Supporting information

Lewis Acid – Catalyzed Formal [3+2] Cycloadditions of N-Tosylaziridines with Electron-rich Alkenes via Selective Carbon-Carbon Bond Cleavage

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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, 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. ClCH₂CH₂Cl (DCE) and CH₂Cl₂ (DCM) were freshly distilled from CaH₂; toluene was freshly distilled prior to use.

	$\frac{Ts}{Ph} CO_2Me}{CO_2Me} + \frac{1}{1a}$	Cat. (5 mol Cat. (5 mol 4 Å MS, Solv rt	Phin CC vent 2a	₂Me ⊃₂Me
Entry	Catalyst	Solvent	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	Mg(OTf) ₂	DCM	1	0
2	Yb(OTf) ₃	DCM	1	72
3	$Sc(OTf)_3$	DCM	1	68
4	$Sn(OTf)_2$	DCM	3	49
5	Fe(OTf) ₃	DCM	3	31
6	$Ni(ClO_4)_2 6H_2O$	DCM	1	78
7	In(OTf) ₃	DCM	1	67
8	$Y(OTf)_3$	DCM	1	81
9	$Y(OTf)_3$	DCE	1	73
10	Y(OTf) ₃	toluene	1	70
11^{c}	ZnCl ₂	DCM	3	47
^{<i>a</i>} All reaction	ons were performed with	h 0.4 mmol of 1 a	a, 3,4-dihydro-21	<i>H</i> -pyran (2 eq.) and

Table 1. C	Optimization	of the	reaction	conditions. ^a

^{*a*} All reactions were performed with 0.4 mmol of **1a**, 3,4-dihydro-2*H*-pyran (2 eq.) and 5 mol % of catalyst, 4 Å molecular sieves (200 mg) in 4 mL of solvent at rt. ^{*b*} Isolated yield and *d*. *r*.>20:1 ^{*c*} 10 mol% of catalyst.

Synthesis of aziridine:

Aziridines were prepared according to the literature (Fan, R.; Ye, Y. *Adv. Synth. Catal.* **2008**, *350*, 1526-1530).

1. (4aR*,5R*,7aS*)-dimethyl 5-phenyl-6-tosylhexahydropyrano[3,2c]pyrrole-7,7(7aH)-dicarboxylate (2a).



The reaction of aziridine **1a** (155.7 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % of Y(OTf)₃(10.7 mg, 0.02 mmol) in DCM(4 mL) was carried out at r.t. for 1 h to afford 153.6 mg of **2a** in 81% yield, white solid. m.p. 186-188 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (d, *J* = 8.0 Hz, 2 H), 7.02-7.12 (m, 3 H), 6.96 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 6.8 Hz, 2 H), 5.38 (d, *J* = 8.8 Hz, 1 H), 3.97-4.06 (m, 1 H), 3.95(s, 6 H), 3.83(d, *J* = 11.6 Hz, 1 H), 3.29 (t, *J* = 12.0 Hz, 1 H), 2.72-2.83 (m, 1 H), 2.27(s, 3 H), 1.75 (d, *J* = 12.4 Hz, 1 H), 1.52-1.68 (m, 1 H), 1.44 (d, *J* = 13.6 Hz, 1 H), 0.53- 0.68 (m, 1 H), ¹³C NMR (100 MHz, CDCl₃): δ = 168.9, 166.9, 142.9, 137.1, 136.9, 128.3, 128.1, 127.9, 127.0, 126.5, 83.9, 75.3, 69.1, 64.9, 53.5, 43.2, 25.0, 24.6, 21.3 ppm. IR (neat) *v*/cm⁻¹ : 3028, 2953, 2923, 2855, 1756,1731, 1599, 1456, 1436, 1344, 1236, 1057, 959, 913. MS (EI, 70 eV) m/z (%): 473 [M⁺] (0.02), 91 (100); HRMS calcd for C₂₄H₂₇NO₇S: 473.1508, found:473.1509.

2. (4aR*,5R*,7aS*)-dimethyl 5-(4-chlorophenyl)-6-tosylhexahydropyrano[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (2b).



