

**Synthesis and Reactivity of Unique Heterocyclic Structures
en route to Substituted Diamines**

Supplementary Material

(19 pages)

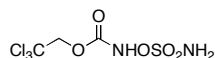
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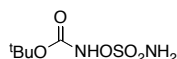
General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using glassware that was flame-dried under vacuum (~1 Torr). Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (~15 Torr) by rotary evaporation. Solvents were purified by passage under 12 psi N₂ through activated alumina columns. Chromatography was performed on Silicycle Silia-P Silica Gel (40–63 μm). Compounds purified by chromatography were typically applied to the adsorbent bed using the indicated solvent conditions with a minimum amount of added chloroform as needed for solubility. High performance liquid chromatography (HPLC) was performed on a Hewlett-Packard 1100 Series. Thin layer chromatography was performed on Whatman Partisil K6F Silica Gel 60 Å plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching or by staining with ninhydrin, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM).

Nuclear magnetic resonance (NMR) spectra were acquired on either a Varian Mercury-400 operating at 400 and 100 MHz or a Varian Inova-500 operating at 500 and 125 MHz for ¹H and ¹³C, respectively, and are referenced internally according to residual solvent signals. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet), integration, coupling constant (Hz). Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Thermo-Nicolet IR300 spectrometer as thin films using NaCl salt plates or as KBr pellets and are reported in frequency of absorption. High-resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

General procedures and characterization data for all new compounds

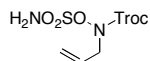


Formic acid (1.65 mL, 43.5 mmol, 2.0 equiv) was added dropwise to ice-cold chlorosulfonyl isocyanate (3.77 mL, 43.5 mmol, 2.0 equiv) with vigorous stirring. When the evolution of gas had ceased, 10 mL of CH₃CN was added. The mixture was stirred at 0 °C for 2 h and then at room temperature for 6 h. NOTE: Solidification of the reaction mixture may occur prior to the addition of CH₃CN. The reaction flask was placed in an ice bath and a solution of TrocNHOH¹ (6.25 g, 21.7 mmol) in 35 mL of DMA was added dropwise. The solution was warmed to room temperature and stirred for 12 h. The reaction was quenched by the addition of 500 mL of H₂O, transferred to a separatory funnel, and extracted with 2 x 300 mL of EtOAc. The combined organic extracts were washed successively with 3 x 300 mL of H₂O and 2 x 200 mL of saturated aqueous NaCl, dried over MgSO₄, and concentrated under reduced pressure to afford TrocNHOSO₂NH₂ (5.94 g, 95%) as a white solid. mp = ~140 °C (decomp); TLC R_f = 0.51 (30% EtOAc/PE); ¹H NMR (CD₃CN, 400 MHz) δ 9.68 (br s, 1H), 6.19 (br s, 2H), 4.88 (s, 2H) ppm; ¹³C NMR (CD₃CN, 100 MHz) δ 155.6, 95.4, 75.5 ppm; IR (thin film) ν 3627, 3282, 2965, 1763, 1395, 1245, 1196, 1123, 1067, 737 cm⁻¹; HRMS (ES⁺) calcd for C₃H₅Cl₃N₂O₅SNa⁺ 308.8883 found 308.8884 (MNa⁺).

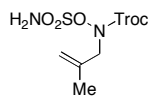


Formic acid (2.62 mL, 68.9 mmol, 2.0 equiv) was added dropwise to ice-cold chlorosulfonyl isocyanate (6.0 mL, 68.9 mmol, 2.0 equiv) with vigorous stirring. When the evolution of gas had ceased, 15 mL of CH₃CN was added. The mixture was stirred at 0 °C for 2 h and then at room temperature for 6 h. NOTE: Solidification of the reaction mixture may occur prior to the addition of acetonitrile. The reaction flask was placed in an ice bath and a solution of BocNHOH² (4.59 g, 34.5 mmol) in 55 mL of DMA was added dropwise. The solution was warmed to 25 °C and stirred for 12 h. The reaction was quenched by the addition of 500 mL of H₂O, transferred to a separatory funnel, and extracted with 6 x 100 mL of EtOAc. The combined organic extracts were washed successively with 4 x 300 mL of H₂O and 2 x 200 mL of saturated aqueous NaCl, dried over MgSO₄, and concentrated under reduced pressure. The resulting white solid was suspended in cold chloroform, triturated, and filtered to afford BocNHOSO₂NH₂ (5.54 g, 76%). mp = ~140 °C (decomp); TLC R_f = 0.31 (2:1 hexanes/EtOAc); ¹H NMR (CD₃CN, 400 MHz) δ 8.88 (br s, 1H), 6.01 (br s, 2H), 1.48 (s, 9H) ppm; ¹³C NMR (CD₃CN, 100 MHz) δ 165.6, 131.9, 127.9, 115.6, 56.7 ppm; IR (KBr pellet) ν 3340, 3299, 3188, 2983, 2954, 2849, 2825, 1597, 1498, 1388, 1354, 1268, 1195, 1161, 733 cm⁻¹; HRMS (ES⁺) calcd for C₅H₁₂N₂O₅SNa⁺ 235.0365 found 235.0363 (MNa⁺).

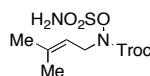
General procedure for substrate preparation using Mitsunobu conditions. Neat diethyl azodicarboxylate (0.20 mL, 1.3 mmol, 1.3 equiv) was added dropwise to an ice-cold solution of alcohol (1.0 mmol), TrocNHOSO₂NH₂ (0.37 g, 1.3 mmol, 1.3 equiv), and PPh₃ (0.34 g, 1.3 mmol, 1.3 equiv) in 5 mL of THF. The yellow solution was warmed to room temperature and stirred until the alcohol was completely consumed, as determined by TLC (10–15 h). All volatile materials were then removed under reduced pressure. The oily residue was redissolved in 2.0 mL of a 1:1 hexanes/EtOAc solution and concentrated. The desired product was isolated following purification by chromatography on silica gel (conditions given below).



Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (100%): TLC R_f = 0.57 (1:1 hexanes/EtOAc); ¹H NMR (CD₃CN, 400 MHz) δ 6.22 (br s, 2H), 5.99-5.87 (m, 1H), 5.36-5.26 (m, 2H), 4.91 (s, 2H), 4.37 (br d, 2H, J = 4.1 Hz) ppm; ¹³C NMR (CD₃CN, 100 MHz) δ 156.0, 131.3, 120.4, 95.4, 76.3, 55.7 ppm; IR (thin film) ν 3351, 3258, 3107, 2963, 2923, 1759, 1562, 1393, 1320, 1228, 1194, 1151, 1091, 941, 726, 705 cm⁻¹; HRMS (ES⁺) calcd for C₆H₉Cl₃N₂O₅SNa⁺ 348.9196 found 348.9193 (MNa⁺).

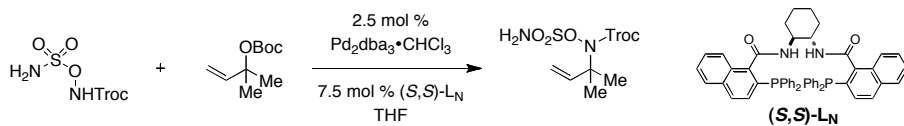


Purified by chromatography on silica gel (gradient elution: 5:1 hexanes/EtOAc→4:1 hexanes/EtOAc); white solid (100%): TLC R_f = 0.59 (1:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 5.25 (br s, 2H), 5.01-4.94 (m, 2H), 4.84 (s, 2H), 4.38 (s, 2H), 1.76 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 155.1, 137.9, 115.1, 94.4, 76.0, 57.9, 20.3 ppm; IR (thin film) ν 3369, 3275, 3088, 2975, 1741, 1396, 1344, 1229, 1198, 1110, 807, 744 cm⁻¹; HRMS (ES⁺) calcd for C₇H₁₁Cl₃N₂O₅SNa⁺ 362.9352 found 362.9350 (MNa⁺).

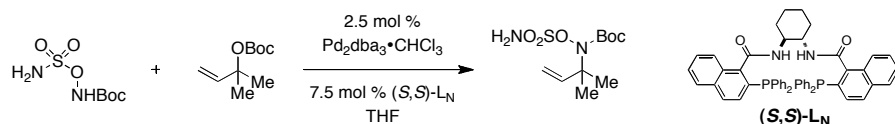


Purified by chromatography on silica gel (5:1 hexanes/EtOAc); white solid (100%): TLC R_f = 0.70 (1:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 5.35-5.30 (m, 2H), 4.84 (s, 3H), 4.39 (d, 2H, J = 7.2 Hz), 1.75 (s, 3H), 1.72 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 155.6, 140.3, 115.7, 94.5, 75.9, 50.8, 26.0, 18.2 ppm; IR (thin film) ν 3371, 3277, 2972, 1742, 1397, 1338, 1237, 1192, 803, 743, 721, 614 cm⁻¹; HRMS (ES⁺) calcd for C₈H₁₃Cl₃N₂O₅SNa⁺ 376.9508 found 376.9488 (MNa⁺).

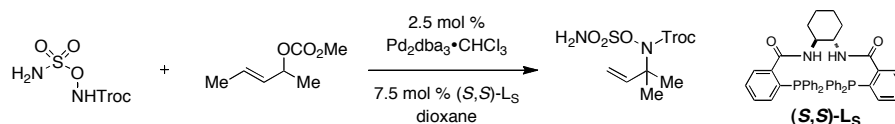
Procedures for substrate preparation using Pd-catalyzed allylic amination conditions.



