# Enantioselective Hydrogenation of Cyclic Tetrasubstituted-Olefinic Dehydroamino Acid Derivatives

# **Supporting Information**

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#### 1. General Considerations

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, unless otherwise noted. All ligands and Rh precursors were stored in a nitrogen-filled glove box before use. Chiral ligand intermediates were prepared according to our reported procedures.

<sup>1</sup>H NMR, <sup>31</sup>P NMR, <sup>19</sup>F NMR and <sup>13</sup>C NMR data were recorded on a Bruker-Ultrashield PLUS400 NMR or a 500 MHz Agilent spectrometer with CDCl3 or (CD<sub>3</sub>)<sub>2</sub>SO as the solvent. <sup>1</sup>H chemical shifts were referenced to CDCl3 at 7.26 ppm and (CD<sub>3</sub>)<sub>2</sub>SO at 2.50. <sup>13</sup>C chemical shifts were referenced to CDCl3 at 77.16 ppm and (CD<sub>3</sub>)<sub>2</sub>SO at 39.52. <sup>31</sup>P chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O at 0.0 ppm as external standard and obtained with <sup>1</sup>H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). MS was measured on Agilent 7890A/5975C Series GC/MSD mass spectrometer. HPLC yield were determined on Agilent 1200 Infinity Series.

### 2. Attached Optimization

 Table S1. Other investigation on asymmetric hydrogenation of N-(4-methyl-2-oxo-5,6-dihydro-2H-pyran-3-yl)acetamide (1a)

NHAc Me NHAc Me Rh(cod) <sub>2</sub> BF <sub>4</sub> (1 mol %) ligand (1.1 mol %) H <sub>2</sub> (1000 psi), 60 °C, THF, 3 h					
1a			2a		
Entries <sup>a</sup>	Ligand	Solvent	Yields (%)	Ee (%) <sup>b</sup>	
1	ArcPhos(L1)	THF	99	90	
2	ArcPhos(L1)	DCM	99	70	
3	ArcPhos(L1)	EtOAc	0	ND	
4	ArcPhos(L1)	CH <sub>3</sub> CN	0	ND	
5	ArcPhos(L1)	DCE	99	62	
6	ArcPhos(L1)	<sup>i</sup> PrOH	25	70	
7	ArcPhos(L1)	MTBE <sup>c</sup>	<5	ND	
8	ArcPhos(L1)	$CPME^{c}$	<5	ND	

<sup>*a*</sup>Unless otherwise specified, the reactions were carried out at 60 °C under H<sub>2</sub> (1000 psi) in THF (0.5 mL) for 3 h with **2a** (0.1 mmol) in the presence of rhodium precursor (1 µmol, 1 mol %) and ligand (1.1 µmol, 1.1 mol %); <sup>*b*</sup>Determined by chiral HPLC using a Chiralpak OJ-3 column. <sup>*c*</sup>MTBE and CPME perform badly for poor solubility.

#### 3. Substrate Preparation





**5**: To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound **3** (1 equiv), dry DCM (30 mL), under N<sub>2</sub> atmosphere. By

slowly adding DBU (2.1 equiv) in DCM via syringe at 0 °C, then the mixture was allowed to react at room temperature for ten minutes. Place the system at 0 °C and slowly drop 3-tert-butyldimethylsiloxypropionaldehyde **4** (1.5 equiv) in DCM for 5 minutes. Then the reaction was kept at 0°C for 10 minutes with TLC monitored (even room temperature or long reaction time will lead to increase of  $\beta$ -elimination by-products). DBU was washed with water, and the mixture was extracted with water (20 mL) and DCM (10 mL x 3), washed with saturated brine, dried over anhydrous sodium sulfate, concentrated, and column chromatography (PE:EA=1:1) to obtain desired product as white solid in 88% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (s, 1H), 6.62 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.35 (dd, *J* = 7.5, 6.0 Hz, 2H), 2.07 (s, 3H), 0.87 (s, 10H), 0.04 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.6 (s), 165.0 (s), 133.5 (s), 127.5 (s), 62.0 (s), 52.3 (s), 31.8 (s), 25.9 (s), 23.2 (s), 18.3 (s), -5.4 (s). ESI-MS: m/z 316. [M+H]<sup>+</sup>, 254.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>13</sub>H<sub>13</sub>NNaO<sub>3</sub>]<sup>+</sup>: 254.0788; found: 254.0788.



**6**: To a 250 mL Schlenk tube equipped with a mechanical stirrer was charged with compound **5** (1 equiv), DCM (30 mL), under N<sub>2</sub> atmosphere. By slowly adding NBS (1.1 equiv) in portions at 0 °C, the mixture turned pale yellow gradually and then was allowed to react at room temperature for 1 hour. Place

the system at 0 °C and slowly drop TEA (1.5 equiv) for 5 minutes, and the addition should be very slow at first. The suspension would turn brown to black then pale-yellow solution. Then the reaction was kept at room temperature for 30 minutes with TLC monitored. The mixture was extracted with 1 N HCl solution (20 mL) and DCM (10 mL x 3), washed with saturated brine, dried over anhydrous sodium sulfate,

concentrated, and column chromatography (PE:EA=3:1) to obtain desired product as pale yellow solid in 90% yield. The *Z/E* ratio was 2:1 determined by <sup>1</sup>H-NMR. (*Z*)-**6**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (s, 1H), 3.85 - 3.75 (m, 5H), 2.98 (t, *J* = 6.4 Hz, 2H), 2.11 (s, 3H), 0.88 (s, 9H), 0.05 (s, 5H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.9 (s), 162.8 (s), 123.7 (s), 123.2 (s), 61.2 (s), 52.7 (s), 39.7 (s), 25.8 (s), 22.9 (s), 18.2 (s), -5.4 (s). ESI-MS: m/z 394.2, 396.2 [M+H]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>15</sub>H<sub>29</sub>BrNO<sub>4</sub>Si]<sup>+</sup>: 394.1044, 396.1026; found: 394.1046, 396.025.



**7**: To a 250 mL Schlenk tube equipped with a mechanical stirrer was charged with Z/E mixture of compound **6** (1 equiv), dry THF (30 mL), under N<sub>2</sub> atmosphere. After slowly adding HF/pyr (2 equiv) through syringe at 0 °C, the mixture turned pale yellow gradually and then was allowed to react at room temperature for

one day. The forming white salt removed through filtration and the organic layer was concentrated. The mixture was purified through column chromatography (PE:EA=1:4) to obtain desired product as white solid in 45% yield (No olefin isomerization and cyclization process of (*E*)-**7** was monitored).<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  9.38 (s, 1H), 4.36 (t, *J* = 6.0 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H), 1.93 (s, 3H).<sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  168.6 (s), 159.8 (s), 137.1 (s), 127.1 (s), 65.9 (s), 34.5 (s), 22.8 (s). ESI-MS: m/z 234.0, 236.0 [M+H]<sup>+</sup>, 256.0, 258.0 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>7</sub>H<sub>8</sub>BrNNaO<sub>3</sub>]<sup>+</sup>: 255.9580; found: 255.9582.





**1p**: To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound **6** (1.0 equiv),  $Pd_2(dba)_3$  (0.03 equiv),  $PCy_3$  (0.06 equiv), trimethylboroxine (2.0 equiv), KF (2.0 equiv) and dioxane (10 mL), the resulting mixture was

purged with nitrogen and stirred under 100°C for 1 day. After full conversion of starting material monitored by TLC, the solvent was removed under vacuum. The mixture was then extracted with H<sub>2</sub>O/EtOAc (three times). The combined organic layers were concentrated and purified by silica gel column chromatography (PE/EA=1:1) to give the desired (*E*)-**1p** in 48% yield ((*Z*)-**1p** was obtained in 23% yield). (*E*)-**1p**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.57 (s, 1H), 3.74 (s, 3H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.58 - 2.52 (m, 2H), 2.08 (s, 3H), 1.84 (s, 3H), 1.75 - 1.67 (m, 3H), 0.89 (s, 9H), 0.04 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5 (s),  $\delta$  165.1 (s), 148.8 (s), 121.3 (s), 62.9 (s), 51.8 (s), 31.5 (s), 31.1 (s), 25.9 (s), 23.1 (s), 20.4 (s), 18.3 (s), -5.3 (s). ESI-MS: m/z 316.2 [M+H]<sup>+</sup>, 338.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>15</sub>H<sub>29</sub>NNaO4Si]<sup>+</sup>: 338.1758; found: 338.1763.





**2a**: ① To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound **7** (1.0 equiv),  $Pd(OAc)_2$  (0.03 equiv), BI-DIME (0.06 equiv), trimethylboroxine (2.0 equiv),  $K_3PO_4$  (2.0 equiv) and dioxane (10 mL), the resulting mixture was purged with nitrogen and stirred under 80 °C for 3 h. After full conversion of

starting material monitored by TLC, the solvent was removed under vacuum. The mixture was then extracted with H<sub>2</sub>O/EtOAc (three times). The combined organic layers were concentrated and purified by silica gel column chromatography to give the desired product compound as white solid in 93% yield. 2 To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound 7 (1.0 equiv), TBAF in THF (1.5 equiv.) and THF (10 mL). The solution was kept at r.t. for 3 h. The mixture was then extracted with H<sub>2</sub>O/EtOAc (three times). The combined organic layers were concentrated and purified by silica gel column chromatography to give the desired product compound as white solid in 82% yield. 3 To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound 7 (1.0 equiv), HF/pyr (2.0 equiv.) and THF (10 mL). The solution was kept at r.t. for 24 h. The mixture was then extracted with H<sub>2</sub>O/EtOAc (three times). The combined organic layers were concentrated and purified by silica gel column chromatography to give the desired product compound as white solid in 75% yield.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (s, 1H), 4.41 (t, J = 6.2 Hz, 2H), 2.59 (t, J = 6.2 Hz, 2H), 2.14 (s, 3H), 1.91 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.0 (s), 164.0 (s), 146.4 (s), 120.4 (s), 77.3 (s), 77.0 (s), 76.8 (s), 65.4 (s), 30.5 (s), 23.6 (s), 20.5 (s). ESI-MS: m/z 191.95 [M+Na]+; HRMS (ESI) calculated for [M+Na]<sup>+</sup>:192.0631; found: 192.0631.



Produce A: To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound 7 (1.0 equiv),  $Pd(OAc)_2$  (0.03 equiv), BI-DIME (0.06 equiv), alkenyl boric acid or vinylboronic acid trifluoroborate potassium (2.0 equiv), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv) and dioxane (10 mL), the resulting mixture was purged with nitrogen and stirred under 80°C for 3h. After full conversion of starting material monitored by TLC, the solvent

was removed under vacuum. The mixture was then extracted with  $H_2O/EtOAc$  (three times). The combined organic layers were concentrated and purified by silica gel column chromatography to give the desired product compound **8x**.

Produce B: To a 10 mL round-bottom flask equipped with a mechanical stirrer was charged with compound **8x** (**x**=**b**-**l**, 1 equiv),  $Pd(OH)_2/C$  (20%, <0.5% H<sub>2</sub>O, 10% wt%) and dry THF (2 ml), the resulting mixture was purged with hydrogen and stirred under 10 atm, 30 °C for 6 h. After full conversion of starting material monitored by TLC, the solid magazines were removed by filtration through kieselguhr and washed with THF, then the combined organic layer was concentrated to afford pure product.





