SUPPLEMENTARY INFORMATION

A Highly Efficient Methodology of Asymmetric Epoxidation based on a Novel Chiral Sulfur Ylide

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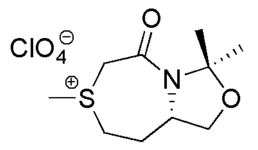
EXPERIMENTAL PROCEDURES

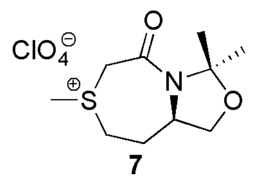
General Techniques. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone, and methylene chloride (CH_2Cl_2) and benzene (PhH) from calcium hydride. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. All solutions used in workup procedures were saturated unless otherwise noted. All reagents were purchased at highest commercial quality and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid or *p*-anisaldehyde solution and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25, 0.50 or 1 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on a

Bruker Advanced-400 instrument and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; b, broad. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. High resolution mass spectra (HRMS) were recorded on a Kratos MS 80 RFA mass spectrometer under fast atom bombardment (FAB) conditions.



6

Sulfonium Salt 6. To a stirred suspension of $NaBH_4$ (31.5 g, 0.80 mol, 2.4 equiv) in THF (300 mL) was added portionwise L-Methionine (**3**) (50.0 g, 0.34 mol, 1.0 equiv) at 0ºC. Then, a solution of I_2 (85.0 g, 0.34 mol, 1.0 equiv) in THF (200 mL) was added dropwise for 1.5 h and after that, the resulting reaction mixture was refluxed for 17 h. After this time, the crude mixture was left to warm to room temperature before addition of MeOH. The solvents were then evaporated and the resulting solid was treated with a 20% aqueous KOH solution (370 mL) under reflux for 6 h. After cooling, the aqueous solution was extracted with CH_2Cl_2 (5 x 300 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvents removed by reduced pressure. Distillation of the resulting crude product (140ºC/0.12 mm Hg) afforded the corresponding L-methioninol (30 g, 65%) as a colorless oil. A solution of L-methioninol (30.0 g, 0.22 mol, 1.0 equiv) in dry acetone (500 mL) was treated with 3Å molecular sieves (15 g) and CSA (2.55 g, 11.0 mmol, 0.05 equiv) and refluxed for 12 h. After this time, the resulting reaction mixture was allowed to warm to room temperature, filtrated and the resulting filtrate treated with TEA (1.53 mL). After removal of the solvents by concentration, the crude product was purified by distillation (bp: 84ºC/0.04 mmHg) to obtain the corresponding N,O-acetal (38 g, 99%) as a colorless oil. A solution of this acetonide (38.0 g, 0.22 mol) and TEA (45.8 mL, 0.33 mol, 1.5 equiv) in CH_2Cl_2 (400 mL) was cooled to 0ºC. Then, a solution of chloroacetyl chloride (26.3 mL, 0.33 mol, 1.5 equiv) in CH_2Cl_2 (50 mL) was added dropwise for 15 minutes. The resulting mixture was stirred at 0ºC for additional 20 minutes, after which a saturated aqueous $NaHCO_3$ solution (200 mL) was added. After separation of both phases, the aqueous solution was extracted with CH_2Cl_2 (2 x 200 mL), and the combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The resulting brown oil was then dissolved in dry acetone (200 mL) and treated with $NaClO_4$ (29.6 g, 0.24 mol, 1.1 equiv) at 40ºC for 48 h. After this time, the resulting suspension was cooled and filtered, and the solid washed with dry acetone. The organic solution was then concentrated under reduced pressure to obtain a syrup, which was dissolved in water, and the aqueous solution extracted twice with CH_2Cl_2. The aqueous solution was concentrated to dryness under reduced pressure to obtain a highly hydroscopic solid, which was purified by crystallization from MeOH. After drying under high vacuum, it was recovered sulfonium salt **6** (48.5 g, 70% from acetal) as a white solid: m p 155-157 ^{o}C; $[\alpha]^{18}_{D}$ = -2.08 (*c* 0.43, DMSO); IR (thin film) ν_{max}: 3015, 2988, 2940, 2886, 1668, 1426, 1410 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ = 1.54 (s, 3 H, $C(CH_3)_2$), 1.63 (s, 3 H, $C(CH_3)_2$), 2.31 (m, 1 H, $SCH_2\mathit{CH_2}$), 2.49 (dt, *J* = 15.6, 3.2 Hz, 1 H, $SCH_2\mathit{CH_2}$,), 3.05 (s, 3 H, SCH_3), 3.63 (dt, *J* = 15.6, 3.2 Hz, 1 H, CH_2O), 3.83-4.00 (m, 4 H, $\mathit{CH_2}S\mathit{CH_2}$), 4.32 (dd, *J* = 9.1, 6.5 Hz, 1 H, CHN), 4.35 (dd, *J* = 16.7, 6.5 Hz, 1 H, CH_2O); ^{13}C NMR (100 MHz, D_2O) δ = 161.0, 97.4, 69.3, 57.3, 45.7, 43.5, 30.4, 26.1, 24.6, 22.0. Elemental Analysis for $C_{10}H_{18}ClNO_6S$: Calcd: 38.04% C, 5.75% H, 4.44% N, 10.15% S, 30.40% O; Found: 37.48% C, 5.26% H, 4.55% N, 10.25% S, 30.72% O.



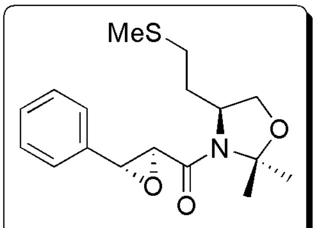
7

Sulfonium Salt 7. Sulfonium salt **7** (22 g, 70% overall yield) was prepared from D-methionine (**4**) (25 g, 0.17 mol) in exactly the same way as described above for **6**. [**7**]: white solid; m p 155-157 ^{o}C; $[\alpha]^{18}_{D}$ = +3.88 (*c* 0.46, DMSO); IR (thin film) ν_{max}: 3015, 2988, 2940, 2886, 1668, 1426, 1410 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ = 1.54 (s, 3 H, $C(CH_3)_2$), 1.63 (s, 3 H, $C(CH_3)_2$), 2.31 (m, 1 H, $SCH_2\mathit{CH_2}$), 2.49 (dt, *J* = 15.6, 3.2 Hz, 1 H, $SCH_2\mathit{CH_2}$,), 3.05 (s, 3 H, SCH_3), 3.63 (dt, *J* =

15.6, 3.2 Hz, 1 H, CH_2O), 3.83-4.00 (m, 4 H, CH_2SCH_2), 4.32 (dd, *J* = 9.1, 6.5 Hz, 1 H, CHN), 4.35 (dd, *J* = 16.7, 6.5 Hz, 1 H, CH_2O); ^{13}C NMR (100 MHz, D_2O) δ = 161.0, 97.4, 69.3, 57.3, 45.7, 43.5, 30.4, 26.1, 24.6, 22.0.

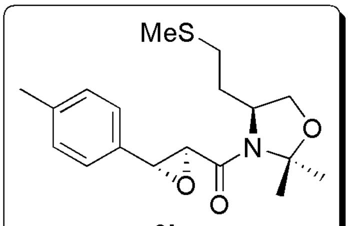
Epoxy amides 9a-j, 11a-i, 11k and 18-24. General Procedure A. To a suspension of sulfonium salt **6** or **7** (1.2 equiv) in *t*BuOH (0.1 M) was added a 3.0 M aqueous NaOH solution (1.2 equiv) at room temperature. After 3 h at this temperature, a solution of aldehyde (**8a-j**, **13**-**15**) (1.0 equiv) in *t*BuOH (0.1 M) was added and the resulting reaction mixture was stirred overnight. The crude mixture was then diluted with CH_2Cl_2 and water, and after decantation, the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography (silica gel, 50% AcOEt in hexanes) to obtain the corresponding pure epoxy amide in yields according to the indicated in Tables 1 and 2. Analysis by NMR and GC-MS of pure epoxy amides allowed to establish the stereochemical yields.

General Procedure B. A solution of sulfonium salt **6** or **7** (1.5 equiv) in H_2O (0.1 M) was treated with a 5.0 M aqueous NaOH solution (1.5 equiv). After 0.5 h, a solution of aldehyde (**8k**, **16**, **17**) (1.0 equiv) in CH_2Cl_2 (0.5 M) was added and the resulting two-phase system was vigourously stirred at room temperature for 48 h. After this time, both phases were separated, and the aqueous phase extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography (silica gel, 50% AcOEt in hexanes) to obtain the corresponding pure epoxy amide in yields according to the indicated in Tables 1 and 2. Analysis by NMR and GC-MS of pure epoxy amides allowed to establish the stereochemical yields.



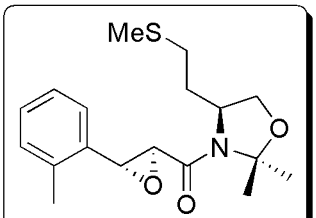
9a

Epoxy Amide 9a: 75%; white solid; m.p. 66-68ºC; R*f* = 0.50 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +126.9 (*c* 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.25 (m, 5 H), 4.23 (ddd, *J* = 10.5, 5.0, 3.1 Hz, 1 H), 4.00 (d, *J* = 1.8 Hz, 1 H), 3.94 (ddd, *J* = 9.1, 5.1, 1.2 Hz, 1 H), 3.78 (d, *J* = 9.1 Hz, 1 H), 3.58 (d, *J* = 1.8 Hz, 1 H), 2.35-2.29 (m, 1 H), 2.20 (ddd, *J* = 14.0, 9.5, 6.0 Hz, 1 H), 1.95-1.85 (m, 2 H), 1.59 (s, 3 H), 1.49 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 135.4, 128.8, 128.6, 125.7, 95.9, 66.9, 57.9, 57.5, 55.8, 34.0, 30.6, 26.3, 22.9, 14.9; FAB HRMS (NBA) *m/e* 344.1302, M+Na$^+$ calcd for $C_{17}H_{23}NO_3S$ 344.1296.



9b

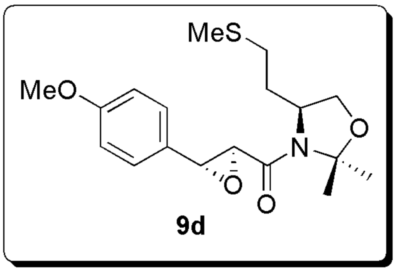
Epoxy Amide 9b: 80%; white solid; m.p. 95.5-96.6ºC; R*f* = 0.25 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +120.6 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max}: 2983, 2921, 1642, 1514, 1442, 1414 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 8.1 Hz, 2 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 4.27 (ddd, *J* = 10.3, 4.8, 3.1 Hz, 1 H), 4.07 (d, *J* = 1.8 Hz, 1 H), 3.99 (ddd, *J* = 9.1, 5.1, 1.3 Hz, 1 H), 3.84 (d, *J* = 9.2 Hz, 1 H), 3.61 (d, *J* = 1.8 Hz, 1 H), 2.41-2.32 (m, 1 H), 2.32-2.20 (m, 2 H), 2.29 (s, 3 H), 2.00-1.88 (m, 1 H), 1.64 (s, 3 H), 1.58 (s, 3 H), 1.53 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 138.6, 132.3, 129.2, 125.6, 95.8, 66.8, 57.9, 57.4, 55.7, 34.0, 30.6, 26.2, 22.9, 22.1, 14.9; FAB HRMS (NBA) *m/e* 358.1455, M+Na$^+$ calcd for $C_{18}H_{25}NO_3S$ 358.1453.



9c

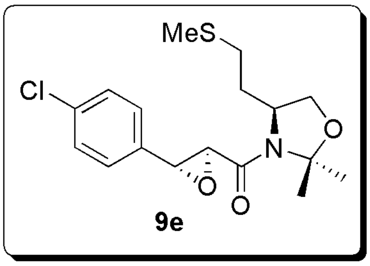
Epoxy Amide 9c: 79%; colorless oil; R*f* = 0.20 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +55.3 (*c* 1.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21-7.08 (m, 4 H), 4.31 (ddd, *J* = 10.5, 4.9, 3.0

Hz, 1 H), 4.24 (bs, 1 H), 3.99 (dd, *J* = 9.2, 5.2 Hz, 1 H), 3.84 (d, *J* = 9.2 Hz, 1 H), 3.50 (d, *J* = 1.4 Hz, 1 H), 2.46-2.39 (m, 1 H), 2.39 (s, 3 H), 2.36-2.24 (m, 2 H), 2.03-1.93 (m, 1 H), 1.65 (s, 3 H), 1.57 (s, 3 H), 1.55 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 136.1, 133.7, 130.0, 128.2, 126.2, 123.9, 95.8, 66.8, 56.9, 57.9, 55.7, 33.9, 28.5, 26.2, 22.8, 18.8, 14.7; FAB HRMS (NBA) *m/e* 358.1462, M+Na$^+$ calcd for $C_{18}H_{25}NO_3S$ 358.1453.



9d

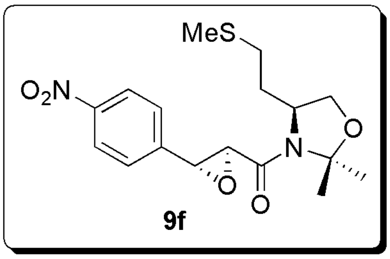
Epoxy Amide 9d: 70%; white solid; m. p. 96.0-97.5ºC; R_f = 0.14 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = +130.0 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.7 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 4.28 (ddd, *J* = 8.2, 4.6, 3.1 Hz, 1 H), 4.02 (d, *J* = 1.6 Hz, 1 H), 3.98 (ddd, *J* = 8.3, 1.6 Hz, 1 H), 3.84 (d, *J* = 9.2 Hz, 1 H), 3.77 (s, 3 H), 3.62 (d, *J* = 1.6 Hz, 1 H), 2.36 (ddd, *J* = 13.5, 6.4, 5.0 Hz, 1 H), 2.24 (ddd, *J* = 15.4, 9.3, 6.2 Hz, 1 H), 1.97-1.88 (m, 1 H), 1.65 (s, 6 H), 1.67-1.56 (m, 1 H), 1.54 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 160.1, 127.3, 127.1, 114.1, 95.8, 66.8, 57.8, 57.3, 55.7, 55.2, 34.0, 30.6, 26.2, 22.9, 15.0; FAB HRMS (NBA) *m/e* 374.1412, M+Na$^+$ calcd for $C_{18}H_{25}NO_4S$ 374.1402.



