Enantioselective synthesis of chiral oxazolines from unactivated ketones and isocyanoacetate esters by synergistic silver/organocatalysis

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SUPPORTING INFORMATION

Table of Contents:

General Experimental Methods S2
Typical procedures and characterization data for compounds 3-5 S2
NMR spectra and Chiral analysis chromatograms for compounds 3-5 S17
X-Ray structure for compound 3d S81
General Experimental Methods

Formal [3+2] cycloaddition reactions were carried out in round bottom flasks closed with a stopper. Starting materials, including ketones and tert-butyl isocyanoacetate were obtained from commercial sources. Methyl tert-Butyl ether (MTBE) was stored over 4 Å MS. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. Melting points were determined in capillary tubes. NMR spectra were run at 300 MHz for $^1$H and at 75 MHz for $^{13}$C NMR using residual non-deuterated solvent (CHCl$_3$) as internal standard ($\delta$ 7.26 and 77.0 ppm, respectively). Chemical shifts are given in ppm. The carbon type was determined by DEPT experiments. High resolution mass spectra (ESI) were recorded on a Q-TOF spectrometer equipped with an electrospray source with a capillary voltage of 3.3 kV (ESI). Specific optical rotations were measured using sodium light (D line 589 nm). Chiral HPLC analyses were performed in a chromatograph equipped with a UV diode-array detector using chiral stationary phase columns from Daicel or Phenomenex.

Typical procedures and characterization data for compounds 3

General procedure for the enantioselective formal [3+2] cycloaddition reaction

Squaramide SQ4 (6.6 mg, 0.0125 mmol) and silver oxide (1.5 mg, 0.0063 mmol) were introduced in 25 mL round bottom flask followed by MTBE (8 mL) and ketone 1 (0.25 mmol). The flask was closed with a stopper and introduced in an ice bath. After 5 min, tert-butyl isocyanoacetate 2 (48 $\mu$L, 0.330 mmol) was added and the mixture was stirred at 0 °C until consumption of the ketone 1 (TLC). After this time, the reaction mixture was filtered through a short pad of silica gel and concentrated under reduced pressure. A small aliquot was analyzed by $^1$H NMR to determine the diastereomer ratio and by HPLC to determine the enantiomeric excess of products 3. The remaining crude was chromatographed on silica gel eluting with hexane:EtOAc mixtures (9:1 to 8:2) to obtain the separated diastereomers cis-3 and trans-3.

The racemic products were obtained by a similar procedure using N-[3,5-bis(trifluoromethyl)phenyl]-N’-(3-dimethylaminopropyl)squaramide as a substitutive for SQ4.
**tert-Butyl 5-methyl-5-phenyl-4,5-dihydrooxazole-4-carboxylate (3a)**

Obtained 61.8 mg (95%). The enantiomeric excess (minor isomer: 91%, major isomer: 99%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 95:5, 1 mL/min, trans-(4R,5S)-3a (minor diastereomer): minor enantiomer, *t*<sub>r</sub> = 15.5 min, major enantiomer, *t*<sub>r</sub> = 22.1 min; cis-(4R,5R)-3a (major diastereomer): minor enantiomer, *t*<sub>r</sub> = 20.4 min, major enantiomer, *t*<sub>r</sub> = 30.5 min.

cis-(4R,5R)-3a (major diastereomer): *R* <sub>f</sub> = 0.18 (7:3 hexane/EtOAc); colorless oil; [α]<sup>25</sup> <sub>D</sub> = –174.3 (c 0.65, CHCl<sub>3</sub>, 99% ee); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.32-7.27 (5H, m, Ar), 7.15 (1H, d, *J* = 2.1 Hz, N=CHO), 4.49 (1H, d, *J* = 2.1 Hz, CH), 1.80 (3H, s, CH<sub>3</sub>), 0.97 (9H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.5 (C), 156.0 (CH), 139.6 (C), 128.0 (CH), 127.9 (CH), 125.8 (CH), 88.3 (C), 81.4 (C), 78.7 (CH), 28.6 (CH<sub>3</sub>), 27.1 (CH<sub>3</sub>); HRMS (ESI) *m/z*: 262.1434 [M+H]<sup>+</sup>, C<sub>15</sub>H<sub>20</sub>NO<sub>3</sub> requires 262.1438.

trans-(4R,5S)-3a (minor diastereomer): *R*<sub>f</sub> = 0.28 (7:3 hexane/EtOAc); colorless oil; [α]<sup>25</sup> <sub>D</sub> = –98.4 (c 0.72, CHCl<sub>3</sub>, 91% ee), Lit. [α]<sup>25</sup> <sub>D</sub> = –72.6 (c 1.0, CHCl<sub>3</sub>, 88% ee); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.48-7.46 (2H, m, Ar), 7.41-7.32 (2H, m, Ar), 7.30-7.27 (1H, m, Ar), 7.08 (1H, d, *J* = 2.1 Hz, N=CHO), 4.70 (1H, d, *J* = 2.1 Hz, CH), 1.66 (3H, s, CH<sub>3</sub>), 1.56 (9H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.5 (C), 155.3 (CH), 145.3 (C), 128.6 (CH), 127.7 (CH), 124.0 (CH), 87.8 (C), 82.5 (C), 77.9 (CH), 28.0 (CH<sub>3</sub>), 24.7 (CH<sub>3</sub>).

tert-Butyl 5-methyl-5-(p-tolyl)-4,5-dihydrooxazole-4-carboxylate (3b)

Obtained 54.6 mg (79%). The enantiomeric excess (minor isomer: 90%, major isomer 99%) was determined by HPLC (Chiracel IC), hexane:iPrOH 90:10, 1 mL/min, trans-(4R,5S)-3b (minor diastereomer): minor enantiomer, *t*<sub>r</sub> = 20.5 min, major enantiomer, *t*<sub>r</sub> = 26.0 min. cis-(4R,5R)-3b (major diastereomer): minor enantiomer, *t*<sub>r</sub> = 24.7 min, major enantiomer, *t*<sub>r</sub> = 28.2 min.

cis-(4R,5R)-3b (major diastereomer): *R* <sub>f</sub> = 0.18 (7:3 hexane/EtOAc); white solid, m.p. 57-59 °C; [α]<sup>25</sup> <sub>D</sub> = –100.8 (c 1.86, CHCl<sub>3</sub>, 99% ee); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.21 (2H, d, *J* = 8.4 Hz, Ar), 7.15 (1H, d, *J* = 1.8 Hz, N=CHO), 7.11 (2H, d, *J* = 8.1 Hz, Ar), 4.47 (1H, d, *J* = 1.8 Hz, CH), 2.3 (3H, s, CH<sub>3</sub>), 1.78 (3H, s, CH<sub>3</sub>), 0.98 (9H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.6 (C), 156.1 (CH), 137.6 (C), 136.6 (C), 128.6 (CH), 125.8 (CH), 88.3 (C), 81.4 (C), 78.7 (CH), 28.5 (CH<sub>3</sub>), 27.1 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>); HRMS (ESI) *m/z*: 276.1593 [M+H]<sup>+</sup>, C<sub>16</sub>H<sub>22</sub>NO<sub>3</sub> requires 276.1594.
**trans-(4R,5S)-3b (minor diastereomer):** \( R_f = 0.25 \) (7:3 hexane/EtOAc); colorless oil;
[\(\alpha\)]\(_D\)\(^{25}\) \(-194.5 \) (c 0.37, CHCl\(_3\), 90% ee); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 7.35 \) (2H, d, \( J = 8.1 \) Hz, Ar), 7.18 (2H, d, \( J = 8.1 \) Hz, Ar), 7.07 (1H, d, \( J = 2.1 \) Hz, N=CHO), 4.68 (1H, d, \( J = 2.1 \) Hz, CH), 2.35 (3H, s, CH\(_3\)), 1.64 (3H, s, CH\(_3\)), 1.55 (9H, s, CH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta 168.6 \) (C), 155.4 (CH), 142.4 (C), 137.5 (C), 129.3 (CH), 124.0 (CH), 87.8 (C), 82.4 (C), 77.9 (CH), 28.0 (CH\(_3\)), 24.6 (CH\(_3\)), 21.0 (CH\(_3\)); HRMS (ESI) \( m/z \): 276.1593 [M+H]\(^+\), \( C_{16}H_{22}NO_3 \) requires 276.1594.

**tert-Butyl 5-(4-methoxyphenyl)-5-methyl-4,5-dihydrooxazole-4-carboxylate (3c)**

Obtained 51.1 mg (70%). The enantiomeric excess (minor isomer: 90%, major isomer: 98%) was determined by HPLC using a chiral column (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, **trans-(4R,5S)-3c (minor diastereomer):** minor enantiomer, \( t_r = 18.3 \) min, major enantiomer, \( t_r = 21.8 \) min; **cis-(4R,5R)-3c (major diastereomer):** minor enantiomer, \( t_r = 19.9 \) min, major enantiomer, \( t_r = 22.8 \) min.