**8b**: Prepared according to procedure A with vinylboronic acid trifluoroborate potassium as white solid in 72% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (s, 1H), 6.55 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.62 (d, *J* = 17.5 Hz, 1H), 5.56 (d, *J* = 10.8 Hz, 1H), 4.47 (t, *J* = 6.2 Hz, 2H), 2.74 (t, *J* = 6.2 Hz, 2H), 2.17 (s, 3H). <sup>13</sup>C NMR (126 MHz,

CDCl<sub>3</sub>)  $\delta$  168.7 (s), 164.6 (s), 140.2 (s), 132.3 (s), 121.3 (s), 120.2 (s), 77.3 (s), 77.3 (s), 76.9 (d, J = 32.0 Hz), 65.6 (s), 24.1 (s), 23.7 (s). ESI-MS: m/z 182.0 [M+H]<sup>+</sup>, 204.0 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>9</sub>H<sub>11</sub>NNaO<sub>3</sub>]<sup>+</sup>: 204.0631; found: 204.0634. bp 82-87 °C



**1b**: Prepared according to procedure B as white solid in 95% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (s, 1H), 4.40 (t, *J* = 6.2 Hz, 2H), 2.57 (t, *J* = 6.2 Hz, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 2.12 (s, 3H), 1.08 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (s),  $\delta$  164.2 (s), 151.6 (s), 119.4 (s), 65.5 (s), 27.5 (s), 26.6 (s), 23.6 (s), 10.4 (s).

ESI-MS: m/z 184.0  $[M+H]^+$ , 206.0  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_9H_{13}NNaO_3]^+$ : 206.0788; found: 206.0791.





**8c**: Prepared according to procedure A as white solid in 84% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (s, 1H), 6.26 (m, 1H), 6.18 (m, 1H), 4.42 (t, *J* = 6.2 Hz, 2H), 2.70 (t, *J* = 6.2 Hz, 2H), 2.16 (s, 3H), 1.91 (d, *J* = 6.1 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.7 (s), 164.9 (s), 141.6 (s), 135.3 (s), 127.2 (s), 118.1 (s), 65.4 (s), 24.8 (s), 23.7 (s), 19.2 (s). ESI-MS: m/z 196.1  $[M+H]^+$ , 218.1  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_{10}H_{13}NNaO_3]^+$ : 218.0788; found: 218.0786.



**1c**: Prepared according to procedure B as white solid in 97% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 (s, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 2.55 (t, *J* = 6.1 Hz, 2H), 2.27 - 2.20 (m, 2H), 2.11 (s, 3H), 1.50 (dd, *J* = 15.3, 7.5 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5 (s), 164.1 (s), 150.9 (s), 120.0 (s), 77.2

(d, J = 32.0 Hz), 77.0 (s), 76.9 (d, J = 32.0 Hz), 65.5 (s), 35.5 (s), 28.0 (s), 23.5 (s), 19.4 (s), 14.1 (s). ESI-MS: m/z 198.1 [M+H]<sup>+</sup>, 220.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>10</sub>H<sub>15</sub>NNaO<sub>3</sub>]<sup>+</sup>: 220.0944; found: 220.0938.





**8d**: Prepared according to procedure A as white solid in 35% yield (An undesired side product was formed with condition of procedure A). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (s, 1H), 5.13 (d, *J* = 20.9 Hz, 2H), 4.43 (t, *J* = 6.1 Hz, 2H), 2.67 (t, *J* = 6.1 Hz, 2H), 2.07 (s, 3H), 1.92 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.0 (s), 164.4 (s), 146.2 (s), 141.5 (s), 119.0 (s), 117.2 (s), 65.6 (s), 28.3 (s), 23.7 (s),

20.0 (s). ESI-MS: m/z 196.1  $[M+H]^+$ , 218.1  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_{10}H_{13}NNaO_3]^+$ : 218.0788; found: 218.0792.



1d: Prepared according to procedure B as white solid in 96% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.96 (s, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 2.84 (m, 1H), 2.51 (t, *J* = 6.1 Hz, 2H), 2.12 (s, 3H), 1.08 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.0 (s), 164.2 (s), 156.4 (s), 118.4 (s), 65.6 (s), 30.6 (s), 23.5 (s), 23.2 (s), 19.6 (s). ESI-MS: m/z 198.1 [M+H]<sup>+</sup>, 220.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for

 $[M+Na, C_{10}H_{15}NNaO_3]^+$ : 220.0944; found: 220.0946.





**8e**: Prepared according to procedure A as white solid in 98% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (s, 1H), 5.84 (s, 1H), 4.35 (t, J = 6.1 Hz, 2H), 2.70 (t, J = 5.8 Hz, 2H), 2.05 (s, 3H), 1.82 (s, 3H), 1.73 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.3 (s), 164.2 (s), 144.7 (s), 142.3 (s), 121.4 (s), 119.7 (s), 77.4 (s), 77.1 (s), 76.9 (s), 65.6 (s), 29.2 (s), 27.7 (s), 23.3 (s), 20.8 (s). ESI-MS: m/z 210.1 [M+H]<sup>+</sup>, 232.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>11</sub>H<sub>16</sub>NO<sub>3</sub>]<sup>+</sup>: 210.1125; found: 210.1130.



**1e**: Prepared according to procedure B as white solid in 95% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (s, 1H), 4.38 (t, *J* = 6.1 Hz, 2H), 2.54 (t, *J* = 6.1 Hz, 2H), 2.17 (d, *J* = 7.4 Hz, 2H), 2.10 (s, 3H), 1.84 (td, *J* = 7.4, 8.3 Hz, 1H), 0.86 (t, *J* = 8.3 Hz, 6H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5 (s), 164.0 (s), 150.5 (s), 120.7 (s), 65.5

(s), 42.7 (s), 28.5 (s), 25.8 (s), 23.5 (s), 22.5 (s). ESI-MS: m/z 212.1  $[M+H]^+$ , 234.1 $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+H, C_{1q}H_{18}NO_3]^+$ : 212.1281; found: 212.1281.





**8f**: Prepared according to procedure A as white solid in 91% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (s, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.19 - 6.11 (m, 1H), 4.43 (t, *J* = 6.2 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.20 (dd, *J* = 14.3, 7.1 Hz, 2H), 2.15 (s, 3H), 1.45 (dd, *J* = 14.8, 7.4 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

δ 168.6 (s), 164.9 (s), 141.6 (s), 140.3 (s), 126.0 (s), 118.3 (s), 65.4 (s), 35.5 (s), 24.8 (s), 23.7 (s), 22.1 (s), 13.7 (s). ESI-MS: m/z 224.1 [M+H]<sup>+</sup>, 246.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>12</sub>H<sub>17</sub>NNaO<sub>3</sub>]<sup>+</sup>: 246.1101; found: 246.1106.



**1f**: Prepared according to procedure B as white solid in 95% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.22 (s, 1H), 4.38 (t, J = 6.2 Hz, 2H), 2.55 (t, J = 6.2 Hz, 2H), 2.24 (m, 2H), 2.11 (s, 3H), 1.45 (m, 2H), 1.32 - 1.22 (m, 5H), 0.87 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.6 (s), 164.2 (s), 151.4 (s), 119.8

(s), 65.5 (s), 33.4 (s), 31.7 (s), 28.0 (s), 25.7 (s), 23.5 (s), 22.4 (s), 13.9 (s).ESI-MS: m/z 226.1 [M+H]<sup>+</sup>, 248.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>12</sub>H<sub>19</sub>NNaO<sub>3</sub>]<sup>+</sup>: 248.1257; found: 248.1262.





**8g**: Prepared according to procedure A as white solid in 92% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (s, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.0, 7.7 Hz, 1H), 4.43 (t, *J* = 6.2 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.15 (s, 3H), 2.11 (t, *J* = 6.9

Hz, 2H), 1.70 (dt, J = 13.4, 6.7 Hz, 1H), 0.90 (d, J = 6.6 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.7 (s), 164.9 (s), 141.6 (s), 139.3 (s), 126.9 (s), 118.4 (s), 65.4 (s), 42.7 (s), 28.4 (s), 24.9 (s), 23.7 (s), 22.4 (s). ESI-MS: m/z 238.1 [M+H]<sup>+</sup>, 260.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>13</sub>H<sub>19</sub>NNaO<sub>3</sub>]<sup>+</sup>: 260.1257; found: 260.1256.



**1g**: Prepared according to procedure B as white solid in 96% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 (s, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 2.56 (t, *J* = 6.1 Hz, 2H), 2.23 (dd, *J* = 16.5, 8.6 Hz, 2H), 2.12 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 1H), 1.46 (t, *J* = 7.9 Hz, 2H), 1.18 - 1.12 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H). <sup>13</sup>C NMR

(126 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (s), 164.2 (s), 150.9 (s), 119.8 (s), 77.1 (d, J = 31.9 Hz), 76.8 (s), 65.5 (s), 38.7 (s), 33.7 (s), 28.1 (s), 27.8 (s), 23.7 (d, J = 24.5 Hz), 22.5 (s).ESI-MS: m/z 240.2 [M+H]<sup>+</sup>, 262.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>13</sub>H<sub>21</sub>NNaO<sub>3</sub>]<sup>+</sup>: 262.1414; found: 262.1415.





**8h**: Prepared according to procedure A as white solid in 83% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (t, *J* = 7.4 Hz, 3H), 7.21 (dd, *J* = 22.4, 7.3 Hz, 3H), 6.27 (d, *J* = 12.7 Hz, 2H), 4.42 (t, *J* = 6.2 Hz, 2H), 3.56 (d, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 6.2 Hz, 2H), 2.15 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5 (s),

164.8 (s), 140.8 (s), 138.6 (s), 138.0 (s), 128.7 (d, J = 16.9 Hz), 127.0 (s), 126.5 (s), 119.0 (s), 77.3 (s), 76.9 (d, J = 32.0 Hz), 76.8 - 76.4 (m), 39.7 (s), 24.9 (s), 23.7 (s). ESI-MS: m/z 272.2 [M+H]<sup>+</sup>, 294.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>16</sub>H<sub>17</sub>NNaO<sub>3</sub>]<sup>+</sup>: 294.1101; found: 294.1105.



**1h:** Prepared according to procedure B as white solid in 98% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.32 - 7.17 (m, 4H), 4.44 (t, *J* = 6.1 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 6.1 Hz, 2H), 2.40 - 2.32 (m, 2H), 2.13 (s, 3H), 1.91 - 1.84 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 

168.6 (s), 164.0 (s), 150.8 (s), 141.3 (s), 128.4 (s), 128.4 (s), 126.1 (s), 120.2 (s), 77.3 (s), 77.1 (s), 76.8 (s), 65.4 (s), 35.6 (s), 32.9 (s), 28.0 (s), 27.6 (s), 23.4 (s). ESI-MS: m/z 274.2  $[M+H]^+$ , 296.2  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_{16}H_{19}NNaO_3]^+$ : 296.1257; found: 296.1260.





**8i**: Prepared according to procedure A as white solid in 72% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (s, 1H), 6.29 (s, 1H), 4.42 (t, *J* = 6.1 Hz, 2H), 2.77 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 2H), 2.11 (s, 3H), 1.94 - 1.87 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.2 (s), 165.4 (s), 142.0 (s), 140.6 (s), 139.3 (s), 118.3 (s), 65.4 (s), 32.8 (d, *J* = 2.5 Hz), 28.4 (s), 23.9 (s), 23.7 (s). ESI-MS:

m/z 222.1  $[M+H]^+$ , 244.1  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_{12}H_{15}NNaO_3]^+$ : 244.0944; found: 244.0947. bp 186-189 °C



**1**i: Prepared according to procedure B as white solid in 96% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.08 (s, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 2.96 - 2.85 (m, 1H), 2.52 (t, *J* = 6.1 Hz, 2H), 2.11 (s, 3H), 1.95 -1.87 (m, 2H), 1.73 - 1.66 (m, 2H), 1.63 (m, 2H), 1.39 (d, *J* = 2.4 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.1 (s), 164.1 (s), 155.2 (s), 119.4 (s), 65.7 (s), 42.3 (s), 30.4 (s), 26.0 (s), 24.4 (s), 23.6 (s). ESI-

MS: m/z 246.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na,  $C_{12}H_{17}NNaO_3$ ]<sup>+</sup>: 246.1101; found: 246.1104.