9e

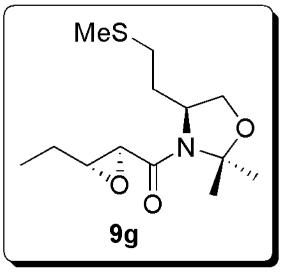
Epoxy Amide 9e: 85%; white solid; m. p. 104.1-106.2ºC; R_f = 0.23 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = +116.5 (*c* 4.8, CH_2Cl_2); IR (neat) ν_{max}: 2978, 2938, 2883, 2845, 1659, 1609, 1582, 1515, 1443, 1422 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H), 4.13 (ddd, *J* = 10.4, 4.9, 3.0 Hz, 1 H), 3.92 (d, *J* = 1.8 Hz, 1 H), 3.85 (ddd, *J* = 9.1, 5.2, 1.2 Hz, 1 H), 3.69 (d, *J* = 9.2 Hz, 1 H), 3.46 (d, *J* = 1.8 Hz, 1 H), 2.30-2.21 (m, 1 H), 2.18-2.07 (m, 1 H), 1.85 (ddd, *J* = 15.9, 10.7, 5.4 Hz, 1 H), 1.49 (s, 6 H), 1.50-1.40 (m, 1 H), 1.39 (s, 3 H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ = 163.0, 160.0, 127.2, 114.0, 95.8, 66.9, 57.8, 57.3, 55.7, 55.2, 34.0, 30.7, 26.2, 22.9, 15.0; FAB HRMS (NBA) *m/e* 378.0911, M+Na$^+$ calcd for $C_{17}H_{22}ClNO_3S$ 378.0907.



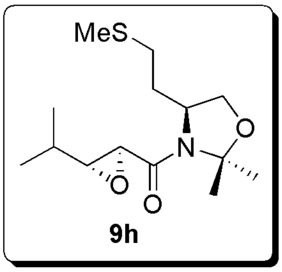
9f

Epoxy Amide 9f: 84%; yellow solid; m. p. 116.5-120.1ºC; R_f = 0.23 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = +127 (*c* 2.4, CH_2Cl_2); IR (neat) ν_{max}: 3110, 3083, 2979, 2936, 2878, 1636, 1604, 1521, 1441, 1416, 1344 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 4.29 (ddd, *J* = 10.4, 4.8, 3.0 Hz, 1 H), 4.21 (d, *J* = 1.7 Hz, 1 H), 4.00 (ddd, *J* = 9.1, 5.1, 1.1 Hz, 1 H), 3.85 (d, *J* = 9.1 Hz, 1 H), 3.65 (d, *J* = 1.7 Hz, 1 H), 2.43 (dt, *J* = 13.5, 5.4 Hz, 1 H), 2.28 (ddd, *J* = 13.5, 9.9, 5.4 Hz, 1 H), 1.97-1.87 (m, 1 H), 1.69 (s, 3 H), 1.65 (s, 3 H), 1.55 (s, 3 H), 1.54-1.41 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.9, 147.9, 142.7, 126.5, 123.7, 95.8, 66.8, 57.5, 56.6, 55.7, 34.1, 30.4, 26.0, 22.7, 15.1; FAB HRMS (NBA) *m/e* 389.1152, M+Na$^+$ calcd for $C_{17}H_{22}N_2O_5S$ 389.1147.



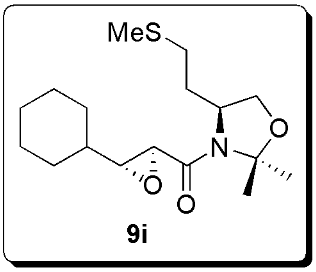
9g

Epoxy Amide 9g: 61%; colorless oil; R_f = 0.32 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = +11.6 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.21 (ddd, *J* = 8.1, 4.9, 3.1 Hz, 1 H), 3.92 (ddd, *J* = 9.2, 5.2, 1.3 Hz, 1 H), 3.80 (d, *J* = 9.2 Hz, 1 H), 3.27 (d, *J* = 2.0 Hz, 1 H), 3.06 (dt, *J* = 6.3, 1.8 Hz, 1 H), 2.50 (ddd, *J* = 12.7, 7.3, 5.1 Hz, 1 H), 2.37 (ddd, *J* = 13.2, 8.7, 7.0 Hz, 1 H), 2.02 (s, 3 H), 2.00-1.97 (m, 1 H), 1.71-1.65 (m, 2 H), 1.55-1.44 (m, 1 H), 1.55 (s, 3 H), 1.43 (s, 3 H), 0.95 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.0, 95.7, 66.8, 59.2, 55.7, 53.4, 34.3, 30.7, 26.1, 24.4, 22.8, 15.8, 9.6; FAB HRMS (NBA) *m/e* 296.1305, M+Na$^+$ calcd for $C_{13}H_{23}NO_3S$ 296.1296.



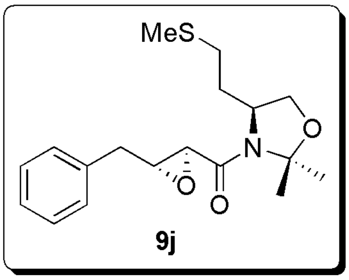
9h

Epoxy Amide 9h: 95%; yellow oil; $R_f = 0.37$ (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_{D} = +10.5$ (*c* 1.1, CH_2Cl_2); IR (neat) ν_{max}: 2981, 2934, 2921, 2873, 1644, 1421, 1397 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.25 (ddd, *J* = 10.5, 5.0, 3.1 Hz, 1 H), 3.94 (ddd, *J* = 9.2, 5.3, 1.5 Hz, 1 H), 3.84 (d, *J* = 9.2 Hz, 1 H), 3.32 (d, *J* = 2.0 Hz, 1 H), 2.96 (dd, *J* = 6.5, 2.0 Hz, 1 H), 2.55 (ddd, *J* = 12.9, 7.4, 5.1 Hz, 1 H), 2.41 (ddd, *J* = 13.0, 8.6, 7.1 Hz, 1 H), 2.06 (s, 3 H), 2.03-1.99 (m, 1 H), 1.76-1.72 (m, 1 H), 1.59 (ds, *J* = 7.0, 6.5 Hz, 1 H), 1.59 (s, 3 H), 1.47 (s, 3 H), 0.98 (d, *J* = 7.0 Hz, 3 H), 0.96 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 95.8, 66.8, 63.4, 55.8, 52.8, 34.6, 30.9, 29.9, 26.3, 22.9, 18.7, 18.4, 16.1; FAB HRMS (NBA) *m/e* 310.1458, $M+Na^+$ calcd for $C_{14}H_{25}NO_3S$ 310.1453.



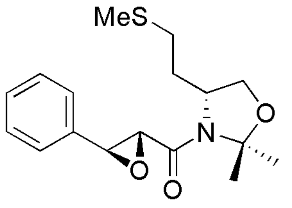
9i

Epoxy Amide 9i: 44%; colorless oil; $R_f = 0.33$ (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_{D} = +14$ (*c* 0.4, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.23 (ddd, *J* = 10.5, 4.8, 3.0 Hz, 1 H), 3.92 (ddd, *J* = 9.1, 5.2, 1.3 Hz, 1 H), 3.81 (d, *J* = 9.1 Hz, 1 H), 3.32 (d, *J* = 2.0 Hz, 1 H), 2.93 (dd, *J* = 6.5, 2.0 Hz, 1 H), 2.55-2.46 (m, 1 H), 2.42-2.35 (m, 1 H), 2.04 (s, 3 H), 1.84-1.57 (m, 6 H), 1.56 (s, 3 H), 1.44 (s, 3 H), 1.34-1.22 (m, 1 H), 1.20-0.99 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 95.7, 66.8, 62.4, 55.8, 52.5, 39.3, 34.5, 30.8, 29.2, 29.0, 26.3, 26.0, 25.5, 25.4, 22.9, 16.0; FAB HRMS (NBA) *m/e* 350.1774, $M+Na^+$ calcd for $C_{17}H_{29}NO_3S$ 350.1766.



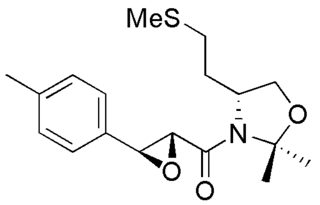
9j

Epoxy Amide 9j: 74%; yellow oil; $R_f = 0.38$ (silica gel, 40% AcOEt in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.15 (m, 5 H), 4.13 (ddd, *J* = 10.3, 4.7, 3.1 Hz, 1 H), 3.90 (ddd, *J* = 8.8, 5.3, 1.5 Hz, 1 H), 3.81 (d, *J* = 9.1 Hz, 1 H), 3.41-3.34 (m, 1 H), 3.23 (d, *J* = 1.9 Hz, 1 H), 2.99 (dd, *J* = 14.9, 4.4 Hz, 1 H), 2.88 (dd, *J* = 14.9, 5.7 Hz, 1 H), 2.51-2.41 (m, 1 H), 2.40-2.25 (m, 1 H), 2.00 (s, 3 H), 1.99-1.89 (m, 1 H), 1.74-1.58 (m, 1 H), 1.55 (s, 3 H), 1.44 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 163.6, 135.9, 129.0, 128.5, 126.8, 95.7, 58.0, 55.8, 53.2, 37.3, 34.5, 33.4, 30.7, 26.3, 22.9, 16.0; FAB HRMS (NBA) *m/e* 358.1461, M+Na$^+$ calcd for $C_{18}H_{25}NO_3S$ 358.1453.



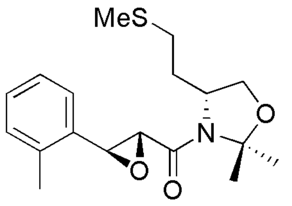
11a

Epoxy Amide 11a: 82%; colorless oil; R_f = 0.42 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = -109 (*c* 0.2, CH_2Cl_2); FAB HRMS (NBA) *m/e* 344.1297, M+Na$^+$ calcd for $C_{17}H_{23}NO_3S$ 344.1296.



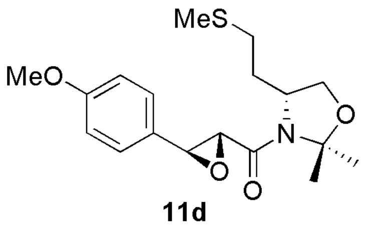
11b

Epoxy Amide 11b: 80%; white solid; m.p. 96-97.1ºC; R_f = 0.28 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = -128 (*c* 0.3, CH_2Cl_2); FAB HRMS (NBA) *m/e* 358.1457, M+Na$^+$ calcd for $C_{18}H_{25}NO_3S$ 358.1453.



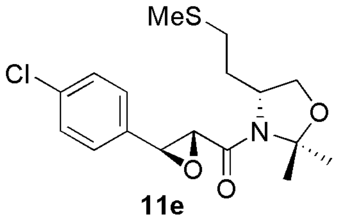
11c

Epoxy Amide 11c: 70%; colorless oil; R_f = 0.21 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = -58.4 (*c* 0.4, CH_2Cl_2); FAB HRMS (NBA) *m/e* 358.1456, M+Na$^+$ calcd for $C_{18}H_{25}NO_3S$ 358.1453.



11d

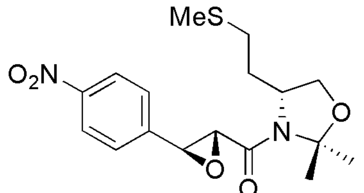
Epoxy Amide 11d: 75%; white solid; m. p. 93.6-95.7ºC; R_f = 0.14 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = -115.1 (*c* 0.4, CH_2Cl_2); FAB HRMS (NBA) *m/e* 374.1408, M+Na$^+$ calcd for $C_{18}H_{25}NO_4S$ 374.1402.



11e

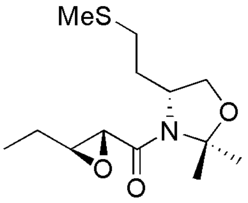
Epoxy Amide 11e: 85%; white solid; m. p. 103.8-106.2ºC; R_f = 0.23 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = -118.2 (*c*

4.8, CH_2Cl_2); FAB HRMS (NBA) *m/e* 378.0909, M+Na^+ calcd for $C_{17}H_{22}ClNO_3S$ 378.0907.



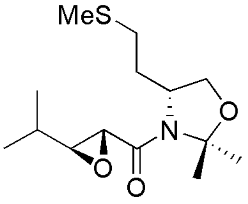
11f

Epoxy Amide 11f: 85%; yellow solid; m. p. 117.0-120.2ºC; R_f = 0.23 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = -127 (*c* 2.4, CH_2Cl_2); FAB HRMS (NBA) *m/e* 389.1149, M+Na^+ calcd for $C_{17}H_{22}N_2O_5S$ 389.1147.



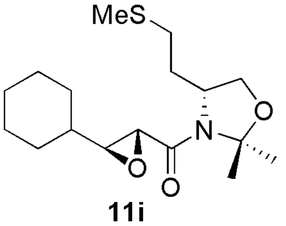
11g

Epoxy Amide 11g: 63%; colorless oil; R_f = 0.32 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = -11.0 (*c* 4.6, CH_2Cl_2); FAB HRMS (NBA) *m/e* 296.1301, M+Na^+ calcd for $C_{13}H_{23}NO_3S$ 296.1296.



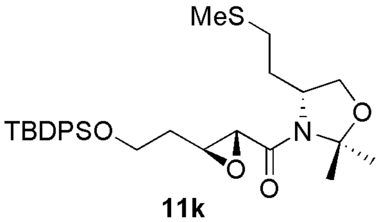
11h

Epoxy Amide 11h: 61%; colorless oil; R_f = 0.37 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = -8.8 (*c* 4.1, CH_2Cl_2); FAB HRMS (NBA) *m/e* 310.1449, M+Na^+ calcd for $C_{14}H_{25}NO_3S$ 310.1453.



11i

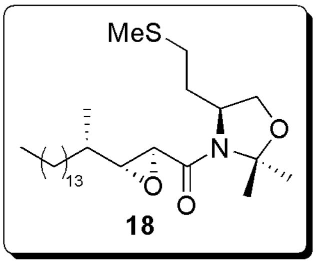
Epoxy Amide 11i: 45%; colorless oil; R_f = 0.33 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = -13.3 (*c* 0.3, CH_2Cl_2); FAB HRMS (NBA) *m/e* 350.1769, M+Na^+ calcd for $C_{17}H_{29}NO_3S$ 350.1766.



