Electronic Supplementary Information

Asymmetric dual catalysis via fragmentation of a single rhodium precursor complex

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1. General Information

All reactions were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Solvents were distilled under argon from calcium hydride (CH₃CN, CH₂Cl₂) or sodium/benzophenone (THF, toluene). Rhodium complex rac-Rh2 and Δ-Rh2,¹ Wittig reagents S1a-c,² glyoxylates S2a and S2c-d,³α,α-disubstituted aldehydes 3b-j⁵ and α, β-unsaturated acyl imidazole 2b-c⁶,⁷ were prepared according to published procedures. All other reagents were purchased from Acros, Aldrich, Alfa and J&K, and used without further purification. Column chromatography was performed with silica gel (300-400 mesh, Yantai Jiangyou Silica Gel Development Co., Ltd). ¹H and ¹³C NMR spectra were recorded on a Bruker AM (400 MHz) or a Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: CDCl₃ = 7.26 ppm (¹H NMR), 77.0 ppm (¹³C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0T FT-MS instrument using ESI technique. Optical rotations were measured on an Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL. Enantioselectivities were determined by chiral HPLC and diastereoselectivities were determined by ¹H NMR.
2. Synthesis of the Substrates and Racemic Products

2.1 Synthesis of α,β-Unsaturated Acyl Imidazoles

General Procedure. The α,β-unsaturated acyl imidazole substrates 2a-f were synthesized following published methods. Accordingly, to a solution of S1a-c (5.0 mmol) in CH$_2$Cl$_2$ (25 mL) was added corresponding glyoxylate S2a-d (6.0 mmol). The reaction was stirred for 12 hours at room temperature. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 5:1 to 3:1) to afford 2a-f.

(E)-tert-butyl 4-oxo-4-(1-phenyl-1H-imidazol-2-yl)but-2-enoate (2a)

Following the general procedure, reaction of Wittig reagent S1a (2.23 g, 5.0 mmol) and tert-butyl glyoxylate S2a (0.781 g, 6.0 mmol) afforded 2a as a pale yellow solid (1.07 g, 3.59 mmol, yield: 72%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, $J = 15.9$ Hz, 1H), 7.48 (t, $J = 3.2$ Hz, 3H), 7.37 (d, $J = 0.5$ Hz, 1H), 7.34-7.28 (m, 2H), 7.25 (d, $J = 0.6$ Hz, 1H), 6.78 (d, $J = 15.8$ Hz, 1H), 1.52 (s, 9H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.6, 164.6, 143.2, 138.0, 136.0, 134.0, 130.5, 129.1, 129.0, 128.0, 125.8, 81.7, 28.0.

IR (film) $\nu_{\text{max}}$: 2918, 2850, 1716, 1673, 1631, 1492, 1446, 1404, 1369, 1306, 1149, 1042, 974, 858, 764, 737, 692, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_2$O$_3$Na (M+Na)$^+$: 321.1210, found: 321.1211.

(E)-ethyl 4-oxo-4-(1-phenyl-1H-imidazol-2-yl)but-2-enoate (2d)

Following the general procedure, reaction of Wittig reagent S1a (2.23 g, 5.0 mmol) and ethyl glyoxylate S2b (0.613 g, 6.0 mmol) afforded 2d as a pale yellow solid (1.06 g, 3.92 mmol, yield: 78%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J = 15.9$ Hz, 1H), 7.49 (t, $J = 3.1$ Hz, 3H), 7.38 (s, 1H), 7.31 (q, $J = 2.8$ Hz, 2H), 7.27 (s, 1H), 6.85 (d, $J = 15.8$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H) 1.33 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.1, 165.4, 143.2, 138.0, 136.9, 131.8, 130.6, 129.1, 129.0, 128.1, 125.8, 61.2, 14.1.

IR (film) $\nu_{\text{max}}$: 2917, 2849, 2283, 1720, 1673, 1492, 1445, 1402, 1299, 1040, 762, 691, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{15}$H$_{14}$N$_2$O$_3$Na (M+Na)$^+$: 293.0897, found: 293.0899.
(E)-methyl 4-oxo-4-(1-phenyl-1H-imidazol-2-yl)but-2-enoate (2e)

\[
\begin{array}{c}
\text{\(E\)-methyl 4-oxo-4-(1-phenyl-1H-imidazol-2-yl)but-2-enoate (2e)}
\end{array}
\]

Following the general procedure, reaction of Wittig reagent S1a (2.23 g, 5.0 mmol) and methyl glyoxylate S2c (0.528 g, 6.0 mmol) afforded 2e as a pale yellow solid (0.961 g, 3.75 mmol, yield: 75%).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.36 (d, \(J = 15.9\) Hz, 1H), 7.49 (s, 3H), 7.38 (s, 1H), 7.31 (d, \(J = 3.1\) Hz, 2H), 7.27 (s, 1H), 6.85 (d, \(J = 15.9\) Hz, 1H), 3.82 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 178.0, 165.8, 143.1, 137.9, 137.2, 131.2, 130.6, 129.1, 129.0, 128.2, 125.8, 52.2.

IR (film) \(\nu_{\text{max}}\): 2918, 2849, 1725, 1699, 1668, 1631, 1557, 1538, 1493, 1444, 1401, 1301, 1169, 1155, 1088, 1043, 974, 914, 804, 756, 701, 689, 678, 557, 523 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{14}\)H\(_{12}\)N\(_2\)O\(_3\)Na (M+Na): 279.0740, found: 279.0744.

(E)-isopropyl 4-oxo-4-(1-phenyl-1H-imidazol-2-yl)but-2-enoate (2f)

\[
\begin{array}{c}
\text{\(E\)-isopropyl 4-oxo-4-(1-phenyl-1H-imidazol-2-yl)but-2-enoate (2f)}
\end{array}
\]

Following the general procedure, reaction of Wittig reagent S1a (2.23 g, 5.0 mmol) and isopropyl glyoxylate S2d (0.697 g, 6.0 mmol) afforded 2f as a pale yellow solid (0.995 g, 3.50 mmol, yield: 70%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.28 (d, \(J = 15.9\) Hz, 1H), 7.49 (t, \(J = 3.1\) Hz, 3H), 7.38 (s, 1H), 7.31
(q, J = 2.7 Hz, 2H), 7.27 (s, 1H), 6.83 (d, J = 15.9 Hz, 1H), 5.22-5.06 (m, 1H), 1.30 (d, J = 6.2 Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.2, 164.9, 143.2, 138.0, 136.6, 132.5, 130.5, 129.1, 129.0, 128.1, 125.8, 68.8, 21.7.

IR (film) $\nu_{max}$: 2917, 2849, 1716, 1673, 1492, 1445, 1402, 1295, 1042, 762, 691, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{16}$H$_{16}$N$_2$O$_3$Na (M+Na)$^+$: 307.1053, found: 307.1050.

### 2.2 Synthesis of the Racemic Products as HPLC References

**General Procedure.** To a solution of 2a-f (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) was added the racemic rhodium complex $\text{rac-Rh}_2$ (1.66 mg, 0.0020 mmol) in a glass vial. After being stirred at room temperature for 30 min, 3a-p (0.30 mmol) and N-methylbenzylamine (0.020 mmol) were added. The reaction mixture was stirred at 20 °C for 12 h. After evaporation of the volatile organic solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, $n$-hexane/ethyl acetate = 5:1 to 3:1) to afford the racemic products $\text{rac-4a-u}$ as HPLC reference for the determination of enantiomeric excess in the asymmetric reaction.
3. Synthesis of Rhodium Catalyst $\Delta_{\text{Rh}}$-$\text{Sc}$-$\text{Rh1}$

Compound $\Delta_{\text{Rh}}$-$\text{Sc}$-$\text{Rh1}$.\(^1\) 5-tert-butyl-2-phenylbenzo[d]oxazole (1.030 g, 4.1 mmol) was added to RhCl$_3$·3H$_2$O (418.5 mg, 2.0 mmol) in a mixture of 2-ethoxyethanol and water (3:1, 92.0 mL). The reaction mixture was heated at 120 °C for 24 h under an atmosphere of argon. The resulting precipitate was collected by centrifugation, washed with methanol and dried to obtain the rhodium dimer (779.62 mg, 0.61 mmol, yield: 61%) as a pale yellow solid.

Subsequently, to a solution of NaOMe (40.5 mg, 0.75 mmol) in MeOH (16.0 mL), (S)-3-amino-3-phenylpropanoic acid (49.6 mg, 0.30 mmol) was added in one portion. The mixture was stirred for 30 min, to which rhodium dimer (201.3 mg, 0.150 mmol) was added. The mixture was stirred and heated at 50 °C for 12 h to give a clear, yellow solution. The solvent was removed in vacuo and the mixture of two diastereoisomers was washed with CH$_2$Cl$_2$/Et$_2$O (1:20, v/v) until the filtrate was almost colorless. The residual insoluble solid was dissolved in CH$_2$Cl$_2$. After filtering, the filtrate was dried and collected as $\Delta_{\text{Rh}}$-$\text{Sc}$-$\text{Rh1}$ (92.1 mg, 0.117 mmol, yield: 39%). The total yield in two steps is 24%. The absolute configuration of the rhodium (III) complex was assigned as $\Delta_{\text{Rh}}$-$\text{Sc}$ by its X-ray crystal structure.

