Supporting Information for

Highly enantioselective Pd-catalyzed indole allylic alkylation using binaphthyl-based phosphoramidite-thioether ligands

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. $^1$H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts were reported on the delta ($\delta$) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers (CDCl$_3$: 77.0 ppm). Mass spectra were measured on a MS spectrometer (EI). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer by ESI. Enantiomeric ratios were determined by chiral HPLC with chiral columns (chiralpak AS-H column, chiralpak AD-H column, chiralcel OJ-H column, chiralpak IC-H column or chiralcel OD-H column) with hexane and $i$-PrOH as solvents. Optical rotations were measured with a polarimeter.

2. Preparation and Spectral Data of Ligands

2.1 General procedure for the preparation of secondary amine

\[
\text{Aminosulfide (2.0 mmol) and aldehyde (2.0 mmol) were dissolved in DCE (10 mL) in a flask. Then, NaB(OAc)$_3$H (1.4 eq, 2.8 mmol) was added and stirred at room temperature until the aminosulfide was totally consumed. Then was purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding products.}
\]

2.2 Characterization data of secondary amine

**(1S,2R)-N-benzyl-1,2-diphenyl-2-(o-tolylthio)ethan-1-amine (6a)**

87% yield; white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 6.74 (m, 19H), 4.25 (d, $J = 7.7$ Hz, 1H), 4.03 (d, $J = 7.7$ Hz, 1H), 3.59 (d, $J = 13.5$ Hz, 1H), 3.34 (d, $J = 13.6$ Hz, 1H), 2.16 (s, 3H), 1.95 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.5, 139.9, 139.8, 139.1, 132.9, 128.6, 128.0, 127.9, 127.8, 127.4, 127.2, 126.9, 126.6, 125.8, 65.4, 60.2, 51.2.

**(1S,2R)-N-benzyl-2-((4-bromophenyl)thio)-1,2-diphenylethan-1-amine (6b)**

67% yield; white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.08 (m, 15H), 7.08 – 7.01 (m, 2H), 6.91 – 6.83 (m, 2H), 4.31 (d, $J = 7.7$ Hz, 1H), 4.01 (d, $J = 7.7$ Hz, 1H), 3.61 (d, $J = 13.6$ Hz, 1H), 3.34 (d, $J = 13.6$ Hz, 1H), 1.92 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.0, 139.6, 138.5, 133.9, 133.5, 131.3, 128.6, 128.2, 128.1, 128.0, 127.8, 127.6, 127.4, 126.7, 120.9, 77.3, 77.0, 76.6, 65.5, 60.9, 51.0.
(1S,2R)-2-((4-bromophenyl)thio)-N-(cyclohexylmethyl)-1,2-diphenylethan-1-amine (6c)

90% yield; white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)

- 7.30 – 7.14 (m, 12H), 6.95 – 6.89 (m, 2H), 4.31 (d, \(J = 7.5\) Hz, 1H), 3.97 (d, \(J = 7.5\) Hz, 1H), 2.12 (d, \(J = 6.7\) Hz, 2H), 1.69 – 1.52 (m, 5H), 1.45 (d, \(J = 12.9\) Hz, 1H), 1.36-1.25 (m, 1H), 1.20-0.95 (m, 3H), 0.85 – 0.55 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

- 140.8, 138.9, 134.3, 133.4, 132.6, 131.5, 128.7, 128.2, 128.2, 127.9, 127.5, 120.8, 67.1, 60.8, 54.2, 37.6, 31.2, 31.1, 26.6, 25.9.

2.3 General procedure for the preparation of ligands

PCl\(_3\) (1.0 eq, 1.0 mmol) and Et\(_3\)N (1.1 eq, 1.1 mmol) were mixed in toluene (5 mL). Then, aminosulfide (1.0 mmol) was added in toluene (1 mL) and stirred for 7 h at 70 °C. Then, the mixture was cooled to 0 °C, Et\(_3\)N (3.3 eq, 3.3 mmol) and \(R\)-BINOL (1.0 mmol) in toluene (1 mL) were added and stirred at room temperature until the aminosulfide was totally consumed. Then, the mixture was purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding ligand.