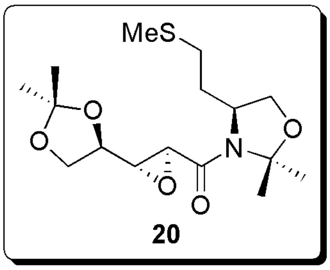
11k

Epoxy Amide 11k: 71%; colorless oil; R_f = 0.45 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = -11.3 (*c* 0.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.70-7.60 (m, 2

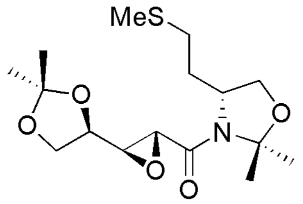
H), 7.40-7.35 (m, 3 H), 4.25 (ddd, *J* = 10.3, 4.7, 3.1 Hz, 1 H), 3.92 (ddd, *J* = 9.1, 5.3, 1.3 Hz, 1 H), 3.81 (d, *J* = 9.1 Hz, 1 H), 3.80-3.70 (m, 2 H), 3.46-3.40 (m, 2 H), 2.51-2.43 (m, 1 H), 2.39-2.32 (m, 1 H), 2.03 (s, 3 H), 1.98-1.92 (m, 1 H), 1.71-1.62 (m, 3 H), 1.58 (s, 3 H), 1.49 (s, 3 H), 0.95 (s, 9 H); FAB HRMS (NBA) *m/e* 550.2418, M+Na$^+$ calcd for $C_{29}H_{41}NO_4SSi$ 550.2423.



Epoxy Amide 18: 60%; colorless oil; R_f = 0.20 (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D$ = +4.0 (*c* 0.2, CH_2Cl_2); IR (neat) ν_{max}: 3275, 2919, 2850, 1656, 1551, 1467 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.00-3.95 (m, 1 H), 3.87 (d, *J* = 9.2 Hz, 1 H), 3.66 (dd, *J* = 9.2, 3.6 Hz, 1 H), 3.35 (d, *J* = 1.9 Hz, 1 H), 3.00 (dd, *J* = 6.2, 1.9 Hz, 1 H), 2.61-2.53 (m, 1 H), 2.47 (t, *J* = 7.4 Hz, 1 H), 2.14 (s, 3 H), 1.90-1.70 (m, 2 H), 1.62 (s, 3 H), 1.50 (s, 3 H), 1.24-1.21 (m, 27 H), 0.98 (d, *J* = 7.0 Hz, 3 H), 0.85 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.0, 95.9, 66.9, 64.8, 64.4, 62.9, 35.5, 34.6, 33.3, 31.9, 30.9, 29.7, 29.6, 29.4, 22.7, 16.5, 16.3, 16.1, 14.1; FAB HRMS (NBA) *m/e* 492.3491, M+Na$^+$ calcd for $C_{27}H_{51}NO_3S$ 492.3487.

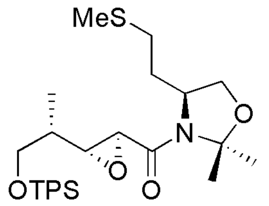


Epoxy Amide 20: 62%; colorless oil; R_f = 0.40 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = +5.5 (*c* 3.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.21 (ddd, *J* = 8.5, 4.6, 3.3 Hz, 1 H), 4.11-4.00 (m, 1 H), 3.95 (dd, *J* = 9.1, 5.2 Hz, 1 H), 3.88-3.79 (m, 3 H), 3.48 (d, *J* = 1.8 Hz, 1 H), 3.18 (dd, *J* = 6.4, 1.8 Hz, 1 H), 2.50 (ddd, *J* = 12.7, 7.4, 5.1 Hz, 1 H), 2.40 (ddd, *J* = 13.4, 8.4, 7.2 Hz, 1 H), 2.04 (s, 3 H), 2.00-1.94 (m, 1 H), 1.88-1.76 (m, 1 H), 1.55 (s, 3 H), 1.44 (s, 3 H), 1.35 (s, 3 H), 1.25 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 109.8, 95.6, 75.1, 66.8, 66.7, 57.6, 55.8, 52.1, 33.8, 30.6, 26.3, 26.0, 22.9, 22.6, 15.5; FAB HRMS (NBA) *m/e* 368.1511, M+Na$^+$ calcd for $C_{16}H_{27}NO_5S$ 368.1508.



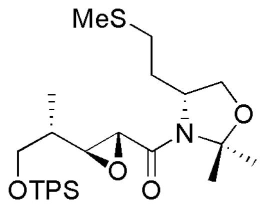
21

Epoxy Amide 21: 50%; colorless oil; R$_f$ = 0.38 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = -15.6 (*c* 1.5, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.24 (ddd, J = 8.5, 4.6, 3.8 Hz, 1 H), 4.16-4.07 (m, 2 H), 3.97-3.93 (m, 1 H), 3.87 (dd, J = 7.0, 5.8 Hz, 1 H), 3.83 (d, J = 9.0 Hz, 1 H), 3.55 (d, J = 1.8 Hz, 1 H), 3.22 (dd, J = 3.1, 1.8 Hz, 1 H), 2.52 (ddd, J = 13.0, 8.0, 5.4 Hz, 1 H), 2.44-2.37 (m, 1 H) 2.05 (s, 3 H), 2.03-1.96 (m, 1 H), 1.76-1.68 (m, 1 H), 1.56 (s, 3 H), 1.45 (s, 3 H), 1.32 (s, 3 H), 1.27 (s, 3 H).



22

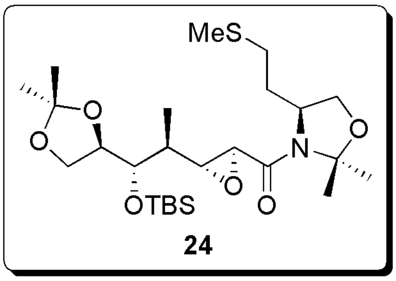
Epoxy Amide 22: 71%; colorless oil; R$_f$ = 0.46 (silica gel, 25% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +11.7 (*c* 0.5, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.62-7.58 (m, 4 H), 7.38-7.30 (m, 6 H), 4.22 (ddd, J = 8.5, 4.7, 3.0 Hz, 1 H), 3.91 (ddd, J = 9.2, 4.9, 1.3 Hz, 1 H), 3.81 (d, J = 9.2 Hz, 1 H), 3.64 (dd, J = 9.9, 6.2 Hz, 1 H), 3.60 (dd, J = 9.9, 5.5 Hz, 1 H), 3.37 (d, J = 1.9 Hz, 1 H), 3.26 (dd, J = 5.9, 2.0 Hz, 1 H), 2.45-2.39 (m, 1 H), 2.32 (ddd, J = 15.3, 8.8, 6.6 Hz, 1 H), 1.98 (s, 3 H), 1.94-1.89 (m, 1 H), 1.82 (sep, J = 6.5 Hz, 1 H), 1.65-1.62 (m, 1 H), 1.59 (s, 3 H), 1.48 (s, 3 H), 0.99 (s, 9 H), 0.97 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 163.9, 135.5, 133.3, 129.6, 127.6, 95.6, 66.8, 66.1, 60.2, 55.6, 52.9, 37.2, 34.4, 30.8, 26.8, 26.7, 26.2, 22.8, 19.1, 15.9, 12.6; FAB HRMS (NBA) *m/e* 564.2581, M+Na$^+$ calcd for $C_{30}H_{43}NO_4SSi$ 564.2580.



23

Epoxy Amide 23: 62%; colorless oil; R$_f$ = 0.52 (silica gel, 25% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = -7.5 (*c* 0.4, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.61-7.58 (m, 4 H), 7.38-7.31 (m, 6 H), 4.23 (ddd, J = 8.5, 4.5, 3.7 Hz, 1 H), 3.94 (dd, J = 9.2, 5.2 Hz, 1 H), 3.83 (d, J = 9.1 Hz, 1 H), 3.69-3.58 (m, 2 H), 3.33 (d, J = 1.8 Hz, 1 H), 3.19 (dd, J = 7.2, 1.8 Hz, 1

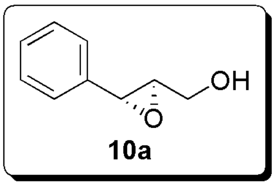
H), 2.52-2.47 (m, 1 H), 2.44-2.35 (m, 1 H), 2.03 (s, 3 H), 1.82-1.79 (m, 1 H), 1.68-1.60 (m, 2 H), 1.60 (s, 3 H), 1.48 (s, 3 H), 1.00 (s, 9 H), 0.98 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.0, 135.5, 133.4, 129.6, 127.6, 95.7, 66.8, 65.9, 60.0, 55.7, 52.6, 37.9, 34.5, 30.7, 26.8, 26.7, 26.2, 22.8, 19.2, 15.9, 13.0; FAB HRMS (NBA) *m/e* 564.2576, M+Na$^+$ calcd for $C_{30}H_{43}NO_4SSi$ 564.2580.



24

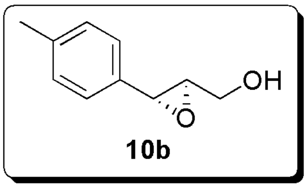
Epoxy Amide 24: 48%; colorless oil; R$_f$ = 0.45 (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D$ = +15.4 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.25 (ddd, *J* = 8.5, 4.5, 3.2 Hz, 1 H), 4.10 (c, *J* = 6.5 Hz, 1 H), 3.99 (dd, *J* = 8.2, 6.1 Hz, 1 H), 3.93 (dd, *J* = 8.9, 5.0 Hz, 1 H), 3.84 (d, *J* = 9.1 Hz, 1 H), 3.81-3.77 (m, 2 H), 3.30-3.28 (m, 2 H), 2.58-2.52 (m, 1 H), 2.44-2.37 (m, 1 H), 2.10 (s, 3 H), 2.07-1.99 (m, 1 H), 1.82-1.75 (m, 1 H), 1.69-1.63 (m, 1 H), 1.59 (s, 3 H), 1.47 (s, 3 H), 1.34 (s, 3 H), 1.26 (s, 3 H), 1.01 (d, *J* = 7.2 Hz, 3 H), 0.82 (s, 9 H), 0.03 (s, 3 H), 0.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.9, 108.8, 95.7, 76.1, 74.4, 67.1, 66.7, 59.2, 55.8, 53.3, 41.0, 34.6, 30.9, 26.5, 26.3, 25.7, 25.2, 22.8, 17.9, 16.0, 11.5, -4.3, -4.5; FAB HRMS (NBA) *m/e* 540.2802, M+Na$^+$ calcd for $C_{25}H_{47}NO_6SSi$ 540.2791.

Epoxy Alcohols 10, 12, 25-29. General Procedure A. A solution of epoxy amide (1.0 equiv) in THF (0.1 M) was treated with Red-Al (0.6 equiv) at -10ºC. After 30 min, the reaction mixture was quenched by addition of a saturated aqueous Na/K tartrate solution and the aqueous phase was extracted twice with Et_2O. The combined organic extracts were dried ($MgSO_4$), filtered and concentrated and the obtained crude epoxy aldehyde was dissolved in MeOH (0.1 M) and treated with excess of sodium borohydride (8.0 equiv) at 0ºC. After 15 min, the reaction mixture was diluted with water and extracted with Et_2O three times. The combined organic layer was dried ($MgSO_4$), filtered and concentrated and the resulting crude product was purified by flash column chromatography (silica gel, 20% AcOEt in hexanes) to obtain the corresponding epoxy alcohol. **General Procedure B.** A solution of epoxy amide (1.0 equiv) in THF (0.1 M) was treated with lithium triethylborohydride (Super-H) (1 M in THF, 3.0 equiv) at room temperature. The reaction mixture was stirred at room temperature until the reaction was complete as judged by TLC (ca. 0.5 h). The excess of Super-H was carefully quenched by addition of MeOH, and the resulting solution was diluted with Et_2O and washed with saturated aqueous NH_4Cl solution. The organic phase was separated, the aqueous layer was extracted with Et_2O (twice), and the combined organic extracts were washed with brine, dried ($MgSO_4$) and filtered. Concentration under reduced pressure provided a crude product that was purified by flash column chromatography (silica gel, 20% AcOEt in hexanes) to afford the corresponding epoxy alcohol.



10a

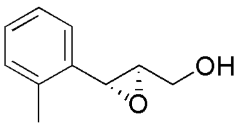
Epoxy Alcohol 10a: Procedure B (67%); colorless oil; R_f = 0.37 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = +57.3 (*c* 1.5, CH_2Cl_2) (*lit.*[1] $[\alpha]^{25}_D$ = +51.0 (*c* 1.0, $CHCl_3$), *ee* 99.1%); IR (neat) ν_{max}: 3396, 3062, 3031, 2960, 2920, 2880 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.24 (m, 5 H), 4.00-3.91 (m, 1 H), 3.88 (d, J = 2.0 Hz, 1 H), 3.78 (d, J = 2.0 Hz, 1 H), 3.18-3.13 (m, 1 H), 1.87 (bs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.5, 128.3, 128.1, 127.5, 62.3, 61.2, 55.6; FAB HRMS (NBA) *m/e* 173.0584, M+Na$^+$ calcd for $C_9H_{10}O_2$ 173.0578.



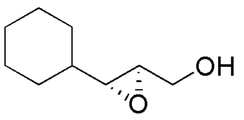
10b

Epoxy Alcohol 10b: Procedure B (80%); white solid; m. p. 57.1-58.5ºC; R_f = 0.45 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = +40.2 (*c* 1.0, CH_2Cl_2) (*lit.*[2] $[\alpha]^{25}_D$ = +36.7 (*c* 2.0, $CHCl_3$), *ee* 99%); IR (neat) ν_{max}: 3339, 2921, 2866 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19-7.09 (m, 4 H), 4.02 (ddd, J = 12.7, 5.2, 2.4 Hz, 1 H), 3.88 (d, J = 2.2 Hz, 1 H), 3.77 (ddd, J = 12.7, 7.6, 3.9 Hz, 1 H), 3.21 (dt, J = 4.0, 2.3 Hz, 1 H), 2.33 (s, 3 H), 1.92 (dd, J = 7.6, 5.4 Hz, 1 H); ^{13}C

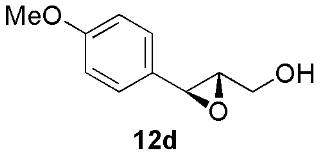
NMR (100 MHz, $CDCl_3$) δ = 138.2, 133.5, 129.2, 125.7, 62.2, 61.2, 55.6, 21.2; FAB HRMS (NBA) *m/e* 187.0737, M+Na$^+$ calcd for $C_{10}H_{12}O_2$ 187.0735.


10c

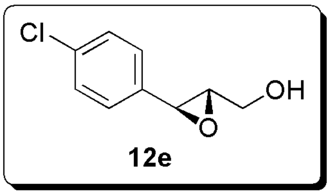
Epoxy Alcohol 10c: Procedure B (73%); colorless oil; R_f = 0.50 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = -0.63 (*c* 1.0, CH_2Cl_2); IR (neat) ν_{max}: 3395, 3023, 2919, 2868 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20-7.12 (m, 4 H), 4.05 (d, *J* = 2.3 Hz, 1 H), 3.85-3.78 (m, 1 H), 3.88 (d, *J* = 2.2 Hz, 1 H), 3.77 (ddd, *J* = 12.7, 7.6, 3.9 Hz, 1 H), 3.21 (dt, *J* = 4.0, 2.3 Hz, 1 H), 2.33 (s, 3 H), 1.92 (dd, *J* = 7.6, 5.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2, 133.5, 129.2, 125.7, 62.2, 61.2, 55.6, 21.2; FAB HRMS (NBA) *m/e* 187.0737, M+Na$^+$ calcd for $C_{10}H_{12}O_2$ 187.0735.