\(^1\)H NMR (500 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 1.4$ Hz, 1H), 7.78 (d, $J = 6.8$ Hz, 1H), 7.72 (d, $J = 6.8$ Hz,
1H), 7.67 (q, J = 5.2 Hz, 2H), 7.60 (dd, J = 8.8, 1.7 Hz, 1H), 7.54 (dd, J = 8.8, 1.5 Hz, 1H), 7.31 (t, J = 7.1 Hz, 2H), 7.27 (s, 1H), 7.17 (q, J = 12.2 Hz, 3H), 7.05-6.95 (m, 2H), 6.93-6.84 (m, 2H), 6.65 (d, J = 7.7 Hz, 1H), 6.36 (d, J = 7.7 Hz, 1H), 4.82 (t, J = 12.2 Hz, 1H), 3.63 (d, J = 10.9 Hz, 1H), 2.88 (d, J = 16.9 Hz, 1H), 2.55 (t, J = 12.5 Hz, 1H), 2.42 (q, J = 11.3 Hz, 1H), 1.40 (s, 9H), 1.18 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.3, 172.4, 171.2, 166.4, 166.2, 164.2, 163.9, 151.5, 150.0, 148.3, 143.8, 138.3, 137.7, 135.0, 133.5, 131.3, 130.6, 129.0, 128.0, 125.8, 125.7, 125.1, 123.8, 123.5, 123.1, 123.0, 115.0, 111.7, 110.7, 110.6, 56.2, 47.3, 35.5, 35.0, 31.7, 31.4.

IR (film) $\nu_{\text{max}}$: 2923, 2852, 1736, 1659, 1589, 1524, 1449, 1428, 1383, 1261, 1088, 1037, 1015, 932, 805, 738, 557 cm$^{-1}$.

HRMS (ESI) calcd for C$_{43}$H$_{42}$N$_3$O$_4$RhNa (M+Na)$^+$: 790.2123, found: 790.2130.

CD (MeOH): $\lambda$, nm ($\Delta\varepsilon$, M$^{-1}$cm$^{-1}$) 391 (+46), 338 (-65), 297 (+73), 253 (-37), 230 (+10), 214 (-77), 202 (+7).

**Figure S1.** CD spectrum of complex $\Delta_{\text{Rh}}$-$\text{S}_\text{C}$-$\text{Rh}$1 recorded in CH$_3$OH (0.20 mM)
4. Asymmetric Michael Addition Catalyzed by $\Delta_{\text{Rh-S}_{\text{C}}}$-Rh1

4.1 Optimization of the Asymmetric Michael Addition Catalyzed by $\Delta_{\text{Rh-S}_{\text{C}}}$-Rh1

**General Procedure.** To a solution of 2a (29.8 mg, 0.10 mmol) in the indicated solvent (0.10 mL) were added the catalyst $\Delta_{\text{Rh-S}_{\text{C}}}$-Rh1 (3.84 mg, 0.0050 mmol), the indicated additive and 3a (0.041 mL, 0.30 mmol) stepwise. The reaction mixture was stirred for the indicated time at the indicated temperature. After evaporation of the solvent, the crude product was used directly for determination of the conversion and diastereomeric ratio by $^1$H NMR as well as ee values by chiral HPLC.

**Table S1.** Conditions optimization of the asymmetric Michael-Stork addition.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Additive</th>
<th>$T$ (°C)</th>
<th>$t$ (h)</th>
<th>Conv. (%)$^a$</th>
<th>d.r.$^a$</th>
<th>ee (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>10 mol% NH$_4$PF$_6$</td>
<td>50</td>
<td>3</td>
<td>&gt;95</td>
<td>2.5:1</td>
<td>98.7/94</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>20 mol% NH$_4$PF$_6$</td>
<td>50</td>
<td>3</td>
<td>&gt;95</td>
<td>2.7:1</td>
<td>99.1/94</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>40 mol% NH$_4$PF$_6$</td>
<td>50</td>
<td>3</td>
<td>&gt;95</td>
<td>2.5:1</td>
<td>98.6/92</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>5 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>2.2:1</td>
<td>97/98</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>10 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>3.7:1</td>
<td>97.7/98</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>20 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>3.4:1</td>
<td>99.0/95</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>40 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>3.6:1</td>
<td>98.4/89</td>
</tr>
<tr>
<td>8</td>
<td>DCE</td>
<td>80 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>2.7:1</td>
<td>96/57</td>
</tr>
<tr>
<td>9</td>
<td>THF</td>
<td>40 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>2.9:1</td>
<td>97/97.5</td>
</tr>
<tr>
<td>10</td>
<td>Toluene</td>
<td>40 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>3.5:1</td>
<td>97.8/96</td>
</tr>
<tr>
<td>11</td>
<td>CH$_3$CN</td>
<td>40 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>2.9:1</td>
<td>97/85</td>
</tr>
<tr>
<td>12</td>
<td>MTBE</td>
<td>40 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>3:1</td>
<td>97.5/97</td>
</tr>
<tr>
<td>13</td>
<td>IPA</td>
<td>40 mol% TFA</td>
<td>50</td>
<td>2</td>
<td>&gt;95</td>
<td>2.8:1</td>
<td>97.5/96</td>
</tr>
<tr>
<td>14</td>
<td>DCE</td>
<td>40 mol% TFA</td>
<td>20</td>
<td>4</td>
<td>&gt;95</td>
<td>4.7:1</td>
<td>98.8/86</td>
</tr>
<tr>
<td>15</td>
<td>DCE</td>
<td>40 mol% TFA</td>
<td>0</td>
<td>14</td>
<td>&gt;95</td>
<td>5.8:1</td>
<td>98.9/90</td>
</tr>
<tr>
<td>16</td>
<td>DCE</td>
<td>40 mol% TFA</td>
<td>-20</td>
<td>49.5</td>
<td>85</td>
<td>5.6:1</td>
<td>98.6/74</td>
</tr>
</tbody>
</table>

$^a$Determined by $^1$H NMR spectroscopy. $^b$Determined by HPLC analysis on a chiral stationary phase. DCE = 1,2-dichloroethane, MTBE = tert-butyl methyl ether, IPA = isopropanol, TFA = trifluoroacetic acid.
4.2 Control Experiments

**General Procedure for Table 1.** To a solution of 2a (29.8 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the indicated catalyst (0.0050 mmol) and 3a (0.041 mL, 0.30 mmol) stepwise. The reaction mixture was stirred for the indicated time at 0 or 50 °C. After evaporation of the volatile organic solvent, the crude product was used directly for determination of the conversion and diastereomeric ratio by $^1$H NMR as well as enantiomeric excess by chiral HPLC.

**General Procedure for Table S2.** To a solution of 2c (23.6 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst $\Delta$Rh-S$_{C}$-Rh1 with different ee values (25, 50, 75, 90 or 95% ee, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and 3a (0.041 mL, 0.30 mmol) stepwise. The reaction mixture was stirred for the indicated time for 14 h at 0 °C. After evaporation of the volatile organic solvent, the crude product was used directly for determination of the conversion and diastereomeric ratio by $^1$H NMR as well as enantiomeric excess by chiral HPLC.

**Table S2.** The relationship between ee values of $\Delta$Rh-$S_{C}$-Rh1 and ee values of the major diastereomer of 4c.

<table>
<thead>
<tr>
<th>Entry</th>
<th>ee values of $\Delta$Rh-$S_{C}$-Rh1 (%)</th>
<th>Conv. (%)</th>
<th>ee values of the major diastereomer of 4c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>&gt;95</td>
<td>-11</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>&gt;95</td>
<td>-16</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>&gt;95</td>
<td>-8</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>&gt;95</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>&gt;95</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>&gt;99</td>
<td>&gt;95</td>
<td>95</td>
</tr>
</tbody>
</table>
Figure S2. The relationship between ee values of $\Delta_{\text{Rh}}$-$S_C$-$\text{Rh1}$ and ee values of the major diastereomer of 4c.

4.3 Substrate Scope with $\Delta_{\text{Rh}}$-$S_C$-$\text{Rh1}$

Method A. To a solution of 2a-f (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst $\Delta_{\text{Rh}}$-$S_C$-$\text{Rh1}$ (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and 3a-e or 3g-i (0.30 mmol). The reaction mixture was stirred for 14 h at 0 °C. After evaporation of the
solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 5:1 to 3:1) to afford the product 4a-j or 4l-n.

**Method B.** To a solution of 2a (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst $\Delta$Rh$_{\text{S-C-Rh1}}$ (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and 3f or 3j (0.30 mmol). The reaction mixture was stirred for 48 h or 36 h at 20 °C. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 5:1 to 3:1) to afford the product 4k or 4o.

**Method C.** To a solution of 2a (0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst $\Delta$Rh$_{\text{S-C-Rh1}}$ (3.84 mg, 0.0050 mmol), NH$_4$PF$_6$ (0.010 mmol) and 3k-p (0.30 mmol). The reaction mixture was stirred for 10 h at 20 °C. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 3:1 to 1:1) to afford the product 4p-u.

**Compound 4a**

Following **Method A,** reaction of 2a (29.8 mg, 0.10 mmol) and 3a (0.041 mL, 0.30 mmol) afforded 4a (37.6 mg, 0.0869 mmol, yield: 87%). The diastereomeric ratio was determined as 5.8:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.9%/90% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 92:8, flow rate: 0.4 mL/min, 25 °C,
$t_r$(major) = 25.3 min, $t_r$(major) = 29.3 min, $t_r$(minor) = 31.6 min, $t_r$(minor) = 73.2 min. $[\alpha]_D^{20} = -127.9^\circ$ (c 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.75 (s, 1H), 7.50-7.46 (m, 3H), 7.40-7.36 (m, 3H), 7.30-7.27 (m, 5H), 7.19 (s, 1H), 4.14 (dd, $J = 11.4$, 1.6 Hz, 1H), 3.87 (q, $J = 11.2$ Hz, 1H), 2.45 (dd, $J = 17.8$, 2.0 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.7, 189.0, 171.2, 142.5, 138.2, 137.2, 129.4, 129.2, 128.9, 128.8, 127.6, 127.0, 126.8, 125.8, 82.5, 55.2, 46.3, 35.5, 27.8, 13.7.