The reaction of aziridine **1b** (169.6 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % of Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 2 h to afford **2b** (167.9 mg) in 82% yield, white solid. m.p.199-201 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.39$ (d, J = 8.0 Hz, 2 H); 6.96 (d, J =8.0 Hz, 2 H), 6.93 (d, J = 8.0 Hz, 2 H), 6.77 (d, J = 8.0 Hz, 2 H), 5.23 (d, J = 8.8 Hz, 1 H), 3.94 (dd, J = 11.6, 4.0 Hz, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.70 (d, J = 11.6 Hz, 1 H), 3.20 (t, J = 12.0 Hz, 1 H), 2.66 (dd, J =20.4, 9.2 Hz, 6 H), 2.23 (s, 3 H), 1.64 (d, J = 12.4 Hz, 1 H), 1.43-1.58 (m, 1 H), 1.37 (d, J = 13.2 Hz, 1 H), 0.47-0.60 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.9$, 166.6, 143.3, 136.9, 135.5, 132.8, 128.4, 128.1, 127.99, 127.95, 83.8, 75.2, 69.0, 64.0, 53.5, 53.4, 43.0, 25.0, 24.5, 21.2 ppm; IR (neat) ν/cm^{-1} : 3040, 2957, 2861, 1757, 1738, 1491, 1435, 1293, 1164, 1040, 958. MS (EI, 70 eV) m/z (%): 507 [M⁺] (0.03), 91 (100); HRMS calcd for C₂₄H₂₆CINO₇S: 507.1119, found: 507.1122.

3. (4aR*, 5R*, 7aS*)-dimethyl 5-(4-bromophenyl)-6-tosylhexahydro pyrano[3, 2-c]pyrrole-7,7(7aH)-dicarboxylate (2c).



The reaction of aziridine **1c** (187.2 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 μ L, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % of Y(OTf) ₃(10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 2 h to afford **2c** (172.2 mg) in 82% yield, white solid. m.p. 205-207 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.47 (d, *J* = 7.6 Hz, 2 H); 7.19 (d, *J* = 7.6 Hz, 1 H), 7.00 (d, *J* = 7.6 Hz, 2 H), 6.78 (d, *J* = 7.6 Hz, 2 H), 5.28 (d, *J* = 8.8 Hz, 1 H), 4.03 (dd, *J* = 11.2, 4.4 Hz, 1 H), 3.96 (s, 3 H), 3.94 (s, 3 H), 3.78 (d, *J* = 11.2 Hz, 1 H); 3.28 (t, *J* = 12, 1 H), 2.73 (dd, *J* = 21.2, 10.8 Hz, 1 H), 2.32 (s, 3 H), 1.72(d, *J* = 12.4 Hz, 1H), 1.53-1.68 (m, 1 H), 1.46 (d, *J* = 13.6 Hz, 1 H), 0.56-0.69 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.9, 166.6, 142.3, 136.8, 136.0, 130.9, 128.4, 128.3, 128.0, 120.8, 83.8, 75.2, 69.0, 64.0, 53.6 53.4, 43.0; 25.0; 24.5, 21.3 ppm; IR (neat) *v*/cm⁻¹ 2990, 2955, 2867, 2840, 1758, 1738, 1597, 1431, 1291, 1162, 1045, 955. MS (EI, 70 eV) m/z (%): 551 [M⁺] (0.02), 91 (100); HRMS calcd for C₂₄H₂₆BrNO₇S: 551.0613, found: 551.0616.

4. (4aR*, 5R*, 7aS*)-dimethyl 5-(4-nitrophenyl)-6-tosylhexahydropyrano[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (2d).



The reaction of aziridine **1d** (173.6 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol, 5 mol%) in DCM (4 mL) was carried out at r.t. for 2.5 h to afford **2d** (154.2 mg) in 82% yield, pale yellow solid. m.p. 227-229 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 7.6 Hz, 2 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.13 (d, *J* = 7.6 Hz, 2 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 5.41 (d, *J* = 9.2 Hz, 1 H), 4.00-4.10 (m, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 3.75 (d, *J* = 11.2 Hz, 1 H), 3.27 (t, *J* = 12.0 Hz, 1 H), 2.83 (dd, J = 21.6, 11.2 Hz, 1 H), 2.28 (s, 3 H), 1.78 (d, J = 12.4 Hz, 1 H), 1.56 - 1.69 (m, 1 H), 1.48 (d, J = 13.2 Hz, 1 H), 0.49-0.61(m, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.9, 166.4, 146.8, 144.7, 143.8, 136.5, 128.6, 128.1, 127.5, 123.0, 83.7, 75.3, 69.0, 63.9, 53.7, 53.5, 43.1, 25.0, 24.5, 21.2 ppm. IR (neat) <math>\nu/\text{cm}^{-1}$ 2987, 2973, 2901; 1756, 1737, 1600, 1435, 1294, 1234, 1085, 1067, 958. MS (EI, 70 eV) m/z (%): 518 [M⁺] (0.14), 91(100); HRMS calcd for C₂₄H₂₆N₂O₉S: 518.1359, found: 518.1360.