10i

Epoxy Alcohol 10i: Procedure B (98%); colorless oil; R_f = 0.53 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = +25.6 (*c* 1.1, CH_2Cl_2) (*lit.*[3] $[\alpha]^{25}_D$ = +26.4 (*c* 1.3, $CHCl_3$)); IR (neat) ν_{max}: 3400, 2924, 2851 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.88 (dd, *J* = 12.6, 2.5 Hz, 1 H), 3.57 (d, *J* = 12.6, 4.5 Hz, 1 H), 2.96 (dt, *J* = 4.7, 2.5 Hz, 1 H), 2.73 (dd, *J* = 6.8, 2.4 Hz, 1 H), 1.90-1.57 (m, 5 H), 1.33-0.98 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 61.9, 60.2, 57.2, 39.5, 29.6, 28.9, 26.2, 25.6, 25.5; FAB HRMS (NBA) *m/e* 179.1053, M+Na$^+$ calcd for $C_9H_{16}O_2$ 179.1048.

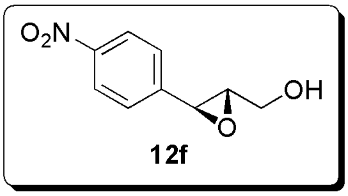

12d

Epoxy Alcohol 12d: Procedure B (80%); colorless oil; R_f = 0.43 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = -12.7 (*c* 1.8, CH_2Cl_2) (*lit.*[4] $[\alpha]^{25}_D$ = -12.5 (*c* 1.1, $CHCl_3$)); IR (neat) ν_{max}: 3481, 2959, 2935, 2882, 2837, 1513 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23-7.15 (m, 2 H), 6.88-6.76 (m, 2 H), 5.07 (d, *J* = 6.2 Hz, 1 H), 4.61-4.53 (m, 1 H), 4.31 (dd, *J* = 13.4, 6.0 Hz, 1 H), 3.78 (s, 3 H), 3.57-3.54 (m, 1 H), 2.31 (bs, 1 H); FAB HRMS (NBA) *m/e* 203.0687, M+Na$^+$ calcd for $C_{10}H_{12}O_3$ 203.0684.



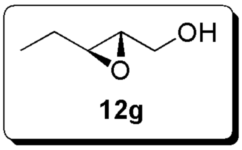
12e

Epoxy Alcohol 12e: Procedure B (69%); colorless oil; $R_f = 0.38$ (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_{D} = -38.5$ (*c* 1.5, CH_2Cl_2) (*lit.*^{5} $[\alpha]^{25}_{D} = -32.3$ (*c* 1.0, $CHCl_3$), *ee* 97%); IR (neat) ν_{max}: 3405, 2960, 2934, 2879, 1493 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.30$ (d, $J = 6.5$ Hz, 2 H), 7.19 (d, $J = 8.6$ Hz, 2 H), 4.02 (d, $J = 12.7$ Hz, 1 H), 3.89 (d, $J = 2.2$ Hz, 1 H), 3.77-3.71 (m, 1 H), 3.15 (dt, $J = 3.8$, 2.2 Hz, 1 H), 2.06 (bs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta =$ 135.2, 134.1, 128.7, 127.0, 62.5, 61.0, 54.9; FAB HRMS (NBA) *m/e* 207.0193, M+Na$^+$ calcd for $C_9H_9O_2Cl$ 207.0189.



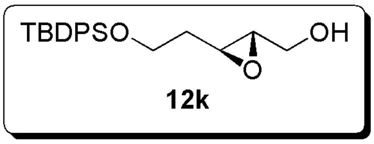
12f

Epoxy Alcohol 12f: Procedure B (59%); colorless oil; $R_f = 0.26$ (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_{D} = -28.2$ (*c* 1.1, CH_2Cl_2) (*lit.*^{5} $[\alpha]^{25}_{D} = -25.0$ (*c* 1.0, $CHCl_3$), *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.17$ (d, $J = 8.8$ Hz, 2 H), 7.42 (d, $J = 8.8$ Hz, 2 H), 4.08-4.04 (m, 2 H), 3.81 (dd, $J = 12.8$, 3.5 Hz, 1 H), 3.20-3.18 (m, 1 H), 2.20 (bs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 147.8$, 144.4, 126.4, 123.7, 63.0, 60.7, 54.3.



12g

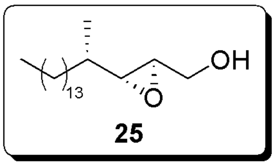
Epoxy Alcohol 12g: Procedure A (56%); colorless oil; $R_f = 0.18$ (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_{D} = -34.1$ (*c* 1.0, EtOH) (*lit.*^{3} $[\alpha]^{25}_{D} = -31.3$ (*c* 0.6, EtOH)); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 3.90$ (ddd, $J = 12.6$, 5.9, 2.1 Hz, 1 H), 3.63 (ddd, $J = 12.6$, 7.2, 4.5 Hz, 1 H), 3.03-2.86 (m, 2 H), 1.93 (t, $J = 7.2$ Hz, 1 H), 1.80-1.45 (m, 2 H), 1.00 (t, $J = 7.2$ Hz, 3 H).



12k

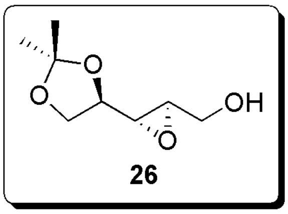
Epoxy Alcohol 12k: Procedure B (75%); colorless oil; $R_f = 0.41$ (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_{D} = -20.2$ (*c* 0.5, $CHCl_3$) (*lit.*^{6} $[\alpha]^{25}_{D} = -16.7$ (*c* 1.0, $CHCl_3$), ee = 83%);^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.65$-

7.62 (m, 4 H), 7.43-7.35 (m, 6 H), 3.89 (dd, $J = 12.5, 2.4$ Hz, 1 H), 3.82-3.75 (m, 2 H), 3.60 (dd, $J = 12.5, 4.2$ Hz, 1 H), 3.11 (ddd, $J = 8.0, 5.7, 2.3$ Hz, 1 H), 2.98-2.94 (m, 1 H), 1.79 (q, $J = 5.7$ Hz, 1 H), 1.59 (bs, 1 H), 1.03 (s, 9 H).



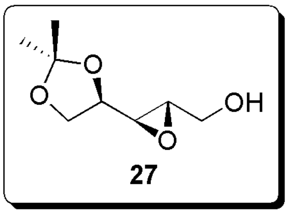
25

Epoxy Alcohol 25[7]: Procedure B (79%); white solid; $R_f = 0.16$ (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D = +17.3$ (c 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 3.89$ (dd, $J = 12.4, 1.1$ Hz, 1 H), 3.59 (dd, $J = 12.4, 3.2$ Hz, 1 H), 2.95 (ddd, $J = 4.8, 2.7, 2.1$ Hz, 1 H), 2.69 (dd, $J = 7.0, 2.1$ Hz, 1 H), 1.86-1.78 (m, 1 H), 1.36-1.17 (m, 26 H), 0.99 (d, $J = 6.4$ Hz, 3 H), 0.85 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 61.7$, 60.6, 58.3, 35.5, 33.6, 31.9, 29.8, 29.66, 29.63, 29.56, 29.3, 27.2, 22.7, 17.2, 14.1; FAB HRMS (NBA) m/e 321.2775, $M+Na^+$ calcd for $C_{19}H_{38}O_2$ 321.2769.



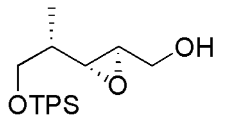
26

Epoxy Alcohol 26: Procedure B (75%); colorless oil; $R_f = 0.46$ (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D = +30.0$ (c 1.1, $CHCl_3$) (*lit.*[3] $[\alpha]^{25}_D = +35.9$ (c 1.4, $CHCl_3$)); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4.13$-4.04 (m, 2 H), 3.96-3.84 (m, 2 H), 3.65 (ddd, $J = 12.8, 6.7, 4.3$ Hz, 1 H), 3.09-3.03 (m, 2 H), 1.80 (bs, 1 H), 1.42 (s, 3 H), 1.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 109.9$, 75.3, 66.8, 61.0, 57.1, 55.2, 26.4, 25.2.



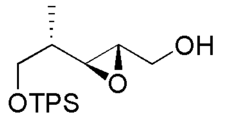
27

Epoxy Alcohol 27: Procedure B (71%); colorless oil; $R_f = 0.54$ (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D = -19.5$ (c 0.8, $CHCl_3$) (*lit.*[8] $[\alpha]^{23}_D = -21.4$ (c 1.8, $CHCl_3$)); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4.12$-4.02 (m, 2 H), 3.93 (dd, $J = 12.9, 2.5$ Hz, 1 H), 3.84-3.80 (m, 1 H), 3.68 (dd, $J = 12.9, 3.8$ Hz, 1 H), 3.15-3.06 (m, 2 H), 1.79 (bs, 1 H), 1.40 (s, 3 H), 1.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 110.0$, 75.1, 66.0, 60.8, 55.3, 55.0, 26.3, 25.5.



28

Epoxy Alcohol 28: Procedure B (75%); colorless oil; $R_f = 0.48$ (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D = +18.9$ (c 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.60$-7.58 (m, 4 H), 7.58-7.33 (m, 6 H), 3.87 (dd, $J = 12.6, 2.2$ Hz, 1 H), 3.56 (dd, $J = 10.2, 5.6$ Hz, 1 H), 3.55-3.51 (m, 2 H), 3.01 (ddd, $J = 4.4, 2.2$ Hz, 1 H), 2.85 (dd, $J = 7.3, 2.2$ Hz, 1 H), 1.68 (bs, 1 H), 1.61 (sep, $J = 7.0$ Hz, 1 H), 0.99 (s, 9 H), 0.93 (d, $J = 7.0$ Hz, 3 H).

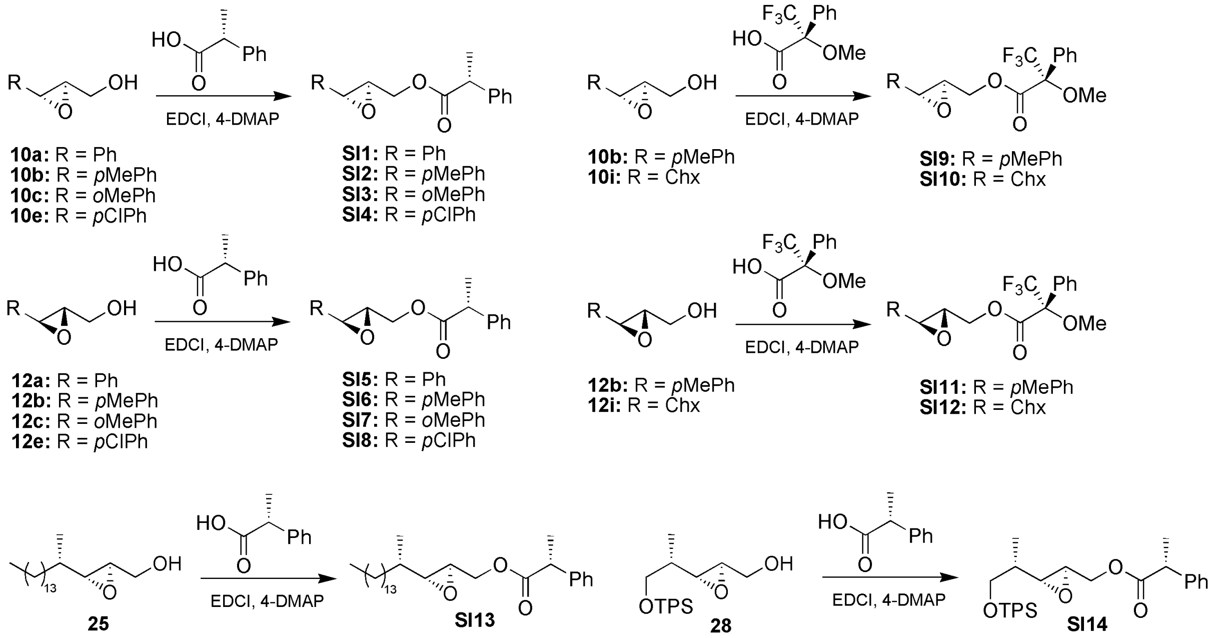


29

Epoxy Alcohol 29: Procedure B (75%); colorless oil; $R_f = 0.45$ (silica gel, 20% AcOEt in hexanes); $[\alpha]^{25}_D = -14.7$ (c 1.7, CH_2Cl_2) (*lit.*[9] $[\alpha]^{25}_D = -5.6$ (c 1.0, $CHCl_3$)); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.62$-7.59 (m, 4 H), 7.37-7.33 (m, 6 H), 3.86 (dd, $J = 12.5, 1.9$ Hz, 1 H), 3.65 (dd, $J = 10.0, 5.3$ Hz, 1 H), 3.61 (dd, $J = 10.0, 4.9$ Hz, 1 H), 3.56 (dd, $J = 12.6, 4.0$ Hz, 1 H), 2.96-2.94 (m, 2 H), 1.65-1.62 (m, 2 H), 0.99 (s, 9 H), 0.92 (d, $J = 7.0$ Hz, 3 H).

Mosher Esters SI1-SI14. General Procedure: To a solution of (*R*)-(+)-α-Methylphenyl acetic acid or (*R*)-(+)-α-Methoxy-α-trifluoromethylphenyl acetic acid (1.5 equiv) and EDCI (1.5 equiv) in CH_2Cl_2 (0.02 M) was added a solution of the epoxy alcohol (1.0 equiv) in CH_2Cl_2 (0.1 M) at 25°C. Then, a solution of 4-DMAP (0.05 equiv) in CH_2Cl_2 (0.005 M) was dropwise added to the crude mixture and was stirred for 12 h. After this time, a saturated aqueous $NaHCO_3$ solution was added, the organic phase diluted with Et_2O and separated. The aqueous layer was extracted with Et_2O (twice), and the combined organic extracts were washed with brine, dried ($MgSO_4$) and filtered. Concentration under reduced pressure provided a crude product that was purified by flash column chromatography (silica gel, 5% AcOEt in hexanes) to afford the corresponding epoxy esters which were analyzed by NMR and HPLC techniques (Scheme 1).

Scheme 1. *Synthesis of Mosher Esters from Epoxy Alcohols.*



Epoxy Ester SI1: 67%; colorless oil; R_f = 0.45 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = -85.0 (*c* 0.4, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.26 (m, 8 H), 7.14-7.12 (m, 2 H), 4.40 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.09 (dd, *J* = 12.4, 5.2 Hz, 1 H), 3.74 (c, *J* = 7.1 Hz, 1 H), 3.59 (d, *J* = 2.0 Hz, 1 H), 3.16 (ddd, *J* = 5.2, 3.2, 2.0 Hz, 1 H), 1.48 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 128.7, 128.5, 128.4, 127.5, 127.3, 125.7, 63.8, 59.3, 56.1, 45.3, 18.4.