2.4 Characterization data of ligands

N-benzyl-N-((1S,2R)-2-(naphthalen-2-ylthio)-1,2-diphenylethyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L4)

75% yield; white solid; melting point 142 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)

- 7.89 (t, \(J = 9.2\) Hz, 2H), 7.71 (d, \(J = 6.7\) Hz, 3H), 7.64 (d, \(J = 8.9\) Hz, 1H), 7.55 (t, \(J = 7.4\) Hz, 2H), 7.48 (d, \(J = 7.3\) Hz, 1H), 7.38 (t, \(J = 7.8\) Hz, 1H), 7.35-7.09 (m, 13H), 7.05-6.90 (m, 2H), 6.90-6.75 (m, 6H), 6.68 (d, \(J = 8.8\) Hz, 1H), 5.02 (d, \(J = 12.0\) Hz, 1H), 4.29 (dd, \(J = 17.7, 12.2\) Hz, 1H), 3.81 (d, \(J = 14.4\) Hz, 1H), 2.88 (d, \(J = 14.4\) Hz, 1H), 1.98 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

- 150.3, 149.2, 141.3, 140.1, 139.5, 136.8, 135.1, 133.3, 132.7, 132.4, 131.4, 130.3, 129.9, 129.8, 129.3, 128.9, 128.3, 128.0, 127.8, 127.6, 127.2, 127.0, 126.8, 126.0, 125.8, 124.8, 124.4, 124.1, 121.6, 65.4 (d, \(J = 65.5\) Hz), 57.2 (d, \(J = 57.2\) Hz), 48.6, 20.5 (d, \(J = 20.5\) Hz). \(^3\)P NMR (160 MHz CDCl\(_3\)) \(\delta\) 137.9. HRMS m/z: anal. calcd for C\(_{48}\)H\(_{37}\)NO\(_2\)PS [M-H]: 722.2277, found: 722.2269.

N-((1S,2R)-2-((4-bromophenyl)thio)-1,2-diphenylethyl)-N-(cyclohexylmethyl)-2,6-diiododinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L5)

60% yield; white solid; melting point 136 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\)

- 8.47 (s, 1H), 8.28 (s, 1H), 7.76 (d, \(J = 8.3\) Hz, 1H), 7.73 – 7.64 (m, 2H), 7.50 – 7.29 (m, 6H), 7.26 (s, 1H), 7.21 (t, \(J = 7.6\) Hz, 2H), 7.18 – 7.11 (m, 4H), 7.02 (dd, \(J = 14.8, 8.7\) Hz, 2H), 6.88 – 6.76 (m, 2H), 5.29 (d, \(J = 6\) Hz 1H), 4.61 (dd, \(J = 20.0, 11.0\) Hz, 1H), 2.55 (s, 1H), 2.30 (s, 1H), 1.24 (dd, \(J = 75.8, 31.9\) Hz, 6H), 1.02 (d, \(J = 11.2\) Hz, 1H), 0.70 (d, \(J = 10.2\) Hz, 2H), 0.24 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

- 149.7, 147.8, 140.0, 139.6, 139.4, 139.2, 135.2, 134.9, 133.1, 132.4, 132.3, 132.2, 131.4, 131.3, 131.1, 130.3, 130.0, 129.6, 128.9, 128.3, 128.3, 127.3, 127.0, 126.9, 126.8, 126.7, 126.5, 126.3, 125.6, 125.1, 124.4, 121.8, 121.1, 91.5, 91.5, 90.0, \(\delta\) 58.50 (d, \(J = 22.6\) Hz), 51.9, 34.2, 30.9.
30.3, 26.0, 25.8, 25.3. \(^{31}P\) NMR (160 MHz CDCl\(_3\)) \(\delta\) 143.56. HRMS m/z: anal. calcd for C\(_{48}\)H\(_{37}\)NO\(_2\)PS [M+K]\(^+\): 1083.9343, found:1083.9342.

N-((1S,2R)-2-((4-bromophenyl)thio)-1,2-diphenylethyl)-N-(cyclohexylmethyl)-2,6-diphenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L6)

\[ \text{63\% yield; w\hite solid; melting point 151 °C} \]
\[ \text{^1H NMR (400 MHz, CDCl}_3\text{))} \quad \delta \]
\[ 8.05 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.81-7.65 (m, 4H), 7.56-7.35 (m, 10H), 7.32-7.25 (m, 2H), 7.19-7.01 (m, 6H), 6.94 (t, J = 7.6 Hz, 2H), 6.78-6.59 (m, 4H), 6.25-6.13 (m, 2H), 4.40 (dd, J = 9.1, 3.4 Hz, 1H), 4.16 (dd, J = 7.1, 3.4 Hz, 1H), 2.55-2.41 (m, 1H), 1.84 (dt, J = 13.7, 3.9 Hz, 1H), 1.54 (d, J = 4.0 Hz, 1H), 1.46 (s, 1H), 1.43 – 1.36 (m, 2H), 1.28 (d, J = 14.8 Hz, 1H), 0.97 – 0.79 (m, 6H), 0.67 (t, J = 11.4 Hz, 1H). \]
\[ \text{^13C NMR (101 MHz, CDCl}_3\text{))} \quad \delta \]
\[ 148.1, 148.0, 146.9, 139.8, 138.2, 138.1, 135.1, 134.4, 133.9, 132.5, 132.2, 131.4, 131.4, 131.1, 131.0, 130.5, 130.1, 130.0, 129.9, 129.1, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.3, 127.2, 127.1, 126.9, 126.9, 126.8, 125.9, 125.6, 125.5, 124.9, 124.5, 122.7, 119.8, 67.59 (d, J = 18.8 Hz), 57.40 (d, J = 41.4 Hz), 49.2, 34.0, 31.0, 30.2, 26.3, 25.7, 25.6. \]

