

Supporting Information:

Syn Monomer Synthesis:

*4-Methyl-3-(4-methyl-pentanoyl)-5-phenyl-oxazolidin-2-one (7)*¹: 4-methyl-5-phenyl-oxazolidin-2-one was synthesized as described previously¹. To a stirred solution of 4-methyl-5-phenyl-oxazolidin-2-one (8.9 g, 50 mmol) in THF (150 mL) was added dropwise *n*-BuLi (1.6 M in hexanes, 31.6 mL, 50.5 mmol) followed by 4-methylpentanoyl chloride (7.40 g, 55.0 mmol) at -78 °C¹. The reaction was stirred at -78 °C for 30 minutes and then warmed to room temperature. The mixture was quenched with sat. aqueous NH₄Cl (100 mL), the organic solvent was removed under vacuum and the aqueous solution was extracted with CH₂Cl₂ (250 mL x 3). The organic layers were combined, dried (MgSO₄), filtered, and concentrated to give compound **7** which was used without further purification.

(4*R*, 5*S*): ¹H NMR (400 MHz, C₆D₆) δ 7.00 (m, 3H), 6.82 (m, 2H), 4.67 (d, *J* = 7.4 Hz, 1H), 4.23 (dd, *J* = 6.8, 6.7 Hz, 1H), 3.09 (ddd, *J* = 6.4, 9.2, 15.7 Hz, 1H), 2.98 (ddd, *J* = 7.1, 9.2, 16.8 Hz, 1H), 1.69 (m, 2H), 1.58 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 6H), 0.56 (d, *J* = 6.6 Hz, 3H); HRMS (ES+) Calcd for [C₁₆H₂₂O₃N]⁺ 276.1599. Found 276.1612.

(4*S*, 5*R*): ¹H NMR (400 MHz, C₆D₆) δ 7.00 (m, 3H), 6.84 (m, 2H), 4.70 (d, *J* = 7.4 Hz, 1H), 4.23 (dd, *J* = 6.8, 6.7 Hz, 1H), 3.10 (ddd, *J* = 6.4, 9.2, 15.7 Hz, 1H), 2.99 (ddd, *J* = 7.1, 9.2, 16.8 Hz, 1H), 1.70 (m, 2H), 1.59 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 6H), 0.59 (d, *J* = 6.6 Hz, 3H); HRMS (ES+) Calcd for [C₁₆H₂₂O₃N]⁺ 276.1599. Found 276.1613.

3-Hydroxy-2-isobutyl-pent-4-enethioic acid S-benzyl ester (syn-3)^{2,3}: To a stirred solution of compound **7** (15.4 g, 50.0 mmol) in CH₂Cl₂ (200 mL) was added dropwise dibutylboron triflate (1.0 M in CH₂Cl₂, 55.0 mL, 55.0 mmol) followed by diisopropylethylamine (10.5 mL, 60.0 mmol) at 0 °C. The solution was cooled to -78 °C, acrolein (16.7 mL, 250 mmol) was added over a period of five minutes and the solution was stirred for 1 hour at -78 °C. The solution was warmed to 0 °C and stirred for 30 minutes. The reaction was quenched with an ice-cooled mixture of MeOH (167 mL) and 30% H₂O₂ (33 mL). The organic solvents were removed under vacuum and the resulting solution was extracted with CH₂Cl₂ (300 mL x 3). Organic layers were combined, washed with 1.0 M NaHCO₃ (300 mL), dried (MgSO₄), filtered, and concentrated under vacuum. The crude aldol product was used without further purification. To a stirred solution of benzylmercaptan (11.3 mL, 100 mmol) in CH₂Cl₂ (75 mL) was added dropwise *n*-BuLi (1.6 M in hexanes, 62.5 mL, 100 mmol) followed by AlMe₃ (2.0 M in toluene, 50 mL, 100 mmol) at 0 °C and the solution was stirred for 30 minutes. The crude product from above was then added dropwise in ice-cooled THF (50 mL) and the reaction was stirred for 2 hrs. The reaction was

quenched with aqueous HCl (1.0 M, 200 mL) at 0 °C and stirred for 30 minutes while warming to room temperature. The solution was extracted with EtOAc (200 mL x 3), dried (MgSO₄), filtered, and concentrated under vacuum. The chiral auxiliary was removed by crystallization from a mixture of EtOAc/hexanes, and the remaining material was purified by flash chromatography (13% EtOAc/hexanes + 0.2% MeOH) providing 8.0 g (58% from 4-methyl-5-phenyl-oxazolidin-2-one) of **syn-3**.

(2*S*, 3*R*): ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.35 (m, 5H), 5.84 (ddd, J = 4.9, 10.7, 16.6 Hz, 1H), 5.31 (ddd, J = 1.4, 1.4, 17.1 Hz, 1H), 5.20 (ddd, J = 1.4, 1.4, 10.8 Hz, 1H), 4.36 (m, 1H), 4.21 (d, J = 13.7 Hz, 1H), 4.15 (d, J = 13.7 Hz, 1H), 2.85 (ddd, J = 3.9, 3.9, 8.8 Hz, 1H), 2.32 (d, J = 3.4 Hz, 1H), 1.79 (ddd, J = 4.9, 10.7, 15.6 Hz, 1H), 1.58-1.66 (m, 1H), 1.42 (ddd, J = 3.4, 9.2, 13.1 Hz, 1H), 0.93 (s, 3H), 0.92 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 202.1, 137.5, 137.4, 129.1, 128.9, 127.6, 117.0, 74.0, 57.5, 36.6, 33.6, 26.2, 23.8, 22.0; IR (film) 3465 (m, br), 3063 (w), 3029 (w), 2956 (s), 2929 (m, sh), 2869 (m, sh), 1681 (s), 1454 (m), 1386 (w), 1368 (w), 1239 (w), 1029 (m), 990 (m, sh), 929 (w), 888 (w), 751 (w), 701 (s) cm⁻¹; [α]_D +3.3 (0.01 g/mL, CH₂Cl₂); HRMS (CI+) Calcd for [C₁₆H₂₃O₂S + NH₄]⁺ 296.1684. Found 296.1689.

(2*R*, 3*S*): ¹H NMR (500 MHz, CDCl₃) δ 7.26-7.34 (m, 5H), 5.84 (ddd, J = 5.9, 10.3, 16.1 Hz, 1H), 5.31 (ddd, J = 1.4, 1.4, 15.4 Hz, 1H), 5.21 (ddd, J = 1.0, 1.0, 10.3 Hz, 1H), 4.36 (m, 1H), 4.20 (d, J = 13.7 Hz, 1H), 4.15 (d, J = 14.2 Hz, 1H), 2.84 (ddd, J = 4.9, 11.7, 15.1 Hz, 1H), 2.31 (d, J = 3.9 Hz, 1H), 1.79 (ddd, J = 4.9, 11.7, 15.1 Hz, 1H), 1.58-1.64 (m, 1H), 1.41 (ddd, J = 3.9, 9.3, 14.7 Hz, 1H), 0.93 (s, 3H), 0.91 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 202.1, 137.5, 137.4, 129.1, 128.9, 127.6, 117.0, 74.0, 57.5, 36.6, 33.6, 26.2, 23.8, 22.0; IR (film) 3457 (m, br), 3064 (w), 3030 (w), 2869 (m, sh), 1683 (s), 1496 (w), 1454 (w), 1386 (w), 1368 (w), 1237 (w), 1028 (m), 990 (w, sh), 928 (w), 888 (w), 751 (w), 700 (m) cm⁻¹; [α]_D -1.8 (0.01 g/mL, CH₂Cl₂); HRMS (CI+) Calcd for [C₁₆H₂₃O₂S + NH₄]⁺ 296.1684. Found 296.1693.

3-(tert-Butyl-dimethyl-silyloxy)-2-isobutyl-pent-4-enoic acid (**8**)^{4,17}: To a stirred solution of compound **syn-3** (4.50 g, 16 mmoles) in DMF (4.0 mL) was added TBDMSCl (3.0 g, 20 mmoles) and imidazole (2.2 g, 32 mmoles). The reaction was stirred for 14 hrs at room temperature. The reaction was quenched by the addition of sat. aqueous NaHCO₃ (5 mL), extracted with CH₂Cl₂ (10 mL x 3) and the combined organic layers were dried (MgSO₄), filtered, and concentrated under vacuum. The crude material was used without further purification. To a stirred solution of the crude product from above (5.3 g, 13 mmoles) in THF (160 mL), MeOH (50 mL) and H₂O (50 mL) was added 1.2 g of LiOH followed by 9.0 mL of H₂O₂ (30% in H₂O) at 0°C. The reaction was warmed to room temperature and stirred for 8 hrs. The reaction was quenched with Na₂SO₃ (1.0 M in H₂O, 156 mL) at 0 °C and stirred for 30 minutes while warming to room temperature. The solution was

acidified to pH 2 with KHSO_4 (1.0 M in H_2O , 200 mL), extracted with CH_2Cl_2 (200 mL x 3) dried (MgSO_4), filtered, and the combined organic layers were concentrated under vacuum. The residue was purified by flash chromatography (13% EtOAc/hexanes + 0.2% AcOH) to give 4.6 g (98%) of compound **8**.

(2*S*, 3*R*): ^1H NMR (400 MHz, C_6D_6) δ 5.89 (ddd, $J = 6.8, 10.4, 17.2$ Hz, 1H), 5.18 (d, $J = 18.2$ Hz, 1H), 5.00 (d, $J = 11.4$ Hz, 1H), 4.38 (dd, $J = 6.5, 6.5$ Hz, 1H), 2.71 (ddd, $J = 3.7, 6.4, 10.4$ Hz, 1H), 1.88 (ddd, $J = 4.6, 10.7, 13.6$ Hz, 1H), 1.68 (m, 1H), 1.49 (ddd, $J = 3.7, 9.6, 13.4$ Hz, 1H), 0.99 (s, 12H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.5$ Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H); HRMS (CI+) Calcd for $[\text{C}_{15}\text{H}_{30}\text{O}_3\text{Si} + \text{NH}_4]^+$ 304.2308. Found 304.2308.

(2*R*, 3*S*): ^1H NMR (400 MHz, C_6D_6) δ 5.89 (ddd, $J = 6.8, 10.4, 17.2$ Hz, 1H), 5.18 (d, $J = 18.2$ Hz, 1H), 5.00 (d, $J = 11.4$ Hz, 1H), 4.38 (dd, $J = 6.5, 6.5$ Hz, 1H), 2.71 (ddd, $J = 3.7, 6.4, 10.4$ Hz, 1H), 1.88 (ddd, $J = 4.6, 10.7, 13.6$ Hz, 1H), 1.68 (m, 1H), 1.49 (ddd, $J = 3.7, 9.6, 13.4$ Hz, 1H), 0.99 (s, 12H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.5$ Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H); HRMS (CI+) Calcd for $[\text{C}_{15}\text{H}_{30}\text{O}_3\text{Si} + \text{NH}_4]^+$ 304.2308. Found 304.2316.

(2-Hydroxy-1-isobutyl-but-3-enyl)-carbamic acid 9H-fluoren-9-ylmethyl ester (**syn-2**)^{5,6}: To a stirred solution of compound **8** (5.00 g, 17.5 mmol) in acetonitrile (88 mL) was added triethylamine (2.67 mL, 19.2 mmol) followed by diphenylphosphoryl azide (4.07 mL, 19.2 mmol) at room temperature. The solution was refluxed for 30 minutes then cooled to room temperature and CuCl (433 mg, 4.40 mmol) was added followed by 9-fluorenylmethanol (10.3 g, 52.4 mmol). The reaction was stirred for 2 hours, quenched by addition of sat. aqueous NaHCO_3 (100 mL), and extracted (100 mL x 3) with EtOAc. The organic layers were combined, dried (MgSO_4), filtered, and concentrated under vacuum. The residue was partially purified by flash chromatography (6% EtOAc/hexanes) to remove polar impurities. The non-polar fractions were concentrated and dissolved in THF (35 mL), AcOH (105 mL) and H_2O (35 mL). The solution was heated to 45 °C and stirred for 4 hours. The solvent was removed under vacuum by azeotropic distillation with toluene and the residue was purified by flash chromatography (20% EtOAc/hexanes + 0.2% MeOH) to give 3.3 g (51%) of compound **syn-2**.

(1*S*, 2*R*): ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.8$ Hz, 2H), 7.59 (d, $J = 7.3$ Hz, 2H), 7.41 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.32 (dd, $J = 7.6, 7.6$ Hz, 2H), 5.82 (ddd, $J = 5.4, 10.5, 16.6$ Hz, 1H), 5.33 (d, $J = 17.1$ Hz, 1H), 5.24 (d, $J = 10.7$ Hz, 1H), 4.71 (d, $J = 8.8$ Hz, 1H), 4.49 (dd, $J = 6.8, 10.7$ Hz, 1H), 4.43 (dd, $J = 6.8, 10.7$ Hz, 1H), 4.22 (dd, $J = 6.8, 6.8$ Hz, 1H), 4.21 (m, 1H), 3.86 (ddd, $J = 4.2, 9.3, 13.4$ Hz, 1H), 1.61 (m, 1H), 1.23-1.33 (m, 2H), 0.92 (d, $J = 6.3$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 378 K) δ 156.7, 144.0, 144.0, 141.4, 141.4, 136.8, 127.6,

127.0, 127.0, 124.9, 124.9, 119.9, 116.6, 75.5, 66.7, 54.2, 47.7, 39.1, 25.0, 23.5, 21.8; FTIR (film) 3323, 3067, 2954, 1692, 1543, 1450, 1267, 738 cm^{-1} ; $[\alpha]_{\text{D}}$ -18.7 (0.02 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{23}\text{H}_{28}\text{O}_3\text{N}]^+$ 366.2069. Found 366.2066.