**8j**: Prepared according to procedure A as white solid in 92% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 (s, 1H), 5.90 (s, 1H), 4.40 (t, *J* = 6.1 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.12 (d, *J* = 5.8 Hz, 4H), 2.06 (s, 3H), 1.68 - 1.62 (m, 2H), 1.62 - 1.57 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.0 (s), 164.9 (s), 147.7 (s), 135.2 (s), 129.8 (s), 118.1 (s), 65.5 (s), 28.3 (s), 26.1 (s), 25.7 (s), 23.6 (s), 22.6 (s),

21.6 (s). ESI-MS: m/z 236.1 [M+H]<sup>+</sup>, 258.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>10</sub>H<sub>14</sub>NNaO<sub>3</sub>]<sup>+</sup>: 258.1101; found: 258.1106. bp 155-157 °C



**1j**: Prepared according to procedure B as white solid in 95% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.03 (s, 1H), 4.37 (t, *J* = 6.1 Hz, 2H), 2.51 (t, *J* = 6.1 Hz, 2H), 2.46 (t, *J* = 11.7 Hz, 1H), 2.12 (s, 3H), 1.82 - 1.74 (m, 4H), 1.34 - 1.10 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 169.2 (s), 164.3 (s), 156.1 (s), 118.7 (s), 65.6 (s), 41.4 (s), 29.5 (s), 25.9 (s), 25.9 (s), 24.5 (s), 23.5 (s). ESI-MS: m/z 238.1 [M+H]<sup>+</sup>,

260.2  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+H, C_{13}H_{20}NO_3]^+$ : 238.1438; found: 238.1436.





**8k**: Prepared according to procedure A as white solid in 82% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (s, 1H), 6.00 (t, *J* = 6.4 Hz, 1H), 4.38 (t, *J* = 6.1 Hz, 2H), 2.63 (t, *J* = 6.0 Hz, 2H), 2.33 - 2.28 (m, 2H), 2.20 (dd, *J* = 10.6, 6.3 Hz, 2H), 2.04 (s, 3H), 1.74 (dt, *J* = 11.7, 5.9 Hz, 2H), 1.56 - 1.45 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.9 (s), 164.6 (s), 150.1 (s), 141.9 (s), 134.3

(s), 117.8 (s), 65.6 (s), 32.2 (s), 30.7 (s), 29.1 (s), 29.0 (s), 27.0 (s), 26.4 (s), 23.6 (s). ESI-MS: m/z 250.1  $[M+H]^+$ , 272.2  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+H, C_{14}H_{19}NO_3]^+$ : 272.1257; found: 272.1264.



**1k**: Prepared according to procedure B as white solid in 98% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.99 (s, 1H), 4.36 (t, J = 6.1 Hz, 2H), 2.60 (t, J = 10.2 Hz, 1H), 2.53 (t, J = 6.1 Hz, 2H), 2.12 (s, 3H), 1.79 - 1.73 (m, 4H), 1.61 (d, J = 6.0 Hz, 2H), 1.55 - 1.45 (m, 4H), 1.42 (dd, J = 19.9, 8.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.1 (s), 164.4 (s), 157.3 (s), 117.4 (s), 77.1 (d, J = 5.0 Hz, 2H).

32.0 Hz), 76.8 (s), 76.8 (s), 65.7 (s), 42.3 (s), 32.0 (s), 27.8 (s), 27.6 (s), 24.4 (s), 23.5 (s). ESI-MS: m/z 252.1 [M+H]<sup>+</sup>, 274.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>14</sub>H<sub>21</sub>NNaO<sub>3</sub>]<sup>+</sup>: 274.1414; found: 274.1416.





**8**I: Prepared according to procedure A as white solid in 76% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (s, 1H), 5.83 (s, 1H), 4.40 (t, *J* = 6.1 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 2H), 2.04 (s, 3H), 1.90 (s, 2H), 1.40 (t, *J* = 6.3 Hz, 2H), 0.91 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.1 (s), 164.9 (s), 148.1 (s), 133.9 (s), 129.0 (s), 118.3 (s), 65.5 (s), 39.6 (s), 35.3 (s), 28.5 (s), 28.2 (s),

28.1 (s), 23.5 (s). ESI-MS: 264.3  $[M+H]^+$ , 286.3  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_{15}H_{21}NNaO_3]^+$ : 286.1414; found: 286.1419.



**11**: Prepared according to procedure B as white solid in 92% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.42 (s, 1H), 4.76 (m, 1H), 4.44 -4.26 (m, 2H), 2.85 (m, 1H), 2.09 (s, 3H), 2.04 - 1.95 (m, 1H), 1.88 (m, 1H), 1.45 - 1.32 (m, 5H), 1.18 (m, 2H), 1.07 (m, 2H), 0.87 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.7 (s), 170.1 (s), 65.8 (s), 50.5 (s), 39.1 (s), 38.6 (s), 37.4 (s), 36.6

(s), 32.9 (s), 29.8 (s), 26.1 (s), 23.8 (s), 23.1 (s), 21.3 (s). ESI-MS: m/z 266.3 [M+H]<sup>+</sup>, 288.4 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>15</sub>H<sub>23</sub>NNaO<sub>3</sub>]<sup>+</sup>: 288.1570; found: 288.1574.





**8m**: Prepared according to procedure A as white solid in 86% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (s, 1H), 5.86 (s, 1H), 4.42-4.34 (m, 2H), 2.60-2.65 (m, 2H), 2.08-2.25 (m, 3H), 2.03 (s, 3H), 1.76-1.59 (m, 3H), 1.23 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.1 (s), 164.8 (s), 148.0 (s), 134.8 (s), 129.5 (s), 118.3 (s), 65.5 (s), 34.1 (s), 30.7 (s), 28.4 (s),

27.7 (s), 26.0 (s), 23.5 (s), 21.5 (s). ESI-MS: 272.3 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>14</sub>H<sub>19</sub>NNaO<sub>3</sub>]<sup>+</sup>: 272.157; found: 272.1262.



**1m**: Prepared according to procedure B as white solid in 98% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (s, 1H), 4.37 (m, 2H), 2.55 (m, 2H), 2.42 (m, 1H), 2.12 (s, 3H), 1.80 - 1.66 (m, 3H), 1.50 (m, 2H), 1.26 (m, 1H), 0.93 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.15 (s), 164.21 (s), 156.19 (s), 119.0 (s), 118.8 (s), 65.6 (s), 41.6 (s), 41.0 (s), 34.5 (s), 32.2 (s), 31.1 (s), 29.4 (s),

26.3 (s), 24.7 (s), 24.5 (s), 23.5 (s), 23.4 (s), 22.5 (s), 17.4 (s). ESI-MS: 274.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>14</sub>H<sub>21</sub>NNaO<sub>3</sub>]<sup>+</sup>: 274.1414; found: 274.1417.





**1n**: Prepared according to procedure A with **11** (2 equiv) as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 - 7.28 (m, 5H), 7.10 (s, 1H), 4.56 (t, *J* = 6.1 Hz, 2H), 2.92 (t, *J* = 6.1 Hz, 2H), 1.95 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.9 (s), 164.2 (s), 145.5 (s), 137.0 (s), 129.3 (s), 128.6 (s), 126.8 (s), 120.3 (s), 65.6

(s), 30.1 (s), 23.3 (s). ESI-MS: m/z 232.1  $[M+H]^+$ , 254.1  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+Na, C_{13}H_{13}NNaO_3]^+$ : 254.0788; found: 254.0788.





13: To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound 12 (1 equiv), dry DCM (30 mL), under  $N_2$  atmosphere. By slowly adding DBU (2.1 equiv) in DCM via syringe at 0 °C, then the mixture was allowed to react at room temperature for ten minutes. Place

the system at 0 °C and slowly drop 3-tert-butyldimethylsiloxypropionaldehyde **4** (1.5 equiv) in DCM for 5 minutes. Then the reaction was kept at 0°C for 10 minutes with TLC monitored (even room temperature or long reaction time will lead to increase of  $\beta$ -elimination by-products). DBU was washed with water, and the mixture was extracted with water (20 mL) and DCM (10 mL x 3), washed with saturated brine, dried over anhydrous sodium sulfate, concentrated, and column chromatography (PE:EA=5:1) to obtain desired product as white solid in 83% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.55 (s, 1H), 6.44 (s, 1H), 3.75 (s, 3H), 3.70 (t, *J* = 6.0 Hz, 2H), 2.39 (dd, *J* = 13.0, 6.0 Hz, 2H), 1.43 (s, 9H), 0.87 (s, 9H), 0.04 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.3 (s), 153.2 (s), 130.8 (s), 128.4 (s), 80.30 (s), 62.20 (s), 52.15 (s), 31.34 (s), 28.15 (s), 25.86 (s), 18.24 (s), -5.45 (s). ESI-MS: m/z 382.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>17</sub>H<sub>33</sub>NNaO<sub>5</sub>Si]<sup>+</sup>: 382.2020; found: 382.2021.



**1o**: To a 150 mL Schlenk tube equipped with a mechanical stirrer was charged with compound (*E*)-**15** (1 equiv), dry THF (30 mL), TBAF (2 equiv) in THF solution under N<sub>2</sub> atmosphere. The mixture was kept at room temperature overnight. The solution was concentrated and purified by column chromatography (PE:EA=1:1)

to afford desired product as white solid in 83% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.36 (s, 1H), 4.35 (t, *J* = 6.2 Hz, 2H), 2.52 (t, *J* = 6.2 Hz, 2H), 1.91 (s, 3H), 1.44 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.0 (s), 153.0 (s), 144.9 (s), 121.0 (s), 80.5 (s), 65.3 (s), 30.3 (s), 28.1 (s), 19.9 (s). ESI-MS: m/z 250.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>11</sub>H<sub>17</sub>NNaO<sub>4</sub>]<sup>+</sup>: 250.1050; found: 250.1054.

#### 4. General procedures for asymmetric hydrogenation

To a 4-mL vial equipped with a magnetic stirring bar was charged cyclic dehydroamino acid derivative (0.1 mmol),  $[Rh(L1)(cod)]BF_4$  (1 mol %) and dry THF (0.5 mL) in glove box. After stirred for 5 min at room temperature, the reaction mixture was transferred to an autoclave. The autoclave was purged with hydrogen three times and charged to 1000 psi. The mixture was stirred at 60 °C for 3 h, and depressurized carefully in a well-ventilated hood. A crude reaction sample was passed through celite to remove metal precipitate and directly analyzed by chiral HPLC to determine the conversions and ee values. The hydrogenation products were isolated in quantitative yields.



**2a**:Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl3)  $\delta$  6.39 (s, 1H), 4.79 (t, *J* = 6.5 Hz, 1H), 4.41 - 4.34 (m, 2H), 2.93 - 2.84 (m, 1H), 2.31 (m, 1H), 2.07 (s, 3H), 1.72 - 1.63 (m, 1H), 0.91 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.2 (s),

170.0 (s), 65.9 (s), 52.4 (s), 29.3 (s), 28.0 (s), 23.0 (s), 16.8 (s). ESI-MS: m/z 172.00  $[M+H]^+$ ; HRMS (ESI) calculated for  $[M+H, C_8H_{14}NO_3]^+$ : 172.0968; found: 172.0960. 90% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 11.47$  min (major),  $t_2 = 13.05$  min. T = 20 min.  $[\alpha]_D^{25}$  -103.6 (c 0.13, CHCl<sub>3</sub>).