**cis-(4R,5R)-3c (major diastereomer):** \( R_f = 0.18 \) (7:3 hexane/EtOAc); white solid, m.p. 68-69 °C; [\(\alpha\)]\(_D\)\(^{25}\) \(-146.9 \) (c 1.3, CHCl\(_3\), 98% ee); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 7.27 \) (2H, d, \( J = 9 \) Hz, Ar), 7.18 (1H, d, \( J = 1.8 \) Hz, N=CHO), 6.88 (2H, d, \( J = 9 \) Hz, Ar), 4.50 (1H, d, \( J = 1.8 \) Hz, CH), 3.80 (3H, s, CH\(_3\)), 1.82 (3H, s, CH\(_3\)), 1.04 (9H, s, CH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta 167.6 \) (C), 159.3 (C), 156.0 (CH), 131.7 (C), 127.2 (CH), 113.4 (CH), 88.1 (C), 81.4 (C), 78.6 (CH), 55.3 (CH\(_3\)), 28.6 (CH\(_3\)), 27.3 (CH\(_3\)); HRMS (ESI) \( m/z \): 292.1547 [M+H]\(^+\), \( C_{16}H_{22}NO_4 \) requires 292.1543.

**trans-(4R,5S)-3c (minor diastereomer):** \( R_f = 0.25 \) (7:3 hexane/EtOAc); Colorless oil; [\(\alpha\)]\(_D\)\(^{25}\) \(-159.9 \) (c 0.47, CHCl\(_3\), 90% ee), Lit.\(^1\) [\(\alpha\)]\(_D\)\(^{25}\) \(-61.9 \) (c 0.8, CHCl\(_3\), 88% ee); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 7.38 \) (2H, d, \( J = 9.0 \) Hz, Ar), 7.06 (1H, d, \( J = 1.8 \) Hz, N=CHO), 4.68 (1H, d, \( J = 2.1 \) Hz, CH), 3.81 (3H, s, CH\(_3\)), 1.64 (3H, s, CH\(_3\)), 1.55 (9H, s, CH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta 168.6 \) (C), 159.0 (C), 155.6 (CH), 137.4 (C), 125.4 (CH), 113.9 (CH), 87.7 (C), 82.4 (C), 80.0 (CH), 55.3 (CH\(_3\)), 28.0 (CH\(_3\)), 24.6 (CH\(_3\)).

**trans-(4R,5S)-3b (minor diastereomer):** \( R_f = 0.25 \) (7:3 hexane/EtOAc); colorless oil; [\(\alpha\)]\(_D\)\(^{25}\) \(-194.5 \) (c 0.37, CHCl\(_3\), 90% ee); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 7.35 \) (2H, d, \( J = 8.1 \) Hz, Ar), 7.18 (2H, d, \( J = 8.1 \) Hz, Ar), 7.07 (1H, d, \( J = 2.1 \) Hz, N=CHO), 4.68 (1H, d, \( J = 2.1 \) Hz, CH), 2.35 (3H, s, CH\(_3\)), 1.64 (3H, s, CH\(_3\)), 1.55 (9H, s, CH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta 168.6 \) (C), 155.4 (CH), 142.4 (C), 137.5 (C), 129.3 (CH), 124.0 (CH), 87.8 (C), 82.4 (C), 77.9 (CH), 28.0 (CH\(_3\)), 24.6 (CH\(_3\)), 21.0 (CH\(_3\)); HRMS (ESI) \( m/z \): 276.1593 [M+H]\(^+\), \( C_{16}H_{22}NO_3 \) requires 276.1594.

**tert-Butyl 5-(4-bromophenyl)-5-methyl-4,5-dihydrooxazole-4-carboxylate (3d)**

Obtained 89.7 mg (99%). The enantiomeric excess (major isomer: 98%, minor isomer: 93%) was determined by HPLC using a chiral column (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, **cis-(4R,5R)-3d (major diastereomer):** minor enantiomer, \( t_r = 10.8 \) min, major enantiomer, \( t_r = 11.5 \) min; **trans-**
(4R,5S)-3d (minor diastereomer): major enantiomer, t<sub>r</sub> = 13.4 min, minor enantiomer, t<sub>r</sub> = 16.9 min.

cis-(4R,5R)-3d (major diastereomer): R<sub>f</sub> = 0.18 (7:3 hexane/EtOAc); white solid, m.p. 73-74 °C; [α]<sup>25</sup><sub>D</sub> = -98.9 (c 1.5, CHCl₃, 98% ee); <sup>1</sup>H NMR (300 MHz, C₆D₆) δ 7.24 (2H, d, J = 9 Hz, Ar), 6.99 (2H, d, J = 9 Hz, Ar), 6.65 (1H, d, J = 1.8 Hz, N=CHO), 4.41 (1H, d, J = 1.8 Hz, CH), 1.26 (3H, s, CH₃), 0.93 (9H, s, CH₃); <sup>13</sup>C NMR (75 MHz, C₆D₆) δ 167.4 (C), 155.5 (CH), 139.8 (C), 131.3 (CH), 128.2 (CH), 122.0 (C), 87.8 (C), 81.0 (C), 79.5 (CH), 28.5 (CH₃), 27.3 (CH₃). HRMS (ESI) <sup>m/z</sup>: 340.0542 [M+H]<sup>+</sup>, C₁₅H₁₉BrNO₃+ requires 340.0543.

trans-(4R,5S)-3d (minor diastereomer): R<sub>f</sub> = 0.28 (7:3 hexane/EtOAc); Colorless oil; [α]<sup>25</sup><sub>D</sub> = -102.0 (c 1.0, CHCl₃, 93% ee), Lit.1 <sup>m/z</sup>: 307.1285 [M+H]<sup>+</sup>, C₁₅H₁₉N₂O₅+ requires 307.1288.

tert-Butyl 5-methyl-5-(4-nitrophenyl)-4,5-dihydrooxazole-4-carboxylate (3e)

Obtained 76.4 mg (95%). The enantiomeric excess (minor isomer: 95%, major isomer 96%) was determined by HPLC (Chiracel IC), hexane/iPrOH 90:10, 1 mL/min, cis-(4R,5R)-3e (major diastereomer): major enantiomer, t<sub>r</sub> = 23.4 min, minor enantiomer, t<sub>r</sub> = 26.9 min. trans-(4R,5S)-3e (minor diastereomer): major enantiomer, t<sub>r</sub> = 58.6 min, minor enantiomer, t<sub>r</sub> = 83.3 min.

cis-(4R,5R)-3e (major diastereomer): R<sub>f</sub> = 0.10 (7:3 hexane/EtOAc); white solid, m.p. 102-103 °C; [α]<sup>25</sup><sub>D</sub> = -257.1 (c 0.5, CHCl₃, 96% ee); <sup>1</sup>H NMR (300 MHz, CCl₃) δ 8.20 (2H, d, J = 9.0 Hz, Ar), 7.54 (2H, d, J = 9.0 Hz, Ar), 7.18 (1H, d, J = 1.8 Hz, N=CHO), 4.57 (1H, d, J = 1.8 Hz, CH), 1.82 (3H, s, CH₃), 1.00 (9H, s, CH₃); <sup>13</sup>C NMR (75 MHz, CCl₃) δ 167.0 (C), 155.8 (CH), 147.4 (C), 146.9 (C), 127.0 (CH), 123.2 (CH), 87.2 (C), 78.9 (CH), 28.7 (CH₃), 27.3 (CH₃); HRMS (ESI) <sup>m/z</sup>: 307.1285 [M+H]<sup>+</sup>, C₁₅H₁₉N₂O₅+ requires 307.1288.

trans-(4R,5S)-3e (minor diastereomer): R<sub>f</sub> = 0.20 (7:3 hexane/EtOAc); colorless oil; [α]<sup>25</sup><sub>D</sub> = -60.3 (c 1.3, CHCl₃, 95% ee), Lit.1 [α]<sup>25</sup><sub>D</sub> = -86.5 (c 1.0, CHCl₃, 90% ee); <sup>1</sup>H NMR (300 MHz, CCl₃) δ 8.23 (2H, d, J = 9.0 Hz, Ar), 7.67 (2H, d, J = 9.0 Hz, Ar), 7.09 (1H, d, J = 2.1 Hz, N=CHO), 4.65 (1H, d, J = 2.1 Hz, CH), 1.67 (3H, s, CH₃), 1.57 (9H, s, CH₃); <sup>13</sup>C NMR (75 MHz, CCl₃) δ 167.8 (C), 155.0 (CH), 152.1 (C), 147.4 (C), 125.3 (CH), 124.0 (CH), 87.2 (C), 83.2 (C), 77.7 (CH), 28.0 (CH₃), 24.7 (CH₃).
**tert-Butyl 5-methyl-5-(m-tolyl)-4,5-dihydrooxazole-4-carboxylate (3f)**

