Novel Iminium Ion Equivalents Prepared Through C–H Oxidation for the Stereocontrolled Synthesis of Functionalized Propargylic Amine Derivatives

Supplementary Material
(22 pages)

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General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of nitrogen. Air- and moisture sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (ca. 15 mm Hg) by rotary evaporation. Dichloromethane and acetonitrile were freshly distilled from CaH₂ immediately prior to use. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl immediately prior to use. *N,N*-Dimethylacetamide (DMA) was dried over 4Å molecular sieves and stored under an atmosphere of nitrogen. Boron trifluoride diethyl etherate (BF₃•OEt₂) was distilled from BaSO₄ under vacuum (ca. 15 mm Hg) and stored in a Schlenk flask under an atmosphere of nitrogen. Zinc chloride (ZnCl₂) was fused under vacuum (ca. 1 mm Hg), ground to a fine powder and stored in an inert atmosphere N₂ glovebox. A 1.0 M solution of ZnCl₂ in THF was prepared in a Schlenk flask and stored under an atmosphere of N₂. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35–75 µm) or on Davisil silica gel, grade 643 (200–425 mesh), pH = 7.0 (Fisher Chemicals). Thin-layer chromatography (TLC) was performed on EM Science silica gel 60 F₂₅₄ plates (250 µm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

Nuclear magnetic resonance (NMR) spectra were acquired on a Varian Inova spectrometer operating at 500 and 125 MHz for ¹H and ¹³C respectively and are referenced internally according to residual protio 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; 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 Perkin-Elmer Spectrum-BX FT-IR spectrometer and are reported in terms of frequency of absorption. Sample preparation was done either as a thin film on a NaCl salt plate or as a KBr pellet. High-resolution mass spectra were obtained from the Mass Spectrometry Facility, University of California at San Francisco, supported by the NIH Division of Research and Resources and from the High Resolution Mass Spectrometry Facility, University of California at Riverside.

Experimental procedure and characterization data for sulfamate esters

General Procedure: Formic acid (283 µL, 7.5 mmol, 2.5 equiv) was added to neat ClSO₂NCO (653 µL, 7.5 mmol, 2.5 equiv) at 0 °C with rapid stirring. Vigorous gas evolution was observed during the addition process and within 5 min the mixture solidified. To the resulting white mass was added 3.0 mL of CH₃CN and the contents were then warmed to 23 °C. After stirring for 7 h the mixture was cooled to 0 °C and a solution of alcohol (3.0 mmol) in 2.5 mL of DMA was added via cannula. Transfer of the alcohol was made quantitative with an additional 0.5 mL of DMA. The reaction was warmed to 23 °C and stirred at this temperature until TLC indicated complete consumption of starting material (~ 1 h). The reaction was quenched by the addition of 15 mL of H₂O and poured into a separatory funnel containing 150 mL of Et₂O and 150 mL of H₂O. The organic phase was collected and the aqueous layer was extracted with 3 x 75 mL of Et₂O. The combined organic extracts were washed with 150 mL of H₂O, dried over MgSO₄, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (conditions given below) afforded the desired product.

Purified by chromatography on silica gel (3:2 hexanes/EtOAc); colorless oil (75%): TLC R_f = 0.53 (1:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 500 MHz) δ 5.29 (br s, 2H), 4.45–4.40 (m, 1H), 4.28–4.26 (m, 1H), 4.20 (dd, 1H, J = 10.6, 4.6 Hz), 4.14 (dd, 1H, J = 8.6, 6.6 Hz), 3.78 (dd, 1H, J = 8.6, 6.3 Hz), 1.69 (q, 2H, J = 7.7 Hz), 1.65 (q, 2H,

$J = 7.6$ Hz), 0.93 (t, 3H, $J = 7.7$ Hz), 0.91 (t, 3H, $J = 7.5$ Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 114.4, 73.3, 70.6, 66.1, 29.3, 28.9, 8.1, 7.8 ppm; IR (thin film) ν 3271, 2975, 1562, 1461, 1364, 1179, 1089, 987, 817 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{17}\text{NO}_5\text{S}$ 239.0827 found 240.0898 (MH^+).

Purified by chromatography on silica gel (18:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); colorless oil (61%, unoptimized): TLC $R_f = 0.20$ (18:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); ^1H NMR (CDCl_3 , 500 MHz) δ 5.31 (s, 2H), 4.60-4.56 (m, 1H), 4.25 (q, 1H, $J = 7.0$ Hz), 4.11-4.07 (m, 1H), 3.75 (dd, 1H, $J = 8.7, 6.7$ Hz), 1.63-1.57 (m, 1H), 1.52-1.29 (m, 6H), 1.47 (s, 3H), 1.39 (s, 3H), 0.91 (t, 3H, $J = 7.2$ Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 110.2, 85.1, 77.4, 65.7, 30.4, 26.8, 26.1, 25.5, 22.2, 13.8 ppm; IR (thin film) ν 3350, 2959, 2874, 1458, 1373, 1181, 1065, 918 cm^{-1} .

Purified by chromatography on silica gel (4:1 hexanes/ EtOAc); colorless oil (72%): TLC $R_f = 0.67$ (2:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 5.73 (d, 1H, $J = 8.7$ Hz), 5.46 (s, 2H), 4.75 (s, 2H), 4.34-4.29 (m, 2H), 4.20-4.16 (m, 1H), 3.60 (dd, 1H, $J = 9.7, 3.9$ Hz), 3.54 (dd, 1H, $J = 9.8, 5.1$ Hz), 3.41 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.6, 95.2, 74.6, 70.1, 68.9, 59.2, 49.8 ppm; IR (thin film) ν 3281, 2961, 1567, 1454, 1360, 1183, 1088, 926, 859 cm^{-1} ; HRMS (EI) calcd for $\text{C}_7\text{H}_{13}\text{Cl}_3\text{N}_2\text{O}_6\text{S}$ 357.9560 found 322.9872 ($\text{M}^+ - \text{Cl}$).

Purified by chromatography on silica gel (gradient elution: 2:1 $\rightarrow$ 1:1 hexanes/ EtOAc); white solid (75%): TLC $R_f = 0.45$ (1:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 5.29 (s, 2H), 4.91 (s, 1H), 3.46 (t, 1H, $J = 9.5$ Hz), 3.34 (s, 3H), 3.22 (dd, 1H, $J = 9.9, 5.6$ Hz), 2.24 (dd, 1H, $J = 14.3, 2.4$ Hz), 1.92-1.89 (m, 1H), 1.76-1.74 (m, 1H), 1.66-1.45 (m, 4H), 1.37-1.28 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 79.6, 73.0, 58.4, 40.2, 30.2, 24.5, 23.1, 20.0 ppm; IR (thin film) ν 3277, 2936, 3864, 1567, 1450, 1359, 1179, 1108, 1088, 916, 789 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{17}\text{NO}_4\text{S}$ 223.0878 found 191.0609 ($\text{M}^+ - \text{CH}_3\text{OH}$).

Purified by chromatography on silica gel (gradient elution: 2:1 $\rightarrow$ 1:1 hexanes/ EtOAc); colorless oil (72%): TLC $R_f = 0.45$ (1:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 5.52 (br s, 2H), 4.86-4.83 (m, 1H), 3.42 (dd, 1H, $J = 9.1, 5.3$ Hz), 3.36 (s, 3H), 3.21 (t, 1H, $J = 9.2$ Hz), 2.49-2.43 (m, 1H), 1.98-1.90 (m, 3H), 1.76-1.61 (m, 2H), 1.23-1.16 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 87.0, 74.0, 58.8, 45.7, 33.2, 27.7, 23.2 ppm; IR (thin film) ν 3351, 2956, 1722, 1538, 1372, 1184, 1101, 1000, 931, 822 cm^{-1} ; HRMS (EI) calcd for $\text{C}_7\text{H}_{15}\text{NO}_4\text{S}$ 209.0722 found 177.0458 ($\text{M}^+ - \text{CH}_3\text{OH}$).

Experimental procedure and characterization data for oxathiazinane *N,O*-acetals (Figure 2)

General Procedure: To a solution of sulfamate ester (1.25 mmol) in 8.0 mL of CH₂Cl₂ were added sequentially MgO (116 mg, 3.0 mmol, 2.3 equiv), PhI(OAc)₂ (443 mg, 1.4 mmol, 1.1 equiv), and Rh catalyst (2–4 mol% of either Rh₂(OAc)₄ or Rh₂(tpa)₄ as indicated below; tpa = Ph₃CCO₂[−]). The light green suspension was stirred vigorously at 23 °C until TLC indicated the complete consumption of starting material (1–4 h). The reaction was diluted with 10 mL of CH₂Cl₂ and filtered through a pad of Celite (30 x 20 mm). The filter cake was rinsed with 2 x 15 mL of CH₂Cl₂ and the combined filtrates were evaporated under reduced pressure. The isolated material was purified by chromatography on silica gel (conditions given below) to afford the desired oxathiazinane *N,O*-acetal.

