A Regio- and Stereodivergent Route to All Isomers of *vic*-Amino Alcohols

Berit Olofsson and Peter Somfai*

Department of Chemistry, Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden. Fax +46-8-791 2333. E-mail somfai@kth.se

Supporting Information

1. Experimental data for compounds **4b, d-f; 7b,d-f; 9b-f;10b-f; 11a; 12b-f**.
2. Synthesis of *N*-H oxazolidinones **14a-d,f, 15,16**
3. Other compounds (**8, 11a**)

General. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , using the residual peak of CHCl_3 (^1H NMR δ 7.26, ^{13}C NMR δ 77.0), or added TMS (δ 0.00), as internal standard. Chemical shifts are reported in the δ -scale with multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), integration and coupling constants (Hz). Optical rotations, $[\alpha]_{\text{D}}$, were measured at the sodium D line at ambient temperature. Only the strongest/structurally most important peaks (ν , cm^{-1}) are listed in infrared spectra. Analytical thin layer chromatography plates were visualized with UV light and phosphomolybdic acid staining reagent (purchased as a 20 wt% solution in ethanol but diluted to ca 5 wt% before use). Air- and moisture sensitive reactions were carried out in flame-dried, septum-capped flasks under an atmospheric pressure of nitrogen. All liquid reagents were transferred via oven-dried syringes. THF and DME were freshly distilled from sodium-benzophenone ketyl; dichloromethane was freshly distilled from CaH_2 .

1 Experimental data for compounds 4b, d-f; 7b,d-f; 9b-f;10b-f; 11a; 12b-f.

1.1 Ring-closure of amino alcohols 2 to aziridines 4:

(2*S*,3*R*)-2-Benzylloxymethyl-3-vinyl-aziridine (4b):¹ Prepared from **2b** as described for **4a**, isolated in 72% yield.

(2*S*,3*S*)-2-(3-Benzylloxy-1-(*E*)-propenyl)-3-methyl-aziridine (4d):¹ Prepared from *anti*-amino alcohol **2d** in 62% yield as described for **4c**. $[\alpha]_{\text{D}}$: -35.2 (*c* 0.64, CH_2Cl_2).

(2*S*,3*S*)-2-(3-Benzylloxy-1-(*E*)-propenyl)-3-ethyl-2-methyl-aziridine (4e): Prepared from **2e** as described for **4a**, isolated as a colorless oil in 95% yield based on recovered **2e** (37%). ^1H NMR (400 MHz, CDCl_3): δ 7.36-7.27 (m, 5H), 5.74 (dt, 1H, J = 15.5, 6.0 Hz), 5.34 (dt, 1H, J = 15.7, 1.3 Hz), 4.52 (s, 2H), 4.01 (dd, 2H, J = 6.0, 1.3 Hz), 1.88 (t, 1H, J = 6.7 Hz), 1.55-1.40 (m, 2H), 1.28 (s, 3H), 1.00 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 140.0, 138.2, 128.4, 127.8, 127.6, 125.2, 72.4, 70.4, 45.8, 38.4, 22.8, 15.7, 12.0; IR (neat): 3280, 2966, 2872 cm^{-1} ; $[\alpha]_{\text{D}}$: -39.3 (*c* 0.81, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{15}\text{H}_{22}\text{NO}$ (M+H): 232.1701. Found: 232.1702.

(2*R*,3*S*)-2-(1-Benzylloxymethyl-vinyl)-3-(4-methoxy-benzylloxymethyl)-aziridine (4f):² Prepared from **2f** as described for **4a**, isolated in 63% yield.

1.2 Ring opening of vinyloxyepoxides 1 to give oxazolidinones 7:

(4*R*,5*R*)-5-Benzylloxymethyl-3-(toluene-4-sulfonyl)-4-vinyloxazolidin-2-one (7b): Prepared from vinyloxyepoxide **1b** as described for **7a**. Isolated as a yellow oil in 88% yield, in a diastereomeric ratio of 14:1 (NMR analysis). ^1H NMR (400 MHz, CDCl_3 , major isomer): δ 7.87 (d, 2H, J = 8.6 Hz), 7.36-7.21 (m, 7H), 5.87 (ddd, 1H, J = 17.2, 10.2, 7.8 Hz), 5.44 (d, 1H, J = 17.2, Hz), 5.36 (d, 1H, J = 10.2 Hz), 4.81 (dd, 1H, J = 7.8, 3.9 Hz), 4.45 (s, 2H), 4.24 (q, 1H, J = 3.9 Hz), 3.56 (t, 2H, J = 3.9 Hz), 2.38 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 151.3, 145.1, 136.9, 134.8, 134.1, 129.4, 128.4, 128.4, 127.9, 127.8, 119.9, 78.5, 73.5, 68.5, 61.1, 21.7; IR (neat): 2931, 2868, 1780, 1371 cm^{-1} ; HRMS (EI+) Exact mass calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$ (M): 387.1140. Found: 387.1150.

(4*R*,5*R*)-4-(3-Benzylloxy-1-(*E*)-propenyl)-5-methyl-3-(toluene-4-sulfonyl)-oxazolidin-2-one

(7d): Prepared from vinyloxyepoxide **1d** as described for **7c**, isolated as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, 2H, J = 8.4 Hz), 7.39-7.24 (m, 7H), 6.00 (dt, 1H, J = 15.4, 4.9 Hz), 5.71 (ddt, 1H, J = 15.4, 8.7, 1.6 Hz), 4.55 (s, 2H), 4.43 (dd, 1H, J = 8.7, 4.3 Hz), 4.28 (dq, 1H, J = 6.3, 4.3 Hz), 4.07 (dd, 2H, J = 4.9, 1.6 Hz), 2.42 (s, 3H), 1.40 (d, 3H, J = 6.3 Hz); ^{13}C NMR (100 MHz,

CDCl₃): 151.3, 145.4, 137.8, 135.0, 133.3, 129.6, 128.6, 128.5, 127.8, 127.7, 126.9, 76.8, 72.7, 69.0, 65.5, 21.7, 19.4; IR (neat): 2983, 2860, 1784, 1360 cm⁻¹; [α]_D: +13.3 (*c* 1.00, CH₂Cl₂); HRMS (CI+) Exact mass calcd for C₂₁H₂₄NO₅S (M+H): 402.1375. Found: 402.1371.

(4*R*,5*R*)-4-(3-Benzoyloxy-1-(*E*)-propenyl)-5-ethyl-4-methyl-3-(toluene-4-sulfonyl)-oxazolidin-2-one (7e): Prepared from vinyl epoxide **1e** in as described for **7c**, isolated as a colorless oil in 94% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, 2H, *J* = 8.3 Hz), 7.39-7.29 (m, 5H), 7.25 (d, 2H, *J* = 8.3 Hz), 5.97 (dd 1H, *J* = 15.9, 1.4 Hz), 5.86 (dt, 1H, *J* = 15.9, 4.9 Hz), 4.59 (s, 2H), 4.14 (dd, 2H, *J* = 4.9, 1.4 Hz), 4.02 (dd, 1H, *J* = 9.9, 3.1 Hz), 2.41 (s, 3H), 1.63 (s, 3H), 1.54 (m, 2H), 1.00 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 151.9, 145.1, 138.0, 135.9, 132.2, 129.7, 129.4, 128.8, 128.4, 127.8, 127.7, 84.9, 72.4, 69.5, 68.9, 21.6, 21.1, 18.1, 10.5; IR (neat): 2978, 2881, 1782, 1363 cm⁻¹; [α]_D: +28.6 (*c* 1.14, CH₂Cl₂); HRMS (CI+) Exact mass calcd for C₂₃H₂₈NO₅S (M+H): 430.1688. Found: 430.1681.

