Oxidative Ring-Opening of Benzothiazole Derivatives

Ryan E. Moreira, Geoffrey S. Sinclair, Derek J. Schipper

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

General Methods:

Solvents were either reagent grade and/or HPLC grade. Chemical reagents were purchased from Sigma-Aldrich. Reactions were monitored using commercial thin-layer chromatography (TLC) plates. Developed TLC plates were examined under a UV lamp (254 nm). Flash chromatography was performed using 230–400 mesh silica gel. ¹H-NMR spectra were recorded on a Bruker AVANCE300 (300 MHz) δ or Bruker AC300 (300 MHz) δ NMR spectrometers. ¹³C-NMR spectra were broad band decoupled and recorded on a Bruker AVANCE300 (75.5 MHz) δ or Bruker AC300 (75.5 MHz) δ NMR spectrometers using the carbon signal of the deuterated solvent as the internal standard. The following abbreviations are used for NMR peak multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet; br, broad. Chemical shifts are reported in parts per million (ppm) relative to either TMS (δ 0.0) or chloroform (δ 7.25) for ¹H-NMR, and chloroform (δ 77.0) for ¹³CNMR. High resolution mass spectra (HRMS) were obtained via electrospray ionization (ESI) or direct analysis in real time (DART) which were measured on a Thermo Scientific Q ExactiveTM Plus Hybrid Quadrupole-OrbitrapTM at the University of Waterloo Mass Spectrometry Facility. X-ray crystal structure was determined by Dr. Jalil Assoud and figures of X-ray crystal structures were generated using Mercury.

Contents

1.	Synthetic Procedures.....	2
2.	Reaction Profile Data	6
3.	Crystallographic Data	7
4.	Spectral Data of New Compounds	13

1. Synthetic Procedures

GENERAL PROCEDURE A

A 0.2 M solution of benzothiazole **1** (1.00 mmol, 1.0 equiv) in alcohol **2** (5 mL) was stirred vigorously, at which point MMPP (1.00 g, 1.60 mmol, 1.6 equiv) was added. The reaction mixture was stirred at room temperature for 4 hours. The reaction mixture was stirred at room temperature for 4 hours. After the reaction time, H_2O (10 mL) was added to the reaction vessel and the solution was extracted with 3 x CH_2Cl_2 (10 mL). The organic layers were collected, dried over $MgSO_4$, filtered and concentrated to yield the crude product. The product was purified by silica gel column chromatography (1:4 EtOAc/hexanes $\rightarrow$ 2:3 EtOAc/hexanes) to yield purified product **3**.

methyl 2-formamidobenzenesulfonate (3a)

This compound was synthesized following the General Procedure A with benzothiazole **1a** (135 mg) and MeOH (**2a**). This yielded **3a** as a light yellow, waxy solid (97 mg, 0.45 mmol, **45 % yield**). R_f = 0.4 (2:3 EtOAc/hexanes). 1H NMR ($CDCl_3$, 300 MHz) (Rotamer ratio: 2.2:1, Asterisk denotes minor peak) δ 8.97 (br. s, 1H) *8.53 (br. s, 1H) 8.59 (d, 1H, J = 8.58 Hz) 8.50 (s, 1H) 7.93 (d, 1H, J = 7.99 Hz) 7.67 (t, 1H, J = 7.81 Hz) 7.28 (t, 1H, J = 7.80 Hz) 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.6, 138.2, 137.7, 132.3, 126.3, 125.5, 124.2, 59.1. HRMS calculated for $C_8H_{10}NO_4S$ (M+H) 216.0325; Found 216.0326.

ethyl 2-formamidobenzenesulfonate (3b)

This compound was synthesized following the General Procedure A with benzothiazole **1a** (135 mg), EtOH (**2b**) and a reaction time of 22 h. This yielded **3b** as a dull yellow solid (105 mg, 0.46 mmol, **46% yield**). R_f = 0.28 (1:4 EtOAc/hexanes). 1H NMR ($CDCl_3$, 300 MHz) (Rotamer ratio: 2.1:1, Asterisk denotes minor peak) δ 8.97 (br. s, 1H) *8.80 (br. s, 1H) 8.57 (d, 1H, J = 8.67 Hz) 8.48 (s, 1H) 7.93 (d, 1H, J = 7.93 Hz) 7.66 (t, 1H, J = 7.92) 7.29 (t, 1H, J = 7.84 Hz) 4.11 (q, 2H, J = 6.89 Hz) 1.31 (t, 3H, J = 7.02). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 135.8, 135.5, 130.1, 124.3, 123.4(4), 123.4(2), 68.1, 14.7. HRMS calculated for $C_9H_{12}NO_4S$ (M+H) 230.0482; Found 230.0482.