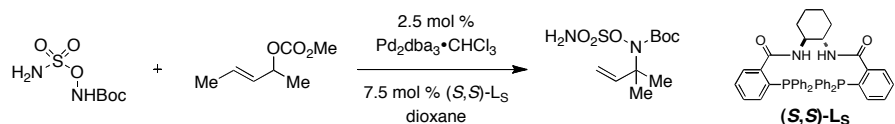
A solution of Pd₂dba₃•CHCl₃ (4.1 mg, 4 μmol, 2.5 mol %) and (S,S)-L_N (10.3 mg, 0.013 mmol, 7.5 mol %) in 0.5 mL of THF was stirred for 20 min at room temperature and then added to a solution of allylic carbonate (40 mg, 0.21 mmol, 1.2 equiv), TrocNHOSO₂NH₂ (50 mg, 0.17 mmol), and Li₂CO₃ (3.2 mg, 0.044 mmol, 0.25 equiv) in 1.0 mL of THF. The reaction was stirred for 12 h then concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 PE/EtOAc) afforded the desired product (45 mg, 85%) as a clear oil. Regioselectivity of branched/linear product > 20:1, as determined by ¹H NMR. TLC R_f = 0.35 (4:1 PE/EtOAc); ¹H NMR (branched product, CDCl₃, 300 MHz) δ 6.09 (dd, 1H, J = 17.5, 10.7 Hz), 5.33 (br s, 2H), 5.09 (d, 1H, J = 17.5 Hz), 5.03 (d, 1H, J = 10.7 Hz), 4.82 (br s, 2H), 1.58 (s, 6H) ppm; ¹³C NMR (CDCl₃, 75 MHz) 156.5, 141.6, 113.7, 94.3, 76.3, 67.7, 28.2 ppm; IR (thin film) ν 3386, 3283, 2963, 174, 1397, 1199 cm⁻¹; HRMS (ES⁺) calcd for C₈H₁₃Cl₃N₂O₅SNa⁺ 376.9508 found 376.9513 (MNa⁺).



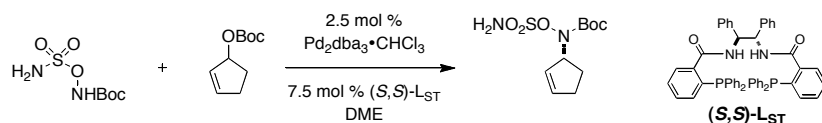
A solution of $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (6.2 mg, 6 μmol , 2.5 mol %) and $(S,S)\text{-L}_N$ (14.2 mg, 0.018 mmol, 7.5 mol %) in 0.5 mL of THF was stirred for 20 min at room temperature and then added to a solution of allylic carbonate (53 mg, 0.28 mmol, 1.2 equiv), $\text{BocNHOSO}_2\text{NH}_2$ (50 mg, 0.24 mmol), and Li_2CO_3 (4.3 mg, 0.059 mmol, 0.25 equiv) in 1.5 mL of THF. The reaction was stirred for 12 h then concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 PE/EtOAc) afforded the desired product (40 mg, 60%) as a clear oil. TLC $R_f = 0.28$ (4:1 PE/EtOAc); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 6.07 (dd, 1H, $J = 17.5, 10.8$ Hz), 5.30 (br s, 2H), 5.09 (d, 1H, $J = 17.5$ Hz), 5.03 (d, 1H, $J = 10.8$ Hz), 1.49-1.47 (m, 15H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 157.4, 143.0, 112.1, 85.0, 66.7, 28.2, 27.3 ppm; IR (thin film) ν 3365, 3278, 2983, 2937, 1723, 1395, 1295, 1198 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_5\text{SNa}^+$ 303.0991 found 303.1001 (MNa^+).



A solution of $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (4.1 mg, 4 μmol , 2.5 mol %) and $(S,S)\text{-L}_S$ (9.0 mg, 0.013 mmol, 7.5 mol %) in 0.5 mL of dioxane was stirred for 20 min at room temperature and then added to a solution of allylic carbonate (30 mg, 0.21 mmol, 1.2 equiv) and $\text{TrocNHOSO}_2\text{NH}_2$ (50 mg, 0.17 mmol) in 0.2 mL of dioxane. The reaction was stirred 12 h then concentrated under reduced pressure. Purification by chromatography on silica gel (15% EtOAc/PE) afforded the desired product (52 mg, 99%, 84% ee) as a clear oil. TLC $R_f = 0.41$ (4:1 PE/EtOAc); $[\alpha]_D^{25} -6.05$ (84% ee, c 0.60, CHCl_3); HPLC $R_t = 14.87$ (major) and 17.93 min (Chiralcel[®] OJ chiral column, $\lambda = 214$ nm, isocratic elution: 90:10 heptane/ PrOH , flow rate = 1.0 mL/min); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 5.83-5.70 (m, 1H), 5.68-5.57 (m, 1H), 5.18 (br s, 2H), 4.89 (d, 1H, $J = 12.0$ Hz), 4.81 (d, 1H, $J = 12.0$ Hz), 4.73-4.62 (m, 1H), 1.70 (d, 3H, $J = 6.2$ Hz), 1.46 (d, 3H, $J = 7.1$ Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) 150.3, 130.1, 128.3, 97.1, 76.0, 62.0, 26.2 ppm; IR (thin film) ν 3376, 3283, 2963, 1741 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_8\text{H}_{13}\text{Cl}_3\text{N}_2\text{O}_5\text{SNa}^+$ 376.9508 found 376.9506 (MNa^+).

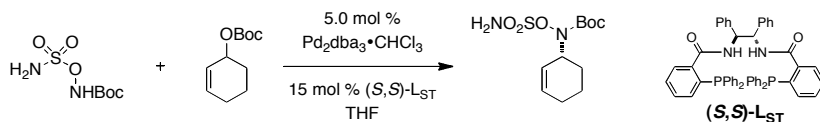


A solution of $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (6.2 mg, 6 μmol , 2.5 mol %) and $(S,S)\text{-L}_S$ (12.5 mg, 0.018 mmol, 7.5 mol %) in 0.5 mL of dioxane was stirred for 20 min at room temperature and then added to a solution of allylic carbonate (41 mg, 0.28 mmol, 1.2 equiv) and $\text{BocNHOSO}_2\text{NH}_2$ (50 mg, 0.24 mmol) in 0.5 mL of dioxane. The reaction was stirred for 12 h then concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 PE/EtOAc) afforded the desired product (63 mg, 95%, 86% ee) as a clear oil. TLC $R_f = 0.70$ (3:2 PE/EtOAc); HPLC $R_t = 18.22$ (major) and 22.59 min (Chiralcel[®] OJ chiral column, $\lambda = 214$ nm, isocratic elution: 95:5 heptane/ PrOH , flow rate = 0.9 mL/min); $^1\text{H NMR}$ (DMSO , 80 $^\circ\text{C}$, 300 MHz) δ 7.63 (s, 2H), 5.69-5.44 (m, 2H), 4.45-4.32 (m, 1H), 1.66 (d, 3H, $J = 5.3$ Hz), 1.44 (s, 9H), 1.31 (d, 3H, $J = 6.9$ Hz) ppm; $^{13}\text{C NMR}$ (DMSO , 75 MHz) 155.8, 122.6, 126.7, 82.0, 60.7, 23.4, 17.5, 16.8 ppm; IR (thin film) ν 3361, 3273, 2980, 2936, 1724, 1396, 1294, 1197 cm^{-1} .



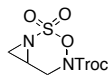
A solution of $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (6.2 mg, 6 μmol , 2.5 mol %) and $(S,S)\text{-L}_{ST}$ (14.2 mg, 18 μmol , 7.5 mol %) in 1.0 mL of DME was stirred for 20 min at 0 $^\circ\text{C}$ and then added to a solution of allylic carbonate (52 mg, 0.28 mmol, 1.2 equiv) and $\text{BocNHOSO}_2\text{NH}_2$ (50 mg, 0.24 mmol) in 3.7 mL of DME. The reaction was stirred at 4 $^\circ\text{C}$ for 12 h then concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 PE/EtOAc) afforded the desired product (49 mg, 75%, 82% ee) as an oil. TLC $R_f = 0.77$ (3:2 PE/EtOAc); $[\alpha]_D^{25} +50.78$ (82% ee, c 0.42,

CHCl₃); HPLC R_t = 23.44 (major) and 13.88 (minor) min (Chiralcel[®] AD chiral column, λ = 214 nm, isocratic elution: 90:10 heptane/ⁱPrOH, 1.0 mL/min); ¹H NMR (CDCl₃, 500 MHz) δ 6.07-6.01 (m, 1H), 5.76-5.68 (m, 1H), 5.29 (br s, 2H), 5.20-5.11 (m, 1H), 2.56-2.45 (m, 1H), 2.35-2.28 (m, 1H), 2.22-2.10 (m, 1H), 2.02-1.90 (m, 1H), 1.51 (s, 9H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 157.1, 136.9, 127.7, 84.6, 69.7, 31.6, 23.2, 26.6 ppm; IR (thin film) ν 3360, 3278, 2979, 2936, 1728, 1395 cm⁻¹; HRMS (ES⁺) calcd for C₁₀H₁₈N₂O₅SNa⁺ 301.0834 found 301.0832 (MNa⁺).

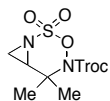


To a flame dried vial containing Pd₂dba₃•CHCl₃ (12 mg, 0.012 mmol, 5.0 mol %) and (S,S)-L₈ (24 mg, 0.034 mmol, 15 mol %) was added 0.5 mL of THF. The catalyst was stirred for 20 minutes at room temperature and then added to a solution of allylic carbonate (50 mg, 0.25 mmol, 1.1 equiv) and BocNHOSO₂NH₂ (49 mg, 0.23 mmol) in 2.0 mL of THF. The reaction was stirred for 24 h then concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 hexanes/EtOAc) afforded the desired product (51 mg, 77%, 88% ee) as a white solid. mp = 65–67 °C; TLC R_f = 0.2 (4:1 hexanes/EtOAc); [α]_D²⁵ 44.8 (88% ee, c. 0.47, CH₂Cl₂); HPLC R_t = 48.3 (minor) and 52.8 (major) min (Chiralcel[®] OD chiral column, λ = 204 nm, isocratic elution: 97:3 heptane/ⁱPrOH, 1.0 mL/min); ¹H NMR (CDCl₃, 500 MHz) δ 5.94-5.81 (m, 1H), 5.71-5.59 (m, 1H), 5.15 (s, 2H), 4.60 (ddd, 1H, J = 8.3, 5.8, 2.5 Hz), 2.10-1.80 (m, 5H) 1.67-1.56 (m, 1H), 1.52 (s, 9H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 156.9, 131.9, 125.5, 84.5, 59.9, 28.1, 25.9, 24.3, 21.1 ppm; IR (thin film) ν 3272, 2932, 1723, 1394, 1371, 1292, 1254, 1194, 1156, 1067, 876, 849, 747 cm⁻¹.