Obtained 60.8 mg (88%). The enantiomeric excess (minor isomer: 97%, major isomer 99%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, trans-(4R,5S)-3f (minor diastereomer): minor enantiomer, t<sub>r</sub> = 8.9 min, major enantiomer, t<sub>r</sub> = 12.4 min. cis-(4R,5R)-3f (major diastereomer): minor enantiomer, t<sub>r</sub> = 10.5 min, minor enantiomer, t<sub>r</sub> = 14.2 min.

cis-(4R,5S)-3f (major diastereomer): Rr = 0.18 (7:3 hexane/EtOAc); white solid, m.p. 75-76 °C; [α]<sub>D</sub><sup>25</sup> =-155.9 (c 1.0, CHCl₃, 99% ee); <sup>1</sup>H NMR (300 MHz, CDCl₃) δ 7.26-7.14 (4H, m, Ar), 7.08-7.06 (1H, m, Ar), 4.48 (1H, d, J = 2.1 Hz, N=CHO), 2.33 (3H, s, CH₃), 1.79 (3H, s, CH₃), 0.99 (9H, s, CH₃); <sup>13</sup>C NMR (75 MHz, CDCl₃) δ 167.5 (C), 156.1 (CH), 139.5 (C), 137.5 (C), 128.5 (CH), 128.0 (CH), 126.5 (CH), 122.8 (CH), 88.3 (C), 81.3 (C), 78.7 (CH), 28.6 (CH₃), 27.1 (CH₃), 21.4 (CH₃); HRMS (ESI) m/z: 276.1594 [M+H]<sup>+</sup>, C₁₆H₂₂NO₃<sup>+</sup> requires 276.1594.

trans-(4R,5S)-3f (minor diastereomer): Rf = 0.30 (7:3 hexane/EtOAc); colorless oil; [α]<sub>D</sub><sup>25</sup> =-92.5 (c 1.0, CHCl₃, 99% ee); <sup>1</sup>H NMR (300 MHz, CDCl₃) δ 7.28-7.26 (3H, m, Ar), 7.13-7.10 (1H, m, Ar), 7.07 (1H, d, J = 1.8 Hz, N=CHO), 4.69 (1H, d, J = 1.8 Hz, CH), 2.38 (3H, s, CH₃), 1.65 (3H, s, CH₃), 1.56 (9H, s, CH₃); <sup>13</sup>C NMR (75 MHz, CDCl₃) δ 168.6 (C), 155.3 (CH), 145.3 (C), 138.3 (C), 128.5 (CH), 128.4 (CH), 124.7 (CH), 121.0 (CH), 87.8 (C), 82.4 (C), 77.9 (CH), 28.0 (CH₃), 24.7 (CH₃), 21.2 (CH₃); HRMS (ESI) m/z: 276.1597 [M+H]<sup>+</sup>, C₁₆H₂₂NO₃<sup>+</sup> requires 276.1594.

cis-(4R,5R)-3g (major diastereomer): Rr = 13.2 min, major enantiomer, t<sub>r</sub> = 19.1 min. cis-(4R,5R)-3g (major diastereomer): minor enantiomer, t<sub>r</sub> = 15.4 min, major enantiomer, t<sub>r</sub> = 20.2 min.

cis-(4R,5S)-3g (major diastereomer): Rr = 0.18 (7:3 hexane/EtOAc); colorless oil; [α]<sub>D</sub><sup>25</sup> =-149.1 (c 1.0, CHCl₃, 99% ee); <sup>1</sup>H NMR (300 MHz, CDCl₃) δ 7.23 (1H, t, J = 8.1 Hz, Ar), 7.16 (1H, d, J = 1.8 Hz, CH), 6.91 (1H, d, J = 7.8 Hz, Ar), 6.88 (1H, m, Ar), 6.81 (1H, dd, J = 8.4, 2.1 Hz, Ar), 4.50 (1H, d, J = 1.8 Hz, N=CHO), 3.80 (3H, s, CH₃), 1.79 (3H, s, CH₃), 1.02 (9H, s, CH₃); <sup>13</sup>C NMR (75 MHz, CDCl₃) δ 167.5 (C), 159.3 (C), 156.1 (CH), 142.2 (C), 129.1 (CH), 118.2 (CH), 113.4 (CH), 111.8 (CH), 88.3 (C), 81.5 (C), 78.7 (CH), 55.3 (CH₃), 28.7 (CH₃), 27.2 (CH₃); HRMS (ESI) m/z: 292.1547 [M+H]<sup>+</sup>, C₁₆H₂₂NO₄<sup>+</sup> requires 292.1543.
**trans-(4R,5S)-3g (minor diastereomer):** \( R_t = 0.25 \) (7:3 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} -88.3 \) (c 0.63, CHCl₃, 91% ee); \(^1H\) NMR (300 MHz, CDCl₃) \( \delta \) 7.30 (1H, t, \( J = 8.1 \) Hz, Ar), 7.08-7.01 (3H, m, Ar), 6.83 (1H, dd, \( J = 7.8, 2.1 \) Hz, Ar), 4.70 (1H, d, \( J = 1.8 \) Hz, N=CHO), 3.82 (3H, s, CH₃), 1.65 (3H, s, CH₃), 1.56 (9H, s, CH₃); \(^13C\) NMR (75 MHz, CDCl₃) \( \delta \) 168.5 (C), 159.8 (C), 155.3 (CH), 147.0 (C), 129.8 (CH), 116.3 (CH), 112.9 (CH), 110.1 (CH), 87.7 (C), 82.5 (C), 77.8 (CH), 55.3 (CH₃), 28.1 (CH₃), 24.8 (CH₃); HRMS (ESI) \( m/z \): 292.1546 [M+H]^+, C₁₆H₂₂NO₄+ requires 292.1543.

**tert-Butyl 5-(3-chlorophenyl)-5-methyl-4,5-dihydrooxazole-4-carboxylate (3h)**

Obtained 55.8 mg (75%). The enantiomeric excess (minor isomer: 91%, major isomer 99%) was determined by HPLC (Chiracel IC), hexane:iPrOH 95:5, 1 mL/min, \(^1H\) NMR (300 MHz, CDCl₃) \( \delta \) 7.30 (1H, t, \( J = 8.1 \) Hz, Ar), 7.08-7.01 (3H, m, Ar), 6.83 (1H, dd, \( J = 7.8, 2.1 \) Hz, Ar), 4.70 (1H, d, \( J = 1.8 \) Hz, N=CHO), 3.82 (3H, s, CH₃), 1.65 (3H, s, CH₃), 1.56 (9H, s, CH₃); \(^13C\) NMR (75 MHz, CDCl₃) \( \delta \) 168.5 (C), 159.8 (C), 155.3 (CH), 147.0 (C), 129.8 (CH), 116.3 (CH), 112.9 (CH), 110.1 (CH), 87.7 (C), 82.5 (C), 77.8 (CH), 55.3 (CH₃), 28.1 (CH₃), 24.8 (CH₃); HRMS (ESI) \( m/z \): 292.1546 [M+H]^+, C₁₆H₂₂NO₄+ requires 292.1543.

**cis-(4R,5R)-3h (major diastereomer):** major enantiomer, \( t_r = 27.2 \) min, minor enantiomer, \( t_r = 29.2 \) min. **trans-(4R,5S)-3h (minor diastereomer):** major enantiomer, \( t_r = 34.7 \) min, minor enantiomer, \( t_r = 39.7 \) min.

**cis-(4R,5R)-3h (major diastereomer):** \( R_f = 0.16 \) (7:3 hexane/EtOAc); white solid, m.p. 74-75 °C; \([\alpha]_D^{25} -160.5 \) (c 1.0, CHCl₃, 99% ee); \(^1H\) NMR (300 MHz, CDCl₃) \( \delta \) 7.34 (1H, bs, Ar), 7.27-7.23 (3H, m, Ar), 7.16 (1H, d, \( J = 1.8 \) Hz, N=CHO), 4.51 (1H, d, \( J = 2.1 \) Hz, CH), 1.79 (3H, s, CH₃), 1.05 (9H, s, CH₃); \(^13C\) NMR (75 MHz, CDCl₃) \( \delta \) 167.2 (C), 155.9 (CH), 141.7 (C), 134.1 (C), 129.4 (CH), 128.0 (CH), 126.3 (CH), 124.0 (CH), 87.7 (C), 81.8 (C), 78.7 (CH), 28.6 (CH₃), 27.2 (CH₃); HRMS (ESI) \( m/z \): 296.1046 [M+H]^+, C₁₅H₁₉ClNO₃+ requires 296.1048.

