A Regio- and Stereodivergent Synthesis of *vic*-Amino Alcohols

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Supporting Information

General. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300/400 MHz, JEOL 270 MHz or Bruker dpx 400/500 MHz spectrometers in $CDCl_3$, using the residual peak of $CHCl_3$ (^{1}H 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 (b=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), integration and coupling constants (Hz). Optical rotations, $[\alpha]_D$, were measured on a Perkin Elmer 343 polarimeter at the sodium D line at ambient temperature. Infrared spectra were recorded on a ATI Mattson FTIR spectrophotometer and only the strongest/structurally most important peaks (ν, cm^{-1}) are listed. High resolution mass spectra were recorded on a JEOL SX-102 spectrometer. Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} plates, the plates were visualized with UV light and phosphomolybdic acid/cerium sulfate staining reagent (purchased from Aldrich as a 20 wt% solution in ethanol but diluted to ca 5 wt% before use). Flash chromatography employed Grace Amicon silica gel 60 (35-70 μm). 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 distilled from sodium-benzophenone ketyl before use; dichloromethane was distilled from CaH_2.

Spectroscopic data for compounds **3a**,**b** and **4a,b** see ref 1.

Representative experimental. Pd(0)-catalyzed ring-opening of vinylepoxide 1d affording oxazolidinone 7d: To a solution of $(dba)_3Pd_2{\cdot}CHCl_3$ (7.6 mg, 7.3 μmol) in THF (1 mL) was added dist. $(^{i}PrO)_3P$ (18 μL, 73 μmol). The mixture was stirred for 20 min before addition of dist. TsNCO (22 μL, 0.146 mmol) and vinylepoxide **1d** (25.0 mg, 73 μmol) in THF (1 mL), and the resultant mixture was stirred for 30 min at r.t. Water was added, and the mixture was extracted with Et_2O. The organic phase was washed with water and brine, dried (Na_2SO_4) and concentrated. Flash chromatography (pentane/EtOAc 5:1→2:1) afforded oxazolidinone **7d** in 93% yield (37.0 mg, 68 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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}; $[\alpha]_D$ + 22.9°

(*c* 0.90, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{29}H_{31}NO_7S$ (M): 537.1821. Found: 537.1826.

Representative experimental. Detosylation and hydrolysis of oxazolidinone 7d into *syn*-amino alcohol 2d: Sodium naphthalide was prepared by stirring naphthalene (200 mg, 1.6 mmol) and small pieces of sodium (50 mg, 2.2 mmol) in freshly dist. DME (3 mL) overnight. To a solution of oxazolidinone **7d** (20.0 mg, 37 μmol) in THF (0.5 mL) at -78 °C was dropwise added sodium naphtalide until the blackish color persisted. The mixture was stirred for 15 min, quenched with EtOH and allowed to reach 0 °C before addition of phosphate buffer (pH 7). The mixture was extracted with Et_2O. The organic phase was washed with water and brine, dried (Na_2SO_4) and concentrated. The diastereomers could be separated by careful flash chromatography (pentane/EtOAc 4:1→1:1) affording the corresponding *N*-H oxazolidinone in 85% yield (12.0 mg, 32 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.17 (m, 7H), 6.83 (d, 2H, *J* = 9.1 Hz), 5.22 (m, 2H), 5.17 (br s, 1H), 4.46 (AB-q, 2H, *J* = 12.1 Hz), 4.43 (m, 3H), 4.28 (d, 1H, *J* = 5.0 Hz), 3.97 (AB-q, 2H, *J* = 11.8 Hz), 3.76 (s, 3H), 3.57 (m, 2H); ^{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}; $[\alpha]_D$ -19.9 (*c* 0.89, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{22}H_{25}NO_5$ (M): 383.1733. Found: 383.1740.

A solution of the *N*-H oxazolidinone (20.0 mg, 52 μmol) in 1M KOH (EtOH/H_2O 2:1) was refluxed for 90 min. Aqueous NaOH (2M) was added, and the mixture was extracted several times with Et_2O. The organic phase was washed with brine, dried (Na_2SO_4) and concentrated. The crude product was pushed through a short silica plug to afford *syn*-amino alcohol **2d** in 86% yield (16.0 mg, 45 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.14 (m, 7H), 6.80 (d, 2H, *J* = 8.8 Hz), 5.12 (m, 2H) 4.44 (m, 2H), 4.39 (br s, 2H), 3.98 (AB-q, 2H, *J* = 12.1 Hz), 3.74-3.68 (m, 1H), 3.73 (s, 3H), 3.52-3.36 (m, 3H), 2.00 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2,, 147.0, 137.8, 130.2, 129.3, 128.4, 127.7, 115.0, 113.8, 73.0, 72.5, 71.7, 71.7, 71.4, 56.2, 55.2; IR (neat) 3373 (br), 2910, 2860 cm^{-1}; $[\alpha]_D$ –6.9 (*c* 1.00, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2019.

