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Supporting information

Nickel(II)-Catalyzed Diastereoselective [3+2] Cycloaddition of *N*-Tosylaziridines and Aldehydes via Selective Carbon-Carbon Bond Cleavage

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Table S1. **Screening reaction conditions**[a]

Entry	Catalyst(5 mol%)	Solvent	Time (h)	Isolated Yield (%)
1[b]	$Sc(OTf)_3$	DCE	1	25
2	$Mg(OTf)_2$	DCE	12	trace
3	$Yb(OTf)_3$	DCE	1	70
4	$Fe(OTf)_3$	DCE	12	9
5	$Cu(OTf)_2$	DCE	3	50
6	MgI_2	DCE	10	11
7	$In(OTf)_3$	DCE	1	44
8	$Sn(OTf)_2$	DCE	1	19
9	$Ni(ClO_4)_2{\cdot}6H_2O$	DCE	1	71
10	$Ni(ClO_4)_2{\cdot}6H_2O$	DCM	1	59
11	$Ni(ClO_4)_2{\cdot}6H_2O$	toluene	1	87
12	$Ni(ClO_4)_2{\cdot}6H_2O$	THF	2	41
13	$Yb(OTf)_3$	toluene	2	84

[a] **1a** (0.2 mmol), **2a** (1.5 equiv.), 5 mol % catalyst, and 100 mg of activated 4 Å MS in 2 mL of solvent at room temperature. [b] dr is more than 20:1 in most cases except entry 1 (d.r. = 2:1).

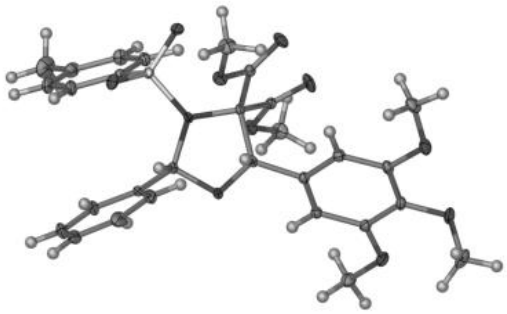

Figure 1. ORTEP representation of **3**.

Two different plausible reaction pathways for the formation *cis*-1,3-oxazolidines and oxazole 4.

From our previous work,[a,b] one stepwise reaction pathway that accounts for this

Ni(II)-catalyzed formal [3+2] cycloaddition is proposed (Scheme 1). The selective coordination of $Ni(ClO_4)_2$ to the dicarboxylates of **1** would give intermediate **IA**, which makes *N*-tosyl aziridine be liable to undergo C-C bond cleavage, providing the metal coordinated azomethine ylide **IB**. The diastereoselective addition of the aldehyde would afford a zwitterionic intermediate **IC**. Subsequent diastereoselective cyclization would produce the *cis*-1,3-oxazolidines and regenerate the catalyst.

Under the thermal condition, aziridine **1a** can also proceed through C-C bond cleavage, leading to the azomethine ylide **ID** (Scheme 2)**.** However, the unavoidable proximity of the generated azomethine ylide **ID** to the C=O bond of either of the ester groups would give the intermediate **IE**, which may go through a rapid 1,5-dipolar electrocyclization process and subsequent elimination would give the oxazole **4**.[c]

References: (a). Li, L.; Wu, X.; Zhang, J. *Chem. Commun*. 2011, **47**, 5049-5051. (b). Chen, Z.; Wei, L.; Zhang, J. *Org. Let.* 2011, **13**, 1170-1173. (c). Pankova, A. S.; Voronin, V. V.; Kuznetsov, M. A. *Tetrahedron Lett*. 2009, **50**, 5990-5993.

General information.

Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^1H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d_3. 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). All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. $ClCH_2CH_2Cl$ (DCE), CH_2Cl_2 (DCM) were freshly distilled from CaH_2; 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 (Renhua Fan, and Yang Ye. *Adv. Synth. Catal.* **2008**, *350*, 1526 – 1530).

Procedure for reactions of aziridine 1a with 3,4,5-trimethoxybenzaldehyde 2a under thermal conditions.

The mixture of **1a** (194.20 mg, 0.5 mmol), **2a** (147 mg, 0.75 mmol), 200 mg of activated 4Å M.S. with toluene (5 mL) in a flame-dried vial was stirred at 90 ^{o}C for 8 hours. After evaporation, the residue was purified by column chromatography (PE:EA = 5:1) on silica gel to afford **4** (66.5 mg) in 57% yield, white solid. m.p. 90 – 94 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 – 7.92 (m, 2 H); 7.51 – 7.45 (m, 3 H); 4.28 (s, 3 H); 3.93 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 161.8, 150.9, 130.4, 128.7, 126.3, 125.9, 107.3, 59.8, 51.8 ppm. MS (EI) m/z (%): 233 [M^+] (2.62), 105 (100); HRMS calcd for $C_{12}H_{11}NO_4$: 233.0688, found: 233.0685. The data is in accordance with that described in the literature. (Lu, L.; Lu, P.; Ma, S. *Eur. J. Org. Chem.* **2007**, 676-680.)

Typical procedure for $Ni(ClO_4)_2{\cdot}6H_2O$ catalyzed cycloaddition reaction.

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In an inert atmosphere, a flame-dried vial was charged with a maganetic stir bar, 200 mg of activated 4Å molecular sieves (M.S.), aldehyde (0.6 mmol, 1.5 equiv), aziridine (0.4 mmol, 1.0 equiv) and 3 mL of toluene. The mixture was allowed to stir at room temperature for 20 minutes, then $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 5 mol %) was added, washed by 1 mL of toluene. The reaction was continued to stir 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 CH_2Cl_2. After evaporation under reduced pressure, the crude product was analyzed by ^{1}H

NMR, which gave the diastereomeric ratio >20:1. The resulting product was purified by flash chromatography to afford the desired product.

