Supporting information

Enantioselective [3+2] Cycloaddition of Azomethine Ylides and Aldehydes via Ni/Bis(oxazoline)-Catalyzed Ring Opening of *N*-Tosylaziridines through Chirality Transfer Approach

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General information.

Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ¹H NMR spectra, ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d₃. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, hep = heptet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Enantiomer ratios were determined using chiral HPLC analysis by comparison with authentic racemic materials. All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirrer bar. CICH₂CH₂Cl (DCE), CH₂Cl₂ (DCM) were freshly distilled from CaH₂; THF and toluene were freshly distilled from sodium metal prior to use. Solid aldehydes were used directly. All other liquid aldehydes were freshly distilled prior to use. Aziridine were prepared according to the literature (X. Wu, L. Li and J. Zhang, *Adv. Synth. Catal.*, 2012, **354**, 3485.).



Figure 1. ORTEP representation of 3lc (CCDC 895347).

| | | СНО | | | | | | | | |
|--|---|------------------|---------|----------|---|---------------|--|--|--|--|
| $\begin{array}{c} Ts \\ N \\ CO_2Me \\ Ph \\ \hline CO_2Me \\ MeO \\ \hline OMe \\ \hline OMe \\ \hline OMe \\ \hline Solvent, 4Å MS \\ \hline OMe \\ \hline Solvent, 4Å MS \\ \hline OMe \\ \hline$ | | | | | | | | | | |
| | 1a | Оме 2а | 011 | | С ₆ H ₂ -(МеС 3аа | 0)-3,4,5 | | | | |
| | | | | | | | | | | |
| Entry | Lewis acid | \mathbf{L}^* | Solvent | Time (h) | Yield $(\%)^b$ | Ee $(\%)^{c}$ | | | | |
| 1 | Ni(ClO ₄) ₂ ·6H ₂ O | L6 | Toluene | 3 | 83 | 11 | | | | |
| 2 | Ni(ClO ₄) ₂ ·6H ₂ O | L7 | Toluene | 3 | 71 | 3 | | | | |
| 3 | Ni(ClO ₄) ₂ ·6H ₂ O | L8 | Toluene | 3 | 81 | racemic | | | | |
| 4 | Ni(ClO ₄) ₂ ·6H ₂ O | L9 | Toluene | 3 | 83 | 42 | | | | |
| 5 | Ni(ClO ₄) ₂ ·6H ₂ O | L1 | Toluene | 3 | 81 | 88 | | | | |
| 6 | Ni(ClO ₄) ₂ ·6H ₂ O | L4 | Toluene | 3 | 79 | 70 | | | | |

Table S1. Screening conditions of reaction between 1a and 2a using Pybox or Box as the chiral ligand.^a

^{*a*} Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), Ni(ClO₄)₂/L (1/1.2, 5 mol%), and 100 mg of activated 4 Å MS in 2 ml of toluene at room temperature. ^{*b*} NMR yield of the crude product (using CH₂Br₂ as internal standard). ^{*c*} Determined by chiral-phase HPLC analysis.



| $\begin{array}{c} Ts \\ Ph \\ CO_2Me \\ 1a \end{array} + \begin{array}{c} CHO \\ Lewis acid/L1 \\ Toluene, 4Å MS \end{array} \xrightarrow{Ph \\ CO_2Me \\ CO_2Me \\ CO_2Me \\ C_6H_4-Me-p \\ 3ac \end{array}$ | | | | | | | | |
|---|---|--------------------|---------|----------|-----------|---------------------|--|--|
| Entry | Lewis acid | Temp/Additive | Solvent | Time (h) | Yield (%) | Ee (%) ^c | | |
| | | (equiv) | | | | | | |
| 1 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/- | DCM | 3 | 68 | 49 | | |
| 2 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/- | DCE | 3 | 67 | 57 | | |
| 3 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/- | DME | 24 | trace | n.d. | | |
| 4 | Ni(ClO ₄) ₂ ·6H ₂ O | -15 °C/- | toluene | 12 | 73 | 53 | | |
| 5 | NiI ₂ | rt/- | toluene | 24 | n.r. | n.d. | | |
| 6 | Ni(OTf) ₂ | rt/- | toluene | 24 | trace | n.d. | | |
| 7 | Ni(BF ₄) ₂ | rt/- | toluene | 4 | 71 | 36 | | |
| 8 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/LiI (0.05) | toluene | 4 | Trace | 42 | | |
| 9 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/P(O)Ph3 (0.20) | toluene | 3 | 55 | 68 | | |
| 10 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/Ca(ClO)2 (0.05) | toluene | 3 | 68 | 55 | | |
| 11 | Ni(ClO ₄) ₂ ·6H ₂ O | rt/PhCOOH (0.20) | toluene | 3 | 71 | 67 | | |

Table S2. Screening reaction conditions using L1 as the chiral ligand.^a

^{*a*} Reaction conditions: **1a** (0.2 mmol), **2c** (1.5 equiv), Lewis acid/**L1** (1/1.2, 5 mol%), and 100 mg of activated 4 Å MS in 2 ml of toluene at room temperature. ^{*b*} Yield of isolated product. ^{*c*} Determined by chiral-phase HPLC analysis. n.d. = not determined.

| Table S3. | Screening | reaction | conditions | using | Pybox | as the | chiral | ligand. ^a |
|-----------|-----------|----------|-------------|-------|-------|--------|--------------------------|----------------------|
| Idole De. | Servening | reaction | contaitions | | | | U 1111 U 1 | |

| Ph CO_2Me + CHO $Lewis acid/L$ Ph N CO_2Me $Toluene, 4Å MS$ O_2Me | | | | | | | | | |
|---|---|--------|-----------------|----------|---------------------------------------|---------------------|--|--|--|
| | 1a | N 2 | /le с | | C ₆ H₄-Me- <i>p</i> 3ac | | | | |
| Entry | Lewis acid | L* | Solvent | Time (h) | Yield $(\%)^b$ | Ee (%) ^c | | | |
| 1 | Ni(ClO ₄) ₂ ·6H ₂ O | L6 | Toluene | 48 | 12 | 39 | | | |
| 2 | Ni(ClO ₄) ₂ ·6H ₂ O | L7 | Toluene | 48 | trace | n.d. | | | |
| 3 | Ni(ClO ₄) ₂ ·6H ₂ O | L8 | Toluene | 48 | trace | n.d. | | | |
| 4 | Ni(ClO ₄) ₂ ·6H ₂ O | L9 | Toluene | 48 | 19 | 23 | | | |

^{*a*} Reaction conditions: **1a** (0.2 mmol), **2c** (1.5 equiv), Ni(ClO₄)₂/**L** (1/1.2, 5 mol%), and 100 mg of activated 4 Å MS in 2 ml of toluene at room temperature. ^{*b*} NMR yield of the crude product (using CH₂Br₂ as internal standard). ^{*c*} Determined by chiral-phase HPLC analysis. n.d. = not determined.

Synthesis of aziridines 1f-1o.

Aziridines were prepared according to the literature (X. Wu, L. Li and J. Zhang, *Adv. Synth. Catal.*, 2012, **354**, 3485).

1. Dineopentyl 3-phenyl-1-tosylaziridine-2,2-dicarboxylate (1f).

White solid, mp = 96 – 98 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 8.4 Hz, 2 H); 7.34 (d, *J* = 8.4 Hz, 2 H); 7.18 – 7.26 (m, 5 H); 4.92 (s, 1 H); 4.05 (d, *J* = 10.4 Hz, 1 H); 4.00 (d, *J* = 10.4 Hz, 1 H); 3.64 (d, *J* = 10.4 Hz, 1 H); 3.44 (d, *J* = 10.4 Hz, 1 H); 2.45 (s, 3 H); 0.99 (s, 9 H); 0.66 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 163.2, 162.6, 144.6, 136.7, 131.2, 129.7, 128.9, 128.5, 127.7, 126.9, 76.5, 75.3, 57.8, 49.7, 31.4, 30.9, 26.4, 25.9, 21.6 ppm. IR (neat) *v*/cm⁻¹ 2959, 2917, 2869, 1739, 1724, 1598, 1476, 1462, 1402, 1375, 1343, 1311, 1298, 1279, 1266, 1166, 1126, 1092, 1045, 981, 968, 935. HRMS (ESI): C₂₇H₃₅NNaO₆S [M+Na]⁺ calcd: 524.2077, found: 524.2139.

2. Dineopentyl 3-(4-isopropylphenyl)-1-tosylaziridine-2,2-dicarboxylate (1g).

White solid, mp = 80 – 83 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (d, *J* = 8.4 Hz, 2 H); 7.34 (d, *J* = 8.4 Hz, 2 H); 7.15 (d, *J* = 8.0 Hz, 2 H); 7.10 (d, *J* = 8.0 Hz, 2 H); 4.90 (s, 1 H); 4.05 (d, *J* = 10.4 Hz, 1 H); 3.99 (d, *J* = 10.4 Hz, 1 H); 3.70 (d, *J* = 10.4 Hz, 1 H); 3.43 (d, *J* = 10.4 Hz, 1 H); 2.83 (hep, *J* = 6.8 Hz, 1 H); 2.44 (s, 3 H); 1.17 (d, *J* = 6.8 Hz, 6 H); 0.99 (s, 9 H); 0.62 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 163.3, 162.8, 149.7, 144.5, 136.8, 129.6, 128.6, 127.7, 126.8, 126.6, 76.4, 75.3, 57.8, 49.9, 33.9, 31.4, 30.9, 26.3, 25.9, 23.8, 21.7 ppm. IR (neat) v/cm⁻¹ 2599, 2905, 2871, 1756, 1703, 1608, 1594, 1479, 1466, 1429, 1401, 1369, 1341, 1293, 1272, 1247, 1224, 1194, 1183, 1164, 1116, 1091, 1030, 1018, 998, 936, 918. HRMS (ESI): C₃₀H₄₁NNaO₆S [M+Na]⁺ calcd: 566.2547, found: 566.2573.

3. Dineopentyl 3-(*p*-tolyl)-1-tosylaziridine-2,2-dicarboxylate (1h).

White solid, mp = 89 – 92 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 4.87 (s, 1 H), 4.03 (d, *J* = 10.4 Hz, 1 H), 3.99 (d, *J* = 10.4 Hz, 1 H), 3.65 (d, *J* = 10.4 Hz, 1 H), 3.46 (d, *J* = 10.4 Hz, 1 H), 2.44 (s, 3 H), 2.27 (s, 3 H), 0.99 (s, 9 H), 0.68 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 163.3, 162.7, 144.5, 138.7, 136.8, 129.6, 129.1, 128.2, 127.7, 126.8, 76.5, 75.3, 57.8, 49.7, 31.4, 31.0, 26.4, 25.9, 21.6, 21.1 ppm. IR (neat) v/cm⁻¹ 2977, 2954, 2868, 1738, 1724, 1686, 1597, 1519, 1478, 1402, 1377, 1365, 1342, 1311, 1297, 1279, 1266, 1168, 1121, 1092, 1043, 1022, 981, 967, 931. HRMS (ESI): C₂₈H₃₇NNaO₆S [M+Na]⁺ calcd: 538.2234, found: 538.2262.