(1*R*, 2*S*): ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.3$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H), 7.41 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.32 (dd, $J = 7.6, 7.6$ Hz, 2H), 5.82 (ddd, $J = 5.4, 10.7, 16.6$ Hz, 1H), 5.33 (d, $J = 17.1$ Hz, 1H), 5.24 (d, $J = 10.7$ Hz, 1H), 4.71 (d, $J = 8.8$ Hz, 1H), 4.49 (dd, $J = 6.8, 10.7$ Hz, 1H), 4.43 (dd, $J = 6.8, 10.7$ Hz, 1H), 4.22 (dd, $J = 6.8, 6.8$ Hz, 1H), 4.21 (m, 1H), 3.86 (ddd, $J = 3.9, 9.3, 13.2$ Hz, 1H), 1.62 (m, 1H), 1.23-1.33 (m, 2H), 0.92 (d, $J = 6.8$ Hz, 3H), 0.90 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 378 K) δ 156.7, 144.0, 143.9, 141.4, 141.4, 136.8, 127.6, 127.5, 127.0, 127.0, 124.9, 119.9, 116.5, 75.5, 66.7, 54.2, 47.6, 39.0, 24.9, 23.5, 21.8 FTIR (film) 3323, 3067, 2954, 1693, 1541, 1450, 1265, 739 cm^{-1} ; $[\alpha]_{\text{D}}$ $+19.6$ (0.02 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{23}\text{H}_{28}\text{O}_3\text{N}]^+$ 366.2069. Found 366.2077.

Anti Monomer Synthesis:

2-(*N*-Benzyl-*N*-mesitylenesulfonyl)amino-1-phenyl-1-propyl 4-methylpentanoate (**4**)⁷: 2-(*N*-benzyl-*N*-mesitylenesulfonyl)amino-1-phenyl-1-propanol was synthesized as described previously. To a stirred solution of 2-(*N*-benzyl-*N*-mesitylenesulfonyl)amino-1-phenyl-1-propanol (4.2 g, 10 mmoles) in THF (43 mL) was added dropwise pyridine (1.1 mL, 13 mmoles) followed by 4-methylpentanoyl chloride (1.6 mL, 12 mmoles) at 0 °C. The reaction was warmed to room temperature and stirred for 16 hours. The reaction was extracted with EtOAc (50 mL x 3). The organic layers were combined, dried (MgSO_4), filtered, and concentrated to give compound **4** which was used without further purification.

(1*S*, 2*R*): ^1H NMR (500 MHz, CDCl_3) δ 7.33 (d, $J = 7.3$ Hz, 2H), 7.16-7.26 (m, 6H), 6.88-6.90 (m, 2H), 6.87 (s, 2H), 5.82 (d, $J = 4.0$ Hz, 1H), 4.73 (B of AB_q , $J_{\text{AB}} = 16.6$ Hz, 1H), 4.60 (A of AB_q , $J_{\text{AB}} = 16.6$ Hz, 1H), 4.03 (dq, $J = 4.1, 6.9$ Hz, 1H), 2.51 (s, 6H), 2.28 (s, 3H), 2.15 (ddd, $J = 6.8, 9.0, 15.9$ Hz, 1H), 2.08 (ddd, $J = 6.9, 8.8, 15.8$ Hz, 1H), 1.45 (m, 1H), 1.38 (m, 2H), 1.12 (d, $J = 7.0$ Hz, 3H), 0.85 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 6.5$ Hz, 3H); HRMS (ES+) Calcd for $[\text{C}_{32}\text{H}_{39}\text{O}_4\text{NS}]^+$ 522.2654. Found 522.2678.

(1*R*, 2*S*): ^1H NMR (500 MHz, CDCl_3) δ 7.33 (d, $J = 7.3$ Hz, 2H), 7.16-7.27 (m, 6H), 6.89-6.91 (m, 2H), 6.88 (s, 2H), 5.82 (d, $J = 4.0$ Hz, 1H), 4.74 (B of AB_q , $J_{\text{AB}} = 16.6$ Hz, 1H), 4.60 (A of AB_q , $J_{\text{AB}} = 16.6$ Hz, 1H), 4.04 (dq, $J = 4.1, 6.9$ Hz, 1H), 2.51 (s, 6H), 2.28 (s, 3H), 2.15 (ddd, $J = 6.8, 9.0, 15.9$ Hz, 1H), 2.08 (ddd, $J = 6.9, 8.8, 15.8$ Hz, 1H), 1.45 (m, 1H), 1.38 (m, 2H), 1.12 (d, $J = 7.0$ Hz,

3H), 0.85 (d, $J = 6.5$ Hz, 3H), 0.84 (d, $J = 6.5$ Hz, 3H); HRMS (ES+) Calcd for $[\text{C}_{32}\text{H}_{38}\text{O}_4\text{NS}+\text{Na}]^+$ 544.2498. Found 544.2502.

(2*R*, 3*R*)-3-Hydroxy-2-isobutyl-pent-4-enoic acid (**5**)^{7,8,9,10}: To a stirred solution of compound **4** (5.6 g, 10 mmoles) in CH_2Cl_2 (75 mL) was added dropwise triethylamine (3.3 mL, 24 mmoles) at 0 °C. The solution was cooled to -78 °C and pre-cooled C_x_2BOTf (1.0 M in CH_2Cl_2 , 20 mL, 20 mmoles) was added dropwise. The solution was stirred for 2 hours, then acrolein (0.80 mL, 12 mmoles) was added dropwise and the reaction was stirred for 1 hour then warmed to 0 °C and stirred for 1 hour. The reaction was quenched with pH 7 phosphate buffer (1.0 M, 40 mL) followed by MeOH (100 mL) and 30% H_2O_2 (10 mL) at 0°C and stirred for 1 hour at room temperature. The organic solvents were removed under vacuum and the resulting solution was extracted with CH_2Cl_2 (150 mL x 3), dried (MgSO_4), filtered, and concentrated under vacuum. The residue was purified by flash chromatography (14% EtOAc/hexanes + 0.2% MeOH) to give 5.2 g (90% from 2-(*N*-benzyl-*N*-mesitylenesulfonyl)amino-1-phenyl-1-propanol) of the aldol product. To a stirred solution of the aldol product (5.2 g, 9.0 mmoles) in MeOH (72 mL) was added aqueous NaOH (2.5 M, 18 mL, 45 mmoles) at room temperature. The solution was stirred for 14 hours then diluted with EtOAc. The organic layer was washed with Na_2CO_3 (150 mL x 3), dried (MgSO_4), filtered, and concentrated under vacuum to give 3.2 g (85%) of the chiral auxiliary. The aqueous layers were combined, acidified with aqueous HCl (1M) to pH 1, extracted with EtOAc (300 mL x 3), dried (MgSO_4), filtered, and concentrated under vacuum to give 1.3 g (87%) of compound **5** which was used without further purification.

(2*S*, 3*S*): ^1H NMR (400 MHz, CDCl_3) δ 5.86 (ddd, $J = 6.4, 10.4, 16.9$, 1H), 5.33 (d, $J = 17.1$ Hz, 1H), 5.23 (d, $J = 10.4$ Hz, 1H), 4.21 (dd, $J = 6.5, 6.5$ Hz, 1H), 2.60 (ddd, $J = 4.6, 6.4, 10.5$ Hz, 1H), 1.65 (m, 2H), 1.35 (m, 1H), 0.93 (d, $J = 6.3$ Hz, 3H), 0.92 (d, $J = 6.2$ Hz, 3H), HRMS (CI+) Calcd for $[\text{C}_9\text{H}_{16}\text{O}_3+\text{NH}_4]^+$ 190.1443. Found 190.1440.

(2*R*, 3*R*): ^1H NMR (400 MHz, CDCl_3) δ 5.85 (ddd, $J = 6.4, 10.4, 17.0$, 1H), 5.32 (d, $J = 17.1$ Hz, 1H), 5.23 (d, $J = 10.4$ Hz, 1H), 4.20 (dd, $J = 6.7, 6.7$ Hz, 1H), 2.59 (ddd, $J = 4.5, 6.9, 11.1$ Hz, 1H), 1.64 (m, 2H), 1.33 (m, 1H), 0.92 (d, $J = 6.3$ Hz, 3H), 0.92 (d, $J = 6.2$ Hz, 3H), HRMS (CI+) Calcd for $[\text{C}_9\text{H}_{16}\text{O}_3+\text{NH}_4]^+$ 190.1443. Found 190.1446.

3-Hydroxy-2-isobutyl-pent-4-enethioic acid *S*-benzyl ester (**anti-3**)¹¹: To a stirred solution of compound **5** (1.94 g, 11.3 mmoles) in CH_2Cl_2 (10.2 mL) was added benzylmercaptan (3.97 mL, 33.9 mmoles) and DMAP (138 mg, 1.10 mmoles) at room temperature. The reaction was cooled to 0 °C and DCC (1.0 M in CH_2Cl_2 , 12.4 mL, 12.4 mmoles) was added dropwise and the reaction

was warmed to room temperature. After stirring for 4 hours at room temperature the solution was diluted with ether and filtered through Celite. The filtrate was concentrated under vacuum and purified by flash chromatography (14% EtOAc/hexanes) to give 2.83 g (90%) of **anti-3**.

(2*S*, 3*S*): ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.31 (m, 5H), 5.84 (ddd, J = 6.0, 10.4, 16.8 Hz, 1H), 5.29 (d, J = 17.1 Hz, 1H), 5.18 (d, J = 10.4 Hz, 1H), 4.22 (dd, J = 6.1, 13.0 Hz, 1H), 4.15 (s, 2H), 2.81 (br dd, J = 5.4, 10.3 Hz, 1H), 2.37 (d, J = 7.1 Hz, 1H), 1.71 (ddd, J = 5.2, 9.7, 14.3 Hz, 1H), 1.61 (m, 1H), 1.37 (ddd, J = 4.9, 8.7, 13.5 Hz, 1H), 0.92 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 6.5 Hz); (100 MHz, CDCl₃) δ 138.3, 137.1, 128.8, 128.6, 127.2, 116.6, 57.0, 38.9, 33.3, 25.6, 23.2, 22.0; FTIR (neat) 3461, 3030, 2957, 1684, 1454, 990, 927, 702 cm⁻¹; [α]_D -20.6 (0.02 g/mL, CH₂Cl₂); HRMS (CI+) Calcd for [C₁₆H₂₃O₂S]⁺ 278.1341. Found 278.1333.

(2*R*, 3*R*): ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.31 (m, 5H), 5.84 (ddd, J = 6.0, 10.4, 16.8 Hz, 1H), 5.29 (d, J = 17.1 Hz, 1H), 5.14 (d, J = 10.4 Hz, 1H), 4.22 (dd, J = 6.1, 13.0 Hz, 1H), 4.15 (s, 2H), 2.81 (br dd, J = 5.4, 10.3 Hz, 1H), 2.39 (d, J = 7.1 Hz, 1H), 1.71 (ddd, J = 5.2, 9.7, 14.2 Hz, 1H), 1.61 (m, 1H), 1.37 (ddd, J = 4.9, 8.7, 13.5 Hz, 1H), 0.92 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 6.5 Hz); (100 MHz, CDCl₃) δ 138.3, 137.1, 128.7, 128.5, 127.2, 116.6, 57.0, 38.8, 33.2, 25.6, 23.2, 21.9; FTIR (neat) 3459, 3030, 2957, 1684, 1454, 990, 927, 702 cm⁻¹; [α]_D +18.7 (0.06 g/mL, CH₂Cl₂); HRMS (CI+) Calcd for [C₁₆H₂₃O₂S]⁺ 278.1341. Found 278.1335.

3-(tert-Butyl-dimethyl-silanyloxy)-2-isobutyl-pent-4-enoic acid (6)^{4,12}: To a stirred solution of compound **5** (134 mg, 0.780 mmoles) in DMF (0.4 mL) was added TBDMSCl (283 mg, 1.87 mmoles) and imidazole (159 mg, 2.34 mmoles) at room temperature and the solution was stirred for 24 hours. The reaction was quenched with sat. aqueous NaHCO₃ (30 mL), extracted with CH₂Cl₂ (30 mL x 3), dried (MgSO₄), filtered, and concentrated under vacuum. The residue was dissolved in THF (2 mL), MeOH (1 mL) and H₂O (1 mL) and stirred for 4 hours at room temperature. The reaction was quenched with aqueous citric acid (pH 4, 5 mL). The solution was extracted with CH₂Cl₂ (10 mL x 3), dried (MgSO₄), filtered, and concentrated under vacuum. The residue was purified by flash chromatography (10% EtOAc/hexanes + 0.5% AcOH) to give 167 mg (75% from compound **4**) of compound **6**.

(2*S*, 3*S*): ¹H NMR (400 MHz, CDCl₃) δ 5.75 (ddd, J = 7.4, 10.3, 17.4 Hz, 1H), 5.22 (d, J = 15.7 Hz, 1H), 5.19 (d, J = 8.9 Hz, 1H), 4.20 (dd, J = 7.2, 7.2 Hz, 1H), 2.56 (ddd, J = 4.3, 6.9, 10.9 Hz, 1H), 1.57 (m, 2H), 1.20 (m, 1H), 0.90 (d, J = 6.3 Hz, 6H), 0.88 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H), HRMS (CI+) Calcd for [C₁₅H₃₀O₃Si+NH₄]⁺ 304.2308. Found 304.2316.

(2*R*, 3*R*): ¹H NMR (400 MHz, CDCl₃) δ 5.74 (ddd, *J* = 7.5, 10.2, 17.4 Hz, 1H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 4.20 (dd, *J* = 7.3, 7.3 Hz, 1H), 2.56 (ddd, *J* = 4.2, 7.3, 11.1 Hz, 1H), 1.56 (m, 2H), 1.20 (m, 1H), 0.90 (d, *J* = 6.2 Hz, 6H), 0.87 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H), HRMS (CI⁺) Calcd for [C₁₅H₃₀O₃Si+NH₄]⁺ 304.2308. Found 304.2308.