Reaction performed with 3 mol% Rh₂(tpa)₄. Purified by chromatography on silica gel (3:2 hexanes/EtOAc); white solid (92%): TLC R_f = 0.58 (1:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 500 MHz) δ 5.51 (d, 1H, *J* = 4.4 Hz), 4.84 (br s, 1H), 4.76 (dd, 1H, *J* = 13.2, 2.1 Hz), 4.72 (dd, 1H, *J* = 13.2, 1.1 Hz), 4.20–4.19 (m, 1H), 1.83 (dq, 2H, *J* = 7.5, 2.5 Hz), 1.66 (q, 2H, *J* = 7.6 Hz), 1.00 (t, 3H, *J* = 7.6 Hz), 0.92 (t, 3H, *J* = 7.6 Hz) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 115.3, 84.4, 70.2, 69.6, 29.6, 28.6, 8.3, 7.9 ppm; IR (thin film) ν 3243, 2946, 1454, 1329, 1178, 1139, 1074, 1027, 944 cm^{−1}; HRMS (EI) calcd for C₈H₁₅NO₅S 237.0671 found 237.0675 (M⁺).

Reaction performed with 4 mol% Rh₂(tpa)₄. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (91%): TLC R_f = 0.75 (8:1 CH₂Cl₂/EtOAc); ¹H NMR (CDCl₃, 500 MHz) δ 5.45 (dd, 1H, *J* = 6.0 Hz), 4.75–4.72 (m, 2H), 4.06 (br d, 1H, *J* = 2.9 Hz), 2.03–1.97 (m, 1H), 1.86–1.79 (m, 1H), 1.59 (s, 3H), 1.57–1.35 (m, 4H), 1.40 (s, 3H), 0.95 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C (CDCl₃, 125 MHz) δ 111.0, 84.5, 81.6, 71.8, 30.0, 27.5, 26.9, 25.4, 22.1, 13.8 ppm; IR (thin film) ν 3287, 2960, 2874, 1378, 1348, 1222, 1178, 1095, 1061, 912 cm^{−1}; HRMS (EI) calcd for C₁₀H₁₉NO₅S 265.0984 found 208.0639 (MH⁺–C₃H₆O).

Reaction performed with 2 mol% Rh₂(OAc)₄. Purified by chromatography on Davisil silica gel, grade 643 (3:2 hexanes/EtOAc); white foam (75%): TLC R_f = 0.55 (3:2 hexanes/EtOAc). The product was isolated as a 1:1 mixture of diastereomers and used in subsequent reactions as such.

Reaction performed with 2 mol% Rh₂(OAc)₄. Purified through rapid filtration through a short column of Davisil silica gel, grade 643 (2:1 hexanes/EtOAc); colorless oil (78%): TLC R_f = 0.46, 0.33 (2:1 hexanes/EtOAc). The product was isolated as a 1:1 mixture of diastereomers and used immediately following isolation. Purification of the

more stable, higher R_f diastereomer was possible by chromatography on Davisil silica gel using 2:1 hexanes/EtOAc as eluent. Characterization data is given for this diastereomer only: ^1H NMR (CDCl_3 , 400 MHz) δ 4.79-4.72 (m, 2H), 4.12 (br d, 1H, $J = 10.0$ Hz), 3.50 (s, 3H), 2.14-2.06 (m, 1H), 1.92-1.82 (m, 2H), 1.75-1.69 (m, 1H), 1.67-1.51 (m, 3H), 1.42-1.23 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 89.7, 79.5, 56.8, 39.0, 30.0, 23.8, 19.7, 16.8 ppm; IR (thin film) ν 3255, 2940, 2865, 1449, 1414, 1373, 1361, 1187, 1136, 1109, 1086, 975, 931, 862 cm^{-1} .

Reaction performed with 2 mol% $\text{Rh}_2(\text{OAc})_4$. Purified by chromatography on Davisil silica gel, grade 643 (3:1 hexanes/EtOAc); colorless oil (90%): TLC $R_f = 0.37, 0.22$ (3:1 hexanes/EtOAc). The product was isolated as a 1:1 mixture of diastereomers and used immediately following isolation. Higher R_f diastereomer: ^1H NMR (CDCl_3 , 400 MHz) δ 4.48 (t, 1H, $J = 9.5$ Hz), 4.43-4.35 (m, 1H), 3.84 (br d, 1H, $J = 9.4$ Hz), 3.52 (s, 3H), 2.21-2.12 (m, 1H), 2.04-1.95 (m, 1H), 1.90-1.72 (m, 4H), 1.39-1.24 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 91.4, 82.8, 56.8, 48.0, 27.6, 21.4, 18.0 ppm; IR (thin film) ν 3243, 2959, 1416, 1354, 1194, 1180, 1103, 1003, 943, 819 cm^{-1} . Lower R_f diastereomer: ^1H NMR (CDCl_3 , 400 MHz) δ 5.07-4.98 (m, 1H), 4.72 (br s, 1H), 4.59 (t, 1H, $J = 3.5$ Hz), 3.51 (s, 3H), 2.20-2.07 (m, 2H), 1.89-1.69 (m, 4H), 1.65-1.56 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 86.3, 82.2, 55.9, 45.0, 28.2, 20.3, 18.3 ppm; IR (thin film) ν 3275, 2959, 1415, 1387, 1325, 1182, 1108, 1066, 1017, 991, 826 cm^{-1} .

Experimental procedures and characterization data for alkynylzinc addition products (eq 1 and Table 1)

Procedure A: To a solution of alkyne (1.06 mmol, 2.1 equiv) in 0.4 mL of THF at 0 $^\circ\text{C}$ was added dropwise 2.5 M $n\text{-BuLi}$ (405 μL , 1.01 mmol, 2.0 equiv) in hexanes. The colorless solution was stirred for 15 min at 0 $^\circ\text{C}$. A 1.0 M solution of ZnCl_2 (1.06 mmol, 2.1 equiv) in THF was added and the mixture was stirred for an additional 20 min after which time $\text{BF}_3 \cdot \text{OEt}_2$ (1.1–3.0 equiv, as indicated below) was added dropwise. The reaction flask was equipped with a reflux condenser and the contents were warmed to 40 $^\circ\text{C}$. A solution of oxathiazinane (0.50 mmol) in 0.7 mL of THF was added via cannula. An additional 0.2 mL of THF was used to ensure quantitative transfer of the oxathiazinane. The colorless solution was stirred at 40 $^\circ\text{C}$ until TLC indicated complete consumption of starting material (0.25–1 h). The reaction was quenched by the addition of 10 mL of saturated aqueous NH_4Cl and transferred to a separatory funnel with 25 mL of Et_2O . The organic phase was collected and washed with 20 mL of 1:1 saturated aqueous NaHCO_3 and saturated aqueous NaCl . The aqueous washings were combined and extracted with 1 x 10 mL of Et_2O . The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. Purification of the isolated material by chromatography on silica gel or by recrystallization (conditions given below) afforded the desired product.

Procedure B: To a solution of alkyne (2.1–4.1 equiv, as indicated below) in 0.6 mL of THF at -78 $^\circ\text{C}$ was added dropwise 2.5 M $n\text{-BuLi}$ (805 μL , 2.01 mmol, 4.0 equiv) in hexanes. The colorless solution was stirred for 20 min at -78 $^\circ\text{C}$. A 1.0 M solution of ZnCl_2 (2.1–4.1 equiv, as indicated below) in THF was added and the mixture was stirred for 5 min before being warmed to 23 $^\circ\text{C}$. After 5 min at 23 $^\circ\text{C}$ the suspension was cooled to 0 $^\circ\text{C}$ and $\text{BF}_3 \cdot \text{OEt}_2$ (1.1–3.0 equiv, as indicated below) was added dropwise. The reaction flask was equipped with a reflux condenser and the contents were warmed to 40 $^\circ\text{C}$. A solution of oxathiazinane (0.50 mmol) in 0.7 mL of THF was added via cannula. An additional 0.2 mL of THF was used to ensure quantitative transfer of the oxathiazinane. The colorless solution was stirred at 40 $^\circ\text{C}$ until TLC indicated complete consumption of starting material (0.25–1 h). The reaction was quenched by the addition of 10 mL of saturated aqueous NH_4Cl and transferred to a separatory funnel with 25 mL of Et_2O . The organic phase was collected and washed with 20 mL of 1:1 saturated aqueous NaHCO_3 and saturated aqueous NaCl . The aqueous washings were combined and extracted with 1 x 10 mL of Et_2O .