4. Dineopentyl 3-(*m*-tolyl)-1-tosylaziridine-2,2-dicarboxylate (1i).

White solid, mp = 101 – 102 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 8.4Hz, 2H); 7.34 (d, *J* = 8.0 Hz, 2 H); 6.96 – 7.18 (m, 4 H); 4.87 (s, 1H); 4.04 (d, *J* = 10.4 Hz, 1 H); 3.99 (d, *J* = 10.8 Hz, 1 H); 3.65 (d, *J* = 10.4 Hz, 1 H); 3.45 (d, *J* = 10.4 Hz, 1 H); 2.45 (s, 3 H), 2.26 (s, 3 H); 0.99 (s, 9 H); 0.67 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 163.3, 162.7, 144.6, 138.2, 136.6, 131.1, 129.6, 128.4, 127.8, 127.6, 123.8, 76.5, 75.3, 57.7, 49.6, 31.4, 31.0, 26.4, 25.9, 21.7, 21.2 ppm. IR(neat) v/cm⁻¹ 2955, 2349, 1759, 1742, 1560, 1520, 1367, 1342, 1312, 1293, 1255, 1234, 1190, 1162, 1125, 1068, 1010, 974, 931, 920. HRMS (ESI): C₂₈H₃₇NNaO₆S [M+Na]⁺ calcd: 538.2234, found: 538.2262.

5. Dineopentyl 3-(4-nitrophenyl)-1-tosylaziridine-2,2-dicarboxylate (1j).

White solid, mp = 109 – 111 °C, ¹H NMR (400 MHz,CDCl₃): δ = 8.14 (d, *J* = 8.4 Hz, 2 H); 7.96 (d, *J* = 8.4 Hz, 2 H); 7.44 (d, *J* = 8.4 Hz, 2 H); 7.37 (d, *J* = 8.4 Hz, 2 H); 4.94 (s, 1 H); 4.06 (d, *J* = 10.4 Hz,1 H); 4.01 (d, *J* = 10.4 Hz, 1 H); 3.64 (d, *J* = 10.4 Hz, 1 H); 3.48 (d, *J* = 10.4 Hz,1 H); 2.47 (s, 3 H); 1.00 (s, 9 H); 0.69 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 162.6, 162.1, 148.3, 145.2, 138.4, 136.0, 129.9, 128.1, 127.8, 123.7, 76.9, 75.7, 57.9, 48.3, 31.4, 31.0, 26.3, 25.9, 21.7 ppm. IR (neat) v/cm⁻¹ 2960, 2886, 2871, 2823, 2361, 2341, 1745, 1608, 1535, 1477, 1451, 1402, 1369, 1357, 1313, 1271, 1252, 1234, 1192, 1171, 1119, 1073, 1034, 1013, 991, 962, 941, 930. HRMS (ESI): C₂₇H₃₄N₂NaO₈S [M+Na]⁺ calcd: 569.1907, found: 569.1928.

6. Dineopentyl 3-(4-chlorophenyl)-1-tosylaziridine-2,2-dicarboxylate (1k).

White solid, mp = 121 - 124 °C, ¹H NMR (400 MHz, CDCl₃): $\delta = 7.95$ (d, J = 8.4 Hz, 2 H); 7.35 (d, J = 8.4 Hz, 2 H); 7.24 (d, J = 8.4 Hz, 2 H); 7.18 (d, J = 8.4 Hz, 2 H); 4.86 (s, 1 H); 4.04 (d, J = 10.4 Hz, 1 H); 3.99 (d, J = 10.4 Hz, 1 H); 3.66 (d, J = 10.4 Hz, 1 H); 3.47 (d, J = 10.4 Hz, 1 H); 2.45 (s, 3 H); 0.99 (s, 9 H); 0.69 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 163.0$, 162.4, 144.9, 136.3, 134.9, 129.7, 128.7, 128.3, 127.7, 76.6, 75.5, 57.7, 48.8, 31.4, 31.0, 26.3, 25.9, 21.7 ppm. IR (neat) v/cm⁻¹ 2954, 2908, 2870, 1740, 1726, 1658, 1597, 1494, 1478, 1402, 1377, 1365, 1323, 1307, 1288, 1168, 1120, 1091, 1042, 1017, 981, 966, 951. HRMS (ESI): C₂₇H₃₄CINNaO₆S [M+Na]⁺ calcd: 558.1688, found: 558.1725.

7. Dineopentyl 3-(4-bromophenyl)-1-tosylaziridine-2,2-dicarboxylate (11).

White solid, mp = 120 - 123 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 8.4 Hz, 2 H); 7.39 (d, *J* = 8.4 Hz, 2 H); 7.35 (d, *J* = 8.0 Hz, 2 H); 7.12 (d, *J* = 8.0 Hz, 2 H);

4.84 (s, 1 H); 4.04 (d, J = 10.4 Hz, 1 H); 3.99 (d, J = 10.4 Hz, 1 H); 3.67 (d, J = 10.4 Hz, 1 H); 3.47 (d, J = 10.4 Hz, 1 H); 2.45 (s, 3 H); 0.99 (s, 9 H); 0.69 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 163.0$, 162.4, 144.9, 136.4, 131.7, 130.3, 129.7, 128.6, 127.7, 123.1, 76.6, 75.5, 57.7, 48.9, 31.4, 31.0, 26.3, 25.9, 21.7 ppm. IR (neat) v/cm⁻¹ 2955, 2869, 1740, 1725, 1591, 1574, 1489, 1479, 1467, 1377, 1366, 1341, 1323, 1306, 1288, 1264, 1167, 1121, 1091, 1071, 1043, 1013, 980, 931. HRMS (ESI): C₂₇H₃₄BrNNaO₆S [M+Na]⁺ calcd: 602.1182, found: 602.1184.

8. Dineopentyl 3-(3-bromophenyl)-1-tosylaziridine-2,2-dicarboxylate (1m)

White solid, mp = 85 – 88 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (d, *J* = 8.0 Hz, 2 H); 7.32 – 7.44 (m, 4 H); 7.08 – 7.22 (m, 2 H); 4.84 (s, 1 H); 4.05 (d, *J* = 10.4 Hz, 1 H); 3.99 (d, *J* = 10.4 Hz, 1 H); 3.68 (d, *J* = 10.4 Hz, 1 H); 3.47 (d, *J* = 10.4 Hz, 1 H); 2.46 (s, 3 H); 0.99 (s, 9 H); 0.70(s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 162.9, 162.4, 144.9, 136.3, 133.6, 132.1, 130.1, 129.9, 129.8, 127.8, 125.7, 122.6, 75.5, 57.8, 48.5, 31.4, 31.0, 26.4, 26.0, 21.7 ppm. IR(neat) v/cm⁻¹ 2961, 2872, 2363, 2332, 1744, 1598, 1570, 1477, 1370, 1345, 1323, 1275, 1253, 1228, 1194, 1166, 1123, 1091, 1040, 994, 927. HRMS (ESI): C₂₇H₃₄BrNNaO₆S [M+Na]⁺ calcd: 602.1182, found: 602.1184.

9. Dineopentyl 3-(naphthalen-2-yl)-1-tosylaziridine-2,2-dicarboxylate (1n).

White solid, mp = 135 - 137 °C, ¹H NMR (400 MHz, CDCl₃): $\delta = 8.00$ (d, J = 8.4 Hz, 2 H); 7.68 – 7.84 (m, 4 H); 7.42 – 7.54 (m, 2 H); 7.29 – 7.42 (m, 3 H); 5.06 (s, 1 H); 4.07 (d, J = 10.4 Hz, 1 H); 4.02 (d, J = 10.4 Hz, 1 H); 3.57 (d, J = 10.4 Hz, 1 H); 3.41 (d, J = 10.4 Hz, 1 H); 2.45 (s, 3 H); 1.01 (s, 9 H); 0.60 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 163.2$, 162.7, 144.7, 136.6, 133.4, 132.9, 129.7, 128.7, 128.4, 128.0, 127.8, 127.7, 126.53, 126.49, 126.4, 124.0, 76.6, 75.4, 57.9, 49.8, 31.4, 30.9, 26.4, 25.9, 21.7 ppm. IR(neat) v/cm⁻¹ 2973, 2887, 1756, 1733, 1697, 1597, 1478, 1405, 1369, 1332, 1314, 1292, 1276, 1227, 1168, 1119, 1089, 1051, 1035, 989, 937, 928, 907. HRMS (ESI): C₃₁H₃₇NNaO₆S [M+Na]⁺ calcd: 574.2213, found: 574.2234.

10. dineopentyl 1-((4-nitrophenyl)sulfonyl)-3-phenylaziridine-2,2-dicarboxylate (10).

White solid, mp = 93 – 94 °C, ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (d, *J* = 8.8 Hz, 2 H); 8.30 (d, *J* = 8.4 Hz, 2 H); 7.18 – 7.34 (m, 5 H); 5.02 (s, 1 H); 4.05 (s, 2 H); 3.65 (d, *J* = 10.4 Hz, 1 H); 3.49 (d, *J* = 10.4 Hz, 1 H); 1.00 (s, 9 H); 0.64 (s, 9 H); ¹³C NMR(100 MHz, CDCl₃): δ = 163.0, 162.2, 150.6, 145.5, 130.5, 129.3, 128.9, 128.7, 126.7, 124.4, 76.9, 75.7, 58.3, 50.7, 31.4, 30.9, 26.3, 25.9 ppm. IR(neat) v/cm⁻¹2961,

2887, 2871, 2361, 2341, 1745, 1608, 1535, 1477, 1451, 1402, 1369, 1357, 1313, 1271, 1252, 1234, 1192, 1171, 1119, 1089, 1034, 1013, 991, 962, 930. HRMS (ESI): C₂₆H₃₂N₂NaO₈S [M+Na]⁺ calcd: 555.1778, found: 555.1772.

Typical procedure for preparation of racemic 1, 3-oxazolidines.



In an inert atmosphere, a flame-dried vial was charged with a maganetic stirrer bar, 100 mg of activated 4Å molecular sieves (M.S.), Ni(ClO₄)₂·6H₂O (2.74 mg, 5 mol %), aldehyde (0.225 mmol, 1.5 equiv), and 2 mL of toluene. The mixture was allowed to be stirred at room temperature for 15 minutes, then aziridine (0.15 mmol, 1.0 equiv) was added. The reaction mixture was continued to be stirred until the reaction was completed (monitored by TLC). The mixture was then passed over a small plug of silica gel eluted with CH₂Cl₂. After evaporation under reduced pressure, the residue was purified by flash chromatography to afford the desired product.

Typical procedure for Ni(ClO₄)₂·6H₂O/Bn-Box catalyzed cycloaddition of aziridine 1 with aldehyde 2.



