Supporting Information for

Development of A New Phosphoramidite-Selenide Ligand for Highly Enantioselective Pd-Catalyzed Asymmetric Allylic Substitution

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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 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 column, chiralpak IA column or chiralpak OD 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 aminoselenide

$$\text{Ph}_2\text{N} + \text{PhSeH} \xrightarrow{1) \text{MeOH, 50 }^\circ\text{C}, \text{N}_2} \text{Ph}_2\text{N} = \text{PhSePh}$$

The aziridine was synthesized according to the reported work.[1] Aziridine (5.0 mmol) and benzeneselenol (6.0 mmol) were dissolved in MeOH (25 mL) in a flask, under N$_2$. Then, warmed to 50 $^\circ$C, and stirred. After the aziridine was totally consumed monitored by TLC ($V_{PE} : V_{EA} = 5:1$), benzaldehyde (7.5 mmol) was added, stirred until the above primary amine was totally consumed monitored by TLC ($V_{PE} : V_{EA} = 10:1$), then the system was cooled to 0 $^\circ$C, NaBH$_4$ (10.0 mmol) was added portion-wisely, stirred for 3 h. After the solvent was evaporated under vacuum, the crude product was added 20 mL NH$_4$Cl (sat, aq.), extracted with CH$_2$Cl$_2$ (3×20 mL), and the organic layer was dried over Na$_2$SO$_4$. After the solvent was evaporated under vacuum, the crude product was purified by flash chromatography ($V_{PE} : V_{EA} = 10:1$), eluting with petroleum ether and ethyl acetate to afford the corresponding products.

2.2 General procedure for the preparation of aminothioether

$$\text{Ph}_2\text{N} + \text{PhSH} \xrightarrow{1) \text{MeOH, reflux}} \text{Ph}_2\text{N} = \text{PhSH}$$

The aziridine was synthesized according to the reported work.[1] Aziridine (5.0 mmol) and thiophenol (6.0 mmol) were dissolved in MeOH (25 mL) in a flask, warmed to reflux, and stirred. After the aziridine was totally consumed monitored by TLC ($V_{PE} : V_{EA} = 5:1$), benzaldehyde (7.5 mmol) was added, stirred until the above primary amine was totally consumed...
monitored by TLC (\(V_{PE}:V_{EA} = 10:1\)), then the system was cooled to 0 °C, NaBH₄ (10.0 mmol) was added portion-wisely, stirred overnight. After the solvent was evaporated under vacuum, the crude product was added 20 mL NH₄Cl (sat, aq.), extracted with CH₂Cl₂ (3×20 mL), and the organic layer was dried over Na₂SO₄. After the solvent was evaporated under vacuum, the crude product was purified by flash chromatography (\(V_{PE}:V_{EA} = 10:1\)), eluting with petroleum ether and ethyl acetate to afford the corresponding products.

2.3 Characterization data of aminoselenide and aminothioether

\((1S,2R)-N\text{-}benzyl\text{-}1,2\text{-}diphenyl\text{-}2\text{-}(phenylselanyl)\text{ethan}\text{-}1\text{-}amine\)  
\[
87\% \text{ yield; white solid; melting point } 86.7 ^\circ \text{C}; \quad [\alpha] -120.283 \text{ (c}=1.0, \text{CHCl}_3). \quad ^1\text{H NMR} (400 MHz, CDCl}_3) \delta 7.35-7.20 (m, 8H), 7.18-7.01 (m, 12H), 4.45 (d, \text{J} = 8.3 \text{ Hz, 1H}), 4.13 (d, \text{J} = 8.3 \text{ Hz, 1H}), 3.61 (d, \text{J} = 13.6 \text{ Hz, 1H}), 3.35 (d, \text{J} = 13.6 \text{ Hz, 1H}), 3.19 (s, 1H). \quad ^{13}\text{C NMR} (100 MHz, CDCl}_3) \delta 140.82, 140.08, 139.46, 135.20, 129.63, 128.91, 128.52, 128.28, 128.23, 128.18, 128.13, 128.11, 127.72, 127.45, 127.15, 126.82, 65.46, 55.99, 51.15.

\((1S,2R)-N\text{-}benzyl\text{-}1,2\text{-}diphenyl\text{-}2\text{-}(phenylthio)\text{ethan}\text{-}1\text{-}amine\)  
\[
86\% \text{ yield; white solid; melting point } 99.1-101.1 ^\circ \text{C}; \quad [\alpha] -85.02 \text{ (c}=1.0, \text{CHCl}_3). \quad ^1\text{H NMR} (400 MHz, CDCl}_3) \delta 7.32-7.12 (m, 13H), 7.10-6.96 (m, 7H), 4.37 (d, \text{J} = 8.1 \text{ Hz, 1H}), 4.04 (d, \text{J} = 7.4 \text{ Hz, 1H}), 3.62 (d, \text{J} = 13.6 \text{ Hz, 1H}), 3.37 (d, \text{J} = 13.6 \text{ Hz, 1H}), 1.92 (s, 1H). \quad ^{13}\text{C NMR} (100 MHz, CDCl}_3) \delta 140.61, 140.20, 139.92, 135.05, 132.29, 128.96, 128.54, 128.42, 128.24, 128.11, 128.06, 127.59, 127.37, 126.89, 126.80, 65.63, 60.96, 51.16.
2.4 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 aminoselenide