**trans-(4R,5S)-3h (minor diastereomer):** \( R_f = 0.28 \) (7:3 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} -82.7 \) (c 0.80, CHCl₃, 91% ee); \(^1H\) NMR (300 MHz, CDCl₃) \( \delta \) 7.32-7.20 (3H, m, Ar), 7.01 (1H, d, \( J = 1.8 \) Hz, N=CHO), 4.60 (1H, d, \( J = 2.1 \) Hz, CH), 1.58 (3H, s, CH₃), 1.51 (9H, s, CH₃); \(^13C\) NMR (75 MHz, CDCl₃) \( \delta \) 168.2 (C), 155.2 (CH), 147.3 (C), 134.6 (C), 130.0 (CH), 127.9 (CH), 124.6 (CH), 122.3 (CH), 87.2 (C), 82.8 (C), 77.8 (CH), 28.0 (CH₃), 24.7 (CH₃); HRMS (ESI) \( m/z \): 296.1043 [M+H]^+, C₁₅H₁₉ClNO₃+ requires 296.1048.

**tert-Butyl 5-methyl-5-(3-nitrophenyl)-4,5-dihydrooxazole-4-carboxylate (3i)**

Obtained 74.6 mg (97%). The enantiomeric excess (minor isomer: 90%, major isomer 95%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, \(^1H\) NMR (300 MHz, CDCl₃) \( \delta \) 7.34 (1H, t, \( J = 8.1 \) Hz, Ar), 7.32-7.20 (3H, m, Ar), 7.01 (1H, d, \( J = 1.8 \) Hz, N=CHO), 4.60 (1H, d, \( J = 2.1 \) Hz, CH), 1.58 (3H, s, CH₃), 1.51 (9H, s, CH₃); \(^13C\) NMR (75 MHz, CDCl₃) \( \delta \) 168.2 (C), 155.2 (CH), 147.3 (C), 134.6 (C), 130.0 (CH), 127.9 (CH), 124.6 (CH), 122.3 (CH), 87.2 (C), 82.8 (C), 77.8 (CH), 28.0 (CH₃), 24.7 (CH₃); HRMS (ESI) \( m/z \): 296.1043 [M+H]^+, C₁₅H₁₉ClNO₃+ requires 296.1048.
cis-(4R,5R)-3i (major diastereomer): R₇ = 0.12 (7:3 hexane/EtOAc); yellow oil; [α]²⁵
–127.0 (c 0.65, CHCl₃, 95% ee); NMR ¹H (300 MHz, CDCl₃) δ 8.25 (1H, t, J = 1.8 Hz, Ar), 8.16 (1H, d, J = 9 Hz, Ar), 7.64 (1H, d, J = 2.1 Hz, Ar), 7.51 (1H, t, J = 8.1 Hz, Ar), 7.19 (1H, d, J = 1.8 Hz, N=CHO), 4.58 (1H, d, J = 1.8 Hz, CH), 1.87 (3H, s, CH₃), 1.00 (9H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.1 (C), 155.8 (CH), 148.0 (C), 142.0 (C), 132.0 (CH), 122.9 (CH), 121.1 (CH), 87.5 (C), 82.2 (C), 78.8 (CH), 28.7 (CH₃), 27.3 (CH₃); HRMS (ESI) m/z: 307.1286 [M+H]⁺, C₁₅H₁₉N₂O₅⁺ requires 307.1288.

trans-(4R,5S)-3i (minor diastereomer): R₇ = 0.20 (7:3 hexane/EtOAc); yellow oil; [α]²⁵
–37.9 (c 0.51, CHCl₃, 90% ee); ¹H NMR (300 MHz, CDCl₃) δ 8.41 (1H, t, J = 1.8 Hz, Ar), 8.19 (1H, dd, J = 8.4, 1.2 Hz, Ar), 7.84 (1H, d, J = 7.8 Hz, Ar), 7.59 (1H, t, J = 7.8 Hz, Ar), 7.10 (1H, d, J = 2.1 Hz, N=CHO), 4.68 (1H, d, J = 2.1 Hz, CH), 1.69 (3H, s, CH₃), 1.60 (9H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.8 (C), 155.05 (CH), 148.5 (C), 147.3 (C), 130.3 (CH), 129.9 (CH), 122.8 (CH), 119.7 (CH), 87.0 (C), 83.3 (C), 77.8 (CH), 28.0 (CH₃), 24.8 (CH₃); HRMS (ESI) m/z: 307.1286 [M+H]⁺, C₁₅H₁₉N₂O₅⁺ requires 307.1288.

tert-butyl 5-methyl-5-(o-tolyl)-4,5-dihydrooxazole-4-carboxylate (3j)

Obtained 63.2 mg (91%). The enantiomeric excess (major isomer: 99%, minor isomer: 89%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, cis-(4R,5R)-3j (major diastereomer): minor enantiomer, tᵣ = 7.6 min, major enantiomer, tᵣ = 10.2 min. trans-(4R,5S)-3j (minor diastereomer): minor enantiomer, tᵣ = 9.3 min, major enantiomer, tᵣ = 11.8 min. Both diastereomers could not be separated by column chromatography.

cis-(4R,5R)-3j (major diastereomer): R₇ = 0.23 (7:3 hexane/EtOAc); white solid, m.p. 53-56 °C; [α]²⁵
–285.9 (c 1.0, CHCl₃, for the diastereomer mixture, dr: 91:9); ¹H NMR (300 MHz, CDCl₃) δ 7.48 (1H, m, Ar), 7.18-7.07 (4H, m, Ar, N=CHO), 4.61 (1H, d, J = 2.1 Hz, CH), 2.41 (3H, s, CH₃), 1.71 (3H, s, CH₃), 0.97 (9H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.4 (C), 155.9 (CH), 138.5 (C), 134.0 (C), 131.9 (CH), 127.8 (CH), 126.3 (CH), 125.7 (CH), 90.1 (C), 81.4 (C), 77.5 (CH), 27.8 (CH₃), 27.0 (CH₃), 22.4 (CH₃); HRMS (ESI) m/z: 276.1593 [M+H]⁺, C₁₆H₁₉N₂O₅⁺ requires 276.1594.

trans-(4R,5S)-3j (minor diastereomer): ¹H NMR (300 MHz, CDCl₃), representative signals taken from the NMR spectrum of the diastereomer mixture, δ 7.50-7.00 (5H, Ar, N=CHO), 4.76 (1H, d, J = 1.8 Hz, CH), 2.49 (3H, s, CH₃), 2.02 (3H, s, CH₃), 1.52 (9H, s, CH₃).
**tert-Butyl 5-(2-methoxyphenyl)-5-methyl-4,5-dihydrooxazole-4-carboxylate (3k)**

Obtained 73.2 mg (99%). The enantiomeric excess (major isomer: 99%, minor isomer: 95%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, **cis-(4R,5R)-3k (major diastereomer)**: minor enantiomer, *t*<sub>r</sub> = 8.2 min, major enantiomer, *t*<sub>r</sub> = 10.7 min. **trans-(4R,5S)-3k (minor diastereomer)**: minor enantiomer, *t*<sub>r</sub> = 12.5 min, major enantiomer, *t*<sub>r</sub> = 21.2 min. Both diastereomers could not be separated by column chromatography.

**cis-(4R,5R)-3k (major diastereomer):**

\[ [\alpha]_D^{25} = -315.0 \] (c 0.85, CHCl<sub>3</sub>, for the diastereomer mixture, dr: 95:5); **1H NMR** (300 MHz, CDCl<sub>3</sub>) \( \delta \) 7.46 (1H, dd, \( J = 7.8, 1.8 \) Hz, Ar), 7.24 (1H, m, Ar), 7.05 (1H, d, \( J = 1.8 \) Hz, N=CHO), 6.92 (1H, td, \( J = 7.5, 1.2 \) Hz, Ar), 6.80 (1H, dd, \( J = 8.1, 1.2 \) Hz, Ar), 4.58 (1H, d, \( J = 1.8 \) Hz, CH), 3.77 (3H, s, CH<sub>3</sub>), 1.61 (3H, s, CH<sub>3</sub>), 0.98 (9H, s, CH<sub>3</sub>); **13C NMR** (75 MHz, CDCl<sub>3</sub>) \( \delta \) 167.6 (C), 155.5 (CH), 154.7 (C), 129.6 (C), 128.6 (CH), 126.0 (CH), 120.4 (CH), 110.3 (CH), 88.4 (C), 80.4 (C), 77.9 (CH), 54.8 (CH<sub>3</sub>), 27.1 (CH<sub>3</sub>), 27.0 (CH<sub>3</sub>); HRMS (ESI) \( m/z \): 292.1545 [M+H]<sup>+</sup>, C<sub>16</sub>H<sub>22</sub>NO<sub>4</sub>+ requires 292.1543.

**trans-(4R,5S)-3k (minor diastereomer):**

**1H NMR** (300 MHz, CDCl<sub>3</sub>), representative signals taken from the NMR spectrum of the diastereomer mixture, \( \delta \) 7.7-7.20 (5H, m, Ar, N=CHO), 4.68 (1H, d, \( J = 1.8 \) Hz, CH), 3.85 (3H, s, CH<sub>3</sub>), 1.52 (9H, s, CH<sub>3</sub>), 1.47 (3H, s, CH<sub>3</sub>).