isopropyl 2-formamidobenzenesulfonate (3c)

This compound was synthesized following the General Procedure A with benzothiazole **1a** (135 mg), *i*-PrOH (**2c**) and a reaction time of 22 h. This yielded **3c** as a white solid (57 mg, 0.24 mmol, **25% yield**). *R*_f = 0.38 (2:3 EtOAc/hexanes). ¹H NMR (CDCl₃, 300 MHz) (Rotamer ratio: 3.1:1, Asterisk denotes minor peak) δ 8.95 (br. s, 1H) *8.77 (br. s, 1H) 8.55 (d, 1H, *J* = 9.00 Hz) 7.94 (d, 1H, *J* = 7.50 Hz) 7.65 (t, 1H, *J* = 7.81 Hz) 7.28 (m, 1H) 4.70 (sept., 1H, *J* = 6.38 Hz) 1.26 (d, 6H, *J* = 6.12 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 159.2, 135.6, 135.3, 129.8, 124.8, 124.4, 123.5, 79.0, 22.8. HRMS calculated for C₁₀H₁₃NO₄S (M+H) 244.0638; Found 244.0638.

butyl 2-formamidobenzenesulfonate (3d)

This compound was synthesized following the General Procedure A with benzothiazole **1a** (135 mg), *n*-BuOH (**2d**) and a reaction time of 22 h. The butanol was removed *in-vacuo* using a toluene:butanol (1:1) azeotrope. This yielded **3d** as a bright yellow solid (77 mg, 0.30 mmol, **30% yield**). *R*_f = 0.30 (1:5 EtOAc/hexanes). ¹H NMR (CDCl₃, 300 MHz) (Rotamer ratio: 2.0:1, Asterisk denotes minor peak) δ 9.00 (br. s, 1H) *8.79 (br. s, 1H) 8.57 (d, 1H, *J* = 8.69 Hz) 8.50 (s, 1H) 7.92 (d, 1H, *J* = 7.72 Hz) 7.66 (t, 1H, *J* = 7.93 Hz) 7.28 (t, 1H, *J* = 7.72 Hz) *4.10 (m, 2H) 4.03 (t, 2H, *J* = 6.74 Hz) 1.61 (quint, 2H, *J* = 6.74 Hz) 1.31 (sext, 2H, *J* = 7.38 Hz) 0.84 (t, 3H, *J* = 7.34 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 159.2, 135.9, 135.5, 130.2, 124.4, 123.4, 123.3, 71.7, 30.8, 18.7, 13.5. HRMS calculated for C₁₁H₁₆NO₄S (M+H) 258.0795; Found 258.0796.

2,2,2-trifluoroethyl 2-formamidobenzenesulfonate (3e)

This compound was synthesized following the General Procedure A with benzothiazole **1a** (135 mg), 2,2,2-trifluoroethanol (**2e**) and a reaction time of 22 h. This yielded **3e** as a light yellow solid (29 mg, 0.11 mmol, **11% yield**). *R*_f = 0.38 (2:3 EtOAc/hexanes). ¹H NMR (CDCl₃, 300 MHz) (Rotamer ratio: 5.4:1, Asterisk denotes minor peak) δ 8.82 (br. s, 1H) *8.76 (br. s, 1H) 8.62 (d, 1H, *J* = 8.36 Hz) 8.51 (s, 1H) *8.037 (m, 1H) 7.93 (d, 1H, *J* = 8.07 Hz) 7.72 (t, 1H, *J* = 7.82 Hz) *7.44 (m, 1H) 7.31 (t, 1H, *J* = 7.83 Hz) *4.43 (m, 2H) 4.36 (q, 2H, *J* = 8.39 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 158.9, 136.4, 136.1, 130.0, 125.7, 124.4, 123.6, 122.6, 121.7, 120.4, 118.2, 65.4, 65.1, 64.8, 64.5. ¹⁹F NMR (CDCl₃, 280 MHz) δ -73.8. HRMS calculated for C₉H₉NO₄SF₃ (M+H) 284.0199; Found 284.0198.