**2b**:Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.52 (s, 1H), 4.86 - 4.76 (m, 1H), 4.39 - 4.31 (m, 2H), 2.58 (m, 1H), 2.21 - 2.12 (m, 1H), 2.04 (s, 3H), 1.78 - 1.69 (m, 1H), 1.57 - 1.49 (m, 1H), 0.91 (m, 1H), 0.87 (m, 3H). <sup>13</sup>C NMR (126 MHz,

CDCl<sub>3</sub>)  $\delta$  172.5 (s), 170.0 (s), 77.3 (s), 52.0 (s), 34.4 (s), 26.3 (s), 23.2 (s), 23.0 (s), 10.8 (s). ESI-MS: m/z 208.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>10</sub>H<sub>19</sub>NNaO<sub>4</sub>]<sup>+</sup>: 240.1206; found: 240.1214. 92% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 10.05$  min (major),  $t_2 = 11.37$  min. T = 20 min. [ $\alpha$ ] $p^{25}$  -30.9 (c 0.10, CHCl<sub>3</sub>).



**2c**:Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.39 (s, 1H), 4.83 - 4.77 (m, 1H), 4.42 - 4.33 (m, 2H), 2.70 (m, 1H), 2.19 (m, 1H), 2.07 (s, 3H), 1.76 (m, 1H), 1.41 (m, 2H), 1.21 (m, 1H), 0.89 (m, 5H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.4 (s),

169.9 (s), 66.0 (s), 52.0 (s), 32.7 (s), 32.5 (s), 26.7 (s), 23.1 (s), 19.5 (s), 14.0 (s). ESI-MS: m/z 200.2 [M+H]<sup>+</sup>, 222.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>11</sub>H<sub>21</sub>NNaO<sub>4</sub>]<sup>+</sup>: 254.1363; found: 254.1370. 90% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 9.32$  min (major),  $t_2 = 10.62$  min. T = 20 min.  $[\alpha]_D^{25}$  -117.7 (c 0.25, CHCl<sub>3</sub>).



**2d**:Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.44 (m, 1H), 4.76 (m, 1H), 4.39 (m, 1H), 4.32 (m, 1H), 2.95 - 2.82 (m, 1H), 2.08 (s, 3H), 1.93 (m, 1H), 1.80 (m, 1H), 0.94 - 0.88 (m, 1H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.70 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.5 (s), 170.1 (s), 65.7 (s), 50.7 (s), 37.1

(s), 26.7 (s), 23.0 (s), 21.6 (s), 20.6 (s), 15.3 (s). ESI-MS: m/z 200.1 [M+H]<sup>+</sup>, 222.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>10</sub>H<sub>17</sub>NNaO<sub>3</sub>]<sup>+</sup>: 222.1101; found:222.1102. 90% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 9.03$  min (major),  $t_2 = 10.57$  min. T = 20 min. [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 25.3 (c 0.24, CHCl<sub>3</sub>).



**2e**:Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.40 (s, 1H), 4.84 (m, *J* = 6.5 Hz, 1H), 4.46 - 4.36 (m, 2H), 2.85 - 2.76 (m, 1H), 2.22 (m, 1H), 2.09 (s, 3H), 1.78 (m, 1H), 1.19 (m, 1H), 1.00 - 0.95 (m, 1H), 0.93 (s, 3H), 0.85 (s, 3H). <sup>13</sup>C NMR

(126 MHz, CDCl<sub>3</sub>)  $\delta$  172.4 (s), 169.8 (s), 66.0 (s), 52.0 (s), 39.4 (s), 30.8 (s), 26.8 (s), 24.8 (s), 24.0 (s), 23.1 (s), 20.8 (s). ESI-MS: m/z 214.1 [M+H]<sup>+</sup>, 236.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>11</sub>H<sub>20</sub>NO<sub>3</sub>]<sup>+</sup>: 214.1438; found: 214.1440. 92% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 8.18 \text{ min (major)}, t_2 = 9.15 \text{ min. T} = 20 \text{ min. } [\alpha]_D^{25}$  -178.1 (c 0.40, CHCl<sub>3</sub>).



**2f**:Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.44 (d, *J* = 5.2 Hz, 1H), 4.82 - 4.77 (m, 1H), 4.37 (m, 2H), 2.66 (m, 1H), 2.21 - 2.14 (m, 1H), 2.06 (s, 3H), 1.76 (m, 1H), 1.43 (m, 1H), 1.26 (m, 6H), 0.86 (m, 4H). <sup>13</sup>C NMR (126)

MHz, CDCl<sub>3</sub>)  $\delta$  172.4 (s), 169.9 (s), 66.0 (s), 52.0 (s), 32.9 (s), 31.7 (s), 30.3 (s), 26.8 (s), 26.0 (s), 23.0 (s), 22.5 (s), 13.9 (s). ESI-MS: m/z 228.2 [M+H]<sup>+</sup>, 250.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>12</sub>H<sub>21</sub>NNaO<sub>3</sub>]<sup>+</sup>: 250.1414; found: 250.1416. 92% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 8.00$  min (major),  $t_2 = 9.82$  min. T = 20 min. [ $\alpha$ ]<sub>D</sub><sup>25</sup> -106.7 (c 0.42, CHCl<sub>3</sub>)



**2g**: Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.39 (s, 1H), 4.79 (t, *J* = 6.6 Hz, 1H), 4.38 (m, 2H), 2.69 (m, 1H), 2.23 - 2.16 (m, 1H), 2.07 (s, 3H), 1.81 - 1.71 (m, 1H), 1.54 - 1.46 (m, 1H), 1.41 (m, 1H), 1.34 (m, 1H), 1.14 (m, 4H), 0.85 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.4 (s),

169.9 (s), 66.0 (s), 52.1 (s), 38.8 (s), 32.9 (s), 30.6 (s), 27.8 (s), 26.8 (s), 24.1 (s), 23.1 (s), 22.7 (s), 22.4 (s). ESI-MS: m/z 242.1  $[M+H]^+$ , 264.4  $[M+Na]^+$ ; HRMS (ESI) calculated for  $[M+MeOH, C_{14}H_{27}NNaO_4]^+$ : 296.1832; found: 296.1839. 91% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 7.47$  min (major),  $t_2 = 8.56$  min. T = 20 min.  $[\alpha]_D^{25}$  -89.7 (c 0.25, CHCl<sub>3</sub>).



**2h**: Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 - 7.24 (m, 2H), 7.16 (m, 3H), 6.38 (d, *J* = 5.3 Hz, 1H), 4.79 (t, *J* = 6.6 Hz, 1H), 4.37 - 4.33 (m, 2H), 2.78 - 2.69 (m, 1H), 2.62 (m, 1H), 2.53 (m, 1H), 2.19 (m, 1H), 2.02 (s, 3H),

1.72 (m, 2H), 1.65 (m, 1H), 1.51 (m, 2H), 1.00 - 0.90 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.3 (s), 169.9 (s), 141.7 (s), 128.4 (s), 128.3 (s), 125.9 (s), 66.0 (s), 51.9 (s), 35.5 (s), 32.6 (s), 29.7 (s), 28.1 (s), 26.8 (s), 23.0 (s). ESI-MS: m/z 276.3 [M+H]<sup>+</sup>, 298.3 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na, C<sub>17</sub>H<sub>25</sub>NNaO<sub>4</sub>]<sup>+</sup>: 330.1676; found: 330.1677. 70% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1$  = 14.00 min (major),  $t_2$  = 17.89 min. T = 20 min. [ $\alpha$ ]<sub>D</sub><sup>25</sup> -140.1 (c 0.28, CHCl<sub>3</sub>).



**2i**: Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.49 (s, 1H), 4.80 (dd, *J* = 7.9, 6.2 Hz, 1H), 4.36 (m, 2H), 2.89 (m, 1H), 2.13 - 2.06 (m, 1H), 2.05 (s, 3H), 1.82 (m, 2H), 1.69 (m, 1H), 1.59 - 1.44 (m, 5H), 1.14 (m, 2H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.1 (s), 170.1 (s), 66.0 (s), 51.9 (s), 40.1 (s), 35.8 (s), 30.6 (s), 27.2

(s), 25.2 (s), 25.2 (s), 24.1 (s), 23.0 (s). ESI-MS: m/z 226.1 [M+H]<sup>+</sup>, 248.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+Na,  $C_{12}H_{19}NNaO_3$ ]<sup>+</sup>: 248.1257; found: 248.1260. 93% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 9.52$  min (major),  $t_2 = 11.14$  min. T = 20 min. [ $\alpha$ ]<sub>D</sub><sup>25</sup> -87.4 (c 0.15, CHCl<sub>3</sub>).



**2j**: Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.44 (d, *J* = 4.5 Hz, 1H), 4.76 (m, 1H), 4.38 (m, 1H), 4.33 - 4.26 (m, 1H), 2.80 (m, 1H), 2.09 (s, 3H), 1.94 (m, 1H), 1.86 (m, 1H), 1.71 (m, 2H), 1.67 - 1.61 (m, 1H), 1.52 - 1.39 (m, 2H), 1.24 (m, 2H), 1.14 (m, 2H), 1.07 - 1.00 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl3)

δ 173.7 (s), 170.1 (s), 65.8 (s), 50.4 (s), 37.4 (s), 37.0 (s), 30.6 (s), 26.5 (s), 26.2 (s), 26.0 (s), 25.7 (s), 23.0 (s), 22.9 (s). ESI-MS: m/z 240.1 [M+H]<sup>+</sup>, 262.1 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>13</sub>H<sub>22</sub>NO<sub>3</sub>]<sup>+</sup>: 240.1594; found: 240.1601. 94% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 8.37$  min (major),  $t_2 = 10.57$  min. T = 20 min. [α]<sub>D</sub><sup>25</sup> -112.3 (c 0.34, CHCl<sub>3</sub>).



**2k:** Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.37 (s, 1H), 4.73 (m, 1H), 4.37 (m, 1H), 4.29 (m, 1H), 2.91 (m, 1H), 2.09 (s, 3H), 2.03 - 1.96 (m, 1H), 1.84 - 1.72 (m, 1H), 1.72 - 1.61 (m, 3H), 1.58 - 1.52 (m, 2H), 1.52 - 1.44 (m, 2H), 1.40 (m, 3H), 1.31 - 1.26 (m, 1H), 1.25 - 1.20 (m, 1H), 1.16 (m, 1H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.7 (s), 170.1 (s), 77.3 (s), 77.1 (s), 76.9 (d, *J* = 31.9 Hz), 65.9 (s), 50.6 (s), 38.8 (d, *J* = 15.5 Hz), 33.0 (s), 27.9 (s), 27.7 (d, *J* = 3.0 Hz), 27.4 (s), 27.2 (d, *J* = 37.7 Hz), 23.3 (s), 22.9 (s). ESI-MS: m/z 254.2 [M+H]<sup>+</sup>, 276.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>15</sub>H<sub>27</sub>NNaO<sub>4</sub>]<sup>+</sup>: 308.1832; found: 308.1838. 92%

ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 8.21$  min (major),  $t_2 = 9.54$  min. T = 20 min.  $[\alpha]_D^{25}$  -108.6 (c 0.54, CHCl<sub>3</sub>).



