Supporting Information

Self-Condensation of *N*-*tert*-butanesulfinyl Aldimines: Application to the Rapid Asymmetric Synthesis of Biologically Important Amine-Containing Compounds

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General Methods. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl. Acetonitrile (CH₃CN), methanol (MeOH), methylene chloride (CH₂Cl₂), and *N,N*-diisopropylethylamine (Hunig's Base) were distilled from CaH₂. Amine-free biosynthesis grade dimethylformamide (DMF) was used without further purification. 1.0 M solutions of sodium and lithium bis(trimethylsilyl)-amide (NaHMDS and LHMDS) were obtained in Sure/SealTM bottles from Aldrich. 1.0 M potassium bis(trimethylsilyl)-amide (KHMDS) was prepared from solid KHMDS and distilled THF. 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was distilled and stored over 3Å molecular sieves. Excluding microwave reactions, all reactions were carried out in flame-dried glassware under an inert nitrogen atmosphere. Reaction progress was monitored by thin layer chromatography. All microwave reactions were performed using a Smith Synthesizer in a septum capped process vial with stirring at 300W. The temperature reported is the maximum temperature the sample reached, and the time reported includes the time required to reach the target temperature. Samples were cooled using 40 psi pressurized air. IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated

total reflectance accessory, and only partial data are listed. Unless otherwise noted, ^1H and ^{13}C NMR spectra were obtained in CDCl_3 . Coupling constants are reported in Hz. The diastereomer ratios of self-condensation products were determined by ^1H -NMR (vide infra). Elemental analyses and mass spectra were obtained from the Microanalytical Laboratory at the University of California, Berkeley.

Bis-imine 3. A solution of cyclohexene (3.00 g, 36.5 mmol, 1.0 equiv) in 91 mL of CH_2Cl_2 was cooled to $-78\text{ }^\circ\text{C}$ and purged with O_2 for 5 min. Ozone was bubbled through the reaction mixture until the solution changed from colorless to blue, at which time the flask was again purged with O_2 until the blue color disappeared. Triphenylphosphine (9.60g, 36.5 mmol, 1.0 equiv) was added, and the reaction mixture was slowly allowed to warm to room temperature overnight. Concentration on a rotary evaporator at $\sim 45\text{ mm Hg}$, keeping the bath at $0\text{ }^\circ\text{C}$, was followed by addition of 3:2 Et_2O :pentane. The mixture was filtered through celite to remove the precipitated $\text{P}(\text{O})\text{Ph}_3$. After concentration and silica gel chromatography with 3:2 Et_2O :pentane provided hexanedial (2.08 g, 50%). To a solution of the hexanedial (2.08 g, 18.2 mmol, 1.0 equiv) in 73 mL of THF was added $\text{Ti}(\text{OEt})_4$ (5-15% isopropanol, 17.7 mL, $\sim 72.8\text{ mmol}$, ~ 4.0 equiv), and (*R_s*)-*tert*-butanesulfinamide (4.41 g, 36.4 mmol, 2.0 equiv). The reaction solution was stirred for 4 h, diluted with 200 mL EtOAc , and the reaction was quenched with 100 mL of brine. After stirring for 5 min, the mixture was filtered through a pad of Celite, which was rinsed with EtOAc . The filtrate was washed with brine, dried

with Na₂SO₄, and concentrated. The crude material was purified by flash chromatography (97/3 CH₂Cl₂/MeOH) to provide **3** as a colorless oil (4.71 g, 80%). [α]_D = -261° (*c* 1.0, CHCl₃). IR: 1084, 1620 cm⁻¹. ¹H NMR (500 MHz): δ 1.19 (s, 18H), 1.70-1.75 (m, 4H), 2.51-2.56 (m, 4H), 8.07 (t, 2H, *J* = 5). ¹³C NMR (125 MHz): δ 22.3, 24.8, 35.7, 56.5, 168.8. MS (FAB): *m/z* 321 (MH⁺). Exact mass calcd for C₁₄H₂₈N₂O₂S₂ requires *m/z* 320.1670, found *m/z* 321.1668 (MH⁺, FAB).