![Chemical structure](image)

![NMR spectra](image)
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of aminothioether
2.5 General procedure for the preparation of P-Se ligand [2]

PCl$_3$ (1.0 eq., 5.0 mmol, 2.0 M in DCM) and DIPEA (6.0 eq., 30.0 mmol) were dissolved in DCM (10 mL), cooled to 0 °C. Then, aminoselenide (1.0 eq., 5.0 mmol) in DCM (5 mL) was added at 0 °C and stirred for 3 h. (R)-BINOL or (S)-BINOL (1.0 eq., 5.0 mmol) in DCM (10 mL, BINOL was dissolved in DCM partly, forming the suspension liquid) was added with a plastic dropper at 0 °C, stirred until the aminoselenide was totally consumed monitored by TLC ($V_{PE}:V_{EA} = 20:1$). The mixture was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the corresponding ligand ($V_{PE}:V_{EA} = 20:1$).

2.6 General procedure for the preparation of P-S ligand [2]

PCl$_3$ (1.0 eq., 5.0 mmol, 2.0 M in DCM) and DIPEA (6.0 eq., 30.0 mmol) were dissolved in DCM (10 mL), cooled to 0 °C. Then, aminothioether (1.0 eq., 5.0 mmol) in DCM (5 mL) was added at 0 °C and stirred for 3 h. (S)-BINOL (1.0 eq., 5.0 mmol) in DCM (10 mL, (S)-BINOL was dissolved in DCM partly, forming the suspension liquid) was added with a plastic dropper at 0 °C, stirred until the aminothioether was totally consumed monitored by TLC ($V_{PE}:V_{EA} = 20:1$). The mixture was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the corresponding ligand ($V_{PE}:V_{EA} = 20:1$).
2.7 Characterization data of ligand

N-benzyl-N-((1S,2R)-1,2-diphenyl-2-(phenylselanyl)ethyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L1)

88% yield; white solid; melting point 78.7 °C; [α]$_D^{29}$ = -196.9 (c = 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (t, $J$ = 7.7 Hz, 2H), 7.80-7.60 (m, 4H), 7.50 (dt, $J$ = 25.1, 7.4 Hz, 3H), 7.37 (t, $J$ = 7.4 Hz, 1H), 7.32-7.01 (m, 14H), 7.00-6.87 (m, 6H), 6.85-6.68 (m, 3H), 5.25 (d, $J$ = 12.1 Hz, 1H), 4.56-4.33 (m, 1H), 3.81 (d, $J$ = 14.4 Hz, 1H), 2.87 (d, $J$ = 12.9 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.28, 150.23, 149.13, 140.03, 139.29, 136.74, 136.04, 132.32, 131.33, 130.47, 130.11, 130.05, 129.94, 129.35, 129.28, 129.24, 128.84, 128.82, 128.39, 128.27, 128.22, 128.09, 127.96, 127.64, 127.62, 127.21, 126.96, 126.79, 126.64, 125.95, 125.92, 124.74, 124.41, 124.01, 123.96, 122.12, 122.10, 122.07, 121.60, 65.35 (d, $J$ = 18.7 Hz), 52.13 (d, $J$ = 29.5 Hz), 48.53.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 138.19. HRMS m/z: anal. calcd for C$_{47}$H$_{37}$NO$_2$PSe [M+H]$^+$: 758.1727, found: 758.1738.

(11bS)-N-benzyl-N-((1S,2R)-1,2-diphenyl-2-(phenylthio)ethyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L2)

83% yield; white solid; melting point 70.9 °C; [α]$_D^{32}$ = -11.4 (c = 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, $J$ = 8.8 Hz, 1H), 7.85 (d, $J$ = 8.2 Hz, 1H), 7.72-7.63 (m, 8H), 7.55 (d, $J$ = 8.9 Hz, 1H), 7.49-7.29 (m, 8H), 7.24 (d, $J$ = 1.6 Hz, 1H), 7.21 (q, $J$ = 3.2 Hz, 5H), 7.16-7.00 (m, 9H), 6.99-6.88 (m, 6H), 6.50 (d, $J$ = 8.8 Hz, 1H), 5.06 (d, $J$ = 12.7 Hz, 1H), 4.87 (dd, $J$ = 15.8, 12.2 Hz, 1H), 3.57 (d, $J$ = 15.0 Hz, 1H), 3.30 (d, $J$ = 15.0 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.72, 149.65, 149.23, 139.55, 139.42, 137.74, 136.42, 132.63, 132.23, 131.28, 130.35, 130.18, 129.71, 129.44, 129.30, 128.95, 128.84, 128.79, 128.23, 128.06, 127.98, 127.92, 127.80, 127.73, 127.00, 126.93, 126.81, 126.78, 125.97, 125.83, 124.74, 124.37, 123.96, 123.90, 122.01, 121.68, 66.11 (d, $J$ = 28.4 Hz), 52.02 (d, $J$ = 22.9 Hz), 49.09. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 143.17. HRMS m/z: anal. calcd for C$_{47}$H$_{37}$NO$_2$PSe [M+H]$^+$: 758.1727, found: 758.1722.