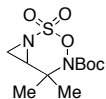
General procedure for Rh-catalyzed aziridination. Solid MgO (2.3 equiv), Rh₂(esp)₂ (2.0 mol %), and PhI(OAc)₂ (1.1 equiv) were added sequentially to a solution of substrate in isopropyl acetate (0.10 M). The resulting blue-green suspension was stirred at room temperature for 4 h, diluted with CH₂Cl₂, and filtered through a small pad of Celite. The flask and filter cake were rinsed with CH₂Cl₂ and the combined filtrates were concentrated under reduced pressure. The isolated blue-green residue was purified by chromatography on silica gel (conditions given below).



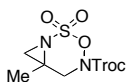
Purified by chromatography on silica gel (2:1 hexanes/EtOAc); clear oil (64%): TLC R_f = 0.33 (1:1 hexanes/EtOAc); ¹H NMR (CD₃CN, 400 MHz) δ 4.93 (d, 1H, J = 12.1 Hz), 4.88 (d, 1H, J = 12.1 Hz), 4.46 (d, 1H, J = 14.5 Hz), 4.12 (dd, 1H, J = 14.5, 4.1 Hz), 3.56 (ddd, 1H, J = 5.2, 5.2, 5.2 Hz), 2.97 (d, 1H, J = 5.0 Hz), 2.81 (d, 1H, J = 5.0 Hz) ppm; ¹³C NMR (CD₃CN, 100 MHz) δ 154.1, 95.2, 76.5, 45.3, 44.7, 35.8 ppm; IR (thin film) ν 1747, 1396, 1258, 1221, 1192, 1117, 800, 652 cm⁻¹; HRMS (ES⁺) calcd for C₇H₁₁Cl₃N₂O₆SNa⁺ 378.9296 found 378.9291 (MNa⁺+CH₃OH).



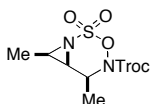
Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white solid (98%): TLC R_f = 0.30 (2:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 4.84 (d, 1H, J = 11.9 Hz), 4.79 (d, 1H, J = 11.9 Hz), 3.05 (dd, 1H, J = 5.0, 5.0 Hz), 2.97 (d, 1H, J = 5.0 Hz), 2.66 (d, 1H, J = 5.0 Hz), 1.76 (s, 3H), 1.75 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 153.6, 94.2, 75.8, 59.7, 53.6, 34.3, 25.2, 24.1 ppm; IR (thin film) ν 2988, 1753, 1391, 1293, 1199, 1183, 1116, 957, 820, 612 cm⁻¹; HRMS (ES⁺) calcd for C₈H₁₁Cl₃N₂O₅SNa⁺ 374.9352 found 374.9355 (MNa⁺).



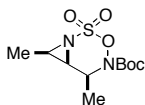
Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white solid (78%): TLC R_f = 0.33 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 2.97-2.93 (m, 2H), 2.60-2.57 (m, 1H), 1.67 (s, 3H), 1.64 (s, 3H), 1.49 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.1, 85.0, 59.0, 53.7, 34.0, 28.1, 25.5, 23.1 ppm; IR (thin film) ν 2983, 2940, 1742, 1389, 1372, 1302, 1263, 1197, 1151, 958, 825 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5\text{SNa}^+$ 301.0834 found 301.0827 (MNa^+).



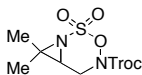
Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white foam (94%): TLC R_f = 0.48 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.83 (s, 2H), 4.53 (d, 1H, J = 14.3 Hz), 3.80 (dd, 1H, J = 14.3, 1.0 Hz), 3.14 (d, 1H, J = 1.0 Hz), 2.65 (dd, 1H, J = 1.0, 1.0 Hz), 1.57 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.9, 94.0, 76.0, 52.2, 48.5, 41.1, 20.9 ppm; IR (thin film) ν 2967, 1773, 1747, 1395, 1227, 1199, 1110, 807 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_7\text{H}_9\text{Cl}_3\text{N}_2\text{O}_5\text{SNa}^+$ 360.9196 found 360.9179 (MNa^+).



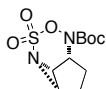
Purified by chromatography on silica gel (4:1 hexanes/EtOAc); clear oil (86%, 3:1 dr): TLC R_f = 0.50 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.85 (s, 2H), 4.79 (q, 1H, J = 6.9 Hz), 3.24 (quint, 1H, J = 5.5 Hz), 2.94 (d, 1H, J = 4.6 Hz), 1.59 (d, 3H, J = 6.9 Hz), 1.41 (d, 3H, J = 5.6 Hz) ppm; IR (thin film) ν 2981, 1775, 1744, 1391, 1301, 1198, 1126, 669 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_8\text{H}_{11}\text{Cl}_3\text{N}_2\text{O}_5\text{SNa}^+$ 374.9352 found 374.9359 (MNa^+).



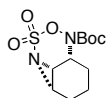
Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (82%): TLC R_f = 0.49 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.66 (q, 1H, J = 6.9 Hz), 3.24 (quint, 1H, J = 5.3 Hz), 2.87 (d, 1H, J = 5.6 Hz), 1.51 (s, 9H), 1.48 (d, 3H, J = 6.9 Hz), 1.38 (d, 3H, J = 5.6 Hz) ppm; IR (thin film) ν 2982, 2937, 1753, 1730, 1386, 1286, 1259, 1197, 1160, 1121, 969, 670 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5\text{SNa}^+$ 301.0834 found 301.0835 (MNa^+).



Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white solid (82%): TLC R_f = 0.38 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.83 (s, 2H), 4.47 (dd, 1H, J = 14.2, 7.6 Hz), 3.88 (dd, 1H, J = 14.2, 4.1 Hz), 3.36 (dd, 1H, J = 7.6, 4.1 Hz), 1.65 (s, 3H), 1.44 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.3, 93.9, 75.6, 50.6, 50.2, 40.2, 26.4, 14.7 ppm; IR (thin film) ν 2979, 1771, 1740, 1387, 1229, 1193, 1109, 961, 794, 741, 717 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_8\text{H}_{11}\text{Cl}_3\text{N}_2\text{O}_5\text{SNa}^+$ 374.9352 found 374.935 (MNa^+).

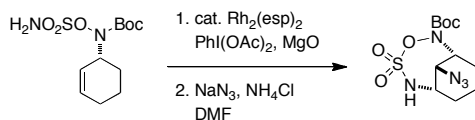


Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white solid (65%): TLC R_f = 0.23 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.92-4.87 (m, 1H), 4.06-4.03 (m, 1H), 3.48-3.46 (m, 1H), 2.63-2.45 (m, 2H), 2.18-2.04 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.4, 85.0, 54.9, 53.7, 53.2, 35.9, 28.1, 24.3 ppm; IR (thin film) ν 2981, 1753, 1726, 1397, 1371, 1309, 1250, 1191, 1155, 1085, 887, 824, 747 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_5\text{SNa}^+$ 299.0678 found 299.0669 (MNa^+).

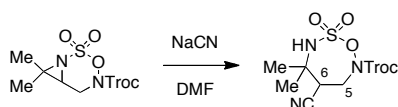


Purified by chromatography on silica gel (gradient elution: 2:1 hexanes/Et₂O→1:1 hexanes/Et₂O; white solid (51%): TLC R_f = 0.40 (1:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 4.84-4.79 (m, 1H), 3.69 (dd, 1H, *J* = 8.4, 5.3 Hz), 3.07-3.03 (m, 1H), 2.45 (dd, 1H, *J* = 15.7, 6.9 Hz), 2.13-2.00 (m, 1H), 1.99-1.91 (m, 2H), 1.68-1.55 (m, 2H), 1.51 (s, 9H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 153.0, 84.6, 44.0, 42.1, 41.8, 28.1, 25.3, 16.8, 15.5 ppm; IR (thin film) ν 2983, 2936, 1758, 1383, 1370, 1287, 1257, 1194, 1183, 1153, 742, 609 cm⁻¹; HRMS (ES⁺) calcd for C₁₁H₁₈N₂O₅SNa⁺ 313.0834 found 313.0839 (MNa⁺).

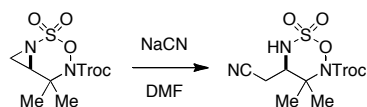
Procedures for Nucleophilic Ring Opening of Aziridines



Solid MgO (29 mg, 0.71 mmol, 2.3 equiv), Rh₂(esp)₂ (9 mg, 12.3 μmol, 4 mol %), and PhI(OAc)₂ (110 mg, 0.34 mmol, 1.1 equiv) were added sequentially to a solution of substrate (91 mg, 0.31 mmol) in 3.1 mL of isopropyl acetate. The resulting blue-green suspension was stirred for 5.5 h, diluted with 1–2 mL CH₂Cl₂, and filtered through a small pad of Celite. The flask and filter cake were rinsed with CH₂Cl₂ and the combined filtrates concentrated under reduced pressure. The residue was redissolved in 3.1 mL of DMF and NH₄Cl (22 mg, 0.34 mmol, 1.1 equiv) and NaN₃ (17 mg, 0.31 mmol) were added sequentially. After stirring at room temperature for 2.5 h, the solution was diluted in 50 mL of EtOAc and transferred to a separatory funnel. The organic phase was washed with 3 x 25 mL of H₂O and 25 mL of saturated NaCl, dried over MgSO₄, and concentrated under reduced pressure. The isolated residue was purified by chromatography on silica gel (6:1 hexanes/EtOAc) to afford the desired product (49 mg, 47%). TLC R_f = 0.27 (2:1 hexanes/EtOAc); ¹H NMR (CD₃CN, 400 MHz, 70 °C) δ 6.07 (br s, 1H), 4.59 (br s, 1H), 4.49 (br s, 1H), 3.68-3.65 (m, 1H), 2.06-1.96 (m, 4H), 1.70-1.63 (m, 2H), 1.51 (s, 9H) ppm; IR (thin film) ν 3273, 2940, 2110, 1717, 1388, 1312, 1256, 1186, 1160, 1120 cm⁻¹. The deposition number for the Cambridge Crystallographic Data Centre is CCDC809399.