Epoxy Ester SI2: 96%; colorless oil; R_f = 0.44 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = -83.2 (*c* 0.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.21 (m, 5 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 4.40 (dd, *J* = 12.4, 3.1 Hz, 1 H), 4.07 (dd, *J* = 12.4, 5.3 Hz, 1 H), 3.73 (c, *J* = 7.2 Hz, 1 H), 3.56 (d, *J* = 2.0 Hz, 1 H), 3.15 (ddd, *J* = 5.3, 3.1, 2.0 Hz, 1 H), 2.28 (s, 3 H), 1.47 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 140.2, 138.2, 133.1, 129.2, 128.7, 127.5, 127.3, 125.6, 63.9, 59.2, 56.1, 45.3, 21.2, 18.4.

Epoxy Ester SI3: 67%; colorless oil; $R_f = 0.41$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D = -42.5$ (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.27$-7.23 (m, 5 H), 7.21-7.06 (m, 4 H), 4.37 (dd, $J = 12.3$, 3.7 Hz, 1 H), 4.19 (dd, $J = 12.3$, 4.9 Hz, 1 H), 3.76 (d, $J = 2.0$ Hz, 1 H), 3.74 (c, $J = 7.1$ Hz, 1 H), 3.02 (ddd, $J = 4.9$, 3.7, 2.0 Hz, 1 H), 2.20 (s, 3 H), 1.48 (d, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 174.2$, 140.2, 140.1, 135.9, 134.5, 129.8, 128.7, 127.8, 127.4, 127.3, 126.1, 124.2, 63.9, 58.4, 54.5, 45.4, 18.7, 18.4.

Epoxy Ester SI4: 90%; colorless oil; $R_f = 0.39$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D = -78.4$ (c 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.26$-7.18 (m, 7 H), 7.01 (d, $J = 8.5$ Hz, 2 H), 4.35 (dd, $J = 12.4$, 3.2 Hz, 1 H), 4.08 (dd, $J = 12.4$, 5.0 Hz, 1 H), 3.70 (c, $J = 7.1$ Hz, 1 H), 3.52 (d, $J = 2.0$ Hz, 1 H), 3.07 (ddd, $J = 5.0$, 3.2, 2.0 Hz, 1 H), 1.45 (d, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 174.1$, 140.2, 134.8, 134.2, 128.7, 128.6, 127.5, 127.3, 126.9, 63.5, 59.4, 55.4, 45.3, 18.4.

Epoxy Ester SI5: 88%; colorless oil; $R_f = 0.45$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D = +22.3$ (c 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.29$-7.20 (m, 8 H), 7.16-7.14 (m, 2 H), 4.40 (dd, $J = 12.3$, 3.3 Hz, 1 H), 4.07 (dd, $J = 12.3$, 5.6 Hz, 1 H), 3.74 (c, $J = 7.1$ Hz, 1 H), 3.61 (d, $J = 1.9$ Hz, 1 H), 3.12 (ddd, $J = 5.6$, 3.3, 1.9 Hz, 1 H), 1.48 (d, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 174.2$, 128.7, 128.5, 128.4, 127.5, 127.2, 125.6, 64.2, 59.2, 56.2, 45.4, 18.5.

Epoxy Ester SI6: 94%; colorless oil; $R_f = 0.44$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D = +24.3$ (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.28$-7.26 (m, 4 H), 7.24-7.20 (m, 1 H), 7.09 (d, $J = 8.5$ Hz, 2 H), 7.04 (d, $J = 8.5$ Hz, 2 H), 4.39 (dd, $J = 12.3$, 3.3 Hz, 1 H), 4.07 (dd, $J = 12.3$, 5.7 Hz, 1 H), 3.74 (c, $J = 7.2$ Hz, 1 H), 3.59 (d, $J = 2.0$ Hz, 1 H), 3.13 (ddd, $J = 5.7$, 3.3, 2.0 Hz, 1 H), 2.29 (s, 3 H), 1.48 (d, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

= 174.2, 140.2, 138.3, 133.1, 129.2, 128.7, 127.5, 127.2, 125.7, 64.4, 59.1, 56.2, 45.4, 21.2, 18.5.

Epoxy Ester SI7: 88%; colorless oil; R*f* = 0.41 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = -23.0 (*c* 1.6, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.26 (m, 4 H), 7.22-7.20 (m, 2 H), 7.14-7.07 (m, 3 H), 4.36 (dd, *J* = 12.2, 3.8 Hz, 1 H), 4.18 (dd, *J* = 12.2, 5.3 Hz, 1 H), 3.76 (d, *J* = 2.0 Hz, 1 H), 3.74 (c, *J* = 7.1 Hz, 1 H), 3.01 (ddd, *J* = 5.3, 3.8, 2.0 Hz, 1 H), 2.23 (s, 3 H), 1.48 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 140.1, 135.9, 134.5, 129.8, 128.7, 127.9, 127.5, 127.3, 126.1, 124.2, 64.3, 58.3, 54.6, 45.4, 18.7, 18.5.

Epoxy Ester SI8: 97%; colorless oil; R*f* = 0.39 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +21.7 (*c* 0.3, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.20 (m, 7 H), 7.06 (d, *J* = 8.5 Hz, 2 H), 4.39 (dd, *J* = 12.3, 3.4 Hz, 1 H), 4.07 (dd, *J* = 12.3, 5.5 Hz, 1 H), 3.70 (c, *J* = 7.2 Hz, 1 H), 3.56 (d, *J* = 2.0 Hz, 1 H), 3.06 (ddd, *J* = 5.5, 3.4, 2.0 Hz, 1 H), 1.48 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 140.2, 134.8, 134.2, 128.7, 128.6, 127.5, 127.3, 127.0, 63.9, 59.3, 55.6, 45.4, 18.4.

Epoxy Ester SI9: 70%; colorless oil; R*f* = 0.30 (silica gel, 5% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +83.0 (*c* 0.3, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.55-7.50 (m, 2 H), 7.43-7.35 (m, 3 H), 7.15-7.09 (m, 4 H), 4.71 (dd, *J* = 12.2, 3.3 Hz, 1 H), 4.35 (dd, *J* = 12.2, 5.2 Hz, 1 H), 3.74 (d, *J* = 2.0 Hz, 1 H), 3.56 (s, 3 H), 3.29 (ddd, *J* = 5.2, 3.3, 2.0 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 138.5, 132.7, 129.7, 129.6, 129.3, 128.5, 127.3, 125.6, 122.9, 73.5, 65.3, 58.4, 56.2, 21.2.

Epoxy Ester SI10: 65%; colorless oil; R*f* = 0.21 (silica gel, 5% AcOEt in hexanes); $[\alpha]^{25}_{D}$ = +131.5 (*c* 0.4, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.51 (dd, *J* = 6.6, 2.6 Hz, 2 H), 7.40-

7.36 (m, 3 H), 4.50 (dd, *J* = 12.0, 3.7 Hz, 1 H), 4.20 (dd, *J* = 12.0, 5.8 Hz, 1 H), 3.54 (s, 3 H), 3.04 (ddd, *J* = 5.8, 3.7, 2.2 Hz, 1 H), 2.62 (dd, *J* = 6.9, 2.2 Hz, 1 H), 1.84-1.48 (m, 4 H), 1.27-0.96 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.6, 129.7, 128.5, 127.3, 126.1, 66.3, 61.0, 55.5, 53.3, 39.4, 29.5, 26.1, 25.5, 25.4.

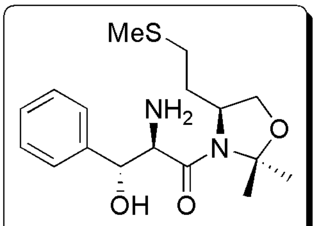
Epoxy Ester SI11: 70%; colorless oil; R_f = 0.30 (silica gel, 5% AcOEt in hexanes); $[\alpha]^{25}_D$ = +20.7 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (bd, *J* = 6.6 Hz, 2 H), 7.41-7.34 (m, 3 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 4.66 (dd, *J* = 12.1, 3.5 Hz, 1 H), 4.37 (dd, *J* = 12.1, 5.6 Hz, 1 H), 3.73 (d, *J* = 2.0 Hz, 1 H), 3.57 (s, 3 H), 3.25 (ddd, *J* = 5.6, 3.5, 2.0 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 138.5, 132.7, 129.7, 129.3, 128.5, 127.3, 127.2, 125.6, 120.3, 73.5, 65.6, 58.3, 56.5, 21.2.

Epoxy Ester SI12: 68%; colorless oil; R_f = 0.21 (silica gel, 5% AcOEt in hexanes); $[\alpha]^{25}_D$ = +33.3 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (dd, *J* = 6.6, 2.5 Hz, 2 H), 7.40-7.36 (m, 3 H), 4.48 (dd, *J* = 12.0, 3.6 Hz, 1 H), 4.21 (dd, *J* = 12.0, 6.2 Hz, 1 H), 3.55 (s, 3 H), 3.03 (ddd, *J* = 6.0, 3.6, 2.2 Hz, 1 H), 2.62 (dd, *J* = 6.2, 2.2 Hz, 1 H), 1.84-1.54 (m, 4 H), 1.29-0.95 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.5, 129.6, 128.4, 127.2, 66.5, 61.0, 55.5, 53.3, 39.4, 29.6, 29.4, 28.8, 26.1, 25.5, 25.3.

Epoxy Ester SI13: 81%; colorless oil; R_f = 0.55 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D$ = +22.5 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.20 (m, 5 H), 4.23 (dd, *J* = 12.2, 3.4 Hz, 1 H), 3.92 (dd, *J* = 12.2, 6.0 Hz, 1 H), 3.70 (c, *J* = 7.2 Hz, 1 H), 2.88 (ddd, *J* = 6.0, 3.4, 2.0 Hz, 1 H), 2.40 (dd, *J* = 6.9, 2.0 Hz, 1 H), 1.45 (d, *J* = 7.2 Hz, 3 H), 1.29-1.24 (m, 1 H), 1.24-1.18 (m, 26 H), 0.90 (d, *J* = 6.2 Hz, 3 H), 0.82 (t, *J* = 7.0 Hz, 3 H).

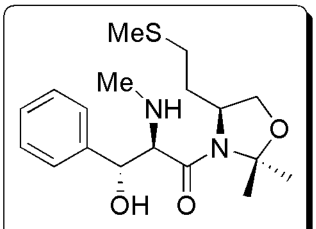
Epoxy Ester SI14: 84%; colorless oil; $R_f = 0.40$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_{D} = +7.0$ (c 0.3, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.59$-7.56 (m, 4 H), 7.39-7.30 (m, 6 H), 7.25-7.22 (m, 5 H), 4.32 (dd, $J = 12.3, 2.6$ Hz, 1 H), 3.85 (dd, $J = 12.3, 6.4$ Hz, 1 H), 3.69 (c, $J = 7.1$ Hz, 1 H), 3.52 (dd, $J = 10.1, 5.6$ Hz, 1 H), 3.48 (dd, $J = 10.1, 7.1$ Hz, 1 H), 2.97 (ddd, $J = 6.4, 2.6, 2.2$ Hz, 1 H), 2.65 (dd, $J = 7.0, 2.2$ Hz, 1 H), 1.54 (sep, $J = 7.0$ Hz, 1 H), 1.45 (d, $J = 7.1$ Hz, 3 H), 0.98 (s, 9 H), 0.88 (d, $J = 6.9$ Hz, 3 H).

Amino Alcohols 30-42. General Procedure. A solution of epoxy amide (1.0 equiv) in methanol (0.1 M) was treated with the corresponding amine (5.0 equiv) and the reaction mixture was refluxed at 70ºC for a period of 6-8 h. After this time, the crude mixture was cooled to room temperature and concentrated under vacuum. Flash column chromatography (silica gel, $CH_2Cl_2 \rightarrow$ 2-5% MeOH in CH_2Cl_2) afforded the corresponding amino alcohol in a range of 60-85% yields.



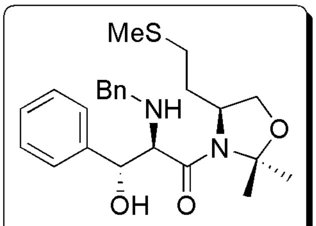
30

Amino Alcohol 30: 69%; colorless oil; $R_f = 0.37$ (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_{D} = +63.8$ (c 0.9, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.33$-7.23 (m, 5 H), 4.23 (bs, 2 H), 4.01 (ddd, $J = 10.6, 4.7, 2.4$ Hz, 1 H), 3.76 (ddd, $J = 9.1, 4.8, 1.4$ Hz, 1 H), 3.68 (d, $J = 9.1$ Hz, 1 H), 2.64 (bs, 3 H), 2.36 (ddd, $J = 13.1, 7.7, 5.3$ Hz, 1 H), 2.26 (ddd, $J = 13.1, 8.3, 7.4$ Hz, 1 H), 2.03 (s, 3 H), 1.76-1.67 (m, 1 H), 1.49 (s, 3 H), 1.47-1.44 (m, 1 H), 1.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 169.0$, 128.6, 128.0, 127.5, 95.3, 73.5, 66.9, 59.1, 56.4, 33.7, 30.9, 26.2, 22.7, 16.0; FAB HRMS (NBA) m/e 361.1558, $M+Na^+$ calcd for $C_{17}H_{26}N_2O_3S$ 361.1562.



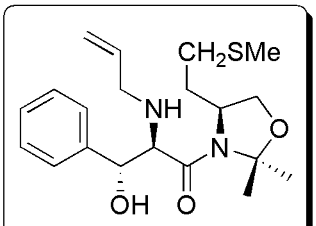
31

Amino Alcohol 31: 72%; colorless oil; R_f = 0.42 (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ = +83.1 (*c* 1.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.21 (m, 5 H), 4.29 (d, *J* = 4.9 Hz, 1 H), 3.92 (ddd, *J* = 10.7, 4.0, 1.9 Hz, 1 H), 3.88 (d, *J* = 4.9 Hz, 1 H), 3.67 (dd, *J* = 9.0, 4.6 Hz, 1 H), 3.62 (d, *J* = 9.1 Hz, 1 H), 3.39 (bs, 2 H), 2.26 (s, 3 H), 2.23-2.16 (m, 2 H), 1.98 (s, 3 H), 1.56-1.51 (m, 2 H), 1.48 (s, 3 H), 1.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.1, 137.8, 128.6, 128.2, 128.1, 95.3, 72.0, 67.8, 66.8, 56.4, 33.7, 33.5, 30.8, 26.1, 22.7, 16.0; FAB HRMS (NBA) *m/e* 375.1719, M+Na$^+$ calcd for $C_{18}H_{28}N_2O_3S$ 375.1718.



