Supporting Information

A New Synthesis of γ -Lactams Based on the Reaction of Vinyl Sulfilimines with Dichloroketene

Qiu Wang, Shinji Nara and Albert Padwa*

Department of Chemistry, Emory University, Atlanta, Georgia 30322

chemap@emory.edu

General Experimental Section Paragraph: Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen. The microwave reactor and reaction vessels were purchased from CEM Corporation. All solids were recrystallized from ethyl acetate/hexane for analytical data.

3,3-Dichloro-1-(toluene-4-sulfonyl)-1,3-dihydroindol-2-one (10). To a mixture of 0.3 g (1.1 mmol) of sulfilimine **9**¹ and 0.65 g of Zn-Cu in 20 mL of THF was slowly added 0.44 mL (4.0 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through a Celite column with an aqueous NaHCO₃ solution and washed with EtOAc. The combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.051 g (14%) of **10** as a clear oil; IR (neat) 1773, 1464, 1377, and 1180 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 2.44 (s, 3H), 7.30 (td, 1H, J = 8.0 and 0.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.48 (td, 1H, J = 8.0 and 0.8 Hz), 7.63 (dd, 1H, J = 8.0 and 0.8 Hz), 7.92 (d, 1H, J = 8.0 Hz) and 7.98 (d, 2H, J = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 22.0, 73.9, 114.5, 125.5, 126.5, 128.3, 128.5, 130.3, 132.8, 13.2, 136.6, 146.8, and 166.5.

Another fraction isolated from the chromatographic column contained 0.089 g (22%) of a yellow oil whose structure was assigned as *N*-[2,2-dichloro-2-(2-methylsulfanylphenyl)acetyl]-4-toluenesulfonamide (**12**): IR (neat) 1667, 1431, 1190, 1086, and 660 cm⁻¹; ¹H-NMR (DMSO-*d*₆, 400 MHz) δ 2.19 (s, 3H), 2.41 (s, 3H), 7.37 (t, 1H, *J* = 8.0 Hz), 7.44 (d, 2H, *J* = 8.2 Hz), 7.48 (t, 1H, *J* = 8.0 Hz), 7.58 (d, 1H, *J* = 8.0 Hz), 7.81 (d, 2H, *J* = 8.2 Hz), and 7.91 (d, 1H, *J* = 8.0 Hz); ¹³C-NMR (DMSO-*d*₆, 100 MHz) δ 18.4, 21.1, 86.2, 126.6, 127.9, 128.1, 129.4, 130.9, 132.0, 135.8, 136.4, 137.7, 144.4, and 163.2.

In addition to compounds **10** and **12**, 0.021g (17%) of thioanisole **11** was isolated as a colorless oil: ¹H-NMR (CDCl₃, 300 MHz) δ 2.40 (s, 3H), 7.05 (m, 1H), 7.20–7.33 (m, 4H).

S-Ethyl-*N*-(toluene-4-sulfonyl)-*S*-1-naphthylsulfilimine (13**).** To a solution of 1.5 g (8.0 mmol) of 1-ethylthionaphthalene² in 50 mL of MeCN at rt was added 2.2 g (8.0 mmol) of chloramine-T trihydrate. After stirring at rt for 21 h, the reaction mixture was poured into EtOAc. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was recrystallized from EtOAc/hexane to give 2.1 g (73%) of **13** as a white solid; mp 134–136 °C; IR (KBr) 3047, 1282, 1139, 1089, 983, 810, and 766 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.22 (t, 3H, *J* = 7.2 Hz), 2.31 (s, 3H), 3.03–3.20 (m, 2H), 7.11 (d, 2H, *J* = 8.2 Hz), 7.57–7.77 (m, 3H), 7.75 (d, 2H, *J* = 8.2 Hz), 7.95 (dd, 1H, *J* = 7.6 and 2.0 Hz), 8.01 (d, 1H, *J* = 8.0 Hz), 8.05 (d, 1H, *J* = 8.0 Hz), and 8.28 (dd, 1H, *J* = 7.6 and 1.2 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 7.6, 21.3, 46.9, 121.3, 125.6, 126.2, 126.3, 127.1, 128.1, 129.0, 129.2, 129.2, 129.7, 132.6, 133.7, 141.2, and 141.5; Anal. Calcd. for C₁₉H₁₉NO₂S₂: C, 63.83; H, 5.36; N, 3.92. Found: C, 63.56; H, 5.28; N, 3.93.

3,3-Dichloro-9*b*-ethylthio-1-(toluene-4-sulfonyl)-1,3,3*a*,9*b*-tetrahydrobenzo-[*g*]indol-2-one (14**).** To a mixture of 0.1 g (0.28 mmol) of sulfilimine **13** and 0.15 g of Zn-Cu in 14 mL of THF at 0 °C was slowly added 0.2 mL (1.8 mmol) of trichloroacetyl

chloride. After stirring at rt for 45 min, the reaction mixture was filtered and EtOAc added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.074 g (56%) of **14** as a colorless solid; mp 172-174 °C; IR (neat) 2927, 1754, 1372, 1223, 1176, 1049, 980, and 663 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 0.91 (t, 3H, *J* = 7.5 Hz), 1.94–2.05 (m, 1H), 2.48 (s, 3H), 2.75–2.86 (m, 1H), 3.28 (d, 1H, *J* = 5.1 Hz), 5.99 (dd, 1H, *J* = 9.3 and 5.7 Hz), 6.88 (d, 1H, *J* = 9.3 Hz), 7.17 (d, 1H, *J* = 7.8 Hz), 7.30–7.40 (m, 4H), 7.98 (d, 1H, *J* = 7.8 Hz), and 8.24 (d, 2H, *J* = 8.1 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 13.1, 21.8, 27.2, 59.0, 78.4, 79.5, 117.7, 127.7, 127.9, 129.0, 129.2, 129.5, 129.9, 130.7, 131.0, 133.0, 134.8, 145.8, and 164.7; Anal. Calcd. for C₂₁H₁₉Cl₂NO₃S₂: C, 53.85; H, 4.09; N, 2.99. Found: C, 53.73; H, 4.07; N, 2.87.

S-1-Ethyl-S-2-furyl-N-(toluene-4-sulfonyl)sulfilimine (15). To a solution of 2.6 g (21 mmol) of 2-(ethylthio)furan³ in 100 mL of EtOH was added 5.7 g (20 mmol) of chloramine-T trihydrate. The mixture was stirred at rt for 1h and concentrated under reduced pressure. The residue was recrystallized from EtOAc/hexane to give 2.9 g (49%) of **15** as a white solid; mp 127-129 °C; IR (neat) 3131, 1280, 1139, 967, and 748 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.20 (t, 3H, *J* = 7.2 Hz), 2.31 (s, 3H), 3.30 (dq, 1H, *J* = 12.8 and 7.2 Hz), 3.38 (dq, 1H, *J* = 12.8 and 7.2 Hz), 6.43 (dd, 1H, *J* = 3.6 and 2.0 Hz), 6.85 (dd, 1H, *J* = 3.6 and 0.8 Hz), 7.13 (d, 2H, *J* = 8.0 Hz), 7.59 (dd, 1H, *J* = 2.0 and 0.8 Hz), and 7.65 (d, 2H, *J* = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 7.9, 21.5, 44.1, 112.1, 119.1, 126.3, 129.2, 141.1, 141.8, 141.9, and 148.6; Anal. Calcd. for C₁₃H₁₅NO₃S₂: C, 52.50; H, 5.08; N, 4.71. Found: C, 52.66; H, 5.03; N, 4.78.