***syn*-Amino alcohol 2a:**
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.24 (m, 5H), 5.82 (ddd, 1H, *J* = 17.3, 10.4, 6.9 Hz), 5.20 (d, 1H, *J* = 17.3 Hz), 5.11 (d, 1H, *J* = 10.4 Hz), 4.56 (AB-q, 2H, *J* = 11.9 Hz), 3.58 (m, 2H), 3.50 (m, 1H), 3.40 (br t, 1H, *J* = 6.9 Hz), 2.00 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 137.8, 128.3, 127.6, 115.9, 73.5, 73.0, 71.7, 56.2; IR (neat): 3356 (br), 2904, 2864 cm^{-1}; $[\alpha]_D$: -9.1 (*c* 0.65, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{12}H_{18}NO_2$ (M+H): 208.1338. Found: 208.1340.

***syn*-Amino alcohol 2b:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.16 (m, 5H), 5.78 (ddd, 1H, *J* = 17.2, 10.5, 7.4 Hz), 5.19 (dt, 1H, *J* = 17.2, 1.2 Hz), 5.13 (dt, 1H, *J* = 10.5, 1.2 Hz), 3.32 (ddd, 1H, *J* = 10.2, 7.4, 3.1 Hz), 3.14 (t, 1H, *J* = 7.4 Hz), 2.88 (ddd, 1H, *J* = 13.9, 10.2, 5.1 Hz), 2.69 (ddd, 1H, *J* = 13.9, 10.2, 7.0 Hz), 2.17 (br s, 3H), 1.85 (m, 1H), 1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 139.9, 128.3, 128.2, 125.6, 115.8, 73.2, 59.5, 35.7, 32.2; IR (neat): 3357 (br), 2920, 2860 cm^{-1}; $[\alpha]_D$: -27.5 (*c* 0.63, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{12}H_{18}NO$ (M+H): 192.1388. Found: 192.1377.

***syn*-Amino alcohol 2c:**
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.27 (m, 5H), 7.25 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 5.75 (dd, 1H, *J* = 15.6, 4.8 Hz), 5.69 (dd, 1H, *J* = 15.6, 6.0 Hz), 4.56 (AB-q, 2H, *J* = 12.1 Hz), 4.42 (s, 2H), 3.95 (d, 2H, *J* = 4.8 Hz), 3.80 (s, 3H), 3.59-3.40 (m, 4H), 1.96 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 138.0, 130.2, 129.4, 128.4, 128.3, 127.8, 113.8, 77.2, 73.5, 73.3, 72.0, 71.8, 69.9, 55.3; IR (neat): 3583, 3357 (br), 2920, 2856 cm^{-1}; $[\alpha]_D$: -20.3 (*c* 1.10, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2021.

Representative experimental. Aminolysis of vinylepoxide 1d affording *anti*-amino alcohol 3d: Vinylepoxide **1d** (15.0 mg, 86 μmol) in NH_4OH (25%, 2.5 mL) was subjected to focused microwave irradiation at 30W for 8 min. The solvent was evaporated at reduced pressure and the crude product chromatographed (EtOAc/MeOH 6:1+1% NH_3) to give *anti*-amino alcohol **3d** in 86% yield (13.5 mg, 38 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.21 (m, 7H), 6.87 (d, 2H, *J* = 8.8 Hz), 5.24 (m, 1H), 5.21 (m, 1H), 4.52 (m, 2H), 4.45 (m, 2H), 4.12 (d, 1H, *J* = 11.8 Hz), 4.00 (d, 1H, *J* = 11.8 Hz), 3.83 (m, 1H), 3.78 (s, 3H), 3.63 (d, 1H, *J* = 6.0 Hz), 3.53 (m, 2H), 2.18 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 146.2, 137.7, 130.2, 129.3, 128.4, 127.7, 115.9, 113.8, 73.0, 72.6, 72.1, 71.4, 71.3, 57.4, 55.2; IR (neat): 3369 (br), 2910, 2860 cm^{-1}; $[\alpha]_D$ +0.8 (*c* 1.00, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2043.