**tert-Butyl 5-(2-chlorophenyl)-5-methyl-4,5-dihydrooxazole-4-carboxylate (3l)**

Obtained 74.2 mg (99%). The enantiomeric excess (minor isomer: 92%, major isomer 97%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, **cis-(4R,5R)-3l (major diastereomer)**: minor enantiomer, *t*<sub>r</sub> = 7.7 min, major enantiomer, *t*<sub>r</sub> = 9.9 min. **trans-(4R,5S)-3l (minor diastereomer)**: minor enantiomer, *t*<sub>r</sub> = 9.1 min, major enantiomer, *t*<sub>r</sub> = 13.8 min. Both diastereomers could not be separated by column chromatography.

**cis-(4R,5R)-3l (major diastereomer):**

\[ [\alpha]_D^{25} = -275.9 \] (c 1.1, CHCl<sub>3</sub>, for the diastereomer mixture, dr: 92:8); **1H NMR** (300 MHz, CDCl<sub>3</sub>) \( \delta \) 7.69 (1H, dd, \( J = 7.5, 1.5 \) Hz, Ar), 7.42-7.20 (5H, m, Ar, N=CHO), 4.79 (1H, s, CH), 1.78 (3H, s, CH<sub>3</sub>), 1.11 (9H, s, CH<sub>3</sub>); **13C NMR** (75 MHz, CDCl<sub>3</sub>) \( \delta \) 167.4 (C), 155.4 (CH), 139.2 (C), 130.4 (CH), 130.2 (C), 129.0 (CH), 127.5 (CH), 127.0 (CH), 89.4 (C), 81.4 (C), 77.1 (CH), 27.2 (CH<sub>3</sub>), 26.3 (CH<sub>3</sub>); HRMS (ESI) \( m/z \): 296.1046 [M+H]<sup>+</sup>, C<sub>15</sub>H<sub>19</sub>ClNO<sub>3</sub>+ requires 296.1048.
trans-(4R,5S)-3l (minor diastereomer): $^1$H NMR (300 MHz, CDCl$_3$), representative signals taken from the NMR spectrum of the diastereomer mixture, δ 7.7-7.20 (5H, m, Ar, N=CHO), 4.92 (1H, s, CH), 1.87 (3H, s, CH$_3$), 1.53 (9H, s, CH$_3$).

tert-Butyl 5-methyl-5-(2-nitrophenyl)-4,5-dihydrooxazole-4-carboxylate (3m)

Obtained 76.9 mg (99%). The enantiomeric excess (major isomer: 95%, minor isomer: 30%) was determined by HPLC (Chiracel IC), hexane:iPrOH 90:10, 1 mL/min, cis-(4R,5R)-3m (major diastereomer): major enantiomer, $t_r$ = 31.5 min, minor enantiomer, $t_r$ = 35.4 min. trans-(4R,5S)-3m (minor diastereomer): major enantiomer, $t_r$ = 50.5 min, minor enantiomer, $t_r$ = 102.4 min. Both diastereomers could not be separated by column chromatography.

cis-(4R,5R)-3m (major diastereomer): $R_f = 0.14$ (7:3 hexane/EtOAc); yellow oil; [α]$^D_{D25}$ = -77.2 (c 0.87, CHCl$_3$, for the diastereomer mixture, dr: 71:29); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.87 (1H, dd, $J = 8.1$, 1.5 Hz, Ar), 7.81 (1H, dd, $J = 8.1$, 1.5 Hz, Ar), 7.59 (1H, m, Ar), 7.43 (1H, m, Ar), 7.06 (1H, d, $J = 1.8$ Hz, N=CHO), 4.84 (1H, d, $J = 2.1$ Hz, CH), 1.64 (3H, s, CH$_3$), 1.10 (9H, s, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.4 (C), 154.7 (CH), 147.1 (C), 135.8 (C), 133.0 (CH), 128.7 (CH), 128.6 (CH), 125.0 (CH), 88.7 (C), 81.6 (C), 78.6 (CH), 27.7 (CH$_3$), 27.2 (CH$_3$); HRMS (ESI) $m/z$: 307.1284 [M+H]$^+$, C$_{15}$H$_{19}$N$_2$O$_5$+ requires 307.1288.

trans-(4R,5S)-3m (minor diastereomer): $^1$H NMR (300 MHz, CDCl$_3$), signals taken from the NMR spectrum of the diastereomer mixture, δ 7.68 (1H, dd, $J = 7.8$, 1.2 Hz, Ar), 7.57-7.39 (3H, m, Ar), 6.89 (1H, d, $J = 2.1$ Hz, N=CHO), 4.87 (1H, d, $J = 2.1$ Hz, CH), 1.76 (3H, s, CH$_3$), 1.53 (9H, s, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$), signals taken from the NMR spectrum of the diastereomer mixture, δ 167.8 (C), 154.7 (CH), 148.5 (C), 136.5 (C), 131.5 (CH), 128.9 (CH), 127.5 (CH), 123.9 (CH), 86.9 (C), 82.3 (C), 78.1 (CH), 27.9 (CH$_3$), 24.0 (CH$_3$).

tert-Butyl 5-methyl-5-(thiophen-2-yl)-4,5-dihydrooxazole-4-carboxylate (3n)

Obtained 54.4 mg (81%). The enantiomeric excess (minor isomer: 92%, major isomer 98%) was determined by HPLC (Lux Celullose 4) hexane:iPrOH 90:10, 1 mL/min, trans-(4R,5S)-3n (minor diastereomer): minor enantiomer, $t_r$ = 11.9 min, major enantiomer, $t_r$ = 17.5 min, cis-(4R,5R)-3n (major diastereomer): minor enantiomer, $t_r$ = 16.0 min, major enantiomer, $t_r$ = 22.4 min.

trans-(4R,5S)-3n (major diastereomer): $R_f = 0.27$ (7:3 hexane/EtOAc); Colourless oil; [α]$^D_{D25}$ = -143.6 (c 1.22, CHCl$_3$, 98% ee); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.26 (1H, dd, $J =$
5.0, 1.5 Hz, Ar), 7.07 (1H, dd, J = 3.6, 1.2 Hz, Ar), 7.02 (1H, d, J = 1.8 Hz, N=CHO), 6.98 (1H, dd, J = 5.0, 3.6 Hz, Ar), 7.02 (1H, d, J = 1.8 Hz, CH), 1.74 (3H, s, CH₃), 1.52 (9H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.9 (C), 155.1 (CH), 148.3 (C), 127.0 (CH), 125.0 (CH), 123.4 (CH), 85.9 (C), 82.6 (C), 78.3 (CH), 28.0 (CH₃), 24.1 (CH₃); HRMS (ESI) m/z: 268.1003 [M+H]^+, C₁₃H₁₈NO₃S⁺ requires 268.1002.

cis-(4R,5R)-3n (minor diastereomer): Rₜ = 0.15 (7:3 hexane/EtOAc); Colourless oil; [α]D²⁵ ≈ -93.8 (c 1.00, CHCl₃, 92% ee); ¹H NMR (300 MHz, CDCl₃) δ 7.22 (1H, dd, J = 3.9, 2.4 Hz, Ar), 7.11 (1H, d, J = 1.8 Hz, N=CHO), 6.97-6.95 (2 H, m, Ar), 4.53 (1H, d, J = 1.8 Hz, CH), 1.91 (3H, s, CH₃), 1.12 (9H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.2 (C), 155.6 (CH), 142.9 (C), 126.9 (CH), 125.5 (CH), 124.9 (CH), 86.4 (C), 81.7 (C), 78.8 (CH), 29.3 (CH₃), 27.3 (CH₃); HRMS (ESI) m/z: 268.1003 [M+H]^+, C₁₃H₁₈NO₃S⁺ requires 268.1002.

tert-Butyl 5-isopropyl-5-phenyl-4,5-dihydrooxazole-4-carboxylate (3o)

Obtained 45.9 mg (63%). The enantiomeric excess (major isomer: 97%) was determined by HPLC (Chiracel AD-H), hexane/iPrOH 90:10, 1 mL/min, cis-(4R,5R)-3o (major diastereomer): minor enantiomer, tᵣ = 5.6 min, major enantiomer, tᵣ = 6.0 min. trans-(4R,5S)-3o (minor diastereomer): minor enantiomer, tᵣ = 7.1 min, major enantiomer, tᵣ = 4.8 min.

cis-(4R,5R)-3o (major diastereomer): Rₜ = 0.20 (7:3 hexane/EtOAc); Colourless oil; [α]D²⁵ ≈ -218.2 (c 0.45, CHCl₃, 97% ee, for the diastereomer mixture, dr: 98:2); ¹H NMR (300 MHz, CDCl₃) δ 7.24-7.16 (5H, m, Ar), 7.08 (1H, d, J = 1.5 Hz, N=CHO), 4.58 (1H, d, J = 1.5 Hz, CH), 2.23 (1H, sept, J = 6.9 Hz, CH), 0.94 (9H, s, CH₃), 0.91 (3H, d, J = 6.9 Hz, CH₃), 0.66 (3H, d, J = 6.9 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 168.1 (C), 156.3 (CH), 139.0 (C), 127.9 (CH), 127.3 (CH), 126.0 (CH), 93.5 (C), 81.4 (C), 76.5 (CH), 38.1 (CH), 27.2 (CH₃), 17.2 (CH₃), 16.2 (CH₃); HRMS (ESI) m/z: 290.11754 [M+H]^+, C₁₇H₂₄NO₃⁺ requires 290.1751.