S-1-Butyl-S-2-(furan-3-acetoxymethyl)-N-(toluene-4-sulfonyl)sulfilimine (16). To a solution of 3 g (35 mmol) of furan-3-methanol in 200 mL of Et₂O at 0 °C was added 30 mL (75 mmol) of *n*-BuLi (2.5 M in hexane). After stirring at rt for 1 h, 6.7 mL (35

mmol) of *n*-butyl-disulfide was added. Stirring was continued at rt for 15 h and then the reaction was quenched with a saturated aqueous NH_4Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure to give 4.5 g of an oil⁴. This material was dissolved in 100 mL of CH_2Cl_2 and 1.0 mL (12 mmol) of pyridine, and 4.9 mL (52 mmol) of Ac_2O were added. After stirring at rt for 18 h, the reaction was quenched with HCl (1.0 M) and extracted with EtOAc. The organic layer was washed with a saturated aqueous NaHCO_3 solution, brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 1.9 g (24%) of 2-butylthio-3-acetoxymethylfuran as a yellow oil; IR (neat) 2959, 1743, 1376, 1228, 1023, and 736, cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 0.89 (t, 3H, J = 7.5 Hz), 1.36–1.45 (m, 2H), 1.48–1.57 (m, 2H), 2.08 (s, 3H), 2.74 (t, 2H, J = 7.2 Hz), 5.02 (s, 2H), 6.47 (d, 1H, J = 1.8 Hz), and 7.46 (d, 1H, J = 1.8 Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 13.6, 20.9, 21.5, 31.9, 35.7, 58.4, 112.2, 125.4, 143.8, 145.0, and 171.0.

To a solution of 1.1 g (4.6 mmol) of above sulfide in 20 mL of EtOH at rt was added 1.3 g (4.6 mmol) of chloramine-T trihydrate. After stirring at 50 °C for 21 h, the reaction was concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.38 g (20%) of **16** as a yellow oil; IR (neat) 2960, 1743, 1282, 1225, 1142, 1090, 960, 815, 753, and 660 cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 0.87 (t, 3H, J = 7.2 Hz), 1.34–1.44 (m, 2H), 1.51–1.66 (m, 2H), 2.07 (s, 3H), 2.36 (s, 3H), 3.24 (ddd, 1H, J = 12.5, 8.7 and 6.6 Hz), 3.59 (ddd, 1H, J = 12.5, 8.4 and 5.4 Hz), 4.84 (d, 1H, J = 13.2 Hz), 5.04 (d, 1H, J = 13.2 Hz), 6.48 (d, 1H, J = 1.9 Hz), 7.17 (d, 2H, J = 8.3 Hz), 7.59 (d, 1H, J = 1.9 Hz), and 7.69 (d, 2H, J = 8.3 Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 13.4, 20.7, 21.2, 21.3, 25.0, 48.3, 56.1, 112.7, 126.3, 129.1, 130.1, 139.7, 141.0, 141.7, 148.2, and 170.4.

4,4-Dichloro-6a-ethylthio-6-(toluene-4-sulfonyl)-3a,4,6,6a-tetrahydrofuro-[2,3-b]pyrrol-5-one (17). To a mixture of 0.25 g (0.8 mmol) of sulfilimine **15** and 1.1 g of Zn-Cu in 15 mL of THF was slowly added 0.47 mL (4.2 mmol) of trichloroacetyl chloride at 0°C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution and washed with EtOAc. The aqueous layer was washed with EtOAc and the combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.2 g (58%) of **17** as a white solid; mp 133-134 °C; IR (neat) 3114, 1762, 1618, 1377, and 907 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.34 (t, 3H, *J* = 7.2 Hz), 2.42 (s, 3H), 2.28 (dq, 1H, *J* = 11.6 and 7.2 Hz), 2.90 (dq, 1H, *J* = 11.6 and 7.2 Hz), 4.43 (t, 1H, *J* = 2.4 Hz), 5.17 (dd, 1H, *J* = 2.8 and 2.4 Hz), 6.40 (dd, 1H, *J* = 2.8 and 2.4 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), and 8.01 (d, 2H, *J* = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 13.9, 22.0, 25.9, 66.4, 80.3, 102.8, 106.1, 129.5, 129.7, 134.2, 146.3, 146.5, and 163.5; Anal. Calcd. for C₁₅H₁₅Cl₂NO₄S₂: C, 44.12; H, 3.70; N, 3.43. Found: C, 44.07; H, 3.61; N, 3.36.

3a-Acetoxymethyl-6a-butythio-4,4-dichloro-6-(toluene-4-sulfonyl)-4,5,6,6a-tetrahydrofuro[2,3-b]pyrrol-5-one (18). To a mixture of 0.1 g (0.25 mmol) of sulfilimine **16** and 0.07 g of Zn-Cu in 13 mL of THF at 0 °C was added dropwise 0.1 mL (0.90 mmol) of trichloroacetyl chloride. After stirring at rt for 30 min, the reaction mixture was filtered and EtOAc added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.05 g (40%) of **18** as a pale yellow oil; IR (KBr) 2957, 1763, 1752, 1381, 1224, 1077, 1032, 815, and 676 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 0.96 (t, 3H, *J* = 7.1 Hz), 1.41–1.54 (m, 2H), 1.61–1.75 (m, 2H), 2.09 (s, 3H), 2.45 (s, 3H), 3.01–3.18 (m, 2H), 4.53 (d, 1H, *J* = 12.0 Hz), 4.86 (d, 1H, *J* = 12.0 Hz), 5.23 (d, 1H, *J* = 3.2 Hz), 6.41 (d, 1H, *J* = 3.2 Hz), 7.34 (d, 2H, *J* = 7.5 Hz), and 8.02 (d, 2H, *J* = 7.5 Hz); ¹³C-

NMR (CDCl₃, 100 MHz) δ 13.6, 20.8, 21.8, 22.0, 31.3, 31.7, 63.6, 67.9, 82.3, 106.4, 107.5, 129.4, 129.5, 134.1, 145.6, 146.1, 163.5, and 170.2.

S-2-Benzo[*b*]furan-S-ethyl-N-(toluene-4-sulfonyl)sulfilimine (19). To a solution of 2.5 g (21 mmol) of benzo[*b*]furan in 200 mL of Et₂O at 0 °C was added 10 mL (25 mmol) of *n*-BuLi (2.5 M in hexane). After stirring at rt for 30 min, 2.3 mL (21 mmol) of *n*-ethyldisulfide was added. Stirring was continued at rt for 20 h and the reaction was quenched with a saturated aqueous NH₄Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 2.4 g (64%) of 2-(ethylthio)benzo[*b*]furan as a yellow oil; IR (neat) 2926, 1528, 1445, 1252, 1160, 924, and 749 cm⁻¹; ¹H-NMR (CDCl₃, 600 MHz) δ 1.33 (t, 3H, *J* = 7.2 Hz), 2.96 (q, 2H, *J* = 7.2 Hz), 6.80 (s, 1H), 7.21 (t, 1H, *J* = 7.8 Hz), 7.26 (t, 1H, *J* = 7.8 Hz), 7.44 (d, 1H, *J* = 7.8 Hz), 7.50 (d, 1H, *J* = 7.8 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 15.1, 28.9, 110.9, 111.0, 120.3, 122.8, 124.3, 128.6, 150.4, and 156.3.