In an inert atmosphere, a flame-dried vial was charged with a maganetic stirrer bar, 150 mg of activated 4Å molecular sieves (M.S.), Ni(ClO₄)₂·6H₂O (5.48 mg, 5 mol%), Bn-Box (6.52 mg, 6 mol%) and 3 mL of toluene. The mixture was allowed to be stirred for 3 h at room temperature. Then, aldehyde **2** (0.45 mmol, 1.5 equiv) was added, followed by aziridine **1** (0.25 mmol, 1.0 equiv). The mixture was continued to be stirred at room temperature until the complete consumption of the aziridine

(determined by TLC analysis). The reaction mixture was then passed over a small plug of silica gel eluted with CH₂Cl₂. After evaporation under reduced pressure, the residue was purified by flash chromatography (eluent, PE : EA = 10:1) to afford the product **3** and enantiomeric excess was determined by chiral HPLC. (Note: For some cases, it was not possible to separate the desired products and the starting aromatic aldehydes using flash chromatography, as they appeared as single spots when isolated by thin layer chromatography. Thus, the aldehydes can be transformed into the corresponding oximes by mixing the crude products with NH₂OH HCl (2 equiv, respected to the excess amount of the aldehyde), NaOAc (2 equiv), EtOH (2 mL), which was stirred at room temperature for 1-2 h before flash chromatography.)

1. (2*S*,5*R*)-dineopentyl 2-phenyl-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3fc).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fc** (174.0 mg) in 90% yield, white solid. m.p. 133 – 136 °C; $[\alpha]_{20}^{D} = -57.4$ (c = 1.0, CHCl₃); ee = 93% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 7.47 min, t_{major} = 9.95 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49$ (d, J = 7.2 Hz, 2 H); 7.18 – 7.32 (m, 3 H); 7.06 – 7.18 (m, 6 H); 6.89 (d, J = 8.4 Hz, 2 H); 6.17 (s, 1 H); 5.76 (s, 1 H); 4.21 (d, J= 10.4 Hz, 1 H); 4.08 (d, J = 10.4 Hz, 1 H); 3.91 (d, J = 10.4 Hz, 1 H); 2.91 (d, J =10.4 Hz, 1 H); 2.31 (s, 3 H); 2.29 (s, 3 H); 1.16 (s, 9 H); 0.73 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 166.6, 142.7, 138.9, 137.6, 133.7, 131.3, 129.9, 129.0, 128.3, 128.2, 127.9, 126.5, 92.7, 87.3, 77.4, 76.2, 75.8, 31.6, 30.9, 26.8, 26.2, 21.4, 21.2 ppm. IR (neat) ν/cm^{-1} 2988, 2955, 1763, 1731, 1600, 1527, 1476, 1462, 1398, 1368, 1346, 1289, 1249, 1232, 1181, 1157, 1078, 1036, 1008, 964, 925. HRMS (ESI): C₃₅H₄₃NNaO₇S [M+Na]⁺ calcd: 644.2652, found: 644.2647.

Procedure for synthesis of 3fa in a gram level scale.

In a flame-dried nitrogen-flushed flask, a solution of Ni(ClO₄)₂·6H₂O (58.5 mg, 2 mol%), Bn-Box ligand (63.8 mg, 2.2 mol%), and 1g 4Å M.S. in dry toluene (60 mL) was stirred for 4 h, then **2c** (1.44 g, 12 mmol) was added to this mixture, followed by aziridine **1f** (4.01g, 8 mmol). The mixture was continued to be stirred for 18 h at room temperature. After filtration to remove the 4Å M.S., the solution was concentrated under reduced pressure. Then, the residue was purified by flash chromatography (PE:EA = 10:1) to afford **3fc** (4.3 g) in 85% yield, white solid, ee = 93% (chiral HPLC analysis), and the ¹H NMR and ¹³C NMR spectra were in accordance with the previous data.

2. (2*S*,5*R*)-dineopentyl 2-(4-isopropylphenyl)-5-(*p*-tolyl)-3-tosyloxazolidine -4,4-dicarboxylate (3gc).



The reaction of **1g** (163.1 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was

carried out at r.t. for 12 hours to afford **3gc** (176.5 mg) in 89% yield, white solid. m.p. 147 – 151 °C; $[\alpha]_{20}^{D} = -36.8$ (c = 1.0, CHCl₃); ee = 89% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 7.55 min, t_{major} = 11.05 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.38$ (d, J = 8.0 Hz, 2 H); 7.22 (d, J = 8.0 Hz, 2 H); 7.16 (d, J = 8.4 Hz, 2 H); 7.11 (d, J = 8.0 Hz, 2 H); 6.96 (d, J = 8.0 Hz, 2 H); 6.87 (d, J = 8.4 Hz, 2 H); 6.15 (s, 1 H); 5.74 (s, 1 H); 4.21 (d, J = 10.4 Hz, 1 H); 4.08 (d, J = 10.4 Hz, 1 H); 3.92 (d, J = 10.4 Hz, 1 H); 2.92 (d, J = 10.4 Hz, 1 H); 2.78 – 2.90 (m, 1 H); 2.31 (s, 3 H); 2.28 (s, 3 H); 1.23 (s, 3 H); 1.21 (s, 3 H); 1.16 (s, 9 H); 0.73 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.0$, 166.7, 150.8, 142.3, 138.8, 137.8, 131.5, 131.0, 129.8, 129.0, 128.3, 128.2, 126.5, 125.9, 92.5, 87.2, 77.5, 76.2, 75.8, 34.0, 31.6, 30.9, 26.8, 26.2, 24.1, 23.9, 21.4, 21.2 ppm. IR (neat) ν /cm⁻¹ 2960, 2870, 1758, 1739, 1614, 1598, 1516, 1497, 1467, 1434, 1393, 1368, 1341, 1298, 1236, 1217, 1203, 1154, 1089, 1078, 1059, 1041, 1020, 1007, 975, 938, 927. HRMS (ESI): C₃₈H₄₉NNaO₇S [M+Na]⁺ calcd: 686.3122, found: 686.3127.

3. (2S,5R)-dineopentyl 2,5-di-(p-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3hc).



The reaction of **1h** (154.6 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 18 hours to afford **3hc** (179.0 mg) in 94% yield, white solid. m.p. 146 – 149 °C; $[\alpha]_{20}^{D} = -46.4$ (c = 1.0, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 8.34 min, t_{major} = 11.69 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.35$ (d, J = 8.0 Hz, 2 H); 7.22 (d, J = 8.0 Hz, 2 H); 7.16 (d, J = 8.4 Hz, 2 H); 7.11 (d, J = 8.0 Hz, 2 H); 6.90 (t, J = 7.8 Hz, 4 H); 6.12 (s, 1 H); 5.73 (s, 1 H); 4.20 (d, J = 10.4 Hz, 1 H); 4.08 (d, J = 10.4 Hz, 1 H); 3.90 (d, J = 10.4 Hz, 1 H); 2.93 (d, J = 10.4 Hz, 1 H); 2.31 (s, 6 H); 1.16 (s, 9 H); 0.73 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.0$, 166.6, 142.5, 139.9, 138.8, 137.8, 131.4, 130.8, 129.7, 128.9, 128.4, 128.3, 128.1, 126.5, 92.5, 87.2, 77.4, 76.2, 75.8, 31.5, 30.9, 26.7, 26.2, 21.4, 21.2, 21.1 ppm. IR (neat) ν /cm⁻¹ 2956, 2869, 1761, 1736, 1617, 1598, 1516, 1476, 1464, 1368, 1345, 1309, 1289, 1247, 1227, 1212, 1154, 1089, 1036, 1006, 970, 940, 926. HRMS (ESI): C₃₆H₄₅NNaO₇S [M+Na]⁺ calcd: 658.2809, found: 658.2810.

4. (2*S*,5*R*)-dineopentyl 2-(*m*-tolyl)-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3ic).



The reaction of **1i** (154.6 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3ic** (169.3 mg) in 89% yield, white solid. m.p. $158 - 161 \, {}^{\circ}\text{C}$; $[\alpha]_{20}^{D} = -63.1$ (c = 1.0, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/ⁱPrOH = 85/15, 0.8 mL/min, t_{minor} = 8.25 min, t_{major} = 13.34 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.18 - 7.30$ (m, 4 H); 7.17 (d, J = 8.0 Hz, 2 H); 7.12 (d, J = 7.6 Hz, 2 H); 7.05 (d, J = 4.4 Hz, 2 H); 6.90 (d, J = 8.0 Hz, 2 H); 6.11 (s, 1 H); 5.72 (s, 1 H); 4.21 (d, J = 10.4 Hz, 1 H); 4.09 (d, J = 10.4 Hz, 1 H); 3.91 (d, J =10.4 Hz, 1 H); 2.95 (d, J = 10.4 Hz, 1 H); 2.31 (s, 3 H); 2.30 (s, 3 H); 2.14 (s, 3 H); 1.16 (s, 9 H); 0.73 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.1$, 166.6, 142.5, 138.9, 137.7, 137.6, 133.3, 131.4, 130.7, 130.3, 129.0, 128.3, 128.1, 127.7, 127.2, 126.6, 92.7, 87.2, 77.5, 76.2, 75.8, 31.6, 30.9, 26.8, 26.2, 21.3, 21.2, 21.0 ppm. IR (neat) ν /cm⁻¹ 2958, 2904, 2870, 1764, 1735, 1599, 1518, 1475, 1399, 1367, 1347, 1310, 1288, 1251, 1231, 1213, 1173, 1154, 1092, 1075, 1039, 1011, 971, 939, 908. HRMS (ESI): C₃₆H₄₅NNaO₇S [M+Na]⁺ calcd: 658.2809, found: 658.2807.

5. (2*S*,5*R*)-dineopentyl 2-(4-nitrophenyl)-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3jc).



The reaction of **1j** (163.9 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 72 hours to afford **3jc** (154.5 mg) in 77% yield, white solid. m.p. $182 - 185 \, {}^{\circ}$ C; $[\alpha]_{20}{}^{D} = -33.1(c = 1.0, CHCl_3)$; ee = 96% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/ⁱPrOH = 85/15, 0.8 mL/min, t_{minor} = 7.80 min, t_{major} = 11.43 min); ¹H NMR (400 MHz, CDCl_3): δ = 7.95 (d, *J* = 8.8 Hz, 2 H); 7.70 (d, *J* = 8.4 Hz, 2 H); 7.11 - 7.24 (m, 6 H); 6.92 (d, *J* = 8.0 Hz, 2 H); 6.23 (s, 1 H); 5.80 (s, 1 H); 4.23 (d, *J* = 10.4 Hz, 1 H); 4.08 (d, *J* = 10.4 Hz, 1 H); 3.91 (d, *J* = 10.0 Hz, 1 H); 2.92 (d, *J* = 10.0 Hz, 1 H); 2.33 (s, 3 H); 2.30 (s, 3 H); 1.16 (s, 9 H); 0.72 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.6, 166.3, 148.8, 143.8, 140.8, 139.3, 137.3, 130.9, 130.7, 129.2, 128.5, 128.2, 126.4, 122.8, 91.1, 87.9, 77.4, 76.4, 76.1, 31.6, 30.9, 26.8, 26.1, 21.3, 21.2 ppm. IR (neat) v/cm⁻¹ 2957, 2869, 1763, 1739, 1525, 1477, 1370, 1346, 1288, 1228, 1202, 1156, 1089, 1034, 1007, 920. HRMS (ESI): C₃₅H₄₂N₂NaO₉S [M+Na]⁺ calcd: 689.2503, found: 689.2506. 6. (2*S*,5*R*)-dineopentyl 2-(4-chlorophenyl)-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3kc).



