H), 5.11-5.03 (m, 2H), 4.35-4.30 (m, 1H), 3.51 (m, 1H), 3.09-3.08 (m, 1H), 0.98 (s, 6H), 0.90 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ: 154.6, 150.1, 146.8, 137.4, 136.1, 129.6, 129.0, 128.7, 128.4, 125.8, 124.6, 146.8, 137.4, 136.1, 129.6, 129.0, 128.7, 128.4, 125.8, 124.6, 124.1, 123.4, 83.7, 67.5, 48.0, 41.3, 24.4, 24.3 ppm; HRMS (ESI-TOF) m/z calcd for C₂₉H₃₂BN₂O₆ (M + H)⁺: 515.2358, found 515.2368.

4,4,5,5-tetramethyl-2-((1S,2S)-1-(naphthalen-2-yl)-2-(4-nitrophenyl)propyl)-1,3,2-dioxaborolane (3y): The general procedure A was followed using (E)-2-(prop-1-en-1-yl)naphthalene (1j, 34 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3y as a colorless solid (56 mg, 67% yield, >20:1 dr): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); ¹H NMR (CDCl₃, 400 MHz) δ: 7.82-7.76 (m, 4H), 7.58-7.56 (m, 2H), 7.52-7.41 (m, 5H), 3.42-3.34 (m, 1H), 2.71 (d, J = 11.7 Hz, 1H), 1.08 (d, J = 6.8 Hz, 3H), 0.88 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ: 151.7, 138.5, 133.8, 132.0, 128.0, 127.9, 127.5, 127.4, 125.8, 125.14, 125.10, 83.3, 42.8, 24.3, 24.0, 21.8 ppm; HRMS (ESI-TOF) m/z calcd for C₂₅H₂₇BNO₄ (M - H)⁻: 415.2069, found 415.2075.

4,4,5,5-tetramethyl-2-((1S,2R)-1-(naphthalen-2-yl)-2-(4-nitrophenyl)pentyl)-1,3,2-dioxaborolane (3z): The general procedure A was followed using (E)-2-(pent-1-en-1-yl)naphthalene (1k, 39 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol).
Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product \(3z\) as a colorless solid (35 mg, 39% yield, >20:1 dr): \(R_f = 0.6\) (EtOAc : petroleum ether = 1 : 10); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 8.19 (d, \(J = 8.0\) Hz, 2H), 7.83-7.81 (m, 3H), 7.76 (s, 1H), 7.52-7.42 (m, 5H), 3.31 (t, \(J = 11.2\) Hz, 1H), 1.54-1.50 (m, 1H), 1.40-1.31 (m, 1H), 1.03-0.91 (m, 2H), 0.87 (s, 6H), 0.86 (s, 6H), 0.64 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 153.9, 146.5, 138.0, 133.8, 132.1, 129.3, 128.0, 127.6, 127.52, 127.47, 125.9, 125.2, 123.3, 83.4, 48.0, 37.2, 24.3, 24.1, 20.2, 13.7 ppm; HRMS (ESI-TOF) \(m/z\) calcd for C\(_{27}\)H\(_{33}\)BNO\(_4\) (M + H): 445.2539, found 445.2550.

4,4,5,5-tetramethyl-2-((1\(S\),2\(R\))-1-(naphthalen-2-yl)-2-(4-nitrophenyl)heptyl)-1,3,2-dioxaborolane (3aa): The general procedure A was followed using (\(E\))-2-(hept-1-en-1-yl)naphthalene (1l, 45 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3aa as a colorless solid (37 mg, 39% yield, >20:1 dr): \(R_f = 0.6\) (EtOAc : petroleum ether = 1 : 10); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 8.19 (d, \(J = 8.0\) Hz, 2H), 7.81-7.80 (m, 3H), 7.75 (s, 1H), 7.52-7.42 (m, 5H), 3.29 (t, \(J = 11.2\) Hz, 1H), 2.78 (d, \(J = 12.0\) Hz, 1H), 1.56 (m, 1H), 1.41-1.33 (m, 1H), 1.04-0.90 (m, 6H), 0.87 (s, 6H), 0.86 (s, 6H), 0.69 (t, \(J = 5.2\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 153.9, 146.5, 138.0, 133.8, 132.1, 129.3, 128.0, 127.6, 127.52, 127.47, 125.9, 125.2, 123.3, 83.4, 48.0, 37.2, 24.3, 24.1, 22.4, 13.9 ppm; HRMS (ESI-TOF) \(m/z\) calcd for C\(_{29}\)H\(_{37}\)BNO\(_4\) (M + H): 473.2852, found 473.2862.