5. (4aR*, 5R*, 7aS*)-dimethyl 5-*p*-tolyl-6-tosylhexahydropyrano[3,2c]pyrrole-7,7(7aH)-dicarboxylate (2e).



The reaction of aziridine **1e** (161.2 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % of Y(OTf) ₃(10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford **2e** (162.0 mg) in 83% yield, white solid. m.p.133-135 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (d, *J* = 7.6 Hz, 2 H), 6.97 (d, *J* = 7.6 Hz, 2 H), 6.88 (d, *J* = 7.6 Hz, 2 H), 6.76 (d, *J* = 7.6 Hz, 2 H), 5.32 (d, *J* = 8.4 Hz, 1 H), 3.98-4.04 (m, 1 H), 3.94 (s, 6 H), 3.84 (d, *J* = 11.6 Hz, 1 H), 3.28 (t, *J* = 12.0 Hz, 1 H), 2.68- 2.78 (m, 1 H), 2.28 (s, 3 H), 2.24 (s, 3 H), 1.72(d, *J* = 13.2 Hz, 1 H), 1.52-1.67 (m, 1 H), 1.43(d, *J* = 14.0 Hz, 1 H), 0.57-0.69 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.0, 167.0 142.9, 137.3, 136.7, 133.9, 128.6, 128.3, 128.2, 126.6, 84.0, 75.3, 69.1, 64.8, 53.5, 43.2, 25.1, 24.7, 21.3, 20.9 ppm. IR (neat) *v*/cm⁻¹ 2955, 2925, 2861, 1757, 1739, 1598, 1515, 1435, 1234, 1163, 1151, 1039, 957. MS (EI, 70 eV) m/z (%): 487 [M⁺] (0.08), 91 (100); HRMS calcd for $C_{24}H_{29}NO_7S$: 487.1665, found: 487.1664.

6. (4aR*, 5R*, 7aS*)-dimethyl 5-(4-isopropylphenyl)-6-tosylhexahydropyrano[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (2f).



The reaction of aziridine **1f** (172.8 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃(10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford **2f** (165.1 mg) in 80% yield, white solid. m.p.161-163 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.42 (d, *J* = 7.6 Hz, 2 H), 6.91 (t, *J* = 8.4 Hz, 4 H), 6.76 (d, *J* = 7.6 Hz, 2 H), 5.34 (d, *J* = 8.8 Hz, 1 H), 4.01- 4.08 (m, 1 H), 3.95 (s, 6 H), 3.86 (d, *J* = 11.6 Hz, 1 H), 3.31 (t, *J* = 12.4 Hz, 1 H), 2.68-2.82 (m, 2 H), 2.25 (s, 3 H), 1.73 (d, *J* = 12.4 Hz, 1 H), 1.52-1.65 (m, 1 H), 1.44 (d, *J* = 13.6 Hz, 1 H), 1.16 (d, *J* = 6.8 Hz, 6 H), 0.62-0.72(m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.0, 167.0, 147.7, 142.6, 137.3, 134.2, 128.2, 128.1, 126.7, 125.9, 84.1, 75.3, 69.2, 64.8, 53.5, 43.3, 33.6, 25.0, 24.7, 24.0, 23.8, 21.3 ppm; IR (neat) *v*/cm⁻¹ 2987, 2925, 2868, 1758, 1598, 1435, 1295, 1196, 1038, 940; MS (EI, 70 eV) m/z (%): 515 [M⁺] (0.43), 91 (100), HRMS calcd for C₂₇H₃₃NO₇S: 515.1978, found: 515.1976.

7. (4aR*, 5R*, 7aS*)-dimethyl 5-(2-bromophenyl)-6-tosylhexahydropyrano[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (2g).



The reaction of aziridine **1g** (187.2 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 10 mol % Y(OTf) ₃(21.4 mg, 0.04 mmol) in DCM(4 mL) was carried out at r.t. for 1 h to afford **2g** (150.4 mg) in 68% yield, white solid. m.p. 188-190 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.33-7.42 (m, 3 H), 6.82-6.91 (m, 4 H), 6.74- 6.82 (m, 1 H), 5.75 (d, *J* = 8.8 Hz, 1 H), 3.92-3.95 (m, 1 H), 3.91 (s, 3 H), 3.86 (s, 3 H), 3.78 (d, *J* = 11.6 Hz, 1 H), 3.22 (t, *J* = 12.0 Hz, 1 H), 2.63-2.76 (m, 1 H), 2.18 (s, 3 H), 1.99 (d, *J* = 12.8 Hz, 1 H), 1.43-1.59 (m, 1 H), 1.34 (d, *J* = 13.6 Hz, 1 H), 0.51-0.65 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.0, 166.6, 143.1, 136.6, 136.2, 132.5, 128.8, 128.44, 128.39, 128.0, 127.1, 122.5, 83.8, 75.3, 69.2, 63.7, 53.6, 53.4, 43.3, 24.4, 24.3, 21.2 ppm; IR (neat) *v*/cm⁻¹. 2952, 2873, 2852, 1766, 1738, 1664, 1597, 1339, 1265, 1089, 988, 932; MS (EI, 70 eV) m/z (%): 551 [M⁺] (0.02), 91 (100); HRMS calcd for C₂₄H₂₆BrNO₇S: 551.0613, found: 551.0611.