Intramolecular self-condensation product 2. Bisimine **3** (1.00 g, 3.12 mmol, 1.0 equiv) was dissolved in 20.8 mL of THF and cooled to -78 °C. NaHMDS (1.0 M in THF, 3.10 mL, 1.0 equiv) was added dropwise, and the reaction mixture was stirred at -78 °C for 3 h. Upon quenching the reaction with 20% AcOH/THF, the reaction mixture was allowed to warm to room temperature, diluted with an equal volume EtOAc, and washed with 1N NaHCO₃ and brine. The organic layer was dried with Na₂SO₄ and concentrated. Purification of the crude oil via flash chromatography (98/2 EtOAc/MeOH) provided **2** as a white solid (810 mg, 81%, as a 78:3:8:11 mixture of diastereomers). A single recrystallization using hexanes and toluene provided **2** in (>95:5 dr) in 50% yield from **3**. Major diastereomer: mp = 144-146 °C. [α]_D = -127° (*c* 1.0, CHCl₃). IR: 1057, 1619 cm⁻¹. ¹H NMR (*d*₆-DMSO 500 MHz): δ 1.06 (s, 9H), 1.08 (s, 9H), 1.58-1.72 (m, 4H), 1.84-1.87 (m, 1H), 1.98-2.02 (m, 1H), 2.88-2.92 (m, 1H), 3.63-3.67 (m, 1H), 5.23 (d, 1H, *J* = 8), 7.91 (d, 1H, *J* = 5.5). (Minor diastereomers: 7.98 (d, *J* =

6.0); 8.00 (d, $J = 5.0$); 8.07 (d, $J = 5.0$)) ^{13}C NMR (d_6 -DMSO, 125 MHz): δ 22.2, 22.9, 23.0, 27.8, 34.4, 52.1, 55.3, 56.4, 61.4, 171.3. MS (ESI): m/z 321 (MH^+). Exact mass calcd for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$ requires m/z 320.1670, found m/z 321.1668 (MH^+ , FAB). Single crystals suitable for X-ray diffraction were obtained by recrystallization of **2** from hot toluene (Figure 1).

Nitrile 4. Imine **2** (300 mg, 0.936 mmol) was divided in half, and each portion was dissolved in 2.4 mL acetonitrile, added to a 2-5 mL process vial, and capped with a septum. The vials were placed in a Smith Synthesizer cavity and subjected to microwave irradiation at 150 °C for 15 min (normal absorption). Upon cooling, the vessels were uncapped and the contents were combined and concentrated. The crude oil was purified by flash chromatography (98/2 EtOAc/MeOH) to provide **4** as a white solid (157 mg, 78%). mp = 77-80 °C. $[\alpha]_{\text{D}} = +22.7^\circ$ (c 1.0, CHCl_3). IR: 1030, 2236 cm^{-1} . ^1H NMR (500 MHz): δ 1.22 (s, 9H), 1.60-1.64 (m, 1H), 1.81-1.87 (m, 2H), 1.89-1.95 (m, 1H), 2.11-2.19 (m, 1H), 2.24-2.31 (m, 1H), 2.66-2.71 (m, 1H), 3.23 (d, 1H, $J = 6.5$), 3.70-3.96 (m, 1H). ^{13}C NMR (125 MHz): δ 22.2, 22.4, 28.2, 33.5, 36.5, 56.0, 62.0, 121.1. MS (EI): m/z 214 (M^+). Exact mass calcd for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{OS}_2$ requires m/z 214.1140, found m/z 214.1144 (M^+ , EI). The stereochemistry of **4** was inferred from that of precursor **2**, which was determined by X-ray crystallography, and was confirmed by conversion of **4** to literature compound **1** (*vide infra*).