To a solution of 1.3 g (7.1 mmol) of above sulfide in 40 mL of EtOH at rt was added 2 g (4.6 mmol) of chloramine-T trihydrate. After stirring at rt for 15 h, the reaction was quenched with H₂O and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was recrystallized from EtOAc/hexane to give 1.1 g (46%) of **19** as a colorless solid; mp 129-130 °C; IR (KBr) 2975, 1278, 1145, 1087, 966, 751 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.30 (t, 3H, *J* = 7.6 Hz), 2.27 (s, 3H), 3.38–3.52 (m, 2H), 7.08 (d, 2H, *J* = 8.0 Hz), 7.23 (brs, 1H), 7.31 (td, 1H, *J* = 7.8 and 1.2 Hz), 7.28 (td, 1H, *J* = 7.8 and 1.2 Hz), 7.48 (brd, 1H, *J* = 7.8 Hz), 7.58 (brd, 1H, *J* = 7.8 Hz), and 7.70 (d, 2H, *J* = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 7.6, 21.3, 44.0, 112.0, 115.2, 122.5, 124.3, 126.0, 126.2, 127.6, 129.0, 140.8, 141.7, 144.5, and 156.8; Anal. Calcd. for C₁₇H₁₇NO₃S₂: C, 58.77; H, 4.93; N, 4.03. Found: C, 58.54; H, 4.83; N, 4.01.

S-2-(1-*tert*-Butoxycarbonyl-3-methyl)indolyl-S-ethyl-(toluene-4-sulfonyl)sulfilimine (20). To a solution of 0.16 g (0.55 mmol) of 1-*tert*-butoxycarbonyl-2-ethylthio-3-methylindole⁵ in 15 mL of EtOH was added 0.16 g (0.55 mmol) of chloramine-T trihydrate. The mixture was stirred at rt for 1h and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.12 g (48%) of **20** as a white solid; mp 158-160 °C; IR (neat) 2974, 1712, 1370, 1143, and 956 cm⁻¹; ¹H-NMR (CDCl₃, 600 MHz) δ 1.39 (t, 3H, *J* = 7.2 Hz), 1.69 (s, 9H), 2.18 (s, 3H), 2.54 (s, 3H), 3.40 (dq, 1H, *J* = 12.6 and 7.2 Hz), 3.49 (dq, 1H, *J* = 12.6 and 7.2 Hz), 6.97 (d, 2H, *J* = 8.4 Hz), 7.28 (td, 1H, *J* = 8.4 and 1.2 Hz), 7.41 (td, 1H, *J* = 8.4 and 1.2 Hz), 7.47 (d, 1H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), and 7.90 (d, 1H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 8.7, 10.1, 21.4, 28.4, 47.0, 86.6, 115.3, 119.9, 123.6, 123.8, 126.2, 127.6, 128.5, 129.0, 130.4, 135.7, 141.1, 141.5, and 150.0; Anal. Calcd. for C₂₃H₂₈N₂O₄S₂: C, 59.97; H, 6.13; N, 6.08. Found: C, 60.08; H, 5.96; N, 6.05.

3,3-Dichloro-8a-ethylthio-1-(toluene-4-sulfonyl)-1,3,3a,8a-tetrahydro-2H-benzofuro[2,3-*b*]pyrrol-2-one (21). To a mixture of 0.3 g (0.9 mmol) of sulfilimine **19** and 0.28 g of Zn-Cu in 45 mL of THF at rt was slowly added 0.4 mL (3.5 mmol) of trichloroacetyl chloride. After stirring at rt for 45 min, the reaction mixture was filtered and EtOAc added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.2 g (52%) of **21** as a colorless solid; mp 126-128 °C; IR (KBr) 2968, 1757, 1595, 1478, 1379, 1258, 1115, 983, and 749 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.30 (t, 3H, *J* = 7.8 Hz), 2.42 (s, 3H), 2.75–2.94 (m, 2H), 4.80 (s, 1H), 7.00 (d, 1H, *J* = 7.5 Hz), 7.04 (t, 1H, *J* = 7.5 Hz), 7.31 (d, 2H, *J* = 7.8 Hz), 7.33 (t, 1H, *J* = 7.5 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), and 8.06 (d, 2H, *J* = 7.8 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 13.6, 21.8, 25.8, 65.6, 80.2, 106.5, 110.8, 121.2, 122.8, 128.0, 129.4, 129.5, 131.4, 133.9, 146.2, 157.5, and

163.2; Anal. Calcd. For $C_{19}H_{17}Cl_2NO_4S_2$: C, 49.78; H, 3.74; N, 3.06. Found: C, 49.49; H, 3.78; N, 3.03.

***tert*-Butyl 3,3-dichloro-8a-ethylthio-3a-methyl-2-oxo-1-(toluene-4-sulfonyl)-2,3,3a,8a-tetrahydro-1*H*-pyrrolo[2,3-*b*]indole-8-carboxylate (22).** To a mixture of 0.013 g (0.028 mmol) of sulfilimine **20** and 0.04 g of Zn-Cu in 5 mL of THF was slowly added 0.015 mL (0.14 mmol) of trichloroacetyl chloride at rt. The reaction mixture was stirred at 25 °C for 10 min, filtered through Celite with a saturated aqueous $NaHCO_3$ solution and washed with EtOAc. The aqueous layer was washed with EtOAc and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.09 g (56%) of **22** as a colorless oil; IR (neat) 1760, 1722, 1485, 1349, 1179, and 1081 cm^{-1} ; 1H -NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, 3H, J = 7.6 Hz), 1.53 (s, 3H), 1.61 (s, 9H), 2.42 (s, 3H), 2.85 (dq, 1H, J = 11.2 and 7.6 Hz), 3.49 (dq, 1H, J = 11.2 and 7.6 Hz), 7.13 (td, 1H, J = 7.6 and 0.8 Hz), 7.25–7.29 (m, 3H), 7.33 (td, 1H, J = 7.6 and 0.8 Hz), 7.52 (d, 1H, J = 7.6 Hz), and 8.15 (d, 2H, J = 8.4 Hz); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ 13.1, 17.7, 21.9, 27.4, 28.6, 65.0, 83.8, 86.1, 96.6, 117.8, 124.4, 124.5, 128.1, 129.4, 130.1, 130.2, 135.8, 142.4, 145.6, 150.2, and 165.1.

(*Z*)-S-2-Phenylethenyl-S-phenyl-*N*-(toluene-4-sulfonyl)sulfilimine (24). To a solution of 0.75 g (3.5 mmol) of (*Z*)-phenyl styryl sulfide and 0.09 g (0.18 mmol) of hexadecyl-tributylphosphonium bromide in 50 mL of CH_2Cl_2 was slowly added 1 g (3.5 mmol) of chloramine-T trihydrate. The reaction mixture was stirred at room temperature for 24 h, the solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography to give 0.47 g (35%) of **24** as a colorless oil; IR (neat) 3058, 1445, 1283, 1141 and 959 cm^{-1} ; 1H -NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 6.32 (d, 1H, J = 10.4 Hz), 7.09 (d, 2H, J = 8.0 Hz), 7.16 (d, 1H, J = 10.4 Hz), 7.37–7.43 (m, 5H), 7.45–7.50 (m, 3H), 7.65 (dd, 2H, J = 8.0 and 1.6 Hz)

and 7.70 (d, 2H, $J = 8.0$ Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 21.6, 126.2, 126.3, 126.6, 129.1, 129.3, 129.7, 130.1, 130.5, 132.2, 132.7, 136.3, 141.6, 141.7, and 141.8.