(4*S*,5*R*)-4-(1-Benzoyloxymethylvinyl)-5-(4-methoxybenzyloxymethyl)-3-toluene-4-sulfonyl)-oxazolidin-2-one (7f): Prepared from vinyl epoxide **1f** as described for **7c**, isolated as a colorless oil in 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, 2H, *J* = 8.3 Hz), 7.34-7.22 (m, 5H), 7.17 (d, 2H, *J* = 8.3 Hz), 7.08 (d, 2H, *J* = 8.4 Hz), 6.82 (d, 2H, *J* = 8.4 Hz), 5.30 (s, 1H), 5.29 (s, 1H), 4.88 (d, 1H, *J* = 3.3 Hz), 4.44 (s, 2H), 4.38 (q, 1H, *J* = 3.3 Hz), 4.27 (s, 2H), 4.07 (AB-q, 2H, *J* = 11.9 Hz), 3.78 (s, 3H), 3.42 (br d, 2H, *J* = 2.9 Hz), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.8, 152.5, 145.7, 143.5, 137.9, 135.1, 129.8, 129.6, 129.0, 129.0, 128.9, 128.3, 116.7, 114.3, 79.8, 73.5, 73.4, 73.4, 71.8, 69.0, 61.5, 55.7, 55.7, 22.1; IR (neat) 2953, 2864, 1719, 1365 cm⁻¹; [α]_D + 22.9° (*c* 0.90, CH₂Cl₂); HRMS (EI+) Exact mass calcd for C₂₉H₃₁NO₇S (M): 537.1821. Found: 537.1826.

1.3 Detosylation of 7 to *N*-H oxazolidinones 9:

(4*R*,5*R*)-5-Benzoyloxymethyl-3-(toluene-4-sulfonyl)-4-vinyloxazolidin-2-one (9b): Prepared from oxazolidinone **7b** as described for **9a**, isolated as a yellow oil in 75% yield. ¹H NMR (300 MHz, CDCl₃): δ 7.40-7.29 (m, 5H), 5.82 (ddd, 1H, *J* = 17.3, 10.2, 7.2 Hz), 5.68 (br s, 1H), 5.34-5.23 (m, 2H), 4.61 (AB-q, 1H, *J* = 12.1 Hz), 4.36 (dt, 1H, *J* = 6.6, 4.1 Hz), 4.25 (br t, 1H, *J* = 6.6 Hz), 3.70 (dd, 1H, *J* = 11.0, 4.1 Hz), 3.64 (dd, 1H, *J* = 11.0, 4.1 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 158.5, 137.3, 135.5, 128.3, 127.8, 127.6, 118.6, 80.8, 73.6, 69.0, 57.2; IR (neat): 3292 (br), 2924, 2866 cm⁻¹; [α]_D: -25.9 (*c* 0.51, CH₂Cl₂); HRMS (EI+) Exact mass calcd for C₁₃H₁₆NO₃ (M+H): 234.1130. Found: 234.1123.

(4*S*,5*R*)-5-Benzoyloxymethyl-4-[3-(4-methoxy-benzyloxy)-1-(*E*)-propenyl]-oxazolidin-2-one (9c): Prepared from oxazolidinone **7c** as described for **9a**, isolated as a yellow oil in 72% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.24 (m, 5H), 7.25 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 5.80 (dt, 1H, *J* = 15.4, 5.0 Hz), 5.71 (ddt, 1H, *J* = 15.4, 7.3, 1.0 Hz), 5.60 (br s, 1H), 4.58 (AB-q, 2H, *J* = 12.1 Hz), 4.44 (s, 2H), 4.34 (dt, 1H, *J* = 6.8, 4.2 Hz), 4.24 (br t, 1H, *J* = 7.1 Hz), 3.97 (dd, 2H, *J* = 5.0, 1.0 Hz), 3.80 (s, 3H), 3.67 (dd, 1H, *J* = 11.1, 4.2 Hz), 3.60 (dd, 1H, *J* = 11.1, 4.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 159.3, 158.4, 137.5, 131.4, 129.9, 129.7, 129.5, 128.5, 127.9, 127.7, 113.9, 80.9, 73.5, 72.4, 69.0, 68.9, 56.2, 55.3; IR (neat): 3288 (br), 2929, 2860, 1757 cm⁻¹; [α]_D: -62.0 (*c* 0.20, CH₂Cl₂); HRMS (CI+) Exact mass calcd for C₂₂H₂₆NO₅ (M+H): 384.1811. Found: 384.1808.

(4*R*,5*R*)-4-(3-Benzoyloxy-1-(*E*)-propenyl)-5-methyl-oxazolidin-2-one (9d): Prepared from oxazolidinone **7d** as described for **9a**, isolated as a colorless oil in 61% yield from **1d**. ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.27 (m, 5H), 5.86 (dt, 1H, *J* = 15.5, 5.1 Hz), 5.70 (ddt, 1H, *J* = 15.5, 7.7, 1.4 Hz), 5.31 (br s, 1H), 4.53 (s, 2H), 4.32 (dq, 1H, *J* = 7.2, 6.3 Hz), 4.03 (dd, 2H, *J* = 5.1, 1.4 Hz), 3.91 (br t, 1H, *J* = 7.4 Hz), 1.43 (d, 3H, *J* = 6.3 Hz); ¹³C NMR (100 MHz, CDCl₃): 158.5, 137.8, 131.7, 129.1, 128.5, 127.8, 127.8, 78.9, 72.8, 69.4, 62.0, 18.9; IR (neat): 3292, 2931, 2860,

1751 cm^{-1} ; $[\alpha]_{\text{D}}$: +31.4 (*c* 0.70, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ (M+H): 248.1287. Found: 248.1291.

(4*R*,5*R*)-4-(3-Benzoyloxy-1-(*E*)-propenyl)-5-ethyl-4-methyl-oxazolidin-2-one (9e): Prepared from oxazolidinone **7e** as described for **9a**, isolated as a colorless oil in 80% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.37–7.27 (m, 5H), 5.84 (dt, 1H, *J* = 15.7, 5.1 Hz), 5.76 (d, 1H, *J* = 15.7 Hz), 5.35 (br s, 1H), 4.53 (s, 2H), 4.11 (dd, 2H, *J* = 9.9, 3.7 Hz), 4.03 (app. d, 1H, *J* = 4.7 Hz), 1.69 (m, 1H), 1.55 (m, 1H), 1.29 (s, 3H), 1.05 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 158.7, 137.7, 133.8, 128.4, 127.9, 127.8, 127.8, 86.8, 72.7, 69.6, 61.1, 21.8, 20.2, 10.8; IR (neat): 3275, 2974, 2879, 1749 cm^{-1} ; $[\alpha]_{\text{D}}$: -6.0 (*c* 1.18, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ (M+H): 276.1600. Found: 276.1602.