(2-Hydroxy-1-isobutyl-but-3-enyl)-carbamic acid 9*H*-fluoren-9-ylmethyl ester (**anti-2**)^{4,5,6}: To a stirred solution of compound **6** (115 g, 0.40 mmoles) in acetonitrile (2 mL) was added triethylamine (61 μL, 0.44 mmoles) followed by diphenylphosphoryl azide (94 μL, 0.44 mmoles) at room temperature. The solution was refluxed for 30 minutes then cooled to room temperature and CuCl (10 mg, 0.1 mmoles) was added followed by 9-fluorene-methanol (286 mg, 1.50 mmoles). The reaction was stirred for 2 hours, quenched by addition of saturated NaHCO₃ (5 mL), and extracted (5 mL x 3) with EtOAc. The organic layers were combined, dried (MgSO₄), filtered, and concentrated under vacuum. The residue was partially purified by flash chromatography (6% EtOAc/hexanes) to remove polar impurities. The non-polar fractions were concentrated and dissolved in THF (0.6 mL), AcOH (1.8 mL) and H₂O (0.6 mL). The solution was heated to 55 °C and stirred for 4 hours. The solvent was removed under vacuum by azeotropic distillation with toluene and the residue was purified by flash chromatography (20% (EtOAc/hexanes + 0.2% MeOH) to give 147 mg (59% from compound **6**) of compound **anti-2**.

(1*S*, 2*S*): ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.40 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 2H), 5.87 (ddd, *J* = 5.9, 10.3, 16.6 Hz, 1H), 5.28 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.7 Hz, 1H), 4.85 (d, *J* = 9.3 Hz, 1H), 4.44 (dd, *J* = 6.8, 10.7 Hz, 1H), 4.38 (dd, *J* = 6.8, 10.7 Hz, 1H), 4.21 (dd, *J* = 6.8, 6.8 Hz, 1H), 4.09 (m, 1H), 3.75 (ddd, *J* = 3.9, 9.8, 14.4 Hz, 1H), 1.63 (m, 1H), 1.46 (ddd, *J* = 4.4, 10.3, 14.1 Hz, 1H), 1.36 (ddd, *J* = 4.4, 9.3, 13.7 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 378 K) δ 156.5, 144.1, 144.0, 141.4, 138.1, 127.6, 127.0, 124.9, 119.9, 116.3, 74.9, 66.6, 53.7, 47.7, 41.2, 25.0, 23.3, 22.1; FTIR (neat) 3407, 3341, 3066, 2955, 1699, 1518, 1450, 1249, 739 cm⁻¹; [α]_D -24.5 (0.01 g/mL, CH₂Cl₂); HRMS (ES⁺) Calcd for [C₂₃H₂₈O₃N]⁺ 366.2069. Found 366.2055.

(1*R*, 2*R*): ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.40 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.31 (dd, *J* = 7.3, 7.3 Hz, 2H), 5.87 (ddd, *J* = 5.9, 10.3, 16.6 Hz, 1H), 5.29 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* = 9.8 Hz, 1H), 4.45 (dd, *J* = 6.8, 10.7 Hz, 1H), 4.39 (dd, *J* = 6.8, 10.7 Hz, 1H), 4.21 (dd, *J* = 6.6, 6.6 Hz, 1H), 4.10 (m, 1H), 3.76 (ddd, *J* = 4.2, 9.8, 13.9 Hz, 1H), 1.61 (m, 1H), 1.47 (ddd, *J* = 4.9, 10.3, 14.6 Hz, 1H), 1.36 (ddd, *J* = 4.6, 9.3, 13.9 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 378 K) δ 156.5, 144.0, 143.9, 141.3, 138.1, 127.5, 126.9, 124.9, 119.8, 116.1, 74.8, 66.6, 53.6, 47.6, 41.1, 25.0, 23.3, 22.1; FTIR

(neat) 3407, 3348, 3066, 2955, 1699, 1517, 1450, 1249, 739 cm^{-1} ; $[\alpha]_{\text{D}} +25.2$ (0.05 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{23}\text{H}_{28}\text{O}_3\text{N}]^+$ 366.2069. Found 366.2082.

Synthesis of the Units 11

*3-({1-[1-(9H-Fluoren-9-ylmethoxycarbonylamino)-3-methyl-butyl]-allyloxy}-dimethyl-silanyloxy)-2-isobutyl-pent-4-enethioic acid S-benzyl ester (9)*¹³: To a stirred solution of dichlorodimethylsilane (1.70 mL, 14.5 μmoles) in pyridine (4.80 mL) was added dropwise compound *anti-2* (0.11 M in pyridine, 6.6 mL, 0.72 μmoles) at room temperature. The reaction was stirred for 2 hours, then the volatiles were removed under high vacuum. To the solid residue was added *anti-3* (0.15 M in pyridine, 4.7 mL, 0.72 μmoles) at room temperature. The reaction was stirred for 1.5 hours and the solvent was removed under high vacuum. The solid residue was dissolved in diethyl ether (10 mL) and H_2O (10 mL) and the organic layer was extracted with diethyl ether (10 mL x 2), dried (MgSO_4), filtered, and concentrated under vacuum. The residue was purified by flash chromatography (5% EtOAc/hexanes) to give 437 mg (86%) of compound **9**.

(2*S*, 3*R*, 6*S*, 7*R*): $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 7.58 (d, $J = 7.2$ Hz, 2H), 7.52 (dd, $J = 5.9, 5.9$ Hz, 2H), 7.16-7.25 (m, 6H), 7.04 (dd, $J = 7.5, 7.5$ Hz, 2H), 6.97 (dd, $J = 7.3, 7.3$ Hz, 1H), 5.98 (ddd, $J = 7.0, 10.3, 17.2$ Hz, 1H), 5.66 (ddd, $J = 5.1, 10.5, 16.4$ Hz, 1H), 5.26 (d, $J = 17.1$ Hz, 1H), 5.20 (d, $J = 16.9$ Hz, 1H), 5.01 (d, $J = 10.4$ Hz, 1H), 5.01 (d, $J = 10.3$ Hz, 1H), 4.68 (d, $J = 9.8$ Hz, 1H), 4.48-4.55 (m, 3H), 4.40 (m, 1H), 4.11 (dd, $J = 6.4, 6.4$ Hz, 1H), 4.06 (m, 1H), 4.06 (d, $J = 13.8$ Hz, 1H), 3.99 (d, $J = 13.8$ Hz, 1H), 3.02 (ddd, $J = 3.6, 6.2, 10.2$ Hz, 1H), 1.97 (ddd, $J = 4.6, 10.6, 13.7$ Hz, 1H), 1.70 (m, 1H), 1.60 (m, 1H), 1.49 (ddd, $J = 3.7, 9.5, 13.4$ Hz, 1H), 1.26 (dd, $J = 7.1, 7.1$ Hz, 1H), 0.95 (d, $J = 6.5$ Hz, 3H), 0.86-0.89 (m, 9H), 0.15 (s, 3H), 0.13 (s, 3H); HRMS (ES+) Calcd for $[\text{C}_{41}\text{H}_{54}\text{O}_5\text{NSiS}]^+$ 700.3492. Found 700.3520.

(2*R*, 3*S*, 6*S*, 7*R*): $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.58 (d, $J = 6.8$ Hz, 2H), 7.53 (d, $J = 6.8$ Hz, 2H), 7.16-7.25 (m, 6H), 7.04 (dd, $J = 7.6$ Hz, 2H), 6.98 (dd, $J = 6.7, 13.9$ Hz, 1H), 5.91 (ddd, $J = 6.8, 10.3, 17.1$ Hz, 1H), 5.65 (ddd, $J = 4.9, 10.5, 16.4$ Hz, 1H), 5.25 (d, $J = 17.1$ Hz, 1H), 5.17 (d, $J = 17.1$ Hz, 1H), 5.00 (d, $J = 10.3$ Hz, 1H), 4.99 (d, $J = 10.3$ Hz, 1H), 4.92 (d, $J = 9.8$ Hz, 1H), 4.51-4.55 (m, 3H), 4.40 (m, 1H), 4.13 (dd, $J = 6.3$ Hz, 1H), 4.08 (d, $J = 13.8$ Hz, 1H), 4.05 (m, 1H), 3.99 (d, $J = 13.7$ Hz, 1H), 3.01 (ddd, $J = 3.7, 5.9, 10.1$ Hz, 1H), 2.03 (ddd, $J = 4.4, 10.7, 14.4$ Hz, 1H), 1.70 (m, 1H), 1.65 (m, 1H), 1.52 (ddd, $J = 3.7, 9.5, 13.4$ Hz, 1H), 1.24-1.40 (m, 2H), 0.97 (d, $J = 6.3$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 6H), 0.88 (d, $J = 6.3$ Hz, 3H), 0.15 (s, 3H), 0.11 (s, 3H); HRMS (ES+) Calcd for $[\text{C}_{41}\text{H}_{54}\text{O}_5\text{NSiS}]^+$ 700.3492. Found 700.3460.

(2*R*, 3*R*, 6*S*, 7*R*): ¹H NMR (500 MHz, CDCl₃) 7.76 (d, *J* = 7.5 Hz, 2H), 7.62 (dd, *J* = 7.6, 11.6 Hz, 2H), 7.39 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.22-7.32 (m, 7H), 5.77 (ddd, *J* = 5.0, 10.5, 16.4 Hz, 1H), 5.71 (ddd, *J* = 7.7, 10.3, 17.5, 1H), 5.46 (d, *J* = 9.6 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.13-5.18 (m, 3H), 4.48 (dd, *J* = 7.2, 10.5 Hz, 1H), 4.39 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.37 (m, 1H), 4.31 (dd, *J* = 7.1, 10.5 Hz, 1H), 4.24 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.17 (d, *J* = 13.8 Hz, 1H), 4.13 (d, *J* = 14.1 Hz, 1H), 3.76 (m, 1H), 2.80 (ddd, *J* = 3.3, 8.5, 11.4 Hz, 1H), 1.56-1.65 (m, 2H), 1.49 (m, 1H), 1.41 (ddd, *J* = 3.6, 11.3, 14.7 Hz, 1H), 1.21 (ddd, *J* = 2.8, 10.2, 13.6 Hz, 1H), 1.09 (ddd, *J* = 3.3, 10.0, 13.3 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H), 0.06 (s, 3H), -0.01 (s, 3H); HRMS (FAB+) Calcd for [C₄₁H₅₃O₅NSiS + Na]⁺ 722.3311. Found 722.3297.

(2*S*, 3*S*, 6*S*, 7*R*): ¹H NMR (500 MHz, CDCl₃) 7.76 (d, *J* = 7.8 Hz, 2H), 7.61 (dd, *J* = 8.1, 8.1 Hz, 2H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.20-7.32 (m, 7H), 5.79 (ddd, *J* = 4.9, 10.3, 17.1 Hz, 1H), 5.70 (ddd, *J* = 7.3, 10.1, 17.3, 1H), 5.26 (d, *J* = 17.1 Hz, 1H), 5.26 (d, *J* = 9.8 Hz, 1H), 5.16 (m, 1H), 5.15 (d, *J* = 16.6 Hz, 1H), 5.13 (d, *J* = 9.8 Hz, 1H), 4.45 (dd, *J* = 7.1, 10.5 Hz, 1H), 4.31-4.36 (m, 3H), 4.24 (dd, *J* = 6.3, 13.2 Hz, 1H), 4.16 (d, *J* = 13.7 Hz, 1H), 4.10 (d, *J* = 14.2 Hz, 1H), 3.77 (m, 1H), 2.80 (ddd, *J* = 3.4, 8.8, 11.2 Hz, 1H), 1.62 (m, 1H), 1.57 (ddd, *J* = 3.9, 11.2, 15.1 Hz, 1H), 1.50 (m, 1H), 1.39 (ddd, *J* = 3.9, 11.5, 14.6 Hz, 1H), 1.23 (ddd, *J* = 2.9, 10.3, 13.7 Hz, 1H), 1.12 (ddd, *J* = 3.7, 10.0, 13.4 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.3 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.03 (s, 3H), 0.02 (s, 3H); HRMS (FAB+) Calcd for [C₄₁H₅₃O₅NsiS+Na]⁺ 722.3311. Found 722.3294.

(2*S*, 3*R*, 6*S*, 7*S*): ¹H NMR (400 MHz, C₆D₆) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.48 (dd, *J* = 8.5, 8.5 Hz, 2H), 7.12-7.24 (m, 6H), 7.05 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 5.95 (ddd, *J* = 6.8, 10.3, 17.1 Hz, 1H), 5.74 (ddd, *J* = 5.9, 10.7, 16.9 Hz, 1H), 5.22 (d, *J* = 15.3 Hz, 1H), 5.19 (d, *J* = 16.7 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 2H), 4.61 (d, *J* = 9.7 Hz, 1H), 4.53 (m, 1H), 4.52 (dd, *J* = 6.2, 10.8 Hz, 1H), 4.42 (dd, *J* = 6.4, 10.9 Hz, 1H), 4.26 (m, 1H), 4.07 (d, *J* = 13.9 Hz, 1H), 4.04 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.99 (m, 1H), 3.99 (d, *J* = 13.8 Hz, 1H), 3.00 (ddd, *J* = 3.8, 6.4, 10.3 Hz, 1H), 2.00 (ddd, *J* = 4.2, 10.2, 14.0 Hz, 1H), 1.71 (m, 1H), 1.62 (m, 1H), 1.53 (ddd, *J* = 3.7, 9.6, 13.4 Hz, 1H), 1.33 (ddd, *J* = 4.2, 9.4, 13.7 Hz, 1H), 1.25 (ddd, *J* = 4.5, 10.0, 14.1 Hz, 1H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.89-0.90 (m, 9H), 0.15 (s, 3H), 0.13 (s, 3H); HRMS (ES+) Calcd for [C₄₁H₅₄O₅NSiS]⁺ 700.3492. Found 700.3523.