(11bS)-N-benzyl-N-((1S,2R)-1,2-diphenyl-2-(phenylthio)ethyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L3)

90% yield; white solid; melting point 70.7-72.9 °C; [α]$_D^{26}$ = 32.45 (c = 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J$ = 8.8 Hz, 1H), 7.89 (d, $J$ = 8.2 Hz, 1H), 7.70 (d, $J$ = 8.2 Hz, 1H), 7.58 (d, $J$ = 8.8 Hz, 1H), 7.45-7.33 (m, 7H), 7.33-7.26 (m, 4H), 7.21 (d, $J$
= 5.6 Hz, 2H), 7.13 (qd, J = 15.6, 14.9, 7.0 Hz, 8H), 7.05-6.98 (m, 2H), 6.91 (t, J = 8.5 Hz, 4H), 6.58 (d, J = 8.8 Hz, 1H),
4.89 (d, J = 11.7 Hz, 1H), 4.66 (dd, J = 16.5, 11.9 Hz, 1H), 3.55 (d, J = 15.0 Hz, 1H), 3.29 (d, J = 15.0 Hz, 1H). $^{13}$C NMR
(100 MHz, CDCl$_3$) $\delta$ 149.90, 149.83, 149.34, 139.77, 139.52, 137.70, 133.94, 133.85, 132.78, 132.40, 131.43, 130.48,
130.23, 129.74, 129.65, 129.62, 129.50, 129.14, 129.08, 128.31, 128.27, 128.04, 127.99, 127.90, 127.69, 127.41, 127.14,
127.09, 127.05, 126.90, 126.02, 125.87, 124.80, 124.42, 124.08, 124.03, 122.08, 122.06, 121.82, 121.71, 66.29 (d, J = 27.8
Hz), 57.84 (d, J = 21.4 Hz), 49.23 (d, J = 4.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 143.89. HRMS m/z: anal. calcd for
C$_{47}$H$_{37}$NO$_2$PS [M+H]$^+$:710.2283, found: 710.2277.

2.8 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 (162 MHz, CDCl$_3$) spectra of
product L1
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{31}$P NMR (162 MHz, CDCl$_3$) spectra of product L2
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{31}$P NMR (162 MHz, CDCl$_3$) spectra of product L3
3. Detailed Optimization of Reaction Conditions

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (b) (%)</th>
<th>ee (c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_3)CN</td>
<td>20 min</td>
<td>94</td>
<td>-75</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>24 h</td>
<td>68</td>
<td>-60</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>24 h</td>
<td>72</td>
<td>-57</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>24 h</td>
<td>81</td>
<td>-68</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>24 h</td>
<td>90</td>
<td>-43</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>24 h</td>
<td>91</td>
<td>-63</td>
</tr>
<tr>
<td>7</td>
<td>CHCl(_3)</td>
<td>24 h</td>
<td>84</td>
<td>-44</td>
</tr>
<tr>
<td>8</td>
<td>DME</td>
<td>24 h</td>
<td>81</td>
<td>-68</td>
</tr>
</tbody>
</table>

\(a\) Unless otherwise noted, reactions were carried out with 1a (0.3 mmol), 2a (0.2 mmol), [Pd(C\(_3\)H\(_5\)Cl\(_2\)](0.01 mmol), L1 (0.02 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 S1, among all the solvents tested, the reaction in CH\(_3\)CN gave the best result in terms of reaction efficiency and enantioselectivity, and was thus selected for further optimization studies.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Time (h)</th>
<th>Yield (b) (%)</th>
<th>ee (c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cs(_2)CO(_3)</td>
<td>20 min</td>
<td>92</td>
<td>-75</td>
</tr>
<tr>
<td>2</td>
<td>K(_2)CO(_3)</td>
<td>9 h</td>
<td>65</td>
<td>-76</td>
</tr>
<tr>
<td>3</td>
<td>K(_2)PO(_4)</td>
<td>24 h</td>
<td>59</td>
<td>-63</td>
</tr>
<tr>
<td>4</td>
<td>BSA (3.0 eq.)+LiOAc (0.3 eq.)</td>
<td>1.5 h</td>
<td>88</td>
<td>-63</td>
</tr>
<tr>
<td>5</td>
<td>BSA (3.0 eq.)+KOAc (0.3 eq.)</td>
<td>30 min</td>
<td>91</td>
<td>-74</td>
</tr>
</tbody>
</table>

\(a\) Unless otherwise noted, reactions were carried out with 1a (0.30 mmol), 2a (0.2 mmol), [Pd(C\(_3\)H\(_5\)Cl\(_2\)](0.01 mmol), L1 (0.02 mmol), base (0.60 mmol) in CH\(_3\)CN (2.0 mL) at 40 °C. \(b\) Isolated yield. \(c\) Determined by chiral HPLC.

