Supplementary Information for:

**Efficient Synthesis of Optically Active \(\alpha\)-Quaternary Amino Acids by Highly Diastereoselective [2,3]-Rearrangement of Allylic Ammonium Ylides**

Ting-Shun Zhu, and Ming-Hua Xu*

*Shanghai Institute of Materia Medica, Chinese Academy of Sciences,
555 Zuchongzhi Road, Shanghai 201203

xumh@mail.shcnc.ac.cn

---

**Table of Contents**

1. General.....................................................................................................................2
2. General Procedure for the Synthesis of Amines 2...................................................2
3. General Procedure for the Synthesis of Ammonium Salts .........................6
4. Optimization of the reaction conditions.............................................................12
5. General Procedure for the Asymmetric [2,3]-Rearrangement......................13
6. X-ray Crystal Structure of Rearrangement Product 4a and 4k .....................28
7. General Procedure for Double Bond Elaboration via Heck Reaction ............29
8. General Procedure for Removal of Chiral Auxiliary.......................................30
9. Copies of \(^1\)H NMR and \(^13\)C NMR spectra.....................................................39
1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or argon. NMR spectra were recorded on a Mercury 300 spectrometer (300 MHz for \( ^1H \)) and Variant MR-400 (100 MHz for \( ^{13}C \)). Chemical shifts are reported in \( \delta \) ppm referenced to an internal SiMe\(_4\) standard for \(^1H\) NMR and chloroform-\( d \) (\( \delta 77.00 \)) for \(^{13}C\) NMR. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. HPLC was performed on a JASCO 2000 instrument by using Daicel columns. LC-MS are performed on an Agilent 1100 instrument by column 20RBAX SB-C18 (4.6X30mm, 3.5\( \mu \)m).

2. General Procedure for the Synthesis of Amines 2

2.1 General Synthetic Procedure for Amines 2a-j

![Chemical diagram]

To a 50 mL flask was added dibromo compound 1\(^1\) (440 mg, 1 mmol), methyl amino acid hydrogen chloride (1.5 mmol), NaHCO\(_3\) (330 mg, 3 mmol) and 20 mL of acetonitrile. The reaction was stirred under reflux for about 4 hours and monitored by TLC for completion. The mixture was then cooled to room temperature, diluted with CH\(_2\)Cl\(_2\), and filtrated through Celite. The filtrate was washed three times with water and brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding \( N,N \)-disubstituted amine product 2.

\((S)-2a\), light yellow solid, yield 99%;

\(^1H\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 3.22 (d, 1H, \( J = 16.2 \) Hz, CH\(_2\)-COOMe), 3.30 (d, 2H, \( J = 12.3 \) Hz, Ar-CH\(_2\)), 3.44 (d, 1H, \( J = 16.2 \) Hz, CH\(_2\)-COOMe), 3.76 (d, 2H, \( J = 12.3 \) Hz, Ar-CH\(_2\)), 3.78 (s, 3H, COOCH\(_3\)), 7.26-7.29 (m, 2H, Ar-H), 7.44-7.49 (m, 4H, Ar-H), 7.57 (d, 2H, \( J = 8.4 \) Hz, Ar-H), 7.95(d, 4H, \( J = 8.1 \) Hz, Ar-H).

\((S)-2a^*\), colorless oil yield 94%;

\(^1H\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 2.81(dd, 2H, \( J = 18.9 \) Hz, 16.2 Hz, CH\(_2\)-COOMe), 3.16(d, 2H, \( J = 12.6 \) Hz, ArCH\(_2\)), 3.42(s, 3H, COOCH\(_3\)), 4.01(d, 2H, \( J = 12.6 \) Hz, ArCH\(_2\)), 7.26-7.32 (m, 2H, Ar-H), 7.40-7.60 (m, 10H, Ar-H), 7.61 (d, 4H, \( J = 6.9 \) Hz, Ar-H), 7.95-7.98(m,

---

(S, L)-2b (S for the confirmation of Chiral auxiliary, L for the confirmation of amino acid), colorless oil, yield 95%;

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 1.54 \text{ (d, 3H, } J = 6.9 \text{ Hz, CH-CH}_3) \], 3.42 \text{ (d, 2H, } J = 12.6 \text{ Hz, Ar-CH}_2) \], 3.40- 3.48 \text{ (m, 1H, CH-CH}_3 \text{)}, 3.67 \text{ (s, 3H, COOCH}_3 \text{)}, 3.90 \text{ (d, 2H, } J = 12.6 \text{ Hz, Ar-CH}_2) \], 7.25-7.28 \text{ (m, 2H, Ar-H)}, 7.46-7.51 \text{ (m, 4H, Ar-H)}, 7.60 \text{ (d, 2H, } J = 8.4 \text{ Hz, Ar-H)}, 7.98 \text{ (d, 4H, } J = 8.4 \text{ Hz, Ar-H).} \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 16.6, 51.9, 53.2, 61.4, 125.4, 125.7, 127.4, 128.1, 128.2, 128.3, 131.2, 133.1, 135.0, 174.5 ppm.

(S, rac)-2b, colorless oil, yield 94% (including two isomers);

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 1.54 \text{ (d, 3H, } J = 6.9 \text{ Hz, CH-CH}_3) \], 3.42 \text{ (d, 2H, } J = 12.6 \text{ Hz, Ar-CH}_2) \], 3.40- 3.48 \text{ (m, 1H, CH-CH}_3 \text{)}, 3.67 \text{ (s, 3H, COOCH}_3 \text{)}, 3.90 \text{ (d, 2H, } J = 12.6 \text{ Hz, Ar-CH}_2) \], 7.25-7.28 \text{ (m, 2H, Ar-H)}, 7.46-7.51 \text{ (m, 4H, Ar-H)}, 7.60 \text{ (d, 2H, } J = 8.4 \text{ Hz, Ar-H)}, 7.98 \text{ (d, 4H, } J = 8.4 \text{ Hz, Ar-H).} \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 16.6, 51.9, 53.2, 61.4, 125.4, 125.7, 127.4, 128.1, 128.2, 128.3, 131.2, 133.1, 135.0, 174.5 ppm.

(S, L)-2c, colorless oil, yield 92%;

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 3.18 \text{ (d, 2H, } J = 7.5 \text{ Hz, Ph-CH}_2) \], 3.42 \text{ (s, 3H, COOCH}_3 \text{)}, 3.57 \text{ (d, 2H, } J = 12.0 \text{ Hz, Ar-CH}_2) \], 3.71 \text{ (t, } J = 7.5 \text{ Hz, CHCOMe)}, 3.92 \text{ (d, 2H, } J = 12.3 \text{ Hz, Ar-CH}_2) \], 7.20-7.28 \text{ (m, 7H, Ar-H)}, 7.42-7.48 \text{ (m, 4H, Ar-H)}, 7.55 \text{ (d, 2H, } J = 8.4 \text{ Hz, Ar-H)}, 7.94 \text{ (dd, 4H, } J = 8.1 \text{ Hz, 8.1 Hz, Ar-H).} \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 37.1, 51.4, 53.2, 68.4, 125.4, 125.7, 126.4, 127.5, 128.1, 128.2, 128.3, 128.4, 129.2, 131.2, 133.1, 133.2, 134.9, 137.7, 172.9 ppm.

(S, rac)-2d, colorless oil, yield 99% (including two isomers);

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 0.86-1.01 \text{ (m, 6H, CH(CH}_3 \text{)})}, 1.65-1.79 \text{ (m, 3H, CH.CH(CH}_3 \text{)})}, 3.30-3.40 \text{ (m, 1H, N-CH)}, 3.46 \text{ and } 3.55 \text{ (d, } J = 12.3 \text{ Hz, Ar-CH}_2) \], 3.55 \text{ and } 3.58 \text{ (s, 3H, COOCH}_3 \text{)}, 3.80 \text{ and } 3.84 \text{ (d, 2H, } J = 12.3 \text{ Hz, Ar-CH}_2) \], 7.22-7.28 \text{ (m, 2H, Ar-H)}, 7.43-7.48 \text{ (m, 4H, Ar-H)}, 7.54 and 7.58 \text{ (d, 2H, } J = 8.1 \text{ Hz, Ar-H}), 7.95 \text{ (d, 4H, } J = 8.1 \text{ Hz, Ar-H).}

(S, L)-2e, colorless oil, yield 92%;

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 2.14-2.21 \text{ (m, 2H, Ph-CH}_2-CH_2) \], 2.73 \text{ (t, } 2H, J = 7.8 \text{ Hz, Ph-CH}_2) \], 3.31 \text{ (t, } J = 7.5 \text{ Hz, N-CH)}, 3.55 \text{ (d, 2H, } J = 12.6 \text{ Hz, Ar-CH}_2) \], 3.58 \text{ (s, 3H, COOCH}_3 \text{)}, 3.81 \text{ (d, } 2H, J = 12.6 \text{ Hz, Ar-CH}_2), 7.24-7.35 \text{ (m, 7H, Ar-H)}, 7.35-7.51 \text{ (m, 4H, Ar-H)}, 7.60 \text{ (d, 2H, } J = 8.4 \text{ Hz, Ar-H)}, 7.96-8.01 \text{ (m, 4H, Ar-H).} \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 31.9, 32.0, 51.4, 51.7, 65.0, 125.4, 125.7, 126.0, 127.5, 128.2, 128.3, 128.4, 128.5, 131.2, 133.0, 133.4, 134.8, 141.5, 173.7 ppm.

(S, L)-2f, light yellow powder, yield 90%;

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 2.06-2.11 \text{ (m, 2H, S-CH}_2-CH_2) \], 2.11 \text{ (s, 3H, S-CH}_3 \text{)}, 2.53-2.60 \text{ (m, 2H, S-CH}_2-CH_2) \], 3.45-3.50 \text{ (m, 1H, N-CH)}, 3.51 \text{ (d, 2H, } J = 12.6 \text{ Hz, Ar-CH}_2) \], 3.54 \text{ (s, 3H, COOCH}_3 \text{)}, 3.77 \text{ (d, } 2H, J = 12.6 \text{ Hz, Ar-CH}_2), 7.21-7.28 \text{ (m, 2H, Ar-H), 7.46-7.61 \text{ (m, 4H, Ar-H)})}.\]
7.41-7.48 (m, 4H, Ar-H), 7.54 (d, 2H, J = 8.4 Hz, Ar-H), 7.94 (d, 4H, J = 8.4 Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.5, 29.6, 30.5, 51.5, 52.7, 64.4, 125.4, 125.7, 127.5, 128.1, 128.2, 128.4, 131.2, 133.0, 134.8, 173.5 ppm.

(S.L)-2g', white solid, yield 96%;

$^{1}$H NMR (300 MHz, CDCl$_3$) δ 3.44-3.49 (m, 1H, N-CH), 3.49 (s, 3H, COOCH$_3$), 3.65 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 3.80 (d, 2H, J = 12.3 Hz, Ar-CH$_2$), 3.80-3.94 (m, 2H, CH$_2$OH), 7.23-7.28 (m, 2H, Ar-H), 7.41-7.49 (m, 2H, Ar-H), 7.52 (d, 2H, J = 8.7 Hz, Ar-H), 7.92-7.97 (m, 4H, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 51.5, 52.5, 59.6, 65.7, 125.6, 125.8, 127.5, 127.9, 128.2, 128.6, 131.3, 133.0, 133.1, 134.9, 172.4 ppm.