8. (4aR*, 5R*, 7aS*)-dimethyl 5-m-tolyl-6-tosylhexahydropyrano-[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (2h).



The reaction of aziridine **1h** (161.2 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 μ L, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford **2h** (154.2 mg) in 76 % yield, white solid. m.p. 198-200 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.45 (d, *J* = 7.6 Hz, 2 H), 6.97 (t, *J* = 8.0 Hz, 3 H), 6.89 (d, *J* = 7.2 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 1 H), 6.62 (s, 1 H), 5.35 (d, *J* = 8.8 Hz, 1 H), 4.02 (dd, *J* = 12.0, 4.4 Hz, 1 H), 3.95 (s, 6 H), 3.82 (d, *J* = 11.6 Hz, 1 H), 3.30 (t, *J* = 12.0 Hz, 1 H), 2.75 (dd, *J* = 20.8, 9.6 Hz, 1 H), 2.27 (s, 3 H), 2.10 (s, 3 H), 1.75 (d, *J* = 12.8 Hz, 1 H), 1.53 – 1.69 (m, 1 H), 1.45 (d, *J* = 13.6 Hz, 1 H), 0.58- 0.71 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.9, 166.9, 142.8, 137.4, 137.2, 136.6, 128.2, 128.1, 127.8, 127.6, 127.4, 123.8, 84.0, 75.3, 69.1, 64.8, 53.4, 53.4, 43.1, 25.1, 24.7, 21.2, 21.1 ppm; IR (neat) *v*/cm⁻¹. 2961, 2921, 2852, 1748, 1599, 1492, 1456, 1432, 1352, 1260, 1162; MS (EI, 70 eV) m/z (%): 487 [M⁺] (0.66), 91 (100); HRMS calcd for C₂₅H₂₉NO₇S: 487.1665, found: 487.1663.

9. (4aR*, 5R*, 7aS*)-diethyl 5-phenyl-6-tosylhexahydropyrano[3,2c]pyrrole-7,7(7aH)-dicarboxylate (1i).



The reaction of aziridine **1i** (166.8 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford **2i** (170.1 mg) in 82% yield, white solid. m.p. 164-166 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (d, *J* = 7.6 Hz, 2 H), 7.02-7.14 (m, 3 H), 6.95 (d, *J* = 7.6 Hz, 2 H), 6.90 (d, *J* = 7.2 Hz, 2 H), 5.35 (d, *J* = 8.8 Hz, 1 H), 4.32-4.53 (m, 4 H), 3.97- 4.06 (m, 1 H), 3.83 (d, *J* = 11.6 Hz, 1 H), 3.27 (t, J = 12.0 Hz, 1 H), 2.69-2.81 (m, 1 H), 2.26 (s, 3 H), 1.72 (t, J = 12.8 Hz, 1 H), 1.51-1.62 (m, 1 H), 1.32-1.48 (m, 7 H), 0.55- 0.68.(m, 1 H); ¹³C NMR (400 MHz, CDCl₃): $\delta = 168.4$, 166.3, 142.8, 137.4, 137.1, 128.3, 128.1, 127.9, 126.9, 126.7, 84.0, 75.3, 69.0, 64.9, 62.5, 62.4, 43.2, 25.2, 24.8, 21.3, 14.03, 14.00 ppm; IR (neat) ν/cm^{-1} 2980, 2929, 2853, 1762, 1676, 1597, 1494, 1242, 1094, 1030. m/z (%): 501[M⁺] (0.02), 91 (100); HRMS calcd for C₂₆H₃₁NO₇S: 501.1821, found: 501.1818.

10. (4aR*, 5R*, 7aS*)-diisopropyl 5-phenyl-6-tosylhexahydropyrano [3,2-c]pyrrole-7,7(7aH)-dicarboxylate (1j).