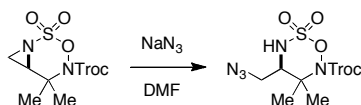


To a solution of aziridine (70 mg, 0.20 mmol) in 2.0 mL of DMF was added NaCN (11 mg, 0.22 mmol, 1.1 equiv). After stirring for 1 h, the solution was diluted in 50 mL of EtOAc and transferred to a separatory funnel. The organic phase washed with 2 x 50 mL of H₂O and 50 mL of saturated NaCl, dried over MgSO₄, and concentrated under reduced pressure. The isolated residue was purified by chromatography on silica gel (2:1 hexanes/EtOAc) to afford the desired product as a white foam (46 mg, 61%). TLC R_f = 0.53 (1:1 hexanes/EtOAc); ¹H NMR (CD₃CN, 400 MHz) δ 6.63 (br s, 1H), 4.92 (s, 2H), 4.28 (d, 1H, *J* = 1.2 Hz), 4.27 (s, 1H), 3.29 (dd, 1H, *J* = 4.9, 4.9 Hz), 1.54 (s, 3H), 1.53 (s, 3H) ppm; ¹³C NMR (CD₃CN, 100 MHz) δ 155.2, 118.5, 95.2, 76.8, 56.7, 51.3, 43.4, 25.8, 25.7 ppm; IR (thin film) ν 3263, 2961, 2261, 1747, 1433, 1397, 1379, 1307, 1244, 1188, 1167, 804, 722, 611 cm⁻¹; the regiochemistry of the aziridine opening was determined based on 2- and 3-bond couplings between the nitrile carbon and carbons C5 and C6. As expected, 4-bond coupling of the nitrile carbon to the methyl protons was negligible; see associated ¹H, HSQC, and HMBC spectra (note: these spectra were taken in CD₃OD).

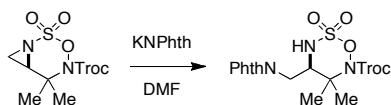


To a solution of aziridine (68 mg, 0.19 mmol) in 2.0 mL of DMF was added NaCN (10 mg, 0.21 mmol, 1.1 equiv). After stirring for 1 h, the solution was diluted in 50 mL of EtOAc, transferred to a separatory funnel, and washed with 100 mL of saturated NaCl. The aqueous layer was extracted with 4 x 25 mL of EtOAc. The combined organic

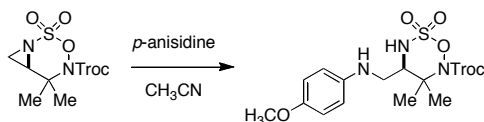
extracts were dried over MgSO_4 and concentrated under reduced pressure. The isolated residue was purified by chromatography on Davisil silica gel (2:1 hexanes/EtOAc) to afford the desired product, as a white solid (48 mg, 66%). TLC R_f = 0.42 (1:1 hexanes/EtOAc); ^1H NMR (CD_3OD , 400 MHz) δ 4.93-4.87 (m, 2H), 3.85 (br dd, 1H, J = 11.1, 3.7 Hz), 2.98 (dd, 1H, J = 16.9, 4.3 Hz), 2.75 (dd, 1H, J = 16.9, 11.1 Hz), 1.57 (s, 3H), 1.55 (s, 3H) ppm; IR (thin film) ν 3418, 3177, 3028, 2962, 2268, 1759, 1373, 1303, 1278, 1202, 1111, 1054, 715 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_9\text{H}_{12}\text{Cl}_3\text{N}_3\text{O}_5\text{SNa}^+$ 401.9455 found 401.9458 (MNa^+). Structural determination of the product was confirmed based on the absence of coupling between the nitrile nitrogen and the methyl protons in a ^{15}N HMBC experiment.



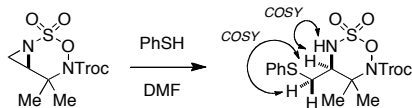
To a solution of aziridine (70 mg, 0.20 mmol) in 2.0 mL of DMF was added NaN_3 (11 mg, 0.20 mmol). After stirring for 1 h, the solution was diluted in 50 mL of EtOAc and transferred to a separatory funnel. The organic phase was washed with 2 x 50 mL of H_2O and 50 mL of saturated NaCl, dried over MgSO_4 , and concentrated under reduced pressure. The isolated residue was purified by chromatography on silica gel (4:1 hexanes/EtOAc) to afford the desired azide product as a clear oil (66 mg, 84%). TLC R_f = 0.56 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.34 (br d, 1H, J = 6.1 Hz), 4.81 (s, 2H), 3.69 (br s, 1H), 3.62-3.52 (m, 2H), 1.58 (s, 6H) ppm; IR (thin film) ν 3269, 2960, 2108, 1738, 1437, 1382, 1292, 1202, 1120, 801, 742, 720 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_8\text{H}_{12}\text{Cl}_3\text{N}_5\text{O}_5\text{S}$ 417.9523 found 417.9518 (MNa^+).



Aziridine (50 mg, 0.14 mmol, 1.0 equiv) and potassium phthalimide (31 mg, 0.17 mmol, 1.2 equiv) were combined in 0.3 mL of DMF and the solution was stirred for 12 h. The reaction was diluted with 5 mL of H_2O and the mixture transferred to a separatory funnel. The aqueous layer was extracted with 5 x 3 mL of Et_2O . The combined organic fractions were dried over MgSO_4 and concentrated under reduced pressure. The isolated residue was purified by chromatography on silica gel (3:2 PE/EtOAc) to afford the desired product (63 mg, 90%) as a white solid. mp = 180 $^\circ\text{C}$ (decomp); TLC R_f = 0.43 (30% EtOAc/PE); ^1H NMR (CDCl_3 , 400 MHz) δ 7.93-7.86 (m, 2H), 7.81-7.76 (m, 2H), 5.35 (d, 1H, J = 11.5 Hz), 4.83 (d, 1H, J = 11.6 Hz), 4.80 (d, 1H, J = 12.1 Hz), 3.91 (br s, 1H), 3.86-3.79 (m, 2H), 1.74 (s, 3H), 1.69 (s, 3H) ppm; ^{13}C NMR (125 MHz, acetone- d_6) δ 168.2, 153.3, 139.1, 134.6, 131.9, 122.9, 94.8, 75.1, 61.1, 36.4, 33.7, 18.4 ppm; IR (thin film) ν 3187, 2922, 1725, 1707, 1453, 1380, 1303, 1200 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{16}\text{H}_{16}\text{Cl}_3\text{N}_3\text{O}_7\text{SNa}^+$ 521.9672 found 521.9681 (MNa^+).

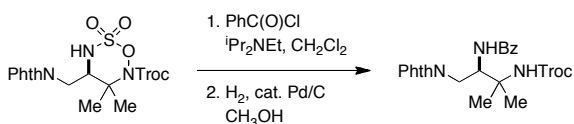


A solution of aziridine (50 mg, 0.14 mmol) and *p*-anisidine (39 mg, 0.31 mmol, 2.0 equiv) in 0.5 mL of CH_3CN was stirred at 68 $^\circ\text{C}$ for 24 h. Following this time, the reaction mixture was concentrated under reduced pressure. The isolated residue was dissolved in a minimal amount of toluene and the product was purified by chromatography on silica gel (gradient elution: 4:1 hexanes/EtOAc \rightarrow 3:2 hexanes/EtOAc) to afford the desired amine as a yellow foam (60 mg, 81%). TLC R_f = 0.35 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 6.80 (d, 2H, J = 8.8 Hz), 6.65 (d, 2H, J = 8.8 Hz), 4.81 (s, 2H), 3.75 (s, 3H), 3.74-3.63 (m, 1H), 3.37 (dd, 1H, J = 13.2, 3.3 Hz), 3.11 (dd, 1H, J = 13.2, 9.5 Hz), 1.60 (s, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.2, 140.6, 115.4, 115.1, 94.3, 75.4, 64.8, 62.2, 55.7, 43.9, 22.0, 19.5 ppm; IR (thin film) ν 3260, 2957, 1738, 1514, 1441, 1381, 1292, 1237, 1202, 1119 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{15}\text{H}_{20}\text{Cl}_3\text{N}_3\text{O}_6\text{SNa}^+$ 498.0036 found 498.0044 (MNa^+).



To a solution of aziridine (50 mg, 0.14 mmol) in 300 μ L of DMF was added thiophenol (31 mg, 0.28 mmol, 2.0 equiv). The reaction was stirred at for 5 h then concentrated under high vacuum (\sim 1 Torr). Purification of the isolated residue by chromatography on silica gel (gradient elution: 100% hexanes \rightarrow 4:1 hexanes/EtOAc) afforded the desired product (63 mg, 98%) as a clear oil. TLC R_f = 0.22 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.37-7.34 (m, 2H), 7.29-7.14 (m, 3H), 5.23 (d, 1H, J = 9.2 Hz), 4.69 (s, 2H), 3.54-3.45 (m, 1H), 3.00 (dd, 1H, J = 14.0, 3.8 Hz), 2.80 (dd, 1H, J = 14.0, 9.7 Hz), 1.47 (s, 3H), 1.37 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.0, 133.6, 131.8, 129.4, 128.0, 94.2, 75.4, 62.2, 60.5, 34.5, 19.4(2) ppm; IR (thin film) ν 3270, 2958, 1739, 1439, 1381, 1300, 1202, 1116, 1066, 800, 742 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{14}\text{H}_{17}\text{Cl}_3\text{N}_2\text{O}_5\text{SNa}^+$ 484.9542 found 484.9537 (MNa^+).