IR (film) $\nu_{\text{max}}$: 2925, 2853, 2720, 1726, 1689, 1597, 1527, 1494, 1447, 1410, 1368, 1344, 1304, 1235, 1154, 1075, 1035, 1002, 968, 931, 914, 884, 844, 764, 697, 554, 523 cm$^{-1}$.

HRMS (ESI) calcd for C$_{26}$H$_{28}$N$_2$O$_4$Na (M+Na)$^+$: 455.1941, found: 455.1942.

**Compound 4b**

Following **Method A**, reaction of 2b (20.8 mg, 0.10 mmol) and 3a (0.041 mL, 0.30 mmol) afforded 4b (23.9 mg, 0.0698 mmol, yield: 70%). The diastereomeric ratio was determined as 3.9:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96%/78% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 90:10, flow rate: 0.8 mL/min, 25 °C,
t_r(major) = 24.2 min, t_r(major) = 27.6 min, t_r(minor) = 33.9 min, t_r(minor) = 49.4 min. [α]D³⁰ = -86.7° (c 1.0, CHCl₃).

Analytic data of the major diastereomer:

¹H NMR (500 MHz, CDCl₃) δ 9.80 (s, 1H), 7.37 (d, J = 2.8 Hz, 4H), 7.26 (t, J = 3.6 Hz, 1H), 7.10 (s, 1H), 6.99 (s, 1H), 4.25-4.19 (m, 1H), 4.18-4.10 (m, 2H), 3.94 (s, 3H), 3.85-3.75 (m, 1H), 2.62 (dd, J = 18.2, 2.1 Hz, 1H), 1.54 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 198.9, 190.0, 172.2, 142.2, 136.9, 129.2, 128.8, 128.7, 127.7, 127.1, 61.4, 55.1, 45.3, 36.1, 35.7, 14.0, 13.9.

IR (film) ν_max: 2956, 2921, 2850, 1728, 1678, 1646, 1494, 1467, 1446, 1414, 1371, 1351, 1326, 1289, 1258, 1218, 1180, 1157, 1135, 1080, 1030, 995, 915, 930, 915, 867, 767, 701, 522 cm⁻¹.


Compound 4c

Reaction with 3 equivalents of 3a: Following Method A, reaction of 2c (23.6 mg, 0.10 mmol) and 3a (0.041 mL, 0.30 mmol) afforded 4c (24.4 mg, 0.0659 mmol, yield: 66%). The diastereomeric ratio was determined as 4.0:1 by ¹H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 95%/61% (HPLC: AD-H, 254 nm, n-hexane/isopropanol =
93:7, flow rate: 0.4 mL/min, 25 °C, tᵣ(minor) = 43.0 min, tᵣ(major) = 51.8 min, tᵣ(minor) = 80.7 min, tᵣ(major) = 84.6 min. [α]ₓ D<sup>20</sup> = -94.9° (c 1.0, CHCl₃).

**Reaction with 1.2 equivalents of 3a:** To a solution of 2c (23.6 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst Δ<sub>Rh-Sc-Rh1</sub> (3.84 mg, 0.0050 mmol), trifluoroacetic acid (0.040 mmol) and 3a (0.016 mL, 0.12 mmol). The reaction mixture was stirred for 33 h at 0 °C (Conv. > 95%). After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 5:1 to 3:1) to afford the product 4c (21.2 mg, 0.0539 mmol, yield: 54%). The diastereomeric ratio was determined as 4.2:1 by ¹H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 94%/44%.

**Analytic data of the major diastereomer:**

¹H NMR (500 MHz, CDCl₃) δ 9.80 (s, 1H), 7.40-7.37 (m, 4H), 7.30-7.28 (m, 1H), 7.22 (s, 1H), 7.12 (s, 1H), 5.51-5.47 (m, 1H), 4.25-4.22 (m, 1H), 4.19-4.14 (m, 2H), 3.85-3.80 (m, 1H), 2.64 (dd, J = 18.0, 2.2 Hz, 1H), 1.54 (s, 3H), 1.41 (q, J = 6.3 Hz, 6H), 1.19 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 199.0, 190.2, 172.3, 141.6, 136.9, 129.4, 129.2, 127.7, 127.2, 121.1, 61.3, 55.2, 49.2, 45.4, 36.2, 23.5, 23.5, 14.1, 13.9.

IR (film) ν<sub>max</sub>: 2957, 2922, 2850, 1728, 1676, 1494, 1466, 1397, 1371, 1351, 1255, 1180, 1133, 1087, 1027, 986, 929, 916, 764, 700 cm⁻¹.

HRMS (ESI) calcd for C₂₁H₂₆N₂O₄Na (M+Na)<sup>+</sup>: 393.1785, found: 393.1785.
Compound 4d

Following Method A, reaction of 2d (27.0 mg, 0.10 mmol) and 3a (0.041 mL, 0.30 mmol) afforded 4d (31.8 mg, 0.0786 mmol, yield: 79%). The diastereomeric ratio was determined as 3.5:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98.0%/97% (HPLC: AD-H, 254 nm, n-hexane/isopropanol = 90:10, flow rate: 0.8 mL/min, 25 °C, $t_r$(major) = 19.7 min, $t_r$(minor) = 21.6 min, $t_r$(major) = 33.8 min, $t_r$(minor) = 39.2 min). $[\alpha]_D^{20} = -111.7^\circ$ (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.74 (s, 1H), 7.50-7.45 (m, 3H), 7.40-7.35 (m, 3H), 7.30-7.26 (m, 5H), 7.14 (s, 1H), 4.20-4.10 (m, 3H), 3.87 (q, $J = 6.7$ Hz, 1H), 2.55 (dd, $J = 18.0$, 1.6 Hz, 1H), 1.52 (s, 3H), 1.16 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.7, 188.6, 172.1, 142.2, 138.0, 136.8, 129.4, 129.3, 128.9, 128.7, 127.7, 127.6, 127.1, 125.8, 61.4, 55.1, 45.2, 35.6, 14.0, 13.9.

IR (film) $\nu_{max}$: 2955, 2919, 2850, 2934, 1730, 1687, 1493, 1467, 1409, 1377, 1304, 1039, 967 cm$^{-1}$.

HRMS (ESI) calcd for C$_{24}$H$_{24}$N$_2$O$_4$Na (M+Na)$^+$: 427.1628, found: 427.1628.
**Compound 4e**

Following **Method A**, reaction of 2e (25.6 mg, 0.10 mmol) and 3a (0.041 mL, 0.30 mmol) afforded 4e (37.3 mg, 0.0955 mmol, yield: 96%). The diastereomeric ratio was determined as 3.8:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 98.0%/95% (HPLC: IC, 254 nm, $n$-hexane/isopropanol = 60:40, flow rate: 0.8 mL/min, 25 °C, $t_r$(minor) = 17.5 min, $t_r$(major) = 21.1 min, $t_r$(major) = 26.3 min, $t_r$(minor) = 41.2 min). $[\alpha]_D^{20} = -133.5^\circ$ (c 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.74 (s, 1H), 7.50-7.47 (m, 3H), 7.40-7.37 (m, 3H), 7.30-7.26 (m, 5H), 7.16 (s, 1H), 4.20 (dd, $J = 11.2$, 1.7 Hz, 1H), 3.87 (q, $J = 11.3$ Hz, 1H), 3.65 (s, 3H), 2.63 (dd, $J = 18.2$, 2.0 Hz, 1H), 1.54 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.7, 188.5, 172.6, 142.2, 138.0, 136.8, 129.4, 129.3, 129.0, 128.9, 127.8, 127.4, 127.1, 125.8, 55.2, 52.0, 45.2, 35.9, 14.1.

IR (film) $\nu_{max}$: 2955, 2918, 2850, 1732, 1687, 1494, 1467, 1410, 1377, 1040 cm$^{-1}$.

HRMS (ESI) calcd for C$_{23}$H$_{22}$N$_2$O$_4$Na (M+Na)$^+$: 413.1472, found: 413.1474.
**Compound 4f**

Following **Method A**, reaction of **2f** (28.4 mg, 0.10 mmol) and **3a** (0.041 mL, 0.30 mmol) afforded **4f** (35.2 mg, 0.0841 mmol, yield: 84%). The diastereomeric ratio was determined as 3.9:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 98.1%/93% (HPLC: IC, 254 nm, n-hexane/isopropanol = 80:20, flow rate: 1 mL/min, 25 °C, $t_{r}$(major) = 18.9 min, $t_{r}$(minor) = 22.8 min, $t_{r}$(major) = 35.4 min, $t_{r}$(minor) = 64.1 min). $[\alpha]_{D}^{20} = -129.3^\circ$ (c 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.77 (s, 1H), 7.50-7.46 (m, 3H), 7.40-7.36 (m, 3H), 7.30-7.27 (m, 5H), 7.16 (d, $J = 1.0$ Hz, 1H), 5.02-4.98 (m, 1H), 4.17 (dd, $J = 11.3$, 2.2 Hz, 1H), 3.90 (q, $J = 11.3$ Hz, 1H), 2.54 (dd, $J = 18.0$, 2.3 Hz, 1H), 1.55 (s, 3H), 1.20 (d, $J = 6.3$ Hz, 3H), 1.16 (d, $J = 6.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.7, 188.8, 171.6, 142.4, 138.1, 137.1, 129.4, 129.3, 128.9, 128.8, 128.7, 127.7, 127.1, 125.8, 69.4, 55.2, 45.5, 35.7, 21.6, 21.4, 14.0.