The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. Purification of the isolated material by chromatography on silica gel or by recrystallization (conditions given below) afforded the desired product.

Prepared according to procedure **A** using 3.0 equiv of $\text{BF}_3 \cdot \text{OEt}_2$ and purified by chromatography on silica gel (3:2 hexanes/EtOAc); off-white solid (92%): TLC R_f = 0.63 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 4.95 (d, 1H, J = 11.0 Hz), 4.74 (dt, 1H, J = 12.5, 1.8 Hz), 4.70 (dq, 1H, J = 11.0, 2.1 Hz), 4.59 (dd, 1H, J = 12.5, 1.8 Hz), 3.72-3.71 (m, 1H), 2.70 (dd, 1H, J = 2.9, 2.2 Hz), 2.27 (dt, 2H, J = 7.1, 2.2 Hz), 1.56-1.50 (m, 2H), 1.45-1.38 (m, 2H), 0.94 (t, 3H, J = 7.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 89.5, 74.4, 72.6, 62.7, 52.9, 30.1, 21.9, 18.2, 13.5 ppm; IR (thin film) ν 3524, 3257, 2959, 2933, 2873, 2244, 1427, 1366, 1180, 1019, 797 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{15}\text{NO}_4\text{S}$ 233.0722 found 234.0799 (MH^+).

Prepared according to procedure **A** using 3.0 equiv of $\text{BF}_3 \cdot \text{OEt}_2$ and purified by chromatography on silica gel (2:1 hexanes/EtOAc); white foam (85%): TLC R_f = 0.50 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 7.70-7.68 (m, 4H), 7.49-7.41 (m, 6H), 4.83 (br s, 1H), 4.71-4.63 (m, 2H), 4.53 (dd, 1H, J = 12.4, 1.7 Hz), 3.81 (t, 2H, J = 6.5 Hz), 3.63-3.62 (m, 1H), 2.67 (br s, 1H), 2.51 (dt, 2H, J = 6.5, 2.1 Hz), 1.09 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 135.5, 133.2, 129.9, 127.8, 86.7, 74.3, 73.9, 62.6, 61.9, 52.9, 26.7, 22.7, 19.2 ppm; IR (thin film) ν 3524, 3259, 2931, 2858, 2360, 1428, 1369, 1190, 1112, 1021, 795, 707 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_5\text{SSi}$ 459.1536 found 402.0832 ($\text{M}^+ - \text{C}_4\text{H}_9$).

Prepared according to procedure **A** using 3.0 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and purified by chromatography on silica gel (3:2 hexanes/EtOAc); colorless oil (82%): TLC R_f = 0.32 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 7.41-7.34 (m, 5H), 5.40 (br s, 1H), 4.68 (d, 1H, J = 11.1 Hz), 4.63 (d, 1H, J = 11.0 Hz), 4.59 (s, 2H), 4.43 (d, 1H, J = 12.6 Hz), 4.24 (s, 2H), 3.77 (br s, 1H), 3.54 (s, 1H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 136.6, 128.6, 128.4, 128.3, 83.4, 79.5, 74.8, 72.5, 62.4, 57.3, 52.6 ppm; IR (thin film) ν 3257, 2866, 1428, 1368, 1190, 1064, 1021, 798 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_5\text{S}$ 297.0671 found 297.0664 (M^+).

Prepared according to procedure **A** using 1.1 equiv of $\text{BF}_3 \cdot \text{OEt}_2$ and purified by chromatography on silica gel (2:1 hexanes/EtOAc); colorless oil (71%, 12:1 cis/trans mixture): TLC R_f = 0.85_{minor}, 0.59_{major} (1:1 hexanes/EtOAc); Major diastereomer: ^1H NMR (CDCl_3 , 500 MHz) δ 5.17 (dd, 1H, J = 8.6, 5.7 Hz), 4.38-4.36 (m, 1H), 3.64 (dd, 1H, J = 2.4, 0.8 Hz), 2.27 (dt, 2H, J = 7.0, 2.2 Hz), 1.93-1.88 (m, 1H), 1.76-1.71 (m, 1H), 1.57-1.37 (m, 8H), 0.96 (t, 3H, J = 7.1 Hz), 0.93 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 89.1, 84.1, 73.3, 66.7, 53.2, 30.3(2), 26.6,

22.1, 21.9, 18.4, 13.8, 13.5 ppm; IR (thin film) ν 3508, 3273, 2958, 2873, 2243, 1429, 1374, 1185, 1057, 999, 885 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{S}$ 289.1348 found 290.1412 (MH^+). Minor diastereomer: ^1H NMR (CDCl_3 , 500 MHz) δ 4.66 (dd, 1H, $J = 8.4, 5.9$ Hz), 4.62-4.58 (m, 2H), 3.59-3.58 (m, 1H), 2.34 (d, 1H, $J = 2.7$ Hz), 2.26 (dt, 2H, $J = 7.0, 1.6$ Hz), 1.99-1.95 (m, 1H), 1.80-1.64 (m, 1H), 1.56-1.24 (m, 8H), 0.96-0.93 (m, 6H) ppm; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{S}$ 289.1348 found 289.1353 (M^+).

^1H NMR nOe (CDCl_3 , 500 MHz):

Prepared according to procedure **B** using 2.6 equiv of $\text{BF}_3 \cdot \text{OEt}_2$, 4.1 equiv of alkyne, and 4.1 equiv of ZnCl_2 . Purified by chromatography on silica gel (15:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); white foam (70%, 8:1 cis/trans mixture): TLC $R_f = 0.34$ (3:2 Hex/ EtOAc); Major diastereomer: ^1H NMR (CDCl_3 , 500 MHz) δ 7.81 (d, 2H, $J = 8.2$ Hz), 7.39 (d, 2H, $J = 8.3$ Hz), 6.32 (d, 1H, $J = 9.0$ Hz), 5.40 (d, 1H, $J = 9.0$ Hz), 4.84-4.73 (m, 4H), 4.60 (dd, 1H, $J = 12.2, 2.1$ Hz), 4.12 (t, 2H, $J = 5.7$ Hz), 4.05 (dd, 1H, $J = 8.9, 2.0$ Hz), 2.59 (t, 2H, $J = 5.8$ Hz), 2.48 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.7, 145.4, 132.4, 130.0, 127.9, 95.2, 94.3, 86.7, 83.5, 74.7, 74.5, 67.3, 51.0, 21.7, 19.8 ppm; IR (thin film) ν 3359, 2960, 2256, 1731, 1538, 1434, 1360, 1191, 1097, 977, 906, 729 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{Cl}_3\text{N}_2\text{O}_8\text{S}_2$ 547.9648 found 512.9956 ($\text{M}^+ - \text{Cl}$).

Prepared according to procedure **A** using 1.1 equiv of $\text{BF}_3 \cdot \text{OEt}_2$ and purified by chromatography on silica gel (4:1 hexanes/ EtOAc); colorless oil (76%): TLC $R_f = 0.40$ (4:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 5.28 (s, 1H), 4.89 (d, 1H, $J = 5.1$ Hz), 4.10-4.08 (m, 2H), 2.20 (dt, 2H, $J = 7.1, 2.2$ Hz), 2.12-2.10 (m, 1H), 1.80-1.72 (m, 3H), 1.65-1.45 (m, 5H), 1.42-1.34 (m, 3H), 0.88 (t, 3H, $J = 7.3$ Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 86.6, 80.9, 75.9, 51.3, 39.5, 30.4, 30.2, 24.5, 24.1, 21.8, 19.7, 18.3, 13.5 ppm; IR (thin film) ν 3274, 2938, 2865, 2235, 1430, 1372, 1133, 1070, 965, 919, 877, 811 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3\text{S}$ 271.1242 found 271.1239 (M^+).