The reaction of 1k (160.8 mg, 0.3 mmol), 2c (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford 3kc (194.3 mg) in 99% yield, white solid. m.p. $168 - 171 \text{ °C}; \ [\alpha]_{20}^{D} = -27.1(c = 0.5, \text{ CHCl}_3); \text{ ee} = 94\% \text{ (chiral HPLC analysis:}$ Chiralcel OZ3, *n*-hexane/^{*i*}PrOH = 95/5, 0.8 mL/min, $t_{minor} = 5.77$ min, $t_{major} = 11.67$ min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.41$ (d, J = 8.4 Hz, 2 H); 7.16 – 7.24 (m, 4 H); 7.13 (d, J = 8.0 Hz, 2 H); 7.07 (d, J = 8.4 Hz, 2 H); 6.96 (d, J = 8.4 Hz, 2 H); 6.12 (s, 1 H); 5.74 (s, 1 H); 4.21 (d, J = 10.4 Hz, 1 H); 4.07 (d, J = 10.4 Hz, 1 H); 3.91 (d, J =10.4 Hz, 1 H); 2.91 (d, J = 10.4 Hz, 1 H); 2.34 (s, 3 H); 2.32 (s, 3 H); 1.16 (s, 9 H); 0.72 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.69$, 166.65, 143.1, 139.1, 137.5, 136.1, 132.4, 131.14, 131.06, 129.1, 128.4, 128.2, 128.0, 126.5, 91.7, 87.4, 77.4, 76.3, 75.9, 31.6, 30.9, 26.8, 26.2, 21.4, 21.2 ppm. IR (neat) v/cm⁻¹ 2965, 2864, 1904, 1760, 1736, 1599, 1547, 1520, 1493, 1478, 1424, 1367, 1349, 1262, 1234, 1214, 1158, 1090, 1034, 1018, 963, 943. HRMS (ESI): C₃₅H₄₂ClNNaO₇S [M+Na]⁺ calcd: 678.2263, found: 678.2248.

7. (2*S*,5*R*)-dineopentyl 2-(4-bromophenyl)-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dica-rboxylate (3lc).



The reaction of **11** (174.2 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3lc** (178.0 mg) in 85% yield, white solid. m.p. $167 - 170 \ ^{\circ}$ C; $[\alpha]_{20}^{D} = -24.7$ (c = 0.5, CHCl₃); ee = 95% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/ⁱPrOH = 85/15, 0.8 mL/min, t_{minor} = 6.28 min, t_{major} = 7.61 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.34$ (d, J = 8.4 Hz, 2 H); 7.16 – 7.28 (m, 6 H); 7.12 (d, J = 8.0 Hz, 2 H); 6.96 (d, J = 8.0 Hz, 2 H); 6.10 (s, 1 H); 5.74 (s, 1 H); 4.21 (d, J = 10.4 Hz, 1 H); 4.07 (d, J = 10.4 Hz, 1 H); 3.91 (d, J = 10.4 Hz, 1 H); 2.92 (d, J = 10.4 Hz, 1 H); 2.35 (s, 3 H); 2.32 (s, 3 H); 1.16 (s, 9 H); 0.72 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.7$, 166.6, 143.2, 139.1, 137.5, 132.8, 131.4, 131.04, 130.96, 129.1, 128.4, 128.2, 126.4, 124.4, 91.8, 87.4, 77.4, 76.3, 75.9, 31.6, 30.9, 26.8, 26.1, 21.4, 21.1 ppm. IR (neat) ν/cm^{-1} 2979, 2949, 2870, 1760, 1736, 1597, 1518, 1478, 1422, 1368, 1343, 1235, 1208, 1158, 1088, 1045, 1037, 1010, 972, 939, 928. HRMS (ESI): C₃₅H₄₂BrNNaO₇S [M+Na]⁺ calcd: 722.1758, found: 722.1703.

8. (2*S*,5*R*)-dineopentyl 2-(3-bromophenyl)-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3mc).



The reaction of 1m (174.2 mg, 0.3 mmol), 2c (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 38 hours to afford **3mc** (176.7 mg) in 84% yield, white solid. m.p. $167 - 171 \text{ °C}; [\alpha]_{20}^{D} = -64.2$ (c = 1.0, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 6.91 min, t_{major} = 9.13 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.53$ (s, 1 H); 7.43 (d, J = 7.6 Hz, 1 H); 7.36 (d, J = 8.0 Hz, 1 H); 7.18 – 7.30 (m, 4 H); 7.13 (d, J = 8.0 Hz, 2 H); 7.05 (t, J = 8.0Hz, 1 H); 6.96 (d, J = 8.0 Hz, 2 H); 6.08 (s, 1 H); 5.73 (s, 1 H); 4.21 (d, J = 10.4 Hz, 1 H); 4.08 (d, *J* = 10.4 Hz, 1 H); 3.92 (d, *J* = 10.4 Hz, 1 H); 2.95 (d, *J* = 10.4 Hz, 1 H); 2.34 (s, 3 H); 2.32 (s, 3 H); 1.16 (s, 9 H); 0.73 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.8, 166.5, 143.3, 139.1, 137.3, 135.8, 133.0, 132.8, 131.1, 129.3, 129.1, 128.6,$ 128.5, 128.1, 126.5, 122.2, 91.7, 87.4, 77.2, 76.3, 75.9, 31.6, 30.9, 26.8, 26.2, 21.5, 21.2 ppm. IR (neat) v/cm⁻¹ 2959, 2884, 2869, 1756, 1735, 1598, 1578, 1518, 1476, 1437, 1367, 1346, 1292, 1263, 1230, 1213, 1157, 1081, 1037, 968, 939, 921, 906. HRMS (ESI): C₃₅H₄₂BrNNaO₇S [M+Na]⁺ calcd: 722.1758, found: 722.1766.

9. (2*S*,5*R*)-dineopentyl 2-(naphthalen-2-yl)-5-(*p*-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (3nc).



The reaction of **1n** (165.5 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018

mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3nc** (188.0 mg) in 93% yield, white solid. m.p. 202 – 205 °C; $[\alpha]_{20}^{D} = -9.4$ (c = 0.5, CHCl₃); ee = 89% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/[/]PrOH = 90/10, 0.8 mL/min, t_{minor} = 9.82 min, t_{major} = 18.09 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.96$ (s, 1 H); 7.75 (t, J = 7.0 Hz, 2 H); 7.44 – 7.53 (m, 4 H); 7.27 (d, J = 8.0 Hz, 2 H); 7.14 (d, J = 8.0 Hz, 2 H); 7.07 (d, J = 8.0 Hz, 2 H); 6.53 (d, J = 8.4 Hz, 2 H); 6.31 (s, 1 H); 5.80 (s, 1 H); 4.24 (d, J = 10.4 Hz, 1 H); 2.33 (s, 3 H); 2.07 (s, 3 H); 1.19 (s, 9 H); 0.75 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.0$, 166.8, 142.6, 139.0, 137.4, 134.3, 132.4, 131.4, 130.9, 130.2, 129.1, 128.4, 128.2, 128.0, 127.7, 127.4, 126.8, 126.6, 126.0, 125.9, 92.7, 87.4, 77.5, 76.2, 75.9, 31.6, 30.9, 26.8, 26.2, 21.18, 21.15 ppm. IR (neat) ν /cm⁻¹ 2987, 2971, 2901, 1752, 1738, 1601, 1477, 1452, 1406, 1379, 1347, 1246, 1179, 1158, 1075, 1067, 1047, 1006, 977, 963. HRMS (ESI): C₃₉H₄₅NNaO₇S [M+Na]⁺ calcd: 694.2809, found: 694.2786.

10. (2*S*,5*R*)-dineopentyl 3-((4-nitrophenyl)sulfonyl)-2-phenyl-5-(*p*-tolyl)oxazolidine-4,4-dicarboxylate (3oc).



The reaction of **1o** (159.8 mg, 0.3 mmol), **2c** (54.1 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 60 hours to afford **3oc** (153.5 mg) in 78% yield, white solid. m.p. $188 - 190 \, ^{\circ}$ C; [α]₂₀^D = -83.5 (*c* = 1.0, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 12.06 min, t_{major} = 15.12 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.91$ (d, J = 8.4 Hz, 2 H); 7.47 (d, J = 7.6 Hz, 2 H); 7.40 (d, J = 8.8 Hz, 2 H); 7.31 (t, J = 7.4 Hz, 1 H); 7.04 – 7.25 (m, 6 H); 6.20 (s, 1 H); 5.77 (s, 1 H); 4.22 (d, J = 10.4 Hz, 1 H); 4.10 (d, J = 10.4 Hz, 1 H); 3.93 (d, J = 10.0 Hz, 1 H); 2.89 (d, J = 10.0 Hz, 1 H); 2.33 (s, 3 H); 1.18 (s, 9 H); 0.72 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.6$, 166.4, 149.2, 145.9, 139.3, 133.2, 130.9, 130.5, 130.1, 129.5, 129.2, 128.1, 126.5, 122.7, 92.7, 87.5, 77.7, 76.6, 76.2, 31.6, 30.9, 26.8, 26.1, 21.2 ppm. IR (neat) ν /cm⁻¹ 2957, 2901, 2867, 1757, 1735, 1607, 1526, 1478, 1464, 1399, 1359, 1314, 1270, 1236, 1217, 1161, 1089, 1075, 1051, 1013, 1001, 963, 927. HRMS (ESI): C₃₄H₄₀N₂NaO₉S [M+Na]⁺ calcd: 675.2347, found: 675.2336.

11. (2*S*,5*R*)-dineopentyl 2-phenyl-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (3fa).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2a** (88.3 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fa** (190.2 mg) in 91% yield, white solid. m.p. 135 – 138 °C; $[\alpha]_{20}^{D} = -35.6$ (c = 1.0, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel ADH, *n*-hexane/^{*i*}PrOH = 80/20, 0.8 mL/min, t_{minor} = 6.55 min, t_{major} = 5.80 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.50$ (d, J = 7.2 Hz, 2 H); 7.28 – 7.37 (m, 1 H); 7.02 – 7.23 (m, 4 H); 6.90 (d, J = 8.4 Hz, 2 H); 6.56 (s, 2 H); 6.20 (s, 1 H); 5.75 (s, 1 H); 4.25 (d, J = 10.4 Hz, 1 H); 4.07 (d, J = 10.4 Hz, 1 H); 3.97 (d, J = 10.4 Hz, 1 H); 3.81 (s, 3 H); 3.80 (s, 6 H); 2.98 (d, J = 10.0 Hz, 1 H); 2.29 (s, 3 H); 1.17 (s, 9 H); 0.76 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.8$, 166.5, 153.2, 142.8, 138.3, 137.5, 133.8, 129.9, 129.8, 128.3, 128.1, 127.9, 103.4, 92.8, 87.1, 77.2, 76.3, 76.0, 60.7, 56.0, 31.6, 31.0, 26.7, 26.2, 21.4 ppm. IR (neat) *v*/cm⁻¹ 2958, 2869, 2841, 1760, 1736, 1587, 1499, 1462, 1421, 1398, 1367, 1347, 1325, 1236, 1158, 1104, 1093, 1046, 998, 985, 957, 939, 909. HRMS (ESI): C₃₇H₄₇NNaO₁₀S [M+Na]⁺ calcd: 720.2813, found: 720.2836.