IR (film) $\nu_{max}$: 2956, 2924, 2852, 1727, 1689, 1597, 1494, 1447, 1410, 1375, 1341, 1304, 1261, 1224, 1180, 1147, 1107, 1075, 1036, 1002, 968, 931, 914, 871, 767, 698, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{25}$H$_{26}$N$_2$O$_4$Na (M+Na)$^+$: 441.1785, found: 441.1787.
Compound 4g

Following Method A, reaction of 2a (29.8 mg, 0.10 mmol) and 3b (64.0 mg, 0.30 mmol) afforded 4g (50.6 mg, 0.0990 mmol, yield: 99%). The diastereomeric ratio was determined as 5.4:1 by \(^1\)H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.7%/93% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 92:8, flow rate: 0.4 mL/min, 25 °C, t\(_{r}\) (major) = 21.5 min, t\(_{r}\) (major) = 25.8 min, t\(_{r}\) (minor) = 35.5 min, t\(_{r}\) (minor) = 51.9 min). \([\alpha]_\text{D}^{20} = -136.5^\circ\ (c\ 1.0,\ \text{CHCl}_3)\).

Analytic data of the major diastereomer:

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.68 (s, 1H), 7.50-7.46 (m, 5H), 7.30-7.24 (m, 5H), 7.16-7.15 (m, 1H), 4.07 (dd, \(J = 11.1, 2.2\) Hz, 1H), 3.84 (q, \(J = 11.1\) Hz, 1H), 2.42 (dd, \(J = 17.8, 2.3\) Hz, 1H), 1.50 (s, 3H), 1.37 (s, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 198.2, 188.7, 170.9, 142.3, 138.1, 136.3, 132.3, 129.7, 129.5, 128.9, 128.8, 127.0, 125.8, 122.0, 82.7, 54.9, 46.1, 35.4, 27.8, 13.8.

IR (film) \(v_{\text{max}}\): 2922, 2851, 1726, 1688, 1597, 1493, 1448, 1410, 1368, 1344, 1304, 1235, 1153, 1038, 1008, 968, 914, 766, 693, 522 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{26}\)H\(_{27}\)BrN\(_2\)O\(_4\)Na (M+Na\(^+\)): 533.1046, found: 533.1049.
Compound 4h

Following **Method A**, reaction of 2a (29.8 mg, 0.10 mmol) and 3c (57.1 mg, 0.30 mmol) afforded 4h (45.7 mg, 0.0935 mmol, yield: 94%). The diastereomeric ratio was determined as 2.5:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97%/95% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 25 °C, $t_r$(major) = 11.2 min, $t_r$(major) = 12.2 min, $t_r$(minor) = 16.5 min, $t_r$(minor) = 22.5 min). $[^{[\alpha]}]_D^{20} = -115.6^\circ$ (c 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.69 (s, 1H), 7.46-7.41 (m, 3H), 7.37-7.34 (m, 2H), 7.27-7.20 (m, 5H), 7.14 (s, 1H), 4.12 (d, $J = 11.5$ Hz, 1H), 3.85 (q, $J = 11.7$ Hz, 1H), 2.46 (dd, $J = 17.7$, 1.7 Hz, 1H), 1.50 (s, 3H), 1.38 (s, 9H), 1.27 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.7, 189.3, 171.4, 150.5, 142.5, 138.2, 133.8, 129.4, 128.9, 128.7, 127.7, 126.7, 126.2, 125.7, 82.4, 54.8, 46.2, 34.4, 31.2, 27.8, 22.6, 13.6.

IR (film) $\nu_{max}$: 2962, 2927, 2869, 1726, 1689, 1597, 1505, 1494, 1447, 1410, 1367, 1345, 1304, 1270, 1234, 1155, 1116, 1074, 1036, 1021, 1002, 968, 914, 885, 844, 766, 6932, 579 cm$^{-1}$.

HRMS (ESI) calcd for C$_{30}$H$_{36}$N$_2$O$_4$Na (M+Na)$^+$: 511.2567, found: 511.2569.
Compound 4i

Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3d** (49.3 mg, 0.30 mmol) afforded 4i (41.5 mg, 0.0897 mmol, yield: 90%). The diastereomeric ratio was determined as 4.7:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.6%/95% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 93:7, flow rate: 0.6 mL/min, 25 °C, $t_r$(major) = 23.6 min, $t_r$(major) = 28.3 min, $t_r$(minor) = 30.5 min, $t_r$(minor) = 47.2 min). [α]$_{D}^{20}$ = -166.1° (c 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.67 (s, 1H), 7.45-7.42 (m, 3H), 7.28-7.23 (m, 5H), 7.14 (s, 1H), 6.89-6.84 (m, 2H), 4.08-4.05 (m, 1H), 3.87-3.80 (m, 1H), 3.76 (s, 3H), 2.46 (dd, $J$ = 17.9, 1.9 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 198.5, 189.1, 171.3, 158.9, 142.4, 138.1, 129.4, 129.2, 128.9, 128.8, 128.2, 126.8, 125.7, 114.6, 82.4, 55.2, 54.5, 46.2, 35.4, 27.8, 13.8.

IR (film) $\nu_{\text{max}}$: 2956, 2922, 2850, 1724, 1688, 1608, 1513, 1494, 1447, 1410, 1368, 1344, 1303, 1255, 1186, 1154, 1075, 1033, 1002, 968, 914, 884, 844, 830, 768, 731, 695, 549 cm$^{-1}$.

HRMS (ESI) calcd for C$_{27}$H$_{30}$N$_{2}$O$_{5}$Na (M+Na)$^+$: 485.2047, found: 485.2051.
**Compound 4j**

Following **Method A**, reaction of **2a** (29.8 mg, 0.10 mmol) and **3e** (44.5 mg, 0.30 mmol) afforded **4j** (39.8 mg, 0.0891 mmol, yield: 89%). The diastereomeric ratio was determined as 5.5:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.8%/94% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 93:7, flow rate: 0.6 mL/min, 25 °C, $t_r$(major) = 14.0 min, $t_r$(major) = 16.7 min, $t_r$(minor) = 20.9 min, $t_r$(minor) = 30.4 min). [$\alpha$]$^D_{20}$ = -142.9˚ ($c$ 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.70 (s, 1H), 7.45-7.41 (m, 3H), 7.28-7.20 (m, 4H), 7.14 (d, $J$ = 7.8 Hz, 4H), 4.14-4.08 (m, 1H), 3.83 (q, $J$ = 11.5 Hz, 1H), 2.44 (d, $J$ = 17.8 Hz, 1H), 2.29 (s, 3H), 1.49 (s, 3H), 1.37 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.7, 189.1, 171.3, 142.4, 138.1, 137.4, 134.0, 130.0, 129.3, 128.9, 128.8, 126.9, 126.8, 125.8, 82.4, 54.8, 46.2, 35.5, 27.8, 20.9, 13.7.

IR (film) $\nu_{max}$: 2924, 2852, 1725, 1689, 1597, 1494, 1448, 1410, 1368, 1344, 1304, 1235, 1154, 1038, 1002, 968, 914, 845, 813, 767, 722, 694, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{27}$H$_{30}$N$_2$O$_4$Na (M+Na)$^+$: 469.2098, found: 469.2101.
Compound 4k

Following Method B, reaction of 2a (29.8 mg, 0.10 mmol) and 3f (44.5 mg, 0.30 mmol) afforded 4k (31.5 mg, 0.0705 mmol, yield: 71%). The diastereomeric ratio was determined as 2.3:1 by \(^1\)H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IB column, ee = 89%/86% (HPLC: IB, 254 nm, n-hexane/isopropanol = 92:8, flow rate: 0.4 mL/min, 25 °C, \(t_r\)(major) = 19.8 min, \(t_r\)(major) = 21.3 min, \(t_r\)(minor) = 23.8 min, \(t_r\)(minor) = 26.6 min). [\(\alpha\)]\(_{D}^{20}\) = -89.5° (c 1.0, CHCl\(_3\)).

Analytic data of the major diastereomer:

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.11 (s, 1H), 7.43-7.40 (m, 5H), 7.33-7.23 (m, 3H), 7.18-7.09 (m, 3H), 4.18 (dd, \(J = 11.2, 2.1\) Hz, 1H), 3.82-3.75 (m, 1H), 2.48 (dd, \(J = 17.5, 2.2\) Hz, 1H), 2.38 (s, 3H), 1.57 (s, 3H), 1.37 (s, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 201.3, 189.1, 171.8, 142.6, 138.2, 137.4, 136.4, 132.8, 129.6, 128.8, 128.7, 128.2, 127.8, 126.8, 126.5, 125.7, 82.0, 55.8, 44.9, 36.7, 27.8, 23.1, 17.5.