As shown in Table S2, among the base tested, Cs\(_2\)CO\(_3\) gave the best results (entry 1), and was thus selected for further studies.
**Table S3. Screen of ligands for the enantioselective allylic reaction**

![Chemical structure](image)

<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>L1</td>
<td>30 min</td>
<td>89</td>
<td>-75</td>
</tr>
<tr>
<td>2</td>
<td>L2</td>
<td>20 min</td>
<td>91</td>
<td>87</td>
</tr>
<tr>
<td>3(^d)</td>
<td>L2</td>
<td>30 min</td>
<td>89</td>
<td>90</td>
</tr>
<tr>
<td>4(^d)</td>
<td>L3</td>
<td>30 min</td>
<td>87</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^a\) Unless otherwise noted, reactions were carried out with 1a (0.30 mmol), 2a (0.2 mmol), \([\text{Pd}(\text{C}_3\text{H}_5\text{Cl})_2]\) (0.01 mmol), ligand (0.02 mmol), Cs\(_2\)CO\(_3\) (0.60 mmol) in CH\(_3\)CN (2.0 mL) at 40 \(^\circ\)C. \(^b\) Isolated yield. \(^c\) Determined by chiral HPLC. \(^d\) Room temperature.

As shown in Table S3, both the selenoether and thioether derived ligand could give the desired product in good ee value and good yield, this result also demonstrated that selenoether ligand could be a good choice in the asymmetric catalysis. Thus, the best results in terms of yield and enantioselectivity was obtained using L2 (entry 3).

**Table S4. Screen of the solvents for the enantioselective allylic reaction using L2**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield ( % )</th>
<th>ee ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_3)CN</td>
<td>20 min</td>
<td>91</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>24 h</td>
<td>68</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>24 h</td>
<td>33</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>24 h</td>
<td>83</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>24 h</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>CHCl(_3)</td>
<td>24 h</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>DME</td>
<td>24 h</td>
<td>86</td>
<td>79</td>
</tr>
</tbody>
</table>

\(^a\) Unless otherwise noted, reactions were carried out with 1a (0.3 mmol), 2a (0.2 mmol), \([\text{Pd}(\text{C}_3\text{H}_5\text{Cl})_2]\) (0.01 mmol), L2 (0.02 mmol), Cs\(_2\)CO\(_3\) (0.60 mmol) in solvent (2.0 mL) at 40 \(^\circ\)C. \(^b\) Isolated yield. \(^c\) Determined by chiral HPLC.

As shown in Table S4, among all the solvents tested, the reaction in CH\(_3\)CN gave the best result in terms of reaction efficiency and enantioselectivity, and was thus selected for further optimization studies.
As shown in Table S5, among all the base tested, the reaction using Cs$_2$CO$_3$ as base gave the best result in terms of reaction efficiency and enantioselectivity, and was thus selected for further optimization studies.

As shown in Table S6, the best results in terms of yield and enantioselectivity was obtained with 5 mol% [Pd(C$_3$H$_5$)$_2$Cl]$_2$.

As shown in Table S7, the best results in terms of yield and enantioselectivity was obtained with 5 mol% [Pd(C$_3$H$_5$)$_2$Cl]$_2$. 

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**Table S5. Screen of the base for the enantioselective allylic reaction using L2**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cs$_2$CO$_3$</td>
<td>20 min</td>
<td>91</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>K$_2$CO$_3$</td>
<td>24 h</td>
<td>62</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>K$_2$PO$_4$</td>
<td>24 h</td>
<td>71</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>BSA (3.0 eq.)+CsOAc (0.3 eq.)</td>
<td>30 min</td>
<td>95</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>BSA (3.0 eq.)+KOAc (0.3 eq.)</td>
<td>30 min</td>
<td>92</td>
<td>66</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, reactions were carried out with 1a (0.30 mmol), 2a (0.2 mmol), [Pd(C$_3$H$_5$)$_2$Cl]$_2$ (0.01 mmol), L$_2$ (0.02 mmol), base (0.60 mmol) in CH$_3$CN (2.0 mL) at 40 °C. $^b$ Isolated yield. $^c$ Determined by chiral HPLC.

**Table S6. Effect of ratio of Pd to ligand on the enantioselective allylic reaction using L2**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>x:y</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L$_2$</td>
<td>5:10</td>
<td>30 min</td>
<td>89</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>L$_2$</td>
<td>2.5:5</td>
<td>5 h</td>
<td>85</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>L$_2$</td>
<td>1.25:2.5</td>
<td>24 h</td>
<td>86</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>L$_2$</td>
<td>0.625:1.25</td>
<td>24 h</td>
<td>81</td>
<td>87</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, reactions were carried out with 1a (0.30 mmol), 2a (0.2 mmol), [Pd(C$_3$H$_5$)$_2$Cl]$_2$ (0.002x mmol), L$_2$ (0.002y mmol), Cs$_2$CO$_3$ (0.60 mmol) in CH$_3$CN (2.0 mL) at room temperature. $^b$ Isolated yield. $^c$ Determined by chiral HPLC.