32

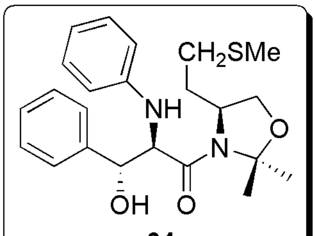
Amino Alcohol 32: 75%; pale yellow oil; R_f = 0.56 (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ = +45.4 (*c* 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.26 (m, 5 H), 7.24-7.17 (m, 5 H), 4.32 (d, *J* = 5.0 Hz, 1 H), 4.05 (d, *J* = 5.0 Hz, 1 H), 3.93 (ddd, *J* = 10.7, 4.6, 2.3 Hz, 1 H), 3.81 (d, *J* = 13.1 Hz, 1 H), 3.73 (ddd, *J* = 9.1, 4.9, 1.1 Hz, 1 H), 3.63 (d, *J* = 9.1 Hz, 1 H), 3.52 (d, *J* = 13.1 Hz, 1 H), 2.25-2.13 (m, 2 H), 1.96 (s, 3 H), 1.55-1.46 (m, 2 H), 1.44 (s, 3 H), 1.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.0, 128.7, 128.5, 128.4, 128.3, 127.3, 95.2, 71.6, 66.6, 64.9, 56.3, 50.3, 33.3, 30.7, 26.0, 22.6, 15.9; FAB HRMS (NBA) *m/e* 451.2029, M+Na$^+$ calcd for $C_{24}H_{32}N_2O_3S$ 451.2031.



33

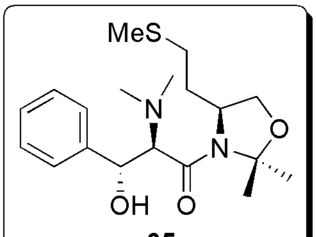
Amino Alcohol 33: 93%; colorless oil; R_f = 0.58 (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ = +64.9 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.21 (m, 5 H), 5.85-5.75 (m, 1 H), 5.05 (dd, *J* = 17.3, 1.6 Hz, 1 H), 5.01 (dd, *J* = 10.3, 1.0 Hz, 1 H), 4.26 (d, *J* = 5.2 Hz, 1 H), 3.97 (d, *J* = 5.2 Hz, 1 H), 3.92 (ddd, *J* = 10.7, 4.6, 2.0 Hz, 1 H), 3.71 (ddd, *J* = 9.1, 4.9, 1.3 Hz, 1 H), 3.62 (d, *J* = 9.1 Hz, 1 H), 3.19 (dd, *J* = 14.0, 5.8 Hz, 1 H), 2.94 (dd, *J* =

14.0, 6.3 Hz, 1 H), 2.23 (ddd, J = 13.0, 7.8, 5.4 Hz, 1 H), 2.20-2.16 (m, 1 H), 1.98 (s, 3 H), 1.61-1.49 (m, 2 H), 1.43 (s, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 169.1, 136.1, 128.5, 128.2, 128.1, 125.7, 116.3, 95.1, 71.8, 66.6, 65.0, 56.3, 49.3, 33.3, 30.7, 26.0, 22.6, 15.9; FAB HRMS (NBA) *m/e* 401.1881, M+Na$^+$ calcd for $C_{20}H_{30}N_2O_3S$ 401.1875.



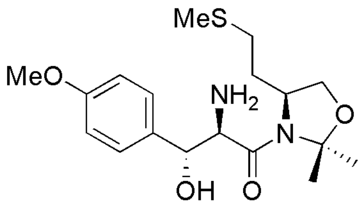
34

Amino Alcohol 34: 54%; yellow oil; R$_f$ = 0.55 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = +45.0 (c 1.7, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.31-7.29 (m, 1 H), 7.26-7.18 (m, 5 H), 7.05 (d, J = 7.2 Hz, 1 H), 7.03 (d, J = 7.2 Hz, 1 H), 6.64 (d, J = 7.3 Hz, 2 H), 4.83 (d, J = 4.3 Hz, 1 H), 4.44 (d, J = 4.3 Hz, 1 H), 3.95 (ddd, J = 10.7, 4.6, 2.3 Hz, 1 H), 3.81 (ddd, J = 9.1, 4.9, 1.4 Hz, 1 H), 3.67 (d, J = 9.1 Hz, 1 H), 2.27-2.09 (m, 2 H), 1.99 (s, 3 H), 1.50 (s, 3 H), 1.49-1.43 (m, 2 H), 1.44 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 169.2, 129.1, 128.7, 128.0, 127.6, 95.3, 71.2, 66.7, 61.7, 56.4, 32.9, 30.8, 25.9, 22.5, 16.1; FAB HRMS (NBA) *m/e* 437.1872, M+Na$^+$ calcd for $C_{23}H_{30}N_2O_3S$ 437.1875.



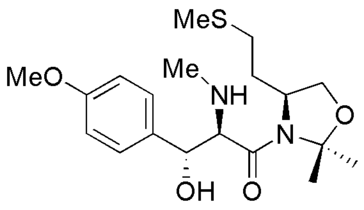
35

Amino Alcohol 35: 68%; colorless oil; R$_f$ = 0.57 (silica gel, 2% MeOH in CH$_2$Cl$_2$); $[\alpha]^{25}_D$ = +53.9 (c 1.4, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.29-7.22 (m, 5 H), 4.70 (d, J = 4.6 Hz, 1 H), 3.95 (ddd, J = 10.3, 4.5, 2.6 Hz, 1 H), 3.61 (d, J = 4.6 Hz, 1 H), 3.54 (d, J = 8.8 Hz, 1 H), 3.16 (ddd, J = 8.9, 4.7, 1.4 Hz, 1 H), 2.38 (dd, J = 7.9, 7.1 Hz, 2 H), 2.23 (s, 6 H), 2.05 (s, 3 H), 1.97-1.89 (m, 1 H), 1.85-1.79 (m, 1 H), 1.47 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 167.7, 129.4, 128.1, 127.9, 95.7, 73.3, 73.0, 66.8, 56.0, 43.6, 34.5, 31.1, 26.3, 22.6, 15.7; FAB HRMS (NBA) *m/e* 389.1876, M+Na$^+$ calcd for $C_{19}H_{30}N_2O_3S$ 389.1875.



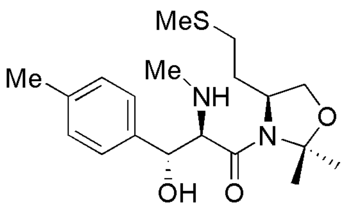
36

Amino Alcohol 36: 65%; colorless oil; $R_f = 0.35$ (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D = +54.0$ (*c* 0.8, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.25$ (d, $J = 8.5$ Hz, 2 H), 6.81 (d, $J = 8.5$ Hz, 2 H), 4.20 (bs, 2 H), 4.01 (ddd, $J = 10.5$, 4.6, 2.1 Hz, 1 H), 3.78 (ddd, $J = 9.0$, 4.8, 1.3 Hz, 1 H), 3.74 (s, 3 H), 3.69 (d, $J = 9.1$ Hz, 1 H), 2.60 (bs, 3 H), 2.36 (ddd, $J = 13.1$, 7.8, 5.3 Hz, 1 H), 2.26 (ddd, $J = 13.1$, 7.8 Hz, 1 H), 2.03 (s, 3 H), 1.78-1.69 (m, 1 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.45-1.35 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 169.1$, 159.3, 132.6, 128.6, 114.0, 95.3, 73.5, 66.9, 58.5, 56.4, 55.3, 33.7, 30.9, 26.2, 22.7, 16.0; FAB HRMS (NBA) *m/e* 391.1674, $M+Na^+$ calcd for $C_{18}H_{28}N_2O_4S$ 391.1668.



37

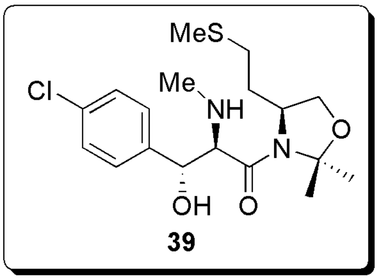
Amino Alcohol 37: 83%; colorless oil; $R_f = 0.44$ (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D = +75.7$ (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.17$ (d, $J = 8.6$ Hz, 2 H), 6.80 (d, $J = 8.7$ Hz, 2 H), 4.26 (d, $J = 5.1$ Hz, 1 H), 3.95 (ddd, $J = 10.6$, 4.6, 2.4 Hz, 1 H), 3.82 (d, $J = 5.1$ Hz, 1 H), 3.74 (s, 3 H), 3.72-3.70 (m, 1 H), 3.64 (d, $J = 9.1$ Hz, 1 H), 3.25 (bs, 1 H), 2.24 (s, 3 H), 2.23-2.15 (m, 2 H), 1.99 (s, 3 H), 1.59-1.52 (m, 1 H), 1.46 (s, 3 H), 1.43 (s, 3 H), 1.16-1.01 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 169.3$, 159.4, 129.3, 114.0, 95.3, 72.0, 67.1, 66.8, 56.5, 55.3, 33.6, 33.5, 30.8, 26.1, 22.7, 16.0; FAB HRMS (NBA) *m/e* 405.1831, $M+Na^+$ calcd for $C_{19}H_{30}N_2O_4S$ 405.1824.



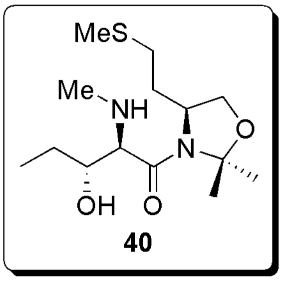
38

Amino Alcohol 38: 71%; colorless oil; $R_f = 0.52$ (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D = +8.2$ (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.15$ (d, $J = 8.5$ Hz, 2 H), 7.08 (d, $J = 8.7$ Hz, 2 H), 4.33 (d, $J = 5.0$ Hz, 1 H), 4.23 (bs, 2 H), 3.95 (ddd, $J = 10.6$, 4.6, 2.6 Hz, 1 H), 3.92 (d, $J = 5.0$ Hz, 1 H), 3.70 (ddd, $J = 9.1$, 4.8, 1.3

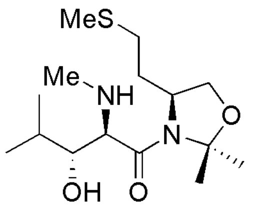
Hz, 1 H), 3.63 (d, *J* = 9.1 Hz, 1 H), 2.28 (s, 3 H), 2.27 (s, 3 H), 2.23-2.18 (m, 2 H), 1.97 (s, 3 H), 1.56-1.48 (m, 1 H), 1.46 (s, 3 H), 1.43 (s, 3 H), 1.17-1.03 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.0, 138.0, 129.3, 128.1, 95.2, 71.8, 67.4, 66.7, 56.4, 33.4, 33.3, 30.6, 26.0, 22.5, 21.0, 15.8; FAB HRMS (NBA) *m/e* 389.1877, M+Na$^+$ calcd for $C_{19}H_{30}N_2O_3S$ 389.1875.



Amino Alcohol 39: 74%; colorless oil; R$_f$ = 0.37 (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ = +144.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 7.19 (d, *J* = 8.7 Hz, 2 H), 4.25 (d, *J* = 5.3 Hz, 1 H), 3.96 (ddd, *J* = 10.6, 4.6, 2.4 Hz, 1 H), 3.84 (d, *J* = 5.3 Hz, 1 H), 3.73 (ddd, *J* = 9.1, 4.8, 1.4 Hz, 1 H), 3.66 (d, *J* = 9.1 Hz, 1 H), 3.50 (bs, 2 H), 2.28 (ddd, *J* = 13.0, 7.8, 5.3 Hz, 1 H), 2.22 (s, 3 H), 2.21 (ddd, *J* = 13.0, 7.5, 5.7 Hz, 1 H), 1.99 (s, 3 H), 1.65-1.57 (m, 1 H), 1.44 (s, 3 H), 1.42 (s, 3 H), 1.13-1.06 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.9, 136.5, 133.7, 129.6, 128.7, 95.3, 72.0, 67.2, 66.8, 56.4, 33.8, 33.7, 30.8, 26.1, 22.6, 16.0; FAB HRMS (NBA) *m/e* 409.1333, M+Na$^+$ calcd for $C_{18}H_{27}ClN_2O_3S$ 409.1329.

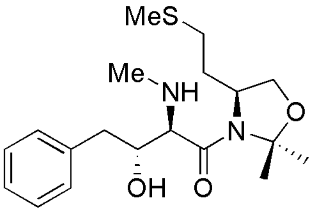


Amino Alcohol 40: 62%; colorless oil; R$_f$ = 0.35 (silica gel, 5% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ = -22.0 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.08 (ddd, *J* = 10.7, 4.7, 2.7 Hz, 1 H), 3.89 (ddd, *J* = 9.1, 4.9, 1.5 Hz, 1 H), 3.81 (d, *J* = 9.1 Hz, 1 H), 3.57 (ddd, *J* = 9.1, 4.9, 3.0 Hz, 1 H), 3.36 (d, *J* = 5.2 Hz, 1 H), 2.70 (bs, 2 H), 2.55 (ddd, *J* = 13.2, 6.8, 4.9 Hz, 1 H), 2.40 (ddd, *J* = 13.2, 9.1, 6.4 Hz, 1 H), 2.37 (s, 3 H), 2.08 (s, 3 H), 2.07-2.00 (m, 1 H), 1.82-1.75 (m, 1 H), 1.61 (s, 3 H), 1.54-1.49 (m, 1 H), 1.48 (s, 3 H), 1.38-1.30 (m, 1 H), 0.96 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.4, 95.4, 73.0, 66.6, 65.6, 56.2, 34.6, 33.7, 30.9, 26.6, 26.5, 22.6, 15.8, 10.4; FAB HRMS (NBA) *m/e* 327.1724, M+Na$^+$ calcd for $C_{14}H_{28}N_2O_3S$ 327.1718.



41

Amino Alcohol 41: 84%; white solid; m.p. 104-106ºC; R_f = 0.33 (silica gel, AcOEt); $[\alpha]^{25}_{D}$ = +16.8 (*c* 1.8, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.15 (ddd, *J* = 10.9, 4.8, 2.6 Hz, 1 H), 3.88 (ddd, *J* = 9.1, 4.9, 1.5 Hz, 1 H), 3.78 (d, *J* = 9.1 Hz, 1 H), 3.40 (ddd, *J* = 7.4, 4.2 Hz, 1 H), 3.28 (d, *J* = 7.4 Hz, 1 H), 2.54 (ddd, *J* = 13.2, 6.8, 5.1 Hz, 1 H), 2.43-2.33 (m, 2 H), 2.31 (s, 3 H), 2.07 (s, 3 H), 2.03-1.97 (m, 1 H), 1.92-1.88 (m, 1 H), 1.87-1.81 (m, 1 H), 1.60 (s, 3 H), 1.58 (s, 3 H), 0.90 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 95.3, 77.1, 66.5, 63.4, 56.1, 34.7, 33.5, 31.0, 30.2, 26.6, 22.5, 22.4, 19.9, 16.0; FAB HRMS (NBA) *m/e* 341.1877, $M+Na^+$ calcd for $C_{15}H_{30}N_2O_3S$ 341.1875.