12. (2*S*,5*R*)-dineopentyl 5-(4-methoxyphenyl)-2-phenyl-3-tosyloxazolidine- 4,4-dicarboxylate (3fb).



The reaction of 1f (150.5 mg, 0.3 mmol), 2b (61.3 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fb** (168.4 mg) in 88% yield, white solid. m.p. 136 - 139 °C; $[\alpha]_{20}^{D} = -61.5$ (c = 0.5, CHCl₃); ee = 90% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, $t_{minor} = 8.33$ min, $t_{maior} = 11.32$ min); ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (d, J = 7.6 Hz, 2 H); 7.24 – 7.30 (m, 3 H); 7.08 - 7.20 (m, 4 H); 6.89 (d, J = 8.4 Hz, 2 H); 6.84 (d, J = 8.8 Hz, 2 H); 6.17 (s, 1 H); 5.73 (s, 1 H); 4.21 (d, J = 10.4 Hz, 1 H); 4.08 (d, J = 10.4 Hz, 1 H); 3.93 (d, J = 10.4Hz, 1 H); 3.78 (s, 3 H); 2.96 (d, J = 10.4 Hz, 1 H); 2.29 (s, 3 H); 1.16 (s, 9 H); 0.75 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 166.6, 160.2, 142.7, 137.6, 133.7, 129.9, 129.8, 128.3, 128.1, 128.0, 127.9, 126.3, 113.8, 92.6, 87.2, 77.4, 76.2, 75.9, 55.3, 31.6, 31.0, 26.8, 26.2, 21.4 ppm. IR (neat) v/cm⁻¹ 2958, 2902, 2885, 1763, 1733, 1614, 1599, 1516, 1461, 1397, 1368, 1342, 1306, 1291, 1248, 1224, 1210, 1173, 1157, 1116, 1090, 1077, 1053, 1033, 1009, 972, 926. HRMS (ESI): C35H43NNaO8S $[M+Na]^+$ calcd: 660.2602, found: 660.2634.

13. (2S,5R)-dineopentyl 2,5-diphenyl-3-tosyloxazolidine-4,4-dicarboxylate (3fd).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2d** (95.4 mg, 0.9 mmol) in the presence of 10 mol % Ni(ClO₄)₂·6H₂O (10.97 mg, 0.03 mmol), Bn-Box ligand (13.05 mg, 0.036 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fd** (162.2 mg) in 89% yield, white solid. m.p. 138 – 141 °C; $[\alpha]_{20}^{D} = -52.2$ (c = 1.0, CHCl₃); ee = 90% (chiral HPLC analysis: Chiralcel OZ3, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 5.04 min, t_{major} = 8.63 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49$ (d, J = 7.2 Hz, 2 H); 7.22 – 7.40 (m, 6 H); 7.05 – 7.20 (m, 4 H); 6.89 (d, J = 8.0 Hz, 2 H); 6.19 (s, 1 H); 5.79 (s, 1 H); 4.22 (d, J = 10.4 Hz, 1 H); 2.29 (s, 3 H); 1.17 (s, 9 H); 0.73 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 166.5, 142.7, 137.6, 134.4, 133.7, 129.9, 129.8, 129.1, 128.4, 128.3, 128.2, 127.9, 126.6, 92.8, 87.2, 77.4, 76.3, 75.8, 31.6, 31.0, 26.8, 26.2, 21.4 ppm. IR (neat) ν/cm^{-1} 2973, 2902, 1741, 1598, 1496, 1463, 1400, 1370, 1349, 1333, 1293, 1241, 1214, 1159, 1094, 1081, 1067, 1051, 1039, 1007, 976, 961, 940, 926. HRMS (ESI): C₃₄H₄₁NNaO₇S [M+Na]⁺ calcd: 630.2496, found: 630.2495.

14. (2S,5R)-dineopentyl5-(3-methoxyphenyl)-2-phenyl-3-tosyloxazolidine-4,4-
dicarboxylate (3fe).



The reaction of 1f (150.5 mg, 0.3 mmol), 2e (61.3 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 24 hours to afford **3fe** (130.2 mg) in 68% yield, white solid. m.p. 118 - 121 °C; $[\alpha]_{20}^{D} = -39.2$ (c = 0.5, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 8.43 min, t_{major} = 9.83min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49$ (d, J = 7.2 Hz, 2 H); 7.20 - 7.38 (m, 2 H); 7.07 - 7.20 (m, 4 H); 6.73 - 7.07 (m, 5 H); 6.18 (s, 1 H); 5.77 (s, 1 H); 4.22 (d, J =10.4 Hz, 1 H); 4.08 (d, J = 10.4 Hz, 1 H); 3.94 (d, J = 10.4 Hz, 1 H); 3.75 (s, 3 H); 2.92 (d, J = 10.4 Hz, 1 H); 2.29 (s, 3 H); 1.16 (s, 9 H); 0.74 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.8$, 166.5, 159.6, 142.7, 137.6, 135.9, 133.7, 129.9, 129.4, 128.3, 128.2, 127.9, 118.8, 114.6, 112.2, 92.8, 87.0, 77.4, 76.3, 75.9, 55.2, 31.6, 31.0, 26.8, 26.2, 21.4 ppm. IR (neat) v/cm⁻¹ 2956, 2938, 1759, 1739, 1599, 1494, 1467, 1370, 1357, 1281, 1260, 1238, 1214, 1163, 1155, 1096, 1086, 1072, 1035, 1003, 976, 963, 931, 921, 911. HRMS (ESI): C₃₅H₄₃NNaO₈S [M+Na]⁺ calcd: 660.2602, found: 660.2634.

15. (2S,5R)-dineopentyl5-(4-isopropylphenyl)-2-phenyl-3-tosyloxazolidine-4,4-
dicarboxylate (3ff).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2f** (66.7 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3ff** (169.8 mg) in 87% yield, white solid. m.p. 102 - 105 °C; $[\alpha]_{20}^{D} = -48.0$ (c = 1.0, CHCl₃); ee = 94% (chiral HPLC analysis: Chiralcel ADH, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 4.59 min, t_{major} = 7.57 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.58$ (d, J = 6.8 Hz, 2 H); 7.30 - 7.42 (m, 3 H); 7.12 - 7.31 (m, 6 H); 6.97 (d, J = 8.0 Hz, 2 H); 6.28 (s, 1 H); 5.85 (s, 1 H); 4.32 (d, J= 10.4 Hz, 1 H); 4.17 (d, J = 10.4 Hz, 1 H); 4.00 (d, J = 10.4 Hz, 1 H); 2.92 - 3.08 (m, 1 H); 2.90 (d, J = 10.4 Hz, 1 H); 2.37 (s, 3 H); 1.30 (d, J = 6.8 Hz, 6 H); 1.26 (s, 9 H); 0.80 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.9, 166.6, 149.8, 142.6, 137.6, 133.8, 131.8, 129.9, 129.8, 128.21, 128.16, 127.8, 126.7, 126.4, 92.7, 87.3, 77.4, 76.2, 75.8, 33.9, 31.6, 30.9, 26.8, 26.2, 23.9, 23.8, 21.4 ppm. IR (neat) v/cm⁻¹ 2960, 2886, 2870, 1749, 1732, 1598, 1515, 1462, 1396, 1368, 1349, 1279, 1259, 1236, 1212, 1156, 1079, 1053, 1032, 965, 940, 923, 876, 832. HRMS (ESI): C₃₇H₄₇NNaO₇S [M+Na]⁺ calcd: 672.2965, found: 672.2973.

16. (2S,5R)-dineopentyl5-(4-bromophenyl)-2-phenyl-3-tosyloxazolidine-4,4-di-
carboxylate (3fg).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2g** (166.5 mg, 0.9 mmol) in the presence of 10 mol % Ni(ClO₄)₂6H₂O (10.97 mg, 0.03 mmol), Bn-Box ligand (13.05 mg, 0.036 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 24 hours to afford **3fg** (139.2 mg) in 68% yield, white solid. m.p. 152 – 155 °C; $[\alpha]_{20}^{D}$ = -42.9 (*c* = 0.5, CHCl₃); ee = 90% (chiral HPLC analysis: Chiralcel OZ3, *n*-hexane/ⁱPrOH = 85/15, 0.4 mL/min, t_{minor} = 9.89 min, t_{major} = 15.37 min); ¹H NMR (400 MHz, CDCl₃): δ = 7.41 – 7.50 (m, 4 H); 7.19 – 7.37 (m, 3 H); 7.04 – 7.18 (m, 4 H); 6.90 (d, *J* = 8.0 Hz, 2 H); 6.15 (s, 1 H); 5.73 (s, 1 H); 4.20 (d, *J* = 10.4 Hz, 1 H); 4.10 (d, *J* = 10.4 Hz, 1 H); 3.92 (d, *J* = 10.4 Hz, 1 H); 3.00 (d, *J* = 10.4 Hz, 1 H); 2.29 (s, 3 H); 1.15 (s, 9 H); 0.76 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.9, 166.4, 142.9, 137.5, 133.51, 133.47, 131.5, 130.0, 129.8, 128.4, 128.3, 128.2, 128.0, 123.2, 92.8, 86.5, 77.3, 76.5, 76.0, 31.6, 31.0, 26.8, 26.2, 21.4 ppm. IR (neat) ν/cm^{-1} 2960, 2883, 2871, 1742, 1599, 1578, 1491, 1463, 1396, 1370, 1348, 1331, 1291, 1255, 1217, 1156, 1095, 1072, 1048, 1005, 979, 963, 927. HRMS (ESI): C₃₄H₄₀BrNNaO₇S [M+Na]⁺ calcd: 708.1601, found: 708.1625.

17. (2*S*,5*R*)-dineopentyl 5-(4-iodophenyl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (3fh).