To a 25 mL flask was added 2g' (40 mg, 0.1 mmol), DIEA(70 μL, 4 eq), MOMCl (12 μL, 1.5 eq) and CH$_2$Cl$_2$ (5 mL). The reaction was stirred under room temperature and monitored by TLC for completion. The mixture was then quenched with NH$_4$Cl (aq, saturated), extracted for three times with CH$_2$Cl$_2$. The organic layer was washed with water and brine, dried over anhydrous Na$_2$SO$_4$, and concentrated. Purification by flash column chromatography on silica gel (eluted with 5:1 hexane/ethyl acetate) afforded the MOM-protected product 2g (40 mg, 92%)

$^{1}$H NMR (300 MHz, CDCl$_3$) δ 3.39 (s, 3H, OCH$_2$OCH$_3$), 3.48 (d, 2H, J = 12.0 Hz, Ar-CH$_2$), 3.53-3.57 (m, 1H, CH$_2$OMOM), 3.68 (s, 3H, COOCH$_3$), 3.78 (d, 2H, Ar-CH$_2$), 3.79-3.84 (m, 1H, CH$_2$OMOM), 3.95-4.01 (m, 1H, N-CH), 4.62 (s, 1H, OCH$_2$OCH$_3$), 7.25-7.28 (m, 2H, Ar-H), 7.43-7.48 (m, 4H, Ar-H), 7.58 (d, 2H, J = 8.4 Hz, Ar-H), 7.93-7.97 (m, 4H, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 51.8, 53.3, 55.3, 65.7, 66.7, 96.6, 125.5, 125.7, 127.4, 128.1, 128.2, 128.4, 131.2, 132.9, 133.1, 134.9, 172.2 ppm.

(S,L)-2h, white solid, yield 91%;

$^{1}$H NMR (300 MHz, CDCl$_3$) δ 3.03 (d, 2H, J = 6 Hz, Ph-CH$_2$), 3.46 (d, 2H, J = 12.3 Hz, Ar-CH$_2$), 3.48 (s, 3H, COOCH$_3$), 3.44-3.49 (m, 1H, N-CH), 3.85 (d, 2H, J = 12.4 Hz, Ar-CH$_2$), 6.70 (d, 2H, J = 8.1Hz, Ph-H), 7.00 (d, 2H, J = 8.1Hz, Ph-H), 7.23-7.29 (m, 2H, Ar-H), 7.44-7.49 (m, 4H, Ar-H), 7.57 (d, 2H, J = 8.4 Hz, Ar-H), 7.97 (d, 4H, J = 8.4 Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 36.2, 51.6, 53.3, 68.8, 115.3, 125.5, 125.7, 127.5, 128.15, 128.24, 128.4, 129.2, 130.3, 131.2, 133.0, 133.1, 134.9, 154.4, 173.1 ppm.
(S,L)-2i, white solid, yield 92%;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.0-3.3 (m, 2H, Ph-CH$_2$),
3.47-3.50 (m, 1H, N-CH), 3.42 and 3.45 (s, 3H, COOCH$_3$),
3.54-3.70 (m, 2H, Ar-CH$_2$), 3.86-4.01 (m, 2H, Ar-CH$_2$),
7.0-7.3 (m, 6H, Ar-H), 7.47-7.52 (m, 4H, Ar-H), 7.58-7.70 (m,
3H, Ar-H), 7.98 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.17 (b, 1H, NH).

$^{13}$C NMR (100 MHz, CDCl$_3$) 26.5, 51.4, 53.2, 67.4, 111.0, 111.6, 118.7, 119.3, 121.9, 122.7, 125.4,
125.7, 127.4, 127.5, 128.2, 128.2, 128.4, 131.2, 133.0, 133.3, 134.9, 136.0, 173.4 ppm.

(S,L)-2j, white solid, yield 93%;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.19 (d, 2H, $J = 12.3$ Hz, ArCH$_2$), 3.63
(s, 3H, COOCH$_3$), 3.77 (d, 2H, $J = 12.0$ Hz, ArCH$_2$), 4.01 (s, 1H,
NCHCOOMe), 7.21-7.27 (m, 2H, Ar-H), 7.38-7.48 (m, 9H, Ar-H),
7.65 (d, 2H, $J = 6.9$ Hz, ArH), 7.94 (d, 4H, $J = 8.1$ Hz, ArH). $^{13}$C NMR
(100 MHz, CDCl$_3$) 52.4, 53.9, 71.8, 125.5, 125.7, 125.5, 125.7, 125.7,
125.7, 127.4, 128.0, 128.3, 128.3, 128.6, 128.6, 128.9, 131.2, 132.8, 133.2, 135.1,
136.0, 172.5 ppm.

2.2 Synthetic Procedure for Amine 2k

Under nitrogen atmosphere, to a solution of (S)-2a (36.5 mg, 0.1 mmol) in dry THF at -78$^\circ$C
was added LiHMDS (1.0 M in THF, 0.15 mL, 1.5 eq). The mixture was allowed to warm and
stirred at 0$^\circ$C for 1h, and then cooling to -78$^\circ$C again, 1-bromo -4-(bromomethyl)-benzene (50 mg,
2 eq) was added and the mixture was allowed to warm to room temperature slowly and stirred for
another 6h. The reaction was quenched with water, and extracted with ethyl acetate for 3 times.
The organic layer was washed with NaHCO$_3$ (aq, saturated) and brine, dried over anhydrous
Na$_2$SO$_4$, and concentrated. Purification by flash column chromatography on silica gel (eluted with
10:1 hexane/ethyl acetate) afforded a colorless oil 2k (36 mg, 67%).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.95-3.18 (m, 2H, Ph-CH$_2$), 3.44 (s, 3H, COOCH$_3$), 3.42-3.51 (m,
1H, N-CH), 3.50 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 3.82 (d, 2H, $J = 12.4$ Hz, Ar-CH$_2$), 7.05 (d, 2H, $J =
8.4$Hz, Ph-H), 7.24-7.27 (m, 2H, Ar-H), 7.37 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.42-7.47 (m, 4H, Ar-H),
7.54 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.94 (d, 2H, $J = 8.4$ Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
36.4, 51.4, 53.0, 59.0, 67.9, 71.7, 120.3, 125.5, 125.7, 127.4, 128.0, 128.2, 128.4, 130.8,
131.0, 131.2, 131.3, 131.5, 133.0, 133.04, 133.2, 134.8, 134.9, 136.8, 172.7 ppm.
2.3 Synthetic Procedure for Amine 2l

Under nitrogen atmosphere, to a solution of (S)-2a (36.5 mg, 0.1 mmol) in dry THF at -78°C was added LiHMDS (1.0 M in THF, 0.15 mL, 1.5 eq). The mixture was allowed to warm and stirred at 0°C for 1h, and then cooling to -78°C again, 2-(2-(bromomethyl)phenyl)-1,3-dioxolane (48 mg, 2 eq) was added and the mixture was allowed to warm to room temperature slowly and stirred for another 6h. The reaction was quenched with water, extracted with ethyl acetate for 3 times. The organic layer was washed with NaHCO₃ (aq, saturated) and brine, dried over anhydrous Na₂SO₄, and concentrated.

The above obtained residue was dissolved in acetone and drops of concentrated HCl was added. After further stirring at room temperature for 3h, the reaction was quenched with NaHCO₃ (aq, saturated), extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na₂SO₄, and concentrated. Purification by flash column chromatography on silica gel (eluted with 10:1 hexane/ethyl acetate) afforded a colorless oil 2l (30 mg, 62%).

3. General Procedure for the Synthesis of Ammonium Salts

To a 25 mL flask was added the amine substrates 2 (0.2 mmol), allyl bromide (0.4 mmol) and 5 mL of acetonitrile. The reaction was stirred at room temperature for 1-2 days, monitored by TLC for completion. The mixture was then diluted with CH₂Cl₂, concentrated under vacuum, removing the solvent and allyl bromide. The residue was purified by flash column chromatography on silica gel afforded the corresponding ammonium salts 3.

3a, white solid, yield 96%;

₁H NMR (300 MHz, CDCl₃) δ 3.77 (d, 2H, J = 12.0 Hz), 3.78 (s, 3H), 4.25 (dd, 1H, J = 7.2 Hz, 13.5 Hz), 4.44 (d, 1H, J = 17.4 Hz), 4.72 (dd, 1H, J = 7.5 Hz, 13.5 Hz), 5.30 (d, 1H, J = 13.2 Hz), 5.48 (d, 1H, J = 17.7 Hz), 5.66 (d, 1H, J = 17.7 Hz), 5.75 (d, 1H, J = 9.3 Hz), 5.87 (d, 1H, J = 12.9 Hz), 6.40-6.54 (m, 1H), 7.38-7.44 (m, 4H), 7.59-7.62 (m, 2H), 7.74 (d, 4H, J = 7.8 Hz, Ar-H), 10.26 (s, 1H, -CHO)
Hz), 8.01-8.05 (m, 2H), 8.13 (d, 2H, J = 8.4 Hz), 8.26 (d, 1H, J = 7.8 Hz); 13C NMR (100 MHz, CDCl3) δ 53.2, 57.2, 62.6, 63.1, 64.2, 124.6, 125.6, 125.9, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.1, 128.5, 128.6, 129.2, 130.2, 130.6, 131.0, 131.1, 134.37, 134.44, 136.5, 137.0 ppm. ESI-MS: 408.1 (M+-Br); HRMS (ESI) for C28H26N1O2 (M+-Br): calcd 408.1964, found 408.1954.

3a', white solid, yield 82%;
1H NMR (300 MHz, CDCl3) δ 3.28 (s, 3H), 3.34 (d, 1H, J = 8.1 Hz), 3.52-3.59 (m, 2H), 3.75-3.83 (m, 2H), 4.57-4.70 (m, 1H), 4.93 (dd, 2H, J = 14.7 Hz, 16.8 Hz), 5.11 (d, 1H, J = 9.9 Hz), 5.48 (d, 1H, J = 12.9 Hz), 5.70 (d, 1H, J = 14.1 Hz), 7.26-7.45 (m, 10H), 7.58-7.67 (m, 6H), 8.01-8.06 (m, 3H), 8.11 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 52.3, 54.1, 56.7, 58.6, 60.3, 123.0, 123.7, 123.8, 127.3, 127.5, 127.6, 127.7, 127.9, 128.0, 128.2, 128.4, 128.5, 130.0, 130.5, 130.7, 131.0, 131.4, 134.0, 137.8, 138.4, 138.6, 138.7, 139.7, 140.8, 164.9 ppm. ESI-MS: 560.2 (M+-Br); HRMS (ESI) for C40H34N1O2 (M+-Br): calcd 560.2590, found 560.2614.

3b, white solid, yield 91%;
1H NMR (300 MHz, CDCl3) δ 3.87 (d, 3H, J = 7.2 Hz), 3.92 (s, 3H), 3.98 (dd, 2H, J = 6.0 Hz, 6.9 Hz), 4.43-4.50 (m, 1H), 4.62-4.69 (m, 1H), 4.88 (d, 1H, J = 7.2 Hz), 5.55-5.69 (m, 3H), 5.82 (d, 2H, J = 12.6 Hz), 6.18-6.32 (m, 1H), 7.32-7.36 (m, 4H), 7.57-7.60 (m, 2H), 8.02 (d, 2H, J = 8.4 Hz), 8.06-8.13 (m, 3H), 8.11 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 14.1, 53.6, 61.2, 62.3, 63.6, 67.0, 125.1, 126.2, 126.8, 126.9, 127.0, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.2, 128.4, 128.5, 128.8, 130.0, 130.9, 131.0, 134.1, 134.2, 136.4, 136.5, 168.5 ppm, ESI-MS: 422.1 (M+-Br); HRMS (ESI) for C29H28N1O2 (M+-Br): calcd 422.2120, found 422.2134.