Diphenyl ((1S,2R)-2-((4-bromophenyl)thio)-1,2-diphenylethyl)(cyclohexylmethyl)phosphoramide (L8)

\[ \text{68\% yield; w\hite solid; melting point 101 °C} \]
\[ \text{^1H NMR (400 MHz, CDCl}_3\text{))} \quad \delta \]
\[ 7.40 (d, J = 6.4 Hz, 2H), 7.34 – 7.20 (m, 5H), 7.20 – 7.06 (m, 8H), 7.00 (d, J = 7.4 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 7.9 Hz, 2H), 6.62 (d, J = 7.9 Hz, 2H), 5.03 (d, J = 11.7 Hz, 1H), 4.68 (dd, J = 19.7, 11.7 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.54 (d, J = 14.3 Hz, 1H), 1.72-1.60 (m, 1H), 1.52-1.42 (m, 1H), 1.25-1.21 (m, 4H), 0.95 – 0.71 (m, 2H), 0.69-0.52 (m, 1H). \]
\[ \text{^13C NMR (100 MHz, CDCl}_3\text{))} \quad \delta \]
\[ 139.5, 139.1, 135.0, 131.2, 129.1, 129.1, 128.8, 128.8, 128.6, 128.6, 128.0, 127.9, 127.7, 127.1, 122.7, 122.5, 120.2, 120.1, 119.8, 119.7, 66.5 (d, J = 23.4 Hz), 57.9 (d, J = 21.3 Hz), 49.9, 35.2, 31.5, 29.8, 26.7, 26.5, 26.2. \]

HRMS m/z: anal. calcd for C\(_{39}\)H\(_{39}\)BrNO\(_2\)PS [M+H]\(^+\): 696.1701, found: 696.1683.
2.5 Copies of $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR Spectra of ligands

$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{31}$P NMR (160 MHz, CDCl$_3$) spectra of product L4
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{31}$P NMR (160 MHz, CDCl$_3$) spectra of product L5
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{31}$P NMR (160 MHz, CDCl$_3$) spectra of product L6
$\text{H NMR (400 MHz, CDCl}_3\text{), }^{13}\text{C NMR (100 MHz, CDCl}_3\text{) and }^{31}\text{P NMR (160 MHz, CDCl}_3\text{) spectra of product L8}$
3. Detailed Optimization of Reaction Conditions

*Table S1. Screen of the bases for the enantioselective allylic reaction*  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>t (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K2CO3 (2.0 eq.)</td>
<td>18</td>
<td>82</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>Cs2CO3 (2.0 eq.)</td>
<td>10</td>
<td>87</td>
<td>71</td>
</tr>
<tr>
<td>3⁺</td>
<td>Cs2CO3 (2.0 eq.)</td>
<td>48</td>
<td>85</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>BSA (2.0 eq.) + LiOAc (0.1 eq.)</td>
<td>24</td>
<td>85</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>BSA (2.0 eq.) + KOAc (0.1 eq.)</td>
<td>24</td>
<td>88</td>
<td>71</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, reactions were carried out with 1a (0.90 mmol), 2a (0.30 mmol), [Pd(C3H5)Cl]2 (0.006 mmol), L3 (0.012 mmol) in CH2Cl2 (2.0 mL).  

b Isolated yield.  

c Determined by chiral HPLC.  

⁺ React at room temperature.

As shown in Table S1, among all the bases, the Cs2CO3 (2 eq.) in CH2Cl2 at 40 °C gave the best result in terms of reaction efficiency, and was thus selected for further optimization studies.

*Table S2. Screen of ligands for the enantioselective allylic reaction*  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L3</td>
<td>24</td>
<td>87</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>L4</td>
<td>24</td>
<td>97</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>L5</td>
<td>24</td>
<td>84</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>L6</td>
<td>24</td>
<td>90</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>L7</td>
<td>24</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>L8</td>
<td>10</td>
<td>85</td>
<td>35</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, reactions were carried out with 1a (0.90 mmol), 2a (0.30 mmol), [Pd(C3H5)Cl]2 (0.006 mmol), ligand (0.012 mmol), Cs2CO3 (0.60 mmol) in CH2Cl2 (2.0 mL) at 40 °C.  

b Isolated yield.  

c Determined by chiral HPLC.