**21**: Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.42 (s, 1H), 4.76 (m, 1H), 4.44 - 4.26 (m, 2H), 2.85 (m, 1H), 2.09 (s, 3H), 2.04 - 1.95 (m, 1H), 1.88 (m, 1H), 1.45 - 1.32 (m, 4H), 1.18 (m, 2H), 1.07 (m, 2H), 0.87 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.7 (s), 170.1 (s), 65.8 (s),

50.5 (s), 39.1(s), 28.6 (s), 37.4 (s), 36.6 (s), 32.9 (s), 29.8 (s), 26.1 (s), 23.8 (s), 23.1 (s), 21.2 (s).ESI-MS: m/z 268.3 [M+H]<sup>+</sup>, 290.3 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>16</sub>H<sub>29</sub>NNaO<sub>4</sub>]<sup>+</sup>: 322.1989; found: 322.1993. 95% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 7.28$  min (major),  $t_2 = 8.21$  min. T = 20 min. [ $\alpha$ ] $_D^{25}$  -119.0 (c 0.32, CHCl<sub>3</sub>).



**2m**: Prepared according to general procedure for asymmetric hydrogenation as white solid in 99% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.40 (s, 1H), 4.76 (m, 1H), 4.39 (m, 1H), 4.31 (m, 1H), 2.83 (m, 1H), 2.09 (s, 3H), 2.02 - 1.93 (m, 1H), 1.93 - 1.78 (m, 2H), 1.72 - 1.64 (m, 1H), 1.55 - 1.39 (m, 4H), 1.35 - 1.28 (m, 1H), 1.20 (m, 1H), 1.08 - 0.99 (m, 1H), 0.88 (m, 4H). <sup>13</sup>C NMR

(126 MHz, CDCl<sub>3</sub>)  $\delta$  173.6 (s), 170.1 (s), 77.3 (s), 77.0 (s), 76.7 (s), 65.9 (d, J = 5.4 Hz), 50.5 (d, J = 9.0 Hz), 37.6 (s), 37.1 (s), 36.7 (s), 36.6 (s), 35.1 (s), 34.5 (s), 32.5 (s), 31.6 (s), 31.1 (s), 30.4 (s), 26.7 (s), 25.4 (s), 24.4 (s), 23.1 (s), 23.0 (s), 22.9 (s), 22.5 (s), 19.9 (s), 17.4 (s). ESI-MS: m/z 254.2 [M+H]<sup>+</sup>, 276.2 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>15</sub>H<sub>27</sub>NNaO<sub>4</sub>]<sup>+</sup>: 308.1832; found: 308.1838. 96% ee. Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min, 210 nm.  $t_1 = 7.43$  min (major),  $t_2 = 8.88$  min ( $t_1 = 8.15$  min (major),  $t_2 = 9.66$  min) T = 20 min.

### 5. Transformation of 2a



To a 25-mL vial equipped with a magnetic stirring bar was charged tetrasubstituted enamides **1a** (1.69 g, 10 mmol), [Rh(**L1**)(cod)]BF<sub>4</sub> (10 mg, 0.1 mol %, TONs = 1000) and dry THF (4 mL) under nitrogen. After stirred for 5 min at room temperature, the reaction mixture was transferred to an autoclave. The autoclave was purged with hydrogen three times and charged to 1000 psi. The mixture was stirred at room temperature for 12 h, and depressurized carefully in a well-ventilated hood. A crude reaction sample was passed through celite to remove metal precipitate and directly

analyzed by chiral HPLC to determine the conversions and ee values. The hydrogenation products were isolated in quantitative yields (1.69 g).



(D)-isoleucine



**16**: **2a** and dry MeOH (1 mL) was added to a dried Schlenk tube, the colorless transparent solution was stirred at room temperature for 1 h. The extra MeOH was removed in vacuo to give the desired product as colorless oil (99% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$  4.40 (d, *J* = 5.5 Hz, 1H), 3.72 (d, *J* = 3.3

Hz, 3H), 3.62 (dd, J = 6.8, 5.4 Hz, 1H), 3.57 (dd, J = 7.7, 6.4 Hz, 1H), 2.18 - 2.09 (m, 1H), 1.99 (s, 3H), 1.70 - 1.62 (m, 1H), 1.45 - 1.36 (m, 1H), 0.95 (d, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>OD)  $\delta$  172.0 (s), 172.0 (s), 59.0 (s), 57.1 (s), 51.0 (s), 34.7 (s), 32.0 (s), 20.8 (s), 15.0 (s). ESI-MS: m/z 226.4 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>9</sub>H<sub>17</sub>NNaO<sub>4</sub>]<sup>+</sup>: 226.1050; found: 226.1056. [ $\alpha$ ]<sub>D</sub><sup>25</sup> -409.8 (c 0.09, CHCl<sub>3</sub>).



**9**: To a dry round-bottom bottle with a stirring bar was added  $I_2$  (1.3 equiv) and DCM (2 mL), then PPh<sub>3</sub> (1.3 equiv) was added at 0 °C, the generated yellow solution was kept for 15 min, then imidazole (2.0 equiv) was added. After 15 min at room temperature, **16** (1.0 equiv) in DCM was added via syringe

dropwise and the generated pale-yellow suspension was kept for about 3 hours. The mixture was concentrated, and column chromatography (PE:EA=3:1) to obtain desired product as white solid in 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.03 (d, *J* = 7.1 Hz, 1H), 4.61 (dd, *J* = 8.4, 5.0 Hz, 1H), 3.76 (s, 3H), 3.29 (d, *J* = 4.9 Hz, 1H), 3.12 (d, *J* = 9.1 Hz, 1H), 2.10 (s, 1H), 2.04 (s, 3H), 2.00 - 1.91 (m, 1H), 1.74 - 1.66 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.1 (s), 169.8 (s), 55.9 (s), 52.4 (s), 37.4 (s), 36.5 (s), 23.3 (s), 15.1 (s), 3.5 (s). ESI-MS: m/z 314.1 [M+H]<sup>+</sup>, 335.9 [M+Na]<sup>+</sup>; HRMS (ESI) calculated for [M+H, C<sub>9</sub>H<sub>16</sub>INNaO<sub>3</sub>]<sup>+</sup>: 336.0067; found: 336.0071. [ $\alpha$ ]<sub>D</sub><sup>25</sup> -163.3 (c 0.11, CHCl<sub>3</sub>).



**17**: To a round-bottom bottle with a stirring bar was added **9** (1.0 equiv) in THF (2 mL) and then Raney Nickel (in H<sub>2</sub>O, 2 equiv). The mixture was kept at room temperature for 1 h and extracted with H<sub>2</sub>O/EtOAc (three times). The combined organic layers were concentrated and purified by silica gel column

chromatography to give the desired product compound as white solid in 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.05 (s, 1H), 4.70 (m, 1H), 3.71 (s, 3H), 2.02 (s, 3H), 1.93 - 1.86 (m, 1H), 1.43 - 1.34 (m, 1H), 1.19 - 1.09 (m, 1H), 0.92 (t, *J* = 6.4 Hz, 3H), 0.84 (d, *J* = 8.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.1 (s), 170.1 (s), 55.3 (s), 52.2 (s), 37.7 (s), 26.1 (s), 23.2 (s), 14.6 (s), 11.7 (s). [ $\alpha$ ]<sub>D</sub><sup>25</sup> -333.8 (c 0.04, CHCl<sub>3</sub>).



**10**: To a sealed tube with a stirring bar was added **17** and conc. HCl (2 mL). The mixture was kept at 80 °C for 3 h. Then, the solvent was removed in vacuo and the mixture was purified through Dowex (H<sup>+</sup> type) to obtain the desired product as white solid (85% yield). <sup>1</sup>H NMR (500 MHz, d<sub>2</sub>o)  $\delta$  3.69 (d, *J* = 3.5

Hz, 1H), 2.02 (m, 1H), 1.39 - 1.34 (m, 1H), 1.34 - 1.25 (m, 1H), 0.94 - 0.88 (m, 6H). <sup>13</sup>C NMR (126 MHz, d<sub>2</sub>o)  $\delta$  174.6 (s), 58.3 (s), 35.5 (s), 25.4 (s), 13.1 (s), 10.9 (s).  $[\alpha]_D^{25}$  -121.4 (c 0.03, H<sub>2</sub>O).

## 6. Original NMR Data of substrates


































































































# 7. Original HPLC Data of substrates

# Rac-2a

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Data File C:\CHEM32\1\DATA\WF\WF 2020-05-25 19-53-03\061-0101.D Sample Name: Ac-Me-Rac
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LC2 7/13/2020 10:16:47 PM 系统

Page 1 of 1

# Chiral-2a

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   Acq. Instrument : LC2
                                            Location : Vial 63
   Injection Date : 6/4/2020 7:44:28 PM
                                              Inj: 1
                                           Inj Volume : 5.000 µl
   Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-06-04 19-09-33\WF-80-20-0.7-5UL-15MIN.M
Last changed : 6/4/2020 7:09:33 PM by 系统
   Acq. Method
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      mAU J
      500 -
      400 -
      300 -
      200 -
                                                                     13.054
      100 -
       0
                            10
                                          11
                                                       12
                                                                     13
   _____
                       Area Percent Report
   _____
                                       _____
   Sorted By
                     :
                           Signal
             :
                         1.0000
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                  Height Area
[mAU] %
   Peak RetTime Type Width
                          Area
    # [min] [mAU*s]
   ----|-----|----|-----|-----|-----|
    1 11.469 MM 0.3621 1.09104e4 502.17953 95.0731
2 13.054 MM 0.3652 565.39850 25.80617 4.9269
   Totals :
                        1.14758e4 527.98570
                         _____
LC2 7/13/2020 10:02:04 PM 系统
                                                                     Page 1 of 1
```

#### Rac-2b

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                                             Seq. Line : 1
                                             Location : Vial 41
   Acq. Instrument : LC2
   Injection Date : 7/13/2020 8:55:04 PM
                                                   Inj: 1
                                            Inj Volume : 5.000 µl

      Acq. Method
      : C:\CHEM32\1\DATA\WF\WF 2020-07-13 20-54-10\WF-80-20-0.7-5UL-25MIN.M

      Last changed
      : 7/13/2020 9:12:33 PM by 系统

                 (modified after loading)
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   Last changed : 7/9/2020 1:50:37 PM by 系统
   Additional Info : Peak(s) manually integrated
          DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-13 20-54-10\041-0101.D)
      mAU ]
                         10:046
      500 -
      450 -
      400 -
      350 -
                                              1.367
      300 -
      250 -
      200 -
      150 -
       100 -
                                        11
                                               11.5
                                                       12
                                                              12.5
                                                                       13
                                                                              13.5
                        10
                                10.5
                9.5
                                                                                     mir
    _____
                             Area Percent Report
   _____
   Sorted By
                            Signal
                      :
             :
                          1.0000
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                   Height Area
[mAU] %
   Peak RetTime Type Width
                           Area
    # [min] [min] [mAU*s]
   1 10.046 BB 0.2318 6763.83154 420.18231 50.1106
2 11.367 BB 0.4361 6733.97607 215.76871 49.8894
   Totals :
                         1.34978e4 635.95102
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LC2 7/13/2020 9:33:35 PM 系统

Page 1 of 1

### Chiral-2b

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                                             Location : Vial 61
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                                                Inj: 1
                                             Inj Volume : 5.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-11 08-04-19\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/11/2020 8:04:19 AM by 系统
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-11 14-02-16\LBW2.M (Sequence Method)
   Last changed : 8/11/2020 2:02:16 PM by 系统
   Additional Info : Peak(s) manually integrated
         DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-08-11 08-04-19\061-0101.D)
      mAU .
350 -
      300 -
      250 -
      200 -
      150 -
       100 -
       50 -
                                                                      12.857
        0.
                                            11
                              10
                                                          12
                                                                        13
                        Area Percent Report
   _____
                                             _____
                          Signal
   Sorted By
                      :
   Multiplier
                      :
                           1.0000
                     :
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
   Peak RetTime Type Width
                           Area
                                   Height Area
                  [min] [mAU*s] [mAU]
    # [min]
                                              8
   ----|-----|-----|------|------|
     1 10.737 BB 0.2561 6497.89063 367.77640 95.7953
     2 12.857 BB 0.3384 285.20709 12.03627 4.2047
                         6783.09772 379.81266
   Totals :
   _____
                                                _____
                         *** End of Report ***
```