3b', white solid, yield 74%;
1H NMR (300 MHz, CDCl3) δ 1.14 (s, 3H), 3.48-3.54 (m, 4H), 3.80 (d, 2H, J = 14.2 Hz), 4.06-4.12 (m, 1H), 4.32 (d, 1H, J = 14.7 Hz), 4.53-4.59 (m, 1H), 4.99 (d, 1H, J = 10.2 Hz), 5.21-5.37 (m, 1H), 5.65 (d, 1H, J = 16.2 Hz), 5.83 (d, 1H, J = 12.0 Hz), 7.39-7.67 (m, 16H), 8.02-8.10 (m, 4H); 13C NMR (100 MHz, CDCl3) δ 14.1, 22.6, 31.9, 53.0, 55.8, 65.6, 123.8, 124.7, 127.4, 127.5, 127.6, 127.7, 127.8, 128.3, 128.4, 128.5, 129.5, 130.8, 131.1, 134.1, 134.2, 136.4, 136.5, 168.5 ppm, ESI-MS: 574.1 (M+-Br); HRMS (ESI) for C41H36N1O2 (M+-Br): calcd 574.2746, found 574.2740.

3c, white solid, yield 81%;
1H NMR (300 MHz, CDCl3) δ 3.20 (t, 1H, J = 12.0 Hz), 3.39 (s, 2H), 3.52 (s, 3H), 3.85-3.90 (m, 1H), 3.97 (d, 1H, J = 13.5 Hz), 4.16 (d, 1H, J = 12.6 Hz), 4.42-4.49 (m, 1H), 4.57-4.64 (m, 1H), 4.87 (dd, 1H, J = 3.3 Hz, 8.4 Hz), 5.54 (dd, 2H, J = 11.1 Hz, 15.0 Hz), 5.69 (d, 1H, J = 13.8 Hz), 5.82 (d, 1H, J = 12.9 Hz), 6.24-6.38 (m, 1H), 7.14-7.19 (m, 5H), 7.27-7.33 (m, 4H), 7.53-7.58 (m, 2H), 7.96-7.99 (m, 2H), 8.05 (dd, 2H, J = 8.4 Hz, 13.8 Hz), 8.20 (dd, 2H, J = 8.7 Hz, 12.3 Hz); 13C NMR (100 MHz, CDCl3) δ 33.6, 53.1, 61.1, 63.5, 64.9, 73.6, 125.1, 126.0, 127.0, 127.1, 127.4, 127.5, 127.6, 128.2, 128.5, 128.6, 128.8, 129.5,
13.0, 130.1, 131.01, 131.03, 132.8, 134.1, 134.2, 136.46, 136.54, 167.2 ppm. ESI-MS: 498.1 (M^+-Br); HRMS (ESI) for C_{35}H_{32}N_1O_2 (M^+-Br): calcd 498.2433, found 498.2441.

**3d**, white solid, yield 96%;

\[
{}^1H\text{ NMR (300 MHz, CDCl}_3): \delta 0.86 (d, 3H, J = 6.3 Hz), 0.93 (d, 3H, J = 6.3 Hz), 1.56 (br, 1H), 2.11-2.32 (m, 2H), 3.79 (d, 1H, J = 12.3 Hz), 4.03 (d, 1H, J = 14.1 Hz), 4.06 (s, 3H), 4.39 (d, 1H, J = 11.1 Hz), 4.50 (dd, 1H, J = 7.2 Hz, 13.8 Hz), 4.72 (dd, 1H, J = 6.9 Hz, 13.8 Hz), 5.24 (d, 1H, J = 13.5 Hz), 5.55 (d, 1H, J = 9.9 Hz), 5.63 (d, 1H, J = 17.1 Hz), 5.86 (d, 1H, J = 12.3 Hz), 6.26-6.40 (m, 1H), 7.33-7.37 (m, 4H), 7.59-7.62 (m, 2H), 7.98-8.16 (m, 5H), 8.33 (d, 1H, J = 8.4 Hz); \]

\[
{}^{13}C\text{ NMR (100 MHz, CDCl}_3): \delta 20.1, 22.9, 25.7, 35.2, 53.3, 61.4, 63.1, 63.6, 71.3, 125.6, 126.1, 126.2, 126.7, 126.8, 127.2, 127.3, 127.4, 127.8, 128.0, 128.28, 128.32, 128.7, 129.6, 129.8, 130.7, 130.8, 133.9, 134.0, 136.3, 136.4, 167.5 ppm. ESI-MS: 464.1 (M^+-Br); HRMS (ESI) for C_{32}H_{34}N_1O_2 (M^+-Br): calcd 464.2590, found 464.2581.

**3e**, white solid, yield 80%;

\[
{}^1H\text{ NMR (300 MHz, CDCl}_3): \delta 2.29-2.37 (m, 1H), 2.78-2.80 (m, 2H), 2.88-2.95 (m, 1H), 3.16 (d, 1H, J = 12.6 Hz), 3.90 (d, 1H, J = 13.5 Hz), 4.02 (s, 3H), 4.37-4.48 (m, 2H), 4.60 (dd, J = 6.6 Hz, 13.2 Hz), 5.33 (d, 1H, J = 11.1 Hz, 19.6 Hz), 5.74 (d, 1H, J = 12.6 Hz), 6.30-6.44 (m, 1H), 6.66 (d, 1H, J = 6.6 Hz), 6.80 (d, 2H, J = 6.3 Hz, 7.5 Hz), 7.04 (d, 2H, J = 7.5 Hz), 7.24-7.36 (m, 4H), 7.53-7.63 (m, 2H), 7.91-8.07 (m, 5H), 8.17 (d, 1H, J = 7.5 Hz); \]

\[
{}^{13}C\text{ NMR (100 MHz, CDCl}_3): \delta 28.9, 31.9, 53.8, 61.1, 62.6, 63.8, 70.0, 125.4, 126.0, 126.3, 126.8, 126.9, 127.2, 127.3, 127.4, 127.5, 127.6, 128.0, 128.2, 128.3, 128.4, 128.5, 128.8, 129.9, 130.9, 134.1, 136.2, 136.3, 138.0, 168.2 ppm. ESI-MS: 512.1 (M^+-Br); HRMS (ESI) for C_{36}H_{34}N_1O_2 (M^+-Br): calcd 512.2590, found 512.2583.

**3f**, light yellow solid; yield 95%; (contains some inseparable sulfur-allylation compounds);

\[
{}^1H\text{ NMR (300 MHz, CDCl}_3): \delta 2.04 (s, 3H), 2.35-2.38 (m, 2H), 3.30 (s, 3H), 3.48-3.60 (m, 3H), 3.74-3.82 (m, 2H), 3.96 (d, 2H, J = 12.3 Hz), 4.09-4.13 (m, 2H), 4.50-4.73 (m, 1H), 5.55-5.61 (m, 1H), 5.78-5.87 (m, 1H), 7.23-7.25 (m, 2H), 7.35-7.46 (m, 4H), 7.56 (d, 2H, J = 8.1 Hz), 7.92-8.01 (4H); \]

\[
{}^{13}C\text{ NMR (100 MHz, CDCl}_3): \delta 21.4, 24.7, 31.3, 52.6, 60.3, 62.8, 62.9, 64.3, 123.5, 124.0, 125.3, 125.6, 125.8, 127.3, 127.6, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 131.1, 132.5, 132.6, 132.9, 134.7, 172.3 ppm. ESI-MS: 482.2 (M^+-Br); HRMS (ESI) for C_{36}H_{34}N_1O_2S_1 (M^+-Br): calcd 482.2154, found 482.2162.

**3g**, white solid, yield 78%;

\[
{}^1H\text{ NMR (300 MHz, CDCl}_3): \delta 3.76-3.78 (m, 1H), 3.88 (s, 3H), 3.96-4.06 (m, 2H), 4.28 (s, 3H), 4.63-4.85 (m, 4H), 5.50 (d, 1H, J = 16.2 Hz), 5.57 (d, 1H, J = 13.2 Hz), 5.69 (d, 1H, J = 9.9 Hz), 6.05 (s, 2H), 6.29-6.38 (m, 1H), 6.48 (d, 1H, J = 13.5 Hz), 7.29-7.34 (m, 4H), 7.59-7.61 (m, 2H), 7.92 (d, 1H, J = 8.7 Hz), 8.04 (d, 2H, J =
$8.1 \text{ Hz}$, $8.14 \text{ (d, 2H, } J = 8.4 \text{ Hz)}$, $8.49 \text{ (d, 1H, } J = 8.4 \text{ Hz)}$; $\text{13C NMR (100 MHz, CDCl}_3 \delta 53.2, 55.2, 61.5, 64.9, 66.5, 71.1, 96.5, 124.9, 125.9, 126.9, 127.2, 127.4, 127.5, 127.7, 128.2, 128.3, 128.5, 128.6, 130.1, 130.2, 131.1, 131.3, 134.3, 136.2, 136.7, 166.8 \text{ ppm. ESI-MS: 482.0 (M}^+\text{-Br); HRMS (ESI) for C}_{31}\text{H}_{32}\text{N}_1\text{O}_4 \text{ (M}^+\text{-Br): calcld 482.2331, found 482.2334.}$

$3h$, white solid, yield 72%;
$\text{1H NMR (300 MHz, CDCl}_3 \delta 3.11 \text{ (t, 1H, } J = 12.6 \text{ Hz), 3.47-3.55 \text{ (m, 4H), 3.99 \text{ (dd, 2H, } J = 9.6 \text{ Hz, 13.5 Hz), 4.34 \text{ (d, 1H, } J = 9.6 \text{ Hz), 4.43-4.50 \text{ (m, 1H), 4.61-4.69 \text{ (m, 1H), 4.99 \text{ (d, 1H, } J = 12.3 \text{ Hz), 5.48 \text{ (d, 1H, } J = 9.9 \text{ Hz), 5.56 \text{ (d, 1H, } J = 16.5 \text{ Hz), 5.82 \text{ (d, 1H, } J = 12.3 \text{ Hz), 6.14-6.28 \text{ (m, 1H), 6.58 \text{ (d, 2H, } J = 8.1 \text{ Hz), 6.77 (d, 2H, } J = 8.1 \text{ Hz), 7.29-7.36 \text{ (m, 4H), 7.52-7.57 \text{ (m, 2H), 7.88-8.09 \text{ (m, 5H), 8.28 (d, 1H, } J = 8.4 \text{ Hz), 8.71 (br, 1H); 13C NMR (100 MHz, CDCl}_3 \delta 32.6, 53.3, 62.0, 63.2, 64.0, 74.0, 116.1, 122.5, 125.3, 125.7, 126.3, 127.0, 127.1, 127.4, 127.6, 128.0, 128.7, 129.0, 130.1, 131.1, 134.2, 134.3, 136.5, 156.8, 167.0 ppm. ESI-MS: 514.1 (M}^+\text{-Br); HRMS (ESI) for C}_{35}\text{H}_{32}\text{N}_1\text{O}_4 \text{ (M}^+\text{-Br): calcld 514.2382, found 514.2388.}$