As shown in Table S2, among the ligands tested, ligand L6 gave the best results (entry 5), and was thus selected for further studies.
Table S3. Screen the solvents for the enantioselective allylic reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>t (h)</th>
<th>Yield (b) (%)</th>
<th>ee (c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>10</td>
<td>90</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>CHCl$_3$</td>
<td>10</td>
<td>80</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>5</td>
<td>88</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>xylenes</td>
<td>5</td>
<td>89</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>mesitylene</td>
<td>5</td>
<td>90</td>
<td>97</td>
</tr>
</tbody>
</table>

$^a$ Unless otherwise noted, reactions were carried out with 1a (0.90 mmol), 2a (0.30 mmol), [Pd(C$_3$H$_5$)Cl]$_2$ (0.006 mmol), L6 (0.012 mmol), Cs$_2$CO$_3$ (0.60 mmol) in solvent (2.0 mL) at 40 °C. $^b$ Isolated yield. $^c$ Determined by chiral HPLC.

As shown in Table S3, among the solvents tested, mesitylene gave the best result in terms of yield and enantioselectivity (entry 5), and was thus selected for further studies.

Table S4. Screen the ratio of indole to allylic acetate

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ratio (x:y)</th>
<th>t (h)</th>
<th>Yield (b) (%)</th>
<th>ee (c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3:1</td>
<td>5</td>
<td>90</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>1.5:1</td>
<td>5</td>
<td>89</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>1:1.5</td>
<td>5</td>
<td>92</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>1:2</td>
<td>5</td>
<td>90</td>
<td>86</td>
</tr>
</tbody>
</table>

$^a$ Unless otherwise noted, reactions were carried out with 1a (0.3x mmol), 2a (0.3y mmol), [Pd(C$_3$H$_5$)Cl]$_2$ (0.006 mmol), L6 (0.012 mmol), Cs$_2$CO$_3$ (0.60 mmol) in mesitylene (2.0 mL) at 40 °C. $^b$ Isolated yield. $^c$ Determined by chiral HPLC.

As shown in Table S4, among the ratio tested, the ratio of 1:1.5 of 1a to 2a gave the best result in terms of yield and enantioselectivity (entry 3), and thus the optimized reaction condition was confirmed: 1 (0.3 mmol), 2 (0.45 mmol), 2 mol% of [Pd(C$_3$H$_5$)Cl]$_2$, 4 mol% of ligand L6, and 2.0 equivalents of Cs$_2$CO$_3$ in mesitylene at 40 °C.
4. General Procedure for Pd-Catalyzed Enantioselective Allylic Substitution

Reactions and Spectral Data

4.1 General procedure for Pd-catalyzed enantioselective allylic substitution reactions

Ligand L6 (11.3 mg, 0.012 mmol, 4 mol%) and [Pd(C₃H₅)Cl]₂ (2.2 mg, 0.006 mmol, 2 mol%) were dissolved in mesitylene (1.0 mL) in a Schlenk tube under Ar. After stirring at room temperature for 1 h, allylic acetate 2 (0.45 mmol) in mesitylene (1.0 mL) was added, followed by indoles 1 (0.3 mmol), Cs₂CO₃ (197 mg, 0.6 mmol). The mixture was stirred at 40 oC until indoles was totally consumed, and then was purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product 3.

4.2 Spectral data of allylic reaction products

(S, E)-3-(1,3-diphenylallyl)-1H-indole (3a) \[1\]

Yield: 90%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90: 10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tᵣ = 20.995 min (minor) for (R)-isomer, tᵣ = 23.581 min (major) for (S)-isomer. ee = 97%. \([\alpha]_D^{21} 255.6 (c = 1.0, CHCl₃)\). \[^1^H\] NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.46 (d, \(J = 7.9 \text{ Hz}, 1H\)), 7.42 – 7.15 (m, 12 H), 7.03-6.95 (m, 1H), 6.89 (dd, \(J = 2.4, 1.0 \text{ Hz}, 1H\)), 6.76 (dd, \(J = 15.7, 7.3 \text{ Hz}, 1H\)), 6.47 (d, \(J = 16, 1H\)), 5.16 (d, \(J = 7.4 \text{ Hz}, 1H\)). \[^{13}^C\] NMR (100 MHz, CDCl₃) δ 143.1, 137.2, 136.4, 132.3, 130.3, 128.3, 128.2, 127.0, 126.6, 126.2, 126.1, 122.4, 119.7, 119.2, 118.5, 111.0, 46.2. MS m/z: anal. calcd for C₂₃H₁₉N [M]⁺: 309.15, found: 309.14.