1. (2R*,5S*)-dimethyl 2-phenyl-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (3).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **3** (203.8 mg) in 87% yield, white solid. m.p. 167 – 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.6 Hz, 2 H); 7.32 (t, *J* = 7.2 Hz, 1 H); 7.19 (t, *J* = 7.6 Hz, 2 H); 7.11 (d, *J* = 7.6 Hz, 2 H); 6.92 (d, *J* = 7.6 Hz, 2 H); 6.53 (s, 2 H); 6.25 (s, 1 H); 5.56 (s, 1 H); 3.91 (s, 3 H); 3.82 (s, 3 H); 3.81 (s, 6 H); 3.34 (s, 3 H); 2.30 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.7, 153.1, 143.0, 138.4, 137.3, 134.0, 129.9, 129.7, 128.4, 128.0, 127.9, 103.4, 93.0, 87.4, 76.8, 60.8, 56.1, 53.8, 52.6, 21.4 ppm. IR (neat) *v*/cm^{-1} 2951, 2846, 1780, 1737, 1594, 1508, 1461, 1403, 1373, 1339, 1237, 1153, 1125, 1089, 1070, 1058, 997, 920. MS (EI) m/z (%): 585 [M^+] (1.87), 234 (100); HRMS calcd for $C_{29}H_{31}NO_{10}S$: 585.1669, found: 585.1669.

Procedure for synthesis of 4aa on a large scale.

In a flame-dried nitrogen-flushed flask, a solution of **1a** (3.90g, 10 mmol), **2a** (2.94g, 15 mmol), and 800 mg 4Å M.S. in dry toluene (40 mL) was stirred for 0.5 h, then $Ni(ClO_4)_2{\cdot}6H_2O$ (36.6 mg, 1 mol %) and 10 mL of toluene were added to this mixture. The mixture was continued to stir for 8 h at room temperature. After filtration to remove the 4Å M.S., the solution was concentrated under reduced pressure. Then, the crude product was purified by flash chromatography (PE:EA = 2:1) to afford **3** (5.19 g) in 89% yield, which was confirmed by ^{1}H NMR and ^{13}C NMR.

2. (2R*,5S*)-dimethyl 2,5-diphenyl-3-tosyloxazolidine-4,4-dicarboxylate (5).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2b** (63.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **5** (133.4 mg) in 67% yield, white solid. m.p. 163 – 177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.6 Hz, 2 H); 7.26 – 7.38 (m, 6 H); 7.17 (t, *J* = 7.2 Hz, 2 H); 7.11 (d, *J* = 7.6 Hz, 2 H); 6.90 (d, *J* = 7.6 Hz, 2 H); 6.26 (s, 1 H); 5.83 (s, 1 H); 4.02 (s, 3 H); 3.23 (s, 3 H); 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.6, 142.9, 137.3, 134.2, 133.8, 129.9, 129.7, 129.0, 128.3, 128.2, 128.0, 129.9, 126.3, 92.9, 87.4, 76.9, 53.8, 52.4, 21.4 ppm. IR (neat) *v*/cm^{-1} 2944, 1766, 1745, 1593, 1508, 1468, 1428, 1342, 1332, 1236, 1159, 1129, 1091, 1082, 1042, 1004, 901. ESI-MS m/z: 518.1 $[M+Na]^+$; HRMS calcd for $C_{26}H_{25}NO_7SNa^+$: 518.1245, found: 518.1244.

3. (2R*,5S*)-dimethyl 2-phenyl-5-(m-tolyl)-3-tosyloxazolidine-4,4-dicarboxylate (6).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2c** (72.1 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **6** (130 mg) in 64% yield, white solid. m.p. 118 – 129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.6 Hz, 2 H); 7.30 (t, *J* = 8 Hz, 1 H); 7.08 – 7.25 (m, 8 H); 6.90 (d, *J* = 8.0 Hz, 2 H); 6.25 (s, 1 H); 5.79 (s, 1 H), 4.02 (s, 3 H); 3.25 (s, 3 H); 2.31 (s, 3 H); 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.6, 142.9, 137.9, 137.3, 134.0, 133.9, 129.9, 129.8, 129.7, 128.3, 128.1, 128.0, 127.9, 126.8, 126.3, 123.5, 92.9, 87.5, 76.9, 53.8, 52.3, 21.4, 21.3 ppm. IR (neat) *v*/cm^{-1} 2951, 1778, 1740, 1598, 1460, 1435, 1339, 1302, 1242, 1224,

1150, 1060, 1049, 992, 910. ESI-MS m/z: 532.1 $[M+Na]^+$; HRMS calcd for $C_{27}H_{27}NO_7SNa^+$: 532.1403, found: 532.1401.

4. (2R*,5S*)-dimethyl 5-(4-isopropylphenyl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (7).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2d** (88.2 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **7** (154.8 mg) in 72% yield, w1hite solid. m.p. 101 – 107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (d, *J* = 7.6 Hz, 2 H); 7.28 (t, *J* = 7.2 Hz, 1 H); 7.23 (d, *J* = 7.6 Hz, 2 H); 7.10 – 7.19 (m, 6 H); 6.89 (d, *J* = 7.6 Hz, 2 H); 6.25 (s, 1 H); 5.80 (s, 1 H); 4.01 (s, 3 H); 3.21 (s, 3 H); 2.88 (hep, *J* = 6.8 Hz, 1 H); 2.28 (s, 3 H); 1.20 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.6, 149.9, 142.8, 137.3, 133.8, 131.6, 129.8, 129.7, 128.2, 127.9, 127.8, 126.3, 126.2, 92.8, 87.4, 77.0, 53.7, 52.3, 33.8, 23.8, 21.3 ppm. IR (neat) ν/cm^{-1} 2959, 1761, 1726, 1597, 1462, 1436, 1401, 1338, 1276, 1235, 1150, 1065, 1039, 939. ESI-MS m/z: 560.2 $[M+Na]^+$; HRMS calcd for $C_{29}H_{31}NO_7SNa^+$: 560.1711, found: 560.1714.