(2*R*, 3*S*, 6*S*, 7*S*): ¹H NMR (400 MHz, C₆D₆) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.48 (dd, *J* = 7.4, 13.3 Hz, 2), 7.12-7.24 (m, 6H), 7.05 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 5.93 (ddd, *J* = 6.8, 10.3, 17.1 Hz, 1H), 5.74 (ddd, *J* = 5.9, 10.7, 16.9 Hz, 1H), 5.21 (d, *J* = 16.4 Hz, 1H), 5.19 (d, *J* = 16.5 Hz, 1H), 5.03 (d, *J* = 10.5 Hz, 1H), 5.02 (d, *J* = 10.3 Hz, 1H), 4.63 (d, *J* = 9.6 Hz, 1H), 4.52-4.54 (m, 2H), 4.42 (dd, *J* = 6.5, 10.8 Hz, 1H), 4.22 (m, 1H), 4.09 (d, *J* = 13.8 Hz, 1H), 4.05 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.01 (m, 1H), 4.00 (d, *J* = 13.8 Hz, 1H), 3.02 (ddd, *J* = 3.7, 6.3, 10.3 Hz, 1H), 2.00 (ddd, *J* = 4.5, 9.0, 11.4 Hz, 1H), 1.72 (m, 1H), 1.62 (ddd, *J* = 4.7, 8.2, 11.5 Hz, 1H), 1.54 (ddd, *J* = 3.7, 9.6, 13.4 Hz, 1H), 1.31 (m, 2H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.89-0.91 (m, 9H), 0.16 (s, 3H), 0.13 (s, 3H); HRMS (ES+) Calcd for [C₄₁H₅₄O₅NSiS]⁺ 700.3492. Found 700.3473.

(2*R*, 3*R*, 6*S*, 7*S*): ¹H NMR (500 MHz, C₆D₆) δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.14-7.23 (m, 6H), 7.04 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.98 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.80 (ddd, *J* = 6.3, 11.2, 17.1 Hz, 1H), 5.76 (ddd, *J* = 7.3, 10.3, 17.6 Hz, 1H), 5.26 (dd, *J* = 1.5, 17.1 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 5.06 (dd, *J* = 1.5, 10.7 Hz, 1H), 5.03 (d, *J* = 11.2 Hz, 1H), 5.00 (d, *J* = 10.3 Hz, 1H), 4.58 (dd, *J* = 8.1, 8.1 Hz, 1H), 4.48 (dd, *J* = 6.6, 11.0 Hz, 1H), 4.44 (dd, *J* = 7.1, 11.5 Hz, 1H), 4.21 (m, 1H), 4.15 (d, *J* = 13.7 Hz, 1H), 4.11 (d, *J* = 14.2 Hz, 1H), 4.03-4.09 (m, 2H), 2.99 (ddd, *J* = 3.4, 8.3, 11.5 Hz, 1H), 1.79 (ddd, *J* = 4.2, 11.2, 13.4 Hz, 1H), 1.65-1.72 (m, 2H), 1.32-1.42 (m, 2H), 1.21 (ddd, *J* = 3.4, 10.0, 13.4 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H), 0.19 (s, 3H), 0.12 (s, 3H); HRMS (ES+) Calcd for [C₄₁H₅₄O₅NSiS]⁺ 700.3492. Found 700.3525.

(2*S*, 3*S*, 6*S*, 7*S*): ¹H NMR (400 MHz, C₆D₆) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 (dd, *J* = 7.4, 11.4 Hz, 2H), 7.15-7.24 (m, 6H), 7.06 (dd, *J* = 7.5, 7.6 Hz, 2H), 6.99 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.80 (ddd, *J* = 6.2, 10.9, 16.7 Hz, 1H), 5.74 (ddd, *J* = 7.3, 10.3, 17.3 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 5.04 (d, *J* = 10.5 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.91 (d, *J* = 9.7 Hz, 1H), 4.60 (dd, *J* = 7.9, 7.9 Hz, 1H), 4.51 (dd, *J* = 6.4, 10.8 Hz, 1H), 4.44 (dd, *J* = 6.7, 10.8 Hz, 1H), 4.19 (m, 1H), 4.14 (d, *J* = 13.7 Hz, 1H), 4.07 (d, *J* = 13.8 Hz, 1H), 4.06-4.13 (m, 2H), 2.98 (ddd, *J* = 3.1, 8.2, 11.1 Hz, 1H), 1.80 (ddd, *J* = 3.8, 8.5, 10.4 Hz, 1H), 1.65-1.70 (m, 2H), 1.35 (dd, *J* = 7.1, 7.1 Hz, 2H), 1.22 (ddd, *J* = 3.5, 9.9, 13.4 Hz, 1H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.16 (s, 3H), 0.15 (s, 3H); HRMS (ES+) Calcd for [C₄₁H₅₄O₅NSiS]⁺ 700.3492. Found 700.3477.

(2*S*, 3*R*, 6*R*, 7*R*): ¹H NMR (400 MHz, C₆D₆) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.48 (dd, *J* = 7.4, 12.3 Hz, 2H), 7.15-7.24 (m, 6H), 7.05 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.98 (dd, *J* = 7.3, 7.3 Hz, 1H), 5.93 (ddd, *J* = 6.8, 10.3, 17.1 Hz, 1H), 5.74 (ddd, *J* = 5.9, 10.7, 16.9 Hz, 1H), 5.20 (d, *J* = 17.1 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 5.01 (d, *J* = 10.3 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 1H),

4.50-4.53 (m, 2H), 4.42 (dd, $J = 6.5, 10.9$ Hz, 1H), 4.22 (m, 1H), 4.09 (d, $J = 13.8$ Hz, 1H), 4.05 (dd, $J = 6.2, 6.2$ Hz, 1H), 4.01 (m, 1H), 4.00 (d, $J = 13.9$ Hz, 1H), 3.00 (ddd, $J = 3.8, 6.3, 10.3$ Hz, 1H), 2.00 (ddd, $J = 4.2, 10.2, 14.0$ Hz, 1H), 1.71 (m, 1H), 1.62 (m, 1H), 1.53 (ddd, $J = 3.6, 9.6, 13.4$ Hz, 1H), 1.30 (m, 1H), 1.29 (m, 1H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.91-0.89 (m, 9H), 0.15 (s, 3H), 0.13 (s, 3H); HRMS (ES+) Calcd for $[\text{C}_{41}\text{H}_{53}\text{O}_5\text{NSiS} + \text{Na}]^+$ 722.3311. Found 722.3282.

(2*R*, 3*S*, 6*R*, 7*R*): ^1H NMR (500 MHz, C_6D_6) δ 7.57 (d, $J = 7.3$ Hz, 2H), 7.47 (dd, $J = 8.6, 8.6$ Hz, 2H), 7.13-7.24 (m, 6H), 7.05 (dd, $J = 7.5, 7.5$ Hz, 2H), 6.97 (dd, $J = 7.3, 7.3$ Hz, 1H), 5.95 (ddd, $J = 6.9, 10.3, 17.1$ Hz, 1H), 5.74 (ddd, $J = 5.6, 10.4, 16.6$ Hz, 1H), 5.27 (d, $J = 15.6$ Hz, 1H), 5.19 (d, $J = 5.9$ Hz, 1H), 5.03 (d, $J = 10.6$ Hz, 2H), 4.58 (d, $J = 9.6$ Hz, 1H), 4.53 (m, 1H), 4.52 (dd, $J = 6.2, 10.9$ Hz, 1H), 4.43 (dd, $J = 6.4, 10.9$ Hz, 1H), 4.26 (m, 1H), 4.07 (d, $J = 13.9$ Hz, 1H), 4.00-4.07 (m, 2H), 4.00 (d, $J = 13.8$ Hz, 1H), 3.00 (ddd, $J = 3.5, 6.1, 10.1$ Hz, 1H), 2.01 (ddd, $J = 4.5, 10.6, 14.3$ Hz, 1H), 1.72 (m, 1H), 1.61 (m, 1H), 1.53 (ddd, $J = 3.5, 9.5, 13.3$ Hz, 1H), 1.33 (ddd, $J = 4.0, 9.2, 14.3$ Hz, 1H), 1.25 (ddd, $J = 4.9, 10.5, 14.5$ Hz, 1H), 1.00 (d, $J = 6.5$ Hz, 3H), 0.88-0.91 (m, 9H), 0.16 (s, 3H), 0.13 (s, 3H); HRMS (ES+) Calcd for $[\text{C}_{41}\text{H}_{54}\text{O}_5\text{NSiS}]^+$ 700.3492. Found 700.3471.

(2*R*, 3*R*, 6*R*, 7*R*): ^1H NMR (500 MHz, C_6D_6) δ 7.57 (d, $J = 7.3$ Hz, 2H), 7.52 (dd, $J = 7.4, 11.4$ Hz, 2H), 7.15-7.24 (m, 1H), 7.06 (dd, $J = 7.5, 7.5$ Hz, 2H), 6.98 (dd, $J = 7.3, 7.3$ Hz, 1H), 5.80 (ddd, $J = 5.7, 10.5, 16.6$ Hz, 1H), 5.74 (ddd, $J = 7.3, 10.2, 17.4$ Hz, 1H), 5.25 (d, $J = 17.1$ Hz, 1H), 5.14 (d, $J = 17.1$ Hz, 1H), 5.04 (d, $J = 10.5$ Hz, 1H), 5.01 (d, $J = 10.1$ Hz, 1H), 4.91 (d, $J = 9.7$ Hz, 1H), 4.60 (dd, $J = 7.9, 7.9$ Hz, 1H), 4.52 (dd, $J = 6.4, 10.8$ Hz, 1H), 4.43 (dd, $J = 6.7, 10.8$ Hz, 1H), 4.19 (m, 1H), 4.14 (d, $J = 13.7$ Hz, 1H), 4.07 (d, $J = 13.8$ Hz, 1H), 4.03-4.10 (m, 2H), 2.98 (ddd, $J = 3.3, 8.4, 10.8$ Hz, 1H), 1.81 (ddd, $J = 4.1, 11.2, 13.6$ Hz, 1H), 1.65-1.71 (m, 2H), 1.35 (dd, $J = 7.2, 7.2$ Hz, 2H), 1.22 (ddd, $J = 3.4, 9.9, 13.4$ Hz, 1H), 1.04 (d, $J = 6.5$ Hz, 3H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.86 (d, $J = 6.5$ Hz, 3H), 0.81 (d, $J = 6.6$ Hz, 3H), 0.16 (s, 3H), 0.15 (s, 3H); HRMS (ES+) Calcd for $[\text{C}_{41}\text{H}_{54}\text{O}_5\text{NSiS}]^+$ 700.3492. Found 700.3478.

(2*S*, 3*S*, 6*R*, 7*R*): ^1H NMR (500 MHz, C_6D_6) δ 7.56 (d, $J = 7.3$ Hz, 2H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 7.4$ Hz, 1H), 7.14-7.23 (m, 6H), 7.04 (dd, $J = 7.5, 7.5$ Hz, 2H), 6.96 (dd, $J = 7.3, 7.3$ Hz, 1H), 5.81 (ddd, $J = 5.6, 10.4, 16.5$ Hz, 1H), 5.76 (ddd, $J = 7.4, 10.2, 17.4$ Hz, 1H), 5.26 (d, $J = 17.2$ Hz, 1H), 5.14 (d, $J = 17.1$ Hz, 1H), 5.06 (d, $J = 10.5$ Hz, 1H), 5.03 (d, $J = 10.0$ Hz, 1H), 4.98 (d, $J = 9.8$ Hz, 1H), 4.58 (dd, $J = 7.9, 7.9$ Hz, 1H), 4.48 (dd, $J = 6.6, 11.0$ Hz, 1H), 4.44 (dd, $J = 7.1, 11.5$ Hz, 1H), 4.21 (m, 1H), 4.15 (d, $J = 13.8$ Hz, 1H), 4.11 (d, $J = 13.8$ Hz, 1H), 4.03-4.09 (m, 2H), 2.98 (ddd, $J = 3.3, 8.5, 11.4$ Hz, 1H), 1.79 (ddd, $J = 4.1, 11.2, 13.6$ Hz, 1H), 1.66-1.71 (m, 2H), 1.32-1.40 (m, 2H), 1.21 (ddd, $J = 3.5, 9.8, 13.4$ Hz, 1H), 1.03 (d, $J = 6.5$ Hz, 3H), 0.93 (d, $J =$

6.6 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H), 0.19 (s, 3H), 0.12 (s, 3H); HRMS (ES+) Calcd for $[C_{41}H_{54}O_5NSiS]^+$ 700.3492. Found 700.3522.

(2*S*, 3*R*, 6*R*, 7*S*): 1H NMR (400 MHz, C_6D_6) δ 7.58 (d, J = 6.8 Hz, 2H), 7.53 (d, J = 6.8 Hz, 2H), 7.16-7.25 (m, 6H), 7.04 (dd, J = 7.6 Hz, 2H), 6.98 (dd, J = 7.3, 14.6 Hz, 1H), 5.91 (ddd, J = 6.8, 10.3, 17.1 Hz, 1H), 5.66 (ddd, J = 5.1, 10.5, 16.8 Hz, 1H), 5.25 (d, J = 17.6 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 5.00 (d, J = 10.7 Hz, 1H), 4.99 (d, J = 10.3 Hz, 1H), 4.92 (d, J = 9.8 Hz, 1H), 4.52-4.56 (m, 3H), 4.40 (m, 1H), 4.13 (dd, J = 6.3 Hz, 1H), 4.07 (d, J = 13.7 Hz, 1H), 4.05 (m, 1H), 3.99 (d, J = 13.7 Hz, 1H), 3.01 (ddd, J = 3.4, 5.9, 10.0 Hz, 1H), 2.03 (ddd, J = 4.6, 10.7, 13.9 Hz, 1H), 1.71 (m, 1H), 1.65 (m, 1H), 1.52 (ddd, J = 3.4, 9.5, 13.2 Hz, 1H), 1.37 (ddd, J = 3.9, 11.7, 14.6 Hz, 1H), 1.29 (ddd, J = 3.2, 10.3, 13.7 Hz, 1H), 0.97 (d, J = 6.3 Hz, 3H), 0.90 (d, J = 6.3 Hz, 6H), 0.88 (d, J = 6.8 Hz, 3H), 0.15 (s, 3H), 0.11 (s, 3H); HRMS (ES+) Calcd for $[C_{41}H_{54}O_5NSiS]^+$ 700.3492. Found 700.3477.