(S, E)-3-(1,3-diphenylallyl)-2-phenyl-1H-indole (3b) \[1\]

Yield: 70%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 85: 15 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tᵣ = 6.860 min (major) for (S)-isomer, tᵣ = 7.438 min (minor) for (R)-isomer. ee = 82%. \([\alpha]_D^{21} 312 (c = 1.0, CHCl₃)\). \[^1^H\] NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.56 – 7.46 (m, 2H), 7.41 (t, \(J = 7.4 \text{ Hz}, 2H\)), 7.37 – 7.29 (m, 5H), 7.26 – 7.20 (m, 4H), 7.19 – 7.03 (m, 4H), 6.96 (t, \(J = 7.5 \text{ Hz}, 1H\)), 6.86 (dd, \(J = 15.7, 7.3 \text{ Hz}, 1H\)), 6.46 – 6.28 (m, 1H), 5.26 (d, \(J = 7.3 \text{ Hz}, 1H\)). \[^{13}^C\] NMR (100 MHz, CDCl₃) δ 143.3, 137.3, 136.4, 132.3, 130.3, 128.3, 128.2, 127.0, 126.6, 126.2, 126.1, 122.4, 121.9, 119.7, 119.2, 118.5, 111.0, 46.2. MS m/z: anal. calcd for C₂₉H₂₃N [M]⁺: 385.18, found: 385.51.

(S, E)-3-(1,3-diphenylallyl)-2-methyl-1H-indole (3c) \[1\]

Yield: 82%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95: 5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tᵣ = 33.353 min (major) for (S)-isomer, tᵣ = 35.932 min (major) for (R)-isomer. ee = 95%. \([\alpha]_D^{21} 163.9 (c = 1.0, CHCl₃)\). \[^1^H\] NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.21 – 7.03 (m, 10 H), 6.97 (d, \(J = 8.3 \text{ Hz}, 1H\)), 6.91 (t, \(J = 7.6 \text{ Hz}, 1H\)), 6.73 – 6.52 (m, 3H), 6.09 (d, \(J = 15.8 \text{ Hz}, 1H\)), 5.31 (d, \(J = 6.5 \text{ Hz}, 1H\)), 2.40 (s, 3H). \[^{13}^C\] NMR (100 MHz, CDCl₃) δ 143.2, 137.3, 135.1, 132.0, 131.5, 130.4, 128.3, 128.1, 128.1, 127.8, 126.9, 126.1, 125.9, 121.9, 121.0, 119.5, 113.7, 110.8, 45.2. MS m/z: anal. calcd for C₂₄H₂₁N [M]⁺: 323.17, found: 323.44.
(S, E)-(3-((4-methoxybenzyl)oxy)prop-1-ene-1,3-diyl) dibenzene (3d) [1]

Yield: 99%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 91:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 14.322 min (major) for (S)-isomer, tR = 16.066 min (minor) for (R)-isomer. ee = 86%. [α]D 25 185 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.62 (s, 1H), 7.28 – 7.00 (m, 11H), 7.00 – 6.87 (m, 2H), 6.73 – 6.52 (m, 3H), 6.09 (d, J = 15.8 Hz, 1H), 5.31 (d, J = 6.5 Hz, 1H), 2.40 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 188.0, 143.8, 137.2, 136.6, 133.7, 130.8, 130.4, 128.6, 128.3, 128.2, 128.1, 126.9, 126.1, 126.1, 125.3, 123.3, 122.0, 121.0, 118.6, 108.9, 46.5, 20.5. MS m/z: anal. calcld for C32H23N [M]+: 332.17, found: 323.21.

(S, E)-4-bromo-3-(1,3-diphenylallyl)-1H-indole (3e) [1]

Yield: 82%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 16.107 min (major) for (S)-isomer, tR = 18.383 min (minor) for (R)-isomer. ee = 93%. [α]D 23 220 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.92 (s, 1H), 7.49 (d, J = 1.8 Hz, 1H), 7.41 – 6.98 (m, 12H), 6.81 (d, J = 2.5 Hz, 1H), 6.63 (dd, J = 15.7, 7.3 Hz, 1H), 6.36 (d, J = 15.7 Hz, 1H), 5.01 (d, J = 7.3 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 142.8, 137.2, 135.2, 132.0, 130.7, 128.5, 128.3, 127.2, 126.5, 126.3, 124.9, 123.8, 122.2, 118.3, 112.7, 112.6, 45.8. MS m/z: anal. calcld for C32H18BrN [M]+: 387.06, found: 387.15.

(S, E)-(3-((4-chlorobenzyl)oxy)prop-1-ene-1,3-diyl) dibenzene (3f) [1]

Yield: 80%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 34.259 min (minor) for (R)-isomer, tR = 39.353 min (major) for (S)-isomer. ee = 97%. [α]D 23 203.7 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.79 (s, 1H), 7.38 – 7.10 (m, 16H), 6.94 – 6.82 (m, 2H), 6.78 (d, J = 2.4 Hz, 1H), 6.65 (dd, J = 15.7, 7.3 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 5.01 (d, J = 7.3 Hz, 1H), 4.91 (s, 2H). 13C NMR (100 MHz, CDCl3) δ 152.6, 143.0, 137.3, 137.2, 132.2, 131.7, 130.3, 128.3, 128.3, 128.2, 127.5, 127.4, 127.0, 126.9, 126.2, 126.1, 126.1, 118.1, 112.7, 111.7, 103.1, 70.7, 46.2. MS m/z: anal. calcld for C32H19ClNO [M]+: 415.19, found: 415.27.