(*E*)-S-2-Phenylethenyl-S-phenyl-*N*-(toluene-4-sulfonyl)sulfilimine (25). To a solution of 1.5 g (5.1 mmol) of sulfilimine **9** in 100 mL of THF at -78 °C was slowly added 2.1 mL (5.1 mmol) of *n*-BuLi solution (2.4 M hexane), 0.6 g (5.1 mmol) of potassium *tert*-butoxide and 0.74 mL (5.1 mmol) of diethyl chlorophosphate. After stirring at -78 °C for 10 min, 0.5 mL (5.1 mmol) of phenyl acetaldehyde was added dropwise and the mixture was warmed to 0 °C for 40 min. A saturated aqueous NH_4Cl solution was added and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.38 g (20%) of **25** as a colorless oil; ^1H -NMR (CDCl_3 , 300 MHz) δ 2.28 (s, 3H), 6.58 (d, 1H, $J = 15.3$ Hz), 7.13 (d, 2H, $J = 8.1$ Hz), 7.30-7.36 (m, 6H), 7.43-7.49 (m, 3H), 7.64-7.69 (m, 2H), and 7.76 (d, 2H, $J = 8.1$ Hz); ^{13}C -NMR (CDCl_3 , 75 MHz) δ 21.5, 122.6, 126.4, 126.9, 128.2, 129.1, 129.4, 130.1, 130.9, 132.4, 132.7, 135.4, 141.5, 141.6, and 141.8.

S-Phenyl-S-1,2-dimethylpropenyl-*N*-(toluene-4-sulfonyl)sulfilimine (26). To a solution of 0.85 g (4.8 mmol) of 1,2-dimethylpropenylbenzene sulfide⁶ in 100 mL of EtOH at rt was added 0.13 mL (2.3 mmol) of AcOH and 1.3 g (4.8 mmol) of chloramine-T trihydrate. After stirring at rt for 20 h, the reaction mixture was quenched with H_2O and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.91 g (55%) of **26** as a white solid; mp 92 - 94 °C; IR (KBr) 2950, 1282, 1140, 1088, 965, 822, 761, and 653 cm^{-1} ; ^1H -NMR (CDCl_3 , 400 MHz) δ 1.67 (s, 3H), 1.83 (s, 3H), 2.16 (s, 3H), 2.36 (s, 3H), 7.19 (d, 2H, $J = 8.2$ Hz), 7.46-7.49 (m, 3H), 7.54-7.57 (m, 2H), and 7.79 (d, 2H, $J = 8.2$ Hz); ^{13}C -

NMR (CDCl₃, 100 MHz) δ 10.5, 21.3, 22.1, 22.3, 125.9, 126.3, 126.8, 129.0, 129.5, 131.1, 133.5, 141.4, 141.8, and 147.7.

3,3-Dichloro-5-phenylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (27). To a mixture of 0.1 g (0.34 mmol) of sulfilimine **23**⁷ and 0.72 g of Zn-Cu in 16 mL of THF was slowly added 0.3 mL (2.8 mmol) of trichloroacetyl chloride in 2 mL of THF at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, filtered through Celite with a saturated aqueous NaHCO₃ solution and washed with EtOAc. The aqueous layer was washed with EtOAc and the combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.085 g (61%) of **27** as a white solid; mp 122-124 °C; IR (neat) 1760, 1374, 1173 and 663 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 2.43 (s, 3H), 2.98 (dd, 1H, *J* = 14.8 and 3.6 Hz), 3.26 (dd, 1H, *J* = 14.8 and 7.2 Hz), 5.59 (dd, 1H, *J* = 7.2 and 3.6 Hz), 7.32-7.44 (m, 7H), and 8.12 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 22.0, 48.5, 64.8, 78.7, 129.6, 129.7, 1129.9, 130.0, 130.7, 134.1, 134.9, 146.6 and 163.8.

(Z)-3,3-Dichloro-4-phenyl-5-phenylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (28). To a mixture of 0.05 g (0.13 mmol) of sulfilimine **24** and 0.17 g of Zn-Cu in 5 mL of THF was slowly added 0.075 mL (0.66 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution and washed with EtOAc. The combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.042 g (60%) of **28** as a colorless oil; IR (neat) 1765, 1373, 1175, and 1088 cm⁻¹; ¹H-NMR (CDCl₃, 600 MHz) δ 2.47 (s, 3H), 4.35 (d, 1H, *J* = 6.0 Hz), 5.79 (d, 1H, *J* = 6.0 Hz), 7.18-7.26 (m, 5H), 7.34-7.41 (m, 5H), 7.63 (d, 2H, *J* = 7.2 Hz), and 8.15 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 22.1, 59.4, 72.7, 82.4, 128.7, 128.8, 129.4, 130.0, 130.8, 130.9, 133.4, 134.0, 134.3, 146.6, and 163.6.

(E)-3,3-Dichloro-4-phenyl-5-phenylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one

(29). To a mixture of 0.06 g (0.17 mmol) of sulfilimine **25** and 0.21 g of Zn-Cu in 5 mL of THF was slowly added 0.09 mL (0.83 mmol) of trichloroacetyl chloride at 0°C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution and washed with EtOAc. The combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.048 g (59%) of **29** as a colorless oil; IR (neat) 1764, 1375, 1173, and 1085 cm⁻¹; ¹H-NMR (CDCl₃, 600 MHz) δ 2.47 (s, 3H), 3.54 (d, 1H, *J* = 8.4 Hz), 5.66 (d, 1H, *J* = 8.4 Hz), 7.03 (d, 2H, *J* = 8.4 Hz), 7.21–7.26 (m, 4H), 7.34 (td, 1H, *J* = 7.8 and 0.6 Hz), 7.38–7.43 (m, 5H), and 8.16 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 22.0, 59.6, 67.4, 83.4, 128.9, 129.5, 129.6, 129.7, 130.0, 130.1, 134.6, 135.8, 146.5, and 163.7.

3,3-Dichloro-4,4,5-trimethyl-1-(toluene-4-sulfonyl)-5-(phenylthio)pyrrolidin-2-one

(30). To a mixture of 0.2 g (0.57 mmol) of sulfimide **26** and 0.75 g of Zn-Cu in 20 mL of THF at 0 °C was slowly added 0.32 mL (2.9 mmol) of trichloroacetyl chloride in 9 mL of THF. After stirring at 0 °C for 10 min, the reaction mixture was quenched with NaHCO₃ and the mixture was filtered and EtOAc added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.15 g (59%) of **30** as a colorless solid; mp 113–115 °C; IR (KBr) 2993, 1754, 1368, 1263, 1176, 1086, 752, and 653 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.26 (s, 3H), 1.63 (s, 3H), 1.68 (s, 3H), 2.45 (s, 3H), 7.35 (d, 2H, *J* = 8.4 Hz), 7.39–7.44 (m, 3H), 7.77 (dd, 2H, *J* = 8.0 and 1.3 Hz), and 8.18 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 19.9, 21.8, 24.0, 24.7, 54.1, 82.5, 88.4, 128.0, 129.3, 129.7, 130.0, 131.1, 134.4, 138.5, 145.7, and 164.4; Anal. Calcd. for C₂₀H₂₁Cl₂NO₃S₂: C, 52.40; H, 4.62; N, 3.06. Found: C, 52.27; H, 4.70; N, 3.07.