5. (2R*,5S*)-dimethyl 5-(4-methoxyphenyl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (8).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2e** (81.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4

mL) was carried out at r.t. for 1 hour to afford **8** (192.3 mg) in 92% yield, white solid. m.p. 144 - 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 2 H); 7.29 (t, *J* = 7.2 Hz, 1 H); 7.23 (d, *J* = 7.6 Hz, 2 H); 7.16 (t, *J* = 7.6 Hz, 2 H); 7.10 (d, *J* = 7.6 Hz, 2 H); 6.90 (d, *J* = 7.6 Hz, 2 H); 6.84 (d, *J* = 7.6 Hz, 2 H); 6.23 (s, 1 H); 5.76 (s, 1 H); 4.00 (s, 3 H); 3.76 (s, 3 H); 3.30 (s, 3 H); 2.28 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.6, 166.0, 142.8, 137.3, 133.8, 129.8, 129.7, 128.2, 127.9, 127.8, 127.7, 126.1, 113.5, 92.7, 87.3, 76.7, 55.1, 53.7, 52.4, 21.3 ppm. IR (neat) *v*/cm^{-1} 2952, 2842, 1780, 1752, 1340, 1238, 1151, 1062, 1022, 928. ESI-MS m/z: 548.1 $[M+Na]^+$; HRMS calcd for $C_{27}H_{27}NO_8SNa^+$: 548.1349, found: 548.1350.

6. (2R*,5S*)-dimethyl 5-(2-methoxyphenyl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (9).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2f** (81.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **9** (115.4 mg) in 55% yield, white solid. m.p. 189 - 196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.6 Hz, 2 H); 7.24 – 7.32 (m, 3 H); 7.12 (d, *J* = 8.0 Hz, 4 H); 6.84 – 6.89 (m, 4 H); 6.24 (s, 1 H); 6.12 (s, 1 H); 4.01 (s, 3 H); 3.79 (s, 3 H); 3.20 (s, 3 H); 2.27 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 166.9, 156.8, 142.7, 137.4, 133.8, 129.8, 128.1, 128.1, 127.8, 125.5, 123.5, 120.3, 109.8, 92.5, 83.0, 76.3, 55.4, 53.2, 52.2, 21.3. IR (neat) *v*/cm^{-1} 2948, 1765, 1747, 1604, 1491, 1460, 1438, 1402, 1341, 1287, 1247, 1155, 1091, 1067, 1043, 973. ESI-MS m/z: 548.1 $[M+Na]^+$; HRMS calcd for $C_{27}H_{27}NO_8SNa^+$: 548.1349, found: 548.1350.

7. (2R*,5S*)-dimethyl 5-(4-chlorophenyl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (10).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2g** (168.7 mg, 1.2 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)\cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 3 hours to afford **10** (105.0 mg) in 50% yield, white solid. m.p. 161 – 171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.6 Hz, 2 H); 7.29 – 7.33 (m, 3 H); 7.26 (d, *J* = 8.0 Hz, 2 H); 7.17 (t, *J* = 7.2 Hz, 2 H); 7.10 (d, *J* = 7.6 Hz, 2 H); 6.91 (d, *J* = 8.0 Hz, 2 H); 6.24 (s, 1 H); 5.79 (s, 1 H); 4.01 (s, 3 H); 3.31 (s, 3 H); 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 166.4, 143.0, 137.2, 134.9, 133.7, 132.8, 123.0, 129.7, 128.4, 128.3, 127.9, 127.7, 93.0, 86.6, 77.2, 53.9, 52.5, 21.4 ppm. IR (neat) *v*/cm^{-1} 2951, 1758, 1741, 1598, 1497, 1467, 1427, 1300, 1329, 1226, 1213, 1165, 1155, 1101, 1070, 1040, 998, 939. ESI-MS m/z: 552.1 $[M+Na]^+$; HRMS calcd for $C_{26}H_{24}ClNO_7SNa^+$: 552.0859, found: 552.0854.

8. (2R*,5S*)-diisopropyl 5-(4-bromophenyl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (11).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2h** (293 mg, 1.2 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2\cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 3 hours to afford **11** (139.0 mg) in 55% yield, white solid. m.p. 147 - 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.42 (m, 4 H); 7.22 (t, *J* = 7.2 Hz, 1 H); 7.04 – 7.12 (m, 4 H); 7.02 (d, *J* = 7.2 Hz, 2 H); 6.83 (d, *J* = 8.0 Hz, 2 H); 6.15 (s, 1 H); 5.69 (s, 1 H); 3.92 (s, 3 H); 3.22 (s, 3 H); 2.21 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 166.4, 143.0, 137.2, 133.6, 133.3, 131.3, 130.0, 129.6, 128.3, 128.0, 127.9, 127.9, 123.0, 92.9, 86.6, 76.6, 53.9, 52.4, 21.3 ppm. IR

(neat) ν/cm^{-1} 2950, 1755, 1740, 1596, 1491, 1431, 1352, 1278, 1214, 1156, 1098, 1043, 1010, 985, 944. ESI-MS m/z: 596.0 $[M+Na]^+$; HRMS calcd for $C_{26}H_{24}BrNO_7SNa^+$: 596.0369, found: 596.0349.