ethyl 2-acetamidobenzenesulfonate (3h)

This compound was synthesized following the General Procedure A with 2-methylbenzothiazole **1b** (149 mg), ethanol (**2b**) and a reaction time of 22 h. This yielded **3h** as a pale yellow solid (43 mg, 0.18 mmol, **18% yield**). $R_f = 0.24$ (1:4 EtOAc/hexanes). ^1H NMR (CDCl_3 , 300 MHz) δ 8.96 (br. s, 1H) 8.46 (d, 1H, $J = 8.38$ Hz) 7.88 (dd, 1H, $J = 7.98$, 1.45 Hz) 7.65-7.59 (m, 1H) 7.21 (t, 1H, $J = 7.68$ Hz) 4.08 (q, 2H, $J = 7.11$ Hz) 2.22 (s, 3H) 1.27 (t, 3H, $J = 7.12$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.8, 137.0, 135.3, 129.9, 123.7, 123.4, 123.2, 68.0, 25.2, 14.8. HRMS calculated for $\text{C}_{10}\text{H}_{14}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) 244.0644; Found 244.0639.

ethyl 2-ureidobenzenesulfonate (3i)

This compound was synthesized following the General Procedure A with 2-aminobenzothiazole **1c** (149 mg), ethanol (**2b**), MMPP (3.2 equiv), and a reaction time of 22 h. This yielded **3i** as an orange solid (40mg, 0.16 mmol, **16% yield**). $R_f = 0.25$ (1:1 EtOAc/hexanes). ^1H NMR (CDCl_3 , 300 MHz) δ 7.90 (d, 1H, $J = 7.1$ Hz) 7.70 (d, 1H, $J = 6.8$ Hz) 7.59-7.55 (m, 2H) 5.98 (br, 3H), 4.38 (q, 2H, $J = 7.2$ Hz) 1.37 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.9, 168.2, 133.3, 132.0, 130.9, 130.3, 129.9, 128.8, 62.0, 13.9. HRMS calculated for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ ($\text{M}+\text{H}$) 245.05905; Found 245.05909.

ethyl 4-bromo-2-formamidobenzenesulfonate (3j)

This compound was synthesized following the General Procedure A with 5-bromobenzothiazole **1d** (214 mg), ethanol (**2b**) and a reaction time of 22 h. This yielded **3j** as a pale yellow solid (100 mg, 0.33 mmol, **33% yield**). $R_f = 0.25$ (1:4 EtOAc/hexanes). ^1H NMR (CDCl_3 , 300 MHz) δ 9.01 (br. s, 1H) 8.82 (s, 1H) 8.45 (s, 1H) 7.75 (d, 1H, $J = 8.44$ Hz) 7.40 (d, 1H, $J = 8.44$ Hz) 4.11 (q, 2H, $J = 7.02$ Hz) 1.30 (t, 3H, $J = 7.06$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.2, 136.7, 131.1, 130.5, 127.5, 126.0, 122.0, 68.4, 14.8. HRMS calculated for $\text{C}_9\text{H}_9\text{BrNO}_4\text{S}$ ($\text{M}+\text{H}$) 307.9587; Found 307.9586.

ethyl 2-formamido-4-nitrobenzenesulfonate (3k)

This compound was synthesized following the General Procedure A with 5-nitrobenzothiazole **1e** (180 mg), ethanol (**2b**) and a reaction time of 22 h. This yielded **3k** as a bright yellow solid (52 mg, 0.19 mmol, **19% yield**). R_f = 0.42 (2:3 EtOAc/hexanes). ^1H NMR (CDCl_3 , 300 MHz) δ 9.31 (br. s, 1H) 8.91-8.89 (m, 1H) 8.80 (d, 1H, J = 2.62 Hz) 8.60 (br. s, 1H) 8.49 (dd, 1H, J = 9.18, 2.61 Hz) 4.25 (q, 2H, J = 7.11 Hz) 1.37 (t, 3H, J = 7.10 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.1, 142.6, 140.8, 130.1, 125.7, 123.7, 123.0, 69.1, 14.7. HRMS calculated for $\text{C}_9\text{H}_{11}\text{N}_2\text{O}_6\text{S}$ ($\text{M}+\text{H}$) 275.0338; Found 275.0333.

ethyl 2-formamido-5-nitrobenzenesulfonate (3l)