$3i$, white solid, yield 80%;
$\text{1H NMR (300 MHz, CDCl}_3 \delta 3.34 \text{ (s, 3H), 3.41-3.52 \text{ (m, 2H), 3.80 (d, 1H, } J = 12.9 \text{ Hz), 3.95 (d, 1H, } J = 13.2 \text{ Hz), 4.36 (d, 1H, } J = 7.5 \text{ Hz), 4.49-4.56 \text{ (m, 1H), 4.65-4.72 \text{ (m, 1H), 4.87 (d, 1H, } J = 13.2 \text{ Hz), 5.50 (dd, 2H, } J = 11.1 \text{ Hz, 17.4 Hz), 5.95 (d, 1H, } J = 12.6 \text{ Hz), 6.10-6.19 \text{ (m, 1H), 6.56 (t, 1H, } J = 7.5 \text{ Hz), 6.75 (t, 1H, } J = 6.9 \text{ Hz), 6.85 (d, 1H, } J = 6.9 \text{ Hz), 6.86 (s, 1H), 7.34-7.43 \text{ (m, 5H), 7.58 (dd, 2H, } J = 8.4 \text{ Hz, 6.6 Hz), 7.79 (d, 1H, } J = 8.4 \text{ Hz), 7.95-8.04 \text{ (m, 4H), 8.13 (d, 1H, } J = 8.4 \text{ Hz), 8.41 (d, 1H, } J = 8.1 \text{ Hz), 10.47 (s, 1H); 13C NMR (100 MHz, CDCl}_3 \delta 23.1, 53.3, 62.1, 62.8, 72.6, 104.7, 112.0, 117.1, 118.6121.1, 124.9, 125.4, 126.0, 126.1, 126.4, 126.9, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 128.1, 128.5, 128.9, 130.1, 130.9, 131.4, 134.2, 135.8, 136.4, 136.5, 167.2 \text{ ppm. ESI-MS: 537.1 (M}^+\text{-Br); HRMS (ESI) for C}_{37}\text{H}_{33}\text{N}_2\text{O}_2 \text{ (M}^+\text{-Br): calcld 537.2542, found 537.2515.}$

$3j$, white solid, yield 85%;
$\text{1H NMR (300 MHz, CDCl}_3 \delta 3.64 \text{ (s, 3H), 4.00 (dd, 1H, } J = 14.7 \text{ Hz, 14.4 Hz), 4.28-4.32 \text{ (m, 1H), 4.65 (d, 1H, } J = 12.6 \text{ Hz), 5.29 (d, 1H, } J = 6.3 \text{ Hz), 5.60 (d, 2H, } J = 12.6 \text{ Hz), 5.85 (d, 1H, } J = 16.5 \text{ Hz), 6.32 (d, 1H, } J = 14.1 \text{ Hz), 6.49-6.60 \text{ (m, 2H), 7.16-7.57 \text{ (m, 10H), 7.76-8.15 \text{ (m, 7H); 13C NMR (100 MHz, CDCl}_3 \delta 53.2, 53.3, 58.0, 59.6, 62.4, 66.0, 66.3, 66.8, 72.0, 73.2, 124.9, 125.2, 125.5, 126.0, 126.3, 126.6, 126.7, 126.9, 127.0, 127.1, 127.16, 127.2, 127.36, 127.40, 127.43, 127.5, 127.6, 127.8, 128.17, 128.20, 128.22, 128.33, 128.36, 128.39, 128.43, 128.5, 128.7, 128.8, 129.4, 130.1, 130.2, 130.4, 131.0, 131.2, 131.3, 131.5, 132.3, 133.3, 133.9, 134.12, 134.16, 135.4, 136.2, 136.4, 136.8, 167.3, 167.8 \text{ ppm. ESI-MS: 484.1 (M}^+\text{-Br); HRMS (ESI) for C}_{34}\text{H}_{30}\text{N}_1\text{O}_2 \text{ (M}^+\text{-Br): calcld 484.2277, found 484.2299.}$
**Electronic Supplementary Material (ESI) for Chemical Communications**

This journal is © The Royal Society of Chemistry 2012
3o, white solid, yield 81%;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.86 (d, 3H, $J$ = 6.3 Hz), 0.89 (d, 3H, $J$ = 6.6 Hz), 1.56 (br, 1H), 2.11 (dd, 1H, $J$ = 12.9Hz, 12.0 Hz), 2.33 (dd, 1H, $J$ = 10.5 Hz, 11.1 Hz), 3.85 (d, 1H, $J$ = 12.6 Hz), 4.10 (d, 1H, $J$ = 6.6 Hz), 4.52 (d, 1H, $J$ = 10.8 Hz), 4.62 (dd, 1H, $J$ = 7.2 Hz, 13.5 Hz), 4.83 (dd, 1H, $J$ = 6.9 Hz), 5.44 (d, 1H, $J$ = 13.5 Hz), 6.00 (d, 1H, $J$ = 12.9 Hz), 6.68-6.78 (m, 1H), 6.88 (d, 1H, $J$ = 15.3 Hz), 7.30 (d, 1H, $J$ = 4.2 Hz), 7.36 (br, 6H), 7.53-7.64 (m, 2H), 7.95-8.04 (m, 4H), 8.12 (d, 1H, $J$ = 8.1 Hz), 8.37 (d, 1H, $J$ = 8.7 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.1, 23.1, 25.8, 35.6, 53.8, 61.2, 63.2, 63.8, 71.4, 166.7, 122.9, 126.5, 126.8, 127.0, 127.2, 127.4, 127.5, 127.9, 128.3, 128.4, 128.9, 129.0, 129.0, 130.8, 130.9, 131.5, 133.6, 134.0, 136.3, 136.5, 140.5, 168.0 ppm. ESI-MS: 618.0 (M$^+$/Br); HRMS (ESI) for C$_{38}$H$_{37}$N$_1$O$_2$Br$_1$ (M$^+$/Br): calcd 618.2008, found 618.2015.

3.1 Synthetic Procedure for 7a and 7b

To a 50 mL flask was added dialdehyde compound 6 (440 mg, 1 mmol), methyl amino acids hydrogen chloride (1.5 mmol), NaBH$_3$CN (330 mg, 3 mmol) and 20 mL of methol. The reaction was stirred at rt for about 4 hours for completion. The mixture was diluted with EtOAc, washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding N,N-disubstituted amine. The amine (0.2 mmol) and allyl bromide (0.4 mmol) was dissolved in 5 mL of acetonitrile, and stirred at room temperature for about 2 days. The mixture was then diluted with CH$_2$Cl$_2$, concentrated under vacuum, removing the solvent and allyl bromide. The residue was purified by flash column chromatography on silica gel (eluted with 10:1 CH$_2$Cl$_2$/CH$_3$OH) to afford the corresponding ammonium salts 7a or 7b.

7a, white solid, yield 82%;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.26 (t, 1H, $J$ = 12.0 Hz), 3.61 (s, 1H), 3.72-3.81 (m, 7H), 3.90-4.00 (m, 14H), 4.51-4.66 (m, 2H), 4.80 (d, 1H, $J$ = 9.0 Hz), 5.40 (d, 1H, $J$ = 13.2 Hz), 5.56-5.64 (m, 3H), 6.30-6.43 (m, 1H), 7.24-7.30 (m, 5H), 7.53 (s, 1H), 7.67 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.8, 52.8, 55.9, 56.4, 60.45, 60.46, 60.57, 60.62 62.9, 64.1, 73.0, 110.3, 111.1, 121.9, 122.8,

124.8, 127.2, 127.6, 128.2, 129.0, 132.6, 143.2, 143.3, 151.18, 151.24, 153.3, 166.3 ppm. ESI-MS: 578.1 (M⁺-Br); HRMS (ESI) for C₃₃H₄₀N₁O₂ (M⁺-Br): calcd 578.2754, found 578.2754.

7b, white solid, yield 92%;

^1^H NMR (300 MHz, CDCl₃) δ 0.68 (d, 3H, ^J^ = 6.3 Hz), 0.72 (d, 3H, ^J^ = 6.6 Hz), 1.37 (br, 1H), 1.85-2.05 (m, 2H), 3.31 (d, 1H, ^J^ = 12.6 Hz), 3.51 (s, 6H), 3.57 (d, 1H, 13.8 Hz), 3.73 (s, 3H), 3.75 (s, 6H), 3.80 (d, 6H, ^J^ = 1.5 Hz), 4.12 (d, 1H, ^J^ = 12.9 Hz), 4.22-4.29 (m, 1H), 4.39-4.46 (m, 1H), 4.67 (d, 1H, ^J^ = 13.5 Hz), 5.34-5.45 (m, 3H), 6.02-6.16 (m, 1H), 7.02 (s, 1H), 7.50 (s, 1H); ^1^C NMR (100 MHz, CDCl₃) δ 20.8, 22.7, 25.4, 34.6, 53.6, 55.9, 56.5, 60.5, 60.56, 60.61, 62.7, 63.2, 70.9, 110.0, 111.3, 122.1, 122.3, 122.7, 123.0, 125.4, 127.5, 143.3, 143.4, 151.1, 151.3, 153.0, 153.4, 167.1 ppm. ESI-MS: 544.1 (M⁺-Br); HRMS (ESI) for C₃₀H₄₂N₁O₈ (M⁺-Br): calcd 544.2910, found 544.2896.

4. Optimization of the reaction conditions.

<table>
<thead>
<tr>
<th>entry^a</th>
<th>R</th>
<th>4</th>
<th>solvent</th>
<th>NaH (equiv)</th>
<th>yield^b (%)</th>
<th>de^c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H (3a)</td>
<td>4a</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>80</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>H (3a)</td>
<td>4a</td>
<td>THF</td>
<td>1</td>
<td>74</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>H (3a)</td>
<td>4a</td>
<td>Et₂O</td>
<td>1</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>H (3a)</td>
<td>4a</td>
<td>DME</td>
<td>1</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>H (3a)</td>
<td>4a</td>
<td>DME</td>
<td>1.5</td>
<td>97</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>Me (3b)</td>
<td>4b</td>
<td>DME</td>
<td>1</td>
<td>70</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>Me (3b)</td>
<td>4b</td>
<td>DME</td>
<td>1.5</td>
<td>92</td>
<td>85</td>
</tr>
<tr>
<td>8^d</td>
<td>Me (3b)</td>
<td>4b</td>
<td>DME</td>
<td>1.5</td>
<td>93</td>
<td>78</td>
</tr>
<tr>
<td>9^e</td>
<td>Me (3b)</td>
<td>4b</td>
<td>DME</td>
<td>1.5</td>
<td>89</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>Bn (3c)</td>
<td>4c</td>
<td>DME</td>
<td>1.5</td>
<td>92</td>
<td>98</td>
</tr>
</tbody>
</table>

^aUnless otherwise mentioned all reactions were performed on 0.1 mmol scale with 100 mg of 4Å molecular sieves in 5 mL of solvent at 0 °C. ^bYield of isolated product. ^cDetermined by crude ^1^H NMR. ^dReaction was proceeded at r.t.. ^eReaction was proceeded at -20 °C.
5. General Procedure for the Asymmetric [2,3]-Rearrangement

Under nitrogen atmosphere, the ammonium salts 3 (0.1 mmol), NaH (amounts as indicated in Table 2), and 4Å molecular sieves (100 mg) was added to a Schlenk flask. Dry DME (4 mL) was added at 0 °C and the reaction mixture was stirred at the same temperature for 1-3h. The mixture was then filtrated through Celite before warming to room temperature. The filtrate was washed with sat. aq. NaHCO₃ and brine, dried over anhydrous Na₂SO₄, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding rearrangement product 4 or 8.