***anti*-Amino alcohol 3c:**
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 5H), 7.25 (d, 2H, *J* = 8.7 Hz), 6.87 (d, 2H, *J* = 8.7 Hz), 5.75 (m, 2H), 4.52 (s, 2H), 4.42 (s, 2H), 3.97 (d, 2H, *J* = 4.2 Hz), 3.80 (s, 3H), 3.77 (m, 1H), 3.51 (m, 3H), 2.16 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 138.0, 133.4, 130.3, 129.4, 128.4, 128.3, 127.8, 113.8, 73.5, 72.7, 71.9, 71.7, 70.0, 55.6, 55.3; IR (neat): 3583, 3377 (br), 3922, 2852 cm^{-1}; $[\alpha]_D$: +2.5 (*c* 0.25, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2014.

Representative experimental. Ring-closure of *anti*-amino alcohol 3d into vinylaziridine 4d: To a solution of PPh_3 (50.5 mg, 78 μmol) in THF (1 mL) at 0 °C was added DIAD (15 μL, 78 μmol). After 20 min amino alcohol **3d** (20.0 mg, 56 μmol) in THF (1 mL) was added, and the resultant mixture was refluxed for 24 hours. The solvent was evaporated at reduced pressure, Et_2O was added to the crude

product, and the mixture was stored overnight in the freezer. Precipitated Ph_3PO was removed by filtration and careful flash chromatography on deactivated silica (10% Et_3N during packing), (pentane → pentane/EtOH 10:1) afforded vinylaziridine **4d** in 63% yield (12.0 mg, 35 μmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37–7.23 (m, 7H), 6.87 (m, 2H), 5.18 (br s, 1H), 5.14 (t, 1H, *J* = 1.3 Hz), 4.48 (m, 4H), 4.01 (AB-q, 2H, *J* = 12.1 Hz), 3.79 (s, 3H), 3.58 (m, 1H), 3.46 (dd, 1H, *J* = 9.8, 4.8 Hz), 2.45 (br s, 1H), 2.27 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 143.2, 137.9, 130.2, 129.3, 128.4, 127.7, 127.6, 114.1, 114.0, 114.0, 113.9, 113.8, 72.6, 72.0, 71.4, 55.2, 37.2, 37.2, 37.1, 21.9; IR (neat): 3408 (br), 2933, 2858 cm^{-1}; $[\alpha]_D$ +7.0 (*c* 0.50, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{26}NO_3$ (M+H): 340.1913. Found: 340.1916.

Representative experimental. Solvolysis of vinylaziridine 4d into *anti*-amino alcohol 6d: To a solution of vinylaziridine **4d** (20.0 mg, 59 μmol) in THF (0.5 mL) and H_2O (0.5 mL) was added $HClO_4$ (3.5 μL, 0.59 μmol) and the solution was heated to 50 °C for 3h. Aqueous NaOH (2M) was added, and the mixture was extracted several times with Et_2O. The organic phase was washed with brine, dried (Na_2SO_4) and concentrated.. Flash chromatography (EtOAc/MeOH 10:1+ 1% NH_4OH) yielded amino alcohol **6d** in 71% (14.9 mg, 42 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.21 (m, 7H), 6.88 (d, 2H, *J* = 8.6 Hz), 5.28 (s, 1H), 5.26 (s, 1H), 4.54 (m, 2H), 4.42 (m, 2H), 4.10 (d, 1H, *J* = 6.3 Hz), 4.08 (m, 2H), 3.79 (s, 3H), 3.58 (dd, 1H, *J* = 9.2, 4.3 Hz), 3.52 (dd, 1H, *J* = 9.2, 6.3 Hz), 3.15 (dt, 1H, *J* = 6.3, 4.3 Hz), 1.80 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 144.7, 137.9, 130.0, 129.4, 128.5, 127.8, 127.7, 116.0, 113.9, 77.6, 73.2, 72.6, 71.1, 55.3, 53.0; IR (neat): 3369 (br), 2914, 2860, 2360 cm^{-1}; $[\alpha]_D$: +7.0 (*c* 0.50, CH_2Cl_2); HRMS(CI+): Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2019.