Procedure for N–O Bond Cleavage

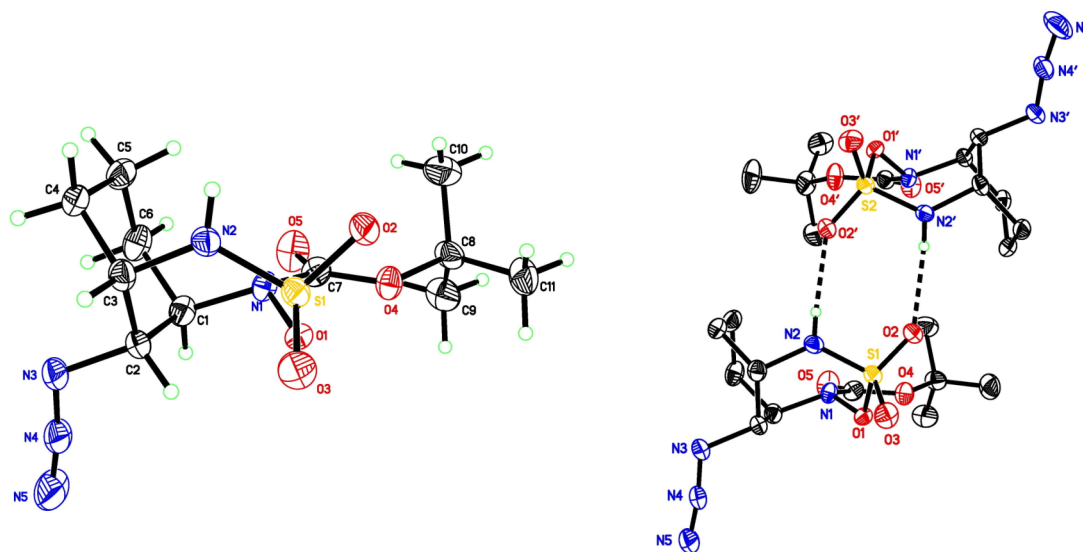


To a solution of oxathiadiazinane (50 mg, 0.10 mmol), *N,N*-dimethyl-4-aminopyridine (5 mg, 0.04 mmol, 0.4 equiv), and Pr_2NEt (29 mg, 0.2 mmol, 2.0 equiv) in 5.0 mL of CH_2Cl_2 was added PhC(O)Cl (21 mg, 0.15 mmol, 1.5 equiv). The mixture was stirred for 1 h then diluted with 30 mL of CH_2Cl_2 and transferred to a separatory funnel. The organic phase was washed with 5 mL of saturated aqueous NH_4Cl and 5 mL of saturated aqueous NaCl , dried over MgSO_4 and concentrated under reduced pressure. The isolated residue was purified by chromatography on silica gel (9:1 PE/EtOAc) to afford the desired product (50 mg, 80%) as a white foam. TLC R_f = 0.48 (30% EtOAc/PE); ^1H NMR (CDCl_3 , 300 MHz) 7.91-7.80 (m, 2H), 7.77-7.68 (m, 2H), 7.65 (d, 2H, J = 7.2 Hz), 7.52 (t, 1H, J = 7.4 Hz), 7.39 (t, 2H, J = 7.7 Hz), 5.28 (br s, 1H), 4.82 (br s, 2H), 4.55 (dd, 1H, J = 14.2, 9.7 Hz), 4.22 (dd, 1H, J = 14.2, 2.2 Hz), 1.90 (s, 3H), 1.81 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.2, 167.8, 154.2, 134.6, 133.6, 132.9, 131.7, 128.6, 128.3, 123.8, 94.2, 75.7, 67.0, 65.2, 60.5, 38.1, 22.9 ppm; IR (thin film) ν 2965, 2920, 1718, 1399, 1375, 1276, 1113 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{23}\text{H}_{20}\text{Cl}_3\text{N}_3\text{O}_8\text{SNa}^+$ 625.9934 found 625.9933 (MNa^+).

Benzoylated oxathiadiazinane (50 mg, 0.083 mmol) and 10% Pd/C (5.0 mg) in 0.5 mL of MeOH was stirred under an atmosphere of H_2 for 12 h. The mixture was then filtered through a pad of Celite and the flask and filter cake were rinsed with MeOH. The combined filtrates were concentrated under reduced pressure. The isolated residue was purified by chromatography on silica gel (30% EtOAc/PE) to afford the desired product (33 mg, 75%) as a clear oil. TLC R_f = 0.70 (30% EtOAc/PE); ^1H NMR (CDCl_3 , 400 MHz) δ 8.08 (d, 1H, J = 9.5 Hz), 7.77 (dd, 2H, J = 5.5, 3.3 Hz), 7.72 (d, 2H, J = 7.8 Hz), 7.65 (dd, 2H, J = 5.8, 2.8 Hz), 7.50-7.35 (m, 3H), 5.39 (br s, 1H), 4.83 (d, 1H, J = 11.8 Hz), 4.68 (d, 1H, J = 11.8 Hz), 4.62 (td, 1H, J = 10.2, 3.3 Hz), 4.01-3.85 (m, 2H), 1.63 (s, 3H), 1.46 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.5, 167.9, 154.6, 134.0, 132.0, 131.5, 128.7, 127.1, 122.4, 95.6, 74.5, 56.1, 39.5, 31.1, 27.0, 24.5 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{23}\text{H}_{22}\text{Cl}_3\text{N}_3\text{O}_5\text{Na}^+$ 548.0523 found 548.0523 (MNa^+).

- (1) TrocNHOH was synthesized by the method of Kirby, G. W.; McGuigan, H.; Mackinnon, J. W. M.; McLean, D.; Sharma, R. P. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1437.
- (2) BocNHOH is commercially available.

X-ray crystallographic data for Azide 11 (Figure 5)



Discussion

The compound crystallizes as colorless rod-like crystals from an ethyl acetate / hexanes solution. There are two crystallographically independent, yet chemically identical molecules of the compound in the asymmetric unit of the primitive, acentric, orthorhombic space group $P2_12_12_1$. The correct enantiomorph of the space group and handedness of the molecule were determined by comparison of the known handedness of the molecule and by comparison of intensities of Friedel pairs of reflections (Flack parameter = 0.01(4), a value of zero (0) indicates the correct handedness, a value of one (1) the inverted absolute configuration). The correct handedness is depicted in the Figures.

The structure of the molecule is as expected. The compound consists of a cyclohexyl ring fused with a sulfonamide ring. The azide and t-butyl ester functionalities are in the expected positions. The hydrogens on the sulfonamide nitrogens (N2 and N2') were located from a difference Fourier map and included in their observed positions. These hydrogens form H-bonds to the sulfonyl oxygen of the other molecule in the asymmetric unit, forming H-bonded dimers of the two independent molecules (see Figures and Table of Hydrogen-bonds).

No unusual bond distances or angles were observed within the molecules.

Data Collection

A fragment of a colorless rod-like crystal of $C_{11}H_{19}N_5O_5S$ having approximate dimensions of $0.32 \times 0.08 \times 0.08$ mm was mounted on a Kapton loop using Paratone N hydrocarbon oil. All measurements were made on a Bruker APEX-II¹ CCD area detector with graphite monochromated Mo-K α radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 9921 centered reflections with $I > 10\sigma(I)$ in the range $2.21 < \theta < 27.59^\circ$ corresponded to a Orthorhombic cell with dimensions:

$$\begin{array}{ll} a = 9.6162(9) \text{ \AA} & \alpha = 90^\circ \\ b = 10.3919(10) \text{ \AA} & \beta = 90^\circ \\ c = 31.833(3) \text{ \AA} & \gamma = 90^\circ \\ V = 3181.1(5) \text{ \AA}^3 & \end{array}$$

For $Z = 8$ and F.W. = 333.37, the calculated density is 1.392 g.cm^{-3} .

Analysis of the systematic absences allowed the space group to be uniquely determined to be:

$$P2_12_12_1$$

The data were collected at a temperature of 150(2) K. Frames corresponding to an arbitrary sphere of data were collected using ω -scans of 0.3° counted for a total of 30 seconds per frame.

Data Reduction

Data were integrated by the program SAINT² to a maximum θ -value of 29.59°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP³. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS⁴. (Tmax = 0.9815, Tmin = 0.9289). Of the 36986 reflections that were collected, 8490 were unique ($R_{\text{int}} = 0.0403$); equivalent reflections were merged. No decay correction was applied.

Structure Solution and Refinement

The structure was solved by direct methods⁵ and expanded using Fourier techniques⁶. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement⁷ was based on 8490 reflections (all data) and 409 variable parameters and converged (largest parameter shift was 0.001 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0346 \text{ for } 7453 \text{ data with } I > 2\sigma(I)$$

$$wR_2 = [(\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w |F_o|^2)]^{1/2} = 0.0711$$

The standard deviation of an observation of unit weight⁸ was 1.020. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.252 and -0.292 e⁻.Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁹. Anomalous dispersion effects were included in Fcalc²; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley¹⁰. The values for the mass attenuation coefficients are those of Creagh and Hubbel¹¹. All calculations were performed using the SHELXTL¹⁻⁶ crystallographic software package of Bruker Analytical X-ray Systems Inc.

References

- (1) APEX-II: Area-Detector Software Package v2.1, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (2006)
- (2) SAINT: SAX Area-Detector Integration Program, 7.34A; Siemens Industrial Automation, Inc.: Madison, WI, (2006)
- (3) XPREP:(v 6.14) Part of the SHELXTL Crystal Structure Determination Package, Siemens Industrial Automation, Inc.: Madison, WI, (1995)
- (4) SADABS: Siemens Area Detector ABSorption correction program v.2.10, George Sheldrick, (2005).
- (5) XS: Program for the Solution of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)
- (6) XL: Program for the Refinement of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)
- (7) Least-Squares:
Function minimized: $\sum w (|F_o|^2 - |F_c|^2)^2$
- (8) Standard deviation of an observation of unit weight:
 $[\sum w (|F_o|^2 - |F_c|^2)^2 / (N_o - N_v)]^{1/2}$
where: N_o = number of observations
 N_v = number of variables
- (9) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
- (10) Creagh, D. C. & McAuley, W. J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (11) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

Crystal data for $C_{11}H_{19}N_5O_5S$; $M_r = 333.37$; Orthorhombic; space group $P2_12_12_1$; $a = 9.6162(9)$ Å; $b = 10.3919(10)$ Å; $c = 31.833(3)$ Å; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 90^\circ$; $V = 3181.1(5)$ Å³; $Z = 8$; $T = 150(2)$ K; $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å; $\mu(\text{Mo-K}\alpha) = 0.234$ mm⁻¹; $d_{\text{calc}} = 1.392$ g.cm⁻³; 36986 reflections collected; 8490 unique ($R_{\text{int}} = 0.0403$); giving $R_1 = 0.0346$, $wR_2 = 0.0711$ for 7453 data with $[I > 2\sigma(I)]$ and $R_1 = 0.0438$, $wR_2 = 0.0750$ for all 8490 data. Residual electron density ($e^- \cdot \text{Å}^{-3}$) max/min: 0.252/ -0.292. An arbitrary sphere of data were collected on a colorless rod-like crystal, having approximate dimensions of $0.32 \times 0.08 \times 0.08$ mm, on a Bruker APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.3° . Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 X for methyl, 1.2 for all others).