S23

The reaction of **1f** (150.5 mg, 0.3 mmol), **2h** (208.8 mg, 0.9 mmol) in the presence of 10 mol % Ni(ClO₄)₂·6H₂O (10.97 mg, 0.03 mmol), Bn-Box ligand (13.05 mg, 0.036 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fh** (171.9 mg) in 78% yield, white solid. m.p. 129 – 131 °C; $[\alpha]_{20}^{D}$ = -61.3 (*c* = 1.0, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/ⁱPrOH = 90/10, 0.8 mL/min, t_{minor} = 7.94 min, t_{major} = 10.01 min); ¹H NMR (400 MHz, CDCl₃): δ = 7.66 (d, *J* = 8.4 Hz, 2 H); 7.45 (d, *J* = 7.2 Hz, 2 H); 7.26 – 7.34 (m, 1 H); 7.08 – 7.22 (m, 6 H); 6.90 (d, *J* = 8.0 Hz, 2 H); 6.15 (s, 1 H); 5.71 (s, 1 H); 4.20 (d, *J* = 10.4 Hz, 1 H); 4.09 (d, *J* = 10.4 Hz, 1 H); 3.92 (d, *J* = 10.4 Hz, 1 H); 3.00 (d, *J* = 10.4 Hz, 1 H); 2.30 (s, 3 H); 1.15 (s, 9 H); 0.76 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.9, 166.4, 142.8, 137.5, 134.2, 133.5, 130.0, 129.8, 129.0, 128.40, 128.35, 128.2, 127.9, 125.3, 95.0, 92.8, 86.5, 76.5, 76.1, 31.6, 31.0, 26.8, 26.2, 21.4 ppm. IR (neat) ν /cm⁻¹ 2961, 2907, 2889, 1743, 1599, 1486, 1461, 1394, 1369, 1348, 1294, 1256, 1240, 1217, 1155, 1100, 1059, 1039, 1004, 979, 958, 941, 927. HRMS (ESI): C₃4H₄₀INNaO₇S [M+Na]⁺ calcd: 756.1462, found: 756.1438.

18. (2S,5S)-dineopentyl5-(furan-2-yl)-2-phenyl-3-tosyloxazolidine-4,4-dicar-
boxylate (3fi).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2i** (45.2 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fi** (167.7 mg) in 94% yield, white solid. m.p. 108 - 111 °C; $[\alpha]_{20}^{D} = -42.7$ (c = 1.0, CHCl₃); ee = 88% (chiral HPLC analysis: Chiralcel OZ3, *n*-hexane/ⁱPrOH = 85/15, 0.8 mL/min, $t_{minor} = 6.88$ min, $t_{major} = 8.34$ min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.36 - 7.62$ (m, 3 H); 7.22 - 7.36 (m, 1 H); 7.19 (d, J = 8.0 Hz, 2 H); 7.13 (t, J = 7.6 Hz, 2 H); 6.91 (d, J = 8.0 Hz, 2 H); 6.38 - 6.48 (m, 1 H); 6.27 - 6.38 (m, 1 H); 6.15 (s, 1 H); 5.83 (s, 1 H); 4.19 (d, J = 10.4 Hz, 1 H); 4.14 (d, J = 10.4 Hz, 1 H); 4.08 (d, J = 10.4 Hz, 1 H); 3.25 (d, J = 10.4 Hz, 1 H); 2.29 (s, 3 H); 1.13 (s, 9 H); 0.87 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.7$, 166.2, 147.7, 143.4, 142.8, 137.5, 133.8, 129.9, 129.8, 128.3, 127.9, 110.6, 109.9, 92.9, 81.3, 77.2, 76.3, 76.2, 31.6, 31.3, 26.7, 26.3, 21.4 ppm. IR (neat) ν/cm^{-1} 2885, 1742, 1703, 1598, 1505, 1478, 1414, 1401, 1368, 1353, 1332, 1238, 1215, 1160, 1095, 1083, 1052, 1037, 1012, 984, 962, 954, 917. HRMS (ESI): C₃₂H₃₉NNaO₈S [M+Na]⁺ calcd: 620.2289, found: 620.2298.

19. (2S,5R)-dineopentyl5-(naphthalen-1-yl)-2-phenyl-3-tosyloxazolidine-4,4-di-
carboxylate (3fj).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2j** (140.6 mg, 0.9 mmol) in the presence of 10 mol % Ni(ClO₄)₂ 6H₂O (10.97 mg, 0.03 mmol), Bn-Box ligand (13.05 mg, 0.036 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 18 hours to afford **3fj** (150.2 mg) in 76% yield, white solid. m.p. 168 – 171 °C; $[\alpha]_{20}^{D}$ = -80.4 (*c* = 1.0, CHCl₃); ee = 86% (chiral HPLC analysis: Chiralcel ADH, *n*-hexane/^{*i*}PrOH = 90/10, 0.5 mL/min, t_{minor} = 10.10 min, t_{major} = 8.85 min); ¹H NMR (400 MHz, CDCl₃): δ = 7.76 – 7.90 (m, 3 H); 7.65 (d, *J* = 7.2 Hz, 1 H); 7.36 – 7.62 (m, 5 H); 7.30 (t, *J* = 7.4 Hz, 1 H); 7.08 – 7.22 (m, 4 H); 6.89 (d, *J* = 8.4 Hz, 2 H); 6.64 (s, 1 H); 6.33 (s, 1 H); 4.34 (d, *J* = 10.4 Hz, 1 H); 4.11 (d, *J* = 10.4 Hz, 1 H); 3.85 (d, *J* = 10.4 Hz, 1 H); 2.29 (s, 3 H); 2.24 (d, *J* = 10.4 Hz, 1 H); 1.25 (s, 9 H); 0.35 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 166.6, 142.8, 137.5, 133.9, 133.7, 131.10, 131.05, 130.0, 129.9, 129.5, 128.9, 128.3, 128.2, 128.0, 126.7, 125.8, 125.1, 124.4, 122.4, 92.8, 84.1, 77.6, 76.8, 75.6, 31.5, 30.5, 26.9, 25.7, 21.4 ppm. IR (neat) ν/cm^{-1} 2958, 2926, 2869, 1963, 1733, 1598, 1513, 1477, 1462, 1400, 1366, 1346, 1324, 1293, 1262, 1227, 1156, 1090, 1080, 1051, 1037, 1008, 962, 921. HRMS (ESI): C₃₈H₄₃NNaO₇S [M+Na]⁺ calcd: 680.2652, found: 680.2639.

20. (2*S*,5*R*)-dineopentyl 2-phenyl-5-((*E*)-styryl)-3-tosyloxazolidine-4,4-dicarboxylate (3fk).



The reaction of 1f (150.5 mg, 0.3 mmol), 2k (59.5 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford 3fk (176.8 mg) in 93% yield, white solid. m.p. 114 - 116 °C; $[\alpha]_{20}^{D} = -34.9$ (c = 1.0, CHCl₃); ee = 85% (chiral HPLC analysis: Chiralcel OZ3, *n*-hexane/ⁱPrOH = 85/15, 0.8 mL/min, t_{minor} = 6.60 min, t_{maior} = 14.35 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.22 - 7.48$ (m, 10 H); 7.13 (t, J = 7.6 Hz, 2 H); 6.94 (d, J = 8.0 Hz, 2 H); 6.71 (d, J = 16.0 Hz, 2 H); 6.30 (dd, $J_1 = 16.0$ Hz, $J_2 =$ 7.2 Hz, 1 H); 6.04 (s, 1 H); 5.29 (d, J = 7.6 Hz, 1 H); 4.11 (s, 2 H); 4.07 (d, J = 10.4Hz, 1 H); 3.82 (d, J = 10.4 Hz, 1 H); 2.31 (s, 3 H); 1.10 (s, 9 H); 0.90 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.0, 166.7, 142.9, 137.5, 135.6, 134.9, 133.9, 129.8, 129.6, 128.5, 128.42, 128.39, 128.3, 127.9, 126.9, 122.0, 92.9, 86.6, 76.8, 76.3, 76.2, 31.5, 31.4, 26.6, 26.4, 21.4 ppm. IR (neat) v/cm⁻¹ 3065, 3030, 2957, 2887, 2869, 1748, 1728, 1684, 1600, 1478, 1460, 1398, 1369, 1342, 1274, 1249, 1233, 1156, 1093, 1065, 1034, 1004, 962, 939, 911. HRMS (ESI): C₃₆H₄₃NNaO₇S [M+Na]⁺ calcd: 656.2652, found: 656.2655.

21. (2S,5R)-dineopentyl 2-phenyl-5-((E)-1-phenylprop-1-en-2-yl)-3- tosyloxazo-

lidine-4,4-dicarboxylate (3fl).



The reaction of 1f (150.5 mg, 0.3 mmol), 2l (65.8 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 18 hours to afford **3fl** (158.4 mg) in 82% yield, white solid. m.p. 137 - 140 °C; $[\alpha]_{20}^{D} = -70.2$ (c = 0.5, CHCl₃); ee = 92% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 95/5, 0.8 mL/min, $t_{minor} = 10.41$ min, $t_{maior} = 11.49$ min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.43$ (d, J = 7.2 Hz, 2 H); 7.28 - 7.36 (m, 3 H); 7.18 - 7.26 (m, 3 H); 7.12 - 7.18 (m, 4 H); 6.92 (d, J = 8.0 Hz, 2 H); 6.65 (s, 1 H); 6.08 (s, 1 H); 5.30 (s, 1 H); 4.28 (d, J = 10.4 Hz, 1 H); 4.15 (d, J = 10.4 Hz, 1 H); 4.03(d, J = 10.4 Hz, 1 H); 3.55 (d, J = 10.4 Hz, 1 H); 2.30 (s, 3 H); 1.92 (s, 3 H); 1.13 (s, 9 H); 0.93 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.2$, 166.8, 142.8, 137.4, 136.5, 134.0, 130.9, 129.9, 129.8, 129.0, 128.3, 128.2, 128.1, 127.9, 127.8, 126.9, 92.6, 89.4, 76.4, 76.1, 31.5, 31.4, 26.7, 26.5, 21.4, 15.8 ppm. IR (neat) v/cm⁻¹ 2959, 2916, 2884, 1758, 1740, 1600, 1495, 1473, 1447, 1411, 1398, 1376, 1366, 1344, 1326, 1306, 1292, 1230, 1156, 1087, 1058, 1037, 1026, 1010, 986, 971, 921, 902. HRMS (ESI): C₃₇H₄₅NNaO₇S [M+Na]⁺ calcd: 670.2809, found: 670.2820.

22. (2*S*,5*R*)-dineopentyl 2-phenyl-5-((*E*)-prop-1-en-1-yl)-3-tosyloxazolidine-4,4dicarboxylate (3fm).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2m** (31.5 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 12 hours to afford **3fm** (168.8 mg) in 99% yield, white solid. m.p. $80 - 83 \, {}^{\circ}$ C; $[\alpha]_{20}^{D} = -26.6$ (c = 0.5, CHCl₃); ee = 69% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 85/15, 0.8 mL/min, t_{minor} = 12.63 min, t_{major} = 11.35 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.30$ (d, J = 7.2 Hz, 2 H); 7.15 – 7.26 (m, 3 H); 7.08 (t, J = 7.6 Hz, 2 H); 6.90 (d, J = 8.0 Hz, 2 H); 5.99 (s, 1 H); 5.82 – 5.96 (m, 1 H); 5.54 – 5.76 (m, 1 H); 5.08 (d, J = 8.0 Hz, 1 H); 4.00 – 4.13 (m, 3 H); 3.92 (d, J = 10.4 Hz, 1 H); 2.28 (s, 3 H); 1.68 – 1.88 (m, 3 H); 1.08 (s, 9 H); 1.02 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 166.8, 142.7, 137.6, 134.0, 132.9, 129.7, 129.5, 128.3, 128.2, 127.8, 124.4, 92.7, 86.9, 76.6, 76.2, 31.5, 31.4, 26.6, 26.5, 21.4, 17.9 ppm. IR (neat) ν /cm⁻¹ 2960, 2870, 1743, 1677, 1598, 1477, 1463, 1403, 1369, 1345, 1306, 1261, 1237, 1217, 1156, 1093, 1051, 1032, 1015, 994, 968, 929, 902. HRMS (ESI): C₃₁H₄₁NNaO₇S [M+Na]⁺ calcd: 594.2496, found: 594.2528.