Amino acid 1. Nitrile **4** (50.0 mg, 0.233 mmol) was dissolved in 2.9 mL of concentrated HCl and heated to 75 °C in a sealed vial for 19 h. The reaction mixture was allowed to cool and was concentrated. The crude residue was triturated with Et₂O to provide **1** as an off-white solid (38.0 mg, 100%). $[\alpha]_D = +25.0^\circ$ (*c* 0.75, H₂O). ¹H NMR (500 MHz, D₂O): δ 1.56-1.78 (m, 4H), 2.05-2.10 (m, 2H), 2.79-2.84 (m, 1H), 3.74-3.79 (m, 1H). ¹³C NMR (125 MHz, D₂O): δ 22.6, 28.5, 30.2, 48.2, 53.8.

General Procedure for the Preparation of (+) and (-) α -Methoxy- α -trifluoromethylphenylacetamides (MTPA amides). The amino acid hydrochloride **1** (1.0 equiv) was dissolved in MeOH (0.1 M) and cooled to 0 °C. Thionyl chloride (5.0 equiv) was added dropwise, and the reaction mixture was stirred at room temperature for 15 h and concentrated. The crude methyl ester was dissolved in CH₂Cl₂ (0.1 M) and Hunig's base (4.0 equiv) was added dropwise. >99% ee (+) or 98% ee (-) MTPA chloride (~2.0 equiv) was added, and the reaction mixture was stirred for 15 h at room temperature. The reaction mixture was quenched with 1N aqueous sodium thiosulfate and diluted with Et₂O. The layers were separated, and the aqueous portion was extracted twice with Et₂O. The organic portions were combined, dried with Na₂SO₄, concentrated, and filtered through a short plug of silica gel with Et₂O eluent. GC/MS analysis on an Agilent Technologies 6890N GC system with an HP-5MS column (50 °C – 3 min; 15 °C/min, 300 °C – 20 min) revealed that the ratio of the (+) MTPA amide methyl ester of

(*S,S*)-**1** (t_r = 18.54 min) to the (+) MTPA amide methyl ester of (*R,R*)-**1** (t_r = 18.60 min) to be greater than 99:1.

3-[1,3]-dioxolan-2-ylpropanal.¹ A mixture of 4-pentenal (10.0 g, 119 mmol, 1.0 equiv) and ethylene glycol (9.90 mL, 178 mmol, 1.5 equiv) in 240 mL of benzene was prepared in a flask fitted with a Dean-Stark apparatus. The reaction solution was heated to 95 °C for 2 h to effect the removal of H₂O via azeotrope. Upon cooling, the reaction mixture was diluted with Et₂O, washed with H₂O, and brine. The Et₂O was removed on a rotary evaporator at ~ 45 mm Hg, keeping the bath at 0 °C, and the remainder of the benzene was removed with a stream of N₂. The colorless, crude oil (13.5 g, 89%) was of sufficient purity to carry on. ¹H NMR (500 MHz): δ 1.76-1.79 (m, 2H), 2.16–2.22 (m, 2H), 3.81-4.01 (m, 4H), 4.88 (t, 1H, J = 4.8), 4.96 (dd, 1H, J = 5, 10), 5.04 (dd, 1H, J = 5, 15), 5.80 – 5.90 (m, 1H).

A solution of the alkene (13.5 g, 105 mmol, 1.0 equiv) in 263 mL of CH₂Cl₂ was cooled to –78 °C and purged with O₂ for 5 min. Ozone was bubbled through the reaction mixture until the solution changed from colorless to blue, at which time the flask was again purged with O₂ until the blue color disappeared. Triphenylphosphine (28.0 g, 105 mmol, 1.0 equiv) was added, and the reaction mixture was slowly allowed to warm to room temperature overnight. Concentration on a rotary evaporator at ~45 mm Hg, keeping the bath at 0 °C, was followed by addition of 1:1 Et₂O:hexanes. The mixture was filtered through celite to remove the precipitated P(O)Ph₃. After concentration and

silica gel chromatography with 1:1 Et₂O:pentane the aldehyde was isolated as a colorless liquid (10.3 g, 75%). ¹H NMR (400 MHz): δ 2.00-2.03 (m, 2H), 2.49-2.53 (m, 2H), 3.78-3.99 (m, 4H), 4.93 (t, 1H, *J* = 4.0), 9.72 (t, 1H, *J* = 1.6). The spectral data are in good agreement with literature reports.¹