Table 1. Crystal data and structure refinement for Azide **11**.

Identification code	Azide 11	
Empirical formula	$C_{11}H_{19}N_5O_5S$	
Formula weight	333.37	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	$a = 9.6162(9)$ Å	$\alpha = 90^\circ$
	$b = 10.3919(10)$ Å	$\beta = 90^\circ$
	$c = 31.833(3)$ Å	$\gamma = 90^\circ$
Volume	$3181.1(5)$ Å ³	
Z	8	
Density (calculated)	1.392 g.cm ⁻³	
Absorption coefficient (μ)	0.234 mm ⁻¹	
F(000)	1408	
Crystal size	$0.32 \times 0.08 \times 0.08$ mm ³	
ω range for data collection	2.06 to 29.59°	
Index ranges	$-12 \leq h \leq 13$, $-14 \leq k \leq 14$, $-44 \leq l \leq 44$	
Reflections collected	36986	
Independent reflections	8490 [$R_{\text{int}} = 0.0403$]	
Completeness to $\theta = 29.59^\circ$	96.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9815 and 0.9289	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8490 / 0 / 409	
Goodness-of-fit on F^2	1.020	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0346$, $wR_2 = 0.0711$	
R indices (all data)	$R_1 = 0.0438$, $wR_2 = 0.0750$	
Absolute structure parameter	0.01(4)	
Largest diff. peak and hole	0.252 and -0.292 e ⁻ · Å ⁻³	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for Azide **11**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
S(1)	0.57985(4)	0.49189(4)	0.29843(1)	0.020(1)
O(1)	0.69549(11)	0.49370(10)	0.33597(3)	0.019(1)
O(2)	0.47093(12)	0.40419(11)	0.30889(4)	0.029(1)
O(3)	0.66708(13)	0.46619(12)	0.26361(4)	0.032(1)
O(4)	0.64565(13)	0.37533(11)	0.40123(4)	0.027(1)
O(5)	0.64874(16)	0.55588(13)	0.44161(4)	0.038(1)
N(1)	0.65149(15)	0.56976(13)	0.37073(4)	0.021(1)
N(2)	0.51626(15)	0.63208(13)	0.29888(4)	0.022(1)
N(3)	0.80330(17)	0.86627(14)	0.31975(5)	0.034(1)
N(4)	0.92758(19)	0.86324(14)	0.32757(6)	0.036(1)
N(5)	1.0418(2)	0.87503(18)	0.33447(8)	0.062(1)
C(1)	0.71569(19)	0.70022(15)	0.36908(5)	0.024(1)
C(2)	0.73289(18)	0.73851(15)	0.32257(5)	0.023(1)
C(3)	0.59231(18)	0.75535(15)	0.30048(5)	0.023(1)
C(4)	0.49965(19)	0.85171(16)	0.32372(5)	0.026(1)
C(5)	0.4839(2)	0.81742(17)	0.37031(6)	0.029(1)
C(6)	0.6243(2)	0.79871(17)	0.39154(6)	0.030(1)
C(7)	0.65027(18)	0.50075(17)	0.40844(5)	0.026(1)
C(8)	0.6109(2)	0.28400(17)	0.43577(5)	0.030(1)
C(9)	0.7219(2)	0.2887(2)	0.46952(6)	0.039(1)
C(10)	0.4679(2)	0.3159(2)	0.45256(8)	0.046(1)
C(11)	0.6116(2)	0.15656(18)	0.41268(7)	0.040(1)
S(2)	0.11227(4)	0.54194(4)	0.31114(1)	0.019(1)
O(1')	0.01135(11)	0.51459(10)	0.35114(3)	0.019(1)
O(2')	0.22705(13)	0.61898(11)	0.32427(4)	0.027(1)
O(3')	0.01394(13)	0.59175(12)	0.28202(4)	0.029(1)
O(4')	0.07690(15)	0.58800(11)	0.42253(4)	0.031(1)
O(5')	0.07621(15)	0.38532(12)	0.44873(3)	0.031(1)
N(1')	0.07065(14)	0.41887(12)	0.37843(4)	0.019(1)
N(2')	0.17092(15)	0.40504(13)	0.29832(4)	0.020(1)
N(3')	-0.10818(16)	0.15660(13)	0.31943(5)	0.027(1)
N(4')	-0.21604(17)	0.15901(14)	0.29913(5)	0.030(1)
N(5')	-0.3156(2)	0.14563(19)	0.28089(7)	0.058(1)
C(1')	0.00593(17)	0.29052(14)	0.37039(5)	0.020(1)
C(2')	-0.03680(17)	0.28271(15)	0.32388(5)	0.020(1)
C(3')	0.08955(17)	0.28425(14)	0.29428(5)	0.021(1)
C(4')	0.18838(18)	0.17401(16)	0.30493(5)	0.026(1)
C(5')	0.23237(19)	0.17660(17)	0.35095(6)	0.028(1)
C(6')	0.10840(19)	0.18226(15)	0.38093(5)	0.024(1)
C(7')	0.07293(18)	0.46139(16)	0.42024(5)	0.023(1)
C(8')	0.0941(2)	0.65177(17)	0.46425(5)	0.033(1)
C(9')	0.2337(2)	0.6131(2)	0.48282(7)	0.043(1)
C(10')	0.0908(3)	0.79293(19)	0.45239(7)	0.054(1)
C(11')	-0.0267(2)	0.6171(2)	0.49238(6)	0.041(1)
H(2)	0.437(2)	0.6324(18)	0.3055(6)	0.027
H(1A)	0.8091	0.6975	0.3828	0.029
H(2A)	0.7894	0.6721	0.3076	0.027
H(3A)	0.6085	0.7867	0.2712	0.028
H(4A)	0.4066	0.8533	0.3104	0.031

H(4B)	0.5404	0.9389	0.3212	0.031
H(5A)	0.4325	0.8870	0.3848	0.035
H(5B)	0.4288	0.7373	0.3729	0.035
H(6A)	0.6090	0.7702	0.4209	0.036
H(6B)	0.6736	0.8823	0.3924	0.036
H(9A)	0.8131	0.2723	0.4569	0.058
H(9B)	0.7024	0.2229	0.4908	0.058
H(9C)	0.7218	0.3739	0.4827	0.058
H(10A)	0.4025	0.3243	0.4291	0.069
H(10B)	0.4717	0.3971	0.4681	0.069
H(10C)	0.4367	0.2469	0.4713	0.069
H(11A)	0.5436	0.1592	0.3898	0.060
H(11B)	0.5873	0.0873	0.4322	0.060
H(11C)	0.7045	0.1408	0.4011	0.060
H(2')	0.252(2)	0.3979(18)	0.3045(6)	0.024
H(1'A)	-0.0788	0.2812	0.3884	0.024
H(2'A)	-0.1019	0.3545	0.3167	0.024
H(3'A)	0.0570	0.2747	0.2646	0.025
H(4'A)	0.1420	0.0910	0.2988	0.031
H(4'B)	0.2721	0.1801	0.2869	0.031
H(5'A)	0.2925	0.2525	0.3558	0.034
H(5'B)	0.2878	0.0986	0.3572	0.034
H(6'A)	0.1431	0.1947	0.4099	0.029
H(6'B)	0.0586	0.0989	0.3800	0.029
H(9'A)	0.3078	0.6324	0.4627	0.064
H(9'B)	0.2333	0.5207	0.4890	0.064
H(9'C)	0.2499	0.6613	0.5088	0.064
H(10D)	0.1684	0.8120	0.4334	0.080
H(10E)	0.0990	0.8456	0.4778	0.080
H(10F)	0.0028	0.8125	0.4382	0.080
H(11D)	-0.1140	0.6280	0.4769	0.061
H(11E)	-0.0268	0.6735	0.5171	0.061
H(11F)	-0.0177	0.5274	0.5014	0.061