23. (2*S*,5*R*)-dineopentyl 5-((*E*)-but-2-en-2-yl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (3fn).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2n** (37.9 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018

mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 20 hours to afford **3fn** (160.2 mg) in 91% yield, white solid. m.p. $108 - 111 \, {}^{\circ}$ C; $[\alpha]_{20}{}^{D} = -30.6$ (c = 1.0, CHCl₃); ee = 87% (chiral HPLC analysis: Chiralcel IC, *n*-hexane/^{*i*}PrOH = 95/5, 0.8 mL/min, t_{minor} = 12.01 min, t_{major} = 12.88 min); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.38$ (d, J = 7.6 Hz, 2 H); 7.23 – 7.40 (m, 1 H); 7.02 – 7.20 (m, 4 H); 6.88 (d, J = 8.4 Hz, 2 H); 6.04 (s, 1 H); 5.69 (q, J = 6.4 Hz, 1 H); 5.13 (s, 1 H); 4.22 (d, J = 10.4 Hz, 1 H); 4.13 (d, J = 10.4 Hz, 1 H); 3.98 (d, J = 10.4 Hz, 1 H); 3.61 (d, J = 10.4 Hz, 1 H); 2.28 (s, 3 H); 1.64 (s, 3 H); 1.61 (d, J = 7.2 Hz, 3 H); 1.11 (s, 9 H); 1.02 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.1$, 142.7, 137.6, 134.1, 129.79, 129.76, 129.1, 128.3, 128.2, 127.8, 123.7, 92.4, 89.6, 76.5, 76.3, 76.2, 31.4, 26.7, 26.5, 21.4, 13.5, 13.2 ppm. IR (neat) ν/cm^{-1} 2961, 2869, 1752, 1738, 1599, 1477, 1461, 1403, 1368, 1344, 1262, 1237, 1210, 1156, 1094, 1052, 1028, 1008, 984, 959, 940. HRMS (ESI): C₃₂H₄₃NNaO₇S [M+Na]⁺ calcd: 608.2652, found: 608.2672.

24. (2*S*,5*R*)-dineopentyl 5-cyclohexenyl-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (3fo).



The reaction of **1f** (150.5 mg, 0.3 mmol), **2o** (49.6 mg, 0.45 mmol) in the presence of 5 mol % Ni(ClO₄)₂·6H₂O (5.48 mg, 0.015 mmol), Bn-Box ligand (6.52 mg, 0.018 mmol), 120 mg of activated 4Å M.S. and using toluene (3 mL) as the solvent was carried out at r.t. for 18 hours to afford **3fo** (145.0 mg) in 79% yield, white solid. m.p. $130 - 133 \, {}^{\circ}$ C; [α]₂₀^D = -41.2 (c = 0.5, CHCl₃); ee = 85% (chiral HPLC analysis: Chiralcel OZ3, *n*-hexane/^{*i*}PrOH = 95/5, 0.8 mL/min, t_{minor} = 6.82 min, t_{major} = 11.89 min); ¹H NMR (400 MHz, CDCl₃): δ = 7.39 (d, J = 7.2 Hz, 2 H); 7.25 – 7.33 (m, 1 H); 7.04 – 7.20 (m, 4 H); 6.90 (d, J = 8.4 Hz, 2 H); 6.01 (s, 1 H); 5.83 – 5.90 (m, 1 H); 5.06 (s, 1 H); 4.40 (d, J = 10.4 Hz, 1 H); 4.11 (d, J =10.4 Hz, 1 H); 4.00 (d, J = 10.4 Hz, 1 H); 3.57 (d, J = 10.4 Hz, 1 H); 2.29 (s, 3 H); 1.84 – 2.16 (m, 4 H); 1.50 – 1.70 (m, 4 H); 1.11 (s, 9 H); 1.04 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.2$, 166.7, 142.7, 137.5, 134.0, 131.4, 129.8, 128.3, 128.1, 127.8, 125.9, 92.3, 88.4, 76.4, 76.1, 75.6, 31.8, 31.4, 26.7, 26.5, 25.6, 24.8, 22.2, 22.0, 21.4 ppm. IR (neat) ν/cm^{-1} 2948, 2900, 1757, 1737, 1598, 1462, 1401, 1369, 1351, 1327, 1308, 1291, 1235, 1214, 1156, 1095, 1040, 1004, 980, 959, 916. HRMS (ESI): C₃₄H₄₅NNaO₇S [M+Na]⁺ calcd: 634.2809, found: 634.2882.

HPLC results

3fc HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fc**



| I | 序号 | 保留时间 | Li, | 肇名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|---|-----|-------|------|-----|---------|---------|--------|-------|-----|
| | | min | | | mAU | mAU*min | % | | |
| ſ | 1 | 7.47 | n.a. | | 81.519 | 22.987 | 49.74 | n.a. | BMB |
| | 2 | 10.07 | n.a. | | 53.559 | 23.223 | 50.26 | n.a. | BMB |
| | 总和: | | | | 135.078 | 46.210 | 100.00 | 0.000 | |

Enantioenriched 3fc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 7.47 | n.a. | 24.529 | 6.871 | 3.56 | n.a. | BMB |
| 2 | 9.95 | n.a. | 416.867 | 185.866 | 96.44 | n.a. | BMB |
| 总和: | | | 441.397 | 192.737 | 100.00 | 0.000 | |

3gc HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3gc**



| 序号 | 保留时间 | | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|-----|---------|---------|--------|-------|------|
| | min | | | mAU | mAU*min | % | | |
| 1 | 7.35 | n.a. | | 8.500 | 1.447 | 1.11 | n.a. | Ru |
| 2 | 7.73 | n.a. | | 201.191 | 63.976 | 48.97 | n.a. | BMB |
| 3 | 11.34 | n.a. | | 123.264 | 65.211 | 49.92 | n.a. | BMB* |
| 总和: | | | | 332.955 | 130.635 | 100.00 | 0.000 | |

Enantioenriched 3gc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 7.55 | n.a. | 46.936 | 10.205 | 5.49 | n.a. | BMB |
| 2 | 11.05 | n.a. | 221.574 | 175.690 | 94.51 | n.a. | BMB |
| 总和: | | | 268.510 | 185.895 | 100.00 | 0.000 | |

3hc HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3hc**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.11 | n.a. | 656.421 | 79.440 | 49.30 | n.a. | BMB |
| 2 | 11.83 | n.a. | 142.592 | 81.684 | 50.70 | n.a. | BMB |
| 总和: | | | 799.013 | 161.124 | 100.00 | 0.000 | |

Enantioenriched 3hc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.34 | n.a. | 19.649 | 6.478 | 4.17 | n.a. | BMB |
| 2 | 11.69 | n.a. | 300.696 | 149.058 | 95.83 | n.a. | BMB |
| 总和: | | | 320.345 | 155.536 | 100.00 | 0.000 | |

3ic HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3ic**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.09 | n.a. | 280.973 | 51.860 | 49.53 | n.a. | BMB |
| 2 | 13.46 | n.a. | 82.024 | 52.849 | 50.47 | n.a. | BMB* |
| 总和: | | | 362.998 | 104.709 | 100.00 | 0.000 | |

Enantioenriched 3ic



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.25 | n.a. | 21.815 | 6.602 | 4.15 | n.a. | BMB |
| 2 | 13.34 | n.a. | 247.066 | 152.448 | 95.85 | n.a. | BMB |
| 总和: | | | 268.881 | 159.049 | 100.00 | 0.000 | |

3jc HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3jc**



3kc HPLC using an OZ3 (*n*-Hexane/*i*PrOH=95/05, flow rate 0.8 ml/min) Racemic **3kc**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 5.77 | n.a. | 102.977 | 53.923 | 49.91 | n.a. | BMB |
| 2 | 12.17 | n.a. | 34.213 | 54.110 | 50.09 | n.a. | BMB |
| 总和: | | | 137.190 | 108.033 | 100.00 | 0.000 | |

Enantioenriched 3kc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 5.77 | n.a. | 42.707 | 21.732 | 3.14 | n.a. | BMB |
| 2 | 11.67 | n.a. | 408.331 | 670.202 | 96.86 | n.a. | BMB* |
| 总和: | | | 451.037 | 691.934 | 100.00 | 0.000 | |
3lc HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3lc**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.27 | n.a. | 94.458 | 23.275 | 49.83 | n.a. | BMB |
| 2 | 7.62 | n.a. | 81.725 | 23.435 | 50.17 | n.a. | BMB* |
| 总和: | | | 176.183 | 46.710 | 100.00 | 0.000 | |

Enantioenriched 3lc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.28 | n.a. | 15.647 | 3.766 | 2.68 | n.a. | BMB |
| 2 | 7.61 | n.a. | 454.907 | 136.778 | 97.32 | n.a. | BMB |
| 总和: | | | 470.554 | 140.544 | 100.00 | 0.000 | |

55.0_WUX #386 [由dell修改] mAU UV VIS 1 WVL:254 nm 7-72-2IC85150830 1 - 6.873 40.0-30.0-2 - 9.240 20.0 10.0--5.0 2.0 4.0 6.0 8.0 10.0 12.0 14.0 16.0 18.9

| 3mc HPLC using an IC (<i>n</i> -Hexane/ <i>i</i> PrOH=85/15, flow rate 0.8 ml/min) |
|--|
| Racemic 3mc |

| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|--------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.87 | n.a. | 48.081 | 11.612 | 50.77 | n.a. | BMB* |
| 2 | 9.24 | n.a. | 22.375 | 11.260 | 49.23 | n.a. | BMB* |
| 总和: | | | 70.456 | 22.873 | 100.00 | 0.000 | |

Enantioenriched 3mc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.91 | n.a. | 32.321 | 8.709 | 4.07 | n.a. | BMB |
| 2 | 9.13 | n.a. | 478.816 | 205.228 | 95.93 | n.a. | BMB |
| 总和: | | | 511.137 | 213.937 | 100.00 | 0.000 | |

3nc HPLC using an IC (*n*-Hexane/*i*PrOH=90/10, flow rate 0.8 ml/min) Racemic **3nc**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 9.85 | n.a. | 85.946 | 54.658 | 49.97 | n.a. | BMB |
| 2 | 18.31 | n.a. | 58.317 | 54.717 | 50.03 | n.a. | BMB |
| 总和: | | | 144.263 | 109.375 | 100.00 | 0.000 | |

Enantioenriched 3nc



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 9.82 | n.a. | 42.732 | 17.184 | 5.55 | n.a. | BMB* |
| 2 | 18.09 | n.a. | 388.248 | 292.681 | 94.45 | n.a. | BMB |
| 总和: | | | 430.981 | 309.865 | 100.00 | 0.000 | |