S-1-Cyclopentenyl-S-phenyl-N-(toluene-4-sulfonyl)sulfilimine (31). To a solution of 0.1 g (0.56 mmol) of 1-(phenylthio)cyclopentene⁸ in 20 mL of ethanol was slowly added 0.16 g (0.56 mmol) of chloramine-T trihydrate which contained 1 drop of acetic acid. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography to give 0.12 g (60%) of **31** as a colorless oil; IR (neat) 1276, 1127, 968, and 661 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.86-1.97 (m, 2H), 2.05-2.18 (m, 1H), 2.34 (s, 3H), 2.40-2.52 (m, 3H), 6.52-6.55 (m, 1H), 7.16 (d, 2H, J = 8.1 Hz), 7.42-7.52 (m, 3H), 7.62 (dd, 2H, J = 7.5 and 2.1 Hz), and 7.74 (d, 2H, J = 8.1 Hz); ¹³C-NMR (CDCl₃, 75 MHz) δ 21.7, 23.0, 29.1, 33.4, 126.4, 126.8, 129.1, 129.3, 132.1, 133.6, 138.0, 141.6, and 143.3.

S-1-Cyclohexenyl-S-phenyl-N-(toluene-4-sulfonyl)sulfilimine (32). To a solution of 0.1 g (0.53 mmol) of 1-(phenylthio)cyclohexene⁸ in 20 mL of ethanol was slowly added 0.15 g (0.53 mmol) of chloramine-T trihydrate which contained 1 drop of acetic acid. The reaction mixture was stirred at room temperature for 8 h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography to give 0.13 g (66%) of **32**⁹ as a colorless oil; IR (neat) 1282, 1142, 1088 and 966 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.44-1.66 (m, 5H), 2.11-2.25 (m, 3H), 2.35 (s, 3H), 6.67-6.71 (m, 1H), 7.16 (d, 2H, J = 8.0 Hz), 7.43-7.49 (m, 3H), 7.61 (dd, 2H, J = 7.6 and 1.6 Hz), and 7.75 (d, 2H, J = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 20.9, 21.3, 21.6, 22.1, 26.5, 126.5, 126.8, 129.2, 129.8, 131.9, 133.3, 135.8, 140.0, 141.6, and 141.9.

S-1-(2-Methyl)-cyclopentenyl-S-phenyl-N-(toluene-4-sulfonyl)sulfilimine (33). To a solution of 0.03 g (0.16 mmol) of 1-(phenylthio)-2-methylcyclopentene⁶ in 10 mL of ethanol was slowly added 0.045 g (0.16 mmol) of chloramine-T trihydrate which contained 1 drop of acetic acid. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was

purified by flash silica gel chromatography to give 0.049 g (86%) of **33** as a colorless oil; IR (neat) 1281, 1141, 1088, 959, and 750 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ 1.67–1.85 (m, 2H), 1.89–1.95 (m, 1H), 1.96 (s, 3H), 2.35 (s, 3H), 2.34–2.49 (m, 2H), 2.64–2.73 (m, 1H), 7.17 (d, 2H, $J = 8.0$ Hz), 7.44–7.48 (m, 3H), 7.56–7.59 (m, 2H), and 7.76 (d, 2H, $J = 8.0$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 15.5, 21.3, 21.6, 28.5, 39.4, 126.1, 126.5, 129.2, 129.7, 129.8, 131.5, 133.7, 141.6, 141.9, and 156.5.

3,3-Dichloro-6a-phenylthio-1-(toluene-4-sulfonyl)-hexahydrocyclopenta-

[b]pyrrol-2-one (34). To a mixture of 0.05 g (0.15 mmol) of sulfilimine **31** and 0.18 g of Zn-Cu in 5 mL of THF was slowly added 0.08 mL (0.72 mmol) of trichloroacetyl chloride at 0°C . The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO_3 solution and washed with EtOAc. The organic layer was washed with brine, dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.041 g (63%) of **34** as a white solid; mp $129\text{--}131^\circ\text{C}$; IR (neat) 1755, 1374, 1175, and 1086 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ 2.00–2.04 (m, 2H), 2.10–2.15 (m, 2H), 2.44 (s, 3H), 2.51 (ddd, 1H, $J = 14.0, 10.0$ and 7.2 Hz), 2.66 (ddd, 1H, $J = 14.0, 7.2$ and 3.6 Hz), 3.04 (t, 1H, $J = 7.2$ Hz), 7.21–7.29 (m, 4H), 7.33 (dt, 1H, $J = 7.2$ and 1.6 Hz), 7.36 (d, 2H, $J = 8.0$ Hz), and 8.14 (d, 2H, $J = 8.0$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 22.0, 25.9, 27.0, 41.5, 59.3, 83.5, 129.8, 129.9, 130.0, 130.3, 134.3, 136.6, 146.3, and 164.9; Anal. Calcd. for $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{NO}_3\text{S}_2$: C, 52.63; H, 4.20; N, 3.07.

Found: C, 52.66; H, 4.09; N, 3.19.

3,3-Dichloro-7a-phenylthio-1-(toluene-4-sulfonyl)octahydroindol-2-one (35). To a mixture of 0.11 g (0.29 mmol) of sulfilimine **32** and 0.37 g of Zn-Cu in 20 mL of THF was slowly added 0.16 mL (1.5 mmol) of trichloroacetyl chloride at 0°C . The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO_3 solution and washed with EtOAc. The combined organic layer was washed with brine, dried over anhydrous MgSO_4 and concentrated under reduced pressure.

The residue was purified by flash silica gel chromatography to give 0.086 g (65%) of **35** as a white solid; mp 176-177 °C; IR (neat) 2935, 1753, 1376, 1176 and 1083 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.60-1.66 (m, 1H), 1.78-1.91 (m, 4H), 2.01-2.05 (m, 1H), 2.27-2.36 (m, 2H), 2.44 (s, 3H), 3.00-3.07 (m, 1H), 7.26-7.29 (m, 4H), 7.33-7.37 (m, 3H), and 8.10 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 20.5, 21.9, 22.0, 34.2, 48.6, 78.3, 84.9, 129.7, 129.8, 129.8, 129.9, 130.3, 134.6, 135.9, 146.1, and 164.0; Anal. Calcd. for C₂₁H₂₁Cl₂NO₃S₂: C, 53.62; H, 4.50; N, 2.98. Found: C, 53.37; H, 4.37; N, 3.02.

3,3-Dichloro-3a-methyl-6a-phenylthio-1-(toluene-4-sulfonyl)hexahydro-cyclopenta[*b*]pyrrol-2-one (36). To a mixture of 0.045 g (0.12 mmol) of sulfilimine **33** and 0.15 g of Zn-Cu in 5 mL of THF was slowly added 0.05 mL (0.48 mmol) of trichloroacetyl chloride at 0°C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution and washed with EtOAc. The aqueous layer was washed with EtOAc and the combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.011 g (20%) of **36** as a colorless oil; IR (neat) 2968, 1758, 1369, and 1176 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.66 (s, 3H), 1.65-1.82 (m, 3H), 1.86-1.94 (m, 1H), 2.07-2.15 (m, 1H), 2.46 (s, 3H), 2.84-2.88 (m, 1H), 7.36 (d, 2 H, *J* = 8.0 Hz), 7.38-7.44 (m, 3H), 7.82-7.85 (m, 2H), and 8.21 (d, 2H, *J* = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 18.3, 21.6, 21.8, 40.1, 41.3, 62.6, 89.6, 113.3, 127.7, 129.4, 129.5, 129.8, 130.2, 135.9, 137.9, 144.1, and 165.9.