tert-Butyl 5-benzyl-5-phenyl-4,5-dihydrooxazole-4-carboxylate (3p)

Obtained 84.7 mg (99%). The enantiomeric excess (major isomer: 97%, minor isomer 95%) was determined by HPLC (Chiracel IC), hexane/iPrOH 90:10, 1 mL/min, trans-(4R,5S)-3p (minor diastereomer): minor enantiomer, tᵣ = 14.3 min, major enantiomer, tᵣ = 28.4 min, cis-(4R,5R)-3p (major diastereomer): minor enantiomer, tᵣ = 22.9 min, major enantiomer, tᵣ = 23.7 min. Both diastereomers could not be separated by column chromatography.
cis-(4R,5R)-3p (major diastereomer): R_f = 0.22 (7:3 hexane/EtOAc); Colorless oil; \([\alpha]_D^{25} = -133.7 (c 0.86, CHCl_3, for the diastereomer mixture, dr: 61:39); \) 1H NMR (300 MHz, CDCl_3) δ 7.42-7.12 (10H, m, Ar), 6.83 (1H, d, J = 1.8 Hz, N=CHO), 4.75 (1H, d, J = 1.8 Hz, CH), 3.40 (2H, d, J = 2.4 Hz, CH_2), 1.08 (9H, s, CH_3); 13C NMR (75 MHz, CDCl_3) δ 167.5 (C), 155.8 (CH), 138.5 (C), 134.5 (C), 130.5 (CH), 127.92 (CH), 127.4 (CH), 126.9 (CH), 126.1 (CH), 90.6 (C), 81.5 (C), 77.4 (CH), 46.9 (CH_2), 28.0 (CH_3), 27.2 (CH_3); HRMS (ESI) m/z: 338.1749 [M+H]^+, C_{21}H_{24}NO_3^+ requires 338.1751.

trans-(4R,5S)-3p (minor diastereomer): 1H NMR (300 MHz, CDCl_3), signals taken from the NMR spectrum of the diastereomer mixture, δ 7.42-7.12 (10H, m, Ar), 6.81 (1H, d, J = 1.8 Hz, N=CHO), 4.95 (1H, d, J = 1.8 Hz, CH), 3.34 (1H, d, J = 13.2 Hz, CH), 3.23 (1H, d, J = 13.2 Hz, CH), 1.70 (9H, s, CH_3); 13C NMR (75 MHz, CDCl_3), signals taken from the NMR spectrum of the diastereomer mixture, δ 168.5 (C), 155.2 (CH), 142.9 (C), 134.8 (C), 130.4 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 126.5 (CH), 124.8 (CH), 89.8 (C), 82.8 (C), 78.8 (CH), 43.4 (CH_2), 28.1 (CH_3), 27.2 (CH_3).

tert-Butyl (R)-5,5-dimethyl-4,5-dihydrooxazole-4-carboxylate (3q)

Obtained 48.0 mg (85%). The enantiomeric excess (96%) was determined by HPLC (Chiracel OD-H), hexane:iPrOH 90:10, 1 mL/min, minor enantiomer, t_r = 4.7 min, major enantiomer, t_c = 5.9 min.

R_f = 0.25 (7:3 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} = -91.9 (c 0.65, CHCl_3, 96% ee); \) 1H NMR (300 MHz, CDCl_3) δ 6.87 (1H, d, J = 1.8 Hz, CH), 4.23 (1H, d, J = 1.8 Hz, N=CHO), 1.50 (3H, s, CH_3), 1.47 (9H, s, CH_3), 1.34 (3H, s, CH_3); 13C NMR (75 MHz, CDCl_3) δ 168.7 (C), 155.8 (CH), 85.1 (C), 82.0 (C), 76.2 (CH), 28.7 (CH_3), 27.9 (CH_3), 22.5 (CH_3); HRMS (ESI) m/z: 200.1283 [M+H]^+, C_{10}H_{18}NO_3^+ requires 200.1281.

tert-Butyl (R)-1-oxa-3-azaspiro[4.5]dec-2-ene-4-carboxylate (3r)

Obtained 59.0 mg (96%). The enantiomeric excess (95%) was determined by HPLC using a chiral column (Chiracel IC), hexane:iPrOH 90:10, 1mL/min, minor enantiomer, t_r = 20.4 min, major enantiomer, t_c = 21.4 min.

R_f = 0.25 (7:3 hexane/EtOAc); Colorless oil; \([\alpha]_D^{25} = -72.6 (c 0.46, CHCl_3, 95% ee); \) 1H NMR (300 MHz, CDCl_3) δ 6.91 (1H, d, J = 1.8 Hz, N=CHO), 4.13 (1H, d, J = 1.8 Hz, CH), 1.84-1.74 (2H, m), 1.68-1.52 (7H, m), 1.47 (9H, s, CH_3), 1.34-1.24 (1H, m); 13C NMR (75 MHz, CDCl_3) δ 168.7 (C), 155.9 (CH), 86.8 (C), 81.9 (C), 76.3 (CH), 37.6
(CH₂), 31.2 (CH₂), 27.9 (CH₃), 24.8 (CH₂), 22.4 (CH₂); HRMS (ESI) m/z: 240.1593 [M+H]⁺, C₁₃H₂₂NO₃⁺ requires 240.1594.

tert-Butyl 5-isobutyl-5-methyl-4,5-dihydrooxazole-4-carboxylate (3s)

Obtained 35.3 mg (71%). The enantiomeric excess (major isomer: 97%, minor isomer: 56%) was determined by HPLC (Chiracel IC), hexane:iPrOH 90:10, 1 mL/min, cis-(4R,5R)-3s (major diastereomer): major enantiomer, tᵣ = 12.2 min, minor enantiomer, tᵣ = 14.6 min, trans-(4R,5S)-3s (minor diastereomer): major enantiomer, tᵣ = 21.7 min, minor enantiomer, tᵣ = 24.1 min.

cis-(4R,5R)-3s (major diastereomer): Rᵣ = 0.18 (7:3 hexane/EtOAc); Colourless oil; [α]D²⁵ −45.4 (c 1.09, CHCl₃, 97% ee); ¹H NMR (300 MHz, CDCl₃) δ 6.89 (1H, d, J = 1.8 Hz, N=CHO), 4.22 (1H, d, J = 1.8 Hz, CH), 1.87 (1H, sept, J = 6.6 Hz, CH), 1.53-1.50 (2H, m), 1.47 (9H, s, CH₃), 1.45 (3H, s, CH₃), 0.94 (3H, d, J = 6.6 Hz, CH₃), 0.93 (3H, d, J = 6.6 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.8 (C), 87.6 (C), 82.0 (C), 78.0 (CH), 28.0 (CH₃), 25.6 (CH₂), 24.8 (CH₃), 24.3 (CH₃), 23.0 (CH₃); HRMS (ESI) m/z: 242.1755 [M+H]⁺, C₁₃H₂₄NO₃⁺ requires 242.1751.

trans-(4R,5S)-3s (minor diastereomer): Rᵣ = 0.27 (7:3 hexane/EtOAc); Colourless oil; [α]D²⁵ −67.7 (c 0.18, CHCl₃, 56% ee); ¹H NMR (300 MHz, CDCl₃) δ 6.89 (1H, d, J = 1.8 Hz, N=CHO), 4.29 (1H, d, J = 1.8 Hz, CH), 1.73 (1H, dd, J = 14.4, 5.1 Hz, CH), 1.63 (1H, m, CH), 1.49 (9H, s, CH₃), 1.33 (3H, s, CH₃), 0.98 (3H, d, J = 6.6 Hz, CH₃), 0.97 (3H, d, J = 6.6 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 168.9 (C), 88.8 (C), 82.0 (C), 75.9 (CH), 49.9 (CH), 28.0 (CH₃), 24.3 (CH₂), 24.2 (CH₃), 23.7 (CH₃), 20.7 (CH₃); HRMS (ESI) m/z: 242.1747 [M+H]⁺, C₁₃H₂₄NO₃⁺ requires 242.1751.

tert-Butyl 5-cyclopropyl-5-methyl-4,5-dihydrooxazole-4-carboxylate (3t)

Obtained 37.3 mg (81%). The enantiomeric excess (major isomer: 97%, minor isomer 87%) was determined by HPLC (Lux Celullose 4), hexane:iPrOH 90:10, 1 mL/min, trans-(4R,5S)-3t (minor diastereomer): minor enantiomer, tᵣ = 9.2 min, major enantiomer, tᵣ = 12.5 min, cis-(4R,5R)-3t (major diastereomer): minor enantiomer, tᵣ = 11.3 min, major enantiomer, tᵣ = 13.2 min.

cis-(4R,5R)-3t (major diastereomer): Rᵣ = 0.15 (7:3 hexane/EtOAc); Colourless oil; [α]D²⁵ −35.2 (c 0.62, CHCl₃, 97% ee); ¹H NMR(300 MHz, CDCl₃) δ 6.84 (1H, d, J = 1.8 Hz, N=CHO), 4.32 (1H, d, J = 1.8 Hz, CH), 1.47 (9H, s, CH₃), 1.46 (3H, s, CH₃), 1.10-1.05 (1H, m, CH), 0.45-0.38 (4H, m, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 168.5
(C), 155.5 (CH), 86.0 (C), 81.7 (C), 76.9 (CH), 28.0 (CH₃), 26.7 (CH₃), 15.5 (CH), 1.8 (CH₂), 1.3 (CH₂); HRMS (ESI) m/z: 226.1437 [M+H]⁺, C₁₂H₂₀NO₃⁺ requires 226.1438.