LC2 8/11/2020 8:34:10 PM 系统

Page 1 of 1
### Rac-2c

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-25 09-51-22\051-0101.D
Sample Name: Ac-nPr-9-23-rac
   _____
   Acq. Operator : 系统
                                             Seq. Line : 1
   Acq. Instrument : LC2
                                              Location : Vial 51
   Injection Date : 7/25/2020 9:52:16 AM
                                                 Inj : 1
                                             Inj Volume : 5.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-25 09-51-22\WF-80-20-0.7-5UL-25MIN.M
Last changed : 7/25/2020 9:51:22 AM by 系统
   Analysis Method : C:\CHEM32\1\METHODS\WT.M
   Last changed : 7/16/2020 7:22:02 PM by 系统
   Additional Info : Peak(s) manually integrated
          DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-25 09-51-22\051-0101.D)
      mAU ქ
                               9
      350 -
      300 -
      250 -
                                           10.644
      200 -
       150 -
       100 -
       50 -
        0-
       -50 -
                                   10
                                                <u>11</u>
                                                             12
                                                                          13
                      ġ
      _____
                                          _____
                        Area Percent Report
   _____
                                          _____
                         Signal
1.0000
1.0000
   Sorted By
                      :
   Multiplier
                   :
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
    Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
   Peak RetTime Type Width
   1 9.710 BV 0.2102 6257.71875 433.93262 49.7234
2 10.644 VV 0.3534 6327.33594 249.92873 50.2766
   Totals :
                         1.25851e4 683.86134
   _____
                             _____
                                            _____
                          *** End of Report ***
```

LC2 7/25/2020 10:41:56 AM 系统

### Chiral-2c

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\063-0601.D
Sample Name: 0814-2c
   _____
  Acq. Operator :系统
                                          Seq. Line : 6
   Acq. Instrument : LC2
                                          Location : Vial 63
   Injection Date : 8/14/2020 3:59:13 PM
                                              Inj: 1
                                          Inj Volume : 5.000 µl
  Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/14/2020 3:43:30 PM by 系统
                 (modified after loading)
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-14 13-51-26\LBW.M (Sequence Method)
   Last changed : 8/14/2020 1:51:26 PM by 系统
   Additional Info : Peak(s) manually integrated
         DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-08-14 14-39-12\063-0601.D)
                      1977.2
      mAU -
                    940
      1000 -
      800 -
      600 -
      400 -
                                    1024.35
      200
                                  132
                                  20100
       0
                                                         12
                                                                     13
                     9
                                10
                                            11
                                                                                mir
   _____
                       Area Percent Report
                                      _____
   _____
   Sorted By
                     :
                          Signal
             :
                        1.0000
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                Height Area
[mAU] %
   Peak RetTime Type Width
                         Area
    # [min] [min] [mAU*s]
   1 8.940 MM 0.2821 1.97712e4 1168.22510 95.0742
2 10.132 MM 0.2723 1024.34680 62.70263 4.9258
   Totals :
                       2.07956e4 1230.92772
                        _____
```

LC2 8/14/2020 4:36:40 PM 系统

#### Rac-2d

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-11 19-55-06\002-0201.D
Sample Name: Ac-iPr-rac
```

```
_____
Acq. Operator :系统
                                            Seq. Line : 2
Acq. Instrument : LC2
                                             Location : Vial 2
Injection Date : 8/11/2020 8:11:16 PM
                                                 Inj: 1
                                            Inj Volume : 5.000 µl
Inj Volume : 5.000 µ1
Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µ1
             : C:\CHEM32\1\DATA\WF\WF 2020-08-11 19-55-06\WF-80-20-0.7-5UL-15MIN.M
Acq. Method
Last changed : 8/11/2020 8:22:46 PM by 系统
                (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-11 14-02-16\LBW2.M (Sequence Method)
Last changed : 8/11/2020 2:02:16 PM by 系统
Additional Info : Peak(s) manually integrated
DAD1 C, Sig=210.4 Ref=360,100 (WFWF 2020-08-11 19-55-06)002-0201.D)
   mAU _
              o,
   350 -
   300 -
                                         9.969
   250 -
   200 -
   150 -
   100 -
    50 -
     0
                                                                             11.5
                              9.5
                                          10
                                                     10.5
                                                                  11
      85
                       Area Percent Report
_____
Sorted By
                          Signal
                    :
Multiplier
                    :
                          1.0000
Dilution
                    :
                          1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	8
1	8.849	BB	0.2031	5531.16895	395.73355	49.6491
2	9.969	BB	0.3406	5609.36328	234.89215	50.3509

Totals :

1.11405e4 630.62570

LC2 8/11/2020 8:27:56 PM 系统

### Chiral-2d

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-11 19-55-06\001-0101.D
Sample Name: Ac-iPr-chiral
   _____
   Acq. Operator : 系统
                                          Seq. Line : 1
   Acq. Instrument : LC2
                                          Location : Vial 1
   Injection Date : 8/11/2020 7:56:01 PM
                                              Inj: 1
                                          Inj Volume : 5.000 µl
  Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-11 19-55-06\WF-80-20-0.7-5UL-25MIN.M
Last changed : 8/11/2020 8:10:15 PM by 系统
                 (modified after loading)
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-11 14-02-16\LBW2.M (Sequence Method)
   Last changed : 8/11/2020 2:02:16 PM by 系统
   Additional Info : Peak(s) manually integrated
         DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-08-11 19-55-06\001-0101.D)
      mAU |
      500 -
      400 -
      300 -
      200 -
      100 -
                                                   10.572
       0
                                                            11
                                       10
                                                                      11.5
                             9.5
                                                 10.5
                   9
        8.5
   _____
                       Area Percent Report
   _____
                                      _____
   Sorted By
                     :
                          Signal
            :
                        1.0000
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                Height Area
[mAU] %
   Peak RetTime Type Width
                         Area
    # [min] [min] [mAU*s]
   1 9.033 BV 0.2176 8322.12402 553.01227 94.8138
2 10.572 VV 0.2854 455.20840 22.56281 5.1862
   Totals :
                       8777.33243 575.57508
                        _____
```

LC2 8/11/2020 8:29:24 PM 系统

#### Rac-2e

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-18 12-03-28\053-0301.D
Sample Name: Ac-i-Bu-9-101-3-rac
```

```
Acq. Operator : 系统
                                       Seq. Line : 3
                                       Location : Vial 53
Acq. Instrument : LC2
Injection Date : 7/18/2020 12:41:44 PM
                                            Inj: 1
                                      Inj Volume : 5.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-18 12-03-28\WF-80-20-0.7-5UL-25MIN.M
Last changed : 7/18/2020 12:04:15 PM by 系统
Analysis Method : C:\CHEM32\1\DATA\TDS\TDS 2020-07-18 08-58-02\TDS.M (Sequence Method)
Last changed : 7/18/2020 8:58:02 AM by 系统
Additional Info : Peak(s) manually integrated
      DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-18 12-03-28\053-0301.D)
   mAU ]
                   23
   350 -
   300 -
                                  888
   250 -
   200 -
   150 -
   100 -
    50 -
    0 -
                                              9.5
                                                         10
                                                                   10.5
     7.5
                8
                          8.5
Area Percent Report
-----
                                    _____
                 : Signal
: 1.0000
: 1.0000
Sorted By
Multiplier
              :
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 C, Sig=210,4 Ref=360,100
              Width Area Height Area
[min] [mAU*s] [mAU] %
Peak RetTime Type Width
 # [min]
----|-----|----|-----|-----|-----|
 1 8.173 BB 0.1689 4431.90479 389.08664 49.9567
  2 8.888 BB 0.2553 4439.58203 247.50140 50.0433
Totals :
                     8871.48682 636.58804
_____
                                         _____
                        _____
```

\*\*\* End of Report \*\*\*

LC2 7/20/2020 9:29:08 AM 系统

#### Chiral-2e

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-29 14-13-43\053-0501.D Sample Name: Ac-iBu-2d
```

```
_____
Acq. Operator : 系统
                                          Seq. Line : 5
                                          Location : Vial 53
Acq. Instrument : LC2
Injection Date : 7/29/2020 3:44:37 PM
                                                Inj: 1
                                      Inj Volume : 10.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 5.000 µl

      Acq. Method
      : C:\CHEM32\1\DATA\WF\WF 2020-07-29 14-13-43\WF-80-20-0.7-10UL-20MIN.M

      Last changed
      : 7/29/2020 2:13:43 PM by 系统

              : 7/29/2020 2:13:43 PM by 系统
Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-07-21 19-22-35\LBW.M (Sequence Method)
Last changed : 7/21/2020 7:22:35 PM by 系统
Additional Info : Peak(s) manually integrated
      DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-29 14-13-43\053-0501.D)
   mAU 🛉
   700 -
   600 -
   500 -
   400 -
   300 -
   200 -
                                        100 -
    0.
                            8.5
                                                  9.5
                                                              10
                                                                         10.5
                                                                                   mir
                    Area Percent Report
_____
                                       _____
Sorted By
                  :
                        Signal
1.0000
             .
:
Multiplier
                        1.0000
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                 Height
Peak RetTime Type Width Area
                                           Area
               [min] [mAU*s] [mAU]
 # [min]
                                            8
1 8.084 VB 0.1912 9202.78027 719.83093 95.8936
  2 9.042 MM 0.2205 394.08899 29.78770 4.1064
                       9596.86926 749.61863
Totals :
```

LC2 7/29/2020 4:42:07 PM 系统

#### Rac-2f

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-18 12-03-28\051-0101.D Sample Name: Ac-n-Pent-RAC-9-101-1
```

```
_____
Acq. Operator : 系统
                                          Seq. Line : 1
                                          Location : Vial 51
Acq. Instrument : LC2
Injection Date : 7/18/2020 12:04:22 PM
                                      Inj : _
Inj Volume : 5.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-18 12-03-28\WF-80-20-0.7-5UL-30MIN.M
Last changed : 7/18/2020 12:23:40 PM by 系统
               (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\TDS\TDS 2020-07-18 08-58-02\TDS.M (Sequence Method)
Last changed : 7/18/2020 8:58:02 AM by 系统
Additional Info : Peak(s) manually integrated
      DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-18 12-03-28\051-0101.D)
   mAU 1
                     053
   250 -
   200 -
                                          9.543
   150 -
   100 -
    50 -
     0
                                                10
                                                               11
                                                                             12
                                                                                   mir
   _____
                    Area Percent Report
_____
                                       _____
Sorted By
                 :
                       Signal
1.0000
1.0000
            :
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                Height Area
Peak RetTime Type Width Area
 # [min] [mAU*s] [mAU]
                                            8
1 8.053 VB 0.1700 3308.05225 288.11914 49.8472
2 9.543 BB 0.3135 3328.33325 151.98228 50.1528
                       6636.38550 440.10143
Totals :
```