The reaction of aziridine **1j** (178.4 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford **2j** (181.1 mg) in 85% yield, white solid. m.p. 161-163°C, ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (d, *J* = 7..6 Hz, 2 H), 7.00-7.12 (m, 3 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 6.89 (d, *J* = 6.8 Hz, 2 H), 5.22-5.34 (m, 3 H), 4.00 (d, *J* = 7.6 Hz, 1 H), 3.77 (d, *J* = 11.6 Hz, 1 H), 3.24 (t, *J* = 12.0 Hz, 1 H), 2.69-2.81 (m, 1 H), 2.25 (s, 3 H), 1.74 (d, *J* = 12.4 Hz, 1 H), 1.48-1.62 (m, 1 H), 1.36-1.48 (m, 10 H), 1.34 (d, *J* = 6.4 Hz, 3 H), 0.53-0.68 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.0, 165.7, 142.7, 137.4, 137.1, 128.3, 128.2, 127.8, 126.8, 126.6, 84.1, 75.4, 70.3, 70.1, 68.9, 64.7, 43.2, 25.2, 24.9, 21.7, 21.60, 21.58, 21.5, 21.3 ppm. IR (neat) ν/cm^{-1} . 2987, 2958, 2868, 1758, 1738, 1598, 1513, 1435, 1383, 1346, 1295, 1228, 1153, 1118, 1038; MS (EI, 70 ev) m/z (%): 529 [M⁺] (0.02), 43 (100); HRMS calcd for $C_{28}H_{35}NO_{67}S$: 529.2134, found: 529.2133.

11. (4aR*, 5R*, 7aS*)-diisopropyl 5-(4-isopropylphenyl)-6-tosylhexahydropyrano[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (2k).



The reaction of aziridine 1k (195.2 mg, 0.4 mmol), 3,4-dihydro-2Hpyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃(10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford 2k (184.9 mg) in 81% yield, colorless oil, ¹H NMR (400 MHz, CDCl₃): $\delta = 7.48$ (d, J = 8.0 Hz, 2 H), 6.90 (d, J = 8.0 Hz, 2 H), 6.87(d, J = 8.0 Hz, 2 H), 6.78 (d, J = 8.0 Hz, 2 H), 5.20-5.32 (m, 3 H),4.00 (d, J = 8.0 Hz, 1 H), 3.82 (d, J = 11.6 Hz, 1 H), 3.26 (t, J = 12.0 Hz, 1 H), 2.64- 2.82 (m, 2 H), 2.23 (s, 3 H), 1.71 (d, J = 12.4 Hz, 1 H), 1.48-1.61 (m, 1 H), 1.29-1.48 (m, 13 H), 1.15 (d, J = 6.8 Hz, 6 H), 0.60-0.72 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.9$, 165.6, 147.3, 142.2, 137.4, 134.2, 128.0, 126.6, 125.6, 84.2, 77.2, 75.2, 70.1, 69.9, 68.8, 64.5, 43.2, 33.4, 25.0, 24.8, 23.9, 23.7, 21.6, 21.5, 21.5, 21.4, 21.1 ppm.IR (neat) v/cm⁻¹. 2982, 2959, 2940, 2868, 1745, 1598, 1514, 1467, 1453, 1374, 1336, 1270, 1237, 1165, 1115, 1031; MS (EI, 70 eV) m/z (%): 571 $[M^+]$ (0.05), 43(100), HRMS calcd for C₃₂H₄₁NO₇S: 571.2604, found: 571.2606.

12. dimethyl 6-(4-nitrophenylsulfonyl)-5-p-tolylhexahydropyrano[2, 3-c]pyrrole-7,7(7aH)-dicarboxylate (2l).



The reaction of aziridine **11** (172.6 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S.and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 2 h to afford **21** (167 mg) in 80% yield, colorless oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.39$ (d, J = 8.0 Hz, 2 H), 6.89 (d, J = 8.0 Hz, 2 H), 6.80 (d, J= 7.2 Hz, 2 H), 6.72 (d, J = 7.2 Hz, 2 H), 5.21 (d, J = 8.4 Hz, 1 H), 4.23-4.44 (m, 4 H), 3.94 (d, J = 10.0 Hz, 1 H), 3.76 (d, J = 11.2 Hz, 1 H), 3.20 (t, J = 12.0 Hz, 1 H), 2.57-2.69 (m, 1 H), 2.20 (s, 3 H), 2.17 (s, 3 H), 1.64 (d, J = 12.8 Hz, 1 H), 1.40-1.58 (m, 1 H), 1.23-1.40 (m, 7 H), 0.48- 0.62 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.3$, 166.3, 142.6, 137.3, 136.5, 133.9, 128.4; 128.2, 128.0, 126.5, 84.0; 75.2, 68.9, 64.7, 62.4, 62.3, 43.1, 25.1, 24.7, 21.2, 20.8, 13.94, 13.90 IR (neat) ν /cm⁻¹ 2988, 2950, 2871, 1745, 1599, 1514, 1440, 1344, 1287, 1272, 1221, 1163, 1113, 1084, 1037. MS (EI) m/z (%): 442 [M⁺-CO₂Et] (1.94), 91 (100), HRMS calcd for C₂₄H₂₈NO₅S[M⁺-CO₂Et]: 442.1688, found: 442.1687.