Imine 5. To a flask charged with freshly flame-dried CuSO₄ (3.00 g, 18.8 mmol, 2.2 equiv) was added 34.0 mL of THF, 3-[1,3]-dioxolan-2-ylpropanal (1.11 g, 8.53 mmol, 1.0 equiv), and *tert*-butanesulfinamide (1.03 g, 8.53 mmol, 1.0 equiv). After stirring at room temperature for 15 h, the reaction mixture was filtered through a pad of Celite, which was washed with CH₂Cl₂. The filtrate was concentrated and the crude product was purified by flash chromatography (50/50 EtOAc/Hex) to give **5** as a colorless oil (1.90 g, 95%). [α]_D = -206° (*c* 1.0, CHCl₃). IR: 1070, 1619 cm⁻¹. ¹H NMR (500 MHz): δ 1.17 (s, 9H), 1.99-2.04 (m, 2H), 2.62-2.66 (m, 2H), 3.83-3.86 (m, 2H), 3.94-3.97 (m, 2H), 4.95 (t, 1H, *J* = 5.0), 8.10 (t, 1H, *J* = 5.0). ¹³C NMR (100 MHz): δ 22.2, 29.2, 30.2, 56.5, 64.9, 65.0, 103.1, 168.6. MS (ESI): *m/z* 234 (MH⁺). Anal. Calcd. for C₁₀H₁₉NO₃S: C, 51.48; H, 8.21; N, 6.00. Found: C, 51.17; H, 8.51; N, 5.89.

Imine self condensation product 6. Imine **5** (2.74 g, 11.8 mmol, 1.0 equiv) and DMPU (1.42 mL, 11.8 mL, 1.0 equiv) were dissolved in 59.0 mL THF, and the mixture was cooled to $-48\text{ }^{\circ}\text{C}$. LHMDS (1.0 M, 5.90 mL, 0.5 equiv) was added dropwise, and the reaction mixture was stirred at $-48\text{ }^{\circ}\text{C}$ for 3 h. The reaction was quenched with 20% AcOH/THF (5 mL), and the resulting solution was allowed to warm to room temperature and was diluted with an equal volume of EtOAc. The organic layer was washed with 1N NaHCO_3 (40 mL) and brine (40 mL), dried over Na_2SO_4 , and concentrated. The crude oil was purified by flash chromatography (97/3 EtOAc/MeOH) to provide **6** as a colorless oil (1.50 g, 55%, as a 91:5:4 mixture of diastereomers). IR: $1044, 1614\text{ cm}^{-1}$. ^1H NMR (500 MHz, d_6 -DMSO): δ 1.09 (s, 18H), 1.55-1.60 (m, 4H), 1.80-1.95 (m, 2H), 2.78-2.79 (m, 1H), 3.34-3.41 (m, 1H), 3.69-4.06 (m, 8H), 4.77-4.82 (m, 2H), 5.15 (d, 1H, $J = 8$), 7.92 (d, 1H, $J = 7.5$). (Minor diastereomers: 7.97 (d, $J = 6.5$); 8.04 (d, $J = 6.0$). ^{13}C NMR (125 MHz, d_6 -DMSO): δ 22.4, 23.3, 27.9, 30.5, 31.8, 46.7, 56.0, 56.7, 60.4, 64.61, 64.64, 64.74, 64.76, 102.7, 103.9, 172.6. MS (ESI): m/z 489 ($\text{M}+\text{Na}$). Exact mass calcd for $\text{C}_{20}\text{H}_{38}\text{N}_2\text{O}_6\text{S}_2$ requires m/z 467.2250, found m/z 467.2260 (MH^+ , FAB).