Table 3. Anisotropic displacement parameters (\AA^2) for Azide **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
S(1)	0.0198(2)	0.0199(2)	0.0201(2)	-0.0014(1)	-0.0012(1)	-0.0027(2)
O(1)	0.0188(6)	0.0204(5)	0.0189(5)	-0.0016(4)	-0.0007(4)	0.0021(5)
O(2)	0.0219(6)	0.0224(6)	0.0418(7)	0.0006(5)	-0.0030(6)	-0.0035(5)
O(3)	0.0388(7)	0.0330(7)	0.0230(6)	-0.0058(5)	0.0058(5)	-0.0015(6)
O(4)	0.0351(7)	0.0227(6)	0.0235(6)	0.0063(5)	-0.0013(5)	0.0012(5)
O(5)	0.0600(10)	0.0359(8)	0.0192(6)	0.0000(5)	-0.0042(6)	0.0002(7)
N(1)	0.0273(7)	0.0179(7)	0.0167(6)	-0.0017(5)	-0.0012(5)	0.0018(5)
N(2)	0.0183(7)	0.0223(7)	0.0262(7)	0.0023(6)	-0.0038(6)	-0.0018(6)
N(3)	0.0251(9)	0.0197(7)	0.0561(10)	0.0054(7)	0.0008(7)	-0.0045(6)
N(4)	0.0314(10)	0.0182(7)	0.0594(11)	-0.0029(7)	0.0008(8)	-0.0053(7)
N(5)	0.0320(12)	0.0257(9)	0.129(2)	-0.0058(11)	-0.0063(12)	-0.0063(8)
C(1)	0.0241(9)	0.0203(8)	0.0272(8)	-0.0022(7)	-0.0073(7)	-0.0006(7)
C(2)	0.0216(9)	0.0177(7)	0.0293(9)	0.0009(6)	0.0019(7)	-0.0033(7)
C(3)	0.0263(9)	0.0206(7)	0.0222(8)	0.0041(6)	0.0007(7)	-0.0007(7)
C(4)	0.0251(9)	0.0199(8)	0.0331(9)	0.0031(7)	-0.0009(7)	0.0031(7)
C(5)	0.0318(10)	0.0237(8)	0.0328(9)	-0.0029(7)	0.0068(8)	0.0055(8)
C(6)	0.0416(11)	0.0231(8)	0.0253(8)	-0.0060(7)	-0.0035(8)	0.0039(8)
C(7)	0.0273(9)	0.0282(9)	0.0214(8)	0.0037(7)	-0.0039(6)	0.0037(7)
C(8)	0.0268(10)	0.0308(9)	0.0308(9)	0.0124(7)	0.0044(8)	-0.0016(8)
C(9)	0.0375(11)	0.0460(12)	0.0333(10)	0.0205(9)	-0.0022(9)	0.0002(10)
C(10)	0.0325(12)	0.0504(13)	0.0551(13)	0.0066(11)	0.0118(10)	0.0002(10)
C(11)	0.0478(13)	0.0274(10)	0.0453(11)	0.0095(8)	0.0072(10)	-0.0044(9)
S(2)	0.0179(2)	0.0180(2)	0.0217(2)	0.0018(1)	0.0004(2)	-0.0009(2)
O(1')	0.0193(6)	0.0180(5)	0.0201(5)	0.0012(4)	0.0009(4)	0.0033(5)
O(2')	0.0219(6)	0.0201(6)	0.0394(7)	-0.0028(5)	0.0027(5)	-0.0039(5)
O(3')	0.0287(7)	0.0311(6)	0.0265(6)	0.0094(5)	-0.0037(5)	0.0036(6)
O(4')	0.0512(8)	0.0213(6)	0.0204(6)	-0.0064(4)	-0.0011(6)	-0.0011(6)
O(5')	0.0445(8)	0.0288(6)	0.0184(6)	0.0006(5)	-0.0016(6)	-0.0017(6)
N(1')	0.0245(7)	0.0157(6)	0.0178(6)	-0.0001(5)	-0.0024(5)	0.0015(5)
N(2')	0.0159(7)	0.0207(7)	0.0237(7)	-0.0036(5)	0.0013(6)	-0.0018(5)
N(3')	0.0223(8)	0.0228(7)	0.0368(8)	-0.0017(6)	-0.0053(7)	-0.0063(6)
N(4')	0.0322(9)	0.0238(7)	0.0342(8)	0.0007(6)	-0.0061(7)	-0.0074(6)
N(5')	0.0494(12)	0.0458(11)	0.0773(14)	0.0103(10)	-0.0367(11)	-0.0182(9)
C(1')	0.0208(8)	0.0184(7)	0.0201(7)	-0.0024(6)	0.0029(6)	-0.0037(6)
C(2')	0.0182(8)	0.0189(8)	0.0230(8)	-0.0028(6)	-0.0012(6)	-0.0023(6)
C(3')	0.0239(9)	0.0194(7)	0.0195(7)	-0.0044(6)	0.0004(7)	-0.0057(7)
C(4')	0.0245(9)	0.0199(8)	0.0327(9)	-0.0057(7)	0.0078(7)	-0.0012(7)
C(5')	0.0239(9)	0.0187(8)	0.0422(10)	0.0004(7)	-0.0043(8)	0.0041(7)
C(6')	0.0316(10)	0.0181(7)	0.0233(8)	0.0015(6)	-0.0031(7)	-0.0003(7)
C(7')	0.0238(8)	0.0235(8)	0.0217(8)	-0.0039(6)	0.0005(6)	-0.0014(7)
C(8')	0.0450(12)	0.0309(9)	0.0243(8)	-0.0129(7)	-0.0053(8)	0.0012(9)
C(9')	0.0388(12)	0.0459(12)	0.0437(12)	-0.0189(10)	-0.0085(10)	-0.0037(10)
C(10')	0.0871(19)	0.0275(10)	0.0460(12)	-0.0159(9)	-0.0077(13)	0.0037(12)
C(11')	0.0418(12)	0.0498(12)	0.0299(10)	-0.0150(9)	-0.0040(9)	0.0073(10)

Table 4. Bond lengths [Å] for Azide **11**.

atom-atom	distance	atom-atom	distance
S(1)-O(3)	1.4153(12)	S(1)-O(2)	1.4278(12)
S(1)-N(2)	1.5800(15)	S(1)-O(1)	1.6327(11)
O(1)-N(1)	1.4241(16)	O(4)-C(7)	1.324(2)
O(4)-C(8)	1.490(2)	O(5)-C(7)	1.202(2)
N(1)-C(7)	1.398(2)	N(1)-C(1)	1.491(2)
N(2)-C(3)	1.476(2)	N(2)-H(2)	0.79(2)
N(3)-N(4)	1.221(2)	N(3)-C(2)	1.493(2)
N(4)-N(5)	1.127(2)	C(1)-C(6)	1.527(2)
C(1)-C(2)	1.542(2)	C(1)-H(1A)	1.0000
C(2)-C(3)	1.534(2)	C(2)-H(2A)	1.0000
C(3)-C(4)	1.531(2)	C(3)-H(3A)	1.0000
C(4)-C(5)	1.533(2)	C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900	C(5)-C(6)	1.522(3)
C(5)-H(5A)	0.9900	C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(8)-C(10)	1.512(3)	C(8)-C(11)	1.515(3)
C(8)-C(9)	1.515(3)	C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800	C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800	C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
S(2)-O(3')	1.4217(12)	S(2)-O(2')	1.4262(13)
S(2)-N(2')	1.5838(14)	S(2)-O(1')	1.6260(11)
O(1')-N(1')	1.4385(16)	O(4')-C(7')	1.318(2)
O(4')-C(8')	1.4934(19)	O(5')-C(7')	1.203(2)
N(1')-C(7')	1.4025(19)	N(1')-C(1')	1.4940(19)
N(2')-C(3')	1.485(2)	N(2')-H(2')	0.81(2)
N(3')-N(4')	1.222(2)	N(3')-C(2')	1.486(2)
N(4')-N(5')	1.129(2)	C(1')-C(6')	1.533(2)
C(1')-C(2')	1.539(2)	C(1')-H(1'A)	1.0000
C(2')-C(3')	1.538(2)	C(2')-H(2'A)	1.0000
C(3')-C(4')	1.527(2)	C(3')-H(3'A)	1.0000
C(4')-C(5')	1.525(2)	C(4')-H(4'A)	0.9900
C(4')-H(4'B)	0.9900	C(5')-C(6')	1.528(3)
C(5')-H(5'A)	0.9900	C(5')-H(5'B)	0.9900
C(6')-H(6'A)	0.9900	C(6')-H(6'B)	0.9900
C(8')-C(11')	1.510(3)	C(8')-C(10')	1.515(3)
C(8')-C(9')	1.521(3)	C(9')-H(9'A)	0.9800
C(9')-H(9'B)	0.9800	C(9')-H(9'C)	0.9800
C(10')-H(10D)	0.9800	C(10')-H(10E)	0.9800
C(10')-H(10F)	0.9800	C(11')-H(11D)	0.9800
C(11')-H(11E)	0.9800	C(11')-H(11F)	0.9800

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for Azide **11**.

atom-atom-atom	angle	atom-atom-atom	angle
O(3)-S(1)-O(2)	119.79(8)	O(3)-S(1)-N(2)	114.24(8)
O(2)-S(1)-N(2)	107.61(8)	O(3)-S(1)-O(1)	99.89(7)
O(2)-S(1)-O(1)	109.65(7)	N(2)-S(1)-O(1)	104.26(7)
N(1)-O(1)-S(1)	111.89(9)	C(7)-O(4)-C(8)	120.43(13)
C(7)-N(1)-O(1)	112.63(12)	C(7)-N(1)-C(1)	120.01(13)
O(1)-N(1)-C(1)	110.76(12)	C(3)-N(2)-S(1)	127.50(12)
C(3)-N(2)-H(2)	117.7(14)	S(1)-N(2)-H(2)	112.3(14)
N(4)-N(3)-C(2)	114.12(15)	N(5)-N(4)-N(3)	172.3(2)
N(1)-C(1)-C(6)	110.78(15)	N(1)-C(1)-C(2)	108.23(13)
C(6)-C(1)-C(2)	109.77(14)	N(1)-C(1)-H(1A)	109.3
C(6)-C(1)-H(1A)	109.3	C(2)-C(1)-H(1A)	109.3
N(3)-C(2)-C(3)	105.71(13)	N(3)-C(2)-C(1)	109.61(14)
C(3)-C(2)-C(1)	112.02(14)	N(3)-C(2)-H(2A)	109.8
C(3)-C(2)-H(2A)	109.8	C(1)-C(2)-H(2A)	109.8
N(2)-C(3)-C(4)	107.22(14)	N(2)-C(3)-C(2)	110.71(13)
C(4)-C(3)-C(2)	111.48(14)	N(2)-C(3)-H(3A)	109.1
C(4)-C(3)-H(3A)	109.1	C(2)-C(3)-H(3A)	109.1
C(3)-C(4)-C(5)	111.90(14)	C(3)-C(4)-H(4A)	109.2
C(5)-C(4)-H(4A)	109.2	C(3)-C(4)-H(4B)	109.2
C(5)-C(4)-H(4B)	109.2	H(4A)-C(4)-H(4B)	107.9
C(6)-C(5)-C(4)	111.83(15)	C(6)-C(5)-H(5A)	109.2
C(4)-C(5)-H(5A)	109.2	C(6)-C(5)-H(5B)	109.2
C(4)-C(5)-H(5B)	109.2	H(5A)-C(5)-H(5B)	107.9
C(5)-C(6)-C(1)	112.86(14)	C(5)-C(6)-H(6A)	109.0
C(1)-C(6)-H(6A)	109.0	C(5)-C(6)-H(6B)	109.0
C(1)-C(6)-H(6B)	109.0	H(6A)-C(6)-H(6B)	107.8
O(5)-C(7)-O(4)	128.40(16)	O(5)-C(7)-N(1)	120.67(16)
O(4)-C(7)-N(1)	110.88(14)	O(4)-C(8)-C(10)	108.97(16)
O(4)-C(8)-C(11)	101.40(14)	C(10)-C(8)-C(11)	111.56(18)
O(4)-C(8)-C(9)	110.16(15)	C(10)-C(8)-C(9)	112.52(17)
C(11)-C(8)-C(9)	111.64(17)	C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5	H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5	H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5	H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5	H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5	C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5	H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5	O(3')-S(2)-O(2')	120.10(7)
O(3')-S(2)-N(2')	113.32(8)	O(2')-S(2)-N(2')	107.71(7)
O(3')-S(2)-O(1')	100.21(7)	O(2')-S(2)-O(1')	109.29(7)
N(2')-S(2)-O(1')	104.91(7)	N(1')-O(1')-S(2)	110.94(9)
C(7')-O(4')-C(8')	119.68(13)	C(7')-N(1')-O(1')	111.19(12)
C(7')-N(1')-C(1')	116.77(13)	O(1')-N(1')-C(1')	110.41(11)
C(3')-N(2')-S(2)	126.44(11)	C(3')-N(2')-H(2')	116.9(14)
S(2)-N(2')-H(2')	111.4(14)	N(4')-N(3')-C(2')	115.11(14)
N(5')-N(4')-N(3')	171.72(19)	N(1')-C(1')-C(6')	110.49(13)
N(1')-C(1')-C(2')	108.85(12)	C(6')-C(1')-C(2')	110.09(13)
N(1')-C(1')-H(1'A)	109.1	C(6')-C(1')-H(1'A)	109.1