LC2 7/20/2020 9:26:27 AM 系统

# Chiral-2f

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-18 12-03-28\052-0201.D
Sample Name: Ac-n-Pent-9-101-2
    Acq. Operator : 系统
                                              Seq. Line : 2
   Acq. Instrument : LC2
                                              Location : Vial 52
   Injection Date : 7/18/2020 12:24:42 PM
                                                   Inj: 1
                                         Inj Volume : 5.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-18 12-03-28\WF-80-20-0.7-5UL-15MIN.M
Last changed : 7/18/2020 12:04:14 PM by 系统
   Analysis Method : C:\CHEM32\1\DATA\TDS\TDS 2020-07-18 08-58-02\TDS.M (Sequence Method)
   Last changed : 7/18/2020 8:58:02 AM by 系统
   Additional Info : Peak(s) manually integrated
         DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-18 12-03-28\052-0201.D)
      mAU –
       400 -
      300 -
       200 -
       100 -
                                                  826
        0
                                                                                 12
                                                    10
                                                                  11
                        8
                                      9
                                                                                       mir
   _____
                                 _____
                        Area Percent Report
   Sorted By
                            Signal
                      :
                   : 1.0000
: 1.0000
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
    Peak RetTime Type Width Area Height
# [min] [mAU*s] [mAU]
   Peak RetTime Type Width
                                               Area
                                                8
   1 8.002 VB 0.1815 5760.46484 468.31638 96.0190
2 9.826 BB 0.2937 238.83366 12.13003 3.9810
   Totals :
                          5999.29851 480.44641
   _____
                                                _____
                          *** End of Report ***
```

LC2 7/20/2020 9:27:38 AM 系统

## Rac-2g

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-25 09-51-22\053-0301.D
Sample Name: Ac-异己基-9-24-rac
   _____
   Acq. Operator : 系统
                                            Seq. Line : 3
   Acq. Instrument : LC2
                                             Location : Vial 53
   Injection Date : 7/25/2020 10:34:13 AM
                                                Inj : 1
                                             Inj Volume : 5.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-25 09-51-22\WF-80-20-0.7-5UL-25MIN.M
Last changed : 7/25/2020 9:51:22 AM by 系统
   Analysis Method : C:\CHEM32\1\METHODS\WT.M
   Last changed : 7/16/2020 7:22:02 PM by 系统
   Additional Info : Peak(s) manually integrated
         DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-25 09-51-22\053-0301.D)
      mAU -
      350 -
      300 -
      250 -
                                                 339
      200 -
      150 -
      100 -
       50 -
        0
                                                                           9.5
                                                     8.5
                               7.5
   _____
                        Area Percent Report
   _____
                                         _____
                         Signal
1.0000
1.0000
   Sorted By
                     :
                     :
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                  Width Area Height Area
[min] [mAU*s] [mAU] %
   Peak RetTime Type Width
    # [min]
   ----|-----|----|-----|-----|-----|
    1 7.519 BB 0.1664 4127.68799 369.18008 49.8015
     2 8.339 BB 0.2850 4160.58936 208.33910 50.1985
   Totals :
                         8288.27734 577.51918
   _____
                                              _____
                             _____
                         *** End of Report ***
```

LC2 7/25/2020 11:09:53 AM 系统

# Chiral-2g

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-17 15-02-09\008-0801.D
Sample Name: 0817-Me-Pent
    _____
   Acq. Operator : 系统
                                                  Seq. Line : 8
   Acq. Instrument : LC2
                                                   Location : Vial 8
   Injection Date : 8/17/2020 5:02:08 PM
                                                       Inj: 1
                                                  Inj Volume : 5.000 µl
   Inj Volume : 5.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-17 15-02-09\WF-80-20-0.7-5UL-15MIN.M
   Last changed : 8/17/2020 3:57:00 PM by 系统
                    (modified after loading)
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-15 23-43-02\LBW.M (Sequence Method)
   Last changed : 8/15/2020 11:43:02 PM by 系统
   Additional Info : Peak(s) manually integrated
DAD1 C, Sig=210.4 Ref=360,100 (WFWF 2020-08-17 15-02-09/008-0801.D)
       mAU 🕇
       1000 -
       800 -
       600 -
       400 -
       200
                                                          437
         0.
                                                                                     9.5
                                                            8.5
          65
                                   7.5
                            Area Percent Report
    _____
   Sorted By
                                Signal
                         :
                               1.0000
   Multiplier
                        :
   Dilution
                         :
                                1.0000
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                     Width Area Height
[min] [mAU*s] [mAU]
    Peak RetTime Type Width
                                                    Area
    # [min]
                                                     8
    1 7.358 VB 0.2274 1.66038e4 1130.19458 95.6818
2 8.437 BB 0.2576 749.34607 42.10359 4.3182
    Totals :
                            1.73532e4 1172.29817
```

LC2 8/17/2020 6:45:28 PM 系统

#### Rac-2h

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-28 15-09-07\091-0101.D
Sample Name: Ac-benbingji-10-32-rac
   _____
   Acq. Operator : 系统
                                             Seq. Line : 1
   Acq. Instrument : LC2
                                              Location : Vial 91
   Injection Date : 7/28/2020 3:10:02 PM
                                                 Inj: 1
                                             Inj Volume : 5.000 µl

      Acq. Method
      : C:\CHEM32\1\DATA\WF\WF 2020-07-28 15-09-07\WF-80-20-0.7-5UL-25MIN.M

      Last changed
      : 7/28/2020 3:09:07 PM by 系统

   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-07-21 19-22-35\LBW.M (Sequence Method)
   Last changed : 7/21/2020 7:22:35 PM by 系统
   Additional Info : Peak(s) manually integrated
          DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-28 15-09-07\091-0101.D)
      mAU 🗂
       70 -
       60 -
                                                                   17.835
       50 -
       40 -
       30 -
       20 -
       10 -
                                                                    18
                   13
                             14
                                                16
                                                          17
                                                                              19
                                       15
   _____
                        Area Percent Report
   _____
                                          _____
   Sorted By
Multiplier
                         Signal
1.0000
1.0000
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                  e Width Area Height Area
[min] [mAU*s] [mAU] %
   Peak RetTime Type Width
    # [min]
   1 14.035 BB 0.3440 1643.74500 72.09856 51.3429
     2 17.835 BB 0.5005 1557.76086 47.26683 48.6571
   Totals :
                         3201.50586 119.36539
   _____
                                               _____
                              _____
                          *** End of Report ***
```

LC2 7/28/2020 4:48:37 PM 系统

### Chiral-2h

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-29 14-13-43\067-0101.D
Sample Name: Ac-bengbingji-2g
   _____
   Acq. Operator : 系统
                                               Seq. Line : 1
   Acq. Instrument : LC2
                                               Location : Vial 67
   Injection Date : 7/29/2020 2:14:38 PM
                                                   Inj: 1
                                              Inj Volume : 20.000 µl
   Inj Volume : 20.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 5.000 µl
               : C:\CHEM32\1\DATA\WF\WF 2020-07-29 14-13-43\WF-80-20-0.7-20UL-30MIN.M
   Acq. Method
   Last changed : 7/29/2020 2:40:35 PM by 系统
                   (modified after loading)
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-07-21 19-22-35\LBW.M (Sequence Method)
   Last changed : 7/21/2020 7:22:35 PM by 系统
   Additional Info : Peak(s) manually integrated
DAD1 C, Sig=210.4 Ref=360,100 (WFWF 2020-07-29 14-13-43\067-0101.D)
      mAU ]
       400 -
       350 -
       300 -
       250 -
       200 -
       150 -
       100 -
                                                                     17.893
        50 -
        0 -
                                                                      18
                   13
                             14
                                       15
                                                  16
                                                            17
                                                                                19
   _____
                         Area Percent Report
   _____
   Sorted By
                             Signal
                       :
                            1.0000
   Multiplier
                      :
   Dilution
                             1.0000
                       :
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                     Height
[mAU]
   Peak RetTime Type Width
                            Area
                                                Area
                 [min] [mAU*s]
    # [min]
                                                 8
   ----|-----|-----|------|------|------|
     1 13.997 BB 0.3404 8993.10547 396.84662 84.6858
2 17.893 BB 0.5022 1626.27808 49.13386 15.3142
```

```
Totals :
```

1.06194e4 445.98048

LC2 7/29/2020 4:51:36 PM 系统

#### Rac-2i

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-06 23-06-18\062-0201.D Sample Name: Ac-Cp-Rac
```

```
_____
Acq. Operator :系统
                                        Seq. Line : 2
                                         Location : Vial 62
Acq. Instrument : LC2
Injection Date : 7/6/2020 11:39:02 PM
                                             Inj: 1
                                       Inj Volume : 20.000 µl
Inj Volume : 20.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 5.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-06 23-06-18\WF-80-20-0.7-20UL-30MIN.M
Last changed : 7/6/2020 11:06:19 FM by 系统
Analysis Method : C:\CHEM32\1\DATA\TYH\TYH 2020-07-13 15-10-31\TYH.M (Sequence Method)
Last changed : 7/13/2020 3:10:31 PM by 系统
Additional Info : Peak(s) manually integrated
      DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-06 23-06-18\062-0201.D)
                     6184.71
   mAU -
                   566
   350 -
   300 -
                                    10.784
   250 -
   200 -
   150 -
   100 -
    50 -
    0
                                       11
                                                                  13
                         10
                                                    12
_____
                             _____
                    Area Percent Report
                                         _____
_____
Sorted By
                        Signal
                  :
                      1.0000
          :
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 C, Sig=210,4 Ref=360,100
Peak RetTime Type Width
                       Area
                               Height Area
 # [min] [min] [mAU*s]
                               [mAU]
                                         8
1 9.566 MM 0.2696 6184.71338 382.35037 50.1564
2 10.784 BB 0.3906 6146.13477 223.64954 49.8436
Totals :
                     1.23308e4 605.99991
```

LC2 7/13/2020 10:42:56 PM 系统

### Chiral-2i

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-17 15-02-09\006-0601.D
Sample Name: 0817-Cp
    _____
   Acq. Operator : 系统
                                                     Seq. Line : 6
    Acq. Instrument : LC2
                                                     Location : Vial 6
    Injection Date : 8/17/2020 4:30:05 PM
                                                         Inj: 1
                                                    Inj Volume : 5.000 µl
   Inj Volume : 5.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-17 15-02-09\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/17/2020 3:57:00 PM by 系统
                     (modified after loading)
    Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-15 23-43-02\LBW.M (Sequence Method)
    Last changed : 8/15/2020 11:43:02 PM by 系统
    Additional Info : Peak(s) manually integrated
DAD1 C, Sig=210.4 Ref=360,100 (WFWF 2020-08-17 15-02-09)006-0601.D)
       mAU 🕇
                         5
       1000
        800 -
        600 -
        400 -
        200
                                                     11.033
         0.
                                                    11
                                                                                     13
                                    10
                                                                     12
                             Area Percent Report
    _____
    Sorted By
                                 Signal
                          :
                                1.0000
    Multiplier
                         :
    Dilution
                          :
                                 1.0000
   Use Multiplier & Dilution Factor with ISTDs
    Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                      Width Area Height
[min] [mAU*s] [mAU]
    Peak RetTime Type Width
                                                       Area
     # [min]
                                                       8
    1 9.342 BB 0.3163 2.35618e4 1134.53796 96.4964
2 11.033 BV 0.3239 855.47681 38.40813 3.5036
```

Totals :

2.44173e4 1172.94610

LC2 8/17/2020 6:49:30 PM 系统

# Rac-2j

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-14 13-16-29\061-0101.D Sample Name: Ac-Cy-Rac
```

```
Acq. Operator : 系统
                                       Seq. Line : 1
                                        Location : Vial 61
Acq. Instrument : LC2
Injection Date : 7/14/2020 1:17:25 PM
                                             Inj: 1
                                       Inj Volume : 5.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-14 13-16-29\WF-80-20-0.7-5UL-25MIN.M
Last changed : 7/14/2020 1:16:29 PM by 系统
Analysis Method : C:\CHEM32\1\DATA\TYH\TYH 2020-07-13 15-10-31\TYH.M (Sequence Method)
Last changed : 7/13/2020 3:10:31 PM by 系统
Additional Info : Peak(s) manually integrated
      DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-14 13-16-29\061-0101.D)
   mAU -
   175 -
   150 -
                                         10.663
   125 -
   100 -
    75 -
    50 -
    25 -
    0
                                  10
                                             11
                                                        12
                                                                    13
Area Percent Report
-----
                                     _____
                 : Signal
: 1.0000
: 1.0000
Sorted By
Multiplier
               :
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 C, Sig=210,4 Ref=360,100
              Width Area Height Area
[min] [mAU*s] [mAU] %
Peak RetTime Type Width
 # [min]
1 8.680 BB 0.1994 2596.59595 192.41283 49.6262
2 10.663 BB 0.3205 2635.70801 120.84343 50.3738
Totals :
                     5232.30396 313.25626
_____
                                         _____
                         _____
                     *** End of Report ***
```