(4*S*,5*R*)-4-(1-Benzoyloxymethylvinyl)-5-(4-methoxybenzyloxymethyl)-oxazolidin-2-one (9f): Prepared from oxazolidinone **7f** as described for **9a**, isolated as a colorless oil in 85% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.32–7.16 (m, 7H), 6.82 (d, 2H, *J* = 8.7 Hz), 5.50 (br s, 1H), 5.20 (br s, 2H), 4.45 (m, 3H), 4.41 (s, 2H), 4.26 (d, 1H, *J* = 5.4 Hz), 3.97 (AB-q, 2H, *J* = 12.1 Hz), 3.75 (s, 3H), 3.58 (dd, 1H, *J* = 10.8, 4.0 Hz), 3.54 (dd, 1H, *J* = 10.8, 4.3 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 159.3, 158.6, 143.7, 137.5, 129.6, 129.3, 128.6, 128.5, 127.9, 127.8, 115.3, 113.8, 80.2, 73.2, 72.8, 70.8, 69.4, 56.5, 55.2; IR (neat): 3288 (br), 2923, 2862, 1755 cm^{-1} ; $[\alpha]_{\text{D}}$: -19.9 (*c* 0.89, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_5$ (M): 383.1733. Found: 383.1740.

1.4 Acylation of vinylaziridines **4** to *N*-acetylaziridines **10**, followed by rearrangement to **11** and *in situ* hydrolysis into hydroxyamides **12**:

(1*S*,2*R*)-*N*-(1-Benzoyloxymethyl-2-hydroxy-3-butenyl)-acetamide (12b): Prepared in two steps from aziridine **4b** as described for **12a**, isolated as a colorless oil in 73% yield. **10b**: ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.25 (m, 5H), 5.52–5.28 (m, 3H), 4.53 (s, 2H), 3.69 (dd, 1H, *J* = 10.9, 4.3 Hz), 3.65 (dd, 1H, *J* = 10.9, 4.7 Hz), 3.08 (dd, 1H, *J* = 8.0, 2.7 Hz), 2.74 (td, 1H, *J* = 4.3, 2.7 Hz), 2.09 (s, 3H). **12b**: ^1H NMR (300 MHz, CDCl_3): δ 7.39–7.27 (m, 5H), 6.12 (br d, 1H, *J* = 7.9 Hz), 5.80 (ddd, 1H, *J* = 17.3, 10.4, 5.2 Hz), 5.31 (dt, 1H, *J* = 17.3, 1.6 Hz), 5.17 (dt, 1H, *J* = 10.4, 1.6 Hz), 4.52 (s, 2H), 4.45 (m, 1H), 4.08 (td, 1H, *J* = 12.6, 4.4 Hz), 3.69 (m, 1H), 3.40 (br s, 1H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.4, 137.3, 137.1, 128.4, 127.9, 127.7, 116.1, 73.6, 73.0, 71.2, 52.5, 23.3; IR (neat) 3338 (br), 3929, 2868, 1653 cm^{-1} ; $[\alpha]_{\text{D}}$: +4.8 (*c* 0.52, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ (M+H): 250.1443. Found: 250.1428.

(1*S*,2*R*)-*N*-[1-Benzoyloxymethyl-2-hydroxy-5-(4-methoxy-benzyloxy)-3-(*E*)-pentenyl]-acetamide (12c): Prepared in two steps from aziridine **4c** as described for **12a**, isolated as a yellow oil in 73% yield. **10c**: ^1H NMR (400 MHz, CDCl_3): δ 7.39–7.26 (m, 5H), 7.25 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 6.04 (dt, 1H, *J* = 15.4, 5.5 Hz), 5.31 (ddt, 1H, *J* = 15.4, 8.6, 1.5 Hz), 4.53 (s, 2H), 4.44 (s, 2H), 4.00 (dd, 2H, *J* = 5.5, 1.5 Hz), 3.81 (s, 3H), 3.70 (dd, 1H, *J* = 10.8, 4.0 Hz), 3.64 (dd, 1H, *J* = 10.8, 4.5 Hz), 3.10 (dd, 1H, *J* = 8.6, 2.8 Hz), 2.74 (td, 1H, *J* = 4.3, 2.8 Hz), 2.09 (s, 3H). **12c**: ^1H NMR (400 MHz, CDCl_3): δ 7.38–7.24 (m, 7H), 6.87 (d, 2H, *J* = 8.7 Hz), 6.09 (br d, 1H, *J* = 8.6 Hz), 5.87 (dtd, 1H, *J* = 15.6, 5.5, 1.3 Hz), 5.69 (ddt, 1H, *J* = 15.6, 5.5, 1.3 Hz), 4.53 (d, 2H, *J* = 2.2 Hz), 4.50 (m, 1H), 4.42 (s, 2H), 4.06 (m, 1H), 3.98 (dd, 2H, *J* = 5.5, 1.3 Hz), 3.80 (s, 3H), 3.71 (dd, 1H, *J* = 9.6, 3.5 Hz), 3.67 (dd, 1H, *J* = 9.6, 4.2 Hz), 1.99 (s, 3H), 1.62 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.0, 159.5, 137.7, 132.1, 131.3, 129.8, 129.3, 129.0, 128.5, 128.2, 114.2, 74.1, 73.1, 72.2, 71.8, 70.1, 55.7, 53.1, 23.4; IR (neat): 3315 (br), 2922, 2856, 1651 cm^{-1} ; $[\alpha]_{\text{D}}$: -1.3 (*c* 0.15, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{23}\text{H}_{30}\text{NO}_5$ (M+H): 400.2124. Found: 400.2124.

(1*S*,2*S*)-*N*-(5-Benzoyloxy-2-hydroxy-1-methyl-3-(*E*)-pentenyl)-acetamide (12d): Prepared in two steps from aziridine **4d** as described for **12a**, isolated as a yellow oil in 74% yield. **10d**: ^1H NMR

(400 MHz, CDCl₃): δ 7.38-7.25 (m, 5H), 6.03 (dt, 1H, J = 15.4, 5.6 Hz), 5.30 (dd, 1H, J = 15.4, 8.6 Hz), 4.51 (s, 2H), 4.02 (d, 2H, J = 5.6 Hz), 2.81 (dd, 1H, J = 8.6, 2.6 Hz), 2.53 (dq, 1H, J = 5.5, 2.6 Hz), 2.07 (s, 3H), 1.32 (d, 3H, J = 5.6 Hz). **12d**: ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.26 (m, 5H), 6.01 (br d, 1H, J = 8.0 Hz), 5.85 (dt, 1H, J = 15.5, 5.6 Hz), 5.73 (dd, 1H, J = 15.5, 5.9 Hz), 4.50 (s, 2H), 4.05 (m, 1H), 4.02 (d, 2H, J = 5.6 Hz), 3.98 (m, 1H), 3.39 (br s, 1H), 1.95 (s, 3H), 1.17 (d, 3H, J = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 170.6, 138.0, 132.7, 128.7, 128.3, 127.7, 127.6, 74.8, 72.2, 69.9, 49.6, 23.3, 17.4; IR (neat): 3303, 2978, 2866, 1647 cm⁻¹; [α]_D: -24.4 (c 1.22, CH₂Cl₂); HRMS (CI+) Exact mass calcd for C₁₅H₂₂NO₃ (M+H): 264.1600. Found: 264.1601.