(3S, E)-3-((4-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (3g) [1]

Yield: 82%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 23.104 min (minor) for (R)-isomer, tR = 28.418 min (major) for (S)-isomer. ee = 98%. [α]D 23 387.6 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.64 (s, 1H), 7.18 (d, J = 7.1 Hz, 4H), 7.14 – 7.08 (m, 3H), 7.08 – 6.98 (m, 3H), 6.97 – 6.93 (m, 1H), 6.70 (d, J = 2.5 Hz, 1H), 6.66 (dd, J = 8.7, 2.5 Hz, 1H), 6.59 (dd, J = 2.6, 1.1 Hz, 1H), 6.54 (dd, J = 15.7, 7.3 Hz, 1H), 6.28 (d, J = 15.8 Hz, 1H), 4.90 (d, J = 7.3 Hz, 1H), 3.54 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 153.6, 143.2, 137.4, 132.4, 131.7, 130.4, 128.4, 128.3, 127.1, 126.3, 126.2, 123.4, 118.0, 111.9, 111.8, 101.7, 55.7, 46.1. MS m/z: anal. calcld for C32H19ClNO [M]+: 439.16, found: 439.21.

(S, E)-(3-((4-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (3h) [1]

Yield: 83%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 16.069 min (minor) for (R)-isomer, tR = 17.578 min (major) for (S)-isomer. ee = 97%. [α]D 21 278.8 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.56 (s, 1H), 7.38 – 7.03 (m, 12H), 6.93 (d, J = 8.3 Hz, 1H), 6.76 – 6.59 (m, 2H), 6.35 (d, J = 15.7 Hz, 1H), 5.03 (d, J = 7.3 Hz, 1H), 2.33 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 152.6, 143.0, 137.3, 137.2, 132.2, 131.7, 130.3, 128.3, 128.3, 128.2, 128.2, 127.5, 127.4, 127.0, 126.9, 126.2, 126.1, 123.3, 118.1, 112.7, 111.7, 103.1, 70.7, 46.2. MS m/z: anal. calcld for C32H19N [M]+: 323.17, found: 323.20.

S14
(S, E)-5-bromo-3-(1,3-diphenallyl)-1H-indole (3i) [1]

Yield: 88%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 16.862 min (minor) for (R)-isomer, t_R = 19.425 min (major) for (S)-isomer. ee = 95%. [α]D²¹ = 278.8 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.34 – 7.08 (m, 12H), 6.81 (d, J = 2.4 Hz, 1H), 6.63 (dd, J = 15.7, 7.3 Hz, 1H), 6.36 (d, J = 15.7 Hz, 1H), 5.01 (d, J = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 137.0, 134.9, 131.8, 130.5, 128.3, 128.3, 127.1, 126.2, 121.2, 121.0, 119.4, 118.2, 111.0, 46.3, 21.8. MS m/z: anal. calcld for C₂₅H₂₃NO₂ [M⁺]: 387.06, found: 387.17.

(S, E)-3-(1,3-diphenallyl)-6-methyl-1H-indole (3j) [1]

Yield: 72%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 22.039 min (minor) for (R)-isomer, t_R = 26.249 min (major) for (S)-isomer. ee = 96%. [α]D²¹ = 429.9 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.35 – 7.10 (m, 11H), 7.03 (s, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.74 – 6.60 (m, 2H), 6.40 (d, J = 15.8 Hz, 1H), 5.05 (d, J = 7.4 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 137.3, 136.9, 132.4, 131.7, 130.2, 128.3, 128.2, 127.0, 126.2, 124.5, 121.8, 121.0, 119.4, 118.2, 111.0, 46.3, 21.8. MS m/z: anal. calcld for C₂₃H₁₈ClN [M⁺]: 323.17, found: 323.22.

(S, E)-6-chloro-3-(1,3-diphenallyl)-1H-indole (3k) [1]

Yield: 73%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 41.833 min (minor) for (R)-isomer, t_R = 43.818 min (major) for (S)-isomer. ee = 97%. [α]D²¹ = 213.7 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.49 (d, J = 1.8 Hz, 1H), 7.41 – 6.98 (m, 12H), 6.81 (d, J = 2.5 Hz, 1H), 6.63 (dd, J = 15.7, 7.3 Hz, 1H), 6.36 (d, J = 15.7 Hz, 1H), 5.01 (d, J = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 137.3, 136.9, 132.4, 131.7, 130.2, 128.3, 128.2, 127.0, 126.2, 124.5, 121.8, 121.0, 119.4, 118.2, 111.0, 46.3, 21.8. MS m/z: anal. calcld for C₂₃H₁₈ClN [M⁺]: 343.11, found: 343.15.