The synthesis of enantioenriched **2l** of : 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) and 5 mol % the Pybox **8** (2,6-bis[(3a*R*, 8a*S*)-(+)-8H-indeno[1,2-d]oxazolin-2-yl)pyridine) (7.9 mg ,0.02 mmol) stirred at r.t. for 2 h in DCM (1 mL). This catalyst solution was transferred to the mixture of aziridine **1l** (172.6 mg, 0.4 mmol), 3,4-dihydro-2*H*-pyran (73 μ L, 0.8 mmol), 150 mg of activated 4Å M.S. in DCM (4 mL). The reaction mixture was stirred at r.t. for 3 hs. After the routine workup, the reaction afforded **2l** (156.5 mg) in 75 % yield with 59% ee. Enantiomeric excess

was determined by HPLC with a Chiralpak OD-H column (hexane: 2propanol = 80:10, 0.8 mL/min, 220 nm); minor enantiomer tr = 8.1 min, major enantiomer tr = 16.4 min.

13. (3S*,5R*)-dimethyl 3-methoxy-3-methyl-5-phenyl-1-tosylpyrrolidine-2,2-dicarboxylate (3a).



The reaction of aziridine **1a** (155.7 mg, 0.4 mmol), 2-methoxyprop-1ene (77µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃(10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 2 h to afford **3a** (129.4 mg) in 70% yield, white solid. m.p. 147-149 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, *J* = 7.6 Hz, 2 H), 7.13 (d, *J* = 7.2 Hz, 2 H), 6.90-7.02 (m, 3 H), 6.86 (d, *J* = 7.6 Hz, 2 H), 5.48 (d, *J* = 10.0 Hz, 1 H), 3.85 (s, 3 H), 3.78 (s, 3 H), 2.68 (dd, *J* = 14.0, 10.0 Hz, 1 H), 2.57 (s, 3 H), 2.20 (s, 3 H), 2.15 (d, *J* = 14.0 Hz, 1 H), 1.28 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 166.6, 142.7, 141.1, 137.5, 128.5, 128.0, 127.6, 127.4, 126.4, 88.8, 85.3, 63.6, 53.2, 52.5, 49.1, 40.4, 21.3, 17.4 ppm;. IR (neat) *v*/cm⁻¹ 2987, 2957, 2927, 2827, 1751, 1730, 1492, 1414, 1334, 1154, 948. MS (EI, 70 eV) m/z (%): 462 [M⁺] (0.04), 91 (100), HRMS calcd for C₂₃H₂₇NO₇S: 461.1508, found: 461.1510.

The enantioenriched **3a** was obtained in 60% yield with 57% ee. Enantiomeric excess was determined by HPLC with a Chiralpak ODH column (hexane: 2-propanol = 85:15, 0.8 mL/min, 220 nm); major enantiomer tr = 11.0 min, minor enantiomer tr = 13.9 min.

14. (3S*, 5R*)-dimethyl 3-methoxy-3-methyl-5-p-tolyl-1-tosylpyrrolidine-2,2-dicarboxylate (3b).



The reaction of aziridine **1e** (161.2 mg, 0.4 mmol), 2-methoxyprop-1ene (77 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 2 h to afford **3b** (131.4 mg) in 69% yield, white solid. m.p. 129-131 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 7.6 Hz, 2 H), 6.95 (d, *J* = 7.6 Hz, 2 H), 6.86 (d, *J* = 7.6 Hz, 2 H), 6.77 (d, *J* = 7.6 Hz, 2 H), 5.43 (d, *J* = 13.6 Hz, 1 H), 3.84 (s, 3 H), 3.77 (s, 3 H), 2.65 (dd, *J* = 13.6, 10.4 Hz, 1 H), 2.62 (s, 3 H), 2.21 (s, 3 H), 2.17 (s, 3 H), 2.13 (d, *J* = 13.6 Hz, 1 H), 1.28 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.8, 166.6, 142.5, 138.2, 137.6, 136.0, 128.5, 128.3, 127.9, 127.4, 88.7, 85.2, 63.5, 53.2, 52.4, 49.2, 40.4, 21.3, 20.9, 17.5 ppm; IR (neat) v/cm⁻¹ 2995, 2952, 2932, 2827, 1753, 1752, 1596, 1515, 1435, 1337, 1274, 1252, 1153, 1101, 1037; MS (EI, 70 eV) m/z (%): 475 [M⁺] (0.06), 91 (100); HRMS calcd for C₂₄H₂₉NO₇S: 475.1665, found: 475.1667.