**Table S7. Temperature effect on the enantioselective allylic reaction using L2**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Temp.</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L$_2$</td>
<td>40 °C</td>
<td>30 min</td>
<td>89</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>L$_2$</td>
<td>RT</td>
<td>30 min</td>
<td>91</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>L$_2$</td>
<td>0 °C</td>
<td>14 h</td>
<td>80</td>
<td>92.7</td>
</tr>
<tr>
<td>4</td>
<td>L$_2$</td>
<td>-20 °C</td>
<td>36 h</td>
<td>75</td>
<td>93</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, reactions were carried out with 1a (0.3 mmol), 2a (0.2 mmol), [Pd(C$_3$H$_5$)$_2$Cl]$_2$ (0.01 mmol), L$_2$ (0.02 mmol), Cs$_2$CO$_3$ (0.60 mmol) in CH$_3$CN (2.0 mL). $^b$ Isolated yield. $^c$ Determined by chiral HPLC.
As shown in Table S7, the best enantioselectivity was obtained at -20 °C. Taking the reaction efficiency, ee value and yield into account, the optimized reaction condition was confirmed as: 1 (0.3 mmol), 2 (0.2 mmol), 5 mol% of [Pd(C3H5Cl)]2, 10 mol% of ligand L2, and 3.0 equivalents of Cs2CO3 in CH3CN at room temperature. The absolute configuration of 3aa was established to be S according to ref. 1.

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 L2 (0.02 mmol, 10 mol%) and [Pd(C3H5Cl)]2 (0.01 mmol, 5 mol%) were dissolved in CH3CN (2.0 mL) in a Schlenk tube under Ar at room temperature. After stirring at room temperature for 1 h, allylic acetate 2 (0.2 mmol) was added, followed by Cs2CO3 (0.6 mmol), stirred for 10 min. 1 (0.3 mmol) was added and stirred at room temperature until 2 was totally consumed monitored by TLC (VPE:VEA = 10:1), and then the above reaction system was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (VPE:VEA = 10:1) to afford the corresponding product.

4.2 Spectral data of allylic reaction products

dimethyl (S,E)-2-(1,3-diphenylallyl)malonate (3aa)

Yield: 89%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 90: 10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 7.564 min (minor), tR = 7.174 min (major), ee = 90%. [α]D24 -10.735 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.32-7.06 (m, 10H), 6.41 (d, J = 15.7 Hz, 1H), 6.26 (dd, J = 15.7, 8.6 Hz, 1H), 4.27-4.11 (m, 1H), 3.88 (d, J = 10.9 Hz, 1H), 3.63 (s, 3H), 3.44 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 168.17, 167.76, 140.12, 136.77, 131.79, 129.06, 128.70, 128.45, 127.83, 127.55, 127.15, 126.35, 57.61, 52.62, 52.44, 49.17.

diethyl (S,E)-2-(1,3-diphenylallyl)malonate (3ba)

Yield: 86%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 7.527 min (minor), tR = 7.389 min.
(major), ee = 88%. [α]D19 -7.37 (c = 0.1, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.41-6.97 (m, 11H), 6.40 (d, J = 15.8 Hz, 1H), 6.26 (dd, J = 15.7, 8.5 Hz, 1H), 4.16-4.04 (m, 3H), 3.94-3.82 (m, 3H), 1.12 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 167.78, 167.35, 140.21, 136.75, 131.59, 129.25, 128.58, 128.39, 127.92, 127.45, 127.02, 126.27, 61.53, 61.31, 57.70, 49.17, 14.08, 13.72.

di-tert-butyl (S,E)-2-(1,3-diphenylallyl)malonate (3ca) [3]

Yield: 82%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 95: 5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 5.489 min (minor), tR = 6.901 (major), ee = 77%. [α]D19 -6.35 (c = 0.1, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.27-7.06 (m, 11H), 6.37 (d, J18 = 15.8 Hz, 1H), 6.26 (dd, J15.7, 8.2 Hz, 1H), 4.14-4.01 (m, 1H), 3.66 (d, J = 10.9 Hz, 1H), 1.34 (s, 9H), 1.14 (s, 9H).

13C NMR (100 MHz, CDCl3) δ 167.20, 166.70, 140.73, 136.99, 131.16, 130.08, 128.45, 128.39, 128.14, 127.29, 126.80, 126.25, 81.75, 81.48, 59.26, 49.02, 27.90, 27.54.

dimethyl (R,E)-2-(1,3-diphenylallyl)-2-methylmalonate (3da) [3]

Yield: 99%. The ee was determined by chiral HPLC (Chiralpak AD, hexane/isopropanol 99:1 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 12.355 min (minor), tR = 14.960 min (major), ee = 93%. [α]D25 19.57 (c = 0.1, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.34-7.06 (m, 10H), 6.61 (dd, J15.7, 9.0 Hz, 1H), 6.39 (d, J = 15.7 Hz, 1H), 4.23 (d, J = 9.0 Hz, 1H), 3.63 (s, 3H), 3.55 (s, 3H), 1.41 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 171.51, 171.28, 139.21, 137.23, 132.77, 129.47, 128.43, 128.24, 127.38, 127.19, 126.36, 59.10, 53.84, 52.48, 52.43, 18.64.