Imine 7. To 3-phenylpropionaldehyde (1.21 mL, 9.08 mmol, 1.1 equiv) dissolved in 33.0 mL of THF was added $\text{Ti}(\text{OEt})_4$ (5-15% isopropanol, 4.00 mL, ~ 16.5 mmol, ~ 2.0 equiv), followed by *tert*-butanesulfinamide (1.00 g, 8.26 mmol, 1.0 equiv). The reaction mixture was stirred for 5 h, diluted with an equal volume of EtOAc, and the reaction was quenched with 10 mL of brine. After stirring for 5 min, the mixture was filtered through a pad of Celite, which was rinsed with EtOAc. The filtrate was washed with brine, dried with Na_2SO_4 , and concentrated. The crude material was purified by flash chromatography (75/25 Hex/EtOAc) to provide **7** as a colorless oil (1.79 g, 91%). $[\alpha]_{\text{D}} = -196^\circ$ (c 1.0, CHCl_3). IR: 1074, 1616 cm^{-1} . ^1H NMR (500 MHz): δ 1.13 (s, 9H), 2.84-2.89 (m, 2H), 2.93-2.99 (m, 2H), 7.18-7.21 (m, 3H), 7.26-7.30 (m, 2H), 8.11 (t, 1H, $J = 5$). ^{13}C NMR (125 MHz): 22.2, 31.3, 37.4, 56.5, 126.2, 128.2, 128.5, 140.2, 168.4. MS (FAB): m/z 238 (MH^+). Anal. Calcd. for $\text{C}_{13}\text{H}_{19}\text{NOS}$: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.39; H, 8.02; N, 6.02.

Self-condensation product 8. Imine **7** (50.0 mg, 0.211 mmol, 1.0 equiv) was dissolved in 1.1 mL of THF and cooled to -48°C . LHMDS (1.0 M in THF, 105 μL , 0.50 equiv) was added dropwise, and the reaction mixture was stirred at -48°C for 3 h. After quenching the reaction with 1 mL of 20% AcOH/THF, the mixture was allowed to warm to room temperature, diluted with an equal volume EtOAc, and washed with 1N NaHCO_3 .

and brine. The organic layer was dried with Na₂SO₄ and concentrated. Purification of the crude oil via flash chromatography (95/5 CH₂Cl₂/MeOH) provided **8** as a colorless oil (34.0 mg, 68%, as a 85:13:2 mixture of diastereomers). IR: 1063, 1614 cm⁻¹. ¹H NMR major diastereomer (400 MHz): δ 1.03 (s, 9H), 1.26 (s, 9H), 1.88-1.95 (m, 1H), 2.09-2.14 (m, 1H), 2.73-2.80 (m, 1H), 2.88-2.92 (m, 3H), 3.14-3.20 (m, 1H), 3.49 (d, 1H, *J* = 6.8), 3.59-3.61 (m, 1H), 7.10-7.36 (m, 10H), 8.02 (d, 1H, *J* = 6). (Minor diastereomers: 8.08 (d, *J* = 5.5); 8.10 (d, *J* = 5.5)) ¹³C NMR major diastereomer (125 MHz): δ 22.1, 22.6, 31.9, 34.3, 34.7, 52.4, 56.2, 56.6, 58.1, 126.1, 126.5, 128.5, 128.61, 128.69, 128.8, 138.2, 140.8, 170.0. MS (ESI): *m/z* 497 (M + Na). Exact mass calcd for C₂₆H₃₈N₂O₂S₂ requires *m/z* 474.2453, found *m/z* 475.2459 (MH⁺, FAB).