IR (film) \(\nu_{max}\): 2925, 2853, 1722, 1689, 1597, 1493, 1447, 1409, 1368, 1345, 1304, 1256, 1233, 1152, 1037, 1002, 967, 914, 845, 762, 727, 693, 522 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{27}\)H\(_{30}\)N\(_2\)O\(_4\)Na (M+Na\(^+\)): 469.2098, found: 469.2098.
Compound 4l

Following **Method A**, reaction of 2a (29.8 mg, 0.10 mmol) and 3g (44.5 mg, 0.30 mmol) afforded 4l (38.9 mg, 0.0871 mmol, yield: 87%). The diastereomeric ratio was determined as 3.4:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97.8%/97.6% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 92:8, flow rate: 0.5 mL/min, 25 °C, $t_r$(major) = 16.0 min, $t_r$(major) = 18.0 min, $t_r$(minor) = 20.4 min, $t_r$(minor) = 44.7 min). $[\alpha]_D^{20} = -141.4^\circ$ (c 1.0, CHCl$_3$).

**Analytic data of the major diastereomer:**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.73 (s, 1H), 7.45-7.41 (m, 3H), 7.27-7.20 (m, 4H), 7.13 (s, 2H), 7.10-7.04 (m, 2H), 4.11 (d, $J$ = 11.1 Hz, 1H), 3.85 (q, $J$ = 11.4 Hz, 1H), 2.44 (d, $J$ = 17.8 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 3H), 1.38 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.9, 189.2, 171.3, 142.6, 138.9, 138.2, 137.0, 129.5, 129.0, 128.9, 128.7, 128.3, 127.7, 126.8, 125.7, 124.0, 82.4, 55.0, 46.3, 35.4, 27.8, 21.6, 13.6.

IR (film) $\nu_{\text{max}}$: 2925, 2853, 1727, 1689, 1598, 1493, 1448, 1410, 1368, 1344, 1304, 1233, 1154, 1075, 1036, 1022, 1002, 968, 930, 914, 844, 765, 694 cm$^{-1}$.

HRMS (ESI) calcd for C$_{27}$H$_{30}$N$_2$O$_4$Na (M+Na$^+$): 469.2098, found: 469.2097.
Following **Method A**, reaction of 2a (29.8 mg, 0.10 mmol) and 3h (56.0 mg, 0.30 mmol) afforded 4m (47.8 mg, 0.0991 mmol, yield: 99%). The diastereomeric ratio was determined as 3.8:1 by \(^1\)H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.3%/95% (HPLC: OD-H, 254 nm, \(n\)-hexane/isopropanol = 92:8, flow rate: 0.7 mL/min, 25 °C, \(t_r\) (major) = 16.4 min, \(t_r\) (major) = 20.8 min, \(t_r\) (minor) = 24.7 min, \(t_r\) (minor) = 28.9 min). \([\alpha]_D^{20} = -169.8^\circ\) (c 1.0, CHCl\(_3\)).

**Analytic data of the major diastereomer:**

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.85 (s, 1H), 7.84-7.76 (m, 4H), 7.50-7.46 (m, 3H), 7.44-7.40 (m, 3H), 7.20-7.18 (m, 3H), 7.09 (d, \(J = 0.9\) Hz, 1H), 4.26 (dd, \(J = 11.2, 2.3\) Hz, 1H), 3.91-3.84 (m, 1H), 2.46 (dd, \(J = 17.9, 2.4\) Hz, 1H), 1.65 (s, 3H), 1.40 (s, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 198.7, 188.9, 171.2, 142.3, 138.1, 134.6, 133.4, 132.3, 129.3, 129.0, 128.9, 128.8, 128.1, 127.4, 126.8, 126.7, 126.5, 126.5, 125.7, 124.1, 82.5, 55.2, 46.3, 35.6, 27.8, 13.9.

IR (film) \(\nu_{max}\): 2924, 2852, 1725, 1689, 1597, 1494, 1448, 1410, 1368, 1344, 1304, 1235, 1154, 1037, 1002, 968, 914, 894, 843, 817, 758, 694, 522, 478 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{30}\)H\(_{30}\)N\(_2\)O\(_4\)Na (M+Na\(^+\)) \(^{\ast}\): 505.2098, found: 505.2100.
**Compound 4n**

Following **Method A**, reaction of 2a (29.8 mg, 0.10 mmol) and 3i (43.0 mg, 0.30 mmol) afforded 4n (32.3 mg, 0.0737 mmol, yield: 74%). The diastereomeric ratio was determined as 3.7:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98.9%/98.5% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 92:8, flow rate: 0.5 mL/min, 25 °C, $t_c$ (major) = 25.3 min, $t_c$ (major) = 26.7 min, $t_c$ (minor) = 29.3 min, $t_c$ (minor) = 42.8 min). \([\alpha]_D^{20} = -132.8^\circ \ (c \ 1.0, \ CHCl_3)\).

**Analytic data of the major diastereomer:**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.58 (s, 1H), 7.45-7.43 (m, 3H), 7.29-7.25 (m, 4H), 7.16 (s, 1H), 7.02-6.97 (m, 1H), 6.93 (d, $J = 3.0$ Hz, 1H), 3.98-3.90 (m, 2H), 2.67 (d, $J = 15.3$ Hz, 1H), 1.56 (s, 3H), 1.37 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.7, 188.9, 170.4, 142.5, 141.6, 138.1, 129.5, 128.9, 128.8, 127.7, 126.9, 126.3, 125.8, 125.7, 82.7, 54.4, 47.1, 35.5, 27.8, 15.0.

IR (film) $\nu_{\text{max}}$: 2923, 2851, 1728, 1689, 1597, 1494, 1448, 1410, 1368, 1344, 1304, 1236, 1153, 1076, 1036, 1002, 968, 914, 884, 844, 767, 695, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{24}$H$_{26}$N$_2$O$_4$SNa (M+Na)$^+$: 461.1505, found: 461.1507.
Compound 4o

Following Method B, reaction of 2a (29.8 mg, 0.10 mmol) and 3j (44.5 mg, 0.30 mmol) afforded 4o (40.8 mg, 0.0915 mmol, yield: 92%). The diastereomeric ratio was determined as 2.0:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IA column, ee = 96%/85% (HPLC: IA, 254 nm, n-hexane/isopropanol = 95:5, flow rate: 0.4 mL/min, 25 °C, t$_r$(major) = 38.7 min, t$_r$(major) = 39.6 min, t$_r$(minor) = 51.7 min, t$_r$(minor) = 55.7 min). [$\alpha$]$_D^{20}$ = -57.0° (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.74 (s, 1H), 7.44-7.38 (m, 4H), 7.29-7.22 (m, 7H), 7.14 (s, 1H), 3.87-3.73 (m, 2H), 3.00 (dd, $J$ = 17.7, 2.0 Hz, 1H), 2.11-1.94 (m, 2H), 1.29 (s, 9H), 0.95 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 200.5, 188.9, 171.7, 142.4, 138.1, 137.0, 129.4, 128.9, 128.7, 128.6, 128.1, 127.5, 126.8, 125.8, 81.6, 58.5, 44.7, 37.4, 27.7, 24.6, 9.0.

IR (film) $\nu_{max}$: 2964, 2925, 2852, 1723, 1689, 1597, 1494, 1447, 1409, 1368, 1304, 1256, 1231, 1153, 1038, 1002, 966, 914, 886, 846, 762, 701, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{27}$H$_{30}$N$_2$O$_4$Na (M+Na)$^+$: 469.2098, found: 469.2099.
Compound 4p

Following Method C, reaction of 2a (29.8 mg, 0.10 mmol) and 3k (0.033 mL, 0.30 mmol) afforded 4p (35.9 mg, 0.0935 mmol, yield: 94%). The diastereomeric ratio was determined as 2:1:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4%/97% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 95:5, flow rate: 0.4 mL/min, 25 °C, $t_r$(major) = 28.4 min, $t_r$(minor) = 29.6 min, $t_r$(minor) = 33.7 min, $t_r$(major) = 36.2 min). $[\alpha]_D^{20} = -59.0^\circ$ (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.58 (s, 1H), 7.44-7.41 (m, 3H), 7.28-7.25 (m, 3H), 7.20 (s, 1H), 3.81 (q, $J$ = 11.1 Hz, 1H), 3.41 (dd, $J$ = 11.2, 3.0 Hz, 1H), 3.00 (dd, $J$ = 17.7, 3.1 Hz, 1H), 1.63-1.54 (m, 2H), 1.33 (s, 9H), 1.03 (s, 3H), 0.81 (t, $J$ = 7.5 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 204.0, 189.3, 171.7, 142.7, 138.2, 129.6, 128.9, 128.7, 126.9, 125.7, 82.0, 50.6, 45.5, 35.1, 27.8, 27.7, 14.1, 8.2.

IR (film) $\nu_{\text{max}}$: 2955, 2918, 2850, 1726, 1691, 1494, 1467, 1410, 1367, 1153, 1041, 967, 764, 556 cm$^{-1}$.

HRMS (ESI) calcd for C$_{22}$H$_{28}$N$_2$O$_4$Na (M+Na)$^+$: 407.1941, found: 407.1943.
Compound 4q

Following Method C, reaction of 2a (29.8 mg, 0.10 mmol) and 3l (0.037 mL, 0.30 mmol) afforded 4q (38.3 mg, 0.0961 mmol, yield: 96%). The diastereomeric ratio was determined as 1.8:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.3%/98.8% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 94:6, flow rate: 0.5 mL/min, 25 °C, $t_r$(major) = 18.0 min, $t_r$(minor) = 19.9 min, $t_r$(minor) = 21.0 min, $t_r$(major) = 22.7 min). [$\alpha$]$^D_{20}$ = -55.1° (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.59 (s, 1H), 7.44-7.43 (m, 3H), 7.29-7.26 (m, 3H), 7.20 (s, 1H), 3.83 (q, $J$ = 11.2 Hz, 1H), 3.40 (dd, $J$ = 11.2, 2.6 Hz, 1H), 3.00 (dd, $J$ = 17.7, 2.7 Hz, 1H), 1.50-1.46 (m, 2H), 1.33 (s, 9H), 1.04 (s, 3H), 0.90-0.84 (m, 5H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 204.1, 189.3, 171.6, 142.7, 138.2, 129.6, 128.9, 128.7, 126.9, 125.7, 82.0, 50.5, 45.6, 37.5, 35.2, 27.7, 17.0, 14.6, 14.6.