(1S,2S)-N-(5-Benzyloxy-1-ethyl-2-hydroxy-2-methyl-3-(E)-pentenyl)-acetamide (12e):

Prepared in two steps from aziridine **4e** as described for **12a**, but with polymer bound DMAP (5.5 mmol N/g, 1 eq) instead of Et₃N in the acetylation. Hydroxyamide **12e** was isolated as a colorless oil in 70% yield. **10e**: ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.27 (m, 5H), 5.94 (dt, 1H, J = 15.6, 5.8 Hz), 5.19 (dt, 1H, J = 15.6, 1.4 Hz), 4.51 (s, 2H), 4.02 (dd, 2H, J = 5.8, 1.4 Hz), 2.43 (t, 1H, J = 6.7 Hz), 2.00 (s, 3H), 1.69-1.45 (m, 2H), 1.43 (s, 3H), 1.17 (t, 3H, J = 7.5 Hz); **12e**: ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.27 (m, 5H), 5.86 (dt, 1H, J = 15.6, 5.2 Hz), 5.80 (d, 1H, J = 15.6 Hz), 5.42 (br d, 1H, J = 9.3 Hz), 4.51 (s, 2H), 4.03 (d, 2H, J = 5.2 Hz), 3.75 (ddd, 1H, J = 11.3, 9.3, 2.9 Hz), 2.63 (s, 1H), 1.99 (s, 3H), 1.77 (dq, 1H, J = 14.1, 7.4, 2.9 Hz), 1.31 (ddq, 1H, J = 14.1, 11.3, 7.4 Hz), 1.26 (s, 3H), 0.93 (t, 3H, J = 7.4 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 171.2, 138.2, 137.9, 128.4, 127.7, 127.6, 125.6, 75.2, 72.2, 70.2, 58.9, 24.3, 23.3, 22.3, 11.1; IR (neat): 3300, 2970, 2873, 1649 cm⁻¹; [α]_D: -32.0 (c 1.25, CH₂Cl₂); HRMS (CI+) Exact mass calcd for C₁₇H₂₆NO₃ (M+H): 292.1913. Found: 292.1913.

(1S,2R)-N-[3-Benzyloxymethyl-2-hydroxy-1-(4-methoxybenzyloxymethyl)-3-butenyl]-acetamide (12f):

Prepared in two steps from aziridine **4f** as described for **12a**, isolated as yellow crystals in 73% yield. **10f**: ¹H NMR (400 MHz, CDCl₃): δ 7.31-7.19 (m, 5H), 7.15 (m, 2H), 6.82 (m, 2H), 5.23 (br s, 1H), 5.18 (br s, 1H), 4.45 (m, 2H), 4.34 (m, 2H), 3.94 (m, 2H), 3.77-3.71 (m, 1H), 3.74 (s, 3H), 3.63 (m, 1H), 3.09 (br s, 1H), 2.74 (br s, 1H), 2.02 (s, 3H). **12f**: mp 84-85 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.29-7.19 (m, 5H), 7.16 (d, 2H, J = 8.7 Hz), 6.81 (d, 2H, J = 8.7 Hz), 6.02 (d, 1H, J = 8.4 Hz), 5.19 (s, 1H), 5.13 (s, 1H), 4.50 (br s, 1H), 4.42 (AB-q, 2H, J = 11.7 Hz), 4.37 (s, 2H), 4.18 (m, 1H), 4.05 (d, 1H, J = 12.2 Hz), 3.95 (d, 1H, J = 12.2 Hz), 3.74 (s, 3H), 3.61 (d, 2H, J = 4.0 Hz), 3.54 (br s, 1H), 1.87 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.4, 159.4, 144.6, 138.0, 129.5, 128.4, 127.7, 114.5, 113.9, 73.3, 72.9, 72.2, 71.3, 55.3, 50.7, 23.2; IR (neat): 3325 (br), 2952, 2858, 1641 cm⁻¹; [α]_D: -5.5 (c 0.43, CH₂Cl₂); HRMS (CI+) Exact mass calcd for C₂₃H₃₀NO₅ (M+H): 400.2124. Found: 400.2129.

2 Synthesis of vinylepoxides 1c-e

2.1 Synthesis of vinylepoxide **1c** from the previously described ester **17**³ (Scheme S1):

Scheme S1

6-(4-Methoxy-benzyloxy)-hexa-2,4-dien-1-ol (18): Ester **17** (1.60 g, 5.8 mmol) in CH₂Cl₂ (35 mL) was cooled to -70 °C before slow addition of DIBAL (1M solution, 14.5 mL, 14.5 mmol). The mixture was stirred at -70 °C for 1.5 h, quenched with MeOH and poured on Rochelle salt. The

mixture was extracted with CH_2Cl_2 ; the organic phase was washed with brine, dried (MgSO_4) and concd. Flash chromatography on deactivated silica (pentane/EtOAc 3:1(1:1)) afforded dienol **18** as a slightly yellow oil in 80% yield (1.09 g, 4.7 mmol). ^1H NMR (400 MHz, CDCl_3): δ 7.26 (m, 2H), 6.87 (d, 2H, $J = 8.7$ Hz), 6.26 (m, 1H), 5.82 (m, 1H), 4.44 (s, 2H), 4.19 (d, 2H, $J = 5.5$ Hz), 4.03 (d, 1H, $J = 5.5$ Hz), 3.80 (s, 3H), 1.42 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 58.6, 132.5, 131.7, 129.7, 129.5, 129.0, 128.9, 113.3, 71.4, 69.7, 62.3, 54.9; IR (neat): 3386, 2935, 2837 cm^{-1} ; $[\alpha]_{\text{D}}$: +0.9 (c 0.95, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{14}\text{H}_{19}\text{O}_3$ (M+H): 235.1334. Found: 235.1342.

(2S,3S)-{3-[3-(4-Methoxy-benzyloxy)-propenyl]-oxiranyl}-methanol (19**):** Molecular sieves (11 mg, 4 Å) in CH_2Cl_2 (3 mL) were cooled to -30 °C before sequential addition of (+)-DIPT (12.0 μL , 53 μmol), $\text{Ti}(\text{O}^i\text{Pr})_4$ (10.5 μL , 35 μmol) and TBHP (2.49 M, 0.30 mL, 0.71 mmol). The mixture was stirred at -25 °C for 30 min, then dienol **18** (83 mg, 0.35 mmol) in CH_2Cl_2 (2 mL) was added, and the mixture was stored in the freezer overnight. The reaction was quenched with water, stirred with 30% NaOH in sat. NaCl and extracted with CH_2Cl_2 . The organic phase was washed with brine, dried (MgSO_4) and concd. Flash chromatography on deactivated silica (pentane /EtOAc 4:1→pure EtOAc) afforded epoxy alcohol **19** as a yellow oil in 67% yield (40.1 mg, 0.16 mmol) based on recovered starting material (30.5 mg, 37%). Enantiomeric purity was measured using chiral HPLC (Chiral Cel OJ, hexane : isopropanol 90:10, 0.5 mL/min) to 95% es. ^1H NMR (400 MHz, CDCl_3): δ 7.25 (m, 2H), 6.88 (d, 2H, $J = 8.6$ Hz), 6.05 (dt, 1H, $J = 15.6, 5.5$ Hz), 5.51 (dd, 1H, $J = 15.6, 8.2$ Hz), 4.44 (s, 2H), 4.00 (dd, 2H, $J = 5.5, 1.4$ Hz), 3.92 (m, 1H), 3.80 (s, 3H), 3.67 (m, 1H), 3.42 (dd, 1H, $J = 8.2, 2.0$ Hz), 3.07 (ddd, 1H, $J = 4.3, 2.3$ Hz), 1.80 (t, 1H, $J = 5.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 159.1, 132.5, 130.0, 129.2, 128.9, 113.7, 72.1, 69.3, 61.1, 60.0, 55.3, 55.1; IR (neat): 3421, 2933, 2862, 1637 cm^{-1} ; $[\alpha]_{\text{D}}$: -14.3 (c 0.90, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ (M): 250.1205. Found: 250.1200.