***anti*-Amino alcohol 6a:**
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.24 (m, 5H), 5.84 (ddd, 1H, *J* = 17.3, 10.4, 6.0 Hz), 5.31 (dt, 1H, *J* = 17.3, 1.7 Hz), 5.20 (dt, 1H, *J* = 10.4, 1.7 Hz), 4.50 (s, 2H), 4.11 (br t, 1H, *J* = 5.8 Hz), 3.51 (m, 2H), 3.06 (br q, 1H, *J* = 6.0 Hz), 2.01 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.3, 128.3, 127.7, 127.6, 116.5, 74.6, 73.5, 72.3, 54.6; IR (neat): 3343 (br), 2908, 2860 cm^{-1}; $[\alpha]_D$: -11.4 (*c* 0.69, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{12}H_{18}NO_2$ (M+H): 208.1338. Found: 208.1344.

***anti*-Amino alcohol 6b:**
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.16 (m, 5H), 5.86 (ddd, 1H, *J* = 17.3, 10.7, 6.1 Hz), 5.34 (dt, 1H, *J* = 17.3, 1.5 Hz), 5.25 (dt, 1H, *J* = 10.7, 1.5 Hz), 4.07 (br s, 1H), 2.94-2.76 (m, 3H), 2.62 (ddd, 1H, *J* = 14.0, 9.9, 6.9 Hz), 1.94 (br s, 3H), 1.91-1.76 (m, 1H); 1.63-1.49 (m, 1H); ^{13}CNMR (67.5 MHz, $CDCl_3$): δ 141.8, 136.6, 128.5, 128.3, 125.9, 117.0, 75.0, 54.5, 35.4, 32.8; IR (neat): 3373 (br), 2922, 2864 cm^{-1}; $[\alpha]_D$: -15.8 (*c* 5.23, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{12}H_{18}NO$ (M+H): 192.1388. Found: 192.1390.

***anti*-Amino alcohol 6c:**
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.24 (m, 7H), 6.88 (d, 2H, *J* = 8.6 Hz), 5.88 (dt, 1H, *J* = 15.6, 5.5 Hz), 5.73 (dd, 1H, *J* = 15.6, 6.0 Hz), 4.52 (s, 2H), 4.44 (s, 2H), 4.15 (br t, 1H, *J* = 5.7 Hz), 4.00 (d, 2H, *J* = 5.5 Hz), 3.81 (s, 3H), 3.54 (dd, 1H, *J* = 9.5, 5.0 Hz), 3.50 (dd, 1H, *J* = 9.5, 6.0 Hz), 3.06 (br q, 1H, *J* = 5.5 Hz), 2.75 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 138.3, 132.1, 130.7, 129.8, 129.6, 128.9, 128.3, 128.2; 114.2, 74.4, 73.9, 72.8, 72.4, 70.2, 55.7, 55.1; IR (neat): 3585, 3357 (br), 2913, 2858 cm^{-1}; $[\alpha]_D$: +11.4 (*c* 0.07, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2020.

Representative experimental. Acetylation, rearrangement and hydrolysis of vinylaziridine 4d into *syn*-hydroxyamide 9d: A solution of vinylaziridine **4d** (25.0 mg, 74 μmol), Et_3N (20 μL, 0.15 mmol) and DMAP (cat.) in CH_2Cl_2 (1.5 mL) was cooled to -78 °C before addition of Ac_2O (8.3 μL, 80 μmol). After 15 min the reaction was quenched with H_2O and the mixture was extracted with Et_2O. The organic phase was washed with water, sat. $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated to give the crude *N*-acetyl vinylaziridine (26.0 mg) that was taken directly on to the next step. ^{1}H NMR (400 MHz, $CDCl_3$): 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);

To a solution of the *N*-acetyl vinylaziridine (20.0 mg, 52 μmol) in THF (1 mL) at -25 °C was added $BF_3{\cdot}OEt_2$ (13.3 μL, 0.104 μmol). After 1.5 h full conversion into the corresponding oxazoline was achieved. H_2O (0.05 mL) was added, and the resultant mixture was stirred at rt for 2 h. Aqueous NaOH (2M) was added, and the mixture was extracted several times with Et_2O. The organic phase was washed with sat. $NaHCO_3$, dried (Na_2SO_4) and concentrated. Flash chromatography (EtOAc) afforded *syn*-hydroxyamide **9d** in 73% yield (15.2 mg. 38 μmol). ^{1}H NMR (500 MHz, $CDCl_3$): 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); ^{13}C NMR (125 MHz, $CDCl_3$): 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}; $[\alpha]_D$: -5.5 (*c* 0.43, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{23}H_{30}NO_5$ (M+H): 400.2124. Found: 400.2129.