^1H NMR nOe (CDCl_3 , 500 MHz):

Prepared according to procedure **A** using 1.1 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and purified by chromatography on silica gel (4:1 hexanes/ EtOAc); colorless oil (80%, 6:1 syn/anti mixture): TLC $R_f = 0.50_{\text{minor}}, 0.28_{\text{major}}$ (4:1 hexanes/ EtOAc); Major diastereomer: ^1H NMR (CDCl_3 , 500 MHz) δ 4.91-4.85 (m, 1H), 4.56 (d, 1H, $J = 4.8$ Hz), 3.87-3.84 (m, 1H), 2.06 (dt, 2H, $J = 6.9, 2.0$ Hz), 1.62-1.14 (m, 11H), 0.78 (t, 3H, $J = 7.2$ Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 88.8, 83.5, 72.5, 49.3, 43.6, 30.5, 28.0, 22.3, 21.8, 18.32, 18.29, 13.5 ppm; IR (thin film) ν 3280, 2959, 2933, 2877,

2247, 1430, 1386, 1357, 1189, 1015, 826 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_3\text{S}$ 257.1086 found 190.0540 ($\text{M}^+ - \text{C}_5\text{H}_7$). Minor diastereomer: ^1H NMR (C_6D_6 , 500 MHz) δ 4.21-4.16 (m, 1H), 4.12-4.07 (m, 1H), 4.00-3.97 (m, 1H), 1.98 (dt, 2H, $J = 6.9, 1.9$ Hz), 1.60-1.47 (m, 2H), 1.40-1.20 (m, 7H), 1.09-1.03 (m, 1H), 0.88 (t, 3H, $J = 7.2$ Hz), 0.67-0.60 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 87.2, 85.5, 74.8, 51.2, 47.8, 30.3, 28.1, 22.2, 21.8, 18.15, 17.8, 13.5 ppm; IR (thin film) ν 3262, 2959, 2933, 2874, 2253, 1428, 1383, 1362, 1190, 1021, 821 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_3\text{S}$ 257.1086 found 190.0542 ($\text{M}^+ - \text{C}_5\text{H}_7$).

Prepared according to procedure **A** using 1.1 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and purified by chromatography on silica gel (4:1 hexanes/EtOAc); white foam (63%, 6:1 syn/anti mixture): TLC $R_f = 0.59_{\text{minor}}, 0.41_{\text{major}}$ (3:1 hexanes/EtOAc); Major diastereomer: ^1H NMR (CDCl_3 , 500 MHz) δ 7.72–7.69 (m, 4H), 7.48-7.40 (m, 6H), 4.95-4.90 (m, 1H), 4.75 (d, 1H, $J = 4.7$ Hz), 4.44-4.41 (m, 1H), 3.83 (dt, 2H, $J = 6.7, 2.0$ Hz), 2.57 (dt, 2H, $J = 6.6, 2.1$ Hz), 2.19-2.10 (m, 2H), 1.84-1.67 (m, 4H), 1.57-1.50 (m, 1H), 1.08 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 135.5, 133.4, 129.7, 127.7, 85.9, 83.5, 73.6, 62.2, 49.3, 43.6, 27.9, 26.7, 22.9, 22.3, 19.1, 18.3 ppm; IR (thin film) ν 3281, 2958, 2881, 2251, 1428, 1385, 1358, 1190, 1112, 1015, 912, 824 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{33}\text{NO}_4\text{SSi}$ 483.1900 found 426.1201 ($\text{M}^+ - \text{C}_4\text{H}_9$).

Prepared according to procedure **B** using 3.0 equiv of $\text{BF}_3 \cdot \text{OEt}_2$, 2.1 equiv of alkyne, and 2.1 equiv of ZnCl_2 . Purified by recrystallization from EtOAc/hexanes; beige powder (70%): TLC $R_f = 0.34$ (2:3 hexanes/EtOAc); ^1H NMR (CD_3OD , 500 MHz) δ 7.85 (d, 2H, $J = 8.3$ Hz), 7.50 (d, 2H, $J = 8.5$ Hz), 4.68 (dd, 1H, $J = 12.3, 1.4$ Hz), 4.56 (br d, 1H, $J = 1.8$ Hz), 4.42 (dd, 1H, $J = 12.3, 2.2$ Hz), 4.12 (t, 2H, $J = 6.5$ Hz), 3.61 (dd, 1H, $J = 4.3, 1.8$ Hz), 2.62 (dt, 2H, $J = 6.47, 2.1$ Hz), 2.50 (s, 3H) ppm; ^{13}C NMR (d_6 -acetone, 125 MHz) δ 146.0, 133.9, 130.9, 128.7, 82.2, 77.2, 76.6, 68.7, 63.2, 53.3, 21.5, 20.0 ppm; IR (KBr pellet) ν 3477, 3220, 2260, 1380, 1353, 1175, 1012, 963 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_7\text{S}_2$ 375.0446 found 375.0442 (M^+).

Experimental procedures and characterization data for 1,7,8-trihydroxyindolizidine synthesis (Scheme 1)

Oxathiazinane **7** (497 mg, 1.32 mmol) was dissolved in 10 mL of THF. Lindlar's catalyst (5 wt% Pd/ CaCO_3 /Pb, 150 mg, 70 μmol , 0.05 equiv) was added and the black suspension was stirred vigorously under 1 atm of H_2 for 40 min. The reaction mixture was filtered through a pad of Celite (30 x 20 mm) and the filter cake was washed with 10 mL of THF. The combined filtrates were concentrated under reduced pressure to an oily residue that was redissolved in 5 mL of THF. To this solution was added dropwise 0.5 M aqueous NaOH (3.2 mL, 1.60 mmol, 1.2 equiv). The colorless mixture was stirred for 10 min then poured into a separatory funnel containing 20 mL of EtOAc and 20 mL of saturated aqueous NaCl. The organic phase was collected and the aqueous layer was extracted with 1 x 20 mL of EtOAc. The organic extracts were combined, dried over MgSO_4 and concentrated under reduced pressure to a pale yellow oil. Purification of this material by chromatography on silica gel (1:1 hexanes/EtOAc) afforded the desired product **7a** as a colorless oil (222 mg, 82%): TLC $R_f = 0.43$ (1:2 hexanes/EtOAc); ^1H NMR

(CDCl₃, 500 MHz) δ 6.18-6.14 (m, 1H), 5.62-5.59 (m, 1H), 4.83 (dd, 1H, J = 12.1, 1.0 Hz), 4.57 (ddd, 1H, J = 12.1, 1.6, 0.7 Hz), 4.38 (q, 1H, J = 2.4 Hz), 3.73 (br d, 1H, J = 4.3 Hz), 3.71-3.66 (m, 1H), 3.35-3.31 (m, 1H), 2.35-2.26 (m, 3H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 129.9, 122.2, 76.1, 64.7, 59.3, 41.7, 24.3 ppm; IR (thin film) ν 3522, 2918, 1373, 1215, 1176, 1124, 971 cm⁻¹; HRMS (EI) calcd for C₇H₁₁NO₄S 205.0409 found 206.0487 (MH⁺).

To a solution of bicyclic oxathiazinane **7a** (142 mg, 0.69 mmol) in 1.5 mL of acetone was added successively NMO (98 mg, 0.84 mmol, 1.2 equiv), DABCO (12 mg, 0.10 mmol, 0.15 equiv), and OsO₄ (4 wt% in H₂O, 220 μ L, 0.05 equiv). The resulting brown solution was stirred for 7 hr then concentrated to dryness under reduced pressure. Purification of the oily residue by chromatography on silica gel (19:1 MeOH/EtOAc) afforded the triol product **8** as a white solid (132 mg, 80%): TLC R_f = 0.25 (19:1 MeOH/EtOAc); ¹H NMR (CD₃OD, 500 MHz) δ 4.78 (dd, 1H, J = 12.0, 1.2 Hz), 4.48 (dd, 1H, J = 12.1, 1.7 Hz), 4.01 (quint, 1H, J = 2.5 Hz), 3.98 (d, 1H, J = 1.5 Hz), 3.83 (dd, 1H, J = 8.8, 2.9 Hz), 3.49 (dd, 1H, J = 8.8, 2.0 Hz), 3.35-3.31 (m, 1H), 3.11 (dt, 1H, J = 11.3, 3.0 Hz), 1.91-1.85 (m, 1H), 1.80-1.73 (m, 1H) ppm; ¹³C NMR (CD₃OH, 125 MHz) δ 78.2, 67.7, 66.2, 62.3, 61.8, 39.3, 28.6 ppm; IR (KBr pellet) ν 3553, 3461, 2946, 2882, 1362, 1284, 1164, 1066, 934 cm⁻¹; HRMS (EI) calcd for C₇H₁₃NO₆S 239.0464 found 240.0542 (MH⁺).