4a, colorless oil, yield 76%;
$$^1$$H NMR (300 MHz, CDCl₃) δ 2.45-2.64 (m, 2H, CH₂CH=CH₂), 3.32 (dd, 1H, J = 6 Hz, 9 Hz), 3.39 (d, 2H, J = 12.3 Hz, Ar-CH₂), 3.61 (s, 3H, COOCH₃), 3.76 (d, 2H, J = 12.3 Hz, Ar-CH₂), 5.08 (dd, 2H, J = 18.6 Hz, 11.1 Hz, CH₂CH=CH₂), 5.70-5.84 (m, 1H, CH₂CH=CH₂), 7.19 (dd, 2H, J = 7.8 Hz, 7.5 Hz, Ar-H), 7.37-7.45 (m, 4H, Ar-H), 7.52 (d, 2H, J = 8.4 Hz, Ar-H), 7.85 (dd, 4H, J = 7.8 Hz, 6.4 Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl₃) δ 35.1, 51.5, 3.1, 66.3, 117.6, 125.4, 125.7, 127.4, 128.1, 128.2, 128.3, 128.4, 131.2, 133.06, 133.13, 133.8, 134.9, 173.1 ppm. ESI-MS: 408.0 [M+H]⁺, HRMS (ESI) for C₂₈H₂₆N₁O₂ [M+H]⁺: calcd 408.1964, found 408.1971.

4a’, colorless oil, yield 68%;
$$^1$$H NMR (300 MHz, CDCl₃) δ 1.78-1.87 (m, 1H, CH₂CH=CH₂), 2.12-2.22 (m, 1H, CH₂CH=CH₂), 3.05 (dd, 1H, J = 5.4Hz, 4.8Hz, CHCOOMe), 3.29 (s, 3H, COOCH₃), 3.38 (d, 2H, J = 12.6Hz, Ar-CH₂), 4.08 (d, 2H, J = 12.6Hz, Ar-CH₂), 4.80 (dd, 2H, J = 17.1Hz, 10.5Hz, CH=CH₂), 5.37-5.51 (m, 1H, CH=CH₂), 7.26-7.30 (m, 2H, ArH), 7.40-7.51 (m, 10H, ArH), 7.52 (d, 4H, J = 6.9 Hz, Ar-H), 7.94-7.96 (m, 4H, Ar-H). $^{13}$C NMR (100 MHz, CDCl₃) δ 33.5, 48.5, 51.1, 66.0, 117.0, 125.7, 125.8, 127.1, 127.5, 128.1, 128.2, 129.4, 130.1, 130.7, 131.7, 132.5, 134.0, 136.2, 140.2, 141.0, 172.0. ESI-MS: 560.1 [M+H]⁺, HRMS (ESI) for C₄₀H₃₃N₁O₂ [M+H]⁺: calcd 560.2590, found 560.2605.

4b, colorless oil, yield 92%;
$$^1$$H NMR (300 MHz, CDCl₃) δ 1.37 (s, 3H, CH₃), 2.58-2.78 (m, 2H, CH₂CH=CH₂), 3.47 (d, 2H, J = 12.6 Hz, Ar-CH₂), 3.52 (s, 3H, COOCH₃), 3.93 (d, 2H, J = 12.6 Hz, Ar-CH₂), 5.12 (dd, 2H, J = 18.6 Hz, 11.1 Hz, CH₂CH=CH₂), 5.75-5.87 (m, 1H, CH₂CH=CH₂), 7.21-7.28 (m, 2H, Ar-H), 7.41-7.48 (m, 4H, Ar-H), 7.52 (d, 2H, J = 8.4 Hz, Ar-H), 7.94 (d, 4H, J =
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.8, 42.6, 49.4, 49.7, 51.4, 65.8, 117.8, 125.3, 125.6, 127.2, 127.5, 128.1, 128.3, 130.1, 131.2, 132.9, 134.1, 134.2, 135.0, 175.3 ppm. ESI-MS: 422.1 [M+H]$^+$, 444.0 [M+Na]$^+$; HRMS (ESI) for C$_{28}$H$_{27}$N$_1$O$_2$ [M+H]$^+$: calcd 422.2120, found 422.2120.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 7.6 min, 8.7 min (maj).

$^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.832 (s, 3H, CCH$_3$), 1.74 (dd, 1H, $J$ = 6.9 Hz, $J$ = 7.2 Hz, CH$_2$CH=CH$_2$), 2.17 (dd, 1H, $J = 6.9$ Hz, $J = 6.6$ Hz, CH$_2$CH=CH$_2$), 3.16 (s, 3H, COOCH$_3$), 3.45 (d, 2H, $J = 12.9$ Hz, NCH$_2$), 4.19 (d, 2H, $J = 12.9$ Hz, NCH$_2$), 4.86 (dd, 2H, $J = 12.9$ Hz, NCH$_2$), 4.91 (d, 2H, $J = 12.9$ Hz, NCH$_2$), 4.86 (dd, 2H, $J = 12.9$ Hz, NCH$_2$), 5.42-5.56 (m, 1H, CH=CH$_2$), 7.22-7.27 (m, 2H, ArH), 7.36-7.49 (m, 10H, ArH), 7.58 (br, 4H, ArH), 7.94 (d, 4H, $J = 5.7$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.9, 40.7, 45.4, 51.1, 66.7, 117.6, 125.6, 125.7, 127.1, 127.5, 128.1, 129.3, 130.3, 132.2, 132.4, 133.9, 136.5, 140.3, 141.2, 174.8 ppm. ESI-MS: 574.3 [M+H]$^+$, 596.3 [M+Na]$^+$; HRMS (ESI) for C$_{41}$H$_{36}$N$_1$O$_2$ [M+H]$^+$: calcd 574.2741, found 574.2715.

LC-MS: detected at 254 nm, Retention time: 63.25 min, 63.3 min (maj).

$^{4b'}$, colorless oil, yield 90%
4c, colorless oil, yield 92%;

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.38-2.46 (m, 1H, CH$_2$CH=CH$_2$), 2.81-2.88 (m, 1H, CH$_2$CH=CH$_2$), 3.30 (d, 1H, $J = 13.5$ Hz, PhCH$_2$), 3.38 (s, 3H, COOCH$_3$), 4.45 (d, 1H, $J = 13.5$ Hz, PhCH$_2$), 3.53 (d, 2H, $J = 12.6$ Hz, Ar-CH$_2$), 4.13 (d, 2H, $J = 12.6$ Hz, Ar-CH$_2$), 5.04 (dd, 2H, $J = 18.3$ Hz, $J = 12.3$ Hz, CH$_2$CH=CH$_2$), 5.88-6.01 (m, 1H, CH$_2$CH=CH$_2$), 7.14-7.29 (m, 7H, Ar-H), 7.44-7.48 (m, 4H, Ar-H), 7.54 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.94 (d, 4H, $J = 8.4$ Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 36.0, 39.2, 49.4, 50.8, 68.0, 117.7, 125.3, 125.6, 126.5, 127.5, 128.2, 128.3, 130.1, 131.2, 132.9, 134.0, 135.2, 137.2, 174.3 ppm. ESI-MS: 498.1 [M+H]$^+$, 520.1 [M+Na]$^+$; HRMS (ESI) for C$_{35}$H$_{32}$N$_1$O$_2$ [M+H]$^+$: calcd 498.2433, found 498.2437.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 3.78 min (maj), 4.15 min.
Colorless oil 4d. yield 95%;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.76 (d, 3H, $J = 6.3$ Hz, CHCH$_3$), 0.98 (d, 3H, $J = 6.3$ Hz, CHCH$_3$), 1.69-1.91 (m, 3H, CH$_2$(CH$_3$)$_2$), 2.53-2.61 (m, 1H, CH$_2$CH=CH$_2$), 3.01-3.08 (m, 1H, CH$_2$CH=CH$_2$), 3.30 (s, 3H, COOCH$_3$), 3.40 (d, 2H, $J = 12.6$ Hz, Ar-CH$_2$), 4.08 (d, 2H, $J = 12.6$ Hz, Ar-CH$_2$), 5.07 (dd, 2H, $J = 18.6$ Hz, 11.1 Hz, CH$_2$CH=CH$_2$), 5.78-5.92 (m, 1H, CH$_2$CH=CH$_2$), 7.23-7.27 (m, 2H, Ar-H), 7.41-7.45 (m, 4H, Ar-H), 7.51 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.92 (d, 4H, $J = 8.4$ Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.7, 24.4, 25.2, 36.1, 42.3, 48.6, 50.6, 65.7, 116.9, 125.3, 125.5, 127.5, 128.1, 128.2, 128.3, 131.2, 132.9, 134.3, 134.4, 135.1, 175.5 ppm. ESI-MS: 464.0 [M+H]$^+$; HRMS (ESI) for C$_{32}$H$_{34}$N$_1$O$_2$ [M+H]$^+$: calculated 464.2584, found 464.2567.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 5.16 min (maj).
**4e**, colorless oil, yield 97%;

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.18 (dd, 2H, $J = 7.5$Hz, 9.6Hz, PhCH$_2$CH$_2$), 2.24-2.52 (m, 1H, CH$_2$CH=CH$_2$), 2.78-3.00 (m, 3H, CH$_2$CH=CH$_2$, PhCH$_2$CH$_2$), 3.39, (s, 3H, COOCH$_3$), 3.49 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 4.12 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 5.04 (dd, 2H, $J = 17.1$ Hz, 10.5 Hz, CH$_2$CH=CH$_2$), 5.88-6.01 (m, 1H, CH$_2$CH=CH$_2$), 7.23-7.34 (m, 7H, Ar-H), 7.44-7.49 (m, 4H, Ar-H), 7.55 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.96 (d, 4H, $J = 8.4$ Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.7, 29.9, 35.3, 37.4, 48.9, 51.1, 66.5, 117.5, 125.3, 125.6, 126.0, 127.5, 128.1, 128.3, 128.4, 128.5, 131.1, 132.9, 134.1, 134.3, 135.1, 142.1, 174.6 ppm. ESI-MS: 512.0 [M+H]$^+$; HRMS (ESI) for C$_{36}$H$_{34}$N$_1$O$_2$ [M+H]$^+$: calcld 512.2584, found 512.2579.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 5.86 min (maj).

**4f**, light yellow oil, yield 88%;

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.13 (s, 3H, SCH$_3$), 2.13-2.19 (m, 2H, CH$_3$CH$_2$S), 2.30-2.39 (m, 1H, CH$_2$CH$_2$S), 2.64-2.72 (m, 2H, CH$_2$CH=CH$_2$, CH$_2$CH$_2$S), 2.80-2.88 (m, 1H, CH$_2$CH=CH$_2$), 3.36, (s, 3H, COOCH$_3$), 3.41 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 4.03 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 5.14 (dd, 2H, $J = 18.3$ Hz, 10.5 Hz, CH$_2$CH=CH$_2$), 5.778-6.89 (m, 1H, CH$_2$CH=CH$_2$), 7.21-7.28 (m, 7H, Ar-H), 7.40-7.46 (m, 4H, Ar-H), 7.51 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.93 (d, 4H, $J = 8.4$ Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.6, 28.2, 33.1, 37.7, 48.9, 51.1, 66.6, 117.8, 125.4, 125.6, 127.5, 128.2, 128.3, 131.2, 132.9, 133.9, 135.2, 174.1 ppm. ESI-MS: 482.0 [M+H]$^+$; HRMS (ESI) for C$_{31}$H$_{32}$N$_1$O$_2$S$_1$ [M+H]$^+$: calcld 482.2154, found 482.2143.
4g, colorless oil, yield 78%.