9. (2R*,5R*)-dimethyl 5-(furan-2-yl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (12).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2i** (57.7 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **12** (154.0 mg) in 80% yield, white solid. m.p. 135 – 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.2 Hz, 3 H); 7.27 (t, *J* = 7.6 Hz, 1 H); 7.14 (t, *J* = 8.0 Hz, 4 H); 6.90 (d, *J* = 8.0 Hz, 2 H); 6.40 (s, 1 H); 6.35 (s, 1 H); 6.22 (s, 1 H); 5.85 (s, 1 H); 3.99 (s, 3 H); 3.54 (s, 3 H); 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 166.7, 147.1, 143.4, 143.0, 137.1, 133.7, 129.9, 129.6, 128.3, 128.1, 127.9, 110.5, 109.9, 93.0, 81.7, 75.4, 53.9, 53.2, 21.4 ppm. IR (neat) ν/cm^{-1} 2952, 1755, 1723, 1459, 1432, 1339, 1278, 1213, 1150, 1092, 1067, 1029, 1016, 943, 917. ESI-MS m/z: 508.1 $[M+Na]^+$; HRMS calcd for $C_{24}H_{23}NO_8SNa^+$: 508.1039, found: 508.1037.

10. (2R*,5S*)-dimethyl 5-(naphthalen-1-yl)-2-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (13).

The reaction of **1a**(155.4 mg, 0.4 mmol), **2j** (187.4 mg, 1.2 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **13** (152.5 mg) in 70% yield, white solid. m.p. 173 - 185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.88 (m, 3 H); 7.61

(d, *J* = 7.2 Hz, 1 H); 7.48 – 7.60 (m, 4 H); 7.41 (t, *J* = 8.0 Hz, 1 H); 7.29 (t, *J* = 7.6 Hz, 1 H); 7.17 (t , *J* = 8.4 Hz, 4 H); 6.90 (d, *J* = 7.6 Hz, 2 H); 6.64 (s, 1 H); 6.37 (s, 1 H); 4.03 (s, 3 H); 2.94 (s, 3 H); 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.6, 167.0, 142.9, 137.3, 133.8, 133.3, 131.0, 130.9, 129.9, 129.8, 129.5, 128.9, 128.3, 128.3, 128.0, 126.8, 125.8, 124.9, 124.1, 122.5, 92.9, 84.7, 77.4, 54.0, 52.2, 21.4 ppm. IR (neat) *v*/cm^{-1} 2948, 1765, 1741, 1597, 1468, 1430, 1344, 1329, 1235, 1155, 1152, 1095, 1073, 1049, 960. ESI-MS m/z: 568.1 $[M+Na]^+$; HRMS calcd for $C_{30}H_{27}NO_7SNa^+$: 568.1339, found: 568.1401.

11. (2R*,5S*)-dimethyl 2-phenyl-5-((E)-styryl)-3-tosyloxazolidine-4,4-dicarboxylate (14).

The reaction of **1a** (155.4 mg, 0.4 mmol), **2k** (79.3 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **14** (181 mg) in 87% yield, white solid. m.p. 110 - 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 7.6 Hz, 4 H); 7.12 – 7.21 (m, 4 H); 7.04 (t, *J* = 7.6 Hz, 4 H); 6.81 (d, *J* = 8.0 Hz, 2 H), 6.61 (d, *J* = 16.0 Hz, 1 H); 6.14 (dd, *J* = 16.0, 6.8 Hz, 1 H); 6.06 (s, 1 H); 6.25 (d, *J* = 6.8 Hz, 1 H); 3.87 (s, 3 H); 3.66 (s, 3 H); 2.17 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 166.8, 142.8, 137.2, 135.5, 134.1, 133.8, 129.7, 129.4, 128.5, 128.3, 128.2, 127.9, 127.8, 126.6, 121.2, 93.0, 86.4, 75.9, 53.7, 52.7, 21.2 ppm. IR (neat) *v*/cm^{-1} 2953, 1766, 1751, 1598, 1494, 1460, 1434, 1339, 1261, 1225, 1151, 1090, 1063, 1030, 962, 922. ESI-MS m/z: 544.1 $[M+Na]^+$; HRMS calcd for $C_{28}H_{27}NO_7SNa^+$: 544.1409, found: 544.1401.

12. (2R*,5S*)-dimethyl 2-(4-nitrophenyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (15).

The reaction of **1b** (173.8 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **15** (249.6 mg) in 99% yield, white solid. m.p. 185 – 202 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.6 Hz, 2 H); 7.75 (d, *J* = 8.0 Hz, 2 H); 7.21 (d, *J* = 7.6 Hz, 2 H); 6.98 (d, *J* = 8.0 Hz, 2 H); 6.52 (s, 2 H); 6.33 (s, 1 H); 5.83 (s, 1 H); 4.00 (s, 3 H); 3.83 (s, 9 H): 3.36 (s, 3 H); 2.32 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 166.6, 153.1, 148.6, 143.9, 141.0, 138.5, 136.7, 130.6, 128.8, 128.5, 127.7, 122.9, 103.1, 91.2, 87.7, 76.5, 60.7, 56.0, 53.8, 52.7, 21.2 ppm IR (neat) ν/cm^{-1} 2918, 2851, 1751, 1724, 1594, 1525, 1466, 1426, 1342, 1280, 1231, 1159, 1126, 1005, 910. MS (EI) m/z (%): 630 [M^+] (1.47), 279 (100); HRMS calcd for $C_{29}H_{30}N_2O_{12}S$: 630.1519, found: 630.1517.

13. (2R*,5S)-dimethyl 2-(4-chlorophenyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (16).

The reaction of **1c** (169.2 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **16** (206.0 mg) in 83% yield, white solid. m.p. 194 – 203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.6 Hz, 2 H); 7.18 (d, *J* = 7.6 Hz, 2 H); 7.13 (d, *J* = 7.6 Hz, 2 H); 6.99 (d, *J* = 7.6 Hz, 2 H); 6.51 (s, 2 H); 6.20 (s, 1 H); 5.75 (s, 1 H); 4.00 (s, 3 H); 3.82 (s, 3 H); 3.81 (s, 6 H); 3.35 (s, 3

H); 2.35 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 166.8, 153.1, 143.4, 138.5, 137.1, 136.1, 132.6, 131.0, 129.4, 128.5, 128.1, 128.0, 103.3, 92.0, 87.5, 76.7, 60.8, 56.1, 53.8, 52.7, 21.4 ppm. IR (neat) ν/cm^{-1} 2948, 2850, 1751, 1723, 1594, 1506, 1467, 1432, 1337, 1281, 1233, 1158, 1128, 1090, 1003, 922, 901. MS (EI) m/z (%): 619 [M^+] (0.93), 268 (100); HRMS calcd for $C_{29}H_{30}ClNO_{10}S$: 619.1279, found: 619.1279.