2-((1\(S\),2\(R\))-1-(6-methoxynaphthalen-2-yl)-2-(4-nitrophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ab): The general procedure A was followed using \((E)\)-2-methoxy-6-(prop-1-en-1-yl)naphthalene (1m, 40 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3ab as a colorless solid (43 mg, 48% yield, >20:1 dr): \(R_f = 0.6\) (EtOAc : petroleum ether = 1 : 10); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 8.18 (d, \(J = 7.7\) Hz, 2H), 7.71-7.67 (m, 3H), 7.52 (d, \(J = 7.7\) Hz, 2H), 7.43 (d, \(J = 8.3\) Hz, 1H), 7.15-7.13 (m, 2H), 3.92 (s, 3H), 3.45-3.39 (m, 1H), 2.66 (d, \(J = 11.5\) Hz, 1H), 1.08 (d, \(J = 6.4\) Hz, 3H), 0.92 (s, 6H), 0.89 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 157.3, 155.7, 146.4, 135.5, 133.1, 129.3, 129.0, 128.5, 128.0, 127.4, 126.9, 123.5, 118.7, 105.6, 83.4, 55.3, 42.8, 24.4, 24.2, 21.6 ppm; HRMS (ESI-TOF) \(m/z\) calcd for C\(_{26}\)H\(_{31}\)BNO\(_5\) (M + H): 447.2332, found 447.2306.
2-((1S,2R)-1-(4-chlorophenyl)-2-(4-nitrophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ac): The general procedure A was followed using (E)-1-chloro-4-(prop-1-en-1-yl)benzene (1n, 30 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3ac as a colorless solid (42 mg, 53% yield, >20:1 dr): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); \( ^1\text{H NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \): 8.17 (d, \( J = 8.1 \) Hz, 2H), 7.46 (d, \( J = 8.1 \) Hz, 2H), 7.29-7.22 (m, 4H), 3.32-3.24 (m, 1H), 2.50 (d, \( J = 11.4 \) Hz, 1H), 1.06 (d, \( J = 6.8 \) Hz, 3H), 0.92 (s, 6H), 0.91 (s, 6H); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 100 MHz) \( \delta \): 155.1, 146.4, 138.9, 131.7, 130.4, 128.6, 128.4, 123.5, 83.5, 42.8, 24.3, 24.1, 21.4 ppm; HRMS (ESI-TOF) \( m/z \) calcd for C\(_{21}\)H\(_{26}\)BNO\(_4\)Cl (M + H\(^+\)): 401.1680, found 401.1681.

methyl 4-((1S,2R)-2-(4-nitrophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) benzoate (3ad): The general procedure A was followed using methyl (E)-4-(prop-1-en-1-yl)benzoate (1o, 35 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ad as a colorless solid (42 mg, 49% yield, >20:1 dr): Rf = 0.2 (EtOAc : petroleum ether = 1 : 10); \( ^1\text{H NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \): 8.17 (d, \( J = 7.8 \) Hz, 2H), 7.99 (d, \( J = 7.5 \) Hz, 2H), 7.48 (d, \( J = 7.8 \) Hz, 2H), 7.38 (d, \( J = 7.5 \) Hz, 2H), 3.91 (s, 3H), 3.39-3.34 (m, 1H), 2.62 (d, \( J = 11.2 \) Hz, 1H), 1.06 (d, \( J = 6.5 \) Hz, 3H), 0.91 (s, 6H), 0.90 (s, 6H); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 100 MHz) \( \delta \): 167.1, 154.9, 146.5, 146.2, 129.8, 129.0, 128.4, 128.0, 123.5, 83.6, 52.0, 42.6, 24.3, 24.1, 21.5 ppm; HRMS (ESI-TOF) \( m/z \) calcd for C\(_{23}\)H\(_{29}\)BNO\(_6\) (M + H\(^+\)): 425.2124, found 425.2119.