diethyl (R,E)-2-(1,3-diphenylallyl)-2-phenylmalonate (3ea) [3]

Yield: 95%. The ee was determined by chiral HPLC (Chiralpak IE, hexane/isopropanol 98:2 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 6.155 min (minor), tR = 6.624 min (major), ee = 88%. [α]D27 22.53 (c = 0.1, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.33-7.29 (m, 2H), 7.25 (d, J = 6.0 Hz, 7H), 7.20-7.09 (m, 4H), 6.96-7.04 (m, 2H), 6.54-6.37 (m, 2H), 4.63 (d, J = 8.9 Hz, 1H), 4.22-4.12 (m, 4H), 1.23-1.14 (m, 6H). 13C NMR (100 MHz, CDCl3) δ 169.73, 169.58, 139.51, 137.45, 135.62, 132.54, 130.56, 129.16, 128.37, 127.56, 127.44, 127.41, 127.23, 126.81, 126.30, 68.09, 61.50, 61.43, 55.33, 13.90, 13.82.

(S,E)-3-(1,3-diphenylallyl)pentane-2,4-dione (3fa) [3]

Yield: 82%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 98:2 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 9.328 min (minor), tR = 9.776 min (major), ee = 90%. [α]D19 -0.783 (c = 0.1, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.36-7.15 (m, 10H), 6.43 (d, J
(S,E)-2-(1,3-diphenallyl)malononitrile (3ga) \(^{[1]}\)

\[
\text{Yield: 80\%. The ee was determined by chiral HPLC (Chiralpak AS-H, hexane/isopropanol 90:10 v/v,}
\]

\[
\text{flow rate 1 mL/min, } \lambda = 254 \text{ nm, 25 }^\circ\text{C}. \text{ Retention times: } t_e = 14.928 \text{ (minor),}
\]

\[
t_R = 16.695 \text{ min (major), ee = 82\%. } \alpha = \text{2.60 (c = 0.1, CHCl}_3\text{).}
\]

\[
\text{1H NMR (400 MHz, CDCl}_3\text{) } \delta 7.50-7.22 \text{ (m, 10H), 6.71 (d, } J = 15.8 \text{ Hz, 1H),}
\]

\[
6.47 \text{ (dd, } J = 15.7, 8.0 \text{ Hz, 1H), 4.14-3.99 (m, 2H).}
\]

\[
\text{13C NMR (100 MHz, CDCl}_3\text{) } \delta 136.57, 135.82, 135.49,
\]

\[
129.41, 128.93, 128.71, 128.60, 127.69, 126.77, 123.93, 111.67, 111.59, 49.78, 30.17.
\]

(R,E)-(4,4-bis(phenylsulfonyl)but-1-ene-1,3-diyl)dibenzene (3ha) \(^{[4]}\)

\[
\text{Yield: 92\%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 80:20 v/v,}
\]

\[
\text{flow rate 1 mL/min, } \lambda = 254 \text{ nm, 25 }^\circ\text{C}. \text{ Retention times: } t_e = 13.415 \text{ (minor),}
\]

\[
t_R = 17.085 \text{ min (major), ee = 90\%. } \alpha = 1.60 (c = 0.1, CHCl}_3\text{).}
\]

\[
\text{1H NMR (400 MHz, CDCl}_3\text{) } \delta 8.01 \text{ (d, } J = 7.8 \text{ Hz, 2H), 7.63 (d, } J = 7.9 \text{ Hz, 2H),}
\]

\[
7.60-7.52 \text{ (m, 2H), 7.47 (t, } J = 7.7 \text{ Hz, 2H), 7.34-7.18 \text{ (m, 10H), 6.88 (dd, } J = 15.8, 9.2 \text{ Hz, 1H), 6.21 (d,}
\]

\[
J = 15.8, 1H), 6.09 (d, } J = 2.6 \text{ Hz, 1H), 4.71 (dd, } J = 9.3, 2.6 \text{ Hz, 1H).}
\]

\[
13C NMR (101 MHz, CDCl}_3\text{) } \delta 140.65, 140.63, 137.99, 136.54, 134.89, 134.51, 133.94, 130.22, 128.94, 128.85, 128.68,
\]

\[
128.65, 128.41, 128.20, 127.76, 127.27, 126.61, 124.33, 89.16, 47.61.
\]

(R,E)-3-(1,3-diphenallyl)-1H-indole (3ia) \(^{[2a]}\)

\[
\text{Yield: 83\%. The ee was determined by chiral HPLC (Chiralpak AD, hexane/isopropanol 90:10 v/v,}
\]

\[
\text{flow rate 1 mL/min, } \lambda = 254 \text{ nm, 25 }^\circ\text{C}. \text{ Retention times: } t_e = 33.742 \text{ (major),}
\]

\[
t_R = 36.211 \text{ min (minor), ee = 71\%. } \alpha = -1.63 (c = 0.1, CHCl}_3\text{).}
\]

\[
\text{1H NMR (400 MHz, CDCl}_3\text{) } \delta 7.85 \text{ (s, 1H), 7.39 (d, } J = 7.9 \text{ Hz, 1H), 7.34-7.10 \text{ (m, 12H),}
\]