Triol **8** (82 mg, 0.34 mmol) and KCN (112 mg, 1.72 mmol, 5.0 equiv) were dissolved in 0.7 mL of 1:1 ⁱPrOH and H₂O. The colorless solution was stirred at 55 °C for 2.5 h then concentrated under reduced pressure to a light brown powder. This material was dissolved in 3 mL of 1.0 M aqueous HCl, stirred for 1.25 h, then concentrated under reduced pressure and dried in vacuo (ca. 1 mm Hg). The isolated solid was redissolved in 1.2 mL of H₂O and to the pale yellow solution was added NaBH₄ (102 mg, 2.70 mmol, 7.9 equiv). The mixture was stirred for 14 h and the reaction was quenched by the addition of 2.6 mL of 1.0 M aqueous HCl. After stirring for 20 min, the pH of the solution was adjusted to ~11 by the addition of 1.0 M aqueous NaOH. The reaction mixture was concentrated under reduced pressure and the solid residue purified by chromatography on Davisil silica gel, grade 643 (2:3 MeOH/EtOAc + 2% conc. NH₄OH) to afford the desired product as an ammonium ion salt. Ion-exchange chromatography on Dowex 1 x 4-400 (OH⁻ form) gave the free base indolizidine **10** as a white crystalline solid (44 mg, 75%): TLC R_f = 0.25 (2:3 MeOH/EtOAc + 2% conc. NH₄OH); ¹H NMR (CD₃OD, 500 MHz) δ 4.34-4.31 (m, 1H), 4.00 (q, 1H, J = 3.0 Hz), 3.73 (dd, 1H, J = 10.0, 3.0 Hz), 3.09 (dt, 1H, J = 8.7, 2.0 Hz), 2.73 (ddd, 1H, J = 10.6, 4.7, 2.2 Hz), 2.28 (dt, 1H, J = 11.5, 3.2 Hz), 2.21-2.10 (m, 3H), 1.82-1.64 (m, 3H) ppm; ¹³C NMR (CD₃OH, 125 MHz) δ 71.3, 69.8, 69.0, 68.7, 53.4, 47.3, 33.4, 32.1 ppm; IR (KBr pellet) ν 3362, 2934, 2810, 1658, 1467, 1318, 1115, 1049 cm⁻¹; HRMS (DI) calcd for C₈H₁₅NO₃ 173.1051 found 173.1059 (M⁺).

Comparison of spectral data for **10** to that reported in Carretero, J. C.; Arrayás, R. G. *J. Org. Chem.* **1998**, *63*, 2993.

Compound **10**:

^1H NMR (D_2O , 500 MHz, DHO referenced at 4.60 ppm) δ 4.16 (ddd, 1H, $J = 7.3, 4.6, 1.7$ Hz, **H**₁), 3.85 (q, 1H, $J = 3.0$ Hz, **H**₇), 3.53 (dd, 1H, $J = 10.3, 3.1$ Hz, **H**₈), 2.84 (dt, 1H, $J = 9.1, 2.0$ Hz), 2.55 (ddd, 1H, $J = 11.5, 4.7, 2.0$ Hz), 2.06-1.89 (m, 4H), 1.66-1.59 (m, 1H), 1.55-1.48 (m, 1H), 1.42-1.35 (m, 1H) ppm.

^{13}C NMR (D_2O , 125 MHz) δ 70.0, 68.2, 67.7, 66.4, 51.9, 45.5, 31.5, 30.0 ppm.

(1*S*, 7*S*, 8*R*, 8*aR*)-1,7,8-trihydroxyindolizidine:

^1H NMR (D_2O , 200 MHz) δ 4.15 (m, 1H), 3.85 (q, 1H, $J = 3.0$ Hz), 3.53 (dd, 1H, $J = 10.2, 3.0$ Hz), 2.83 (td, 1H, $J = 9.1, 2.0$ Hz), 2.55 (ddd, 1H, $J = 11.5, 4.4, 2.3$ Hz), 2.11-1.85 (m, 4H), 1.66-1.33 (m, 3H) ppm.

^{13}C NMR (D_2O , 50 MHz) δ 70.0, 68.2, 67.6, 66.2, 51.9, 45.5, 31.6, 30.0 ppm.

The magnitude of the coupling constant between H_8 and H_{8a} is consistent with a *trans*-diaxial arrangement. For stereochemical assignments in related polyhydroxylated indolizidines, see: (a) Paolucci, C.; Mattioli, L. *J. Org. Chem.* **2001**, *66*, 4787-4794. (b) St. Denis, Y.; Chan, T. H. *Can. J. Chem.* **2000**, *78*, 776-783. (c) Davis, B.; Bell, A. A.; Nash, R. J.; Watson, A. A.; Griffiths, R. C.; Jones, M. G.; Smith, C.; Fleet, G. W. J. *Tetrahedron Lett.* **1996**, *37*, 8565-8568.

X-ray data for Homopropargyl Tosylate-derived Oxathiazinane 7 (Figure 3)

Experimental

Data Collection

A colorless rhombic crystal of C₁₄H₁₇NO₇S₂ was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART¹ CCD area detector with graphite monochromated Mo-K α radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 2121 reflections in the range 4° < 2 θ < 49.36° corresponded to a primitive triclinic cell with dimensions:

$$\begin{array}{ll} a = 6.195(1) \text{ \AA} & \alpha = 99.25(0)^\circ \\ b = 8.218(1) \text{ \AA} & \beta = 98.14(0)^\circ \\ c = 16.58(0) \text{ \AA} & \gamma = 101.06(0)^\circ \\ V = 804.8(0) \text{ \AA}^3 & \end{array}$$

For Z = 2 and F.W. = 375.41, the calculated density is 1.55 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$P-1 \text{ (\#2)}$$

The data were collected at a temperature of -140 $\pm$ 1 °C using the ω scan technique to a maximum 2 θ value of 49.4°. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°, counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT² with box parameters of 1.6 x 0.6. Of the 4079 reflections which were collected, 2554 were unique (R_{int} = 0.039); equivalent reflections were merged. No decay correction was applied.

The linear absorption coefficient, μ , for Mo-K α radiation is 3.7 cm⁻¹. Data were analyzed for agreement and possible absorption using SADABS³. A semi-empirical absorption correction based on 1447 reflections with I > 10 σ (I) was applied that resulted in transmission factors ranging from 0.608 to 0.990. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods⁴ and expanded using Fourier techniques⁵. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier but were fixed at idealized positions. The final cycle of full-matrix least-squares refinement⁶ on F² was based on 2554 observed reflections and 234 variable parameters and converged (largest parameter shift was less than 1% of its esd) with unweighted and weighted agreement factors of:

$$\begin{aligned} R_1 &= \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.048 \\ wR_2 &= [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.129 \end{aligned}$$

Experimental Details

A. Crystal Data

Empirical Formula	$\text{C}_{14}\text{H}_{17}\text{NO}_7\text{S}_2$
Formula Weight	375.41
Crystal Color, Habit	colorless rhombic
Crystal Dimensions	0.35 x 0.15 x 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	2121 ($4^\circ < 2\theta < 49.36^\circ$)
Lattice Parameters	$a = 6.195(1) \text{ \AA}$ $b = 8.218(1) \text{ \AA}$ $c = 16.58(0) \text{ \AA}$ $\alpha = 99.25(0)^\circ$ $\beta = 98.14(0)^\circ$ $\gamma = 101.06(0)^\circ$ $V = 804.8(0) \text{ \AA}^3$
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.549 g/cm^3
F_{000}	392.00
$\mu(\text{MoK}\alpha)$	3.68 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	MoK α ($\lambda = 0.71069$ Å) graphite monochromated
Temperature	−140 °C
Scan Type	ω (0.3°/frame)
Scan Rate	10 sec Frame Exposure
$2\theta_{\max}$	49.4°
No. of Reflections Measured	Total: 4079 Unique: 2554 ($R_{\text{int}} = 0.039$)
Corrections	Absorption, Lorentz, polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 0.00\sigma(I)$)	2554
No. Variables	234
Reflection/Parameter Ratio	10.91
Residuals: R_1 ; wR_2	0.048; 0.129
Goodness of Fit Indicator	1.27
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.44 e [−] /Å ³
Minimum peak in Final Diff. Map	−0.81 e [−] /Å ³