4,4,5,5-tetramethyl-2-((1S,2S)-2-(4-nitrophenyl)-1,2-diphenylethyl)-1,3,2-dioxaborolane (3ae): The general procedure A was followed using methyl (E)-1,2-diphenylethene (1p, 36 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3ae as a colorless solid (50 mg, 58% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); \( ^1\text{H NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \): 8.16 (d, \( J = 8.0 \) Hz, 2H), 7.61 (d, \( J = 8.0 \) Hz, 2H), 7.18-7.02 (m, 10H), 4.59 (d, \( J = 12.6 \) Hz, 1H), 3.28 (d, \( J = 12.6 \) Hz, 1H), 0.99 (s, 6H), 0.90 (s, 6H); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 100 MHz) \( \delta \): 153.0, 146.4, 142.3, 139.5, 129.02, 128.96, 128.4, 128.3, 127.9, 126.4, 125.7, 123.6.
4,4,5,5-tetramethyl-2-((1R,2S)-2-(4-nitrophenyl)-1,2-diphenylethyl)-1,3,2-dioxaborolane (3af): The general procedure A was followed using methyl (Z)-1,2-diphenylethene (1q, 36 mg, 0.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 71 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3af as a colorless solid (57 mg, 66% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.92 (d, $J$ = 8.0 Hz, 2H), 7.43 (d, $J$ = 7.6 Hz, 2H), 7.31 (t, $J$ = 7.2 Hz, 2H), 7.22-7.12 (m, 7H), 7.07-7.04 (m, 1H), 4.59 (d, $J$ = 12.8 Hz, 1H), 3.26 (d, $J$ = 12.8 Hz, 1H), 0.97 (s, 6H), 0.89 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 152.0, 146.0, 143.3, 139.5, 128.9, 128.7, 128.4, 128.1, 126.9, 125.8, 123.3, 83.6, 53.9, 24.2, 24.1 ppm; HRMS (ESI-TOF) m/z calcd for C$_{26}$H$_{29}$BNO$_4$ (M + H)$^+$: 429.2226, found 429.2218.

3a-OH: The general procedure B was followed using 1,2-dihydronaphthalene (1a, 13 mg, 0.10 mmol), Ligand ((R)-L12, 10 mg, 0.01 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 47 mg, 0.20 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3a-OH as a White solid (5 mg, 20% yield, >20:1 dr, 93:7 er): Rf = 0.2 (EtOAc : petroleum ether = 1 : 5); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 8.22 (d, $J$ = 7.9 Hz, 2H), 7.52 (d, $J$ = 7.9 Hz, 2H), 7.34-7.21 (m, 4H), 4.82 (s 1H), 3.19 (d, $J$ = 12.8 Hz, 2H), 3.10-3.04 (m, 1H), 2.99-2.91 (m, 1H), 2.54-2.43 (m, 1H), 2.00-1.97 (m, 1H), 1.55 (s 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 150.8, 146.8, 137.5, 136.2, 130.0, 129.3, 129.2, 128.5, 126.5, 123.5, 70.9, 46.1, 29.3, 21.7 ppm; HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{16}$O$_3$N (M + H)$^+$: 270.1130, found 270.1136; [a]$_D^{23}$ = +96.6 (c = 0.5, CHCl$_3$).

3e-OH: The general procedure B was followed using 1,2-dihydronaphthalene (1a, 13 mg, 0.10 mmol), Ligand ((R)-L12, 10 mg, 0.01 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2e, 45 mg, 0.20 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3e-OH as a yellow solid (7 mg, 28% yield, >20:1 dr, 94:6 er): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.34-7.18 (m, 4H), 6.88 (d, $J$ = 8.0 Hz, 2H), 6.74-6.69 (m, 1H), 4.79 (s, 1H), 3.07-3.01 (m, 2H), 2.96-2.87 (m, 1H), 2.43-2.33 (m, 1H), 1.95-1.93 (m, 1H), 1.55 (s 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 164.4, 164.2, 161.9, 161.8, 150.8, 146.8, 137.5, 136.2, 130.0, 129.3, 129.2, 128.5, 126.5, 123.5, 70.9, 46.1, 29.3, 21.7 ppm; HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{16}$O$_3$N (M + H)$^+$: 270.1130, found 270.1136; [a]$_D^{23}$ = +96.6 (c = 0.5, CHCl$_3$).
(1R, 2S)-7-chloro-2-(3,5-difluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (3ag-OH): The general procedure B was followed using 6-chloro-1,2-dihydronaphthalene (1c, 17 mg, 0.10 mmol), Ligand ((R)-L12, 10 mg, 0.01 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2e, 45 mg, 0.20 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ag-OH as a white solid (6 mg, 21% yield, >20:1 dr, 94:6 er): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); $^{1}$H NMR (CDCl$_3$, 400 MHz) δ: 7.31 (s, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 7.7 Hz, 2H), 6.75-6.71 (m, 1H), 4.73 (s, 1H), 3.05-2.97 (m, 2H), 2.89-2.81 (m, 1H), 2.40-2.31 (m, 1H), 1.95-1.93 (m, 1H), 1.63 (s 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 164.4, 164.3, 162.0, 161.8, 146.5, 146.4, 146.3, 139.0, 134.7, 131.8, 130.5, 129.9, 128.5, 111.22, 111.15, 111.04, 110.97, 102.6, 102.3, 102.0, 70.6, 45.6, 28.8, 21.5 ppm; HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{13}$OF$_2$ (M - H): 259.0934, found 259.0922; $[\alpha]_D^{23}$ = +109.6 (c = 0.7, CHCl$_3$).