Nitrile 9. Imine **6** (100 mg, .214 mmol) was dissolved in 1.1 mL acetonitrile, added to a 2-5 mL process vial, and capped with a septum. The reaction vial was placed in a Smith Synthesizer cavity and subjected to microwave irradiation at 150 °C for 15 min (normal absorption). Upon cooling, the vessel was uncapped, and the contents concentrated. The crude residue was purified by flash chromatography (97/3 CH₂Cl₂/MeOH) to provide **9** as a slightly yellow oil that crystallized upon standing (65.0 mg, 84%). Trituration with Et₂O provided **9** as a colorless white solid. mp = 107-108 °C. [α]_D = -87.4° (*c* 1.0, CHCl₃). IR: 1044, 2235 cm⁻¹. ¹H NMR (500 MHz): δ 1.25 (s,

9H), 1.74-1.79 (m, 1H), 1.85-1.89 (m, 4H), 2.07-2.12 (m, 1H), 3.04-3.07 (m, 1H), 3.46-3.53 (m, 1H), 3.82-3.93 (m, 4H), 3.98-4.03 (m, 4H), 4.10 (d, 1H, $J = 4.5$), 4.94-4.95 (m, 1H), 5.03-5.05 (m, 1H). ^{13}C NMR (125 MHz): δ 22.6, 24.6, 29.0, 32.3, 33.9, 56.1, 56.5, 64.9, 65.02, 65.03, 65.2, 101.5, 103.2, 119.7. MS (ESI): m/z 361 (MH^+). Exact mass calcd for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_5\text{S}$ requires m/z 360.1787, found m/z 361.1797 (MH^+ , FAB). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a solution of **9** in CH_2Cl_2 (Figure 2).

Amine 10. A flask charged with nitrile **9** (195 mg, 0.542 mmol, 1.0 equiv), $\text{BH}_3 \cdot \text{SMe}_2$ (72 μL , 0.758 mmol, 1.4 equiv) and 2.7 mL of THF was fitted with a reflux condenser, nitrogen inlet, and a needle to allow for the release of Me_2S gas. The reaction mixture was heated to 70 $^\circ\text{C}$ for 3.5 h. After allowing the reaction mixture to cool to room temperature, 20% AcOH/THF (1 mL) was added, at which point the evolution of H_2 was observed. The reaction mixture was then concentrated sequentially from toluene (3 mL) and methanol (3 mL). The crude residue was purified by flash chromatography on a short silica gel plug (90/10 $\text{CH}_2\text{Cl}_2/\text{MeOH}$, followed by 85/10/5 $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$) to provide amine **10** as a colorless oil (180 mg, 91%). $[\alpha]_{\text{D}} = -39.4^\circ$ (c 1.8, CHCl_3). IR: 1141, 2877, 2955 cm^{-1} . ^1H NMR (400 MHz): δ 1.24 (s, 9H), 1.58-1.66 (m, 1H), 1.78-1.90 (m, 8H), 2.77-2.79 (m, 2H), 3.48-3.54 (m, 1H), 3.82-4.02

(m, 9H), 4.93-4.95 (m, 2H). ^{13}C NMR (125 MHz): δ 22.8, 27.2, 30.0, 32.0, 41.6, 43.0, 56.0, 57.4, 64.6, 64.7, 64.80, 64.87, 103.4, 103.9. MS (FAB): m/z 365 (MH^+). Exact mass calcd for $\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_5\text{S}$ requires m/z 364.2110, found m/z 365.2105 (MH^+ , FAB).