This compound was synthesized following the General Procedure A with 6-nitrobenzothiazole **1f** (180 mg), ethanol (**2b**) and a reaction time of 22 h. This yielded **3l** as a bright yellow solid (57 mg, 0.21 mmol, **21% yield**). R_f = 0.42 (2:3 EtOAc/hexanes). ^1H NMR (CDCl_3 , 300 MHz) δ 9.32 (br. s, 1H) 8.90 (d, 1H, J = 8.04) 8.80 (d, 1H, J = 2.05 Hz) 8.59 (br. s, 1H) 8.49 (dd, 1H, J = 9.18, 2.55 Hz) 4.24 (q, 2H, J = 7.05 Hz) 1.37 (t, 3H, J = 7.08 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.1, 142.6, 140.8, 130.1, 125.7, 123.7, 123.0, 69.2, 14.7. HRMS calculated for $\text{C}_9\text{H}_{11}\text{N}_2\text{O}_6\text{S}$ ($\text{M}+\text{H}$) 275.03323; Found 275.03350.

isopropyl 2-acetamidobenzenesulfonate (3n)

This compound was synthesized following the General Procedure A with 2-methylbenzothiazole **1b** (149 mg), isopropanol (**2c**) and a reaction time of 22 h. This yielded **3n** as a dull yellow solid (17 mg, 0.07 mmol, **7% yield**). R_f = 0.17 (1:4 EtOAc/hexanes). ^1H NMR (CDCl_3 , 300 MHz) (Rotamer ratio: 7.8:1, Asterisk denotes minor peak) 8.92 (br. s, 1H) 8.43 (d, 1H, J = 8.44 Hz) *8.01 (d, 1H, J = 7.94 Hz) 7.90 (d, 1H, J = 8.04 Hz) *7.75 (m, 1H) 7.62 (t, 1H, J = 7.74 Hz) *7.42 (m, 1H) 7.22 (t, 1H, J = 7.65 Hz) 4.66 (sept., 1H, J = 6.28 Hz) 2.23 (s, 3H) 1.24 (d, 6H, J = 6.23 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) 168.8, 136.8, 135.2, 129.7, 124.7, 123.8, 123.3, 78.7, 25.2, 22.8. HRMS calculated for $\text{C}_{11}\text{H}_{16}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) 258.0795; Found 258.0795.

isopropyl 4-bromo-2-formamidobenzenesulfonate (3o)

Chemical Formula: C₁₀H₁₂BrNO₄S

This compound was synthesized following the General Procedure A with 5-bromobenzothiazole **1d** (214 mg), ethanol (**2c**) and a reaction time of 22 h. This yielded **3o** as a dull yellow solid (87 mg, 0.19 mmol, **19% yield**). R_f = 0.38 (1:4 EtOAc/hexanes). ¹H NMR (CDCl₃, 300 MHz) (Rotamer ratio: 8.5:1, Asterisk denotes minor peak) δ 8.97 (br. s, 1H) 8.81 (s, 1H) *8.79 (br. s, 1H) 8.49 (s, 1H) 7.77 (d, 1H, *J* = 8.43 Hz) *7.57 (m, 1H) 7.41 (d, 1H, *J* = 8.26 Hz) *4.82 (m, 1H) 4.71 (sept., 1H, *J* = 5.4 Hz) 1.27 (d, 6H, *J* = 6.18 Hz). ¹³C NMR (CDCl₃, 100 MHz) 159.1, 136.5, 130.8, 130.2, 127.6, 126.1, 123.4, 79.4, 22.8. HRMS calculated for C₁₀H₁₃NO₄SBr (M+H) 321.9749; Found 321.9743.

2-aminobenzenesulfonic acid (4)

Sulfonic ester **3a** (100 mg, 0.47 mmol) was stirred in MeOH (8 mL) and refluxed for 3 h. Removal of solvent yielded complete conversion to product **4**. ¹H NMR (CD₃OD, 300 MHz) δ 7.82 (d, 1H, *J* = 7.8 Hz) 7.54 (t, 1H, *J* = 7.7 Hz) 7.45 (t, 1H, *J* = 7.2 Hz) 7.35 (d, 1H, *J* = 7.9 Hz). ¹³C NMR (CD₃OD, 100 MHz) δ 138.1, 135.8, 131.7, 131.0, 130.5, 126.9. Characterization data is consistent with authentic samples.

methyl 2-formamidobenzenesulfinate (5)