15. (3S*, 5R*)-dimethyl 5-(4-bromophenyl)-3-methoxy-3-methyl-1tosylpyrrolidine-2,2-dicarboxylate (3c).



The reaction of aziridine **1c** (187.3 mg, 0.4 mmol), (77 μ L, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf) $_3(10.7 \text{ mg},$

0.02 mmol) in DCM (4 mL) was carried out at r.t. for 3 h to afford **3c** (146.8 mg) in 68% yield, white solid. m.p. 130-132 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.43 (d, *J* = 7.2 Hz, 2 H), 7.13 (d, *J* = 7.2 Hz, 2 H), 6.99 (d, *J* = 8.0 Hz, 4 H), 5.48 (d, *J* = 10.4 Hz, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 2.76 (dd, *J* = 13.6, 10.4 Hz, 1 H), 2.65 (s, 3 H), 2.32 (s, 3 H), 2.18 (d, *J* = 13.6 Hz, 1 H), 1.35 (s, 3 H). ¹³C NMR (100MHz, CDCl₃): δ = 168.44, 166.49, 143.11, 140.30, 137.14, 130.49, 129.11, 128.54, 128.11, 120.19, 88.83, 85.19, 62.85, 53.23, 52.50, 49.13, 40.24, 21.30, 17.24 ppm.IR (neat) *v*/cm⁻¹ 2961, 2923, 2852, 1752, 1731, 1596, 1488, 1459, 1435, 1412, 1333, 1196, 1153; MS (EI, 70 eV) m/z (%): 543 [M⁺] (0.17), 91 (100); HRMS calcd for C₂₃H₂₆BrNO₇S: 541.0593, found: 541.0594.

16. Dimethyl 3-ethoxy-5-phenyl-1-tosylpyrrolidine-2,2-dicarboxylate(4)



The reaction of aziridine **1a** (155.7 mg, 0.4 mmol), vinyl ethyl ether (77 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 1 h to afford **4** (140.2 mg) in 80% yield, colorless oil, Major isomer: ¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, *J* = 7.6 Hz, 2 H), 6.99- 7.09 (m, 3 H), 6.94 (d, *J* = 7.2 Hz, 2 H), 6.89 (d, *J* = 7.6 Hz, 2 H), 5.30 (d, *J* = 9.6 Hz, 1 H), 4.53 (dd, *J* = 10.8, 6.8 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 3.57- 3.66 (m, 1 H), 3.32-3.42 (m, 1 H), 2.64 (q, *J* = 11.2 Hz, 1 H), 2.21 (s, 3 H), 2.06 (dd, *J* = 12.0, 6.8 Hz, 1 H), 1.03 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR

(100 MHz, CDCl₃): δ = 169.5, 167.0, 142.9, 141.1, 137.3, 128.4, 128.3, 127.9, 127.1, 126.3, 83.8, 76.6, 66.9, 62.1, 53.2, 52.9, 39.8, 21.3, 15.1 ppm.

Minor isomer ¹H NMR (400 MHz, CDCl₃): $\delta = 7.23$ (d, J = 7.6 Hz, 2 H), 7.12 (d, J = 7.6 Hz, 2 H), 6.91-7.02 (m, 3 H), 6.84 (d, J = 8.0 Hz, 2 H), 5.35 (d, J = 9.2 Hz, 1 H), 4.21 (d, J = 4.8 Hz, 1 H), 3.85 (s, 3 H), 3.80 (s, 3 H), 3.25 (q, J = 6.8 Hz, 2 H), 2.80-2.89 (m, 1 H), 2.20 (s, 3 H), 2.00 (d, J = 13.6 Hz, 1 H), 0.87 (t, J = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.9$, 166.5, 142.6, 140.7, 137.6, 128.3, 128.1, 128.0, 127.6, 126.8, 85.0, 81.6, 65.3, 64.6, 53.4, 52.6, 39.2, 21.3, 14.8 ppm.IR (neat) ν/cm^{-1} 2981, 2950, 2872, 1751, 1733, 1600, 1495, 1439, 1337, 1287, 1237, 1152, 1118, 104 ; MS (EI, 70 eV) m/z (%): 461 [M⁺] (0.01), 91 (100); HRMS calcd for C₂₃H₂₇NO₇S: 461.1508, found: 461.1507.