(2S,3S)-2-Benzyloxymethyl-3-[3-(4-methoxybenzyloxy)-propenyl]-oxirane (1c**):** Epoxy alcohol **19** (180 mg, 0.72 mmol) and freshly prepared Ag_2O (252 mg, 1.1 mmol) were dissolved in toluene (15 mL), BnBr (96 μL , 0.79 mmol) was added and the mixture was heated to 50 °C for 45 min.⁴ Then 0.5 eq Ag_2O (84 mg, 0.36 mmol) was added and the heating continued for 45 min. The mixture was filtered through Celite, concd and purified by flash chromatography on deactivated silica (pentane/EtOAc 4:1→1:2) to afford vinyloxyepoxide **1c** as a colorless oil in 85% yield (114 mg, 0.33 mmol) based on recovered starting material (81.5 mg, 45%). ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.27 (m, 5H), 7.25 (d, 2H, $J = 8.6$ Hz), 6.88 (d, 2H, $J = 8.6$ Hz), 6.04 (dt, 1H, $J = 15.6, 5.5$ Hz), 5.51 (ddt, 1H, $J = 15.6, 8.0, 1.5$ Hz), 4.57 (AB-q, 2H, $J = 11.7$ Hz), 4.45 (s, 2H), 4.01 (dd, 2H, $J = 5.5, 1.5$ Hz), 3.80 (s, 3H), 3.75 (dd, 1H $J = 11.7, 3.1$ Hz), 3.52 (dd, 1H, $J = 11.7, 5.5$ Hz), 3.30 (dd, 1H, $J = 8.0, 2.0$ Hz) 3.11 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.0, 137.6, 132.3, 129.9, 129.2, 129.1, 128.2, 127.6, 113.7, 73.3, 72.0, 69.8, 69.3, 58.7, 55.3, 55.3; IR (neat): 2932, 2856, 1612 cm^{-1} ; $[\alpha]_{\text{D}}$: -1.0 (c 0.37, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{21}\text{H}_{23}\text{O}_4$ (M-H): 339.1596. Found: 339.1599.

2.2 Synthesis of vinyloxyepoxide **1d** from the previously described diene **20**¹ (Scheme S2):

Scheme S2

(2R,3R)-2-(3-Benzyloxy-(E)-propenyl)-3-methyl-oxirane (1d**):** Diene **20** (1.00 g, 5.3 mmol), 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in EDTA (0.4 mM) (52 mL), dimethoxymethane:acetonitrile 2:1 (80 mL), Bu_4NHSO_4 (80 mg, 0.21 mmol) and catalyst **21** (346 mg, 1.3 mmol) were mixed and cooled to 0 °C before dropwise, simultaneous addition of Oxone (3.66 g, 5.9 mmol) in EDTA (0.4 mM, 32 mL)

and K_2CO_3 in H_2O (32 mL) over 90 min.⁵ The reaction was immediately quenched with 80 mL hexane, extracted with 3* Et_2O , washed with brine, dried (Na_2SO_4) and concd. Flash chromatography (pentane/ $EtOAc$ 15:1→10:1) yielded **1d** (687 mg, 3.4 mmol) in 66% based on recovered starting material. The enantioselectivity was >95% as measured by HPLC (Chiral Cel OD-H, hexane : isopropanol 98:2, 0.5 mL/min). $[\alpha]_D$: +28.6 (*c* 1.32, CH_2Cl_2).

2.3 Synthesis of vinyl epoxide **1e** from the previously described dienol **22**⁵ (Scheme S3):

Scheme S3

(4-Methyl-hepta-(E,E)-2,4-dienyloxymethyl)-benzene (23): NaH (60% in oil, 1.39g, 35 mmol) in THF (50 mL) was cooled to $-40\text{ }^{\circ}C$ before addition of **22** and the mixture was allowed to reach rt, stirred 14 h. Quenched with water, extracted with Et_2O , washed with brine, dried ($MgSO_4$) and concd. Flash chromatography (pentane/ $EtOAc$ 25:1→1:1) afforded **23** as a colorless oil in 94% yield (6.43 g, 30 mmol). 1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.26 (m, 5H), 6.27 (d, 1H, J = 15.6 Hz), 5.68 (dt, 1H, J = 15.6, 6.4 Hz), 5.49 (t, 1H, J = 7.2 Hz), 4.52 (s, 2H), 4.08 (d, 2H, J = 6.4 Hz), 2.14 (qvi, 2H, J = 7.5 Hz), 1.75 (s, 3H), 0.99 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.1, 135.2, 132.4, 128.3, 127.8, 127.5, 122.5, 71.9, 71.1, 21.5, 14.0, 12.2; IR (neat): 2966, 2873, 1678 cm^{-1} ; HRMS (CI+) Exact mass calcd for $C_{15}H_{20}O$ (M): 216.1514. Found: 216.1509.

(2R,3R)-2-(3-Benzyloxy-(E)-propenyl)-3-ethyl-2-methyl-oxirane (1e): Vinyl epoxide **1e** was synthesized by epoxidation of diene **23** as described for **1d**. The regioselectivity was complete, giving **1e** as a colorless oil in 100% yield. Enantiomeric selectivity was measured by HPLC (Chiral Cel OD-H, hexane : isopropanol 99:1, 0.5 mL/min) to 95%. 1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.25 (m, 5H), 5.88 (dt, 1H, J = 15.7, 5.8 Hz), 5.58 (dt, 1H, J = 15.7, 1.4 Hz), 4.52 (s, 2H), 4.03 (dd, 2H, J = 5.8, 1.4 Hz), 2.78 (t, 1H, J = 6.4 Hz), 1.70-1.50 (m, 2H), 1.40 (s, 3H), 1.03 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 135.9, 128.3, 127.9, 127.7, 127.6, 72.3, 70.0, 66.5, 58.9, 21.9, 15.2, 10.4; IR (neat): 2970, 2856 cm^{-1} ; $[\alpha]_D$: -8.5 (*c* 1.08, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{15}H_{20}O_2$ (M): 232.1463. Found: 232.1463.

3 Synthesis of N-H oxazolidinones 14-16

Typical procedure for the conversion of amino alcohols to the corresponding oxazolidinones:

To a solution of amino alcohol (0.140 mmol) and iPr_2NEt (37 μL , 0.210 mmol) in CH_2Cl_2 (2 mL) at $0\text{ }^{\circ}C$ was added $(Cl_3CO)_2CO$ (63 mg, 0.210 mmol) and the mixture was stirred overnight. H_2O was added and the mixture was extracted with Et_2O . The organic phase was washed with water and brine, dried (Na_2SO_4) and concd. Flash chromatography (pentane/ $EtOAc$ 1:1) afforded the corresponding N-H oxazolidinone in 92% yield (0.129 mmol).