This compound was synthesized following the General Procedure A with benzothiazole **1a** (135 mg), MeOH (**2a**) and a reaction time of 2 h. This yielded **5** as a light yellow, flakey solid (8.2 mg, 0.04 mmol, **4% yield**). R_f = 0.31 (2:3 EtOAc/hexanes). ¹H NMR (CDCl₃, 300 MHz) (Rotamer ratio: 4.2:1, Asterisk denotes minor peak) δ 10.11 (br. s, 1H) *9.00 (br. s, 1H) *8.75 (d, 1H, *J* = 10.81 Hz) 8.57 (d, 1H, *J* = 8.42 Hz) 8.46 (s, 1H) *7.66 (d, 1H, *J* = 7.47 Hz) 7.54 (t, 1H, *J* = 7.79 Hz) 7.45 (d, 1H, *J* = 7.75 Hz) *7.35 (m, 1H) 7.23 (t, 1H, *J* = 7.59 Hz) 3.66 (s, 3H) *3.64 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 159.6, 138.4, 133.7, 128.1, 127.6, 124.3, 122.9, 51.6. HRMS calculated for C₈H₉NO₃SLi (M+Li) 206.0458; Found 206.0459.

2. Reaction Profile Data

Procedure for NMR kinetic Analysis

A room temperature round bottom flask was charged with benzothiazole (0.22 mL, 2.00 mmol, 1.0 equiv) and methanol (10 mL, 0.2 M). Dodecane (45 μ L, 0.2 mmol, 0.1 eq) was then added to the reaction mixture. The reaction mixture was stirred vigorously at which point MMPP (2.00 g, 3.20 mmol, 1.6 eq) was added. After 5 min, a 0.5 mL aliquot of the reaction mixture was removed, DI H₂O (0.5 mL) was added to the aliquot and the solution was extracted with CH₂Cl₂ (1 mL) 3 times. The organic layers were collected, dried over MgSO₄ and concentrated to yield the crude product. This process was repeated at the following times: 5min, 20 min, 1 hour, 2 hours, 4 hours, 10 hours. After the data was collected, the relative concentrations of product and intermediate were determined by integrating δ 3.64 (**2**) and δ 3.76 (**1**) relative to δ 0.86 (dodecane).

3. Crystallographic Data

Product 3a single crystal x-ray structure

Table S1 - Crystal Data and Details of the Structure Determination

Crystal Data		
Formula	C ₈ H ₉ N O ₄ S	
Formula Weight	215.22	
Crystal System	monoclinic	
Space group (No. 14)	P21/c	
a, b, c [Angstrom]	15.0399(4)	8.2086(2)
alpha, beta, gamma [deg]	90	127.961(2)

V [Ang**3]	
1908.59(10)	
Z	
8	
	D(calc) [g/cm**3]
	1.498
Mu(MoKa) [/mm]	
0.327	
F(000)	
896	
Crystal Size [mm]	0.04 x 0.12 x
0.31	
Data Collection	
Temperature (K)	
296	
Radiation [Angstrom]	MoKa
0.71073	
Theta Min-Max [Deg]	
1.3, 26.0	
Dataset	-18: 18 ; -7: 10 ; -
24: 23	
Tot., Uniq. Data, R(int)	18286, 3749,
0.021	
Observed Data [I > 2.0 sigma(I)]	
2920	
Refinement	
Nref, Npar	
3749, 254	
R, wR2, S	0.0356,
0.0743, 1.17	
w = $\frac{1}{\sigma^2(F_o^2) + (0.0139P)^2 + 1.0065P}$ WHERE P=($F_o^2 + 2FC^2$)/3'	
Max. and Av. Shift/Error	0.00,
0.00	
Min. and Max. Resd. Dens. [e/Ang^3]	-0.30,
0.30	

Table S2 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms

Atom	x	y	z	U(eq)
[Ang^2]				
S1A	0.71615(4)	0.20387(6)	0.67269(4)	0.0430(2)
S2B	0.22022(4)	0.04061(6)	0.56054(3)	0.0425(2)
O1A	0.76926(13)	0.27082(18)	0.63919(10)	0.0548(6)