3,3-Dichloro-5-ethylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (37). To a solution of 0.23 mL (2.4 mmol) of ethyl vinyl sulfide in 50 mL of ethanol, was slowly added 0.57 g (2.0 mmol) of chloramine-T trihydrate which contained 0.1 ml of acetic acid. The reaction mixture was stirred at rt for 1 h, the solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography to

give 0.35 g (70%) of *S*-ethenyl-*S*-phenyl-*N*-(toluene-4-sulfonyl)sulfilimine as a white solid: mp 122-124 °C; IR (neat) 3052, 1275, 1140, 1088, and 966 cm⁻¹; ¹H-NMR (CDCl₃, 600 MHz) δ 1.22 (t, 3H, *J* = 7.2 Hz), 2.36 (s, 3H), 2.86 (dq, 1H, *J* = 12.0 and 7.2 Hz), 2.92 (dq, 1H, *J* = 12.0 and 7.2 Hz), 6.01 (d, 1H, *J* = 9.0 Hz), 6.17 (d, 1H, *J* = 16.2 Hz), 6.33 (dd, 1H, *J* = 16.2 and 9.0 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), and 7.74 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 7.2, 21.6, 44.5, 126.4, 127.4, 129.4, 130.9, 141.5, and 141.9. Anal. Calcd. for C₁₁H₁₅NO₂S₂: C, 51.33; H, 5.87; N, 5.44. Found: C, 51.54; H, 5.91; N, 5.51.

To a mixture of 0.12 g (0.46 mmol) of above sulfilimine and 0.6 g of Zn-Cu in 10 ml of THF was slowly added 0.26 mL (2.3 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through celite into a cold saturated aqueous NaHCO₃ solution and washed with EtOAc. After separating the organic layer, the aqueous layer was washed with EtOAc. The combined organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.11 g (68%) of **37** as a white solid: mp 135-136 °C; IR (neat) 1756, 1371, 1172, 1068, and 960 cm⁻¹; ¹H-NMR (CDCl₃, 600 MHz) δ 1.30 (t, 3H, *J* = 7.2 Hz), 2.45 (s, 3H), 2.89 (dq, 1H, *J* = 12.0 and 7.2 Hz), 2.94 (dq, 1H, *J* = 12.0 and 7.2 Hz), 3.02 (dd, 1H, *J* = 15.0 and 3.6 Hz), 3.39 (dd, 1H, *J* = 15.0 and 7.2 Hz), 5.39 (dd, 1H, *J* = 7.2 and 3.6 Hz), 7.36 (d, 2H, *J* = 8.4 Hz), and 8.05 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃, 150 MHz) δ 14.9, 22.0, 28.4, 50.8, 62.3, 78.7, 129.3, 129.9, 134.3, 146.4, and 163.8. Anal. Calcd. for C₁₃H₁₅Cl₂NO₃S₂: C, 42.39; H, 4.11; N, 3.80. Found: C, 42.41; H, 4.10; N, 3.81.

5-Ethylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (38). To a mixture containing 0.05 g (0.14 mmol) of sulfide **37** and 0.17 g Zn metal in 8 mL of EtOH was added 0.04 mL (0.7 mmol) of acetic acid and 0.1 mL (0.7 mmol) of TEMDA. The mixture was stirred at rt for 1 h and filtered through Celite. The solvent was removed under

reduced pressure and the residue was dissolved in EtOAc and washed with water. The organic layer was separated, dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.034 g (88%) of **38** as a white solid; mp 114-116 °C; IR (neat) 1742, 1359, 1165, 1088 and 814 cm^{-1} ; ^1H -NMR (CDCl_3 , 400 MHz) δ 1.25 (t, 3H, J = 7.2 Hz), 2.14-2.20 (m, 1H), 2.37-2.43 (m, 1H), 2.42 (s, 3H), 2.52-2.75 (m, 4H), 5.49 (d, 1H, J = 7.2 Hz), 7.30 (d, 2H, J = 8.0 Hz), and 8.02 (d, 2H, J = 8.0 Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 14.6, 21.9, 25.6, 29.5, 31.1, 64.7, 129.2, 129.5, 135.5, 145.4, and 172.6; Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}_2$: C, 52.15; H, 5.72; N, 4.68. Found: C, 52.30; H, 5.78; N, 4.66.

2-(tert-Butyl-dimethylsilanyloxy)-1-(toluene-4-sulfonyl)-1H-pyrrole (39). To a solution of 0.06 g (0.2 mmol) of sulfide **38** in 5 mL of CH_2Cl_2 was added 0.07 g (0.4 mmol) of *m*-chloroperbenzoic acid at rt. The reaction mixture was stirred for 2h and was then quenched by a saturated aqueous NaHCO_3 solution. The organic layer was separated, washed with a saturated aqueous NaHCO_3 solution, and dried over MgSO_4 . Concentration under reduced pressure followed by flash silica gel chromatography provided 0.044 g (94%) of 1-(toluene-4-sulfonyl)-1,5-dihydropyrrol-2-one as a white solid: IR (neat) 1716, 1357, 1169, and 799 cm^{-1} ; ^1H -NMR (CDCl_3 , 600 MHz) δ 2.43 (s, 3H), 4.50 (quint, 2H, J = 1.8 Hz), 6.07 (dt, 1H, J = 6.0 and 1.8 Hz), 7.24 (dt, 1H, J = 6.0 and 1.8 Hz), 7.33 (d, 2H, J = 7.8 Hz), and 7.95 (d, 2H, J = 7.8 Hz); ^{13}C -NMR (CDCl_3 , 150 MHz) δ 21.9, 52.5, 127.4, 128.2, 130.0, 135.5, 145.4, 146.7, and 168.5.

To a solution of 0.04 g (0.17 mmol) of above pyrrolinone in 2 mL of CH_2Cl_2 at rt, was added 0.07 mL (0.5 mmol) of 2,6-lutidine and 0.04 mL (0.18 mmol) of TBSOTf. The reaction mixture was stirred at rt for 15 min and was concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.05 g (86%) of **39** as a clear oil: IR (neat) 2930, 1585,

1179, 1154, 843 and 672 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ 0.18 (s, 6H), 0.93 (s, 9H), 2.39 (s, 3H), 5.15 (dd, 1H, $J = 3.6$ and 1.8 Hz), 5.98 (t, 1H, $J = 3.6$ Hz), 6.78 (dd, 1H, $J = 3.6$ and 1.8 Hz), 7.25 (d, 2H, $J = 8.4$ Hz), and 7.71 (d, 2H, $J = 8.4$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ -4.8, 18.4, 21.8, 25.8, 92.3, 109.7, 113.9, 127.5, 129.8, 136.6, 143.4, and 144.7.