\[
7.02-6.93 \text{ (m, 1H), 6.85-6.75 \text{ (m, 1H), 6.76 (dd, } J = 15.7, 7.3 \text{ Hz, 1H), 6.40 (d, } J = 15.7 \text{ Hz, 1H), 6.08 (d,}
\]

\[
J = 7.4 \text{ Hz, 1H).}
\]

\[
13C NMR (100 MHz, CDCl}_3\text{) } \delta 143.10, 137.22, 136.38, 132.29, 130.32, 128.29, 128.23, 126.97, 126.57, 126.20, 126.12, 122.44, 121.90, 119.70, 119.25, 118.45, 110.97, 46.24.
\]

ethyl (3S,E)-2-cyano-3,5-diphenylpent-4-enoate (3ja) \(^{[5]}\)

\[
\text{Yield: 75\%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 90:10 v/v,}
\]

\[
\text{flow rate 1 mL/min, } \lambda = 254 \text{ nm, 25 }^\circ\text{C}. \text{ Retention times: } t_e = 11.236 \text{ (minor),}
\]

\[
t_R = 12.299 \text{ min (major), ee = 92\%. } \alpha = 11.6767 (c = 0.5, CHCl}_3\text{).}
\]

\[
\text{1H NMR (400 MHz, CDCl}_3\text{) } \delta 7.47-7.17 \text{ (m, } 2H), 6.63-6.37 \text{ (m, 2H), 4.27-4.10 \text{ (m, 3H), 3.89 (dd, } J = 14.8, 7.0 \text{ Hz, 1H), 1.16 (td,}
\]

\[
J = 7.2, 2.4 \text{ Hz, 3H).}
\]

\[
13C NMR (100 MHz, CDCl}_3\text{) } \delta 132.29, 130.32, 128.29, 128.23, 126.97, 126.57, 126.20, 126.12, 122.44, 121.90, 119.70, 119.25, 118.45, 110.97, 46.24.
\]
MHz, CDCl$_3$) $\delta$ 164.87, 164.83, 138.77, 138.08, 136.21, 136.14, 134.30, 133.25, 129.02, 128.98, 128.60, 128.11, 128.07, 127.96, 127.66, 127.08, 126.61, 126.58, 125.75, 115.36, 115.32, 62.84, 62.79, 49.41, 49.17, 44.81, 44.50, 13.87.

dimethyl (S,E)-2-(1,3-di-p-tolylallyl)malonate (3ab) [3]

Yield: 85%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 95:5 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 °C). Retention times: $t_r$ = 11.126 min (minor), $t_R$ = 14.079 min (major), ee = 90%. [a]$_{D}^{25}$ -5.10 (c = 0.1, CHCl$_3$). ¹H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (dd, $J$ = 25.0, 7.9 Hz, 4H), 7.01 (dd, $J$ = 17.3, 7.8 Hz, 4H), 6.35 (d, $J$ = 15.7 Hz, 1H), 6.18 (dd, $J$ = 15.7, 8.6 Hz, 1H), 4.18 – 4.09 (m, 1H), 3.85 (d, $J$ = 10.9 Hz, 1H), 3.61 (s, 3H), 3.45 (s, 3H), 2.23 (s, 6H).

¹³C NMR (100 MHz, CDCl$_3$) $\delta$ 168.28, 167.85, 137.29, 137.21, 136.66, 134.06, 131.42, 129.36, 129.10, 128.20, 127.64, 126.24, 57.73, 52.57, 52.42, 48.83, 21.13, 21.02.

dimethyl (S,E)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (3ac) [3]

Yield: 90%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, $\lambda$ = 254 nm, 25 °C). Retention times: $t_R$ = 11.253 min (minor), $t_R$ = 15.350 min (major), ee = 95%. [a]$_{D}^{27}$ 7.76 (c = 0.1, CHCl$_3$). ¹H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 -7.19 (m, 2H), 7.15 (d, $J$ = 8.9 Hz, 6H), 6.33 (d, $J$ = 15.7 Hz, 1H), 6.19 (dd, $J$ = 15.7, 8.4 Hz, 1H), 4.16 (dd, $J$ = 10.8, 8.4 Hz, 1H), 3.82 (d, $J$ = 10.8 Hz, 1H), 3.62 (s, 3H), 3.47 (s, 3H).

¹³C NMR (100 MHz, CDCl$_3$) $\delta$ 167.90, 167.49, 138.43, 135.00, 133.35, 133.03, 131.00, 129.21, 129.13, 128.91, 128.65, 127.56, 57.31, 52.71, 52.59, 48.36.

dimethyl (S,E)-2-(1,3-bis(4-bromophenyl)allyl)malonate (3ad) [3]