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
S(1)	0.227(0)	0.3026(1)	0.8577(1)	1.3(0)
S(2)	0.526(0)	1.2467(1)	1.3060(1)	1.5(0)
O(1)	-0.014(0)	0.278(0)	0.805(0)	1.4(1)
O(2)	0.387(0)	0.347(0)	0.805(0)	1.6(1)
O(3)	0.222(0)	0.155(0)	0.892(0)	1.9(1)
O(4)	-0.184(0)	0.544(0)	0.901(0)	1.4(0)
O(5)	0.384(0)	1.198(0)	1.216(0)	1.4(1)
O(6)	0.756(0)	1.253(0)	1.301(0)	1.9(1)
O(7)	0.461(0)	1.395(0)	1.343(0)	2.2(1)
N(1)	0.256(0)	0.464(0)	0.930(0)	1.2(1)
C(1)	0.205(1)	0.617(0)	0.900(0)	1.2(1)
C(2)	-0.028(1)	0.578(0)	0.847(0)	1.3(1)
C(3)	-0.057(1)	0.431(0)	0.775(0)	1.5(1)
C(4)	0.235(1)	0.759(0)	0.969(0)	1.3(1)
C(5)	0.248(1)	0.882(0)	1.019(0)	1.3(1)
C(6)	0.259(1)	1.037(0)	1.079(0)	1.3(1)
C(7)	0.410(1)	1.045(0)	1.161(0)	1.3(1)
C(8)	0.428(1)	1.076(0)	1.353(0)	1.4(1)
C(9)	0.222(1)	1.064(0)	1.379(0)	1.9(1)
C(10)	0.145(1)	0.927(0)	1.414(0)	2.0(1)
C(11)	0.267(1)	0.804(0)	1.423(0)	1.9(1)
C(12)	0.470(1)	0.818(0)	1.396(0)	1.9(1)
C(13)	0.550(1)	0.953(0)	1.360(0)	1.7(1)
C(14)	0.177(1)	0.653(1)	1.460(0)	2.8(1)
H(1)	0.310(1)	0.648(0)	0.865(0)	1.4(0)
H(2)	-0.050(1)	0.675(0)	0.825(0)	1.5(0)
H(3)	0.044(1)	0.461(0)	0.740(0)	1.7(0)
H(4)	-0.206(1)	0.407(0)	0.746(0)	1.8(0)
H(5)	0.315(1)	1.132(0)	1.056(0)	1.5(0)
H(6)	0.113(1)	1.041(0)	1.089(0)	1.5(0)
H(7)	0.561(1)	1.055(0)	1.153(0)	1.6(0)
H(8)	0.365(1)	0.948(0)	1.183(0)	1.6(0)
H(9)	0.138(1)	1.148(0)	1.374(0)	2.3(0)
H(10)	0.005(1)	0.917(0)	1.432(0)	2.4(0)
H(11)	0.555(1)	0.734(0)	1.401(0)	2.3(0)
H(12)	0.688(1)	0.962(0)	1.340(0)	2.0(0)
H(13)	0.077(1)	0.581(1)	1.414(0)	3.4(0)
H(14)	0.097(1)	0.677(1)	1.504(0)	3.4(0)
H(15)	0.292(1)	0.599(1)	1.478(0)	3.4(0)
H(16)	-0.309(0)	0.481(0)	0.876(0)	1.7(1)
H(17)	0.186(0)	0.438(0)	0.979(0)	1.5(1)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	0.015(0)	0.015(0)	0.019(1)	0.005(0)	0.007(0)	0.002(0)
S(2)	0.026(1)	0.015(0)	0.015(0)	0.003(0)	0.003(0)	0.003(0)
O(1)	0.02(0)	0.01(0)	0.02(0)	0.003(1)	0.005(1)	0.000(1)
O(2)	0.02(0)	0.02(0)	0.02(0)	0.005(1)	0.010(1)	0.002(1)
O(3)	0.03(0)	0.02(0)	0.03(0)	0.011(1)	0.01(0)	0.01(0)
O(4)	0.01(0)	0.02(0)	0.02(0)	0.002(1)	0.004(1)	0.003(1)
O(5)	0.02(0)	0.02(0)	0.01(0)	0.009(1)	0.001(1)	-0.000(1)
O(6)	0.02(0)	0.03(0)	0.02(0)	-0.001(1)	-0.001(1)	0.01(0)
O(7)	0.05(0)	0.02(0)	0.02(0)	0.01(0)	0.01(0)	0.001(1)
N(1)	0.02(0)	0.01(0)	0.01(0)	0.01(0)	0.01(0)	0.00(0)
C(1)	0.02(0)	0.01(0)	0.01(0)	0.00(0)	0.01(0)	0.00(0)
C(2)	0.02(0)	0.02(0)	0.02(0)	0.01(0)	0.01(0)	0.00(0)
C(3)	0.02(0)	0.02(0)	0.02(0)	0.00(0)	0.00(0)	0.01(0)
C(4)	0.01(0)	0.02(0)	0.02(0)	0.00(0)	0.00(0)	0.00(0)
C(5)	0.02(0)	0.01(0)	0.02(0)	0.00(0)	0.00(0)	0.00(0)
C(6)	0.02(0)	0.01(0)	0.02(0)	0.00(0)	0.00(0)	-0.00(0)
C(7)	0.02(0)	0.01(0)	0.02(0)	0.01(0)	0.01(0)	-0.00(0)
C(8)	0.02(0)	0.02(0)	0.01(0)	0.00(0)	0.00(0)	0.00(0)
C(9)	0.03(0)	0.03(0)	0.02(0)	0.01(0)	0.01(0)	0.00(0)
C(10)	0.02(0)	0.03(0)	0.02(0)	0.00(0)	0.01(0)	0.00(0)
C(11)	0.04(0)	0.02(0)	0.01(0)	-0.00(0)	0.00(0)	-0.00(0)
C(12)	0.03(0)	0.02(0)	0.02(0)	0.01(0)	0.00(0)	0.00(0)
C(13)	0.02(0)	0.02(0)	0.02(0)	0.00(0)	0.00(0)	0.00(0)
C(14)	0.05(0)	0.03(0)	0.03(0)	-0.00(0)	0.01(0)	0.01(0)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table 3. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S(1)	O(1)	1.59(0)	S(1)	O(2)	1.44(0)
S(1)	O(3)	1.42(0)	S(1)	N(1)	1.61(0)
S(2)	O(5)	1.58(0)	S(2)	O(6)	1.43(0)
S(2)	O(7)	1.43(0)	S(2)	C(8)	1.75(0)
O(1)	C(3)	1.47(0)	O(4)	C(2)	1.43(0)
O(5)	C(7)	1.48(0)	N(1)	C(1)	1.49(0)
C(1)	C(2)	1.53(0)	C(1)	C(4)	1.47(0)
C(2)	C(3)	1.51(0)	C(4)	C(5)	1.18(0)
C(5)	C(6)	1.47(0)	C(6)	C(7)	1.51(0)
C(8)	C(9)	1.40(1)	C(8)	C(13)	1.39(0)
C(9)	C(10)	1.38(1)	C(10)	C(11)	1.39(1)
C(11)	C(12)	1.39(1)	C(11)	C(14)	1.51(1)
C(12)	C(13)	1.39(0)			

Table 4. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
O(4)	H(16)	0.85	N(1)	H(17)	1.00
C(1)	H(1)	0.95	C(2)	H(2)	0.95
C(3)	H(3)	0.95	C(3)	H(4)	0.95
C(6)	H(5)	0.95	C(6)	H(6)	0.95
C(7)	H(7)	0.95	C(7)	H(8)	0.95
C(9)	H(9)	0.95	C(10)	H(10)	0.95
C(12)	H(11)	0.95	C(13)	H(12)	0.95
C(14)	H(13)	0.95	C(14)	H(14)	0.95
C(14)	H(15)	0.95			

Table 5. Bond angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	S(1)	O(2)	107.3(0)	O(1)	S(1)	O(3)	105.6(0)
O(2)	S(1)	O(3)	120.2(0)	O(1)	S(1)	N(1)	105.8(0)
O(2)	S(1)	N(1)	107.3(0)	O(3)	S(1)	N(1)	109.7(0)
O(5)	S(2)	O(6)	109.1(0)	O(5)	S(2)	O(7)	104.2(0)
O(6)	S(2)	O(7)	119.5(0)	O(5)	S(2)	C(8)	104.0(0)
O(6)	S(2)	C(8)	108.6(0)	O(7)	S(2)	C(8)	110.3(0)
S(1)	O(1)	C(3)	114.2(0)	S(2)	O(5)	C(7)	117.9(0)
S(1)	N(1)	C(1)	113.7(0)	N(1)	C(1)	C(2)	111.3(0)
N(1)	C(1)	C(4)	110.7(0)	C(2)	C(1)	C(4)	111.7(0)
O(4)	C(2)	C(1)	106.9(0)	O(4)	C(2)	C(3)	111.9(0)
C(1)	C(2)	C(3)	111.3(0)	O(1)	C(3)	C(2)	111.6(0)
C(1)	C(4)	C(5)	172.6(0)	C(4)	C(5)	C(6)	178.2(0)
C(5)	C(6)	C(7)	111.9(0)	O(5)	C(7)	C(6)	104.8(0)
S(2)	C(8)	C(9)	119.2(0)	S(2)	C(8)	C(13)	119.7(0)
C(9)	C(8)	C(13)	121.1(0)	C(8)	C(9)	C(10)	118.2(0)
C(9)	C(10)	C(11)	121.8(0)	C(10)	C(11)	C(12)	118.8(0)
C(10)	C(11)	C(14)	120.6(0)	C(12)	C(11)	C(14)	120.5(0)
C(11)	C(12)	C(13)	120.6(0)	C(8)	C(13)	C(12)	119.4(0)