14. (2R*,5S*)-dimethyl 2-(4-bromophenyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (17).

The reaction of **1d** (187 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **17** (270.9 mg) in 97% yield, white solid. m.p. 190 – 209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.6 Hz, 2 H); 7.28 (d, *J* = 7.6 Hz, 2 H); 7.18 (d, *J* = 7.6 Hz, 2 H); 7.00 (d, *J* = 7.6 Hz, 2 H); 6.51 (s, 2 H); 6.18 (s, 1 H); 5.75 (s, 1 H); 4.01 (s, 3 H); 3.82 (s, 3 H); 3.81 (s, 6 H); 3.35 (s, 3 H); 2.37 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 166.8, 153.2, 143.5, 138.5, 137.1, 133.0, 131.3, 131.1, 129.4, 128.5, 128.0, 124.4, 103.3, 92.1, 87.5, 76.8, 60.8, 56.1, 53.9, 52.7, 21.5 ppm. IR (neat) ν/cm^{-1} 2945, 2850, 1749, 1722, 1594, 1507, 1468, 1433, 1422, 1336, 1284, 1234, 1158, 1128, 1089, 1066, 1004, 901. MS (EI) m/z (%): 665 [M^+] (2.33), 312 (100); HRMS calcd for $C_{29}H_{30}BrNO_{10}S$: 665.0753, found: 665.0754.

15. (2R*,5S*)-dimethyl 2-(p-tolyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4- dicarboxylate (18).

The reaction of **1e** (160.9 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **18** (201.3 mg) in 84% yield, white solid. m.p. 190 – 209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.2 Hz, 2 H); 7.14 (d, *J* = 7.2 Hz, 2 H); 6.96 (d, *J* = 7.6 Hz, 2 H); 6.93 (d, *J* = 7.6 Hz, 2 H); 6.53 (s, 2 H); 6.20 (s, 1 H); 5.74 (s, 1 H); 4.01 (s, 3 H); 3.82 (s, 3 H); 3.81 (s, 6 H); 3.35 (s, 3 H); 2.32 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.7, 153.1, 142.8, 140.0, 138.3, 137.3, 130.9, 129. 8, 129.5, 128.5, 128.2, 128.0, 103.3, 92.8, 87.2, 76.8, 60.8, 56.0, 53.8, 52.6, 21.4, 21.2 ppm. IR (neat) *v*/cm^{-1} 2945, 1764, 1745, 1722, 1593, 1509, 1467, 1430, 1337, 1236, 1158, 1130, 1081, 1041, 1004, 947, 901. MS (EI) m/z (%): 599 [M^+] (0.93), 248 (100); HRMS calcd for $C_{30}H_{33}NO_{10}S$: 599.1825, found: 599.1824.

16. (2R*,5S*)-dimethyl 2-(4-isopropylphenyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (19).

The reaction of **1f** (172.2 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **19** (211.1 mg) in 84% yield, white solid. m.p. 199 – 214 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.6 Hz, 2 H); 7.14 (d, *J* = 7.6 Hz, 2 H); 7.10 (d, *J* = 7.6 Hz, 2 H); 6.90 (d, *J* = 7.6 Hz, 2 H); 6.54 (s, 2 H); 6.22 (s, 1 H); 5.74 (s, 1 H); 4.02 (s, 3 H); 3.81 (s, 9 H); 2.86 (hep, *J* = 6.8 Hz, 1 H);

2.28 (s, 1 H); 1.23 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =167.8, 166.7, 153.1, 150.9, 142.6, 138.4, 137.4, 131.1, 129.8, 129.6, 128.2, 128.0, 125.9, 103.4, 92.7, 87.3, 76.9, 60.7, 56.0, 53.7, 52.5, 33.9, 24.0, 23.8, 21.3 ppm. IR (neat) *v*/cm^{-1} 2960, 1750, 1724, 1593, 1507, 1464, 1431, 1340, 1282, 1234, 1157, 1126, 1091, 1070, 1041, 999, 962, 922, 901. MS (EI) m/z (%): 627 [M^+] (1.20), 276 (100); HRMS calcd for $C_{32}H_{37}NO_{10}S$: 627.2138, found: 627.2138.

17. (2R*,5S*)-dimethyl 2-(m-tolyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (20).

The reaction of **1g** (160.9 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **20** (210.6 mg) in 88% yield, white solid. m.p. 139 – 149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1 H); 7.20 (s, 1 H); 7.15 (d, *J* = 7.6 Hz, 2 H); 7.09 (d, *J* = 4.0 Hz, 2 H); 6.92 (d, *J* = 7.6 Hz, 2 H); 6.54 (s, 2 H); 6.19 (s, 1 H); 5.72 (s, 1 H); 4.02 (s, 3 H); 3.82 (s, 3 H); 3.81 (s, 6 H); 3.36 (s, 3 H); 2.30 (s, 3 H); 2.15 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 166.5, 153.0, 142.8, 138.3, 137.5, 137.2, 133.5, 130.5, 130.1, 129.8, 128.1, 127.9, 127.7, 126.8, 103.4, 92.8, 87.1, 76.8, 60.7, 56.0, 53.6, 52.4, 21.2, 20.9 ppm. IR (neat) *v*/cm^{-1} 2945, 2827, 1744, 1719, 1595, 1508, 1463, 1428, 1365, 1332, 1286, 1230, 1157, 1125, 1083, 1013, 959. MS (EI) m/z (%): 599 [M^+] (1.17), 248 (100); HRMS calcd for $C_{30}H_{33}NO_{10}S$: 599.1825, found:599.1826.