(2*R*, 3*S*, 6*R*, 7*S*): 1H NMR (500 MHz, C_6D_6) δ 7.58 (d, J = 7.2 Hz, 2H), 7.52 (dd, J = 5.9, 5.9 Hz, 2H), 7.16-7.25 (m, 6H), 7.04 (dd, J = 7.5, 7.5 Hz, 2H), 6.97 (dd, J = 7.3, 7.3 Hz, 1H), 5.98 (ddd, J = 7.0, 10.2, 17.2 Hz, 1H), 5.66 (ddd, J = 5.2, 10.5, 16.4 Hz, 1H), 5.26 (d, J = 17.1 Hz, 1H), 5.20 (d, J = 16.9 Hz, 1H), 5.02 (d, J = 10.3 Hz, 2H), 4.68 (d, J = 9.7 Hz, 1H), 4.50-4.55 (m, 3H), 4.39 (m, 1H), 4.11 (dd, J = 6.4, 6.4 Hz, 1H), 4.06 (m, 1H), 4.06 (d, J = 13.8 Hz, 1H), 3.99 (d, J = 13.8 Hz, 1H), 3.02 (ddd, J = 3.5, 6.1, 10.1 Hz, 1H), 1.97 (ddd, J = 4.6, 10.6, 13.7 Hz, 1H), 1.70 (m, 1H), 1.60 (m, 1H), 1.49 (ddd, J = 3.6, 9.5, 13.4 Hz, 1H), 1.26 (dd, J = 7.1, 7.1 Hz, 1H), 0.95 (d, J = 6.6 Hz, 3H), 0.86-0.89 (m, 9H), 0.16 (s, 3H), 0.13 (s, 3H); HRMS (ES+) Calcd for $[C_{41}H_{54}O_5NSiS]^+$ 700.3492. Found 700.3523.

(2*R*, 3*R*, 6*R*, 7*S*): 1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.61 (dd, J = 7.7, 7.7 Hz, 2H), 7.39 (dd, J = 7.5, 7.5 Hz, 2H), 7.19-7.31 (m, 7H), 5.79 (ddd, J = 4.9, 10.5, 16.8 Hz, 1H), 5.70 (ddd, J = 7.6, 10.2, 17.5, 1H), 5.26 (d, J = 17.4 Hz, 1H), 5.25 (d, J = 9.4 Hz, 1H), 5.16 (d, J = 10.9 Hz, 1H), 5.15 (d, J = 16.6 Hz, 1H), 5.13 (d, J = 10.7 Hz, 1H), 4.45 (dd, J = 7.2, 10.6 Hz, 1H), 4.31-4.36 (m, 3H), 4.23 (dd, J = 6.9, 6.9 Hz, 1H), 4.16 (d, J = 13.8 Hz, 1H), 4.10 (d, J = 13.8 Hz, 1H), 3.77 (m, 1H), 2.80 (ddd, J = 3.4, 8.5, 11.4 Hz, 1H), 1.48-1.67 (m, 3H), 1.38 (ddd, J = 3.8, 11.4, 14.6 Hz, 1H), 1.23 (ddd, J = 2.7, 10.1, 13.4 Hz, 1H), 1.11 (ddd, J = 3.3, 9.8, 13.3 Hz, 1H), 0.91 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.5 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H), 0.81 (d, J = 6.7 Hz, 3H), 0.03 (s, 3H), 0.02 (s, 3H); HRMS (ES+) Calcd for $[C_{41}H_{54}O_5NSiS]^+$ 700.3492. Found 700.3515.

(2*S*, 3*S*, 6*R*, 7*S*): 1H NMR (500 MHz, C_6D_6) δ 7.57 (dd, J = 6.4, 6.4 Hz, 4H), 7.16-7.24 (m, 6H), 7.07 (dd, J = 7.6, 7.6 Hz, 2H), 6.98 (dd, J = 7.3, 7.3 Hz, 1H), 5.74 (ddd, J = 7.3, 10.1, 17.3 Hz, 1H),

5.68 (ddd, J = 5.2, 10.6, 17.0 Hz, 1H), 5.37 (d, J = 9.7 Hz, 1H), 5.27 (d, J = 17.1 Hz, 1H), 5.14 (d, J = 17.0 Hz, 1H), 5.03 (d, J = 10.7 Hz, 1H), 5.00 (d, J = 11.0 Hz, 1H), 4.59-4.64 (m, 2H) 4.48 (m, 1H), 4.43 (dd, J = 6.7, 10.8 Hz, 1H), 4.18 (d, J = 6.7 Hz, 1H), 4.12 (d, J = 13.7 Hz, 1H), 4.08 (d, J = 13.8 Hz, 1H), 4.08 (m, 1H), 2.99 (ddd, J = 3.4, 8.4, 11.4 Hz, 1H), 1.82 (ddd, J = 4.1, 11.3, 13.6 Hz, 1H), 1.75 (m, 1H), 1.66 (m, 1H), 1.49 (ddd, J = 3.8, 11.6, 14.6 Hz, 1H), 1.32 (ddd, J = 2.8, 10.3, 13.6 Hz, 1H), 1.20 (ddd, J = 3.4, 10.0, 13.5 Hz, 1H), 1.00 (d, J = 6.5 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H), 0.83 (d, J = 6.5 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H), 0.20 (s, 3H), 0.12 (s, 3H); HRMS (ES+) Calcd for [C₄₁H₅₄O₅NSiS]⁺ 700.3492. Found 700.3518.

*7-(9H-Fluoren-9-ylmethoxycarbonylamino)-3,6-dihydroxy-2-isobutyl-9-methyl-dec-4-enethioic acid S-benzyl ester (11)*¹⁴: To a stirred solution of compound **9** (190 mg, 0.27 mmoles) in toluene (9 mL) was added Cl₂(IMes)(PCy₃)Ru=CHPh (23 mg, 0.027 mmoles) dissolved in toluene (9 mL) at room temperature. The reaction was heated to 70 °C for 2 hours then cooled to room temperature. The solvent was removed under vacuum and the residue was partially purified by flash chromatography (5% EtOAc/hexanes to 10% EtOAc/hexanes) to remove polar contaminants. The non-polar fractions were concentrated under vacuum and dissolved in THF (2.6 mL) at 0°C. To this solution was added HF/pyridine (0.097 mL, 3.4 mmoles) and the solution was stirred for 30 minutes at room temperature. The reaction was quenched by addition of aqueous Na₂CO₃ (1.0 M, 10 mL) at 0 °C, extracted with EtOAc (10 mL x 3), dried (MgSO₄), filtered, and concentrated under vacuum. The residue was purified by flash chromatography (25% EtOAc/hexanes) to give 94 mg (56%) of compound **11**.

(2*S*, 3*R*, 6*S*, 7*R*): ¹H NMR (500 MHz, CD₃CN) δ 7.88, (d, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.71 (t, J = 5.3 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.38 (ddd, J = 1.0, 4.4, 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.26-7.34 (m, 5H, Ar_{Bn}-H), 5.62 (dd, J = 9.3, 11.2 Hz, 1H, C₄-H), 5.57 (d, J = 10.2 Hz, 1H, N-H), 5.55 (dd, J = 8.3, 11.3 Hz, 1H, C₅-H), 4.61 (ddd, J = 5.4, 5.4, 10.2 Hz, 1H, C₃-H), 4.43 (dd, J = 7.3, 10.7 Hz, 1H, C₁'-H), 4.39 (ddd, J = 4.9, 4.9, 8.8 Hz, 1H, C₆-H), 4.33 (dd, J = 7.3, 10.7 Hz, 1H, C₁'-H'), 4.28 (t, J = 6.9 Hz, 1H, C₂'-H), 4.18 (d, J = 13.7 Hz, 1H, C₁'-H), 4.08 (d, J = 14.1 Hz, 1H, C₁'-H'), 3.67 (m, 1H, C₇-H), 3.28 (d, J = 4.4 Hz, 1H, C₃-OH), 3.24 (d, J = 4.9 Hz, 1H, C₆-OH), 2.89 (ddd, J = 2.9, 5.9, 9.3 Hz, 1H, C₂-H), 1.71 (ddd, J = 3.4, 11.2, 14.7 Hz, 1H, C₁₁-H), 1.64 (m, 1H, C₁₂-H), 1.54 (m, 1H, C₉-H), 1.47 (ddd, J = 3.5, 9.8, 13.2 Hz, 1H, C₁₁-H'), 1.40 (m, 1H, C₈-H), 1.31 (m, 1H, C₈-H'), 0.91 (d, J = 5.9 Hz, 3H, C₁₃-H), 0.89-0.90 (m, 9H, C₁₄-H, C₁₀-H, C₁₅-H); ¹³C NMR (125 MHz, CDCl₃) δ 201.9, 156.9, 143.9, 143.8, 141.4, 137.1, 132.9, 131.6, 128.8, 128.6, 127.7, 127.2, 127.0, 125.0, 112.0, 71.3, 69.1, 66.6, 57.7, 54.1, 47.4, 39.1, 37.7, 33.4, 26.0, 24.7, 23.6, 21.7, 21.6; IR (film) 3400 (s, br), 3064 (w), 3029 (w), 2955 (s), 2869 (m, sh), 1683 (s), 1517 (m), 1450 (m), 1367 (w), 1245 (m), 1119 (w, sh), 1031

(m), 889 (w), 758 (m, sh), 740 (s), 102 (m, sh) cm^{-1} ; $[\alpha]_{\text{D}} +23.5$ (0.02 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{37}\text{H}_{46}\text{O}_5\text{NS}]^+$ 616.3096. Found 616.3125.

(2*R*, 3*S*, 6*S*, 7*R*): ^1H NMR (500 MHz, CD_3CN) δ 7.89 (d, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.72 (dd, $J = 4.9, 6.9$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.47 (t, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.39 (t, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.28-7.35 (m, 5H, $\text{Ar}_{\text{Bn}}\text{-H}$), 5.66 (d, $J = 9.3$ Hz, 1H, N-H), 5.54 (dd, $J = 8.8, 11.2$ Hz, 1H, $\text{C}_4\text{-H}$), 5.50 (dd, $J = 7.3, 13.6$ Hz, 1H, $\text{C}_5\text{-H}$), 4.52 (dd, $J = 7.3, 13.6$ Hz, 1H, $\text{C}_3\text{-H}$), 4.33-4.42 (m, 3H, $\text{C}_2\text{-H}$, $\text{C}_{1'}\text{-H}$, $\text{C}_{1'}\text{-H}'$), 4.28 (t, $J = 6.8$ Hz, 1H, $\text{C}_2\text{-H}$), 4.15 (s, 2H, $\text{C}_{1''}\text{-H}$, $\text{C}_{1''}\text{-H}'$), 3.65 (m, 1H, $\text{C}_7\text{-H}$), 3.17 (d, $J = 5.4$ Hz, 1H, $\text{C}_3\text{-OH}$), 3.04 (d, $J = 4.9$ Hz, 1H, $\text{C}_6\text{-OH}$), 2.87 (ddd, $J = 2.9, 6.8, 10.3$ Hz, 1H, $\text{C}_2\text{-H}$), 1.71 (m, 1H, $\text{C}_{11}\text{-H}$), 1.65 (m, 1H, $\text{C}_{12}\text{-H}$), 1.50-1.60 (m, 2H, $\text{C}_9\text{-H}$, $\text{C}_{11}\text{-H}'$), 1.43 (ddd, $J = 3.9, 11.2, 14.6$ Hz, 1H, $\text{C}_8\text{-H}$), 1.35 (ddd, $J = 2.9, 10.3, 13.6$ Hz, 1H, $\text{C}_8\text{-H}'$), 0.97 (d, $J = 6.3$ Hz, 3H, $\text{C}_{13}\text{-H}$), 0.89-0.94 (m, 9H, $\text{C}_{14}\text{-H}$, $\text{C}_{10}\text{-H}$, $\text{C}_{15}\text{-H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 202.4, 156.8, 143.9, 141.3, 137.1, 132.4, 132.1, 128.8, 128.6, 127.7, 127.3, 127.0, 125.0, 125.0, 120.0, 71.2, 69.1, 66.5, 58.2, 54.1, 47.4, 38.6, 38.1, 33.3, 25.9, 24.7, 23.6, 21.7, 21.6; IR (film) 3465 (m, br), 3063 (w), 3029 (w), 2956 (s), 2929 (s, sh), 2869 (m, sh), 1681 (s), 1602 (w), 1495 (w), 1453 (w), 1238 (w), 1028 (m), 990 (m, sh), 928 (m), 888 (m), 701 (s) cm^{-1} ; $[\alpha]_{\text{D}} +44.9$ (0.04 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{37}\text{H}_{46}\text{O}_5\text{NS}]^+$ 616.3096. Found 616.3070.

(2*R*, 3*R*, 6*S*, 7*R*): ^1H NMR (500 MHz, CD_3CN) δ 7.89 (d, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.72 (t, $J = 7.8$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.47 (t, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.39 (t, $J = 7.8$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.28-7.35 (m, 5H, $\text{Ar}_{\text{Bn}}\text{-H}$), 5.65 (d, $J = 9.3$ Hz, 1H, N-H), 5.85 (dd, $J = 8.8, 11.2$ Hz, 1H, $\text{C}_5\text{-H}$), 5.45 (t, $J = 10.3$ Hz, 1H, $\text{C}_4\text{-H}$), 4.58 (ddd, $J = 5.3, 5.3, 9.3$ Hz, 1H, $\text{C}_3\text{-H}$), 4.40-4.46 (m, 2H, $\text{C}_2\text{-H}$, $\text{C}_{1'}\text{-H}$), 4.33 (dd, $J = 6.8, 10.7$ Hz, 1H, $\text{C}_{1'}\text{-H}'$), 4.27 (t, $J = 6.9$ Hz, 1H, $\text{C}_2\text{-H}$), 4.21 (d, $J = 14.1$ Hz, 1H, $\text{C}_{1''}\text{-H}$), 4.16 (d, $J = 14.2$ Hz, 1H, $\text{C}_{1''}\text{-H}'$), 3.65 (m, 1H, $\text{C}_7\text{-H}$), 3.24 (d, $J = 2.0$ Hz, 1H, $\text{C}_3\text{-OH}$), 3.24 (d, $J = 2.0$ Hz, 1H, $\text{C}_6\text{-OH}$), 2.79 (ddd, $J = 3.4, 8.8, 11.7$ Hz, 1H, $\text{C}_2\text{-H}$), 1.61-1.70 (m, 2H, $\text{C}_{11}\text{-H}$, $\text{C}_9\text{-H}$), 1.44-1.55 (m, 2H, $\text{C}_8\text{-H}$, $\text{C}_{12}\text{-H}$), 1.30 (ddd, $J = 2.9, 10.2, 13.7$ Hz, 1H, $\text{C}_8\text{-H}'$), 1.15 (ddd, $J = 3.9, 10.3, 13.3$ Hz, 1H, $\text{C}_{11}\text{-H}'$), 0.96 (d, $J = 6.9$ Hz, 3H, $\text{C}_{10}\text{-H}$), 0.90 (d, $J = 6.4$ Hz, 3H, $\text{C}_{13}\text{-H}$), 0.88 (d, $J = 6.3$ Hz, 3H, $\text{C}_{15}\text{-H}$), 0.85 (d, $J = 6.4$ Hz, 3H, $\text{C}_{14}\text{-H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 202.2, 156.9, 143.9, 141.4, 141.3, 137.1, 133.8, 131.8, 128.8, 128.6, 127.7, 127.2, 127.0, 125.0, 120.0, 71.0, 69.3, 66.6, 57.5, 54.1, 47.4, 38.9, 33.4, 25.7, 24.7, 23.6, 23.4, 21.8, 21.6; IR (film) 3401 (m, br), 3064 (w), 3029 (w), 2956 (s), 2869 (m, sh), 1686 (s), 1517 (m), 1467 (w, sh), 1451 (m), 1368 (w), 1245 (m), 1032 (m), 888 (w), 759 (m, sh), 740 (s), 702 (w) cm^{-1} ; $[\alpha]_{\text{D}} +13.7$ (0.04 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{37}\text{H}_{46}\text{O}_5\text{NS}]^+$ 616.3096. Found 616.3092.