Representative experimental. Hydrolysis of hydroxyamide 9d into *syn*-amino alcohol 5d: Hydroxyamide **9d** (12.0 mg, 30 μmol) in 1M KOH (EtOH/H_2O 2:1) was refluxed for 24 hours. Aqueous NaOH (2M) was added, and the mixture was extracted several times with Et_2O. The organic phase was washed with brine, dried (Na_2SO_4) and concentrated. The crude product was pushed through a short silica plug to afford *syn*-amino alcohol **5d** in 84% yield (9.0 mg, 25 μmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.20 (m, 7H), 6.87 (m, 2H), 5.28 (br s, 1H), 5.26 (br s, 1H), 4.55-4.41 (m, 4H),

4.15-3.95 (m, 3H), 3.80 (s, 3H), 3.56 (m, 1H), 3.48 (m, 1H), 3.11 (m, 1H), 1.80 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 145.5, 138.0, 130.0, 129.4, 128.4, 127.7, 114.9, 113.9, 113.8, 73.2, 73.1, 72.8, 72.3, 70.9, 55.3, 52.9; IR (neat): 3361 (br), 2918, 2856 cm^{-1}; $[\alpha]_D$: +7.8 (*c* 0.75, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2022.

***syn*-amino alcohol 5a:**
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5H), 5.82 (ddd, 1H, *J* = 17.3, 10.4, 5.3 Hz), 5.33 (dt, 1H, *J* = 17.3, 1.4 Hz), 5.20 (dt, 1H, *J* = 10.4, 1.4 Hz), 4.54 (AB-q, 2H, *J* = 11.8 Hz), 4.08 (br t, 1H, *J* = 5.3 Hz), 3.60 (dd, 1H, *J* = 9.3, 4.4 Hz), 3.51 (m, 1H), 2.97 (br m, 1H), 2.34 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.6, 128.3, 127.7, 127.6, 116.5, 73.4, 72.7, 72.3, 54.7; IR (neat): 3332 (br), 2912, 2864 cm^{-1}; $[\alpha]_D$: +14.4 (*c* 0.55, CH_2Cl_2); HRMS (EI+) Exact mass calcd $C_{12}H_{18}NO_2$ (M+H): 208.1338. Found: 208.1334.

***syn*-amino alcohol 5b:**
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.21 (m, 5H), 5.83 (ddd, 1H, *J* = 17.3, 10.4, 6.0 Hz), 5.33 (dt, 1H, *J* = 17.3, 1.4 Hz), 5.21 (dt, 1H, *J* = 10.4, 1.4 Hz), 3.85 (br t, 1H, *J* = 6.0 Hz), 2.79 (ddd, 1H, *J* = 15.4, 10.2, 5.8 Hz), 2.67 (m, 2H), 1.94 (m, 1H), 1.58 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 141.6, 138.7, 128.3, 128.2, 125.8, 116.6, 75.4, 54.9, 35.8, 32.7; IR ($CDCl_3$): 3602, 3300 (br), 3155, 2924 cm^{-1}; $[\alpha]_D$: +13.8 (*c* 0.86, CH_2Cl_2); HRMS (EI+) Exact mass calcd for $C_{12}H_{18}NO$ (M+H): 192.1388. Found: 192.1387.

***syn*-amino alcohol 5c:**
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.25 (m, 7H), 6.88 (d, 2H, *J* = 8.4 Hz), 5.88 (dt, 1H, *J* = 15.6, 5.5 Hz), 5.73 (dd, 1H, *J* = 15.6, 4.8 Hz), 4.53 (AB-q, 2H, *J* = 11.8 Hz), 4.44 (s, 2H), 4.08 (m, 1H), 4.01 (d, 2H, *J* = 5.5 Hz), 3.81 (s, 3H), 3.57 (dd, 1H, *J* = 9.0, 4.3 Hz), 3.48 (dd, 1H, *J* = 9.0, 6.3 Hz), 2.94 (m, 1H), 1.86 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 137.6, 132.6, 130.0, 129.5, 128.8, 128.5, 127.9, 127.8, 113.6, 73.5, 72.6, 72.1, 71.9, 69.7, 55.3, 54.5; IR (neat): 3394 (br), 2933, 2858 cm^{-1}; $[\alpha]_D$: +3.8 (*c* 0.29, CH_2Cl_2); HRMS (CI+) Exact mass calcd for $C_{21}H_{28}NO_4$ (M+H): 358.2018. Found: 358.2022.