IR (film) $\nu_{max}$: 2960, 2924, 2851, 1724, 1689, 1597, 1494, 1447, 1410, 1367, 1304, 1250, 1229, 1149, 1039, 967, 914, 846, 765, 692, 522 cm$^{-1}$.

HRMS (ESI) calcd for C$_{23}$H$_{30}$N$_2$O$_4$Na (M+Na)$^+$: 421.2098, found: 421.2099.
Compound 4r

Following Method C, reaction of 2a (29.8 mg, 0.10 mmol) and 3m (0.0480 mL, 0.30 mmol) afforded (41.6 mg, 0.0949 mmol, yield: 95%). The diastereomeric ratio was determined as 1.8:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4%/99.3% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 88:12, flow rate: 0.2 mL/min, 25 °C, $t_1$(major) = 28.8 min, $t_1$(minor) = 31.8 min, $t_2$(minor) = 32.7 min, $t_2$(major) = 34.9 min). $[\alpha]_D^{20} = -39.8'$ (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.60 (s, 1H), 7.44-7.43 (m, 3H), 7.29-7.25 (m, 3H), 7.19 (s, 1H), 5.04-4.95 (m, 1H), 3.82 (q, $J = 11.1$ Hz, 1H), 3.41 (dd, $J = 11.2$, 2.8 Hz, 1H), 3.01 (dd, $J = 17.7$, 2.9 Hz, 1H), 2.01-1.87 (m, 3H), 1.81-1.73 (m, 1H), 1.64 (s, 3H), 1.53 (s, 3H), 1.33 (s, 9H), 1.06 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.8, 189.2, 171.5, 142.7, 138.2, 132.5, 129.6, 128.9, 128.7, 126.9, 125.7, 123.2, 82.0, 50.4, 45.7, 35.2, 35.2, 27.7, 25.6, 22.4, 17.6, 14.4.

IR (film) $\nu_{\text{max}}$: 2922, 2851, 1722, 1689, 1645, 1598, 1494, 1447, 1409, 1367, 1344, 1304, 1244, 1150, 1074, 1038, 1021, 1001, 966, 914, 845, 764, 692 cm$^{-1}$.

HRMS (ESI) calcd for C$_{26}$H$_{34}$N$_2$O$_4$Na (M+Na)$^+$: 461.2411, found: 461.2412.
Compound 4s

Following Method C, reaction of 2a (29.8 mg, 0.10 mmol) and 3n (0.0650 mL, 0.30 mmol) afforded 4s (48.9 mg, 0.0973 mmol, yield: 97%). The diastereomeric ratio was determined as 2.7:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 99.2%/23% (HPLC: IC, 254 nm, n-hexane/isopropanol = 90:10, flow rate: 1 mL/min, 25 °C, $t_{(maj)}$ = 31.2 min, $t_{(maj)}$ = 40.4 min, $t_{(min)}$ = 49.2 min, $t_{(min)}$ = 85.7 min). $[\alpha]_D^{20} = -61.3^\circ$ (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.64 (s, 1H), 7.44-7.43 (m, 3H), 7.30-7.25 (m, 5H), 7.20 (s, 1H), 6.97 (d $J = 8.0$ Hz, 2H), 3.91 (q, $J = 11.0$ Hz, 1H), 3.46 (dd, $J = 11.0$, 2.6 Hz, 1H), 3.28-3.22 (m, 1H), 2.94 (d, $J = 13.8$ Hz, 1H), 2.74 (d, $J = 13.7$ Hz, 1H), 1.33 (s, 9H), 1.27 (s, 9H), 1.04 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 204.0, 189.0, 171.6, 149.6, 142.7, 138.1, 132.2, 130.2, 130.0, 129.7, 128.9, 126.9, 125.7, 125.2, 82.1, 51.4, 45.6, 40.7, 35.6, 34.3, 31.2, 27.7, 15.1.

IR (film) $\nu_{\text{max}}$: 2962, 2927, 2869, 2720, 1725, 1690, 1598, 1494, 1448, 1410, 1367, 1345, 1305, 1246, 1152, 1110, 1074, 1036, 1021, 1002, 967, 914, 874, 844, 803, 766, 693, 571, 524 cm$^{-1}$.

HRMS (ESI) calcd for C$_{31}$H$_{38}$N$_2$O$_4$Na (M+Na)$^+$: 525.2724, found: 525.2720.
Compounds 4t

Following Method C, reaction of 2a (29.8 mg, 0.10 mmol) and 3o (52.0 mg, 0.30 mmol) afforded 4t (46.7 mg, 0.0990 mmol, yield: 99%). The diastereomeric ratio was determined as 4.2:1 by $^1$H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98.2%/97% (HPLC: AD-H, 254 nm, n-hexane/isopropanol = 93:7, flow rate: 0.8 mL/min, 25 °C, $t_c$(minor) = 22.7 min, $t_c$(major) = 27.0 min, $t_c$(major) = 31.6 min, $t_c$(minor) = 58.0 min). [α]$^D_{20}$ = -38.3° (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.43 (s, 1H), 7.44-7.40 (m, 3H), 7.27 (d, J = 1.9 Hz, 1H), 7.25-7.23 (m, 2H), 7.17 (d, J = 0.7 Hz, 1H), 5.94 (s, 1H), 3.73-3.67 (m, 1H), 3.35-3.31 (m, 1H), 3.26-3.19 (m, 1H), 1.43 (s, 3H), 1.43 (s, 9H), 1.39 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 198.9, 188.2, 170.7, 154.7, 142.3, 138.1, 129.7, 128.9, 128.7, 127.0, 125.8, 82.5, 61.9, 44.9, 36.7, 28.2, 27.8, 22.6, 14.1.

IR (film) $\nu_{max}$: 3390, 2976, 2927, 2854, 1716, 1695, 1598, 1494, 1449, 1411, 1393, 1368, 1305, 1259, 1157, 1057, 1036, 967, 914, 845, 802, 761, 693, 521 cm$^{-1}$.

HRMS (ESI) calcd for C$_{25}$H$_{33}$N$_3$O$_6$Na (M+Na)$^+$: 494.2262, found: 494.2260.
Compound 4u

Following Method C, reaction of 2a (29.8 mg, 0.10 mmol) and 3p (52.0 mg, 0.30 mmol) afforded 4u (30.3 mg, 0.0820 mmol, yield: 82%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.2% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 25 °C, t$_r$(minor) = 11.8 min, t$_r$(major) = 13.9 min). [α]$_D^{20}$ = -49.5° (c 1.0, CHCl$_3$).

Analytic data of the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.46 (s, 1H), 7.40-7.32 (m, 3H), 7.24-7.16 (m, 3H), 7.12 (s, 1H), 3.73 (q, J = 11.1 Hz, 1H), 3.22 (d, J =8.8 Hz, 1H), 2.95 (d, J = 16.0 Hz, 1H), 1.27 (s, 9H), 1.00 (d, J = 3.3 Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 203.2, 189.1, 171.5, 142.6, 138.1, 129.6, 128.9, 128.7, 126.9, 125.7, 81.8, 47.3, 45.9, 35.6, 27.7, 20.5, 17.7.

IR (film) ν$_{max}$: 2974, 2923, 1725, 1689, 1641, 1597, 1547, 1493, 1447, 1410, 1368, 1305, 1260, 1146, 1086, 1038, 966, 914, 846, 801, 768, 693, 523 cm$^{-1}$.

HRMS (ESI) calcd for C$_{21}$H$_{26}$N$_2$O$_4$Na (M+Na)$^+$: 393.1785, found: 393.1780.
Additional Substrates with Different β-Substituents on α,β-Unsaturated Acyl Imidazoles

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{iPr} & \quad \text{Me} \\
\text{R} & \quad \text{CHO} \\
2g \ (R = \text{Me}); \\
2h \ (R = \text{Ph}).
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{CHO} \\
\text{N} & \quad \text{N} \\
\text{iPr} & \quad \text{Me} \\
\text{Me} & \quad \text{Ph} \\
3a \\
\Delta_{\text{Rh}-\text{S}} & \quad \text{Rh}1 \ (5 \text{ mol\%}) \\
\text{TFA} & \quad (0.4 \text{ eq}) \\
0 & \quad \text{°C, 40 h}
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{CHO} \\
\text{N} & \quad \text{N} \\
\text{iPr} & \quad \text{Me} \\
\text{Me} & \quad \text{Ph} \\
4w \ (R = \text{Me}), <5\% \text{ Conv.} \\
4v \ (R = \text{Ph}), 11\% \text{ Yield, 8.3:1 d.r., 7\%/66\% ee}
\end{align*}
\]

**Compound 4v**

To a solution of 2g (17.8 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst \(\Delta_{\text{Rh}-\text{S}}\text{-Rh1} \ (3.84 \text{ mg, 0.0050 mmol})\), trifluoroacetic acid (0.040 mmol) and 3a (0.041 mL, 0.30 mmol). The reaction mixture was stirred for 40 h at 0 °C. After evaporation of the volatile organic solvent, the crude product was used directly for determination of the conversion by \(^1\)H NMR (Conv. < 5%).