(S, E)-3-(1,3-diphenallyl)-7-methyl-1H-indole (3l) [1]

Yield: 88%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 21.002 min (major) for (S)-isomer. ee = 96%. [α]D²¹ = 202.3 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (s, 1H), 7.39 – 7.07 (m, 16H), 6.92 – 6.82 (m, 2H), 6.78 (d, J = 2.4 Hz, 1H), 6.65 (dd, J = 15.7, 7.3 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 5.01 (d, J = 7.3 Hz, 1H), 4.91 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 137.4, 136.1, 132.5, 130.4, 128.4, 128.3, 127.1, 126.3, 126.2, 122.5, 122.3, 120.2, 119.5, 118.9, 117.5, 46.2, 16.5. MS m/z: anal. calcld for C₂₃H₂₃NO₂ [M⁺]: 371.17, found: 373.17.

(S, E)-3-(1,3-diphenallyl)-5,6-dimethoxy-1H-indole (3m) [1]

Yield: 99%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: t_R = 34.794 min (minor) for (R)-isomer, t_R = 45.927 min (major) for (S)-isomer. ee = 98%. [α]D²¹ = 71.8 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.38 – 7.02 (m, 10H), 6.75 (s, 1H), 6.69 (s, 1H), 6.67 – 6.56 (m, 2H), 6.40 (d, J = 15.7 Hz, 1H), 5.00 (d, J = 7.3 Hz, 1H), 4.91 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 137.4, 136.1, 132.5, 130.4, 128.4, 128.3, 127.1, 126.3, 126.2, 122.5, 122.3, 120.2, 119.5, 118.9, 117.5, 46.2, 16.5. MS m/z: anal. calcld for C₂₃H₂₃NO₂ [M⁺]: 369.17, found: 369.20.
Yield: 82%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 16.589 min (major) for (S)-isomer, tR = 16.700 min (minor) for (R)-isomer. ee = 98%. [α]D23 155.5 (c = 1.0, CHCl3).

1H NMR (600 MHz, CDCl3) δ 8.04 (s, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.26 (q, J = 8.1 Hz, 8H), 7.19 (t, J = 7.7 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 2.4 Hz, 1H), 6.65 (dd, J = 15.8, 7.2 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 5.08 (d, J = 7.2 Hz, 1H).

13C NMR (100 MHz, CDCl3) δ 141.3, 136.4, 135.5, 132.6, 132.4, 131.9, 129.6, 129.5, 128.4, 128.4, 127.3, 126.3, 122.4, 122.1, 119.5, 119.4, 117.7, 111.1, 45.5. MS m/z: anal. calcd for C23H17Cl2N [M]+: 377.07, found: 377.15.

(R, E)-3-(4-phenylbut-3-en-2-yl)-1H-indole (3o) [1]
Yield: 89%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 32.053 min (minor) for (R)-isomer, tR = 34.850 min (major) for (S)-isomer. ee = 53%. [α]D23 151.6 (c = 1.0, CHCl3).

1H NMR (400 MHz, Chloroform-d) δ 7.93 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 3H), 7.18 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.56 – 6.37 (m, 2H), 3.91 (q, J = 6.6 Hz, 1H), 1.57 (d, J = 6.9 Hz 5H including H 2O).

13C NMR (100 MHz, CDCl3) δ 137.7, 136.5, 135.4, 128.4, 128.1, 126.8, 126.7, 126.1, 121.9, 120.4, 120.3, 119.6, 119.2, 111.1, 34.2, 20.7. MS m/z: anal. calcd for C18H17N [M]+: 247.14, found: 247.14.

(R, E)-3-(4-(pyridin-4-yl)but-3-en-2-yl)-1H-indole
Yield: 89%. The ee was determined by chiral HPLC (Chiralcel AD-H, hexane/isopropanol 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 18.511 min (minor) for (R)-isomer, tR = 23.694 min (major) for (S)-isomer. ee = 41%. [α]D23 -551.5 (c = 1.0, CHCl3).

1H NMR (400 MHz, CDCl3) δ 8.44 (d, J = 5.3 Hz, 2H), 8.34 (s, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.07 (p, J = 7.5 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.67 (dd, J = 15.8, 6.9 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 3.95 (t, J = 7.0 Hz, 1H), 1.57 (d, J = 7.0 Hz, 3H).

13C NMR (100 MHz, CDCl3) δ 149.5, 145.1, 140.4, 136.4, 126.4, 125.8, 121.9, 120.7, 120.5, 119.2, 111.2, 34.4, 20.4. HRMS m/z: anal. calcd for C13H13NO2[M+Na]+: 271.1211, found: 271.1238.