C(2')-C(1')-H(1'A)	109.1	N(3')-C(2')-C(3')	108.40(12)
N(3')-C(2')-C(1')	105.17(12)	C(3')-C(2')-C(1')	112.22(13)
N(3')-C(2')-H(2'A)	110.3	C(3')-C(2')-H(2'A)	110.3
C(1')-C(2')-H(2'A)	110.3	N(2')-C(3')-C(4')	106.68(13)
N(2')-C(3')-C(2')	111.84(12)	C(4')-C(3')-C(2')	110.36(13)
N(2')-C(3')-H(3'A)	109.3	C(4')-C(3')-H(3'A)	109.3
C(2')-C(3')-H(3'A)	109.3	C(5')-C(4')-C(3')	111.89(13)
C(5')-C(4')-H(4'A)	109.2	C(3')-C(4')-H(4'A)	109.2
C(5')-C(4')-H(4'B)	109.2	C(3')-C(4')-H(4'B)	109.2
H(4'A)-C(4')-H(4'B)	107.9	C(4')-C(5')-C(6')	112.59(14)
C(4')-C(5')-H(5'A)	109.1	C(6')-C(5')-H(5'A)	109.1
C(4')-C(5')-H(5'B)	109.1	C(6')-C(5')-H(5'B)	109.1
H(5'A)-C(5')-H(5'B)	107.8	C(5')-C(6')-C(1')	113.15(13)
C(5')-C(6')-H(6'A)	108.9	C(1')-C(6')-H(6'A)	108.9
C(5')-C(6')-H(6'B)	108.9	C(1')-C(6')-H(6'B)	108.9
H(6'A)-C(6')-H(6'B)	107.8	O(5')-C(7')-O(4')	127.83(15)
O(5')-C(7')-N(1')	120.56(15)	O(4')-C(7')-N(1')	111.55(14)
O(4')-C(8')-C(11')	109.63(16)	O(4')-C(8')-C(10')	101.86(14)
C(11')-C(8')-C(10')	111.24(19)	O(4')-C(8')-C(9')	109.05(16)
C(11')-C(8')-C(9')	112.68(16)	C(10')-C(8')-C(9')	111.80(19)
C(8')-C(9')-H(9'A)	109.5	C(8')-C(9')-H(9'B)	109.5
H(9'A)-C(9')-H(9'B)	109.5	C(8')-C(9')-H(9'C)	109.5
H(9'A)-C(9')-H(9'C)	109.5	H(9'B)-C(9')-H(9'C)	109.5
C(8')-C(10')-H(10D)	109.5	C(8')-C(10')-H(10E)	109.5
H(10D)-C(10')-H(10E)	109.5	C(8')-C(10')-H(10F)	109.5
H(10D)-C(10')-H(10F)	109.5	H(10E)-C(10')-H(10F)	109.5
C(8')-C(11')-H(11D)	109.5	C(8')-C(11')-H(11E)	109.5
H(11D)-C(11')-H(11E)	109.5	C(8')-C(11')-H(11F)	109.5
H(11D)-C(11')-H(11F)	109.5	H(11E)-C(11')-H(11F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for Azide **11**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
O(3)-S(1)-O(1)-N(1)	154.52(10)	O(2)-S(1)-O(1)-N(1)	-78.77(11)
N(2)-S(1)-O(1)-N(1)	36.21(11)	S(1)-O(1)-N(1)-C(7)	123.56(12)
S(1)-O(1)-N(1)-C(1)	-98.93(12)	O(3)-S(1)-N(2)-C(3)	-60.82(16)
O(2)-S(1)-N(2)-C(3)	163.57(14)	O(1)-S(1)-N(2)-C(3)	47.16(15)
C(2)-N(3)-N(4)-N(5)	-173.7(18)	C(7)-N(1)-C(1)-C(6)	-72.74(19)
O(1)-N(1)-C(1)-C(6)	153.30(13)	C(7)-N(1)-C(1)-C(2)	166.87(14)
O(1)-N(1)-C(1)-C(2)	32.92(17)	N(4)-N(3)-C(2)-C(3)	-164.90(16)
N(4)-N(3)-C(2)-C(1)	74.2(2)	N(1)-C(1)-C(2)-N(3)	-177.30(13)
C(6)-C(1)-C(2)-N(3)	61.69(18)	N(1)-C(1)-C(2)-C(3)	65.69(17)
C(6)-C(1)-C(2)-C(3)	-55.33(18)	S(1)-N(2)-C(3)-C(4)	-149.43(13)
S(1)-N(2)-C(3)-C(2)	-27.6(2)	N(3)-C(2)-C(3)-N(2)	176.40(13)
C(1)-C(2)-C(3)-N(2)	-64.27(17)	N(3)-C(2)-C(3)-C(4)	-64.34(17)
C(1)-C(2)-C(3)-C(4)	54.99(17)	N(2)-C(3)-C(4)-C(5)	68.31(18)
C(2)-C(3)-C(4)-C(5)	-53.00(19)	C(3)-C(4)-C(5)-C(6)	52.5(2)
C(4)-C(5)-C(6)-C(1)	-54.4(2)	N(1)-C(1)-C(6)-C(5)	-64.33(19)
C(2)-C(1)-C(6)-C(5)	55.1(2)	C(8)-O(4)-C(7)-O(5)	11.5(3)
C(8)-O(4)-C(7)-N(1)	-165.86(14)	O(1)-N(1)-C(7)-O(5)	161.97(16)
C(1)-N(1)-C(7)-O(5)	28.8(2)	O(1)-N(1)-C(7)-O(4)	-20.45(19)
C(1)-N(1)-C(7)-O(4)	-153.62(14)	C(7)-O(4)-C(8)-C(10)	59.7(2)
C(7)-O(4)-C(8)-C(11)	177.48(16)	C(7)-O(4)-C(8)-C(9)	-64.2(2)
O(3')-S(2)-O(1')-N(1')	156.95(9)	O(2')-S(2)-O(1')-N(1')	-75.97(10)
N(2')-S(2)-O(1')-N(1')	39.29(11)	S(2)-O(1')-N(1')-C(7')	129.13(12)
S(2)-O(1')-N(1')-C(1')	-99.59(12)	O(3')-S(2)-N(2')-C(3')	-63.08(15)
O(2')-S(2)-N(2')-C(3')	161.61(13)	O(1')-S(2)-N(2')-C(3')	45.25(15)
C(2')-N(3')-N(4')-N(5')	174.5(14)	C(7')-N(1')-C(1')-C(6')	-80.08(17)
O(1')-N(1')-C(1')-C(6')	151.62(12)	C(7')-N(1')-C(1')-C(2')	158.92(14)
O(1')-N(1')-C(1')-C(2')	30.62(16)	N(4')-N(3')-C(2')-C(3')	-104.31(17)
N(4')-N(3')-C(2')-C(1')	135.49(15)	N(1')-C(1')-C(2')-N(3')	-176.31(12)
C(6')-C(1')-C(2')-N(3')	62.44(16)	N(1')-C(1')-C(2')-C(3')	66.05(16)
C(6')-C(1')-C(2')-C(3')	-55.20(17)	S(2)-N(2')-C(3')-C(4')	-150.09(12)
S(2)-N(2')-C(3')-C(2')	-29.33(19)	N(3')-C(2')-C(3')-N(2')	-177.25(13)
C(1')-C(2')-C(3')-N(2')	-61.54(17)	N(3')-C(2')-C(3')-C(4')	-58.65(16)
C(1')-C(2')-C(3')-C(4')	57.05(17)	N(2')-C(3')-C(4')-C(5')	66.71(17)
C(2')-C(3')-C(4')-C(5')	-54.99(18)	C(3')-C(4')-C(5')-C(6')	52.71(19)
C(4')-C(5')-C(6')-C(1')	-51.66(19)	N(1')-C(1')-C(6')-C(5')	-68.10(17)
C(2')-C(1')-C(6')-C(5')	52.16(18)	C(8')-O(4')-C(7')-O(5')	3.2(3)
C(8')-O(4')-C(7')-N(1')	-173.92(15)	O(1')-N(1')-C(7')-O(5')	156.44(15)
C(1')-N(1')-C(7')-O(5')	28.5(2)	O(1')-N(1')-C(7')-O(4')	-26.2(2)
C(1')-N(1')-C(7')-O(4')	-154.12(15)	C(7')-O(4')-C(8')-C(11')	-61.2(2)
C(7')-O(4')-C(8')-C(10')	-179.13(19)	C(7')-O(4')-C(8')-C(9')	62.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for Azide **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(2')	0.79(2)	2.11(2)	2.8994(19)	176(2)
N(2')-H(2')...O(2)	0.81(2)	2.11(2)	2.9044(19)	167.6(19)