3.1 Oxazolidinones 14 from syn-amino alcohols 6 (Scheme S4):

Scheme S4

(4*R*,5*R*)-4-Phenethyl-5-vinyloxazolidin-2-one (14a): Colorless oil; ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.17 (m, 5H), 5.89 (ddd, 1H, $J = 17.2, 10.4, 7.1$ Hz), 5.58 (br s, 1H), 5.43 (dt, 1H, $J = 17.2, 0.8$ Hz), 5.33 (dt, 1H, $J = 10.4, 0.8$ Hz), 4.60 (br t, 1H, $J = 6.6$ Hz), 3.55 (br q, 1H, $J = 6.6$ Hz), 2.71 (br t, 1H, $J = 7.7$ Hz), 2.02-1.86 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 158.5, 140.0, 133.8, 128.7, 128.2, 126.4, 119.3, 83.0, 57.8, 36.2, 32.1; IR (neat): 3282 (br), 2931, 2862, 1751 cm^{-1} ; $[\alpha]_{\text{D}}$: +40.0 (c 0.37, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ (M): 217.1103. Found: 217.1103.

(4*S*,5*R*)-4-Benzylloxymethyl-5-vinyloxazolidin-2-one (14b): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.27 (m, 5H), 5.90 (ddd, 1H, $J = 17.2, 10.6, 6.6$ Hz), 5.40 (d, 1H, $J = 17.2$ Hz), 5.31 (d, 1H, $J = 10.6$ Hz), 5.26 (br s, 1H), 4.65 (t, 1H, $J = 6.6$ Hz), 4.55 (s, 2H), 3.74 (m, 1H), 3.51 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.0, 137.0, 133.9, 128.5, 128.0, 127.7, 118.8, 79.2, 73.7, 71.2, 57.6; IR (neat): 3296 (br), 2922, 2862, 1757 cm^{-1} ; $[\alpha]_{\text{D}}$: +48.9 (c 0.28, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_3$ (M+H): 234.1130. Found: 234.1129.

(4*S*,5*R*)-4-Benzylloxymethyl-5-[3-(4-methoxy-benzyloxy)-1-(*E*)-propenyl]-oxazolidin-2-one (14c): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.27 (m, 5H), 7.26 (d, 2H, $J = 8.7$ Hz), 6.88 (d, 2H, $J = 8.7$ Hz), 5.93 (dt, 1H, $J = 15.6, 4.8$ Hz), 5.83 (ddt, 1H, $J = 15.6, 6.5, 1.5$ Hz), 5.19 (br s, 1H), 4.67 (br t, 1H, $J = 6.3$ Hz), 4.55 (s, 2H), 4.45 (s, 2H), 4.02 (dt, 2H, $J = 4.0, 1.5$ Hz), 3.81 (s, 3H), 3.74 (m, 1H), 3.52 (dd, 1H, $J = 9.3, 4.5$ Hz), 3.45 (dd, 1H, $J = 9.3, 7.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 159.7, 158.5, 137.6, 132.3, 130.4, 129.8, 129.0, 128.5, 128.2, 127.9, 114.3, 79.1, 74.1, 72.7, 71.6, 69.3, 58.1, 55.7; IR (neat): 3298 (br), 2919, 2860, 1757 cm^{-1} ; $[\alpha]_{\text{D}}$: +31.6 (c 0.38, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5$ (M+H): 384.1811. Found: 384.1815.

(4*S*,5*S*)-5-(3-Benzylloxy-1-(*E*)-propenyl)-4-methyl-oxazolidin-2-one (14d): Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.27 (m, 5H), 5.97 (dtd, 1H, $J = 15.5, 5.0, 0.6$ Hz), 5.83 (ddt, 1H, $J = 15.5, 7.1, 1.4$ Hz), 5.81 (br d, 1H, $J = 3.8$ Hz), 4.54 (s, 2H), 4.51 (app. t, 1H, $J = 7.0$ Hz), 4.07 (dd, 2H, $J = 5.0, 1.0$ Hz), 3.66 (app. qvi, 1H, $J = 6.2$ Hz), 1.28 (d, 3H, $J = 6.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 158.8, 137.9, 132.2, 128.4, 127.8, 127.7, 127.2, 84.0, 72.6, 69.2, 54.1, 19.6; IR (neat): 3290, 2927, 2858, 1749 cm^{-1} ; $[\alpha]_{\text{D}}$: -24.9 (c 0.65, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ (M+H): 248.1287. Found: 248.1287.

(4*S*,5*R*)-5-(1-Benzylloxymethylvinyl)-4-(4-methoxybenzyloxymethyl)-oxazolidin-2-one (14f): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.26 (m, 5H), 7.21 (d, 2H, $J = 8.8$ Hz), 6.83 (d, 2H, $J = 8.8$ Hz), 5.32 (s, 1H), 5.29 (s, 1H), 5.14 (br s, 1H), 4.74 (d, 1H, $J = 5.5$ Hz), 4.48 (s, 2H), 4.42 (s, 2H), 4.14 (d, 1H, $J = 12.3$ Hz), 4.05 (d, 1H, $J = 12.3$ Hz), 3.91 (m, 1H), 3.81 (s, 3H), 3.48 (dd, 1H, $J = 9.3, 4.0$ Hz), 3.42 (dd, 1H, $J = 9.3, 7.6$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 159.5, 159.2, 141.9, 137.6, 129.4, 129.3, 128.5, 127.9, 127.8, 115.4, 114.0, 78.8, 73.2, 72.7, 71.5, 70.1, 56.9, 55.3; IR (neat): 3309 (br), 2924, 2856, 1755 cm^{-1} ; $[\alpha]_{\text{D}}$: +20.0 (c 0.26, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5$ (M+H): 384.1811. Found: 384.1815.

3.2 *Cis*-oxazolidinones 15 from *anti*-amino alcohols 2 (Scheme S5):

Scheme S5

(4*R*,5*S*)-5-Phenethyl-4-vinylloxazolidin-2-one (15a): Low melting solid; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.17 (m, 5H), 5.80 (ddd, 1H, $J = 17.6, 10.2, 7.8$ Hz), 5.48 (br s, 1H), 5.34-5.26 (m, 2H), 4.63 (ddd, 1H, $J = 11.7, 8.2, 3.9$ Hz), 4.26 (br t, 1H, $J = 7.8$ Hz), 2.88 (ddd, 1H, $J = 14.1, 9.4, 5.1$ Hz), 2.69 (ddd, 1H, $J = 14.1, 9.0, 7.4$ Hz), 2.00 (m, 1H), 1.78 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.8, 140.4, 132.8, 128.4, 128.4, 126.1, 119.5, 79.0, 58.2, 32.5, 31.9; IR (neat): 3275 (br), 2953, 2864, 1747 cm^{-1} ; $[\alpha]_{\text{D}}$: -10.4 (c 1.05, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ (M): 217.1103. Found: 217.1103.