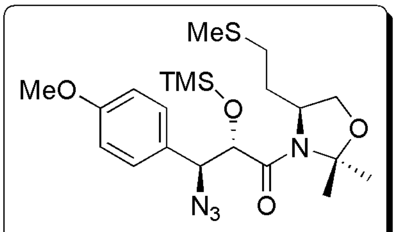


42

Amino Alcohol 42: 65%; yellow oil; R_f = 0.46 (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_{D}$ = +47.1 (*c* 0.9, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.15 (m, 5 H), 3.93-3.86 (m, 2 H), 3.84 (ddd, *J* = 9.1, 5.0, 1.3 Hz, 1 H), 3.75 (d, *J* = 9.1 Hz, 1 H), 3.36 (d, *J* = 6.3 Hz, 1 H), 2.95 (dd, *J* = 14.0, 3.7 Hz, 1 H), 2.85 (bs, 2 H), 2.76 (dd, *J* = 14.0, 9.0 Hz, 1 H), 2.43 (ddd, *J* = 13.9, 7.6, 5.1 Hz, 1 H), 2.39 (s, 3 H), 2.32-2.25 (m, 1 H), 2.05 (s, 3 H), 2.03-1.96 (m, 1 H), 1.73-1.67 (m, 1 H), 1.61 (s, 3 H), 1.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.2, 137.9, 129.2, 128.4, 126.5, 95.4, 72.9, 66.6, 65.3, 56.1, 40.2, 34.6, 33.9, 30.7, 26.6, 22.5, 15.8; FAB HRMS (NBA) *m/e* 389.1868, $M+Na^+$ calcd for $C_{19}H_{30}N_2O_3S$ 389.1875.

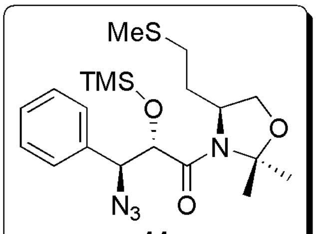
3-Azido 2-Trimethylsilyloxy Amides 43-45. General Procedure. To a solution of epoxy amide (1.0 equiv) in CH_2Cl_2 (0.1 M) was added trimethylsilyl azide (2.5 equiv) and $Yb(OTf)_3$ (0.2 equiv) at 25 ºC. After stirring at this temperature overnight, the reaction mixture was diluted with Et_2O and the resulting organic solution washed with a saturated aqueous

$NaHCO_3$ solution. After separation of both phases, the aqueous layer was extracted with Et_2O (twice), and the combined organic extracts were washed with brine, dried ($MgSO_4$) and filtered. Concentration under reduced pressure provided a crude product that was purified by flash column chromatography (silica gel, 5% AcOEt in hexanes) to afford the corresponding azido trimethylsilyloxy amides.



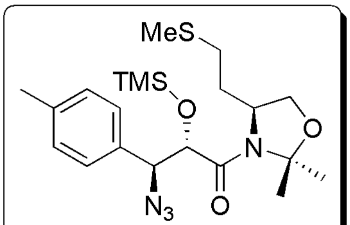
43

3-Azido 2-Trimethylsilyloxy Amide 43: 85%; colorless oil; $R_f = 0.56$ (silica gel, 5% AcOEt in hexanes); $[\alpha]^{25}_D = -61.9$ (*c* 1.6, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.19$ (d, *J* = 8.5 Hz, 2 H), 6.81 (d, *J* = 8.5 Hz, 2 H), 4.92 (d, *J* = 8.8 Hz, 1 H), 4.10 (d, *J* = 8.8 Hz, 1 H), 3.85 (ddd, *J* = 10.5, 4.5, 2.3 Hz, 1 H), 3.75-3.73 (m, 1 H), 3.71 (s, 3 H), 3.64 (d, *J* = 9.1 Hz, 1 H), 2.19-2.10 (m, 2 H), 2.01 (s, 3 H), 1.44 (s, 3 H), 1.38 (s, 3 H), 1.37-1.29 (m, 1 H), 0.80-0.75 (m, 1 H), 0.18 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta =$ 166.5, 159.6, 129.1, 114.2, 95.2, 76.7, 67.7, 66.2, 56.2, 55.2, 32.2, 31.0, 25.9, 22.4, 16.1, 0.3; FAB HRMS (NBA) *m/e* 489.1973, $M+Na^+$ calcd for $C_{21}H_{34}N_4O_4SSi$ 489.1968.



44

3-Azido 2-Trimethylsilyloxy Amide 44: 12%; colorless oil; $R_f = 0.38$ (silica gel, 5% AcOEt in hexanes); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.33$-7.28 (m, 5 H), 4.87 (d, *J* = 9.1 Hz, 1 H), 4.14 (d, *J* = 9.1 Hz, 1 H), 4.07 (ddd, *J* = 9.0, 4.4 Hz, 1 H), 3.87 (ddd, *J* = 9.0, 5.2, 1.0 Hz, 1 H), 3.83 (d, *J* = 9.0 Hz, 1 H), 2.68-2.63 (m, 1 H), 2.38 (ddd, *J* = 13.7, 9.3, 6.5 Hz, 1 H), 2.17 (s, 3 H), 2.15-2.13 (m, 1 H), 1.68 (s, 3 H), 1.65-1.58 (m, 1 H), 1.53 (s, 3 H), 0.20 (s, 9 H).

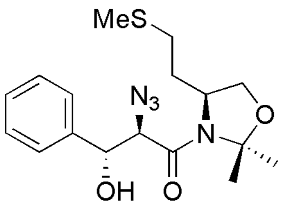


45

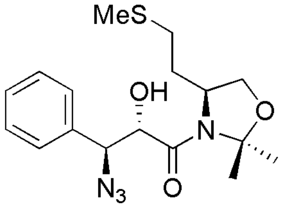
3-Azido 2-Trimethylsilyloxy Amide 45: 15%; colorless oil; R_f = 0.52 (silica gel, 5% AcOEt in hexanes); ^1H NMR (400 MHz,

$CDCl_3$) δ = 7.22-7.13 (m, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 4.95 (d, *J* = 8.7 Hz, 1 H), 4.11 (d, *J* = 8.7 Hz, 1 H), 3.87-3.82 (m, 1 H), 3.75 (ddd, *J* = 9.1, 4.8, 1.6 Hz, 1 H), 3.65 (d, *J* = 9.1 Hz, 1 H), 2.65-2.60 (m, 1 H), 2.25 (s, 3 H), 2.15-2.05 (m, 1 H), 2.01 (s, 3 H), 1.45 (s, 3 H), 1.40 (s, 3 H), 1.30-1.22 (m, 1 H), 0.82-0.79 (m, 1 H), 0.19 (s, 9 H).

Azido Hydroxy Amides 46a/46b and 47. General Procedure. A mixture of epoxy amide (1.0 equiv) and NaN_3 (10.0 equiv) in methanol (0.1 M) was refluxed at 70ºC for a period of 6-8 h. After this time, the crude mixture was cooled to room temperature, diluted with water and extracted with Et_2O three times. The resulting organic solution was washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 20% AcOEt in hexanes) to afford the corresponding azido alcohol.

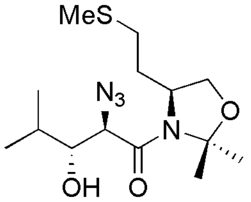


46a



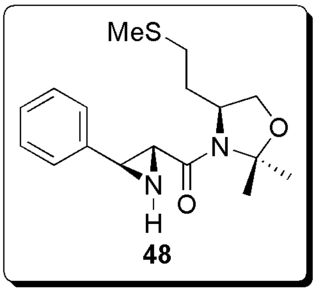
46b

Azido Hydroxy Amides 46a/b: 87% as a 2:1 mixture of regioisomers; yellow solid; R_f = 0.35 (silica gel, 20% AcOEt in hexanes); ^1H NMR (400 MHz, $CDCl_3$) (major isomer) δ = 7.38-7.27 (m, 5 H), 4.85 (d, *J* = 9.1 Hz, 1 H), 4.26 (d, *J* = 9.1 Hz, 1 H), 4.11 (ddd, *J* = 10.0, 5.1 Hz, 1 H), 3.90 (dd, *J* = 9.1, 5.0 Hz, 1 H), 3.81 (d, *J* = 9.1 Hz, 1 H), 2.90 (bs, 1 H), 2.60 (ddd, *J* = 13.2, 5.5 Hz, 1 H), 2.38 (ddd, *J* = 13.5, 8.0 Hz, 1 H), 2.09 (s, 3 H), 2.08-2.05 (m, 1 H), 1.64 (s, 3 H), 1.51 (s, 3 H), 1.47-1.36 (m, 1 H); FAB HRMS (NBA) *m/e* 387.1472, $M+Na^+$ calcd for $C_{17}H_{24}N_4O_3S$ 387.1467.



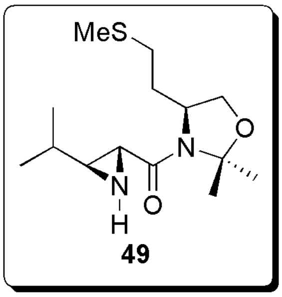
47

2-Azido 3-Hydroxy Amide 47: 76%; colorless oil; R_f = 0.40 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = -69.3 (*c* 2.7, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.12 (ddd, *J* = 10.5, 4.9, 2.9 Hz, 1 H), 3.92 (ddd, *J* = 9.2, 5.2, 1.7 Hz, 1 H), 3.86 (dd, *J* = 7.5, 4.3 Hz, 1 H), 3.77 (d, *J* = 9.2 Hz, 1 H), 3.63 (d, *J* = 7.5 Hz, 1 H), 2.56 (ddd, *J* = 13.4, 4.8 Hz, 1 H), 2.32 (ddd, *J* = 13.5, 10.6, 4.8 Hz, 1 H), 2.07 (s, 3 H), 2.03-1.95 (m, 1 H), 1.91-1.79 (m, 2 H), 1.63 (s, 3 H), 1.49 (s, 3 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 0.93 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 166.8, 95.6, 66.7, 59.6, 56.4, 50.9, 32.9, 30.8, 26.4, 22.5, 19.4, 19.3, 15.9; FAB HRMS (NBA) *m/e* 353.1617, M+Na$^+$ calcd for $C_{14}H_{26}N_4O_3S$ 353.1623.



48

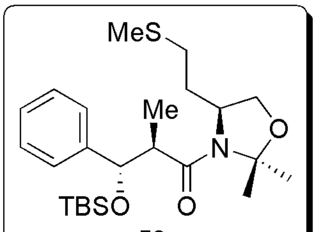
Aziridine 48. A solution of azido alcohols **46a/46b** (20 mg, 0.05 mmol, 1.0 equiv) in THF (2 mL) was treated with Ph$_3$P (22 mg, 0.08 mmol, 1.5 equiv) at room temperature. After 6 h, the reaction mixture was diluted with water and Et$_2$O, the phases were separated and the aqueous phase was extracted with Et$_2$O twice. The combined organic extracts were washed with brine, dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 50% AcOEt in hexanes) to afford aziridine **48** (10 mg, 62%) as a colorless oil: R$_f$ = 0.49 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = -57.0 (*c* 0.5, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.28-7.19 (m, 5 H), 4.08 (ddd, *J* = 10.2, 4.8, 2.8 Hz, 1 H), 3.92 (ddd, *J* = 9.1, 4.9, 1.5 Hz, 1 H), 3.80 (d, *J* = 9.1 Hz, 1 H), 3.08 (bs, 1 H), 2.69 (bs, 1 H), 2.53 (ddd, *J* = 13.5, 6.1, 5.4 Hz, 1 H), 2.32 (ddd, *J* = 13.5, 9.6, 5.8 Hz, 1 H), 2.10-2.03 (m, 1 H), 2.02 (s, 3 H), 1.93-1.88 (m, 1 H), 1.61 (s, 3 H), 1.50 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 165.9, 138.4, 128.4, 127.6, 126.1, 95.5, 67.1, 55.9, 39.94, 39.89, 33.4, 30.9, 26.6, 22.9, 15.8; FAB HRMS (NBA) *m/e* 343.1463, M+Na$^+$ calcd for $C_{17}H_{24}N_2O_2S$ 343.1456.



49

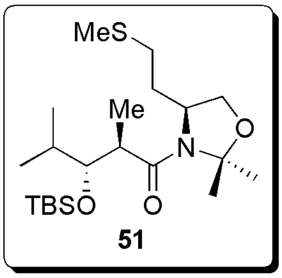
Aziridine 49. A solution of azido alcohol **47** (30 mg, 0.09 mmol, 1.0 equiv) in THF (2 mL) was treated with Ph$_3$P (35 mg, 0.14 mmol, 1.5 equiv) at room temperature. After 6 h, the reaction mixture was diluted with water and Et_2O, the phases were separated and the aqueous phase was extracted with Et_2O twice. The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 2% MeOH in CH_2Cl_2) to afford aziridine **49** (23 mg, 89%) as a colorless oil: $R_f = 0.35$ (silica gel, 2% MeOH in CH_2Cl_2); $[\alpha]^{25}_D = +59.8$ (*c* 1.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4.13$ (ddd, $J = 10.6, 4.8, 2.5$ Hz, 1 H), 3.94 (ddd, $J = 9.1, 4.9, 1.5$ Hz, 1 H), 3.83 (d, $J = 9.1$ Hz, 1 H), 2.58 (ddd, $J = 13.6, 5.3$ Hz, 1 H), 2.43-2.34 (m, 2 H), 2.10-1.97 (m, 1 H), 2.05 (s, 3 H), 1.91-1.84 (m, 2 H), 1.56 (s, 3 H), 1.45 (s, 3 H), 1.38-1.31 (m, 1 H), 0.97 (d, $J = 6.6$ Hz, 3 H), 0.93 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 167.0$, 95.3, 66.9, 55.7, 45.6, 34.8, 33.1, 31.0, 26.4, 22.8, 19.9, 19.8, 15.7; FAB HRMS (NBA) *m/e* 309.1617, $M+Na^+$ calcd for $C_{14}H_{26}N_2O_2S$ 309.1613.