(2*S*, 3*S*, 6*S*, 7*R*): ^1H NMR (500 MHz, CD_3CN) δ 7.89 (d, $J = 6.8$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.71 (dd, $J = 4.4, 6.8$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.47 (t, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.39 (t, $J = 6.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$),

7.27-7.35 (m, 5H, Ar_{Bn}-H), 5.68 (d, J = 9.2 Hz, 1H, N-H), 5.55 (dd, J = 8.8, 11.2 Hz, 1H, C₅-H), 5.45 (t, J = 9.8 Hz, 1H, C₄-H), 4.56 (ddd, J = 5.8, 8.8 Hz, 1H, C₃-H), 4.33-4.41 (m, 3H, C₆-H, C₁-H, C₁'-H'), 4.27 (t, J = 7.3 Hz, 1H, C₂'-H), 4.21 (d, J = 13.6 Hz, 1H, C₁'-H), 4.16 (d, J = 13.5 Hz, 1H, C₁'-H'), 3.63 (m, 1H, C₇-H), 3.24 (d, J = 5.4 Hz, 1H, C₃-OH), 3.21 (d, J = 5.8 Hz, 1H, C₆-OH), 2.79 (ddd, J = 3.4, 8.8, 11.8 Hz, 1H, C₂-H), 1.59-1.68 (m, 2H, C₈-H, C₉-H), 1.50-1.57 (m, 1H, C₁₂-H), 1.44 (ddd, J = 3.9, 11.2, 14.7 Hz, 1H, C₁₁-H), 1.36 (ddd, J = 2.9, 9.7, 13.7 Hz, 1H, C₈-H'), 1.23 (ddd, J = 3.4, 9.8, 13.6 Hz, 1H, C₁₁-H'), 0.96 (d, J = 6.9 Hz, 3H, C₁₀-H), 0.87-0.93 (m, 9H, C₁₃-H, C₁₅-H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.3, 156.9, 143.9, 141.3, 137.1, 133.0, 132.3, 128.8, 128.6, 127.7, 127.3, 127.1, 125.0, 125.0, 120.0, 71.6, 69.4, 66.5, 57.8, 54.3, 47.4, 38.8, 33.4, 25.7, 24.7, 23.6, 23.3, 21.9, 21.6; IR (film) 3392 (m, br), 3064 (w), 3029 (w), 2956 (s), 2869 (w, sh), 1688 (s), 1529 (m), 1451 (m), 1368 (w), 1246 (m), 1120 (w, sh), 1031 (m), 888 (w), 759 (w), 740 (s), 702 (w) cm⁻¹; [α]_D +28.2 (0.02 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3126.

(2*S*, 3*R*, 6*S*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.88 (d, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.72 (t, J = 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.39 (ddd, J = 2.4, 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.26-7.33 (m, 5H, Ar_{Bn}-H), 5.47 (m, 3H, C₃-H, C₄-H, N-H), 4.52-4.56 (m, 1H, C₃-H), 4.39 (dd, J = 6.4, 10.3 Hz, 1H, C₁-H), 4.37 (dd, J = 6.4, 10.3 Hz, 1H, C₁'-H'), 4.30-4.32 (m, 1H, C₆-H), 4.27 (t, J = 7.3 Hz, 2H, C₂-H), 4.21 (d, J = 13.7 Hz, 1H, C₁'-H), 4.15 (d, J = 14.1 Hz, 1H, C₁'-H'), 3.62 (m, 1H, C₇-H), 3.24 (d, J = 4.9 Hz, 1H, C₃-OH), 3.18 (d, J = 4.4 Hz, 1H, C₆-OH), 2.84 (ddd, J = 3.0, 6.9, 10.3 Hz, 1H, C₂-H), 1.70-1.75 (m, 1H, C₁₁-H), 1.61-1.69 (m, 1H, C₉-H), 1.48-1.59 (m, 3H, C₁₁-H', C₈-H, C₁₂-H), 1.28 (ddd, J = 3.9, 9.8, 13.8 Hz, 1H, C₈-H'), 0.97 (d, J = 6.8 Hz, 3H, C₁₃-H), 0.95 (d, J = 6.8 Hz, 3H, C₁₄-H), 0.91 (d, J = 5.9 Hz, 3H, C₁₀-H), 0.90 (d, J = 5.9 Hz, 3H, C₁₅-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.5, 157.1, 144.2, 144.1, 141.6, 137.2, 133.4, 132.5, 129.1, 128.9, 127.9, 127.6, 127.3, 125.3, 120.2, 70.2, 69.5, 66.8, 57.7, 53.7, 47.6, 41.5, 33.7, 26.2, 25.0, 23.9, 23.6, 22.3, 22.0; IR (film) 3400 (m, br), 3065 (w), 2956 (m), 2869 (w, sh), 1717 (m, sh), 1683 (s), 1521 (m), 1451 (m), 1329 (w), 1245 (m), 1117 (w), 1032 (m), 890 (w), 759 (m, sh), 740 (s), 701 (w) cm⁻¹; [α]_D -16.0 (0.01 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3107.

(2*R*, 3*S*, 6*S*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.90 (d, J = 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.72 (t, J = 5.4 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.38 (t, J = 7.4 Hz, 2H, Ar_{Fmoc}-H), 7.26-7.35 (m, 5H, Ar_{Bn}-H), 5.57 (d, J = 9.8 Hz, 1H, N-H), 5.51 (dd, J = 8.8, 11.8 Hz, 1H, C₄-H), 5.46 (dd, J = 7.3, 11.7 Hz, 1H, C₅-H), 4.45 (ddd, J = 3.9, 8.3, 8.3 Hz, 1H, C₃-H), 4.40 (s, 1H, C₁-H), 4.38 (s, 1H, C₁'-H'), 4.36 (ddd, J = 4.3, 4.3, 7.8 Hz, 1H, C₆-H), 4.27 (t, J = 7.4 Hz, 1H, C₂-H), 4.16 (d, J = 14.2 Hz, 1H, C₁'-H), 4.13 (d, J = 13.6 Hz, 1H, C₁'-H'), 3.71 (m, 1H, C₇-H), 3.49 (d, J = 3.9

Hz, 1H, C₃-OH), 3.00 (d, J = 4.9 Hz, 1H, C₆-OH), 2.88 (ddd, J = 3.9, 7.3, 10.8 Hz, 1H, C₂-H), 1.66-1.71 (m, 1H, C₁₁-H), 1.61-1.65 (m, 1H, C₁₂-H), 1.53-1.58 (m, 2H, C₁₁-H', C₉-H), 1.47 (ddd, J = 4.9, 10.7, 14.2 Hz, 1H, C₈-H), 1.34 (ddd, J = 4.4, 9.2, 13.6 Hz, 1H, C₈-H'), 0.96 (d, J = 6.3 Hz, 3H, C₁₃-H), 0.90-0.94 (m, 9H, C₁₄-H, C₁₀-H, C₁₅-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.2, 156.9, 143.9, 143.9, 141.3, 137.2, 133.4, 131.6, 128.8, 128.6, 127.6, 127.2, 127.0, 125.0, 119.9, 69.6, 66.6, 58.2, 53.8, 47.4, 41.0, 38.2, 33.3, 26.0, 24.7, 23.7, 23.2, 22.1, 21.7; IR (film) 3396 (m, br), 3064 (w), 3029 (w), 2956 (s), 2869 (w, sh), 1684 (s), 1521 (m), 1451 (m), 1368 (w), 1250 (m), 1120 (w, sh), 1032 (m), 890 (w), 758 (m, sh), 740 (s), 702 (w) cm⁻¹; [α]_D +10.9 (0.06 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3067.

(2*R*, 3*R*, 6*S*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.89 (d, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.17 (t, J = 6.8 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.38 (dd, J = 3.4, 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.26-7.34 (m, 5H, Ar_{Bn}-H), 5.53 (dd, J = 9.3, 11.2 Hz, 1H, C₅-H), 5.49 (d, J = 9.8 Hz, 1H, N-H), 5.44 (t, J = 9.8 Hz, 1H, C₄-H), 4.55 (ddd, J = 4.9, 4.9, 8.8 Hz, 1H, C₃-H), 4.40 (s, 1H, C₁-H), 4.38 (s, 1H, C₁-H'), 4.35 (ddd, J = 4.4, 4.4, 8.3 Hz, 1H, C₆-H), 4.27 (t, J = 6.9 Hz, 1H, C₂-H), 4.21 (d, J = 13.7 Hz, 1H, C₁-H), 4.16 (d, J = 13.7 Hz, 1H, C₁-H'), 3.63 (m, 1H, C₇-H), 3.21 (d, J = 4.9 Hz, 1H, C₃-OH), 3.20 (d, J = 3.9 Hz, 1H, C₆-OH), 2.79 (ddd, J = 3.4, 8.8, 12.2 Hz, 1H, C₂-H), 1.50-1.67 (m, 3H, C₉-H, C₁₁-H, C₁₂-H), 1.47 (ddd, J = 4.4, 10.8, 15.1 Hz, 1H, C₈-H), 1.30 (ddd, J = 3.9, 9.7, 13.7 Hz, 1H, C₈-H'), 1.21 (ddd, J = 3.4, 9.7, 13.2 Hz, 1H, C₁₁-H'), 0.95 (d, J = 3, 3H, C₁₃-H), 0.90-0.93 (m, 6H, C₁₀-H, C₁₄-H), 0.86 (d, J = 6.3 Hz, 3H, C₁₅-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.3, 156.8, 143.9, 141.3, 137.1, 133.4, 133.3, 128.8, 128.6, 127.6, 127.3, 127.0, 125.0, 119.9, 69.6, 69.5, 66.5, 57.4, 53.5, 47.4, 41.3, 39.0, 33.4, 25.7, 24.7, 23.4, 22.0, 21.8; IR (film) 3401 (m, br), 3064 (w), 2956 (s), 2869 (w, sh), 1685 (s), 1517 (m), 1451 (m), 1368 (w), 1244 (m), 1117 (w), 1044 (s), 890 (w), 759 (w, sh), 740 (m), 701 (w) cm⁻¹; [α]_D -14.2 (0.04 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3069.

(2*S*, 3*S*, 6*S*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.88 (d, J = 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.72 (dd, J = 4.4, 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.39 (ddd, J = 2.9, 2.9, 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.27-7.34 (m, 5H, Ar_{Bn}-H), 5.60 (d, J = 9.8 Hz, 1H, N-H), 5.53 (dd, J = 7.3, 11.2 Hz, 1H, C₅-H), 5.41 (t, J = 10.2 Hz; 1H, C₄-H), 4.49 (ddd, J = 5.9, 5.9, 8.8 Hz, 1H, C₃-H), 4.36-4.39 (m, 3H, C₁-H, C₁-H', C₆-H), 4.27 (t, J = 6.8 Hz, 1H, C₂-H), 4.19 (d, J = 13.6 Hz, 1H, C₁-H), 4.15 (d, J = 14.2 Hz, 1H, C₁-H'), 3.71 (m, 1H, C₇-H), 3.45 (d, J = 4.4 Hz; 1H, C₃-OH), 3.20 (d, J = 4.8 Hz, 1H, C₆-OH), 2.78 (ddd, J = 3.4, 8.8, 11.7 Hz, 1H, C₂-H), 1.58-1.66 (m, 2H, C₁₁-H, C₉-H), 1.51-1.56 (m, 1H, C₁₂-H), 1.47 (ddd, J = 4.4, 10.8, 14.7 Hz, 1H, C₈-H), 1.34 (ddd, J = 3.9, 9.3, 12.7 Hz, 1H, C₈-H'), 1.21 (ddd, J = 3.4, 9.7, 13.6 Hz, 1H, C₁₁-H'), 0.96 (d, J = 6.4 Hz, 3H, C₁₃-H), 0.91-

0.93 (m, 6H, C₁₄-H, C₁₀-H), 0.88 (d, J = 6.9 Hz, 3H, C₁₅-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.1, 157.0, 143.9, 143.8, 141.3, 137.2, 133.9, 132.0, 128.8, 128.6, 127.6, 127.2, 127.0, 125.0, 119.9, 70.3, 69.8, 66.6, 57.7, 54.1, 47.3, 40.7, 33.4, 25.7, 24.8, 23.4, 23.3, 22.0, 21.8; IR (film) 3389 (m, br), 3064 (w), 3029 (w), 2956 (s), 2929 (m, sh), 2869 (m, sh), 1688 (s), 1524 (m), 1497 (w, sh), 1467 (m), 1368 (w), 1251 (m), 1120 (w), 1046 (m), 888 (w), 759 (w), 740 (m), 702 (w) cm⁻¹; [α]_D +15.8 (0.04 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3099.