**Compound 4w**

To a solution of 2h (24.0 mg, 0.10 mmol) in anhydrous 1,2-dichloroethane (0.10 mL) were added the catalyst \(\Delta_{\text{Rh}-\text{S}}\text{-Rh1} \ (3.84 \text{ mg, 0.0050 mmol})\), trifluoroacetic acid (0.040 mmol) and 3a (0.041 mL, 0.30 mmol). The reaction mixture was stirred for 40 h at 0 °C (Conv. < 20%).
evaporation of the solvent, the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 5:1 to 3:1) to afford the product 4w (4.1 mg, 0.011 mmol, yield: 11%). The diastereomeric ratio was determined as 8.3:1 by \(^1\)H NMR. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 7%/60% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 94:6, flow rate: 0.7 mL/min, 25 °C, \(t_r\)(major) = 13.7 min, \(t_r\)(minor) = 15.1 min, \(t_r\)(minor) = 17.4 min, \(t_r\)(major) = 26.5 min).

**Analytic data of the major diastereomer:**

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.75 (s, 1H), 7.22-7.20 (m, 1H), 7.19-7.18 (m, 1H), 7.15-7.13 (m, 1H), 7.12-7.09 (m, 1H), 7.08-7.06 (m, 3H), 6.97-6.94 (m, 3H), 6.85-6.82 (m, 2H), 5.30-5.23 (m, 1H), 4.24-4.21 (m, 1H), 4.04-3.98 (m, 1H), 3.35-3.30 (m, 1H), 1.45 (s, 3H), 1.41 (d, \(J = 6.6\) Hz, 6H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 202.3, 190.5, 142.4, 139.4, 139.0, 129.5, 129.3, 128.5, 127.6, 127.5, 127.2, 126.4, 121.0, 57.6, 49.0, 46.0, 40.4, 29.7, 23.3, 16.1.
5. Stereochemical Assignment of the Products

The absolute and relative configuration of product 4a (the major diastereomer) was assigned as 2R,3S based on single crystal X-ray diffraction of its ester derivative 6a. Absolute and relative configuration of product 4a’ (the minor diastereomer) were assigned as 2R,3R based on single crystal X-ray diffraction of its ester derivative 6a’. See section 6.2 for synthesis of compounds 6a and 6a’, and section 8 for crystallographic data of 6a and 6a’.

HPLC peaks were assigned according to comparison of HPLC traces of the products generated from rac-Rh2, ΔRh-Sc-Rh1, and ΔRh-Rc-Rh1.

Enantiomeric excess of the compound 4a was determined with a Daicel Chiralpak OD-H column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using n-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 254 nm.
Figure S3. HPLC traces of rac-4a/4a', (2R,3S)-4a generated from \( \Delta_{\text{Rh-Sc}} \)-Rh1, and (2S,3R)-4a generated from \( \Lambda_{\text{Rh-Rc}} \)-Rh1.
6. Transformation of the Michael Addition Product

6.1 Transformation to a Chiral γ-Lactone

Compound 5b. A solution of sodium borohydride (19.0 mg, 0.502 mmol) and Na₂CO₃ (88.6 g, 0.836 mmol) in deionized water (0.167 mL) at room temperature was treated with 4b (143 mg, 0.418 mmol, the major diastereomer of 4b after flash chromatography, >99% de, 96% ee) in one portion. The resulting mixture was stirred for 1 h, worked up with saturated NH₄Cl solution, and extracted with ether. The extracts were dried (Na₂SO₄) and the solvent was evaporated in vacuo. The residue was used for the next reaction without further purification.

Subsequently, to a solution of the residue in CH₃CN (4.2 mL) was added 4 Å MS (210 mg) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (0.143 mL, 1.26 mmol) was added and stirred at room temperature for 26 h. After that, methanol (1.04 mL) and DBU (0.094 mL, 0.629 mmol) were added successively at room temperature. After stirring at room temperature for 1 h, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 6:1 to 3:1) to afford 5b (39.9 mg, 0.161 mmol, yield: 39%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 95% (HPLC: OJ, 220 nm, n-hexane/isopropanol = 80:20, flow rate: 1 mL/min, 25 °C, tᵣ(major) = 21.7 min, tᵣ(minor) =
24.7 min). \([\alpha]\)D \(^{20} = +14.1^\circ\) (c 1.0, CHCl\(_3\)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.35-7.30 (m, 2H), 7.44-7.40 (m, 3H), 4.24 (d, \(J = 8.9\) Hz, 1H), 4.16 (d, \(J = 8.9\) Hz, 1H), 3.58 (q, \(J = 3.4\) Hz, 1H), 3.52 (s, 3H), 2.64 (q, \(J = 7.8\) Hz, 1H), 2.38 (dd, \(J = 11.1, 5.1\) Hz, 1H), 1.38 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 176.8, 171.5, 141.0, 129.0, 127.6, 125.6, 78.2, 52.1, 46.5, 46.3, 29.9, 20.6.

IR (film) \(\nu_{\text{max}}:\) 2959, 2923, 2852, 1769, 1731, 1462, 1377, 1260, 1095, 1017, 800 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{14}\)H\(_{16}\)O\(_{4}\)Na (M+Na) \(^+\): 271.0941, found: 271.0944.

### 6.2 Transformation to Ester Derivatives 6a and 6a’ for Crystallography Study

**General Method.** A diastereomeric mixture of 4a and 4a’ (dr = 5.8:1, ee = 98.9%/90%) afforded in the catalytic asymmetric Michael addition was first separated by a silica gel flash chromatography. The isolated single diastereomer 4a or 4a’ was converted to their corresponding ester derivatives through \(N\)-methylation of the imidazole moiety with MeOTf followed by alcoholsylation.

**Compound 6a.** To a solution of 4a (565.5 mg, 1.306 mmol, the major diastereomer, 98.9% ee) in CH\(_3\)CN (13.1 mL) was added 4 Å MS (653 mg) under argon atmosphere. The suspension was
stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (0.22 mL, 1.961 mmol) was added and stirred at room temperature for 26 h. Afterwards, 4-bromobenzyl alcohol (1.466 g, 7.84 mmol) and DBU (0.29 mL, 1.961 mmol) were added in turn at room temperature. The mixture was stirred at room temperature for additional 1 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 6:1 to 3:1) to afford 6a (389.5 mg, 0.821 mmol, yield: 63%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IB column, ee = 82% (HPLC: IB, 220 nm, n-hexane/isopropanol = 92:8, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 15.5 min, t_r(minor) = 16.2 min). [α]_D^{20} = -106.7° (c 1.0, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 9.77 (s, 1H), 7.55-7.46 (m, 2H), 7.43-7.39 (m, 2H), 7.37-7.28 (m, 3H), 7.25-7.17 (m, 2H), 5.03 (s, 2H), 3.94 (d, J = 10.7 Hz, 1H), 2.69 (q, J = 5.3 Hz, 1H), 2.03 (d, J = 16.9 Hz, 1H), 1.46 (s, 3H), 1.44 (s, 9H).

^13C NMR (101 MHz, CDCl_3) δ 198.5, 171.9, 170.9, 136.9, 134.7, 131.6, 129.8, 129.3, 127.8, 127.0, 122.2, 82.7, 65.7, 55.1, 47.1, 31.1, 27.8, 13.7.

IR (film) v_max: 2977, 1730, 1597, 1490, 1446, 1369, 1337, 1260, 1148, 1071, 1014, 886, 843, 802, 763, 700 cm\(^{-1}\).

HRMS (ESI) calcd for C_{24}H_{27}BrO_5Na (M+Na)^+: 497.0934, found: 497.0939.
**Compound 6a'.** To a solution of 4a' (377.5 mg, 0.948 mmol, the minor diastereomer, 90% ee) in CH$_3$CN (9.5 mL) was added 4 Å MS (474.1 mg) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (0.161 mL, 1.422 mmol) was added and stirred at room temperature for 26 h. Afterwards, 4-bromobenzyl alcohol (1.06 g, 5.69 mmol) and DBU (0.213 mL, 1.422 mmol) were added in turn at room temperature. The mixture was stirred at room temperature for additional 1 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (300-400 mesh, n-hexane/ethyl acetate = 6:1 to 3:1) to afford 6a' (296.8 mg, 0.626 mmol, yield: 66%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IB column, ee = 82% (HPLC: OD-H, 220 nm, n-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 25 °C, t$_r$(minor) = 15.6 min, t$_r$(major) = 17.2 min). $[\alpha]_D^{20} = -77.2^\circ$ (c 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.40 (s, 1H), 7.52-7.48 (m, 2H), 7.43-7.38 (m, 2H), 7.37-7.32 (m, 1H), 7.31-7.28 (m, 2H), 7.25-7.23 (m, 2H), 5.08 (s, 2H), 3.64 (q, J = 2.8 Hz, 1H), 2.83 (q, J = 11.5 Hz, 1H), 2.56 (q, J = 2.9 Hz, 1H), 1.60 (s, 3H), 1.06 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 199.0, 171.6, 171.5, 136.7, 134.7, 131.7, 129.9, 128.7, 128.0, 127.9, 122.2, 80.9, 65.7, 54.8, 46.7, 33.4, 27.3, 14.6.

IR (film) $\nu_{\text{max}}$: 2975, 2925, 2851, 1721, 1598, 1490, 1446, 1408, 1368, 1349, 1260, 1149, 1071,
1013, 844, 802, 759, 740, 699, 546 cm$^{-1}$.