O2A	0.62224(13)	0.28500(19)	0.65777(11)	0.0613(6)
O3A	0.81413(11)	0.19298(17)	0.77263(9)	0.0465(5)
O4A	0.96367(13)	-0.29009(19)	0.75918(10)	0.0594(6)
N1A	0.86732(13)	-0.0612(2)	0.68245(11)	0.0410(6)
C1A	0.68004(16)	-0.0005(2)	0.64054(12)	0.0383(6)
O1B	0.11610(12)	-0.04113(18)	0.50206(10)	0.0610(5)
C2A	0.75687(16)	-0.1103(2)	0.64761(12)	0.0372(6)
O2B	0.31904(12)	-0.02296(19)	0.57625(11)	0.0612(6)
C3A	0.72127(18)	-0.2687(3)	0.61924(14)	0.0492(8)
O3B	0.25126(12)	0.04562(18)	0.65265(9)	0.0527(5)
C4A	0.6140(2)	-0.3168(3)	0.58690(15)	0.0614(9)
O4B	0.46656(13)	0.5549(2)	0.72237(11)	0.0741(6)
C5A	0.5397(2)	-0.2090(3)	0.58097(16)	0.0637(9)
C6A	0.57206(18)	-0.0500(3)	0.60741(14)	0.0520(8)
C7A	0.7845(2)	0.1369(3)	0.82650(16)	0.0596(9)
C8A	0.96055(18)	-0.1538(3)	0.73429(14)	0.0456(8)
N1B	0.39708(13)	0.3115(2)	0.65328(11)	0.0465(6)
C1B	0.20335(16)	0.2464(2)	0.53025(12)	0.0353(6)
C2B	0.29273(16)	0.3582(2)	0.57712(12)	0.0354(6)
C3B	0.27208(18)	0.5171(3)	0.54549(14)	0.0438(7)
C4B	0.1671(2)	0.5623(3)	0.47267(14)	0.0490(8)

C5B	0.08012(19)	0.4528(3)	0.42895(14)	0.0522(8)	
C6B	0.09841(17)	0.2947(3)	0.45719(13)	0.0452(7)	
C7B	0.1670(2)	0.1025(3)	0.66047(18)	0.0709(11)	
C8B	0.47454(17)	0.4096(3)	0.71859(15)	0.0539(8)	

Table S3 - Hydrogen Atom Positions and Isotropic Displacement Parameters

Atom	x	y	z	U(iso)
[Ang^2]				
H1AA	0.87580	0.03500	0.66990	0.0490
H3AA	0.77000	-0.34310	0.62200	0.0590
H4AA	0.59160	-0.42390	0.56880	0.0740
H5AA	0.46770	-0.24320	0.55920	0.0760
H6AA	0.52180	0.02360	0.60300	0.0620
H7AA	0.85070	0.13530	0.88590	0.0720
H7AB	0.72960	0.20920	0.82010	0.0720
H7AC	0.75350	0.02900	0.80910	0.0720
H8AA	1.02870	-0.10860	0.75260	0.0550
H1BA	0.41320	0.20950	0.65890	0.0560
H3BA	0.33000	0.59340	0.57390	0.0530
H4BA	0.15510	0.66910	0.45290	0.0590
H5BA	0.00920	0.48540	0.38050	0.0630
H6BA	0.03980	0.21960	0.42730	0.0540

H7BA	0.19710	0.09930	0.72010	0.0850
H7BB	0.14630	0.21240	0.63950	0.0850
H7BC	0.10170	0.03380	0.62700	0.0850
H8BA	0.54050	0.36070	0.76520	0.0650

Table S4 - Bond Distances (Angstrom)

S1A	-O1A	1.420(2)	C3A	-H3AA	0.9300
S1A	-O2A	1.420(2)	C4A	-H4AA	0.9300
S1A	-O3A	1.5707(15)	C5A	-H5AA	0.9300
S1A	-C1A	1.7566(17)	C6A	-H6AA	0.9300
S2B	-C1B	1.7565(17)	C7A	-H7AA	0.9600
S2B	-O1B	1.4171(19)	C7A	-H7AC	0.9600
S2B	-O2B	1.419(2)	C7A	-H7AB	0.9600
S2B	-O3B	1.5634(16)	C8A	-H8AA	0.9300
O3A	-C7A	1.451(4)	C1B	-C2B	1.405(3)
O4A	-C8A	1.210(3)	C1B	-C6B	1.385(3)
N1A	-C2A	1.412(3)	N1B	-H1BA	0.8600
N1A	-C8A	1.350(3)	C2B	-C3B	1.395(3)