(2*S*, 3*R*, 6*R*, 7*R*): ¹H NMR (500 MHz, CD₃CN) 7.88 (d, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.72 (t, J = 5.8 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.38 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.26-7.37 (m, 5H, Ar_{Bn}-H), 5.59 (d, J = 9.3 Hz, 1H, N-H), 5.51 (t, J = 11.2 Hz, 1H, C₄-H), 5.46 (dd, J = 7.3, 11.2 Hz, 1H, C₅-H), 4.45 (ddd, J = 3.9, 3.9, 7.8 Hz, 1H, C₃-H), 4.40 (s, 1H, C₁-H), 4.38 (s, 1H, C₁-H'), 4.36-4.37 (m, 1H, C₆-H), 4.27 (t, J = 6.5, 1H, C₂-H), 4.16 (d, J = 14.2 Hz, 1H, C₁-H), 4.13 (d, J = 13.7 Hz, 1H, C₁-H'), 3.71 (m, 1H, C₇-H), 5.51 (d, J = 3.9 Hz, 1H, C₃-OH), 3.02 (d, J = 4.4 Hz, 1H, C₆-OH), 2.88 (ddd, J = 2.9, 6.9, 9.8 Hz, 1H, C₂-H), 1.67-1.71 (m, 1H, C₁₁-H), 1.61-1.65 (m, 1H, C₉-H), 1.51-1.60 (m, 2H, C₁₁-H', C₁₂-H), 1.47 (ddd, J = 4.8, 10.7, 14.1 Hz, 1H, C₈-H), 1.34 (ddd, J = 4.4, 9.3, 13.7 Hz, 1H, C₈-H'), 0.96 (d, J = 6.8 Hz, 3H, C₁₀-H), 0.90-0.94 (m, 9H, C₁₅-H, C₁₃-H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.6, 157.2, 144.2, 144.1, 141.6, 137.5, 133.8, 131.8, 129.2, 128.9, 127.9, 127.5, 127.3, 125.3, 120.3, 69.8, 66.8, 58.4, 53.9, 47.6, 41.3, 38.5, 33.6, 26.2, 25.0, 24.0, 23.5, 22.4, 21.9; IR (film) 3398 (m, br), 3064 (w), 2956 (s), 2869 (m, sh), 1685 (s), 1520 (m), 1451 (m), 1368 (w), 1250 (m), 1120 (w), 1032 (m), 974 (w), 890 (w), 758 (w, sh), 740 (m), 702 (w) cm⁻¹; [α]_D -9.4 (0.02 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3109.

(2*R*, 3*S*, 6*R*, 7*R*): ¹H NMR (500 MHz, CD₃CN) 7.89 (d, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.72 (t, J = 7.9 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.38 (ddd, J = 2.4, 6.4, 7.9 Hz, 2H, Ar_{Fmoc}-H), 7.25-7.33 (m, 5H, Ar_{Bn}-H), 5.47-5.56 (m, 3H, C₅-H, C₄-H, N-H), 4.51-4.56 (m, 1H, C₃-H), 4.41 (dd, J = 7.3, 10.8 Hz, 1H, C₁-H), 4.37 (dd, J = 6.8, 10.7 Hz, 1H, C₁-H'), 4.31 (ddd, J = 3.9, 3.9, 7.8 Hz, 1H, C₆-H), 4.27 (t, J = 7.3 Hz, 1H, C₂-H), 4.22 (d, J = 13.7 Hz, 1H, C₁-H), 4.15 (d, J = 13.6 Hz, 1H, C₁-H'), 3.62 (m, 1H, C₇-H), 3.22 (d, J = 4.9 Hz, 1H, C₃-OH), 3.16 (d, J = 4.9 Hz, 1H, C₆-OH), 2.84 (ddd, J = 3.4, 6.9, 10.7 Hz, 1H, C₂-H), 1.73 (ddd, J = 3.4, 12.7, 12.7 Hz, 1H, C₁₁-H), 1.60-1.69 (m, 1H, C₉-H), 1.47-1.59 (m, 3H, C₁₁-H', C₈-H, C₁₂-H), 1.30 (ddd, J = 4.4, 9.8, 13.7 Hz, 1H, C₈-H'), 0.97 (d, J = 6.8 Hz, 3H, C₁₀-H), 0.95 (d, J = 6.3 Hz, 3H, C₁₅-H), 0.92 (d, J = 6.4 Hz, 3H, C₁₃-H), 0.89 (d, J = 6.4 Hz, 3H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.2, 157.2, 144.2, 144.1, 141.6, 137.2, 133.0, 132.7, 129.1, 128.9, 127.9, 127.6, 127.3, 125.4, 120.2, 70.0, 69.2, 66.8, 57.9, 53.8, 47.6, 41.3, 33.7, 26.2, 25.0, 24.0, 23.7, 22.3, 22.0; IR (film) 3401 (m, br), 3065 (w), 3029 (w), 2956 (s), 2869 (m, sh), 1681 (s), 1517 (m), 1451 (m), 1368 (w), 1245 (m), 1117 (w),

1033 (m), 973 (w), 890 (w), 758 (m, sh), 740 (s), 701 (w) cm^{-1} ; $[\alpha]_{\text{D}} +14.6$ (0.04 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{37}\text{H}_{46}\text{O}_5\text{NS}]^+$ 616.3096. Found 616.3120.

(2*R*, 3*R*, 6*R*, 7*R*): ^1H NMR (500 MHz, CD_3CN) δ 7.88 (d, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.72 (dd, $J = 4.4, 7.8$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.47 (t, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.38 (ddd, $J = 1.0, 3.0, 8.8$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.26-7.34 (m, 5H, $\text{Ar}_{\text{Bn}}\text{-H}$), 5.59 (d, $J = 9.3$ Hz, 1H, N-H), 5.52 (dd, $J = 7.8, 11.2$ Hz, 1H, $\text{C}_5\text{-H}$), 5.41 (t, $J = 10.2$ Hz, 1H, $\text{C}_4\text{-H}$), 4.49 (ddd, $J = 3.9, 8.8, 8.8$ Hz, 1H, $\text{C}_3\text{-H}$), 4.36-4.46 (m, 3H, $\text{C}_1\text{-H}$, $\text{C}_1\text{-H}'$, $\text{C}_6\text{-H}$), 4.27 (t, $J = 6.9$ Hz, 1H, $\text{C}_2\text{-H}$), 4.19 (d, $J = 13.7$ Hz, 1H, $\text{C}_1\text{-H}$), 4.15 (d, $J = 14.2$ Hz, 1H, $\text{C}_1\text{-H}'$), 3.71 (m, 1H, $\text{C}_7\text{-H}$), 3.45 (d, $J = 4.4$ Hz, 1H, $\text{C}_3\text{-OH}$), 3.19 (d, $J = 4.9$ Hz, 1H, $\text{C}_6\text{-OH}$), 2.78 (ddd, $J = 3.4, 8.7, 11.8$ Hz, 1H, $\text{C}_2\text{-H}$), 1.58-1.68 (m, 2H, $\text{C}_{11}\text{-H}$, $\text{C}_9\text{-H}$), 1.51-1.56 (m, 1H, $\text{C}_{12}\text{-H}$), 1.47 (ddd, $J = 4.9, 10.8, 15.1$ Hz, 1H, $\text{C}_8\text{-H}$), 1.34 (ddd, $J = 4.4, 9.8, 13.7$ Hz, 1H, $\text{C}_8\text{-H}'$), 1.20 (ddd, $J = 3.4, 9.7, 13.6$ Hz, 1H, $\text{C}_{11}\text{-H}'$), 0.96 (d, $J = 6.3$ Hz, 3H, $\text{C}_{10}\text{-H}$), 0.90-0.93 (m, 6H, $\text{C}_{15}\text{-H}$, $\text{C}_{13}\text{-H}$), 0.87 (d, $J = 6.9$ Hz, 3H, $\text{C}_{14}\text{-H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 202.4, 157.3, 144.2, 144.0, 141.6, 137.4, 134.3, 132.2, 129.1, 128.9, 127.9, 127.5, 127.3, 125.3, 120.2, 70.6, 70.0, 66.9, 57.9, 54.4, 47.6, 40.9, 33.7, 26.0, 25.0, 23.8, 23.6, 22.3, 22.1; IR (film) 3390 (m, br), 3064 (w), 2956 (s), 2869 (m, sh), 1687 (s), 1523 (m), 1451 (m), 1368 (w), 1250 (m), 1168 (w), 1046 (m), 887 (w), 759 (w, sh), 740 (m), 702 (w) cm^{-1} ; $[\alpha]_{\text{D}} -8.4$ (0.02 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{37}\text{H}_{46}\text{O}_5\text{NS}]^+$ 616.3096. Found 616.3088.

(2*S*, 3*S*, 6*R*, 7*R*): ^1H NMR (500 MHz, CD_3CN) δ 7.88 (d, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.72 (t, $J = 6.9$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.47 (t, $J = 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.38 (dddd, $J = 1.0, 2.9, 7.3, 7.3$ Hz, 2H, $\text{Ar}_{\text{Fmoc}}\text{-H}$), 7.26-7.35 (m, 5H, $\text{Ar}_{\text{Bn}}\text{-H}$), 5.54 (dd, $J = 9.3, 11.2$ Hz, 1H, $\text{C}_5\text{-H}$), 5.49 (d, $J = 9.3$ Hz, 1H, N-H), 5.44 (t, $J = 10.2$ Hz, 1H, $\text{C}_4\text{-H}$), 4.56 (ddd, $J = 4.9, 8.8, 8.8$ Hz, 1H, $\text{C}_3\text{-H}$), 4.40 (s, 1H, $\text{C}_1\text{-H}$), 4.38 (s, 1H, $\text{C}_1\text{-H}'$), 4.36 (ddd, $J = 4.3, 4.3, 8.8$ Hz, 1H, $\text{C}_6\text{-H}$), 4.27 (t, $J = 6.9$ Hz, 1H, $\text{C}_2\text{-H}$), 4.22 (d, $J = 14.2$ Hz, 1H, $\text{C}_1\text{-H}$), 4.15 (d, $J = 14.2$ Hz, 1H, $\text{C}_1\text{-H}'$), 3.63 (m, 1H, $\text{C}_7\text{-H}$), 3.21 (d, $J = 4.9$ Hz, 1H, $\text{C}_3\text{-OH}$), 3.19 (d, $J = 4.4$ Hz, 1H, $\text{C}_6\text{-OH}$), 2.79 (ddd, $J = 3.4, 8.8, 12.2$ Hz, 1H, $\text{C}_2\text{-H}$), 1.54-1.67 (m, 2H, $\text{C}_{11}\text{-H}$, $\text{C}_9\text{-H}$), 1.50-1.53 (m, 1H, $\text{C}_{12}\text{-H}$), 1.47 (ddd, $J = 4.4, 10.7, 15.1$ Hz, 1H, $\text{C}_8\text{-H}$), 1.30 (ddd, $J = 3.9, 9.7, 13.7$ Hz, 1H, $\text{C}_8\text{-H}'$), 1.21 (ddd, $J = 3.4, 9.8, 13.2$ Hz, 1H, $\text{C}_{11}\text{-H}'$), 0.96 (d, $J = 6.8$ Hz, 3H, $\text{C}_{13}\text{-H}$), 0.92 (t, 6H, $\text{C}_{14}\text{-H}$, $\text{C}_{10}\text{-H}$), 0.86 (d, $J = 6.3$ Hz, 3H, $\text{C}_{15}\text{-H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 202.3, 156.8, 144.0, 143.9, 141.3, 137.1, 133.4, 133.2, 128.8, 128.6, 127.6, 127.3, 127.0, 125.0, 119.9, 69.6, 69.4, 66.5, 57.4, 53.5, 47.4, 41.3, 39.0, 33.4, 25.7, 24.7, 23.4, 23.3, 21.8; IR (film) 3398 (m, br), 3064 (w), 3029 (w), 2956 (s), 2929 (m, sh), 2869 (w, s), 1686 (s), 1516 (m), 1451 (m), 1368 (w), 1245 (m), 1117 (w), 1045 (m), 978 (w), 890 (w), 759 (w), 740 (s), 702 (w) cm^{-1} ; $[\alpha]_{\text{D}} +17.1$ (0.05 g/mL, CH_2Cl_2); HRMS (ES+) Calcd for $[\text{C}_{37}\text{H}_{46}\text{O}_5\text{NS}]^+$ 616.3096. Found 616.3082.

(2*S*, 3*R*, 6*R*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.89 (d, J = 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.72 (dd, J = 4.4, 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.37-7.40 (m, 2H, Ar_{Fmoc}-H), 7.27-7.35 (m, 5H, Ar_{Bn}-H), 5.65 (d, J = 8.8 Hz, 1H, N-H), 5.54 (dd, J = 8.8, 11.2 Hz, 1H, C₄-H), 5.50 (dd, J = 8.3, 11.2 Hz, 1H, C₅-H), 4.53 (dd, J = 6.8, 13.6 Hz, 1H, C₃-H), 4.33-4.42 (m, 3H, C₁-H, C₁-H', C₆-H), 4.28 (t, J = 6.8 Hz, 1H, C₂-H), 4.15 (s, 2H, C₁₁-H, C₁₁-H'), 3.65 (m, 1H, C₇-H), 3.26 (d, J = 5.3 Hz, 1H, C₃-OH), 3.04 (d, J = 4.9 Hz, 1H, C₆-OH), 2.87 (ddd, J = 3.4, 7.3, 10.7 Hz, 1H, C₂-H), 1.61-1.73 (m, 2H, C₁₁-H, C₉-H), 1.50-1.60 (m, 2H, C₁₁-H', C₁₂-H), 1.43 (ddd, J = 3.9, 11.2, 14.2 Hz, 1H, C₈-H), 1.37 (ddd, J = 2.9, 10.3, 13.2 Hz, 1H, C₈-H'), 0.97 (d, J = 6.3 Hz, 3H, C₁₀-H), 0.89-0.94 (m, 9H, C₁₅-H, C₁₃-H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.3, 156.8, 143.9, 141.4, 141.3, 137.1, 132.4, 132.1, 128.8, 128.6, 127.7, 127.3, 127.1, 125.0, 120.0, 71.1, 69.1, 66.5, 58.3, 54.1, 47.4, 38.5, 38.2, 33.4, 26.0, 24.7, 23.7, 21.7, 21.6; IR (film) 3399 (m, br), 3064 (w), 3029 (w), 2955 (s), 2869 (w, sh), 1687 (s), 1518 (m), 1451 (m), 1367 (w), 1246 (m), 1120 (w, sh), 1030 (m), 975 (w, sh), 891 (w), 758 (m, sh), 740 (s), 702 (w) cm⁻¹; [α]_D -33.7 (0.03 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3075.