(4*R*,5*R*)-5-Benzyloxymethyl-4-vinylloxazolidin-2-one (15b): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.27 (m, 5H), 5.87 (ddd, 1H, $J = 17.2, 10.2, 7.0$ Hz), 5.33 (d, 1H, $J = 17.2$ Hz), 5.32 (s, 1H), 5.29 (d, 1H, $J = 10.2$ Hz), 4.81 (dt, 1H, $J = 8.2, 5.5$ Hz), 4.54 (AB-q, 2H, $J = 11.7$ Hz), 4.42 (br t, 1H, $J = 8.2$ Hz), 3.62 (dd, 1H, $J = 9.4, 5.5$ Hz), 3.60 (dd, 1H, $J = 9.4, 5.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 158.3, 137.3, 132.5, 128.3, 127.8, 127.6, 119.4, 78.0, 73.6, 68.1, 57.0; IR (neat): 3309 (br), 2927, 2870, 1757 cm^{-1} ; $[\alpha]_{\text{D}}$: -22.4 (c 0.45, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_3$ (M+H): 234.1130. Found: 234.1133.

(4*R*,5*R*)-5-Benzyloxymethyl-4-[3-(4-methoxy-benzyloxy)-1-(*E*)-propenyl]-oxazolidin-2-one (15c): Slightly yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.25 (m, 5H), 7.24 (d, 2H, $J = 8.7$ Hz), 6.87 (d, 2H, $J = 8.7$ Hz), 5.86 (dt, 1H, $J = 15.6, 4.8$ Hz), 5.78 (dd, 1H, $J = 15.6, 7.3$ Hz), 5.03 (br s, 1H), 4.79 (dt, 1H, $J = 8.3, 5.5$ Hz), 4.53 (d, 2H, $J = 5.1$ Hz), 4.45 (br t, 1H, $J = 7.7$ Hz), 4.44 (s, 2H), 3.96 (d, 2H, $J = 4.8$ Hz), 3.81 (s, 3H), 3.62 (dd, 2H, $J = 10.5, 5.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 159.3, 158.2, 137.4, 132.3, 129.9, 129.4, 128.5, 127.9, 127.8, 126.5, 113.9, 78.1, 73.7, 72.4, 69.1, 68.1, 56.2, 55.3; IR (neat): 3311 (br), 2935, 2862, 1757 cm^{-1} ; $[\alpha]_{\text{D}}$: -2.1 (c 0.33, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5$ (M+H): 384.1811. Found: 384.1808.

(4*S*,5*R*)-4-(3-Benzyloxy-1-(*E*)-propenyl)-5-methyl-oxazolidin-2-one (15d): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.28 (m, 5H), 5.85 (dt, 1H, $J = 15.5, 5.3$ Hz), 5.72 (ddt, 1H, $J = 15.5, 7.7, 1.4$ Hz), 5.61 (br s, 1H), 4.81 (dq, 1H, $J = 7.9, 6.6$ Hz), 4.53 (s, 2H), 4.32 (t, 1H, $J = 7.9$ Hz), 4.05 (dd, 2H, $J = 5.3, 1.4$ Hz), 1.30 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 159.0, 137.8, 131.8, 128.4, 127.8, 127.7, 126.9, 76.3, 72.6, 69.3, 57.6, 16.0; IR (neat): 3288, 2933, 2858, 1747 cm^{-1} ; $[\alpha]_{\text{D}}$: -13.3 (c 1.50, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ (M+H): 248.1287. Found: 248.1292.

(4*S*,5*R*)-4-(3-Benzyloxy-1-(*E*)-propenyl)-5-ethyl-4-methyl-oxazolidin-2-one (15e): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.27 (m, 5H), 5.80 (dt, 1H, $J = 15.7, 5.0$ Hz), 5.71 (dt, 1H, $J = 15.7, 1.2$ Hz), 5.22 (br s, 1H), 4.53 (s, 2H), 4.12 (dd, 2H, $J = 9.7, 4.0$ Hz), 4.06 (dt, 2H, $J = 5.0, 1.2$ Hz), 1.63-1.46 (m, 2H), 1.42 (s, 3H), 1.03 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 158.3, 138.0, 131.5, 128.4, 128.2, 127.8, 127.7, 88.2, 72.6, 69.6, 60.6, 25.7, 23.8, 10.5; IR (neat): 3276, 2972, 2858, 1747 cm^{-1} ; $[\alpha]_{\text{D}}$: +48.1 (c 0.74, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ (M+H): 276.1600. Found: 276.1590.

(4*R*,5*R*)-4-(1-Benzyloxymethylvinyl)-5-(4-methoxybenzyloxymethyl)-oxazolidin-2-one (15f): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.19 (m, 5H), 7.12 (d, 2H, $J = 8.7$ Hz), 6.78 (d, 2H, $J = 8.7$ Hz), 5.26 (s, 1H), 5.22 (s, 1H), 5.19 (br s, 1H), 4.74 (dt, 1H, $J = 8.4, 5.8$ Hz), 4.49 (d, 1H, $J = 8.4$ Hz), 4.39 (s, 2H), 4.31 (AB-q, 2H, $J = 11.4$ Hz), 3.89 (d, 2H, $J = 2.9$ Hz), 3.72 (s, 3H), 3.46 (d, 2H, $J = 5.8$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 159.7, 159.2, 141.7, 138.1, 130.1, 129.8, 128.9, 128.3, 128.2, 116.2, 114.2, 78.4, 73.6, 73.4, 72.2, 68.6, 56.6, 55.7; IR (neat): 3373 (br),

2925, 2864 cm^{-1} ; $[\alpha]_{\text{D}}$: -16.7 (c 0.75, CH_2Cl_2); HRMS (CI+): Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5$ (M+H): 384.1811. Found: 384.1807.

3.3 *Cis*-oxazolidinones **16** from *anti*-amino alcohols **5** (Scheme S6):

Scheme S6

(4*R*,5*S*)-4-Phenethyl-5-vinyloxazolidin-2-one (16a): Low melting solid; ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.14 (m, 5H), 5.90 (ddd, 1H, J = 17.2, 10.4, 7.1 Hz), 5.48 (dt, 1H, J = 17.2, 1.1 Hz), 5.40 (dt, 1H, J = 10.4, 1.1 Hz), 5.05 (br t, 1H, J = 8.0 Hz), 3.88 (td, 1H, J = 8.0, 5.5 Hz), 2.86-2.57 (m, 3H), 1.86-1.76 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 158.0, 140.2, 130.7, 128.7, 128.2, 126.4, 120.3, 80.5, 55.4, 32.9, 32.5; IR (neat): 3327 (br), 2932, 2868, 1749 cm^{-1} ; $[\alpha]_{\text{D}}$: $+9.7$ (c 0.35, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ (M): 217.1103. Found: 217.1111.

(4*S*,5*S*)-4-Benzylloxymethyl-5-vinyloxazolidin-2-one (16b): Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.20 (m, 5H), 5.88 (ddd, 1H, J = 17.2, 10.5, 6.7 Hz), 5.40 (dt, 1H, J = 17.2, 1.2 Hz), 5.29 (d, 1H, J = 10.5, 1.2 Hz), 5.21 (br s, 1H), 5.07 (br t, 1H, J = 8.0 Hz), 4.41 (AB-q, 2H, J = 11.9 Hz), 4.04 (td, 1H, J = 8.3, 3.9 Hz), 3.40-3.29 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.8, 137.6, 130.5, 129.0, 128.5, 128.2, 120.7, 78.9, 74.1, 69.9, 55.5; IR (neat): 3267 (br), 2924, 2858, 1755 cm^{-1} ; $[\alpha]_{\text{D}}$: $+33.0$ (c 0.14, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_3$ (M+H): 234.1130. Found: 234.1121.