18. (2R*,5S*)-dimethyl 2-(2-bromophenyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (21).

The reaction of **1h** (187.0 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **21** (239.2 mg) in 90% yield, white solid. m.p. 204 – 212 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.6 Hz, 1 H); 7.53 (d, *J* = 8.0 Hz, 1 H); 7.29 (d, *J* = 7.2 Hz, 2 H); 7.13 (t, *J* = 7.6 Hz, 1 H); 6.94 – 7.00 (m, 3 H); 6.79 (s, 1 H); 6.49 (s, 2 H); 5.82 (s, 1 H); 4.01 (s, 3 H); 3.82 (s,3 H); 3.80 (s, 6 H); 3.35 (s, 3 H); 2.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 166.9, 153.1, 143.4, 138.4, 136.9, 133.2, 132.5, 131.8, 131.0, 129.5, 128.6, 128.0, 127.2, 124.7, 103.4, 91.3, 87.7, 76.7, 60.8, 56.0, 53.9, 52.7, 21.4 ppm. IR (neat) *v*/cm^{-1} 2950, 2845, 1757, 1736, 1593, 1508, 1456, 1339, 1232, 1152, 1127, 1702, 1006, 947, 902. MS (EI) m/z (%): 665 [M^+] (1.32), 312(100); HRMS calcd for $C_{29}H_{30}BrNO_{10}S$: 665.0753, found: 665.0756.

19. (2R*,5S*)-diethyl 2-phenyl-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (22).

The reaction of **1i** (167.0 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **22** (200.1 mg) in 82% yield, white solid. m.p. 117 – 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.0 Hz, 2 H); 7.30 (t, *J* = 7.2 Hz, 1 H); 7.12 – 7.19 (m, 4 H); 6.90 (d, *J* = 8.0 Hz, 2 H); 6.57 (s, 2 H); 6.24 (s, 1 H); 5.78 (s, 1 H); 4.50 – 4.58 (m, 1 H); 4.40 – 4.48 (m, 1 H); 3.95 – 4.03 (m, 1 H);

3.82 (s, 3 H); 3.80 (s, 6 H); 3.56 – 3.64 (m, 1 H); 2.29 (s, 3 H); 1.45 (t, *J* = 6.8 Hz, 3 H); 0.90 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 166.1, 153.0, 142.7, 138.2, 137.4, 133.9, 129.9, 129.8, 129.6, 128.2, 127.9, 127.8, 103.3, 92.7, 87.1, 76.6, 62.9, 61.9, 60.6, 55.9, 21.3, 13.9, 13.3 ppm. IR (neat) *v*/cm^{-1} 2981, 2935, 1755, 1718, 1595, 1507, 1461, 1427, 1398, 1369, 1338, 1282, 1225, 1152, 1127, 1084, 1056, 999, 914. MS (EI) m/z (%): 613 [M^+] (0.97), 262 (100); HRMS calcd for $C_{31}H_{35}NO_{10}S$: 613.1982, found: 613.1984..

20. (2R*,5S*)-diisopropyl 2-phenyl-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (23).

The reaction of **1j** (177.8 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1 hour to afford **23** (230.6 mg) in 90% yield, white solid. m.p. 156 – 169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.6 Hz, 2 H); 7.29 (t, *J* = 7.2 Hz, 1 H); 7.11 – 7.20 (m, 4 H); 6.90 (d, *J* = 7.6 Hz, 2 H); 6.58 (s, 2 H); 6.20 (s, 1 H); 5.80 (s, 1 H); 5.33 (hep, *J* = 6.0 Hz, 1 H); 4.70 (hep, *J* = 6.0 Hz, 1 H); 3.82 (s ,3 H); 3.79 (s, 6 H); 2.28 (s, 3 H); 1.45 (t, *J* = 6.0 Hz, 6 H); 1.11 (d, *J* = 6.0 Hz, 3 H); 0.73 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 165.6, 152.9, 142.6, 138.0, 137.5, 133.9, 130.0, 129.6, 128.1, 127.8, 127.7, 103.2, 92.6, 87.0, 76.4, 70.9, 69.8, 60.5, 55.8, 21.5, 21.4, 21.2, 21.2, 20.7 ppm. IR (neat) *v*/cm^{-1} 2983, 2928, 1739, 1717, 1596, 1509, 1464, 1421, 1383, 1338, 1277, 1227, 1154, 1128, 1105, 1090, 1014, 928. MS (EI) m/z (%): 641 [M^+] (2.88), 206 (100); HRMS calcd for $C_{33}H_{39}NO_{10}S$: 641.2295, found: 641.2298.

21. (2R*,5S*)-diisopropyl 2-(4-isopropylphenyl)-3-tosyl-5-(3,4,5-trimethoxyphenyl)oxazolidine-4,4-dicarboxylate (24).

The reaction of **1k** (194.9 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 3 hours to afford **24** (246.5 mg) in 90% yield, white solid. m.p. 130 – 142 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* =7.6 Hz, 2 H); 7.18 (d, *J* = 7.6 Hz, 2 H); 7.00 (d, *J* = 7.6 Hz, 2 H); 6.88 (d, *J* = 7.6 Hz, 2 H); 6.59 (s, 2 H); 6.18 (s, 1 H); 5.78 (s, 1 H); 5.35 (hep, *J* = 6.0 Hz, 1 H); 4.72 (hep, *J* = 6.0 Hz, 1 H); 3.82 (s, 3 H); 3.80 (s, 6 H); 2.86 (hep, *J* = 6.8 Hz, 1 H); 2.28 (s, 3 H); 1.45 (t, *J* = 6.0 Hz, 6 H); 1.23 (d, *J* = 6.8 Hz, 6 H); 1.12 (d, *J* = 6.0 Hz, 3 H); 0.75 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 165.8, 153.0, 150.8, 142.3, 138.1, 137.8, 131.2, 130.2, 129.6, 128.1, 128.0, 125.8, 103.4, 92.4, 86.9, 76.6, 71.0, 69.9, 60.6, 56.0, 33.9, 24.0, 23.8, 21.6, 21.5, 21.3, 21.3, 20.8 ppm. IR (neat) ν/cm^{-1} 2980, 2939, 2877, 1740, 1590, 1508, 1464, 1732, 1351, 1238, 1158, 1128, 1102, 1042, 1006, 932. ESI-MS m/z: 706.3 $[M+Na]^+$; HRMS calcd for $C_{36}H_{45}NO_{10}SNa^+$: 706.2642, found: 706.2656.