17. Dimethyl 3-(4-methoxyphenyl)-5-phenyl-1-tosylpyrrolidine-2,2dicarboxylate (5).



The reaction of aziridine **1a** (155.7 mg, 0.4 mmol), 1-methoxy-4vinylbenzene (107.3 mg, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 3 h to afford **5** (146.0 mg) in 73% yield, colorless oil, minor isomer: ¹H NMR (400 MHz, CDCl₃): δ = 7.44 (d, *J* = 8.0 Hz, 2 H), 7.22-7.30 (m, 1 H), 6.96-7.18 (m, 8 H), 6.79 (d, *J* = 7.6 Hz, 2 H), 5.53 (d, *J* = 8.8 Hz, 1 H), 4.08 (dd, *J* = 14.0, 7.5 Hz, 1 H), 3.86 (s, 3 H), 3.74 (s, 3 H), 3.62 (s, 3 H), 3.22 (dd, *J* = 22.4, 13.2 Hz, 1 H), 2.28 (s, 3 H), 1.96 (dd, *J* = 12, 6 Hz, 1 H); Major isomer: ¹H NMR (400 MHz, CDCl₃): δ = 7.22-7.30 (m, 1 H), 6.96-7.18 (m, 8 H), 6.89 (d, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 5.05 (dd, *J* = 10.4, 5.6 Hz, 1 H), 4.19 (dd, *J* = 13.2, 6.0 Hz , 1 H), 3.97 (s, 3 H), 3.76 (s, 3 H), 3.46 (s, 3 H), 2.41-2.60 (m, 3 H), 2.28 (s, 3 H); For two isomer: ¹³C NMR (100 MHz, CDCl₃): δ = 169.2, 169.0, 168.1, 167.6, 159.2, 159.1, 142.9, 142.3, 141.3, 137.9, 137.4, 137.2, 129.6, 129.0, 128.8, 128.3, 128.1, 128.04, 127.95, 127.8, 127.73, 127.65, 127.1, 126.8, 126.2, 126.0, 113.6, 113.4, 78.8, 78.3, 65.1, 63.2, 55.0, 54.9, 53.1, 52.8, 52.6, 52.6, 52.2, 51.0, 40.4, 39.0, 21.2 ppm; IR (neat) *v*/cm⁻¹ 2961, 2919, 2850, 1760, 1726, 1612, 1599, 1515, 1458, 1431, 1338, 1258, 1215, 1182, 1137, 1095, 1033; MS (EI, 70 eV) m/z (%): 523 [M⁺] (1.07), 91 (100), HRMS calcd for C₂₈H₂₉NO₇S: 523.1665, found: 523.1668.

18. (4aR*,5R*,7aS*)-dimethyl 6-(4-nitrophenylsulfonyl)-5-phenyl hexa-hydropyrano[3,2-c]pyrrole-7,7(7aH)-dicarboxylate (7).



The reaction of aziridine **6** (173.6 mg, 0.4 mmol), 3,4-dihydro-2*H*pyran (73 µL, 0.8 mmol), 150 mg of activated 4Å M.S. and 5 mol % Y(OTf)₃ (10.7 mg, 0.02 mmol) in DCM (4 mL) was carried out at r.t. for 2 h to afford **7** (176.3 mg) in 85% yield, white solid. m.p.233-235 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.04-7.18 (m, 3 H), 6.77- 6.88 (m, 2 H), 5.55 (d, *J* = 8.8 Hz, 1 H), 4.02-4.10 (m, 1 H), 3.97 (s, 6 H), 3.82 (d, *J* = 11.2 Hz, 1 H), 3.31 (t, *J* = 12.0 Hz, 1 H), 2.79-2.90 (m, 1 H), 1.77 (d, *J* = 12,4 Hz, 1 H), 1.58-1.69 (m, 1 H), 1.47 (d, *J* = 15.2 Hz , 1 H), 0.57- 0.70 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.9$, 166.7, 149.4, 145.6, 136.3, 129.6, 128.3, 127.7, 126.7, 122.8, 83.9, 75.9, 69.3, 65.5, 53.9, 53.8, 43.4, 25.0, 24.6 ppm. IR (neat) ν/cm^{-1} 2949, 2920, 2868, 2851, 1754, 1741, 1690, 1604, 1526, 1436, 1349, 1252, 1164, 1148, 1120, 1090, 157, 1021. MS (EI) m/z (%): 445 [M⁺- 59] (100),445 (100).

The structure of **2a**:



The structure of **3a**:

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Enantioenriched 3a



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