(1R, 2S)-7-bromo-2-(3,5-difluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (3ah-OH): The general procedure B was followed using 6-bromo-1,2-dihydronaphthalene (1d, 21 mg, 0.10 mmol), Ligand ((R)-L12, 10 mg, 0.01 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2e, 45 mg, 0.20 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ah-OH as a yellow solid (9 mg, 27% yield, >20:1 dr, 95:5 er): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); $^{1}$H NMR (CDCl$_3$, 400 MHz) δ: 7.46 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 7.7 Hz, 2H), 6.75-6.71 (m, 1H), 4.72 (s, 1H), 3.04-2.95 (m, 2H), 2.87-2.78 (m, 1H), 2.40-2.29 (m, 1H), 1.95-1.92 (m, 1H), 1.64 (s 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 164.4, 164.3, 161.9, 161.8, 146.4, 146.3, 146.25, 139.4, 135.2, 132.9, 131.4, 130.8, 119.6, 111.21, 111.15, 111.03, 110.96, 102.6, 102.3, 102.1, 70.5, 45.6, 28.8, 21.4 ppm; HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{12}$BOFCl (M - H): 293.0545, found 293.0536; $[\alpha]_D^{23}$ = +35.2 (c = 0.6, CHCl$_3$).
6. References

7. The data for some failed examples

\[
\begin{align*}
\text{R}^1 \text{R}^2 & + \text{O}_2 \text{N} & \text{N}_2 \text{EF}_4 & + \text{B}_2 \text{Pin}_2 & \xrightarrow{\text{Pd}_2(\text{dba})_3 (2.5 \text{ mol} \%) } \\
& & & \text{toluene, 25 °C, 24 h} & \rightarrow \text{Pin} \text{R}^1 \text{R}^2 \text{N} \text{C}_2 \\
\hline
\text{1} & \text{6} & \text{2a} & \text{3} \\
0\% & 0\% & \text{trace} \\
\end{align*}
\]

*Standard reaction conditions:* \(1 (0.2 \text{ mmol}), \ 2a (0.3 \text{ mmol}), \ \text{B}_2 \text{Pin}_2 (0.3 \text{ mmol}), \ \text{Pd}_2(\text{dba})_3 (2.5 \text{ mol} \%), \ \text{toluene (2 mL)}, \ \text{N}_2, \ 25 ^\circ \text{C}, \ 24 \text{ h}.*
8. The data for 1 mmol scale reaction

\[
R^1 \begin{array}{c} \text{ArN} \text{BF}_4 \\ \text{BPin} \end{array} + R_1 + R_2 \xrightarrow{\text{Pd}_2\text{dba}_3 (2.5 \text{ mol} \%)} \text{toluene, 25 \text{ oC}, 24 \text{ h}} \rightarrow BPin \]

The general procedure for 1 mmol scale reaction: In an oven dried 50 mL Schlenk tube containing a stirring bar was charged with B\(_2\text{Pin}_2\) (1.5 mmol), Pd\(_2\text{dba}_3\) (2.5 mol%), and ArN\(_2\text{BF}_4\) (1.5 mmol). The tube was then evacuated and back-filled under a N\(_2\) flow (this sequence was repeated three times). Anhydrous toluene (10.0 ml), alkene 1 (1.0 mmol) were added subsequently under N\(_2\). The tube was stirred at 25 \text{oC} for 24 h. The reaction was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (EtOAc/petroleum ether) to afford the product 3.

4,4,5,5-tetramethyl-2-(2-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3a): The general procedure for 1 mmol scale reaction was followed using 1,2-dihydronaphthalene (1a, 130 mg, 1.0 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2a, 356 mg, 1.5 mmol). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1 : 20) afforded product 3a as a colorless solid (281 mg, 74% yield, >20:1 dr): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10).