**trans-(4R,5S)-3t (minor diastereomer):** Rₜ = 0.25 (7:3 hexane/EtOAc); Colourless oil; [α]D²⁵ –88.8 (c 0.75, CHCl₃, 87% ee); ¹H NMR (300 MHz, CDCl₃) δ 6.83 (1H, d, J = 1.8 Hz, N=CHO), 4.35 (1H, d, J = 1.8 Hz, CH), 1.49 (9H, s, CH₃), 1.34 (3H, s, CH₃), 1.22-1.17 (1H, m, CH), 0.55-0.42 (4H, m, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 168.8 (C), 155.6 (CH), 86.6 (C), 82.0 (C), 75.1 (CH), 28.0 (CH₃), 21.0 (CH), 1.4 (CH₂), 0.73 (CH₂); HRMS (ESI) m/z: 226.1438 [M+H]⁺, C₁₂H₂₀NO₃⁺ requires 226.1438.

**Methyl 5-methyl-5-phenyl-4,5-dihydrooxazole-4-carboxylate (3u)**

Obtained 45.2 mg (82%). The enantiomeric excess (minor isomer: 84%, major isomer: 96%) was determined by HPLC (Chiralpak AS-H) hexane:iPrOH 95:5, 1mL/min, **trans-(4R,5S)-3u (minor diastereomer):** minor enantiomer, tᵣ = 12.8 min, major enantiomer, tᵣ = 14.2 min; cis-(4R,5R)-3u (major diastereomer): minor enantiomer, tᵣ = 10.8 min, major enantiomer, tᵣ = 28.6 min. Both diastereomers could not be separated by column chromatography.

**cis-(4R,5R)-3u (major diastereomer):** Rᵣ = 0.20 (6:4 hexane/EtOAc); colorless oil; [α]D²⁵ –166.0 (c 0.50, CHCl₃, 96% ee, for the diastereomer mixture, dr = 80:20); ¹H NMR (CDCl₃, 300 MHz) δ 7.48-7.26 (5H, m, Ar), 7.11 (1H, d, J = 1.8 Hz, N=CHO), 4.64 (1H, d, J = 1.8 Hz, CH), 3.15 (3H, s, CH₃), 1.86 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.0 (C), 155.8 (CH), 144.8 (C), 128.7 (CH), 127.8 (CH), 124.0 (CH), 116.0 (C), 108.8 (C), 87.9 (C), 77.6 (CH), 52.4 (CH₃), 24.5 (CH₃).

**Isopropyl 5-methyl-5-phenyl-4,5-dihydrooxazole-4-carboxylate (3v)**

Obtained 48.4 mg (78%). The enantiomeric excess (minor isomer: 90%, major isomer: 97%) was determined by HPLC (Lux Cellulose 4) hexane:iPrOH 90:10, 1mL/min, **trans-(4R,5S)-3v (minor diastereomer):** minor enantiomer, tᵣ = 11.7 min, major enantiomer, tᵣ = 15.5 min; cis-
(4R,5R)-3v (major diastereomer): minor enantiomer, \( t_r = 14.0 \) min, major enantiomer, \( t_r = 17.9 \) min.

cis-(4R,5R)-3v (major diastereomer): \( R_t = 0.22 \) (6:4 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} = -173.9 \) (c 0.57, CHCl\(_3\), 97% ee); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.35-7.26 (5, m, Ar), 7.20 (1H, d, \( J = 1.8 \) Hz, N=CHO), 4.59 (1H, d, \( J = 1.8 \) Hz, CH), 4.47 (1H, sept, \( J = 6.3 \) Hz, CH), 1.84 (3H, s, CH\(_3\)), 0.86 (3H, d, \( J = 6.3 \) Hz, CH\(_3\)), 0.77 (3H, d, \( J = 6.3 \) Hz, CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 168.2 (C), 156.4 (CH), 139.3 (C), 127.9 (CH), 125.6 (CH), 88.4 (C), 78.3 (CH), 68.8 (CH), 28.5 (CH\(_3\)), 21.2 (CH\(_3\)), 21.0 (CH\(_3\)); HRMS (ESI) \( m/z \): 248.1282 [M+H]^+, C\(_{14}\)H\(_{18}\)NO\(_3\)+ requires 248.1281.

trans-(4R,5S)-3v (minor diastereomer): \( R_f = 0.26 \) (6:4 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} = -79.5 \) (c 0.73, CHCl\(_3\), 90% ee); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.49-7.29 (5H, m, Ar), 7.10 (1H, d, \( J = 1.8 \) Hz, N=CHO), 5.20 (1H, sept, \( J = 6.3 \) Hz, CH), 4.76 (1H, d, \( J = 2.1 \) Hz, CH), 1.63 (3H, s, CH\(_3\)), 1.35 (3H, d, \( J = 6.3 \) Hz, CH), 1.33 (3H, d, \( J = 6.3 \) Hz, CH). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 169.0 (C), 155.6 (CH), 145.0 (C), 128.7 (CH), 127.8 (CH), 124.0 (CH), 87.8 (C), 77.5 (CH), 69.3 (CH), 24.5 (CH\(_3\)), 21.9 (CH\(_3\)), 21.8 (CH\(_3\)); HRMS (ESI) \( m/z \): 248.1282 [M+H]^+, C\(_{14}\)H\(_{18}\)NO\(_3\)+ requires 248.1281.

Benzyl 5-methyl-5-phenyl-4,5-dihydrooxazole-4-carboxylate (3w)

Obtained 56.1 mg (76%). The enantiomeric excess (minor isomer: 82%, major isomer: 96%) was determined by HPLC (Lux Cellulose 4) hexane:iPrOH 90:10, 1mL/min, \( t_r = 14.0 \) min, major enantiomer, \( t_r = 17.9 \) min; major enantiomer, \( t_r = 25.2 \) min, major enantiomer, \( t_r = 34.6 \) min.

cis-(4R,5R)-3w (major diastereomer): \( R_f = 0.26 \) (6:4 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} = -118.0 \) (c 0.72, CHCl\(_3\), 96% ee); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.29-7.26 (8H, m, Ar), 7.20 (1H, d, \( J = 1.8 \) Hz, N=CHO), 7.08-7.04 (2H, m, Ar), 4.67 (1H, d, \( J = 1.8 \) Hz, CH), 4.65 (1H, d, \( J = 12.0 \) Hz, CH), 4.36 (1H, d, \( J = 12.0 \) Hz, CH), 1.83 (3H, s, CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 168.6 (C), 156.6 (CH), 139.1 (C), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.04 (CH), 125.3 (CH), 88.4 (C), 78.4 (CH), 66.8 (CH\(_2\)), 28.3 (CH\(_3\)); HRMS (ESI) \( m/z \): 296.1283 [M+H]^+, C\(_{18}\)H\(_{18}\)NO\(_3\)+ requires 296.1281.

trans-(4R,5S)-3w (minor diastereomer): \( R_f = 0.30 \) (6:4 hexane/EtOAc); colorless oil; \([\alpha]_D^{25} = -91.4 \) (c 0.56, CHCl\(_3\), 82% ee); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.45-7.29 (10H, m, Ar), 7.11 (1H, d, \( J = 2.1 \) Hz, N=CHO), 5.30 (2H, s, CH\(_2\)), 4.84 (1H, d, \( J = 2.1 \) Hz, CH), 1.51 (3H, s, CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 169.4 (C), 155.9 (CH), 144.8 (C), 135.1 (C), 128.8 (CH), 128.7 (CH), 128.64 (CH), 128.62 (CH), 127.8 (CH), 127.4 (CH).
88.0 (C), 77.6 (CH), 67.3 (CH₂), 24.4 (CH₃); HRMS (ESI) m/z: 296.1283 [M+H]^+, C₁₈H₁₈NO₃^+ requires 296.1281.