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.77-2.85 (m, 2H, CH$_2$CH=CH$_2$), 2.92-3.00 (m, 2H, CH$_2$CH=CH$_2$), 3.28 (s, 3H, OCH$_2$OCH$_3$), 3.41 (s, 3H, COOCH$_3$), 3.52 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 3.78 (d, 1H, $J = 8.7$ Hz, CH$_2$OMOM), 3.95 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 3.97 (d, 1H, $J = 8.7$ Hz, CH$_2$OMOM), 4.58 (2H, s, OCH$_2$OCH$_3$), 5.11 (dd, 2H, $J = 17.1$ Hz, 9.0 Hz, CH$_2$CH=CH$_2$), 5.78-5.91 (m, 1H, CH$_2$CH=CH$_2$), 7.21-7.28 (m, 2H, Ar-H), 7.41-7.44 (m, 4H, Ar-H), 7.51 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.92 (d, 4H, $J = 8.4$ Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 36.0, 49.4, 51.2, 55.4, 67.7, 68.2, 96.8, 117.8, 125.4, 125.6, 127.5, 128.1, 128.2, 128.3, 131.1, 132.9, 133.9, 134.0, 135.0, 173.5 ppm. ESI-MS: 482.2 [M+H]$^+$, 504.0 [M+Na]$^+$; HRMS (ESI) for C$_{31}$H$_{32}$N$_1$O$_4$ [M+H]$^+$: calced 482.2331, found 482.2343.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 7.80 min, 8.49 min (maj).
4h, light yellow oil, yield 85%;

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.41-2.49 (m, 1H, CH$_2$CH=CH$_2$), 2.83-2.88 (m, 1H, CH$_2$CH=CH$_2$), 2.94 (d, 1H, J = 13.5 Hz, PhCH$_3$), 3.40, (s, 3H, COOCH$_3$), 3.42 (d, 1H, J = 13.5 Hz, PhCH$_3$), 3.57 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 4.14 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 5.10 (dd, 2H, J = 18.3 Hz, 12.3 Hz, CH$_2$CH=CH$_2$), 5.92-6.01 (m, 1H, CH$_2$CH=CH$_2$), 6.69 (d, 2H, J = 8.4 Hz, Ph-H), 7.01 (d, 2H, J = 8.4 Hz, Ph-H), 7.25-7.30 (m, 2H, Ar-H), 7.44-7.50 (m, 4H, Ar-H), 7.56 (d, 2H, J = 8.4 Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 35.8, 38.3, 49.1, 51.0, 68.1, 115.1, 117.7, 125.3, 125.6, 127.5, 128.1, 128.2, 128.3, 128.7, 131.1, 132.9, 133.97, 134.03, 135.1, 154.4, 175.0 ppm. ESI-MS: 514.1 [M+H]$^+$; HRMS (ESI) for C$_{35}$H$_{32}$N$_1$O$_3$ [M+H]$^+$: calcd 514.2382, found 514.2382.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 1.80 min, 2.05 min (maj).
4i, light yellow solid, yield 91%;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.80 (d, 2H, $J = 6.6$ Hz, CH$_2$CH=CH$_2$), 3.26 (d, 1H, $J = 15.0$ Hz, Indole-CH$_2$), 3.36 (s, 3H, COOCH$_3$), 3.48 (d, 1H, $J = 15.0$ Hz, Indole-CH$_2$), 3.56 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 4.21 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 4.98 (dd, 2H, $J = 17.4$ Hz, 10.2 Hz, CH$_2$CH=CH$_2$), 5.86-6.00 (m, 1H, CH$_2$CH=CH$_2$), 7.08 (dd, 1H, $J = 7.2$ Hz, 7.2 Hz, indole-H), 7.17 (dd, 1H, $J = 7.2$ Hz, 7.2 Hz, indole-H), 7.17 (s, 1H, indole-H), 7.25 (dd, 2H, $J = 5.1$ Hz, 9.3 Hz, Ar-H), 7.34 (d, 2H, $J = 8.1$ Hz, indole-H), 7.46(dd, 2H, $J = 5.1$ Hz, 9.3 Hz, Ar-H), 7.53 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.56 (d, 1H, $J = 8.1$ Hz, indole-H), 7.94 (d, 4H, $J = 8.1$ Hz, Ar-H), 8.04 (s, 1H, NH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 28.4, 37.0, 49.1, 51.0, 68.3, 110.8, 110.9, 117.8, 119.0, 119.2, 121.8, 123.3, 125.3, 125.6, 127.5, 128.1, 128.2, 128.2, 128.3, 131.2, 132.9, 134.1, 134.3, 135.2, 135.5, 174.5 ppm. ESI-MS: 537.3 [M+H]$^+$; HRMS (ESI) for C$_{37}$H$_{33}$N$_2$O$_2$ [M+H]$^+$: calcd 537.2536, found 537.2534.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 2.69 min (maj).
4j, white solid, yield 92%;

\[
\begin{align*}
\text{NCOOMe}^* & \\
\text{COOMe} & \\
\end{align*}
\]

\[\delta 2.97-3.15 \text{ (m, 1H, CH}_2\text{CH=CH}_2\text{)}, 3.42, 3.43 \text{ (d, 2H, J = 12.6 Hz, Ar-CH}_2\text{)}, 4.09 \text{ (d, 2H, J = 12.6 Hz, Ar-CH}_2\text{)}, 4.85 \text{ (dd, 2H, J = 18.0 Hz, 9.0 Hz, CH}_2\text{CH=CH}_2\text{), 5.46-5.60 \text{ (m, 1H, CH}_2\text{CH=CH}_2\text{), 7.23-7.28 \text{ (m, 2H, Ar-H), 7.31-7.53 \text{ (m, 1H, Ar-H), 7.95 \text{ (d, 4H, J = 8.4 Hz, Ar-H).}}}}
\]

\[\delta 44.2, 49.4, 51.1, 72.8, 118.0, 125.3, 125.6, 127.1, 127.5, 127.7, 127.9, 128.0, 128.2, 128.3, 131.2, 132.9, 133.4, 134.3, 135.1, 141.0, 172.9 \text{ ppm. ESI-MS: 483.9 [M+H]}^+; \text{HRMS (ESI) for C}_{34}\text{H}_{30}\text{N}_1\text{O}_2 \text{[M+H]}^+:} \text{calcd 484.2271, found 474.2265.}
\]

LC-MS: detected at 254 nm and 214 nm; MeOH / H\text{2O} = 80/20; flow = 1.0 mL/min, Retention time: 3.86 min (maj).
**Signal 1: DAD1 A, Sig=254.16 Ref=360.100**

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*]s</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>6.402 MM</td>
<td>0.2335</td>
<td>64.26478</td>
<td>4.58751</td>
</tr>
</tbody>
</table>

**Signal 2: DAD1 B, Sig=214.16 Ref=360.100**

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*]s</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>6.300 MM</td>
<td>0.2141</td>
<td>65.37462</td>
<td>46.22490</td>
</tr>
<tr>
<td>2</td>
<td>7.016 MM</td>
<td>0.4204</td>
<td>2.26209e4</td>
<td>0.04199</td>
</tr>
</tbody>
</table>

**4k**, colorless solid, yield 92%:

1H NMR (300 MHz, CDCl3) δ 2.41-2.49 (m, 1H, CH₂CH=CH₂), 2.77-2.85 (m, 1H, CH₂CH=CH₂), 3.01 (d, 1H, J = 13.5 Hz, PhCH₂), 3.37 (d, 1H, J = 13.5 Hz, PhCH₂), 3.39, (s, 3H, COOCH₃), 3.52 (d, 2H, J = 12.6 Hz, PhCH₂), 4.12 (d, 2H, J = 12.6 Hz, PhCH₂), 5.10 (dd, 2H, J = 18.3 Hz, 12.3 Hz, CH₂CH=CH₂), 5.85-5.97 (m, 1H, CH₂CH=CH₂), 7.08 (d, 2H, J = 8.4 Hz, Ph-H), 7.28-7.30 (m, 2H, Ar-H), 7.39 (d, 2H, J = 8.4 Hz, Ph-H), 7.45-7.50 (m, 4H, Ar-H), 7.54 (d, 2H, J = 8.4 Hz, Ar-H), 7.96 (d, 2H, J = 8.4 Hz, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ 38.1, 38.4, 49.1, 51.0, 67.8, 118.1, 120.5, 125.7, 125.7, 127.5, 128.1, 128.9, 131.1, 131.2, 132.9, 133.7, 133.8, 135.1, 136.2, 173.9 ppm. ESI-MS: 576.2 [M+H]⁺, HRMS (ESI) for C₈H₈BrN₂O₂ [M+H]⁺: calcd 576.1533, found 576.1532.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H₂O = 80/20; flow = 1.0 mL/min, Retention time: 6.4 min, 7.0 min (maj).
**4l**, light brown solid, yield 92%;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.57-2.72 (m, 2H, CH$_2$CH=CH$_2$), 3.36 (s, 3H, COOCH$_3$), 3.54 (d, 1H, J = 14.4 Hz, ArCH$_2$), 3.54 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 3.81 (d, 1H, J = 14.4 Hz, ArCH$_2$), 4.11 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 4.90 (d, 1H, J = 17.1 Hz, CH$_2$CH=CH$_2$), 5.10 (d, 1H, J = 10.2 Hz, CH$_2$CH=CH$_2$), 5.74-5.85 (m, 1H, 1H, CH$_2$CH=CH$_2$), 7.23-7.28 (m, 2H, Ar-H), 7.39-7.49 (m, 6H, Ar-H), 7.84 (d, 1H, J = 7.5 Hz, Ar-H), 7.93-7.97 (m, 4H, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 33.6, 37.9, 49.3, 51.2, 68.9, 118.4, 125.4, 125.6, 127.0, 127.5, 128.2, 128.4, 131.2, 131.7, 132.9, 133.0, 133.4, 133.7, 135.1, 135.3, 139.8, 173.9, 191.7 ppm. ESI-MS: 526.0 [M+H]$^+$; HRMS (ESI) for C$_{36}$H$_{32}$N$_1$O$_3$ [M+H]$^+$: calcd 526.2376, found 526.2355.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 2.5 min (maj), 3.0 min.

**4m**, light yellow oil, yield 92%;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.71 (d, 3H, J = 6.3 Hz, CHCH$_3$), 0.85 (d, 3H, J = 6.3 Hz, CHCH$_3$), 1.11 (s, 3H, C(CH$_3$)$_2$), 1.16 (s, 3H, C(CH$_3$)$_2$), 1.62-1.93 (m, 3H, CH$_2$CH(CH$_3$)$_2$), 3.59 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 3.81 (s, 3H, COOCH$_3$), 4.12 (d, 2H, J = 12.6 Hz, Ar-CH$_2$), 4.91-4.97 (m, 2H, CH$_2$CH=CH$_2$), 6.11-6.21 (m, 1H, CH$_2$CH=CH$_2$), 7.21-7.27 (m, 2H, Ar-H), 7.42-7.47 (m, 4H, Ar-H), 7.69 (d, 2H, J = 8.4 Hz, Ar-H), 7.93-7.98 (m, 2H, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 23.2, 23.5, 25.1, 25.6, 25.6, 44.2, 46.9, 51.1, 51.7, 111.6, 125.2, 125.4, 127.6, 128.1, 128.1, 129.0, 131.2, 132.7, 134.7, 134.8, 147.3, 176.0 ppm. ESI-MS: 492.1 [M+H]$^+$; HRMS (ESI) for C$_{34}$H$_{38}$N$_1$O$_2$ [M+H]$^+$: calcd 492.2903, found 492.2898.
LC-MS: detected at both 254 nm and 214 nm; MeOH / H2O = 80/20; flow = 1.0 mL/min, Retention time: 6.86 min, 9.95 min (maj).