HRMS (ESI) calcd for C$_{24}$H$_{27}$BrO$_5$Na (M+Na)$^+$: 497.0934, found: 497.0929.
7. Chiral HPLC Traces

7.1 Chiral HPLC Traces of the Michael Addition Products

Enantiomeric excess of the compounds 4b-u and 4w were determined with a Daicel Chiralpak AD-H, IA, IB, IC or OD-H column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using n-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 254 nm.

**Figure S4.** HPLC traces of rac-4b/4b* and (2R,3S)-4b.
Figure S5. HPLC traces of rac-4c/4c' and (2R,3S)-4c.
Figure S6. HPLC traces of rac-4c/4c' and nonrac-4c.
Figure S7. HPLC traces of rac-4c/4c' and nonrac-4c.
**Figure S8.** HPLC traces of rac-4c/4c’ and nonrac-4c.
Figure S9. HPLC traces of rac-4c/4c\textsuperscript{a} and nonrac-4c.
Figure S10. HPLC traces of rac-4c/4c' and nonrac-4c.
Figure S11. HPLC traces of rac-4d/4d’ and (2R,3S)-4d.
Figure S12. HPLC traces of rac-4e/4e* and (2R,3S)-4e.
Figure S13. HPLC traces of rac-4f/4f' and (2R,3S)-4f.
Figure S14. HPLC traces of rac-4g/4g' and (2R,3S)-4g.
Figure S15. HPLC traces of rac-4h/4h’ and (2R,3S)-4h.
Figure S16. HPLC traces of rac-4i/4i' and (2R,3S)-4i.
Figure S17. HPLC traces of rac-4j/4j' and (2R,3S)-4j.
Figure S18. HPLC traces of rac-4k/4k’ and (2R,3S)-4k.
Figure S19. HPLC traces of rac-4l/4l’ and (2R,3S)-4l.
Figure S20. HPLC traces of rac-4m/4m’ and (2R,3S)-4m.
Figure S21. HPLC traces of rac-4n/4n’ and (2R,3R)-4n.
Figure S22. HPLC traces of $\text{rac-4o}/4o^*$ and $(2R,3S)-4o$. 

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<th>#</th>
<th>[min]</th>
<th>[min]</th>
<th>[mAU*s]</th>
<th>[mAU]</th>
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<td>VBA</td>
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<td>51.39439</td>
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Figure S23. HPLC traces of rac-4p/4p’ and (2R,3R)-4p.
Figure S24. HPLC traces of rac-4q/4q’ and (2R,3R)-4q.
Figure S25. HPLC traces of rac-4r/4r’ and (2R,3R)-4r.
Figure S26 HPLC traces of rac-4s/4s' and (2R,3R)-4s.
**Figure S27.** HPLC traces of rac-4t/4t’ and (2R,3R)-4t.
**Figure S28.** HPLC traces of *rac*-4u and (*R*)-4u.
Figure S29. HPLC traces of rac-4w/4w' and nonrac-4w.
7.2 Chiral HPLC Traces of the Transformation Products

Enantiomeric excess of 5b, 6a and 6a’ were determined with a Daicel Chiralpak OJ, IB or OD-H column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using n-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 220 nm.

![HPLC traces of rac-5b and (3R,4S)-5b.](image)

**Figure S30.** HPLC traces of rac-5b and (3R,4S)-5b.
Figure S31. HPLC traces of rac-6a, (2R,3S)-6a (synthesized from product 4a with 98.9% ee) and (2R,3S)-6a (crystal).
Figure S32. HPLC traces of rac-6a’, (2R,3R)-6a’ (synthesized from product 4a’ with 90% ee) and (2R,3R)-6a’ (crystal).
8. Single Crystal X-Ray Diffraction

8.1 Single Crystal X-Ray Diffraction of Rhodium Catalyst $\Delta_{\text{Rh-S}}$-Rh1

Crystals of $\Delta_{\text{Rh-S}}$-Rh1 was obtained by slow diffusion from a solution of the compound in CH$_2$Cl$_2$ layered with Et$_2$O at room temperature for several days. Data were collected on an Oxford Xcalibur, Sapphire3, Gemini ultra detector employing graphite-monochromated Mo-K$\alpha$ radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F$^2$ data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S33. The detailed information is listed in the Table S3. Crystallographic data for $\Delta_{\text{Rh-S}}$-Rh1 has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1465210.

Figure S33. Ortep drawing of rhodium catalyst $\Delta_{\text{Rh-S}}$-Rh1 with 50% probability thermal ellipsoids, the absolute configuration was identified as $\Delta_{\text{Rh-S}}$. 
8.2 Single Crystal X-Ray Diffraction of the Converted Product 6a

Crystals of compound 6a were obtained by recrystallization from a solution of the compound in n-hexane. Diffraction data were collected on a Bruker Apex CCD area detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 203 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on $F^2$ data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S34. The detailed information is listed in the Table S3. Crystallographic data for 6a has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1460793.

![Ortep drawing of 6a](image)

**Figure S34.** Ortep drawing of 6a with 50% probability thermal ellipsoids, the absolute configuration was identified as 2$R$,3$S$. 
8.3 Single Crystal X-Ray Diffraction of the Converted Product 6a'

Crystals of compound 6a' were obtained by recrystallization from a solution of the compound in \( n \)-hexane. Diffraction data were collected on a Bruker Apex CCD area detector employing graphite-monochromated Mo-K\( \alpha \) radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on \( F^2 \) data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S35. The detailed information is listed in the Table S3. Crystallographic data for 6a' has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1472577.

Figure S35. Ortep drawing of 6a' with 50% probability thermal ellipsoids, the absolute configuration was identified as \( 2R,3R \).
Table S3. Data collection and refinement statistics for the compounds ΔRh-Sc-Rh1, 6a and 6a’.

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<td><strong>Empirical formula</strong></td>
<td>C_{43}H_{44}BrN_{3}O_{5}Rh</td>
<td>C_{24}H_{27}BrO_{5}</td>
<td>C_{24}H_{27}BrO_{5}</td>
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<td>475.37</td>
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<td>203(2)</td>
<td>173(2)</td>
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<tr>
<td><strong>Wavelength (Å)</strong></td>
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<td>0.71073</td>
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<td>P2(1)2(1)2(1)</td>
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<td>2</td>
<td>4</td>
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<td>1.013</td>
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<td>R1 = 0.0367, wR2 = 0.0871</td>
<td>R1 = 0.0922, wR2 = 0.1140</td>
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<td>0.031(8)</td>
<td>0.021(13)</td>
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<td>0.438 and -0.209</td>
<td>0.612 and -0.349</td>
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9. References


**10. $^1$H NMR and $^{13}$C NMR Spectra**

10.1 $^1$H NMR and $^{13}$C NMR Spectra of Rhodium Catalyst $\Delta_{\text{Rh-Sc}}$-Rh1

![NMR Spectra](image)

**Figure S36.** $^1$H and $^{13}$C NMR spectrum for $\Delta_{\text{Rh-Sc}}$-Rh1.
10.2 $^1$H NMR and $^{13}$C NMR Spectra of Substrates and Products

Figure S37. $^1$H and $^{13}$C NMR spectrum for 2a.
Figure S38. $^1$H and $^{13}$C NMR spectrum for 2d.
Figure S39. $^1$H and $^{13}$C NMR spectrum for 2e.
Figure S40. $^1$H and $^{13}$C NMR spectrum for 2f.
Figure S41. $^1$H and $^{13}$C NMR spectrum for 4a.
Figure S42. $^1$H and $^{13}$C NMR spectrum for 4b.
Figure S43. $^1$H and $^{13}$C NMR spectrum for 4c.
Figure S44. $^1$H and $^{13}$C NMR spectrum for 4d.
Figure S45. $^1$H and $^{13}$C NMR spectrum for 4e.
Figure S46. $^1$H and $^{13}$C NMR spectrum for 4f.
Figure S47. $^1$H and $^{13}$C NMR spectrum for 4g.
Figure S48. $^1H$ and $^{13}C$ NMR spectrum for 4h.
Figure S49. $^1$H and $^{13}$C NMR spectrum for 4i.
Figure S50. $^1$H and $^{13}$C NMR spectrum for 4j.
Figure S51. $^1$H and $^{13}$C NMR spectrum for 4k.
Figure S52. $^1$H and $^{13}$C NMR spectrum for 4l.
Figure S53. $^1$H and $^{13}$C NMR spectrum for 4m.
Figure S54. $^1$H and $^{13}$C NMR spectrum for 4n.
Figure S55. $^1$H and $^{13}$C NMR spectrum for 4o.
Figure S56. $^1$H and $^{13}$C NMR spectrum for 4p.
Figure S57. $^1$H and $^{13}$C NMR spectrum for 4q.
Figure S58. $^1$H and $^{13}$C NMR spectrum for 4r.
Figure S59. $^1$H and $^{13}$C NMR spectrum for 4s.
Figure S60. $^1$H and $^{13}$C NMR spectrum for 4t.
Figure S61. $^1$H and $^{13}$C NMR spectrum for 4u.
9.3 $^1$H NMR and $^{13}$C NMR Spectra of the Transformation Product

**Figure S62.** $^1$H and $^{13}$C NMR spectrum for 5b.
Figure S63. $^1$H and $^{13}$C NMR spectrum for 6a.
Figure S64. $^1$H and $^{13}$C NMR spectrum for 6a'.
Figure S65. $^1$H and $^{13}$C NMR spectrum for 4w.