LC2 7/14/2020 2:33:51 PM 系统

# Chiral-2j

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-29 14-13-43\052-0401.D
Sample Name: Ac-cy-2i
   _____
   Acq. Operator :系统
                                            Seq. Line : 4
   Acq. Instrument : LC2
                                             Location : Vial 52
   Injection Date : 7/29/2020 3:23:39 PM
                                                Inj: 1
                                           Inj Volume : 10.000 µl
   Different Inj Volume from Sequence ! Actual Inj Volume : 5.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-29 14-13-43\WF-80-20-0.7-10UL-20MIN.M
Last changed : 7/29/2020 2:13:43 PM by 系统
   Acq. Method
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-07-21 19-22-35\LBW.M (Sequence Method)
   Last changed : 7/21/2020 7:22:35 PM by 系统
   Additional Info : Peak(s) manually integrated
          DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-29 14-13-43\052-0401.D)
      mAU
                    448
      500 -
      400 -
      300 -
      200 -
      100 -
                                              10.666
        0
                                                 11
                                                             12
                                                                         13
                                      10
               8
                          9
   _____
                        Area Percent Report
                                                _____
   Sorted By
                            Signal
                      :
   Sortea by
Multiplier :
                          1.0000
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
   Peak RetTime Type Width
                          Area
                                   Height
                                            Area
                                             8
    # [min] [min] [mAU*s]
                                   [mAU]
   ----|-----|-----|-----|
    1 8.448 BB 0.2217 8156.06543 541.42072 96.4624
2 10.666 BB 0.3002 299.11270 14.90228 3.5376
   Totals :
                        8455.17813 556.32300
```

LC2 7/29/2020 4:39:26 PM 系统

#### Rac-2k

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-25 09-51-22\055-0501.D
Sample Name: Ac-cHep-9-25-rac
   _____
   Acq. Operator : 系统
                                           Seq. Line : 5
   Acq. Instrument : LC2
                                            Location : Vial 55
   Injection Date : 7/25/2020 11:08:12 AM
                                               Inj: 1
                                           Inj Volume : 5.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-07-25 09-51-22\WF-80-20-0.7-5UL-25MIN.M
Last changed : 7/25/2020 11:08:21 AM by 系统
                 (modified after loading)
   Analysis Method : C:\CHEM32\1\METHODS\WT.M
   Last changed : 7/16/2020 7:22:02 PM by 系统
   Additional Info : Peak(s) manually integrated
         DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-07-25 09-51-22\055-0501.D)
      mAU -
300 -
      250 -
                                                618
      200 -
      150 -
      100 -
       50 -
        0
                                                                10.5
                                                                          11
                                              9.5
                                                       10
                           8.5
                                     9
         7.5
                  8
   _____
                       Area Percent Report
   Sorted By
Multiplier :
                           Signal
                         1.0000
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                  Height Area
[mAU] %
   Peak RetTime Type Width
                          Area
    # [min] [min] [mAU*s]
   1 8.338 BB 0.1998 4083.20044 301.90570 49.7074
2 9.618 BB 0.2905 4131.27246 203.80452 50.2926
   Totals :
                        8214.47290 505.71022
```

LC2 7/25/2020 12:06:18 PM 系统

### Chiral-2k

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-17 15-02-09\007-0701.D
Sample Name: 0817-cHep
    _____
   Acq. Operator : 系统
                                                      Seq. Line : 7
    Acq. Instrument : LC2
                                                       Location : Vial 7
    Injection Date : 8/17/2020 4:46:05 PM
                                                           Inj: 1
                                                      Inj Volume : 5.000 µl
   Inj Volume : 5.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-17 15-02-09\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/17/2020 3:57:00 PM by 系统
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-15 23-43-02\LBW.M (Sequence Method)
    Last changed : 8/15/2020 11:43:02 PM by 系统
    Additional Info : Peak(s) manually integrated
DAD1 C, Sig=210.4 Ref=360,100 (WFWF 2020-08-17 15-02-09/007-0701.D)
       mAU j
        700 -
        600 -
        500 -
        400 -
        300 -
        200 -
        100 -
                                                               754
         0.
                                                                                10.5
                                                                                             11
                                                         9.5
                                                                     10
           75
                                  8.5
                              Area Percent Report
    _____
    Sorted By
                                  Signal
                           :
                                  1.0000
    Multiplier
                          :
    Dilution
                           :
                                  1.0000
   Use Multiplier & Dilution Factor with ISTDs
    Signal 1: DAD1 C, Sig=210,4 Ref=360,100
    Peak RetTime Type Width Area
                                           Height
                                                       Area
```

#	[min]		[min]	[mAU*s]	[mAU]	8	
1	8.199	BV	0.2472	1.26003e4	768.91077	95.7940	
2	9.754	VB	0.3125	553.23853	25.35692	4.2060	

Totals :

1.31536e4 794.26768

LC2 8/17/2020 6:51:31 PM 系统

### Rac-2l

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-07-28 15-09-07\093-0201.D
Sample Name: Ac-diMe-Cy-10-33-rac
```



LC2 7/28/2020 4:27:58 PM 系统

### Chiral-21

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\002-0201.D
Sample Name: 0814-2j
   _____
   Acq. Operator :系统
                                            Seq. Line : 2
   Acq. Instrument : LC2
                                            Location : Vial 2
   Injection Date : 8/14/2020 2:57:08 PM
                                               Inj: 1
                                           Inj Volume : 5.000 µl
   Inj Volume : 5.000 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/14/2020 2:39:12 PM by 系统
   Acg. Method
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-14 13-51-26\LBW.M (Sequence Method)
   Last changed : 8/14/2020 1:51:26 PM by 系统
   Additional Info : Peak(s) manually integrated
          DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-08-14 14-39-12\002-0201.D)
      mAU ]
                       88
      600 -
      500 -
      400 -
      300 -
      200 -
      100 -
                                           8.080
        0
                                                                         9.5
                              7.5
                                                               9
                                                   8.5
                                         8
        6.5
   _____
                        Area Percent Report
   _____
                                       _____
   Sorted By
                      :
                           Signal
             :
                         1.0000
   Multiplier
   Dilution
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
                                  Height Area
[mAU] %
   Peak RetTime Type Width
                          Area
    # [min] [min] [mAU*s]
   ----|-----|-----|------|
    1 7.166 VB 0.1888 7720.56543 613.55286 97.4269
2 8.080 BB 0.2429 203.90529 11.72408 2.5731
   Totals :
                        7924.47072 625.27694
                         _____
```

LC2 8/14/2020 3:36:21 PM 系统

#### Rac-2m (cis+trans)

Data File C:\CHEM32\1\DATA\WF\WF 2020-08-11 08-04-19\062-0401.D Sample Name: zyx-2n-rac



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#### Chiral-2m (cis+trans)

Data File C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\062-0501.D Sample Name: 0814-2p



# Chiral-2m-isomer

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\062-0501.D
Sample Name: 0814-2p
```

Acq. Operator : 系统	Seq. Line : 5
Acq. Instrument : LC2	Location : Vial 62
Injection Date : 8/14/2020 3:45:13 PM	Inj : 1
	Inj Volume : 5.000 µl
Different Inj Volume from Sequence ! A	Actual Inj Volume : 10.000 µl
Acq. Method : C:\CHEM32\1\DATA\WF\WF 2	2020-08-14 14-39-12\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/14/2020 3:43:30 PM by	系统
(modified after loading)	
Analysis Method : C:\CHEM32\1\DATA\LBW\LBW	/ 2020-08-14 13-51-26\LBW.M (Sequence Method)
Last changed : 8/14/2020 1:51:26 PM by	系统
Additional Info : Peak(s) manually integra	ated
DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-08-14 14-	39-12\062-0501.D)
mAU ]	
400-	
350 8	
300 4	
300 -	
250 -	
200	
200	
150 -	
100-	
50 7	030
	,
0-	
7 7.5 8 8.5	9 9.5 10 10.5 min

\_\_\_\_\_ Area Percent Report

\_\_\_\_\_

Sorted By		:	Signal	
Multiplier		:	1.0000	
Dilution		:	1.0000	
Use Multiplier	δ	Dilution	Factor with	ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	8
1	7.405	BB	0.1776	3510.71533	297.55807	97.8795
2	9.030	VB	0.2534	76.05803	4.04531	2.1205

Totals: 3586.77336 301.60339

LC2 8/14/2020 4:04:37 PM 系统

#### Chiral-2m-isomer

```
Data File C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\062-0501.D
Sample Name: 0814-2p
    Acq. Operator : 系统
                                              Seq. Line : 5
   Acq. Instrument : LC2
                                               Location : Vial 62
   Injection Date : 8/14/2020 3:45:13 PM
                                                   Inj: 1
                                             Inj Volume : 5.000 µl
   Different Inj Volume from Sequence ! Actual Inj Volume : 10.000 µl
   Acq. Method : C:\CHEM32\1\DATA\WF\WF 2020-08-14 14-39-12\WF-80-20-0.7-5UL-15MIN.M
Last changed : 8/14/2020 3:43:30 PM by 系统
                  (modified after loading)
   Analysis Method : C:\CHEM32\1\DATA\LBW\LBW 2020-08-14 13-51-26\LBW.M (Sequence Method)
   Last changed : 8/14/2020 1:51:26 PM by 系统
   Additional Info : Peak(s) manually integrated
          DAD1 C, Sig=210,4 Ref=360,100 (WF\WF 2020-08-14 14-39-12\062-0501.D)
      mAU ]
       400 -
       350 -
       300 -
       250 -
       200 -
       150 -
       100 -
       50 ·
                                                                  9.874
        0.
                   7.5
                                                                     10
                                                                              10.5
                                                          9.5
                                       8.5
   _____
                                           _____
                        Area Percent Report
   _____
   Sorted By
                            Signal
                       :
   Multiplier
                           1.0000
                    :
                            1.0000
   Dilution
                      :
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 C, Sig=210,4 Ref=360,100
   Peak RetTime Type Width
                                    Height
                           Area
                                              Area
                   [min] [mAU*s]
    # [min]
                                     [mAU]
                                                8
    -----
    1 8.117 BV 0.2031 5249.95801 389.88605 98.0077
2 9.874 BB 0.2455 106.72096 6.64102 1.9923
                                      6.64102 1.9923
                          5356.67897 396.52707
   Totals :
```

LC2 8/14/2020 4:05:01 PM 系统