1-(Toluene-4-sulfonyl)-pyrrolidine (40). To a solution of 0.03 g (0.1 mmol) of amide **38** in 2 mL of THF was added 0.3 mL of $\text{BH}_3\cdot\text{THF}$ (1.0 M in THF) at 0 °C. The reaction mixture was stirred for 20 h, quenched with MeOH and concentrated under reduced pressure. Purification by flash silica gel chromatography gave 0.02 g (83%) of **40** as a white solid¹⁰: $^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ 1.73-1.76 (m, 4H), 2.43 (s, 3H), 3.21-3.34 (m, 4H), 7.32 (d, 2H, $J = 7.8$ Hz), and 7.72 (d, 2H, $J = 7.8$ Hz).); $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ 21.7, 25.4, 48.1, 127.8, 130.0, 134.2, and 143.5.

3,3-Dichloro-5-ethylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-ol (41). To a solution of 0.1 g (0.3 mmol) of sulfide **36** in 3 mL of THF at 0 °C, was added 0.8 mL (0.81 mmol) of $\text{BH}_3\cdot\text{THF}$ (1.0M). The reaction was stirred at rt for 12 h and was then quenched with MeOH. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine, dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.084 g (84%) of **41** as a white solid: mp 119-120 °C; IR (neat) 3478, 2970, 1343, 1165, and 1082 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ 0.95 (t, 3H, $J = 7.2$ Hz), 2.31 (dq, 1H, $J = 12.0$ and 7.2 Hz), 2.41 (s, 3H), 2.49 (dq, 1H, $J = 12.0$ and 7.2 Hz), 2.87 (dd, 1H, $J = 14.0$ and 9.2 Hz), 2.98 (dd, 1H, $J = 14.0$ and 6.8 Hz), 3.60 (brs, 1H), 4.99 (dd, 1H, $J = 9.2$ and 6.8 Hz), 5.71 (s, 1H), 7.28 (d, 2H, $J = 8.0$ Hz), and 7.87 (d, 2H, $J = 8.0$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 13.9, 21.8, 23.3, 49.3, 62.9, 86.2, 89.9, 128.0, 130.0, 137.3,

and 144.2; Anal. Calcd. for $C_{13}H_{17}Cl_2NO_3S_2$: C, 42.16; H, 4.63; N, 3.78. Found: C, 42.20; H, 4.54; N, 3.83.

***N*-(4-hydroxybutyl)-4-toluenesulfonamide (42).** To a solution of 0.05 g (0.14 mmol) of sulfide **37** in 2 mL MeOH was added 0.026 g (0.67 mmol) of $NaBH_4$. The reaction mixture was stirred at rt for 20 min, and quenched with water. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by flash silica gel chromatography gave 0.037 g (92%) of *N*-(3,3-dichloro-4-hydroxybutyl)-4-toluenesulfonamide as a white solid: mp 108-109 °C; IR (neat) 3380, 3155, 1305, 1151 and 1048 cm^{-1} ; 1H -NMR ($CDCl_3$, 600 MHz) δ 2.43 (s, 3H), 2.46 (t, 2H, $J = 7.2$ Hz), 2.67 (t, 1H, $J = 7.2$ Hz), 3.30 (q, 2H, $J = 7.2$ Hz), 3.88 (d, 2H, $J = 7.2$ Hz), 4.98 (t, 1H, $J = 7.2$ Hz), 7.32 (d, 2H, $J = 8.4$ Hz), and 7.75 (d, 2H, $J = 8.4$ Hz); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ 21.8, 39.7, 43.7, 72.3, 91.6, 127.3, 130.1, 136.7, and 144.0; Anal. Calcd. for $C_{11}H_{15}Cl_2NO_3S$: C, 42.32; H, 4.84; N, 4.49. Found: C, 42.27; H, 4.79; N, 4.56.

To a mixture containing 0.03 g (0.1 mmol) of above amide and 0.12 g of Zn in 5 mL of EtOH was added 0.03 mL (0.5 mmol) of acetic acid and 0.07 mL (0.5 mmol) of TEMDA. The mixture was stirred at rt for 1 h and filtered through celite. The solvent was removed under reduced pressure and the residue was dissolved in EtOAc and washed with water. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.021 g (88%) of **42** as a colorless oil¹¹: 1H -NMR ($CDCl_3$, 400 MHz) δ 1.64 (m, 1H), 1.70 (quint, 2H, $J = 6.0$ Hz), 2.42 (s, 3H), 3.10 (q, 2H, $J = 6.0$ Hz), 3.70-3.80 (m, 2H), 4.81-4.88 (m, 1H), 7.30 (d, 2H, $J = 8.0$ Hz), and 7.73 (d, 2H, $J = 8.0$ Hz).

6a-Ethylthio-6-(toluene-4-sulfonyl)-3a,4,6,6a-tetrahydrofuro[2,3-*b*]pyrrol-5-one (43). To a mixture containing 0.16 g (0.39 mmol) of sulfide **17** and 0.5 g of Zn

metal in 15 mL of EtOH, was added 0.12 mL (1.9 mmol) of acetic acid and 0.29 mL (1.9 mmol) of TEMDA. The mixture was stirred at rt for 1 h and filtered through celite. The solvent was removed under reduced pressure and the residue was dissolved in EtOAc and washed with water. The organic layer was separated, dried over anhydrous MgSO_4 and concentrated under reduced pressure. Silica gel chromatography gave 0.11 g (84 %) of **43** as a white solid: mp 129-131 °C; IR (neat) 3104, 1740, 1371, 1174, and 1011 cm^{-1} ; ^1H -NMR (CDCl_3 , 400 MHz) δ 1.29 (t, 3H, J = 7.2 Hz), 2.39 (dd, 1H, J = 17.6 and 2.4 Hz), 2.40 (s, 3H), 2.65 (dq, 1H, J = 11.6 and 7.2 Hz), 2.76 (dd, 1H, J = 17.6 and 9.2 Hz), 2.79 (dq, 1H, J = 11.6 and 7.2 Hz), 3.80 (dq, 1H, J = 9.2 and 2.4 Hz), 5.01 (t, 1H, J = 2.4 Hz), 6.35 (t, 1H, J = 2.4 Hz), 7.28 (d, 2H, J = 8.4 Hz), and 7.99 (d, 2H, J = 8.4 Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 13.8, 21.9, 25.0, 35.4, 49.2, 105.6, 108.8, 129.3, 129.4, 135.6, 145.1, 145.4, and 171.3; Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}_2$: C, 53.08; H, 5.05; N, 4.13. Found: C, 53.11; H, 5.08; N, 4.11.

***N*-{2,2-Dichloro-2-[2-(ethylthio)furan-3-yl]-acetyl}-4-toluenesulfonamide (**44**).**

A solution of containing 0.02 g (0.05 mmol) of sulfide **17** and 0.1 mL of TFA in 1 mL of toluene was subjected to microwave irradiation (200 W, 100°C) for 30 min. The resulting mixture was diluted with H_2O and extracted with EtOAc. The organic layer was washed with a saturated aqueous NaHCO_3 , brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.014 g (71%) of amide **44** as a yellow oil: IR (neat) 3255, 1721, 1638, 1408, and 1192 cm^{-1} ; ^1H -NMR (CDCl_3 , 400 MHz) δ 1.40 (t, 3H, J = 7.2 Hz), 2.42 (s, 3H), 3.16 (q, 2H, J = 7.2 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.34 (d, 1H, J = 2.0 Hz), 7.37 (d, 1H, J = 2.0 Hz), and 7.98 (d, 2H, J = 8.0 Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 15.0, 21.9, 25.2, 112.5, 116.4, 128.7, 129.9, 135.3, 143.4, 145.8, 158.5, 166.3, and 176.2.