4n, white solid, yield 90%;

1H NMR (300 MHz, CDCl3): δ 0.69 (d, 3H, J = 6.3 Hz, CHCH3), 0.75 (d, 3H, J = 6.3 Hz, CHCH3), 1.26-1.63 (m, 3H, CH2CH(CH3)2), 3.65 (s, 3H, COOCH3), 3.67 (d, 2H, J = 12.3 Hz, Ar-CH2), 4.06 (d, 2H, J = 12.3 Hz, Ar-CH2), 4.17 (d, 1H, J = 8.1 Hz) 5.03 (dd, 2H, J = 16.8 Hz, 10.5 Hz, CH2CH=CH2), 6.21-6.34 (m, 1H, CH2CH=CH2), 7.23-7.37 (m, 7H, Ar-H), 7.44-7.50 (m, 6H, Ar-H), 7.96-8.01 (m, 4H, Ar-H). 13C NMR (100 MHz, CDCl3): δ 24.2, 25.3, 46.1, 51.4, 52.7, 55.9, 71.8, 116.5, 125.3, 125.5, 126.2, 127.7, 128.2, 128.3, 128.9, 131.3, 131.5, 131.9, 132.7, 134.3, 134.8, 139.7, 140.4, 176.4 ppm. ESI-MS: 540.0 [M+H]+, 561.8 [M+Na]+; HRMS (ESI) for C38H38N1O2 [M+H]+: calcd 540.2897, found 540.2892.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H2O = 80/20; flow = 1.0 mL/min, Retention time: 9.0 min, 10.6 min, 13.8 min (maj).
40, white solid, yield 94%;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.70 (d, 3H, $J = 6.3$ Hz, CH$_3$CH), 0.75 (d, 3H, $J = 6.3$ Hz, CH$_3$CH), 1.29-1.63 (m, 3H, CH$_2$CH<sub>3</sub>), 3.65 (s, 3H, COOCH<sub>3</sub>), 3.66 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 4.02 (d, 2H, $J = 12.3$ Hz, Ar-CH$_2$), 4.13 (d, 1H, $J = 8.1$ Hz) 5.07 (dd, 2H, $J = 16.8$ Hz, $J = 10.5$ Hz, CH$_2$CH=CH$_2$), 6.19-6.31 (m, 1H, CH$_2$CH=CH$_2$), 7.24-7.29 (m, 4H, Ar-H), 7.41-7.50 (m, 8H, Ar-H), 7.96-8.01 (m, 4H, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.8, 25.1, 45.7, 51.1, 52.5, 55.6, 72.1, 116.3, 120.5, 125.4, 125.6, 127.5, 128.0, 128.1, 128.7, 131.1, 131.2, 131.9, 132.9, 134.3, 134.9, 139.9, 140.2, 176.1 ppm. ESI-MS: 617.8 [M+H]$^+$; HRMS (ESI) for C$_{38}$H$_{37}$Br$_1$N$_1$O$_2$ [M+H]$^+$: calcd 618.2002 found 618.2001.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H$_2$O = 80/20; flow = 1.0 mL/min, Retention time: 9.2 min, 10.9 min, 14.2 min (maj).
8a, colorless solid, yield 91%;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.74 (d, 3H, $J = 6.3$ Hz, CHCH$_3$), 0.96 (d, 3H, $J = 6.3$ Hz, CHCH$_3$), 1.64-1.91 (m, 3H, CH$_2$CHCH$_3$), 2.51 (dd, 1H, $J = 8.4$ Hz, 8.1 Hz, CH$_2$CH=CH$_2$), 3.05 (dd, 1H, $J = 4.2$ Hz, 5.7 Hz, CH$_2$CH=CH$_2$), 3.30 (s, 3H, COOCH$_3$), 3.31 (d, 2H, $J = 12.6$ Hz, NCH$_2$), 3.68 (s, 6H, 2×ArOCH$_3$), 3.82 (d, 2H, $J = 12.6$ Hz, NCH$_3$), 3.90 (s, 6H, 2×ArOCH$_3$), 3.94 (s, 6H, 2×ArOCH$_3$), 5.12 (dd, 2H, $J = 7.5$ Hz, 17.7 Hz, CHCH$_2$), 5.82-5.96 (m, 1H, CHCH$_2$), 6.61 (s, 2H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 21.4, 24.4, 25.1, 35.6, 42.1, 48.5, 50.1, 55.9, 60.6, 60.8, 65.2, 108.4, 116.7, 122.9, 131.2, 134.4, 141.0, 150.9, 152.4, 175.6 ppm. ESI-MS: 544.3 [M+H]$^+$, 566.3 [M+Na]$^+$; HRMS (ESI) for C$_{30}$H$_{42}$N$_1$O$_8$ [M+H]$^+$: calcd 544.2905, found 544.2886.

LC-MS: detected at 254 nm, Retention time: 55.3 min, 56.3 min (maj).
8b, white solid, yield 92%;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.35 (dd, 1H, $J = 7.5$ Hz, 7.2 Hz, CH$_2$CH=CH$_2$), 2.82 (dd, 1H, $J = 5.7$ Hz, 5.7 Hz, CH$_2$CH=CH$_2$), 2.96 (d, 1H, $J = 13.8$ Hz, CH$_2$Ph), 3.38-3.47 (m, 6H, CH$_2$Ph, NCH$_3$, COOCH$_3$), 3.68 (s, 6H, 2×ArOCH$_3$), 3.84-3.91 (m, 14H, NCH$_3$, 4×ArOCH$_3$), 5.07 (dd, 2H, $J = 17.1$ Hz, 10.2 Hz, CH=CH$_2$), 5.90-6.03 (m, 1H, CH=CH$_2$), 6.61 (s, 2H, ArH), 7.12 (d, 2H, $J = 7.8$ Hz, Ph-H), 7.20 (t, 3H, $J = 7.5$ Hz, Ph-H), $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 35.5, 38.9, 49.0, 50.3, 55.8, 60.5, 60.8, 67.5, 108.3, 117.5, 122.9, 126.5, 128.1, 129.9, 131.0, 133.9, 137.0, 141.1, 150.9, 152.5, 174.2 ppm. ESI-MS: 578.3 [M+H]$^+$; HRMS (ESI) for C$_{33}$H$_{40}$N$_1$O$_8$ [M+H]$^+$: calcd 578.2754, found 578.2737.

LC-MS: detected at 254 nm, Retention time: 27.2 min, 29.7 min (maj).
6. X-ray Crystal Structure of Rearrangement Product 4a and 4k

**Compound 4a**

**Compound 4k**

CCDC 865414 (4a) & 865415 (4k) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.
7. General Procedure for Double Bond Elaboration via Heck Reaction

Under nitrogen atmosphere, the ammonium salts 4d (46 mg, 0.1 mmol), aryl iodide (0.1 mmol), PdPPh3Cl2 (2.2 mg, 5 mol%), Et3N (21 μL, 0.15 mmol) was mixed in dry DMF (5 mL). The mixture was heated to 90°C and stirred overnight. The solution was then diluted with EtOAc, washed with NaHCO3 (aq, saturated) and brine, dried over anhydrous Na2SO4, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding products.

10, colorless oil, yield 84%;
1H NMR (300 MHz, CDCl3): δ 0.80 (d, 3H, J = 5.7 Hz CH(CH3)2), 0.99 (d, 3H, J = 5.7 Hz CH(CH3)2), 1.74-1.97 (m, 3H, CH2CH2(CH3)2), 2.71 (dd, 1H, J = 7.8 Hz, 8.4 Hz, CH2CH=CH2), 3.16 (dd, 1H, J = 5.1 Hz, 4.8 Hz, CH2CH=CH2), 3.34 (s, 3H, ArOCH3), 4.12 (d, 2H, J = 12.6 Hz, NCH2), 6.07-6.16 (m, 1H, ArCH=CH), 6.41 (d, 1H, J = 16.5 Hz, ArCH=CH), 6.83 (d, 2H, J = 8.4 Hz, ArH), 7.23-7.29 (m, 4H, ArH), 7.56 (dd, 4H, J = 6.3 Hz, 8.1 Hz, ArH), 7.53 (d, 2H, J = 7.8 Hz, ArH), 7.94 (d, 2H, J = 8.1 Hz, ArH). 13C NMR (100 MHz, CDCl3): δ 21.9, 24.4, 25.2, 35.5, 42.6, 48.7, 50.7, 55.2, 66.3, 113.8, 124.3, 125.3, 125.5, 127.1, 127.5, 128.1, 128.2, 128.3, 130.7, 131.1, 131.4, 132.9, 134.3, 135.1, 158.6, 175.6 ppm. ESI-MS: 570.3 [M+H]+; HRMS (ESI) for C39H40N1O3 [M+H]+: calcd 570.3008 found 570.3003.

11, colorless oil, yield 82%;
1H NMR (300 MHz, CDCl3): δ 0.79 (d, 3H, J = 6.3 Hz CH(CH3)2), 0.98 (d, 3H, J = 6.0 Hz CH(CH3)2), 1.40 (t, 3H, J = 7.2 Hz, COOCH2CH3), 1.73-1.99 (m, 3H, CH2CH2CH3), 2.74 (dd, 1H, J = 7.5 Hz, 7.2 Hz, CH2CH=CH2), 3.20 (dd, 1H, J = 4.2 Hz, 4.8 Hz, CH2CH=CH2), 3.35 (s, 3H, COOCH3), 3.48 (d, 2H, J = 12.9 Hz, NCH2), 4.10 (d, 2H, J = 12.3 Hz, NCH2), 4.37 (q, 2H, J = 6.9 Hz, COOCH2CH3), 6.35-6.44 (m, 1H, ArCH=CH), 6.50 (d, 1H, J = 15.9 Hz, ArCH=CH), 7.23-7.28 (m, 2H, ArH), 7.33(d, 2H, J = 8.4 Hz, ArH), 7.45 (dd, 4H, J = 8.7 Hz, 8.1 Hz, ArH), 7.52 (d, 2H, J = 8.4 Hz, 7.93-7.98 (m, 6H, ArH). 13C NMR (100 MHz, CDCl3): δ 14.3, 21.8, 24.5, 25.2, 35.6, 42.7, 48.8, 50.8, 60.8, 66.2, 125.3, 125.6, 125.8, 127.5, 128.1, 128.2, 128.6, 128.9, 131.1, 131.3, 132.9, 134.2, 135.1, 142.2, 166.5, 175.5 ppm. ESI-MS: 612.3 [M+H]+; HRMS (ESI) for C41H42N1O4 [M+H]+: calcd 612.3008 found 612.3003.
8. General Procedure for Removal of Chiral Auxiliary