Yield: 92%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 95:5 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 °C). Retention times: $t_R$ = 19.498 min (minor), $t_R$ = 26.730 min (major), ee = 93%. [a]$_{D}^{27}$ 2.83 (c = 0.1, CHCl$_3$). ¹H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J$ = 7.9 Hz, 2H), 7.39 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.1 Hz, 4H), 6.39 (d, $J$ = 15.7 Hz, 1H), 6.28 (dd, $J$ = 15.7, 8.5 Hz, 1H), 4.22 (t, $J$ = 9.6 Hz, 1H), 3.90 (d, $J$ = 10.8 Hz, 1H), 3.70 (s, 3H), 3.55 (s, 3H). ¹³C NMR (100 MHz, CDCl$_3$) $\delta$ 167.74, 167.33, 138.83, 135.32, 131.74, 131.47, 130.96, 129.48, 129.09, 127.78, 121.39, 121.03, 57.08, 52.62, 52.51, 48.34.

dimethyl (S,E)-2-(1,3-bis(3-bromophenyl)allyl)malonate (3ae) [3]

Yield: 87%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, $\lambda$ = 254 nm, 25 °C). Retention times: $t_R$ = 7.585 min (minor), $t_R$ = 9.915 min (major), ee = 91%. [a]$_{D}^{18}$ -2.65 (c = 0.1, CHCl$_3$). ¹H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (dt, $J$
= 13.0, 1.9 Hz, 2H), 7.33-7.24 (m, 2H), 7.18-7.11 (m, 3H), 7.10-7.04 (m, 1H), 6.33 (d, J = 15.7 Hz, 1H), 6.21 (dd, J = 15.7, 8.5 Hz, 1H), 4.15 (dd, J = 10.8, 8.4 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.64 (s, 3H), 3.49 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 167.79, 167.38, 142.17, 138.59, 131.02, 130.89, 130.62, 130.44, 130.32, 130.02, 129.78, 129.13, 126.49, 125.14, 122.73, 122.70, 57.14, 52.75, 52.63, 48.58.

**dimethyl (S,E)-2-(4-phenylbut-3-en-2-yl)malonate (3af)** [6]
Yield: 73%. The ee was determined by chiral HPLC (Chiralpak IE, hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 9.147 min (minor), tR = 9.687 min (major), ee = 64%. [α]D27 38.98 (c = 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.36-7.24 (m, 4H), 7.23-7.17 (m, 1H), 6.45 (d, J = 15.8 Hz, 1H), 6.12 (dd, J = 15.8, 8.5 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.40 (d, J = 8.8 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 168.62, 168.58, 137.18, 131.26, 130.82, 128.48, 127.36, 126.27, 57.84, 52.33, 52.25, 37.67, 18.43.

Yield: 89%. The ee was determined by chiral HPLC (Chiralpak IA, hexane/isopropanol 99:1 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: tR = 9.404 min (major), tR = 10.209 min (minor), ee = 83%. [α]D27 -1.96 (c = 0.1, CHCl3). 1H NMR (400 MHz, CDCl3) δ 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) δ 142.8, 140.3, 136.8, 132.5, 130.3, 128.6, 128.5, 128.4, 128.2, 127.4, 127.3, 126.9, 126.4, 64.5, 51.3.

5. References


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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 3aa
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ba
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ca
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3da
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ea
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3fa

![NMR Spectra Graph]
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ga
\(^1\)H NMR (400 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectra of product 3ha
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ia
\[^1\text{H}\text{ NMR (400 MHz, CDCl}\text{3)}\text{ and }[^13\text{C}\text{ NMR (100 MHz, CDCl}\text{3)}\text{ spectra of product 3ja}\]
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ab
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ac
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3ad

![Chemical structure of product 3ad](attachment:image)

![1H NMR spectrum of product 3ad](attachment:image)

![13C NMR spectrum of product 3ad](attachment:image)
**1H NMR (400 MHz, CDCl₃) and 13C NMR (100 MHz, CDCl₃) spectra of product 3ae**

![Spectrum Image](Image URL)

**1H NMR (400 MHz, CDCl₃) and 13C NMR (100 MHz, CDCl₃) spectra of product 3ae**

![Spectrum Image](Image URL)

**1H NMR (400 MHz, CDCl₃) and 13C NMR (100 MHz, CDCl₃) spectra of product 3ae**

![Spectrum Image](Image URL)
$^{1}$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3af
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 6
7. Copies of HPLC Chromatograms

**3aa**

<table>
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<th>峰保留时间</th>
<th>类型</th>
<th>峰宽 [min]</th>
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<th>峰面积%</th>
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<th>峰面积</th>
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<th>峰面积</th>
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| 3ad  |                    | 19.408   | BB   | 1.2767     | 186.3353 | 6.3248  | 3.7234  |
|      |                    | 26.730   | BB   | 1.7030     | 4818.0817| 149.0250| 96.2766 |
|      | 总和               |          |      |            | 5004.1450|        |         |

| 3ae  |                    | 7.518    | BB   | 1.0903     | 1180.0062| 1238.7062| 48.6614 |
|      |                    | 9.133    | BB   | 1.0490     | 1204.8294| 1044.9500| 80.3386 |
|      | 总和               |          |      |            | 2480.8354|        |         |

| 3ae  |                    | 7.965    | YY   | 0.8320     | 286.9644 | 26.5016  | 4.3306  |
|      |                    | 9.913    | YY   | 1.6100     | 6446.8042| 472.9647 | 93.9510 |
|      | 总和               |          |      |            | 6732.6086|        |         |