4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (3c): The general procedure for 1 mmol scale reaction was followed using 1,2-dihydronaphthalene (1a, 130 mg, 1.0 mmol) and 4-(trifluoromethyl)phenyl diazonium tetrafluoroborate (2c, 390 mg, 1.5 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 40) afforded product 3c as a colorless solid (346 mg, 86% yield, >20:1 dr): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10).
Conclusion: The X-ray data of 3f and 3ad crystal could support the syn-selectivity of this Pd-catalyzed reaction.
Using 3a-OH as object, the signal of the other isomer could not be found in $^1$H-NMR. So we proposed the d.r. higher than 20:1. To double make sure d.r. of this chemistry, we separated and show all the diastereomers of 3a-OH in the HPLC traces. The detail data was shown at bellow. These data suggested the diastereoselectivity of this reaction is more than 20:1. So HPLC result supported the validity of the conclusion from 1H-NMR data.

Separation of enantiomers by HPLC, Daicel Chiralpak AD-H column, 20 °C, Hexane : i-ProOH = 90:10, 1mL/min, major retention time: $t_1 = 22.6$, minor retention time: $t_2 = 35.7$; er = 93:7.
11. The absolute configuration of the products:

The 3b-OH could be made by present reaction (eq. S1). The data of 3b-OH as bellow:

(1R,2S)-2-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (3b-OH): The general procedure B was followed using 1,2-dihydronaphthalene (1a, 13 mg, 0.10 mmol), Ligand ((R)-L8, 6 mg, 0.01 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (2b, 39 mg, 0.20 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3b-OH as a White solid (9 mg, 40% yield, >20:1 dr, 81:19 er): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.40-7.33 (m, 5H), 7.30-7.18 (m, 4H), 4.79 (s, 1H), 3.13-3.02 (m, 2H), 2.96-2.88 (m, 1H), 2.51-2.40 (m, 1H), 1.98-1.95 (m, 1H), 1.57 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 142.6, 137.6, 136.7, 130.4, 129.1, 128.6, 128.2, 128.1, 126.8, 126.1, 71.3, 46.0, 29.7, 21.5 ppm; \([\alpha]_D^{23}\) = +97.8 (c = 1.1, CHCl\(_3\)).

Separation of enantiomers by HPLC, Daicel Chiralpak AD-H column, 20 °C, Hexane : i-PrOH = 90:10, 1mL/min, major retention time: t\(_1\) = 10.0, minor retention time: t\(_2\) = 18.3; er = 81:19.

Based on the reported \(^1\)H NMR, \(^{13}\)C NMR and \([\alpha]_D^{23}\) data data of 3b-OH (reference: Chem. Sci. 2018, 9, 4505), the absolute configuration of 3b-OH should (1R,2S)-2-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (see as bellow)
### 12. Enantiomeric ratio of products

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Conditions</th>
<th>Retention time (min)</th>
<th>Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Compound 1" /></td>
<td>HPLC, Column Daicel Chiralpak AD-H, 20°C, Hexane :i-PrOH= 90:10, 1mL/min</td>
<td>t₁ = 22.6, t₂ = 35.7</td>
<td>93:7</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Compound 2" /></td>
<td>HPLC, Column Daicel Chiralpak AD-H, 20°C, Hexane :i-PrOH= 95:5, 1mL/min</td>
<td>t₁ = 15.6, t₂ = 19.9</td>
<td>94:6</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Compound 3" /></td>
<td>HPLC, Column Daicel Chiralpak AD-H, 20°C, Hexane :i-PrOH= 98:2, 1mL/min</td>
<td>t₁ = 35.4, t₂ = 78.8</td>
<td>94:6</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Compound 4" /></td>
<td>HPLC, Column Daicel Chiralpak AD-H, 20°C, Hexane :i-PrOH= 98:2, 1mL/min</td>
<td>t₁ = 34.0, t₂ = 89.6</td>
<td>95:5</td>
</tr>
</tbody>
</table>
Separation of enantiomers by HPLC, Daicel Chiralpak AD-H column, 20 °C, Hexane : \textit{i} - PrOH = 90:10, 1mL/min, major retention time: \( t_1 = 22.6 \), minor retention time: \( t_2 = 35.7 \); \( \text{er} = 93:7 \).
Separation of enantiomers by HPLC, Daicel Chiralpak AD-H column, 20 °C, Hexane : i-PrOH = 95:5, 1mL/min, minor retention time: $t_1 = 15.6$, major retention time: $t_2 = 19.9$; $er = 94:6$
Separation of enantiomers by HPLC, Daicel Chiralpak AD-H column, 20 °C, Hexane : i-PrOH = 98:2, 1mL/min, minor retention time: $t_1 = 35.4$, major retention time: $t_2 = 78.8$; er = 94:6
Separation of enantiomers by HPLC, Daicel Chiralpak AD-H column, 20 °C, Hexane : i-PrOH = 98:2, 1mL/min, minor retention time: $t_1 = 34.0$, major retention time: $t_2 = 89.6$; $er = 95:5$