2-Methyl-3-*tert*-Butyldimethylsililoxy Amides 50-53. General Procedure. To a suspension of CuI (5.0 equiv) in THF was added dropwise MeLi (1.6 M in Et_2O, 10.0 equiv) at 0ºC. The resulting colorless solution of Me_2CuLi was added to a solution of epoxy amides **9a,h,i,j** (1.0 equiv) in THF (0.1 M) at 0ºC. The reaction mixture was stirred for 8 h at this temperature and quenched by careful addition of aqueous saturated NH_4Cl solution, followed by dilution with Et_2O. After separation of both phases, the aqueous phase was extracted with Et_2O and the combined organic layers were sequentially washed with aqueous saturated NH_4Cl solution, water and brine. After treatment with $MgSO_4$, the solvents were removed by reduced pressure to obtain crude 2-methyl-3-hydroxy amides which were subjected to the following step without purification. A solution of the hydroxy amides (1.0 equiv) in CH_2Cl_2 (0.1 M) was treated with tertbutyldimethylsilyl trifluoromethanesulphonate (TBSOTf) (1.5 equiv) at 0ºC in the presence of 2,6-lutidine (2.0 equiv). After 0.5 h at 0ºC, the reaction mixture was quenched by addition of MeOH, followed by addition of aqueous saturated NH_4Cl solution and dilution with Et_2O. After separation of both phases, the aqueous phase was extracted with Et_2O twice, the combined organic layers were washed with brine and dried with $MgSO_4$. After filtration, the solvents were removed by reduced pressure to obtain crude products which were purified by flash column chromatography (silica gel, 10% EtOAc in hexanes) to afford the corresponding silyl ethers **50-53**.



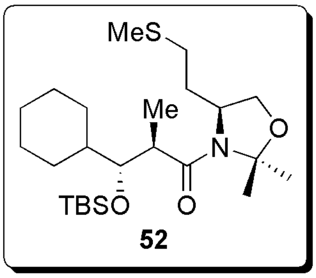
50

2-Methyl-3-*tert*-Butyldimethylsililoxy Amide 50: 56% over two steps; colorless oil; $R_f = 0.57$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D = +12.5$ (c 3.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta =$ 7.25-7.13 (m, 5 H), 4.32 (d, $J = 9.2$ Hz, 1 H), 4.12 (ddd, $J = 11.0$, 4.1, 2.5 Hz, 1 H), 3.86 (ddd, $J = 9.2$, 4.5, 1.5 Hz, 1 H), 3.82 (d, $J = 9.2$ Hz, 1 H), 3.21 (dc, $J =$ 9.2, 7.2 Hz, 1 H), 2.60 (bs, 1 H), 2.42 (bs, 1 H), 2.16 (s, 3 H), 2.12-2.03 (m, 1 H), 1.82-1.75 (m, 1 H), 1.61 (s, 3 H), 1.54 (s, 3 H), 1.15 (d, $J = 7.0$ Hz, 3 H), 0.62 (s, 9 H), -0.19 (s, 3 H), -0.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 168.7$, 143.5, 128.6, 128.2, 126.5, 95.5, 76.3, 66.4, 56.3, 44.8, 34.2, 31.3, 26.4, 25.5, 22.7, 18.4, 18.0, 16.4, -4.6, -4.9; FAB HRMS (NBA) *m/e* 474.2469, $M+Na^+$ calcd for $C_{24}H_{41}NO_3SSi$ 474.2474.



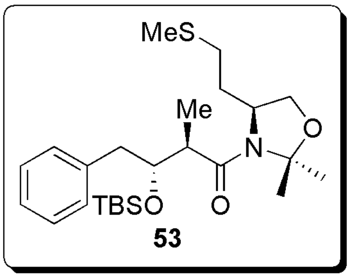
51

2-Methyl-3-*tert*-Butyldimethylsililoxy Amide 51: 64% over two steps; colorless oil; $R_f = 0.31$ (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D = +11.6$ (c 2.3, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4.04$ (ddd, $J = 10.9$, 4.5, 2.1 Hz, 1 H), 3.83-3.79 (m, 2 H), 3.74 (d, $J = 9.1$ Hz, 1 H), 2.67 (dc, $J = 8.8$, 6.9 Hz, 1 H), 2.52 (ddd, $J = 13.0$, 6.7, 5.8 Hz, 1 H), 2.36 (ddd, $J =$ 13.0, 8.9, 6.9 Hz, 1 H), 2.06 (s, 3 H), 2.02-1.94 (m, 1 H), 1.78 (dsep, $J = 7.0$, 1.5 Hz, 1 H), 1.76-1.71 (m, 1 H), 1.54 (s, 3 H), 1.49 (s, 3 H), 0.98 (d, $J = 6.8$ Hz, 3 H), 0.90 (d, $J = 7.0$ Hz, 3 H), 0.84 (d, $J = 7.0$ Hz, 3 H), 0.80 (s, 9 H), -0.02 (s, 3 H), -0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 173.0$, 94.8, 77.8, 66.6, 56.8, 44.1, 32.7, 31.3, 31.2, 26.3, 26.0, 24.2, 19.4, 18.2, 16.3, 16.1, 15.9, -3.7, -3.9; FAB HRMS (NBA) *m/e* 440.2635, M+Na$^+$ calcd for $C_{21}H_{43}NO_3SSi$ 440.2631.



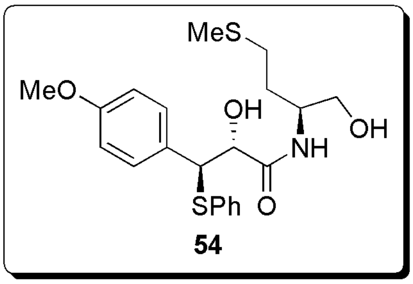
52

2-Methyl-3-*tert*-Butyldimethylsililoxy Amide 52: 60% over two steps; colorless oil; R_f = 0.37 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D$ = +6.9 (*c* 1.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.01 (ddd, *J* = 10.8, 4.5, 2.1 Hz, 1 H), 3.79 (ddd, *J* = 9.0, 4.7, 1.2 Hz, 1 H), 3.74 (d, *J* = 9.0 Hz, 1 H), 3.73 (d, *J* = 9.0 Hz, 1 H), 2.69 (dc, *J* = 9.0, 6.9 Hz, 1 H), 2.53-2.47 (m, 1 H), 2.42-2.33 (m, 1 H), 2.04 (s, 3 H), 2.02-1.95 (m, 1 H), 1.73-1.55 (m, 6 H), 1.52 (s, 3 H), 1.48 (s, 3 H), 1.41-1.38 (m, 1 H), 1.23-1.04 (m, 5 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 0.79 (s, 9 H), -0.02 (s, 3 H), -0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 94.8, 77.8, 66.6, 56.8, 43.6, 42.4, 32.7, 31.1, 29.7, 27.1, 26.9, 26.8, 26.7, 26.3, 26.1, 24.2, 18.2, 16.2, 15.8, -3.79, -3.82; FAB HRMS (NBA) *m/e* 480.2956, M+Na$^+$ calcd for $C_{24}H_{47}NO_3SSi$ 480.2944.



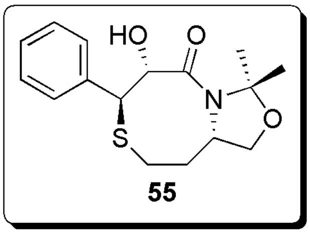
53

2-Methyl-3-*tert*-Butyldimethylsililoxy Amide 53: 52% over two steps; yellow oil; R_f = 0.55 (silica gel, 10% AcOEt in hexanes); $[\alpha]^{25}_D$ = +20.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.18 (m, 5 H), 4.12 (ddd, *J* = 8.4, 4.5, 3.7 Hz, 1 H), 3.80 (ddd, *J* = 9.0, 4.8, 1.5 Hz, 1 H), 3.72-3.69 (m, 1 H), 3.69 (d, *J* = 9.0 Hz, 1 H), 2.98 (dd, *J* = 14.8, 3.5 Hz, 1 H), 2.70 (dd, *J* = 14.8, 4.7 Hz, 1 H), 2.46 (dc, *J* = 8.5, 6.8 Hz, 1 H), 2.22-2.15 (m, 1 H), 2.05-1.98 (m, 1 H), 1.88 (bs, 3 H), 1.87-1.77 (m, 1 H), 1.62-1.55 (m, 1 H), 1.52 (s, 3 H), 1.51 (s, 3 H), 1.00 (d, *J* = 6.8 Hz, 3 H), 0.85 (s, 9 H), -0.02 (s, 3 H), -0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.1, 130.0, 128.0, 126.1, 94.6, 74.3, 66.8, 56.9, 43.8, 39.3, 30.5, 26.3, 25.9, 23.7, 17.9, 14.4, -4.4, -5.0; FAB HRMS (NBA) *m/e* 488.2628, M+Na$^+$ calcd for $C_{25}H_{43}NO_3SSi$ 488.2631.



54

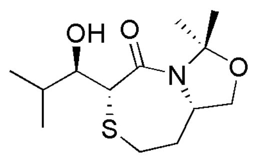
2-Hydroxy 3-Phenylthio Amide 54. To a solution of epoxy amide **9d** (102 mg, 0.29 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added thiophenol (78 μL, 0.73 mmol, 2.5 equiv) and $Yb(OTf)_3$ (54 mg, 0.09 mmol, 0.3 equiv) at 0 °C. After stirring at this temperature for 2 days, the reaction mixture was diluted with Et_2O and the resulting organic solution washed with a saturated aqueous $NaHCO_3$ solution. After separation of both phases, the aqueous layer was extracted with Et_2O (twice), and the combined organic extracts were washed with brine, dried ($MgSO_4$) and filtered. Concentration under reduced pressure provided a crude product that was purified by flash column chromatography (silica gel, 50% AcOEt in hexanes) to afford sulfide **54** (94 mg, 77%) as a colorless oil: R_f = 0.52 (silica gel, AcOEt); $[\alpha]^{25}_D$ = -118.0 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, J = 8.5 Hz, 2 H), 7.20-7.10 (m, 5 H), 7.01 (d, J = 8.8 Hz, 1 H), 6.75 (d, J = 8.5 Hz, 2 H), 4.68 (d, J = 2.6 Hz, 1 H), 4.39 (d, J = 2.6 Hz, 1 H), 3.95-3.92 (m, 1 H), 3.70 (s, 3 H), 3.54 (dd, J = 11.5, 3.6 Hz, 1 H), 3.46 (dd, J = 11.5, 6.5 Hz, 1 H), 3.33 (bs, 1 H), 2.57-2.52 (m, 1 H), 2.48-2.42 (m, 1 H), 1.98 (s, 3 H), 1.73-1.67 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 158.9, 134.2, 131.5, 131.2, 129.4, 128.7, 126.9, 113.8, 75.9, 64.7, 56.2, 55.1, 51.0, 30.4, 29.6, 15.4; FAB HRMS (NBA) *m/e* 444.5635, $M+Na^+$ calcd for $C_{21}H_{27}NO_4S_2$ 444.5632.



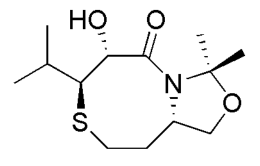
55

Thiocane 55. Treatment of Epoxy Amide 9a with SmI_2. A solution of SmI_2 (0.74 mmol, 2.0 equiv) in THF (7 mL) was added dropwise to a solution of epoxy amide **9a** (120 mg, 0.37 mmol, 1.0 equiv) in THF (10 mL). After stirring for 2 h at room temperature, the reaction mixture was quenched with 0.1 M aqueous HCl solution (5 mL), followed by addition of Et_2O. After separation of both phases, the aqueous solution was extracted with

Et_2O (twice), and the combined organic extracts were washed with brine, dried ($MgSO_4$) and filtered. Concentration under reduced pressure provided a crude product that was purified by flash column chromatography (silica gel, 20% AcOEt in hexanes) to afford compound **55** (42 mg, 37%) as a white solid: $R_f = 0.38$ (silica gel, 20% AcOEt in hexanes); m.p. 182-185ºC; $[\alpha]^{25}_D = -61.6$ (*c* 2.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.31$-7.22 (m, 5 H), 4.69 (d, $J = 10.0$ Hz, 1 H), 4.54 (ddd, $J = 11.5, 4.1$ Hz, 1 H), 4.03 (dd, $J = 8.7, 4.6$ Hz, 1 H), 3.78 (d, $J = 8.7$ Hz, 1 H), 3.77 (d, $J = 10.0$ Hz, 1 H), 2.88 (ddd, $J = 15.6, 5.0, 4.0$ Hz, 1 H), 2.40 (ddd, $J = 14.8, 11.1, 3.4$ Hz, 1 H), 2.20-2.12 (m, 1 H), 1.83 (dddd, $J = 14.8, 11.1, 3.8$ Hz, 1 H), 1.68 (s, 3 H), 1.56 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 170.7$, 139.4, 128.6, 127.8, 127.5, 96.2, 74.0, 68.8, 55.3, 53.7, 36.0, 28.0, 26.4, 23.2; FAB HRMS (NBA) *m/e* 330.1135, $M+Na^+$ calcd for $C_{16}H_{21}NO_3S$ 330.1140.



56



57

Thiepane 56 and Thiocane 57. Treatment of Epoxy Amide 9h with SmI_2. Epoxy amide **9h** (64 mg, 0.23 mmol, 1.0 equiv) was treated with a solution of SmI_2 (0.46 mmol, 2.0 equiv) in THF (5 mL) according to the procedure described above for **9a**, to obtain, after purification by flash column chromatography (silica gel, 20% AcOEt in hexanes) an inseparable mixture of compounds **56** and **57** (50 mg, 80% combined yield, 1:1 mixture) as a colorless oil: $R_f = 0.38$ (silica gel, 20% AcOEt in hexanes); ^1H NMR (400 MHz, $CDCl_3$) (**56** + **57**) $\delta = 4.48$-4.46 (m, 1 H), 4.36 (ddd, $J = 11.8, 4.1$ Hz, 1 H), 4.29 (d, $J = 10.0$ Hz, 1 H), 3.98 (dd, $J = 8.7, 4.7$ Hz, 1 H), 3.73 (d, $J = 8.7$ Hz, 1 H), 3.60 (dd, $J = 5.9, 5.7$ Hz, 1 H), 3.40 (d, $J = 11.1$ Hz, 1 H), 3.28 (d, $J = 11.2$ Hz, 1 H), 2.96 (d, $J = 5.0$ Hz, 1 H), 2.88 (ddd, $J = 15.4, 5.0, 4.0$ Hz, 1 H), 2.62-2.59 (m, 1 H), 2.55 (dd, $J = 10.0, 2.9$ Hz, 1 H), 2.27 (ddd, $J = 14.9, 10.5, 3.2$ Hz, 1 H), 2.11-2.03 (m, 2 H), 1.85-1.74 (m, 5 H), 1.63 (s, 6 H), 1.54 (s, 6 H), 1.01 (d, $J = 7.0$ Hz, 3 H), 0.92 (d, $J = 6.9$ Hz, 3 H), 0.89 (d, $J = 6.7$ Hz, 6 H).

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