Amide 11. 4-Amino-5-chloro-2-methoxybenzoic acid (54.0 mg, 0.266 mmol, 1.0 equiv) and 1-hydroxybenzotriazole hydrate (36.0 mg, 0.266 mmol, 1.0 equiv) were dissolved in 1.30 mL of DMF. 1,3-Dicyclohexylcarbodiimide (55.0 mg, 0.266 mmol, 1.0 equiv) was then added, and the mixture was stirred for 10 min. Amine **10** (97.0 mg, 0.266 mmol, 1.0 equiv) dissolved in a minimum amount of DMF was added to the flask, and the reaction mixture was stirred at room temperature for 16 h. After concentration under high vacuum, the reaction mixture was diluted with EtOAc, filtered through a pad of Celite, and concentrated. The crude residue was purified via silica gel chromatography (95/5 $\text{CH}_2\text{Cl}_2/\text{MeOH}$), to provide **11** as an off-white solid (116 mg, 80%). mp = 147-150 °C. $[\alpha]_{\text{D}} = -6.3^\circ$ (c 1.0, CHCl_3). IR: 1064, 1634 cm^{-1} . ^1H NMR (500 MHz): δ 1.24 (s, 9H), 1.65-1.81 (m, 6H), 2.04 (m, 1H), 3.22-3.28 (m, 1H), 3.44 (m, 1H), 3.69-3.77 (m, 1H), 3.78-4.00 (m, 11H), 4.45 (br s, 2H), 4.87-4.88 (m, 1H), 4.97-4.99 (m, 1H), 6.29 (s, 1H), 7.87-8.00 (m, 1H), 8.06 (s, 1H). ^{13}C NMR (125 MHz): δ 22.9, 27.0, 30.1, 31.6, 38.9, 40.4, 56.0, 56.1, 57.1, 64.7, 64.81, 64.84, 64.9, 97.9, 103.2, 103.8,

111.3, 112.2, 132.9, 146.7, 157.4, 162.4, 164.6. MS (ESI): m/z 548 (MH^+). Exact mass calcd for $C_{24}H_{38}ClN_3O_7S$ requires m/z 548.2197, found m/z 548.2213 (MH^+ , FAB).

SC-53116. A mixture of amide **11** (100 mg, 0.182 mmol), PtO_2 (10.0 mg, 10 wt%), and trifluoroacetic acid (0.180 mL, 10 vol%) was dissolved in EtOH/ H_2O (1/1, 1.80 mL) in a scintillation vial fitted with a stir bar and placed in a Parr apparatus. The Parr apparatus was purged with H_2 gas three times, sealed, and heated at 40 °C for 17 h. The reaction mixture was concentrated, diluted with CH_2Cl_2 , and filtered through a pad of Celite, which removes the majority of the platinum byproduct. The remainder is removed upon purification of the crude residue via silica gel chromatography (90/10 CH_2Cl_2 /MeOH, followed by 80/15/5 CH_2Cl_2 /MeOH/ NH_4OH), which furnishes SC-53116 as a slightly yellow waxy solid (52.0 mg, 88%). $[\alpha]_D = -2.6^\circ$ (c 0.5, MeOH). IR: 1593 cm^{-1} . 1H NMR (CD_3OD , 500 MHz): δ 1.67-1.78 (m, 2H), 1.85-1.90 (m, 1H), 1.95-2.07 (m, 2H), 2.11-2.22 (m, 2H), 2.77-2.89 (m, 2H), 3.11-3.16 (m, 1H), 3.40-3.55 (m, 4H), 3.91 (s, 3H), 6.50 (s, 1H), 7.79 (s, 1H). ^{13}C NMR (125 MHz): δ 25.9 (CH_2), 31.54 (CH_2), 31.56 (CH_2), 42.1 (CH_2), 46.7 (CH), 55.4 (CH_2), 55.7 (CH_2), 56.5 (OCH_3), 71.4 (CH), 98.4 (Ar CH), 111.2 (Ar C), 111.4 (Ar C), 133.1 (Ar CH), 150.4 (Ar C), 159.5 (Ar C), 167.6 (C=O). MS (ESI): m/z 324 (MH^+). Exact mass calcd for $C_{16}H_{22}ClN_3O_2$ requires m/z 323.1478, found m/z 324.1475 (MH^+ , FAB).

Figure 1. X-ray Crystal Structure of **2**.

Figure 2. X-ray Crystal Structure of **9**.

¹ Shiu, L.-H.; Li, Y.-L.; Li, C.-L.; Lao, C.-Y.; Chen, W.-C.; Yu, C.-H.; Liu, R.-S. *J. Org. Chem.* **1999**, *64*, 7552.