Table 6. Bond angles involving hydrogens(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	O(4)	H(16)	112.7(0)	S(1)	N(1)	H(17)	113.8(1)
C(1)	N(1)	H(17)	115.0(0)	N(1)	C(1)	H(1)	107.6(0)
C(2)	C(1)	H(1)	107.7(0)	C(4)	C(1)	H(1)	107.6(0)
O(4)	C(2)	H(2)	108.9(0)	C(1)	C(2)	H(2)	108.9(0)
C(3)	C(2)	H(2)	108.9(0)	O(1)	C(3)	H(3)	109.0(0)
C(2)	C(3)	H(3)	109.0(0)	O(1)	C(3)	H(4)	108.8(0)
C(2)	C(3)	H(4)	108.9(0)	H(3)	C(3)	H(4)	109.5(0)
C(5)	C(6)	H(5)	108.8(0)	C(7)	C(6)	H(5)	108.8(0)
C(5)	C(6)	H(6)	108.9(0)	C(7)	C(6)	H(6)	108.9(0)
H(5)	C(6)	H(6)	109.5(0)	O(5)	C(7)	H(7)	110.7(0)
C(6)	C(7)	H(7)	110.7(0)	O(5)	C(7)	H(8)	110.6(0)
C(6)	C(7)	H(8)	110.6(0)	H(7)	C(7)	H(8)	109.5
C(8)	C(9)	H(9)	120.9(0)	C(10)	C(9)	H(9)	120.9(0)
C(9)	C(10)	H(10)	119.1(0)	C(11)	C(10)	H(10)	119.1(0)
C(11)	C(12)	H(11)	119.7(0)	C(13)	C(12)	H(11)	119.7(0)
C(8)	C(13)	H(12)	120.3(0)	C(12)	C(13)	H(12)	120.3(0)
C(11)	C(14)	H(13)	101.9(0)	C(11)	C(14)	H(14)	114.8(0)
H(13)	C(14)	H(14)	109.5(0)	C(11)	C(14)	H(15)	111.4(0)
H(13)	C(14)	H(15)	109.5(0)	H(14)	C(14)	H(15)	109.4(0)

Table 7. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(2)	S(1)	O(1)	C(3)	-61.1(0)	O(3)	S(1)	O(1)	C(3)	169.5(0)
N(1)	S(1)	O(1)	C(3)	53.2(0)	O(1)	S(1)	N(1)	C(1)	-52.0(0)
O(2)	S(1)	N(1)	C(1)	62.4(0)	O(3)	S(1)	N(1)	C(1)	-165.4(0)
O(6)	S(2)	O(5)	C(7)	52.4(0)	O(7)	S(2)	O(5)	C(7)	-179.0(0)
C(8)	S(2)	O(5)	C(7)	-63.4(0)	O(5)	S(2)	C(8)	C(9)	-76.6(1)
O(5)	S(2)	C(8)	C(13)	101.0(1)	O(6)	S(2)	C(8)	C(9)	167.2(0)
O(6)	S(2)	C(8)	C(13)	-15.2(1)	O(7)	S(2)	C(8)	C(9)	34.5(1)
O(7)	S(2)	C(8)	C(13)	-147.9(0)	S(1)	O(1)	C(3)	C(2)	-58.0(0)
S(2)	O(5)	C(7)	C(6)	-178.4(0)	S(1)	N(1)	C(1)	C(2)	55.3(0)
S(1)	N(1)	C(1)	C(4)	-179.9(0)	N(1)	C(1)	C(2)	O(4)	66.8(0)
N(1)	C(1)	C(2)	C(3)	-55.7(1)	C(4)	C(1)	C(2)	O(4)	-57.5(1)
C(4)	C(1)	C(2)	C(3)	-180.0(0)	N(1)	C(1)	C(4)	C(5)	-171.4(3)
C(2)	C(1)	C(4)	C(5)	-46.8(4)	O(4)	C(2)	C(3)	O(1)	-62.6(0)
C(1)	C(2)	C(3)	O(1)	56.9(1)	C(1)	C(4)	C(5)	C(6)	24.0(1)
C(4)	C(5)	C(6)	C(7)	170.2(1)	C(5)	C(6)	C(7)	O(5)	-174.5(0)
S(2)	C(8)	C(9)	C(10)	178.5(0)	C(13)	C(8)	C(9)	C(10)	1.0(1)
S(2)	C(8)	C(13)	C(12)	-179.3(0)	C(9)	C(8)	C(13)	C(12)	-1.7(1)
C(8)	C(9)	C(10)	C(11)	0.4(1)	C(9)	C(10)	C(11)	C(12)	-0.9(1)
C(9)	C(10)	C(11)	C(14)	-178.8(0)	C(10)	C(11)	C(12)	C(13)	0.2(1)
C(14)	C(11)	C(12)	C(13)	178.1(0)	C(11)	C(12)	C(13)	C(8)	1.1(1)

Table 8. Distances beyond the asymmetric unit out to 3.00 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
S(1)	O(1)	1.59(0)	(1)	S(1)	O(2)	1.44(0)	(1)
S(1)	O(3)	1.42(0)	(1)	S(1)	N(1)	1.61(0)	(1)
S(1)	C(1)	2.60(0)	(1)	S(1)	C(3)	2.56(0)	(1)
S(2)	O(5)	1.58(0)	(1)	S(2)	O(6)	1.43(0)	(1)
S(2)	O(7)	1.43(0)	(1)	S(2)	C(7)	2.62(0)	(1)
S(2)	C(8)	1.75(0)	(1)	S(2)	C(9)	2.73(0)	(1)
S(2)	C(13)	2.72(0)	(1)	O(1)	O(2)	2.44(0)	(1)
O(1)	O(3)	2.40(0)	(1)	O(1)	O(4)	2.94(0)	(1)
O(1)	N(1)	2.55(0)	(1)	O(1)	C(1)	2.93(0)	(1)
O(1)	C(2)	2.47(0)	(1)	O(1)	C(3)	1.47(0)	(1)
O(2)	O(3)	2.48(0)	(1)	O(2)	O(4)	2.92(0)	(1,1,1)
O(2)	N(1)	2.46(0)	(1)	O(2)	C(1)	3.00(0)	(1)
O(2)	C(3)	2.96(0)	(1)	O(3)	N(1)	2.48(0)	(1)
O(4)	N(1)	2.91(0)	(1)	O(4)	N(1)	2.90(0)	(-1,1,0,1,2)
O(4)	C(1)	2.38(0)	(1)	O(4)	C(2)	1.43(0)	(1)
O(4)	C(3)	2.44(0)	(1)	O(4)	C(4)	2.81(0)	(1)
O(5)	O(6)	2.45(0)	(1)	O(5)	O(7)	2.37(0)	(1)
O(5)	C(6)	2.37(0)	(1)	O(5)	C(7)	1.48(0)	(1)
O(5)	C(8)	2.63(0)	(1)	O(6)	O(7)	2.47(0)	(1)
O(6)	C(7)	2.98(0)	(1)	O(6)	C(8)	2.59(0)	(1)
O(6)	C(13)	2.92(0)	(1)	O(7)	C(8)	2.62(0)	(1)
N(1)	C(1)	1.49(0)	(1)	N(1)	C(2)	2.50(0)	(1)
N(1)	C(3)	2.93(0)	(1)	N(1)	C(4)	2.43(0)	(1)
C(1)	C(2)	1.53(0)	(1)	C(1)	C(3)	2.52(0)	(1)
C(1)	C(4)	1.47(0)	(1)	C(1)	C(5)	2.64(0)	(1)
C(2)	C(3)	1.51(0)	(1)	C(2)	C(4)	2.48(0)	(1)
C(4)	C(5)	1.18(0)	(1)	C(4)	C(6)	2.65(0)	(1)
C(5)	C(6)	1.47(0)	(1)	C(5)	C(7)	2.47(0)	(1)
C(6)	C(7)	1.51(0)	(1)	C(8)	C(9)	1.40(1)	(1)
C(8)	C(10)	2.38(0)	(1)	C(8)	C(11)	2.78(0)	(1)
C(8)	C(12)	2.40(0)	(1)	C(8)	C(13)	1.39(0)	(1)
C(9)	C(10)	1.38(1)	(1)	C(9)	C(11)	2.42(1)	(1)
C(9)	C(12)	2.79(1)	(1)	C(9)	C(13)	2.42(1)	(1)
C(10)	C(11)	1.39(1)	(1)	C(10)	C(12)	2.39(1)	(1)
C(10)	C(13)	2.77(1)	(1)	C(10)	C(14)	2.52(1)	(1)
C(11)	C(12)	1.39(1)	(1)	C(11)	C(13)	2.41(1)	(1)
C(11)	C(14)	1.51(1)	(1)	C(12)	C(13)	1.39(0)	(1)
C(12)	C(14)	2.52(1)	(1)				

*ADC (S, L, TX, TY, TZ) represents following things:

S: Symmetry operation number. -S is inversion of operation S.
(1) X,Y,Z

L: Lattice translation.
(1) 0, 0, 0

TX, TY, TZ: Unit cell translation along the x, y, and z directions.