4.3 General procedure for Pd-catalyzed enantioselective allylic etherification and amination reactions

Ligand L6 (11.3 mg, 0.012 mmol, 4 mol%) and [Pd(C5H5)Cl]2 (2.2 mg, 0.006 mmol, 2 mol%) were dissolved in CH2Cl2 (1.0 mL) in a Schlenk tube under Ar. After stirring at room temperature for 1 h, allylic acetate 2a (0.45 mmol) in CH2Cl2 (1.0 mL) was added, followed by benzylamine or benzylalcohol (0.3 mmol), Cs2CO3 (197 mg, 0.6 mmol). The mixture was stirred at 40 °C until indoles was totally consumed, and then was purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product 9 and 11.

4.4 Spectral Data of Allylic Reaction Products

(S,E)-(3-benzyloxy)prop-1-ene-1,3-diyldibenzene (9) [2]
Yield: 95%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, \( \lambda = 254 \) nm, 25 °C). Retention times: \( t_R = 6.028 \) min (major) for (S)-isomer, \( t_R = 6.525 \) min (minor) for (R)-isomer. ee = 98%. \([\alpha]_D^{23} = -15.9 \) (c = 1.0, toluene). ¹H NMR (600 MHz, CDCl₃) \( \delta 7.43 \) (d, \( J = 7.3 \) Hz, 2H), 7.41-7.33 (m, 8H), 7.21-7.28 (m, 4H), 7.24-7.20 (m, 1H), 6.63 (d, \( J = 16.2 \) Hz, 1H), 6.34 (dd, \( J = 16.7, 7.2 \) Hz, 1H), 5.01 (d, \( J = 7.2 \) Hz, 1H), 4.57 (dd, \( J = 15.6, 12.0 \) Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) \( \delta 141.0, 138.3, 136.5, 131.5, 130.2, 128.5, 128.3, 127.7, 127.7, 127.5, 126.9, 126.5, 81.5, 70.0\). HRMS (EI) m/z: calcd for C₂₂H₂₀O \([M]+: 300.1514\), found: 300.1520.

(S,E)-N-benzyl-1,3-diphenylprop-2-en-1-amine (11) [²]

Yield: 90%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, \( \lambda = 254 \) nm, 25 °C). Retention times: \( t_R = 8.627 \) min (minor) for (R)-isomer, \( t_R = 9.228 \) min (major) for (S)-isomer. ee = 97%. \([\alpha]_D^{23} = -19.66 \) (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) \( \delta 7.52 – 7.39 \) (m, 2H), 7.36-7.32 (m, 7H), 7.30 (s, 1H), 7.29 – 7.12 (m, 5H). 6.58 (d, \( J = 15.8 \) Hz, 1H), 6.32 (dd, \( J = 15.9, 7.5 \) Hz, 1H), 4.40 (d, \( J = 7.5 \) Hz, 1H), 3.79 (dd, \( J = 17.6 \) Hz, \( J = 9.2 \) Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) \( \delta 142.8, 140.3, 136.8, 132.5, 130.3, 128.6, 128.4, 128.2, 127.4, 127.3, 127.3, 126.9, 126.4, 64.5, 51.3). MS m/z: anal. calcd for C₂₂H₂₁N \([M]+: 299.17\), found: 299.22.

5. References


6. Copies of $^1$H NMR and $^{13}$C NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3a.
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3b
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3c
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3d
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3e
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) and $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) spectra of product 3f
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3g
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3i
1H NMR (400 MHz, CDCl3) and 13C NMR (100 MHz, CDCl3) spectra of product 3j
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3k
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3l
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3m
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3n
$^{1}$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3o
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3p
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 9
$^1$H NMR (400 MHz, CDCl₃) and $^{13}$C NMR (100 MHz, CDCl₃) spectra of product 11
7. Copies of HPLC Chromatograms

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Peak RetTime Type Width Area Height Area
# [min] [min] mAU s mAU %
1 33.033 BV 0.8531 2.19511e4 397.98581 49.4644
2 35.187 VV 0.9665 2.26265e4 355.25589 50.5356

Peak RetTime Type Width Area Height Area
# [min] [min] mAU s mAU %
1 33.353 BB 0.8097 4.09202e4 739.90649 97.6095
2 35.932 BR 0.7775 1.002.141e2 19.77868 2.3905

Peak RetTime Type Width Area Height Area
# [min] [min] mAU s mAU %
1 14.325 VB 0.4069 1932.80505 73.9610 49.9842
2 16.186 BI 0.5102 2140.22205 40.15617 50.0958

Peak RetTime Type Width Area Height Area
# [min] [min] mAU s mAU %
1 14.322 VB 0.4039 1959.14697 173.35382 7.0750
2 16.064 BB 0.4872 5.92240b4 1834.932b8 92.9250
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