6.1 Debenzylization via Hydrogenation

\[
\begin{align*}
\text{Amine} & \quad (0.1 \text{ mmol}) \quad \text{and} \quad \text{Pd/C (10\%, 11mg)} \quad \text{was added to 5 mL of methanol, and stirred under} \quad \text{H}_2 \quad (4 \text{ atm}) \quad \text{atmosphere at 30°C. After completion, the reaction mixture was filtrated, concentrated. The mixture was dissolved in 5 mL of acetone and to this solution was added K}_2\text{CO}_3 \quad (27.6 \text{ mg, 0.2 mmol), then stirred at room temperature for 1h. After filtration and concentration, the residue was purified via column chromatography on silica gel, affording corresponding benzoyl amino acids.}
\end{align*}
\]

\[
\begin{align*}
4a, R = H & \quad 9a, 76\% \text{ yield, 96\% ee} \\
4b, R = CH_3 & \quad 9b, 82\% \text{ yield, 98\% ee} \\
4c, R = Bn & \\
4d, R = CH_2CH(CH_3)_2 & \\
4e, R = CH_2CH_2Ph & \\
4h, R = CH_2C_6H_4-p-OBz & \\
5a, 92\% \text{ yield, 77\% ee} \\
5b, 87\% \text{ yield, 85\% ee} \\
5c, 89\% \text{ yield, 98\% ee} \\
5d, 87\% \text{ yield, 99\% ee} \\
5e, 88\% \text{ yield, 99\% ee} \\
5e, 88\% \text{ yield, 97\% ee} \\
\end{align*}
\]

\[
\begin{align*}
\text{Amine} \quad 4 \quad (0.1 \text{ mmol}) \quad \text{and} \quad \text{Pd/C (10\%, 11mg) was added to 5 mL of methanol, and stirred under} \quad \text{H}_2 \quad (4 \text{ atm}) \quad \text{atmosphere at 30°C. After completion, the reaction mixture was filtrated, concentrated. The mixture was dissolved in 5 mL of acetone and to this solution was added K}_2\text{CO}_3 \quad (27.6 \text{ mg, 0.2 mmol), then stirred at room temperature for 1h. After filtration and concentration, the residue was purified via column chromatography on silica gel, affording corresponding benzoyl amino acids.}
\end{align*}
\]

6.2 Debenzylization via Oxidation

\[
\begin{align*}
8a, R = Bn & \\
8b, R = CH_2CH(CH_3)_2 & \\
9a, 76\% \text{ yield, 96\% ee} \\
9b, 82\% \text{ yield, 98\% ee} \\
\end{align*}
\]

To a 25 mL flask was added amine \(8\) (0.1 mmol), CAN (0.6 mmol) and 5 mL of acetonitrile. The reaction was stirred at room temperature for about 2 hours for completion. The mixture was then diluted with EtOAc, washed with water and brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and concentrated. The residue was dissolved in 5 mL of acetone and K\textsubscript{2}CO\textsubscript{3} and BzCl was added. After stirring at room temperature for 1 hour, the mixture was diluted with EtOAc, and filtrated through Celite. The filtrate was washed three times with water and brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding benzoylation product \(9\).
5a, colorless oil, yield 92%, ee 77%;

\[\left[\alpha\right]_D^{14} = -20.0 \ (c \ 0.4, \ \text{CHCl}_3)\].

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.92-0.98 (m, 3H, CH$_2$CH$_3$), 1.38-1.44 (m, 2H, CH$_2$CH$_3$), 1.65-1.82 (m, 1H, CH$_2$CH$_3$CH$_3$), 1.85-1.98 (m, 1H, CH$_3$CH$_2$CH$_3$), 3.77 (s, 3H, COOCH$_3$), 4.82-4.86 (m, 1H, N-CH), 6.74 (b, 1H, NH), 7.42-7.51 (m, 3H, Ph-H), 7.80 (d, 2H, $J = 8.1$ Hz, Ph-H).

HPLC: Chiral OD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 12.1 min (maj), 16.6 min
**5b**, white solid, yield 87%, ee 85%;

\[
[\alpha]_{D}^{25} = +12.7 \text{ (c 0.3, CHCl}_3\text{)}; \quad ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 0.88-0.92 (m, 3H, CH\textsubscript{2}CH\textsubscript{3}), 1.09-1.14 (m, 1H, CH\textsubscript{2}CH\textsubscript{3}), 1.28-1.35 (m, 1H, CH\textsubscript{2}CH\textsubscript{3}), 1.71 (s, 3H, NCCH\textsubscript{3}) 1.80-1.89 (m, 1H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 2.36-2.47 (m, 1H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 3.79 (s, 3H, COOCH\textsubscript{3}), 7.06 (b, 1H, NH), 7.42-7.47 (m, 3H, Ph-H), 7.79 (d, 2H, J = 8.1 Hz, Ph-H).

HPLC: Chiral OD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 8.4 min, 9.2 min (maj)
5c, colorless oil, yield 89%, ee 98%;
\([\alpha]_D^{25} = +102.7. (c 0.5, \text{CHCl}_3);^1\text{H NMR (300 MHz, CDCl}_3) \delta 0.89-0.94 (m, 3H, \text{CH}_2\text{CH}_3), 1.00-1.11 (m, 1H, \text{CH}_2\text{CH}_3), 1.30-1.41 (m, 1H, \text{CH}_3\text{CH}_3), 1.88-1.99 (m, 1H, \text{CH}_3\text{CH}_2\text{CH}_3), 2.75-2.86 (m, 1H, \text{CH}_3\text{CH}_2\text{CH}_3), 3.16 (d, 2H, \text{J} = 13.5 \text{ Hz, PhCH}_2), 3.83 (s, 3H, \text{COOCH}_3), 3.94 (d, 2H, \text{J} = 13.5 \text{ Hz, PhCH}_2), 6.96 (b, 1H, NH), 7.01-7.04 (m, 2H, Ph-H), 7.17-7.19 (m, 3H, Ph-H), 7.41 (q, 2H, \text{J} = 7.2 \text{ Hz, Ph-H}), 7.49, (q, 1H, \text{J} = 7.2 \text{ Hz, Ph-H}), 7.69 (d, 2H, \text{J} = 8.4 \text{ Hz, Ph-H}).

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 95/5; flow = 0.7 mL/min; Retention time: 7.8 min, 8.4 min (maj)
5d, colorless oil, yield 87%, ee 99%;
\[ [\alpha]_D^{20} = -14.7 \text{ (c 1.25, CHCl}_3) \];
$^1$H NMR (300 MHz, CDCl$_3$) δ 0.77 (d, 3H, J = 6.6 Hz, CH(CH$_3$)$_2$), 0.85-0.89 (m, 6H, CH$_2$CH$_3$, CH(CH$_3$)$_2$), 0.91-1.00 (m, 1H, CH$_3$CH$_3$), 1.24-1.33 (m, 1H, CH$_2$CH$_3$), 1.51-1.62 (m, 1H, CH(CH$_3$)$_2$), 1.70-1.77 (m, 2H, CH$_2$CH$_2$CH$_3$, CH$_2$CH(CH$_3$)$_2$), 2.59-2.72 (m, 2H, CH$_2$CH$_2$CH$_3$, CH$_2$CH(CH$_3$)$_2$), 3.80 (s, 3H, COOCH$_3$), 7.35 (b, 1H, NH), 7.43-7.50 (m, 3H, Ph-H), 7.79 (d, 2H, J = 8.4 Hz, Ph-H).

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 95/5; flow = 0.7 mL/min; Retention time: 9.8 min, 10.4 min(maj)
5e, colorless oil, yield 88%, ee 99%;
\([\alpha]^{20}_D = -10.7\) (c 0.6, CHCl₃); \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) 0.78-0.89 (m, 6H), 1.12-1.19 (m, 6H), 1.25-1.40 (m, 2H), 1.61-1.83 (m, 6H), 2.58-2.65 (m, 2H), 3.81 (s, 3H, COOCH₃), 7.20 (b, 1H, NH), 7.43-7.49 (m, 3H, Ph-H), 7.80 (d, 2H, \(J = 8.1\) Hz),

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.7 min, 8.8 min (maj)
5h, colorless oil, yield 88%, ee 97%.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.89-0.94 (m, 3H, CH$_2$CH$_3$), 1.04-1.16 (m, 1H, CH$_2$CH$_3$), 1.33-1.41 (m, 1H, CH$_2$CH$_3$), 1.88-1.99 (m, 1H, CH$_2$CH$_2$CH$_3$), 2.75-2.86 (m, 1H, CH$_2$CH$_2$CH$_3$), 3.21 (d, 2H, $J$ = 13.5 Hz, PhCH$_2$), 3.84 (s, 3H, COOCH$_3$), 3.97 (d, 2H, $J$ = 13.5 Hz, PhCH$_2$), 6.99 (b, 1H, NH), 7.06-7.08 (m, 4H, Ph-H), 7.43-7.52 (m, 5H, Ph-H), 7.62, (q, 1H, $J$ = 8.1 Hz, Ph-H), 7.73 (q, 2H, $J$ = 8.1 Hz, Ph-H), 8.17 (d, 2H, $J$ = 8.1 Hz, Ph-H).

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 80/20; flow = 0.7 mL/min; Retention time: 16.2 min, 20.3 min (maj)
9a, colorless oil, yield 82%, ee 98%;

^1^H NMR (300 MHz, CDCl_3) δ 0.79 (d, 3H, J = 6.6 Hz, CH(CH_3)_2), 0.89 (d, 3H, J = 7.2 Hz, CH(CH_3)_2), 1.56-1.65 (m, 1H, CH(CH_3)_2), 1.73-1.80 (m, 1H, CH(CH_3)Pr), 2.49 (dd, 1H, J = 7.8 Hz, 13.8 Hz, CH(CH_3)Pr), 2.49 (dd, 1H, J = 5.4 Hz, 14.1 Hz, CH_2CH=CH_2), 3.44 (dd, 1H, J = 7.2 Hz, 13.8 Hz, CH_2CH=CH_2), 3.80 (s, 3H, COOCH_3), 5.04 (dd, 2H, J = 9.9 Hz, 18.6 Hz, CH_2CH=CH_2), 5.51-5.65 (m, 1H, CH=CH=CH_2), 7.28 (br, 1H, BzNH), 7.41-7.50 (m, 3H, Ph-H), 7.78 (d, 2H, J = 8.4 Hz, Ph-H)

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 9.0 min (maj), 10.5 min
**8b**, white solid, yield 76%, ee 96%;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.71 (dd, 1H, $J = 7.2$ Hz, 14.1 Hz, CH$_2$CH=CH$_2$), 3.21 (d, 1H, $J = 13.5$ Hz, CH$_2$Ph), 3.60 (dd, 1H, $J = 7.2$ Hz, 13.8 Hz, CH$_2$CH=CH$_2$), 3.82 (s, 3H, COOCH$_3$), 3.95 (d, 1H, $J = 13.5$ Hz, CH$_3$Ph), 5.09 (dd, 2H, $J = 10.5$ Hz, 17.4 Hz, CH$_2$CH=CH$_2$), 5.58-5.72 (m, 1H, CH$_2$CH=CH$_2$), 6.92 (br, 1H, BzNH), 7.04-7.06 (m, 2H, Ph-H), 7.18-7.20 (m, 3H, Ph-H), 7.38-7.51 (m, 3H, Ph-H), 7.68 (d, 2H, $J = 7.5$ Hz, Ph-H);

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.7 min, 8.8 min (maj)
9. Copies of $^1$H NMR and $^{13}$C NMR spectra
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

after single crystallization

low de (reacted with 1.2eq NaH)
(S)-4n

N

COOMe

(S)-4n

N

COOMe

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012