3oc HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3oc**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 12.03 | n.a. | 337.149 | 157.316 | 50.30 | n.a. | BMB* |
| 2 | 15.19 | n.a. | 232.032 | 155.428 | 49.70 | n.a. | BMB |
| 总和: | | | 569.181 | 312.744 | 100.00 | 0.000 | |

Enantioenriched 3oc





3fa HPLC using an ADH (*n*-Hexane/*i*PrOH=80/20, flow rate 0.8 ml/min) Racemic **3fa**

| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|--------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 5.79 | n.a. | 36.746 | 9.879 | 50.06 | n.a. | BMb* |
| 2 | 6.54 | n.a. | 32.667 | 9.854 | 49.94 | n.a. | bMB* |
| 总和: | | | 69.412 | 19.733 | 100.00 | 0.000 | |

Enantioenriched 3fa



| 序号 | 保留时间 | 峰名和 | r 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|----------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 5.80 | n.a. | 1057.830 | 214.525 | 95.90 | n.a. | BM * |
| 2 | 6.55 | n.a. | 28.348 | 9.166 | 4.10 | n.a. | MB* |
| 总和: | | | 1086.178 | 223.691 | 100.00 | 0.000 | |

3fb HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fb**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.32 | n.a. | 72.186 | 23.156 | 49.65 | n.a. | BMB |
| 2 | 11.41 | n.a. | 56.092 | 23.478 | 50.35 | n.a. | BMB |
| 总和: | | | 128.277 | 46.634 | 100.00 | 0.000 | |

Enantioenriched 3fb



| | 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|---|-----|-------|------|---------|---------|--------|-------|------|
| | | min | | mAU | mAU*min | % | | |
| I | 1 | 8.33 | n.a. | 14.930 | 4.780 | 5.12 | n.a. | BMB* |
| | 2 | 11.32 | n.a. | 212.385 | 88.634 | 94.88 | n.a. | BMB |
| | 总和: | | | 227.315 | 93.413 | 100.00 | 0.000 | |

3fd HPLC using an OZ3 (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fd**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 5.04 | n.a. | 112.708 | 34.352 | 50.17 | n.a. | BMB |
| 2 | 8.73 | n.a. | 25.214 | 34.121 | 49.83 | n.a. | BMB |
| 总和: | | | 137.922 | 68.473 | 100.00 | 0.000 | |

Enantioenriched 3fd



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 5.04 | n.a. | 24.650 | 7.295 | 5.12 | n.a. | BMB |
| 2 | 8.63 | n.a. | 96.911 | 135.255 | 94.88 | n.a. | BMB |
| 总和: | | | 121.561 | 142.549 | 100.00 | 0.000 | |



3fe HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fe**

| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.43 | n.a. | 53.799 | 16.475 | 4.10 | n.a. | BMB |
| 2 | 9.83 | n.a. | 886.489 | 385.665 | 95.90 | n.a. | BMB* |
| 总和: | | | 940.288 | 402.140 | 100.00 | 0.000 | |

3ff HPLC using an ADH (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3ff**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 4.57 | n.a. | 454.835 | 121.881 | 49.57 | n.a. | BMB* |
| 2 | 7.69 | n.a. | 104.599 | 124.005 | 50.43 | n.a. | BMB |
| 总和: | | | 559.435 | 245.886 | 100.00 | 0.000 | |

Enantioenriched 3ff



Racemic **3fg**



| 戶亏 | 保留时间 | 嘽名栁 | 峰向 | 嘽囬枳 | 相对噻囬松 | 杆茚重 | 矢空 | |
|-----|-------|------|--------|---------|--------|-------|-----|--|
| | min | | mAU | mAU*min | % | | | |
| 1 | 9.89 | n.a. | 36.121 | 19.964 | 45.18 | n.a. | BMB | |
| 2 | 14.17 | n.a. | 11.816 | 4.474 | 10.13 | n.a. | BM | |
| 3 | 15.47 | n.a. | 10.488 | 19.747 | 44.69 | n.a. | MB | |
| 总和: | | | 58.425 | 44.186 | 100.00 | 0.000 | | |

Enantioenriched 3fg



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 9.89 | n.a. | 19.027 | 10.459 | 5.14 | n.a. | BMB |
| 2 | 15.37 | n.a. | 101.182 | 193.140 | 94.86 | n.a. | BMB |
| 总和: | | | 120.208 | 203.599 | 100.00 | 0.000 | |

3fh HPLC using an IC (*n*-Hexane/*i*PrOH=90/10, flow rate 0.8 ml/min) Racemic **3fh**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 7.95 | n.a. | 419.300 | 130.090 | 50.64 | n.a. | BMB* |
| 2 | 10.11 | n.a. | 335.580 | 126.823 | 49.36 | n.a. | BMB* |
| 总和: | | | 754.880 | 256.913 | 100.00 | 0.000 | |

Enantioenriched 3fh



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 7.94 | n.a. | 11.910 | 3.887 | 3.97 | n.a. | BMB |
| 2 | 10.01 | n.a. | 254.307 | 93.926 | 96.03 | n.a. | BMB* |
| 总和: | | | 266.217 | 97.813 | 100.00 | 0.000 | |

3fi HPLC using an OZ3 (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fi**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|----|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.83 | n.a. | 345.397 | 182.877 | 49.96 | n.a. | BM |
| 2 | 8.57 | n.a. | 188.268 | 183.184 | 50.04 | n.a. | MB |
| 总和: | | | 533.665 | 366.061 | 100.00 | 0.000 | |

Enantioenriched 3fi



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.88 | n.a. | 68.424 | 33.384 | 5.80 | n.a. | Ru |
| 2 | 8.34 | n.a. | 552.554 | 542.298 | 94.20 | n.a. | BMB |
| 总和: | | | 620.978 | 575.682 | 100.00 | 0.000 | |

3fj HPLC using an ADH (*n*-Hexane/*i*PrOH=90/10, flow rate 0.5 ml/min) Racemic **3fj**



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|----|
| | min | | mAU | mAU*min | % | | |
| 1 | 8.74 | n.a. | 260.552 | 122.251 | 48.14 | n.a. | BM |
| 2 | 9.84 | n.a. | 267.552 | 118.524 | 46.68 | n.a. | M |
| 3 | 10.71 | n.a. | 14.155 | 6.932 | 2.73 | n.a. | M |
| 4 | 11.52 | n.a. | 11.922 | 6.226 | 2.45 | n.a. | MB |
| 总和: | | | 554.181 | 253.933 | 100.00 | 0.000 | |

Enantioenriched 3fj





3fk HPLC using an OZ3 (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fk**

| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.67 | n.a. | 687.213 | 339.847 | 50.05 | n.a. | BMB |
| 2 | 14.66 | n.a. | 142.715 | 339.218 | 49.95 | n.a. | BMB* |
| 总和: | | | 829.928 | 679.065 | 100.00 | 0.000 | |

Enantioenriched 3fk



| 序号 | 保留时间 | | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|-----|----------|----------|--------|-------|------|
| | min | | | mAU | mAU*min | % | | |
| 1 | 6.60 | n.a. | | 471.128 | 208.184 | 7.65 | n.a. | BMB |
| 2 | 14.35 | n.a. | | 1064.687 | 2511.500 | 92.35 | n.a. | BMB* |
| 总和: | | | | 1535.815 | 2719.684 | 100.00 | 0.000 | |

3fl HPLC using an IC (*n*-Hexane/*i*PrOH=95/05, flow rate 0.8 ml/min) Racemic **3fl**



Enantioenriched 3fl



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|----|
| | min | | mAU | mAU*min | % | | |
| 1 | 10.41 | n.a. | 20.858 | 9.570 | 3.92 | n.a. | BM |
| 2 | 11.49 | n.a. | 452.406 | 234.846 | 96.08 | n.a. | MB |
| 总和: | | | 473.263 | 244.416 | 100.00 | 0.000 | |

160_____WUX #349 [由dell修改] _____mAU 7-45-2IC85150830 UV VIS 1 WVL:254 nm 2 - 12.653 1 - 11.40/7 140-120-100-80-60-40 20 0 min 18.5 -20 2.0 4.0 6.0 8.0 10.0 12.0 14.0 16.0 序号 保留时间 峰名称 峰高 峰面积 相对峰面积 样品量 类型 mAU mAU*min % min 1 11.41 141.639 64.024 49.36 n.a. BMB* n.a. 2 12.65 n.a. 145.431 65.673 50.64 n.a. BMB* 总和: 129.698 100.00 287.070 0.000 Enantioenriched 3fm 250_WUX #358 [由dell修改] mAU 7-45-1IC85150830 UV VIS 1 WVL:254 nm Ts -N CO₂CH₂^tBu ∕─CO₂CH₂^tBu 1 - 11.347 200-0 150-100-3fm 50-2 - 12.627 0min 19.2 -50 2.0 10.0 12.0 14.0 16.0 4.0 6.0 8.0

3fm HPLC using an IC (*n*-Hexane/*i*PrOH=85/15, flow rate 0.8 ml/min) Racemic **3fm**

| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|-----|
| | min | | mAU | mAU*min | % | | |
| 1 | 11.35 | n.a. | 211.933 | 93.221 | 84.60 | n.a. | BMb |
| 2 | 12.63 | n.a. | 38.393 | 16.964 | 15.40 | n.a. | bMB |
| 总和: | | | 250.326 | 110.186 | 100.00 | 0.000 | |



3fn HPLC using an IC (*n*-Hexane/*i*PrOH=95/05, flow rate 0.8 ml/min) Racemic **3fn**

| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|--------|---------|--------|-------|----|
| | min | | mAU | mAU*min | % | | |
| 1 | 12.02 | n.a. | 38.899 | 22.693 | 49.30 | n.a. | BM |
| 2 | 13.17 | n.a. | 36.066 | 23.338 | 50.70 | n.a. | MB |
| 总和: | | | 74.965 | 46.031 | 100.00 | 0.000 | |

Enantioenriched 3fn



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|----|
| | min | | mAU | mAU*min | % | | |
| 1 | 12.01 | n.a. | 37.674 | 20.125 | 6.55 | n.a. | BM |
| 2 | 12.88 | n.a. | 425.630 | 287.355 | 93.45 | n.a. | MB |
| 总和: | | | 463.304 | 307.480 | 100.00 | 0.000 | |

3fo HPLC using an OZ3 (*n*-Hexane/*i*PrOH=95/05, flow rate 0.8 ml/min) Racemic **3fo**



Enantioenriched 3fn



| 序号 | 保留时间 | 峰名称 | 峰高 | 峰面积 | 相对峰面积 | 样品量 | 类型 |
|-----|-------|------|---------|---------|--------|-------|------|
| | min | | mAU | mAU*min | % | | |
| 1 | 6.82 | n.a. | 86.883 | 59.752 | 7.59 | n.a. | BMB |
| 2 | 11.89 | n.a. | 400.798 | 727.456 | 92.41 | n.a. | BMB* |
| 总和: | | | 487.682 | 787.208 | 100.00 | 0.000 | |





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3fd


























