tert-Butyl (2R,3R)-2-amino-3-(4-bromophenyl)-3-hydroxybutanoate (4)

6 M Aqueous HCl (6 drops) was added to a solution of compound 3d (25.0 mg, 0.073 mmol) in MeOH (1 mL). The reaction mixture was stirred at rt for 24 h. The mixture was basified with saturated aqueous NaHCO₃ (1 mL), water was added (10 mL), extracted with EtOAc (3×20 mL), washed with brine (20 mL) and dried over MgSO₄. Removal of the solvent under reduced pressure afforded 22.3 mg (93%) of compound 4. The enantiomeric excess (81%) was determined by HPLC (Lux Cellulose 4), hexane:iPrOH 90:10, 1 mL/min, minor enantiomer, tᵣ = 11.8 min, major enantiomer, tᵣ = 10.0 min. Colorless oil; [α]²⁵[ᵣ]⁻²³.₉ (c 1.1, CHCl₃, 81% ee); **¹H NMR** (300 MHz, CDCl₃) δ 7.43 (2H, d, J = 8.7 Hz, Ar), 7.28 (2H, d, J = 8.7 Hz, Ar), 3.55 (1H, s, CHN), 2.62 (3H, bs, NH₂, OH), 1.59 (3H, s, CH₃), 1.25 (9H, s, CH₃); **¹³C NMR** (75 MHz, CDCl₃) δ 173.0 (C), 143.8 (C), 130.9 (CH), 127.4 (CH), 121.1 (C), 82.3 (C), 62.6 (CH), 27.7 (CH₃), 26.4 (CH₃); HRMS (ESI) m/z: 352.0516 [M+Na]^+, C₁₄H₂₀BrNNaO₃^+ requires 352.0518.

tert-butyl (2R,3R)-3-(4-bromophenyl)-2-formamido-3-hydroxybutanoate (5)

6 M Aqueous HCl (6 drops) was added to a solution of compound 3d (33.0 mg, 0.096 mmol) in THF (1 mL). The reaction mixture was stirred at rt for 24 h. Work up as described in the previous procedure afforded 34.6 mg (99%) of compound 5. The enantiomeric excess (98%) was determined by HPLC (Chiracel IC), hexane:iPrOH 90:10, 1 mL/min, major enantiomer, tᵣ = 5.0 min, minor enantiomer, tᵣ = 9.0 min. White solid; m.p. 130-131 °C; [α]²⁵[ᵣ]+²₂.₈ (c 0.37, CHCl₃, 98% ee); **¹H NMR** (300 MHz, CDCl₃) δ 8.33 (1H, s, CHO), 7.49 (2H, d, J = 8.7 Hz, Ar), 7.33 (2H, d, J = 8.7 Hz, Ar), 6.53 (1H, d, J = 9.3 Hz, OH), 4.96 (1H, dd, J = 9.0, 0.6 Hz, CHN), 3.41 (1H, bs, NH), 1.49 (3H, s, CH₃), 1.14 (9H, s, CH₃); **¹³C NMR** (75 MHz, CDCl₃) δ 170.2 (C), 161.0 (C), 142.9 (C), 131.2 (CH), 127.0 (CH), 121.5 (CH), 83.4 (C), 76.0 (C), 57.7 (CH₃), 27.4 (CH₃); HRMS (ESI) m/z: 380.0461 [M+Na]^+, C₁₄H₂₀BrNNaO₄^+ requires 380.0468.

References

cis-(4R,5R)-3a

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3a

$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3a

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3a

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic product:

Enantioselective reaction:
cis-(4R,5R)-3b

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3b

$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3b

$^1$H NMR, 300 MHz, CDCl$_3$

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
cis-(4R,5R)-3c

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3c

$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3c

$^1$H NMR, 300 MHz, CDCl$_3$

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trans-(4R,5S)-3c

$^{13}$C NMR, 75 MHz, CDCl$_3$

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 cis-(4R,5R)-3d
$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3d

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3d

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![Graph showing racemic reaction results]

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![Graph showing enantioselective reaction results]

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cis-(4R,5R)-3e

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3e

$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3e
$\text{H NMR, 300 MHz, CDCl}_3$

trans-(4R,5S)-3e
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Racemic reaction:

Enantioselective reaction:
cis-(4R,5R)-\(\text{3f}\)

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\(^{13}\text{C NMR, 75 MHz, CDCl}_3\)
trans-(4R,5S)-3f

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3f

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
cis-(4R,5R)-3g

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$^13$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3g
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trans-(4R,5S)-3g
$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

![Racemic reaction graph]

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![Enantioselective reaction graph]

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$^13$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3h

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3h

$^{13}$C NMR, 75 MHz, CDCl$_3$
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![Graph of racemic reaction data.]

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Enantioselective reaction:

![Graph of enantioselective reaction data.]

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cis-(4R,5R)-3i

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3i

$^{13}$C NMR, 75 MHz, CDCl$_3$
$\text{trans-}(4R,5S)-3i$

$^1\text{H NMR, 300 MHz, CDCl}_3$

$\text{trans-}(4R,5S)-3i$

$^{13}\text{C NMR, 75 MHz, CDCl}_3$
Racemic reaction:

Enantioselective reaction:
cis-\((4R,5R)\)-3j

\(^1\)H NMR, 300 MHz, CDCl\(_3\)

\(^{13}\)C NMR, 75 MHz, CDCl\(_3\)
Racemic reaction: 3j

Enantioselective reaction:
cis-(4R,5R)-3k

$^1$H NMR, 300 MHz, CDCl$_3$

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
cis-(4R,5R)-3I

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3I

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
cis and trans-3m

$^1$H NMR, 300 MHz, CDCl$_3$

\[ \text{cis and trans-3m} \]

$^1$H NMR, 300 MHz, CDCl$_3$

\[ \text{cis and trans-3m} \]

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

![Racemic reaction graph]

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Enantioselective reaction:

![Enantioselective reaction graph]

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cis-(4R,5R)-3n

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3n

$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3n

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3n

$^1$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

![Graph showing racemic reaction results.]

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Enantioselective reaction:

![Graph showing enantioselective reaction results.]

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cis-(4R,5R)-3o

$^1$H NMR, 300 MHz, CDCl$_3$

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
$^\text{1}^H$ NMR, 300 MHz, CDCl$_3$

$^\text{13}^C$ NMR, 75 MHz, CDCl$_3$
Racemic reaction:

6: 220 nm, 4 nm Results

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Enantioselective reaction:

10: 223 nm, 4 nm Results

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(R)-3q

$^1$H NMR, 300 MHz, CDCl$_3$

(For NMR spectra)

(R)-3q

$^{13}$C NMR, 75 MHz, CDCl$_3$
Enantioselective reaction:
(R)-3r

$^1$H NMR, 300 MHz, CDCl$_3$

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
cis-(4R,5R)-3s

$^1$H NMR, 300 MHz, CDCl$_3$

 cis-(4R,5R)-3s

$^{13}$C NMR, 75 MHz, CDCl$_3$
$\text{trans-}(4R,5S)-3s$

$^1\text{H NMR, } 300 \text{ MHz, CDCl}_3$

$\text{trans-}(4R,5S)-3s$

$^{13}\text{C NMR, } 75 \text{ MHz, CDCl}_3$
Racemic reaction:

Enantioselective reaction:
cis-(4R,5R)-3t

$^1$H NMR, 300 MHz, CDCl$_3$

cis-(4R,5R)-3t
$^{13}$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3t
$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3t
$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
$\text{cis-}(4R,5R)-3\text{u}$

$\text{H NMR, 300 MHz, CDCl}_3$

$\text{cis-}(4R,5R)-3\text{u}$

$\text{C NMR, 75 MHz, CDCl}_3$
Racemic product:

Enantioselective reaction:
cis-(4R,5R)-3v

$^1$H NMR, 300 MHz, CDCl$_3$

$^1$C NMR, 75 MHz, CDCl$_3$
trans-(4R,5S)-3v

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3v

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic product:

\[
\begin{align*}
\text{Enantioselective reaction:}
\end{align*}
\]

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cis-(4R,5R)-3w

$\text{H NMR, 300 MHz, CDCl}_3$

$\text{C NMR, 75 MHz, CDCl}_3$
trans-(4R,5S)-3w

$^1$H NMR, 300 MHz, CDCl$_3$

trans-(4R,5S)-3w

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic product:

Enantioselective reaction:
(4R,5R)-4
$^1$H NMR, 300 MHz, CDCl$_3$

$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
(4R,5R)-5
$^1$H NMR, 300 MHz, CDCl$_3$

(4R,5R)-5
$^{13}$C NMR, 75 MHz, CDCl$_3$
Racemic reaction:

Enantioselective reaction:
Figure S1. ORTEP plot for the X-Ray structure of compound 5. Flack parameter = 0.019(10), Hooft parameter = 0.037(10)