Table 9. Distances beyond the asymmetric unit out to 3.00 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
S(1)	H(1)	2.77(0)	(1)	S(1)	H(3)	2.75(0)	(1)
S(1)	H(16)	2.92(0)	(1,1,1)	S(1)	H(17)	2.21(0)	(1)
S(2)	H(7)	2.82(0)	(1)	S(2)	H(8)	2.84(0)	(1)
S(2)	H(9)	2.84(0)	(1)	S(2)	H(12)	2.83(0)	(1)
O(1)	H(3)	1.99(0)	(1)	O(1)	H(4)	1.99(0)	(1)
O(1)	H(8)	2.63(0)	(-1,1,0,1,2)	O(1)	H(16)	2.94(0)	(1)
O(1)	H(17)	2.96(0)	(1)	O(2)	H(1)	2.67(0)	(1)
O(2)	H(3)	2.65(0)	(1)	O(2)	H(4)	2.82(0)	(1,1,1)
O(2)	H(16)	2.08(0)	(1,1,1)	O(3)	H(5)	2.74(0)	(1,1,0,-1)
O(3)	H(6)	2.46(0)	(-1,1,0,1,2)	O(3)	H(7)	2.47(0)	(-1,1,1,1,2)
O(3)	H(17)	2.60(0)	(1)	O(4)	H(2)	1.95(0)	(1)
O(4)	H(4)	2.61(0)	(1)	O(4)	H(5)	2.94(0)	(-1,1,0,2,2)
O(4)	H(16)	0.85	(1)	O(4)	H(17)	2.82(0)	(1)
O(4)	H(17)	1.97(0)	(-1,1,0,1,2)	O(5)	H(1)	2.71(0)	(-1,1,1,2,2)
O(5)	H(2)	2.55(0)	(-1,1,0,2,2)	O(5)	H(5)	2.57(0)	(1)
O(5)	H(6)	2.49(0)	(1)	O(5)	H(7)	2.02(0)	(1)
O(5)	H(8)	2.02(0)	(1)	O(6)	H(3)	2.67(0)	(-1,1,1,2,2)
O(6)	H(7)	2.70(0)	(1)	O(6)	H(9)	2.84(0)	(1,1,1)
O(6)	H(12)	2.55(0)	(1)	O(7)	H(4)	2.90(0)	(-1,1,0,2,2)
O(7)	H(9)	2.73(0)	(1)	O(7)	H(11)	2.72(0)	(1,1,0,1)
N(1)	H(1)	2.00(0)	(1)	N(1)	H(16)	2.96(0)	(1,1,1)
N(1)	H(17)	1.00	(1)	C(1)	H(1)	0.95	(1)
C(1)	H(2)	2.05(0)	(1)	C(1)	H(3)	2.71(0)	(1)
C(1)	H(17)	2.12(0)	(1)	C(2)	H(1)	2.03(0)	(1)
C(2)	H(2)	0.95	(1)	C(2)	H(3)	2.03(0)	(1)
C(2)	H(4)	2.03(0)	(1)	C(2)	H(16)	1.92(0)	(1)
C(2)	H(17)	2.90(0)	(1)	C(3)	H(1)	2.69(0)	(1)
C(3)	H(2)	2.03(0)	(1)	C(3)	H(3)	0.95	(1)
C(3)	H(4)	0.95	(1)	C(3)	H(16)	2.47(0)	(1)
C(4)	H(1)	1.98(0)	(1)	C(4)	H(2)	2.67(0)	(1)
C(4)	H(5)	2.87(0)	(-1,1,1,2,2)	C(4)	H(17)	2.63(0)	(1)
C(5)	H(5)	1.99(0)	(1)	C(5)	H(6)	1.99(0)	(1)
C(5)	H(6)	2.90(0)	(-1,1,0,2,2)	C(5)	H(7)	2.73(0)	(1)
C(5)	H(8)	2.65(0)	(1)	C(6)	H(5)	0.95	(1)
C(6)	H(6)	0.95	(1)	C(6)	H(7)	2.05(0)	(1)
C(6)	H(8)	2.05(0)	(1)	C(7)	H(1)	2.90(0)	(-1,1,1,2,2)
C(7)	H(5)	2.03(0)	(1)	C(7)	H(6)	2.03(0)	(1)

Table 9. Distances beyond the asymmetric unit out to 3.00 Å (continued)

atom	atom	distance	ADC	atom	atom	distance	ADC
C(7)	H(7)	0.95	(1)	C(7)	H(8)	0.95	(1)
C(8)	H(8)	2.79(0)	(1)	C(8)	H(9)	2.06(1)	(1)
C(8)	H(12)	2.04(0)	(1)	C(9)	H(9)	0.95	(1)
C(9)	H(10)	2.02(0)	(1)	C(10)	H(9)	2.04(1)	(1)
C(10)	H(10)	0.95	(1)	C(10)	H(13)	2.79(1)	(1)
C(10)	H(14)	2.72(1)	(1)	C(11)	H(4)	2.98(0)	(-1,1,0,1,2)
C(11)	H(10)	2.03(1)	(1)	C(11)	H(11)	2.04(1)	(1)
C(11)	H(13)	1.94(1)	(1)	C(11)	H(14)	2.10(1)	(1)
C(11)	H(15)	2.06(1)	(1)	C(12)	H(4)	2.82(0)	(-1,1,0,1,2)
C(12)	H(11)	0.95	(1)	C(12)	H(12)	2.04(0)	(1)
C(12)	H(13)	2.89(1)	(1)	C(12)	H(15)	2.61(1)	(1)
C(13)	H(8)	2.98(0)	(1)	C(13)	H(10)	2.99(1)	(1,1,1)
C(13)	H(11)	2.04(0)	(1)	C(13)	H(12)	0.95	(1)
C(14)	H(10)	2.67(1)	(1)	C(14)	H(11)	2.67(1)	(1)
C(14)	H(13)	0.95	(1)	C(14)	H(14)	0.95	(1)
C(14)	H(15)	0.95	(1)	H(1)	H(2)	2.30(0)	(1)
H(1)	H(3)	2.54(0)	(1)	H(1)	H(5)	2.67(0)	(-1,1,1,2,2)
H(1)	H(7)	2.50(0)	(-1,1,1,2,2)	H(1)	H(16)	2.95(0)	(1,1,1)
H(1)	H(17)	2.84(0)	(1)	H(2)	H(3)	2.29(0)	(1)
H(2)	H(4)	2.33(0)	(1)	H(2)	H(6)	2.66(0)	(-1,1,0,2,2)
H(2)	H(16)	2.37(0)	(1)	H(3)	H(4)	1.55	(1)
H(3)	H(13)	2.49(1)	(-1,1,0,1,2)	H(4)	H(11)	2.93(0)	(-1,1,0,1,2)
H(4)	H(13)	2.88(1)	(-1,1,0,1,2)	H(4)	H(16)	2.35(0)	(1)
H(5)	H(6)	1.55	(1)	H(5)	H(7)	2.31(0)	(1)
H(5)	H(8)	2.80(0)	(1)	H(6)	H(7)	2.80(0)	(1)
H(6)	H(8)	2.36(0)	(1)	H(7)	H(8)	1.55	(1)
H(9)	H(10)	2.33(1)	(1)	H(9)	H(12)	2.84(1)	(1,1,-1)
H(9)	H(14)	2.99(1)	(-1,1,0,2,3)	H(10)	H(10)	2.46(1)	(-1,1,0,2,3)
H(10)	H(11)	2.84(1)	(1,1,-1)	H(10)	H(12)	2.43(1)	(1,1,-1)
H(10)	H(13)	2.85(1)	(1)	H(10)	H(14)	2.57(1)	(1)
H(11)	H(12)	2.34(0)	(1)	H(11)	H(15)	2.42(1)	(1)
H(13)	H(14)	1.55	(1)	H(13)	H(14)	2.83(1)	(-1,1,0,1,3)
H(13)	H(15)	1.55	(1)	H(14)	H(14)	2.91(1)	(-1,1,0,1,3)
H(14)	H(15)	1.55	(1)	H(16)	H(17)	2.37(0)	(-1,1,0,1,2)
H(17)	H(17)	2.82(1)	(-1,1,0,1,2)				

*ADC (S, L, TX, TY, TZ) represents following things:

S: Symmetry operation number. -S is inversion of operation S.

(1) X,Y,Z

L: Lattice translation.

(1) 0, 0, 0

TX, TY, TZ: Unit cell translation along the x, y, and z directions.