(4*S*,5*S*)-4-Benzylloxymethyl-5-[3-(4-methoxy-benzylloxy)-1-(*E*)-propenyl]-oxazolidin-2-one

(16c): Low melting solid; ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.23 (m, 7H), 6.88 (d, 2H, J = 8.6 Hz), 6.01 (dt, 1H, J = 15.6, 4.4 Hz), 5.76 (dd, 1H, J = 15.6, 7.3 Hz), 5.18 (br s, 1H), 5.13 (br t, 1H, J = 7.5 Hz), 4.51 (d, 2H, J = 3.3 Hz), 4.44 (s, 2H), 4.01 (m, 3H), 3.81 (s, 3H), 3.47 (dd, 1H, J = 9.3, 4.3 Hz), 3.41 (t, 1H, J = 9.3 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 159.8, 158.8, 137.7, 133.7, 130.4, 129.7, 129.0, 128.5, 128.2, 124.0, 114.3, 78.4, 74.1, 72.6, 69.9, 69.3, 55.8, 55.7; IR (neat): 3323 (br), 2927, 2858, 1749 cm^{-1} ; $[\alpha]_{\text{D}}$: $+23.3$ (c 0.36, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5$ (M+H): 384.1811. Found: 384.1808.

(4*S*,5*R*)-5-(3-Benzylloxy-1-(*E*)-propenyl)-4-methyl-oxazolidin-2-one (16d): Slightly yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.27 (m, 5H), 6.00 (dtd, 1H, J = 15.6, 5.1, 0.9 Hz), 5.81 (ddt, 1H, J = 15.6, 7.3, 1.6 Hz), 5.62 (br s, 1H), 5.07 (dt, 1H, J = 7.5, 0.6 Hz), 4.54 (s, 2H), 4.09 (d, 2H, J = 5.1 Hz), 3.99 (app. q, 1H, J = 6.9 Hz), 1.15 (d, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 137.9, 132.9, 128.4, 127.7, 127.7, 124.5, 79.9, 72.4, 69.3, 51.5, 17.0; IR (neat): 3294, 2978, 2858, 1757 cm^{-1} ; $[\alpha]_{\text{D}}$: -0.9 (c 0.91, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ (M+H): 248.1287. Found: 248.1277.

(4*S*,5*R*)-5-(3-Benzylloxy-1-(*E*)-propenyl)-4-ethyl-5-methyl-oxazolidin-2-one (16e): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.27 (m, 5H), 5.95 (dt, 1H, J = 15.7, 5.1 Hz), 5.76 (dt, 1H, J = 15.7, 1.6 Hz), 5.66 (br s, 1H), 4.53 (s, 2H), 4.07 (dd, 2H, J = 5.1, 1.6 Hz), 3.43 (ddd, 1H, J = 9.3, 4.5, 0.6 Hz), 1.54 (s, 3H), 1.49 (m, 1H), 1.40 (m, 1H), 0.94 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 158.3, 138.1, 129.2, 128.4, 128.1, 127.7, 127.7, 84.2, 72.4, 69.6, 64.0, 26.0, 24.9, 10.8; IR (neat): 3259, 2972, 2877, 1747 cm^{-1} ; $[\alpha]_{\text{D}}$: -36.9 (c 0.54, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ (M+H): 276.1600. Found: 276.1598.

(4*S*,5*S*)-5-(1-Benzylloxymethylvinyl)-4-(4-methoxybenzylloxymethyl)-oxazolidin-2-one (16f): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.25 (m, 5H), 7.17 (d, 2H, J = 8.7 Hz), 6.86 (d,

2H, $J = 8.7$ Hz), 5.40 (s, 1H), 5.31 (s, 1H), 5.27 (br s, 1H), 5.17 (d, 1H, $J = 7.8$ Hz), 4.47 (AB-q, 2H, $J = 11.7$ Hz), 4.34 (AB-q, 2H, $J = 11.2$ Hz), 4.02 (AB-q, 2H, $J = 11.9$ Hz), 3.98 (ddd, 1H, $J = 9.4, 7.8, 3.8$ Hz), 3.79 (s, 3H), 3.43 (dd, 1H, $J = 9.4, 3.8$ Hz), 3.26 (t, 1H, $J = 9.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 158.8, 138.8, 129.9, 129.8, 128.9, 128.3, 128.1, 115.6, 114.3, 78.2, 73.7, 73.3, 71.9, 70.2, 55.7, 55.4; IR (neat): 3298 (br), 2924, 2858, 1759 cm^{-1} ; $[\alpha]_{\text{D}}$: +42.0 (c 0.50, CH_2Cl_2); HRMS (EI+): Exact mass calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_5$ (M): 383.1733. Found: 383.1728.

4 Other compounds (8, 11a)

(4*S*,5*R*)-4-(3-Benzoyloxy-(*Z*)-propenyl)-5-methyl-3-(toluene-4-sulfonyl)-oxazolidin-2-one (8):

Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, 2H, $J = 8.4$ Hz), 7.38-7.32 (m, 5H), 7.30 (d, 2H, $J = 8.4$ Hz), 5.99 (dt, 1H, $J = 10.7, 5.9$ Hz), 5.35 (tt, 1H, $J = 10.7, 1.5$ Hz), 5.26 (dd, 1H, $J = 10.7, 7.0$ Hz), 4.71 (qvi, 1H, $J = 6.7$ Hz), 4.57 (d, 2H, $J = 1.3$), 4.25 (ddd, 1H, $J = 13.0, 5.7, 1.8$ Hz), 4.20 (ddd, 2H, $J = 13.0, 6.1, 1.3$ Hz), 2.43 (s, 3H), 1.24 (d, 3H, $J = 6.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 151.5, 145.3, 137.7, 135.1, 133.6, 139.5, 128.7, 128.5, 127.9, 127.7, 124.7, 75.2, 73.0, 65.9, 58.4, 21.7, 15.2; IR (neat): 2980, 2879, 1784, 1367 cm^{-1} ; $[\alpha]_{\text{D}}$: -90.7 (c 1.69, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_5\text{S}$ (M+H): 402.1375. Found: 402.1376.

(4*R*,5*R*)-2-Methyl-4-phenethyl-5-vinyl-4,5-dihydrooxazole (11a): Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.17 (m, 5H), 5.89 (ddd, 1H, $J = 17.3, 10.3, 7.3$ Hz), 5.33 (dt, 1H, $J = 17.2, 1.0$ Hz), 5.24 (dt, 1H, $J = 10.3, 1.0$ Hz), 4.50 (t, 1H, $J = 7.3$ Hz), 3.78 (br q, 1H, $J = 7.3$ Hz), 2.92-2.68 (m, 2H), 2.06 (s, 3H), 2.00-1.81 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 61.9, 136.1, 128.2, 125.8, 117.3, 85.9, 71.7, 37.2, 32.2, 17.1; HRMS (EI+) Exact mass calcd $\text{C}_{14}\text{H}_{17}\text{NO}$ (M): 215.1310. Found: 215.1314.

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