22. (2R*,5S*)-dimethyl 2-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-4,4-dicarboxylate (25).

The reaction of **1b** (173.8 mg, 0.4 mmol), **2b** (63.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 1.5 hours to afford **25** (181.6 mg) in 84% yield, white solid. m.p. 201 – 223 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.6 Hz, 2 H); 7.65 (d, *J* = 7.6 Hz, 2 H); 7.19 – 7.28 (m, 5 H); 7.14 (d, *J* = 7.6 Hz, 2 H); 6.88 (d, *J* =

7.6 Hz, 2 H); 6.25 (s, 1 H); 5.82 (s, 1 H); 3.94 (s, 3 H); 3.16 (s, 3 H); 2.24 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 166.7, 148.8, 144.0, 141.1, 137.0, 133.6, 130.8, 129.4, 128.6, 128.4, 128.0, 126.3, 123.0, 91.4, 87.9, 76.9, 54.0, 52.6, 21.4 ppm. IR (neat) ν/cm^{-1} 2951, 1761, 1736, 1529, 1344, 1234, 1208, 1155, 1086, 1063, 1033, 1016, 967. ESI-MS m/z: 563.1 $[M+Na]^+$; HRMS calcd for $C_{26}H_{24}N_2O_9SNa^+$: 563.1115, found: 563.1095.

23. (2R*,5S*)-dimethyl 5-(4-methoxyphenyl)-2-(4-nitrophenyl)-3-tosyloxazolidine-4,4- dicarboxylate (26).

The reaction of **1b** (173.8 mg, 0.4 mmol), **2e** (81.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **26** (218.0 mg) in 96% yield, white solid. m.p. 155 – 162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.6 Hz, 2 H); 7.71 (d, *J* = 8.0 Hz, 2 H); 7.21 (d, *J* = 7.6 Hz, 4 H); 6.95 (d, *J* = 7.6 Hz, 2 H); 6.88 (d, *J* = 8.0 Hz, 2 H); 6.30 (s, 1 H); 5.83 (s, 1 H); 4.00 (s, 3 H); 3.80 (s, 3 H); 3.32 (s, 3 H); 2.31 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 166.8, 160.3, 148.7, 144.0, 141.1, 137.0, 130.8, 128.6, 128.0, 127.7, 125.5, 122.9, 113.7, 91.2, 87.9, 76.8, 55.3, 53.9, 52.8, 21.4 ppm. IR (neat) ν/cm^{-1} 2947, 2895, 1765, 1743, 1613, 1524, 1433, 1342, 1251, 1235, 1216, 1152, 1080, 1062, 1032, 1018, 969, 908. ESI-MS m/z: 593.1 $[M+Na]^+$; HRMS calcd for $C_{27}H_{26}N_2O_{10}SNa^+$: 593.1213, found: 593.1200.

24. (2R*,5S*)-dimethyl 5-(4-chlorophenyl)-2-(4-nitrophenyl)-3-tosyloxazolidine-4,4-dicarboxylate(27).

The reaction of **1b** (173.8 mg, 0.4 mmol), **2g** (168.7 mg, 1.2 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **27** (161 mg) in 70% yield, white solid. m.p. 167 – 176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.6 Hz, 2 H); 7.70 (d, *J* = 7.6 Hz, 2 H); 7.34 (d, *J* = 7.6 Hz, 2 H); 7.20 – 7.27 (m, 4 H); 6.96 (d, *J* = 8.0 Hz, 2 H); 6.31 (s, 1 H); 5.86 (s, 1 H); 4.01 (s, 3 H); 3.31 (s, 3 H); 2.32 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 166.5, 148.8, 144.1, 140.9, 136.8, 135.3, 132.1, 130.7, 128.6, 128.0, 127.6, 123.0, 91.4, 87.2, 76.6, 54.1, 52.7, 21.4 ppm. IR (neat) *v*/cm^{-1} 2950, 1770, 1738, 1527, 1493, 1344, 1292, 1233, 1213, 1153, 1090, 1072, 1041, 1011, 973, 911. ESI-MS m/z: 597.1 $[M+Na]^+$; HRMS calcd for $C_{26}H_{23}ClN_2O_9SNa^+$: 597.0690, found: 597.0705.

25. (2R*,5S*)-dimethyl-3-((4-nitrophenyl)sulfonyl)-2-phenyl-5-(3,4,5-trimethoxyphenyl)oxazolidine- 4,4-dicarboxylate (28).