(2*R*, 3*S*, 6*R*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.88 (d, J = 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.71 (t, J = 5.8 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.7 Hz, 2H, Ar_{Fmoc}-H), 7.38 (ddd, J = 0.9, 4.4, 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.25-7.34 (m, 5H, Ar_{Bn}-H), 5.61 (dd, J = 8.8, 11.3 Hz, 1H, C₄-H), 5.57 (d, J = 6.8 Hz, 1H, N-H), 5.55 (dd, J = 8.3, 11.3 Hz, 1H, C₅-H), 4.60 (ddd, J = 5.3, 9.2 Hz, 1H, C₃-H), 4.43 (dd, J = 6.9, 10.3 Hz, 1H, C₁-H), 4.38 (ddd, J = 4.4, 9.2, 12.7 Hz, 1H, C₆-H), 4.33 (dd, J = 6.8, 10.7 Hz, 1H, C₁-H'), 4.27 (t, J = 6.9 Hz, 1H, C₂-H), 4.19 (d, J = 13.4 Hz, 1H, C₁₁-H), 4.09 (d, J = 14.1 Hz, 1H, C₁₁-H'), 3.68 (m, 1H, C₇-H), 3.28 (d, J = 4.9 Hz, 1H, C₃-OH), 3.25 (d, J = 4.9 Hz, 1H, C₆-OH), 2.89 (ddd, J = 3.4, 6.4, 9.8 Hz, 1H, C₂-H), 1.71 (ddd, J = 3.4, 11.2, 15.1 Hz, 1H, C₁₁-H), 1.60-1.68 (m, 1H, C₉-H), 1.51-1.58 (m, 1H, C₁₂-H), 1.47 (ddd, J = 3.5, 9.8, 13.2 Hz, 1H, C₁₁-H'), 1.39-1.42 (m, 1H, C₈-H), 1.28-1.33 (m, 1H, C₈-H'), 0.96 (d, J = 6.8 Hz, 3H, C₁₀-H), 0.89-0.92 (m, 9H, C₁₅-H, C₁₃-H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 201.8, 156.9, 143.9, 143.8, 141.4, 137.1, 132.9, 131.6, 128.8, 128.6, 127.7, 127.2, 127.0, 125.0, 120.0, 71.2, 69.0, 66.6, 57.8, 54.1, 47.4, 39.1, 37.7, 33.4, 25.9, 24.7, 23.6, 21.7, 21.6; IR (film) 3400 (m, br), 3064 (w), 3029 (w), 2956 (s), 2869 (w, sh), 1685 (s), 1517 (m), 1451 (m), 1367 (w), 1245 (m), 1119 (w, sh), 1032 (m), 973 (w, sh), 889 (w), 758 (m, sh), 740 (s), 702 (m) cm⁻¹; [α]_D -21.7 (0.04 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3101.

(2*R*, 3*R*, 6*R*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.89 (d, J = 7.3 Hz, 2H, 2H, Ar_{Fmoc}-H), 7.71 (dd, J = 4.4, 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.39 (dt, J = 1.3, 7.8 Hz, 2H, Ar_{Fmoc}-H), 7.26-7.35 (m, 5H, Ar_{Bn}-H), 5.67 (d, J = 9.3 Hz, 1H, N-H), 5.55 (dd, J = 8.8, 11.3 Hz, 1H, C₅-H), 5.45 (t, J = 9.8 Hz, 1H, C₄-H), 4.56 (ddd, J = 5.9, 8.8, 8.8 Hz, 1H, C₃-H), 4.33-4.43 (m, 3H,

C₁'-H, C₁'-H', C₆-H), 4.27 (t, J = 7.3 Hz, 1H, C₂'-H), 4.20 (d, J = 14.1 Hz, 1H, C₁'-H), 4.17 (d, 13.6 Hz, 1H, C₁'-H'), 3.63 (m, 1H, C₇-H), 3.22 (d, J = 5.3 Hz, 1H, C₆-OH), 3.19 (d, J = 5.8 Hz, 1H, C₃-OH), 2.79 (ddd, J = 3.9, 8.8, 12.2 Hz, 1H, C₂-H), 1.61-1.67 (m, 2H, C₁₁-H, C₉-H), 1.50-1.59 (m, 1H, C₁₂-H), 1.44 (ddd, J = 3.9, 11.2, 14.2 Hz, 1H, C₈-H), 1.36 (ddd, J = 2.9, 10.2, 14.2 Hz, 1H, C₈-H'); 1.23 (ddd, J = 3.9, 10.2, 13.2 Hz, 1H, C₁₁-H'), 0.96 (d, J = 6.3 Hz, 3H, C₁₀-H), 0.87-0.93 (m, 9H, C₁₅-H, C₁₃-H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.3, 156.9, 143.9, 141.4, 137.1, 133.0, 132.2, 128.8, 128.6, 127.7, 127.2, 127.1, 127.0, 125.0, 120.0, 71.6, 69.4, 66.5, 57.8, 54.3, 47.4, 38.8, 33.4, 25.7, 24.7, 23.6, 23.3, 21.9, 21.6; IR (film) 3399 (m, br), 3064 (w), 3029 (w), 2956 (s), 2869 (w, sh), 1688 (s), 1529 (m), 1451 (m), 1368 (w), 1246 (m), 1120 (w, sh), 1031 (m), 888 (w), 759 (m, sh), 740 (s), 702 (w) cm⁻¹; [α]_D -20.5 (0.04 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3069.

(2*S*, 3*S*, 6*R*, 7*S*): ¹H NMR (500 MHz, CD₃CN) δ 7.89 (d, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.72 (t, J = 8.3 Hz, 2H, Ar_{Fmoc}-H), 7.47 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.39 (t, J = 7.3 Hz, 2H, Ar_{Fmoc}-H), 7.28-7.35 (m, 5H, Ar_{Bn}-H), 5.65 (d, J = 9.3 Hz, 1H, N-H), 5.58 (dd, J = 8.8, 11.2 Hz, 1H, C₅-H), 5.45 (t, J = 9.7 Hz, 1H, C₄-H), 4.58 (m, 1H, C₃-H), 4.40-4.46 (m, 2H, C₁'-H, C₆-H), 4.33 (dd, J = 6.8, 10.1 Hz, 1H, C₁'-H'), 4.27 (t, J = 6.8 Hz, 1H, C₂'-H), 4.20 (d, J = 13.7 Hz, 1H, C₁'-H), 4.15 (d, J = 14.1 Hz, 1H, C₁'-H'), 3.65 (m, 1H, C₇-H), 3.23 (t_{app}, 2H, C₆-OH, C₃-OH), 2.79 (ddd, J = 3.4, 8.8, 11.7 Hz, 1H, C₂-H), 1.62-1.70 (m, 2H, C₁₁-H, C₉-H), 1.44-1.55 (m, 2H, C₈-H, C₁₂-H), 1.30 (ddd, J = 2.4, 10.2, 13.7 Hz, 1H, C₈-H'), 1.15 (ddd, J = 3.4, 10.2, 13.2 Hz, 1H, C₁₁-H'), 0.96 (d, J = 6.8 Hz, 3H, C₁₀-H), 0.88-0.91 (m, 9H, C₁₅-H, C₁₃-H, C₁₄-H); ¹³C NMR (125 MHz, CDCl₃) δ 202.2, 156.9, 143.9, 141.4, 141.3, 137.1, 133.8, 131.8, 128.8, 128.6, 127.7, 127.2, 127.0, 125.0, 119.9, 71.0, 69.3, 66.6, 57.5, 54.1, 47.4, 38.9, 33.4, 25.7, 24.7, 23.6, 23.4, 21.8, 21.6; IR (film) 3409 (m, br), 3064 (w), 3029 (w), 2956 (s), 2869 (m, sh), 1688 (s), 1513 (w), 1452 (s), 1367 (s), 1246 (m), 1151 (w), 1032 (s), 888 (w), 759 (m, sh), 740 (s), 702 (m) cm⁻¹; [α]_D -12.4 (0.06 g/mL, CH₂Cl₂); HRMS (ES+) Calcd for [C₃₇H₄₆O₅NS]⁺ 616.3096. Found 616.3087.

Synthesis of chimerae 12^{15,16}: To a stirred solution of compound **11** (15 mg, 0.025 mmoles) in THF (0.5 mL) was added diisopropylethylamine (9 μL, 0.05 mmoles) followed by Dhbt-OH (9 mg, 0.05 mmoles) and Hg(OCOFCF₃)₂ (12 mg, 0.028 mmoles) at room temperature. After 5 minutes the solvent was removed under vacuum and the residue was filtered through a short plug of silica (50% EtOAc/hexanes + 1% MeOH) and was concentrated under vacuum to give unit **11** activated for peptide coupling. To resin containing a growing peptide chain with a free amine (3.3 μmoles) was added a solution of activated unit **11** (1.5 mg, 2.3 μmoles) and diisopropylethylamine (0.8 μL, 4.6 μmoles) in NMP (90 μL). After 1 hour, the solution was drained and the resin was washed with NMP (100 μL x 3). The resin was then treated with diisopropylethylamine (5.5 μL,

29 μ moles) and acetic anhydride (10 μ L, 106 μ moles) in NMP (84 μ L) for 30 minutes to cap any free amines. The resin was washed with NMP (100 μ L x 3) and peptide synthesis was continued. The peptides were deprotected and cleaved from the resin using trifluoroacetic acid:triisopropylsilane:water (95:2.5:2.5) for 3 hours at room temperature. The cleavage mixture was collected and cold ether was added to precipitate the peptides. The precipitate was taken up in H₂O with 0.1% TFA, and purified on a Beckmann 5 μ C₁₈ column (4.6 mm x 15 cm) using a linear gradient of acetonitrile in H₂O with 0.1 % (v/v) trifluoroacetic acid and UV detection at 220 nm. The single major product in each case was the desired product **12**. None of the minor products had the mass of **12**, but instead had lower masses, indicating that they arose from incomplete coupling rather than racemization of the stereodiversified unit.

General protocol for formation of Boc protected *syn* and *anti* amino monomers^{5,4}:

To a stirred solution of TBS protected β -hydroxy acid **6/8** (1 eq) in benzene (0.2 M) was added triethylamine (1.1 eq) followed by diphenylphosphoryl azide (1.1 eq) at room temperature. The solution was refluxed for 30 minutes then cooled to room temperature and a mixture of lithium *t*-butoxide (1.5 eq) and *t*-butanol (3 eq) in THF (equal volume to benzene) was added. The reaction was stirred for 15 minutes, quenched by addition of saturated Na₂CO₃, and extracted (3x) with EtOAc. The organic layers were combined, dried (MgSO₄), filtered, and concentrated under vacuum. The residue was partially purified by flash chromatography (6% EtOAc/hexanes) to remove polar impurities. The non-polar fractions were concentrated and dissolved in THF (0.2 M). TBAF (2 eq, 1M in THF) was added and stirred for 2 hours at room temperature, quenched by addition of saturated NaHCO₃, and extracted (3x) with EtOAc. The organic layers were combined, dried (MgSO₄), filtered, and concentrated under vacuum. The residue was purified by flash chromatography (20% EtOAc/hexanes).

References:

- (1) Tietze, L. F.; Eicher, T. *Reactions and Syntheses in the Organic Chemistry Laboratory*; University Science Books:, 1989.
- (2) Evans, D. A.; Gage, J. R.; Leighton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 9434-53.
- (3) Damon, R. E.; Coppola, G. M. *Tetrahedron Lett.* **1990**, *31*, 2849-52.
- (4) Corey, E. J.; Venkateswarlu, A. *J. Amer. Chem. Soc.* **1972**, *94*, 6190-1.
- (5) Shioiri, T.; Yokoyama, Y.; Kasai, Y.; Yamada, S. *Tetrahedron* **1976**, *32*, 2211-17.
- (6) Duggan, M. E.; Imagire, J. S. *Synthesis* **1989**, 131-2.
- (7) Abiko, A.; Liu, J.-F.; Masamune, S. *J. Am. Chem. Soc.* **1997**, *119*, 2586-2587.

- (8) Brown, H. C.; Dhar, R. K.; Ganesan, K.; Singaram, B. *J. Org. Chem.* **1992**, *57*, 499-504.
- (9) Brown, H. C.; Ganesan, K.; Dhar, R. K. *J. Org. Chem.* **1993**, *58*, 147-53.
- (10) Palazzi, C.; Colombo, L.; Gennari, C. *Tetrahedron Lett.* **1986**, *27*, 1735-8.
- (11) Neises, B.; Steglich, W. *Angew. Chem.* **1978**, *90*, 556-7.
- (12) Boger, D. L.; Patane, M. A.; Zhou, J. *J. Am. Chem. Soc.* **1994**, *116*, 8544-56.
- (13) Myers, A. G.; Gin, D. Y.; Rogers, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4697-718.
- (14) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678. Furstner, A.; Thiel, O.; Ackerman, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204-2207. Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247-2250.
- (15) Atherton, E.; Holder, J. L.; Meldal, M.; Sheppard, R. C.; Valerio, R. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2887-94.
- (16) Masamune, S.; Kamata, S.; Schilling, W. *J. Am. Chem. Soc.* **1975**, *97*, 3515-16.
- (17) Koide, K. Ph.D. Dissertation, University of San Diego, CA, 1997