4,4-Dichloro-6a-methyl-6-(toluene-4-sulfonyl)-3a,4,6,6a-tetrahydrofuro[2,3-b]pyrrol-5-one (45). To a solution of 0.04 g (0.10 mmol) of sulfide **17** in 3 mL of CH₂Cl₂ at 0 °C was added 0.085 g (0.5 mmol) of *m*-chloroperbenzoic acid. After stirring at rt for 32 h the mixture was quenched with H₂O and extracted with EtOAc. The organic layer was washed with a saturated aqueous NaHCO₃, brine, and dried over Na₂SO₄. Concentration under reduced pressure followed by flash silica gel chromatography provided 0.03 g (70%) of 4,4-dichloro-6a-ethane-sulfonyl-6-(toluene-4-sulfonyl)-3a,4,6,6a-tetrahydro-furo[2,3-*b*]pyrrol-5-one as a colorless oil: ¹H-NMR (CDCl₃, 400 MHz) δ 1.55 (t, 3H, *J* = 7.6 Hz), 2.45 (s, 3H), 3.72 (dq, 1H, *J* = 14.0 and 7.6 Hz), 3.84 (dq, 1H, *J* = 14.0 and 7.6 Hz), 5.26 (t, 1H, *J* = 2.8 Hz), 5.36 (t, 1H, *J* = 2.8 Hz), 6.48 (t, 1H, *J* = 2.8 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), and 8.07 (d, 2H, *J* = 8.0 Hz).

To a solution of 0.02 g (0.05 mmol) of the above sulfone in 2 mL of CH₂Cl₂ at rt was added 0.1 mL (0.2 mmol) of AlMe₃ (2.0 M in toluene). After heating at reflux for 36 h, the reaction was quenched with a 10% aqueous solution of Rochelle salt and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.013 g (70%) of **45** as a white solid: mp 147-148 °C; IR (KBr) 3116, 1765, 1376, 1191, 1038, 977, 817, and 665 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 2.27 (3H, s), 2.44 (3H, s), 3.97 (1H, t, *J* = 2.4 Hz), 5.01 (1H, t, *J* = 2.4 Hz), 6.22 (1H, t, *J* = 2.4 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 7.96 (2H, d, *J* = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 21.7, 24.7, 65.7, 80.9, 101.6, 102.0, 129.0, 129.5, 134.5, 145.8, 145.9, and 163.7; Anal. Calcd. for C₁₄H₁₃Cl₂NO₄S: C, 46.42; H, 3.62; N, 3.87. Found: C, 46.54; H, 3.71; N, 3.90.

References:

(1) Johnson, C. R.; Mori, K.; Nakanishi, A. *J. Org. Chem.* **1979**, *44*, 2065.

- (2) Node, M.; Nishide, K.; Ohta, K.; Fujita, E. *Tetrahedron Lett.* **1982**, 23, 689.
- (3) Wu, H.-J.; Chuang, C.-T. *J. Org. Chem.* **1998**, 63, 5064.
- (4) Goldman, D.; Liotta, D.; Saindane, S.; Waykole, L.; Bowen, P. *Tetrahedron Lett.* **1983**, 24, 5835.
- (5) Marino, J. P.; Bogdan, S.; Kimura, K. *J. Am. Chem. Soc.* **1992**, 114, 5566.
- (6) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, 105, 5075.
- (7) Rayner, C. P.; Clark, A. J.; Rooke, S. M.; Sparey, T. J.; Taylor, P. C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 79.
- (8) Qian, D. Q.; Shine, H. J.; Guzman-Jimenez, I. Y.; Thurston, J. H.; Whitmire, K. H. *J. Org. Chem.* **2002**, 67, 4030.
- (9) Kakimoto, M.; Yamamoto, T.; Okawara, M. *Tetrahedron Lett.* **1979**, 20, 623.
- (10) Zhu, S.; Jin, G.; Xu, Y. *Tetrahedron* **2003**, 59, 4389.
- (11) Bailey, T. R.; Garigipati, R. S.; Morton, J. A.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, 106, 3240.

3eq. 673-01-0010
[Full 1D NMR run: 8/2/01]

Exp 061-013
 00120 Temp: 000000 0001

Sample: 075-018
 Run Date: 08/11/11

STANDARD LI OBSERVE

NAME: STALL

DATE	TIME	DATE	TIME	DATE	TIME
2007-07-23	10:00	2007-07-23	10:00	2007-07-23	10:00
11:00	12:00	11:00	12:00	11:00	12:00
13:00	14:00	13:00	14:00	13:00	14:00
15:00	16:00	15:00	16:00	15:00	16:00
17:00	18:00	17:00	18:00	17:00	18:00
19:00	20:00	19:00	20:00	19:00	20:00
21:00	22:00	21:00	22:00	21:00	22:00
23:00	24:00	23:00	24:00	23:00	24:00
25:00	26:00	25:00	26:00	25:00	26:00
27:00	28:00	27:00	28:00	27:00	28:00
29:00	30:00	29:00	30:00	29:00	30:00
31:00	32:00	31:00	32:00	31:00	32:00
33:00	34:00	33:00	34:00	33:00	34:00
35:00	36:00	35:00	36:00	35:00	36:00
37:00	38:00	37:00	38:00	37:00	38:00
39:00	40:00	39:00	40:00	39:00	40:00
41:00	42:00	41:00	42:00	41:00	42:00
43:00	44:00	43:00	44:00	43:00	44:00
45:00	46:00	45:00	46:00	45:00	46:00
47:00	48:00	47:00	48:00	47:00	48:00
49:00	50:00	49:00	50:00	49:00	50:00
51:00	52:00	51:00	52:00	51:00	52:00
53:00	54:00	53:00	54:00	53:00	54:00
55:00	56:00	55:00	56:00	55:00	56:00
57:00	58:00	57:00	58:00	57:00	58:00
59:00	60:00	59:00	60:00	59:00	60:00
61:00	62:00	61:00	62:00	61:00	62:00
63:00	64:00	63:00	64:00	63:00	64:00
65:00	66:00	65:00	66:00	65:00	66:00
67:00	68:00	67:00	68:00	67:00	68:00
69:00	70:00	69:00	70:00	69:00	70:00
71:00	72:00	71:00	72:00	71:00	72:00
73:00	74:00	73:00	74:00	73:00	74:00
75:00	76:00	75:00	76:00	75:00	76:00
77:00	78:00	77:00	78:00	77:00	78:00
79:00	80:00	79:00	80:00	79:00	80:00
81:00	82:00	81:00	82:00	81:00	82:00
83:00	84:00	83:00	84:00	83:00	84:00
85:00	86:00	85:00	86:00	85:00	86:00
87:00	88:00	87:00	88:00	87:00	88:00
89:00	90:00	89:00	90:00	89:00	90:00
91:00	92:00	91:00	92:00	91:00	92:00
93:00	94:00	93:00	94:00	93:00	94:00
95:00	96:00	95:00	96:00	95:00	96:00
97:00	98:00	97:00	98:00	97:00	98:00
99:00	100:00	99:00	100:00	99:00	100:00

Seq-J41-3
Pulse Sequence: zgpg30

Exp 310-8

[P15: 56: 100000: 82.00]

20-198
 01100 Sequence: 23001

Ensemble Equivalence: 88:10

Exercice 10 : 20 points

1105 2-2

0153-1-a-2.3
 P0153-1-a-2.3