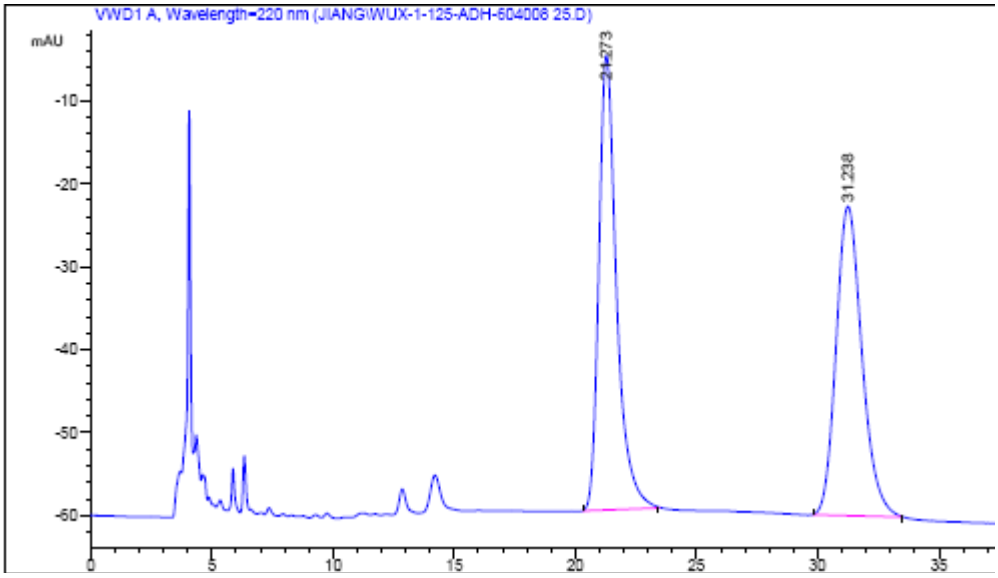
The reaction of **1l** (168.2 mg, 0.4 mmol), **2a** (117.6 mg, 0.6 mmol), 200 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2{\cdot}6H_2O$ (7.2 mg, 0.02 mmol) in toluene (4 mL) was carried out at r.t. for 2 hours to afford **28** (211 mg) in 86% yield, white solid. m.p. 179 - 205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.4 Hz, 2 H); 7.47 (d, *J* = 7.6 Hz, 2 H); 7.33 – 7.40 (m, 3 H); 7.19 (t, *J* = 7.2 Hz, 2 H); 6.52 (s, 2 H); 6.27 (s, 1 H); 5.77 (s, 1 H); 4.04 (s, 3 H); 3.83 (s, 9 H), 3.37 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 166.8, 153.3, 149.3, 145.5, 138.7, 133.3, 130.5, 129.9, 129.3, 129.2, 128.2, 122.8, 103.4, 93.0, 87.7, 77.1, 60.8, 56.1, 54.0, 52.9 ppm. IR (neat)

ν/cm^{-1} 2946, 2846, 1774, 1755, 1591, 1526, 1438, 1349, 1238, 1162, 1124, 1048, 1008, 929. MS (EI) m/z (%): 616 [M^+] (1.86), 234 (100); HRMS calcd for $C_{28}H_{28}N_2O_{12}S$: 616.1363, found: 616.1364.

Procedure for $Ni(ClO_4)_2 \cdot 6H_2O$/Pybox catalyzed cycloaddition of aziridine 1a with 3,4,5-trimethoxybenzaldehyde 2a.

In an inert atmosphere, a flame-dried vial was charged with a maganetic stir bar, 150 mg of activated 4Å molecular sieves (M.S.), $Ni(ClO_4)_2 \cdot 6H_2O$ (6.40 mg, 7 mol%), Pybox **29** (9.8 mg, 10 mol%) and 2 mL of toluene. The mixture was allowed to stir for 2 h at room temperature. Then, aldehyde **2a** (73.5 mg, 0.375 mmol, 1.5 equiv) was added, followed by aziridine **1a** (97.1 mg, 0.25 mmol, 1.0 equiv) and 0.5 mL of toluene. The mixture was continued to stir 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 CH_2Cl_2. After evaporation under reduced pressure, the resulting product was purified by flash chromatography to afford the product **3** (124.6 mg) in 85% yield and enantiomeric excess was determined by chiral HPLC. HPLC analysis: Chiralcel AD-H (hexane/^{i}PrOH = 60/40, 0.8 mL/min), t_{minor} = 22.01 min, t_{major} = 32.41 min, ee = 60%.

Racemic **3**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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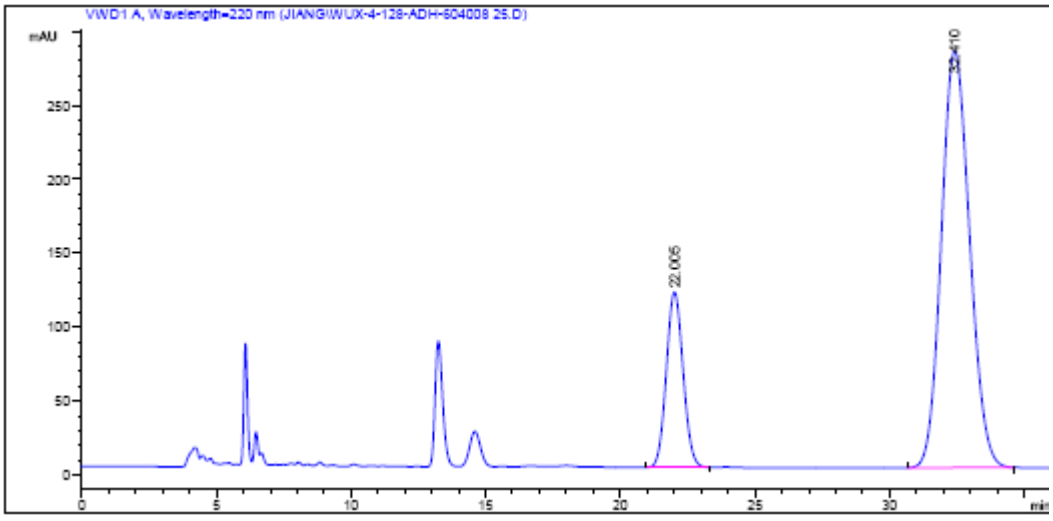
2	31.238	BB	1.1236	2771.81982	37.34698	49.8466
Totals :				5560.69629	92.18271	

Enantioenriched **3**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.005	BB	0.6759	5135.69922	118.51983	19.9734
2	32.410	BB	1.1444	2.05770e4	281.83655	80.0266
Totals :				2.57127e4	400.35638	

Electronic Supplementary Material (ESI) for Chemical Communications