C1A	-C2A	1.404(3)	C3B	-C4B	1.377(4)
N1A	-H1AA	0.8600	C4B	-C5B	1.369(4)
C1A	-C6A	1.388(4)	C5B	-C6B	1.371(3)
C2A	-C3A	1.386(3)	C3B	-H3BA	0.9300
C3A	-C4A	1.379(4)	C4B	-H4BA	0.9300
O3B	-C7B	1.445(4)	C5B	-H5BA	0.9300
C4A	-C5A	1.373(4)	C6B	-H6BA	0.9300
O4B	-C8B	1.206(3)	C7B	-H7BA	0.9600
C5A	-C6A	1.378(3)	C7B	-H7BB	0.9600
N1B	-C8B	1.345(3)	C7B	-H7BC	0.9600
N1B	-C2B	1.399(3)	C8B	-H8BA	0.9300

Table S5 - Bond Angles (Degrees)

O1A	-S1A	-O2A	119.63(11)	C2B	-N1B	-C8B	126.73(18)
O1A	-S1A	-O3A	103.66(11)	C2A	-C3A	-H3AA	120.00
O1A	-S1A	-C1A	109.95(11)	C4A	-C3A	-H3AA	120.00
O2A	-S1A	-O3A	109.56(11)	C3A	-C4A	-H4AA	120.00

O2A	-S1A	-C1A	108.98(12)	C5A	-C4A	-H4AA
119.00						
O3A	-S1A	-C1A	103.83(8)	C4A	-C5A	-H5AA
120.00						
O1B	-S2B	-O2B	119.35(11)	C6A	-C5A	-H5AA
120.00						
O1B	-S2B	-O3B	110.08(11)	C1A	-C6A	-H6AA
120.00						
O1B	-S2B	-C1B	108.90(10)	C5A	-C6A	-H6AA
120.00						
O2B	-S2B	-O3B	103.32(10)	O3A	-C7A	-H7AB
109.00						
O2B	-S2B	-C1B	109.96(12)	O3A	-C7A	-H7AC
109.00						
O3B	-S2B	-C1B	104.11(9)	H7AA	-C7A	-H7AB
109.00						
S1A	-O3A	-C7A	116.98(17)	H7AA	-C7A	-H7AC
109.00						
C2A	-N1A	-C8A	124.86(19)	H7AB	-C7A	-H7AC
109.00						
S1A	-C1A	-C2A	121.59(19)	O3A	-C7A	-H7AA
110.00						
C2A	-N1A	-H1AA	117.00	O4A	-C8A	-H8AA
117.00						
C8A	-N1A	-H1AA	118.00	N1A	-C8A	-H8AA
117.00						
S1A	-C1A	-C6A	117.52(18)	S2B	-C1B	-C2B
121.73(15)						
C2A	-C1A	-C6A	120.89(18)	S2B	-C1B	-C6B
117.43(17)						
C1A	-C2A	-C3A	118.1(2)	C2B	-C1B	-C6B
120.83(18)						

N1A -C2A -C3A 120.8(2) C2B -N1B -H1BA 117.00
N1A -C2A -C1A 121.11(16) C8B -N1B -H1BA 117.00
C2A -C3A -C4A 120.5(3) N1B -C2B -C1B 120.87(16)
S2B -O3B -C7B 118.24(15) C1B -C2B -C3B 117.3(2)
C3A -C4A -C5A 121.0(2) N1B -C2B -C3B 121.9(2)
C4A -C5A -C6A 119.9(3) C2B -C3B -C4B 120.9(2)
C1A -C6A -C5A 119.6(3) C3B -C4B -C5B 121.1(2)
O4A -C8A -N1A 126.1(3) C4B -C5B -C6B 119.4(2)
C1B -C6B -C5B 120.4(2) C5B -C6B -H6BA 120.00
O4B -C8B -N1B 126.2(2) O3B -C7B -H7BA 109.00
C2B -C3B -H3BA 120.00 O3B -C7B -H7BB 109.00
C4B -C3B -H3BA 120.00 O3B -C7B -H7BC 109.00
C3B -C4B -H4BA 119.00 H7BA -C7B -H7BB 109.00
C5B -C4B -H4BA 119.00 H7BA -C7B -H7BC 110.00
C4B -C5B -H5BA 120.00 H7BB -C7B -H7BC 109.00

C6B	-C5B	-H5BA	120.00	O4B	-C8B	-H8BA
117.00						
C1B	-C6B	-H6BA	120.00	N1B	-C8B	-H8BA
117.00						

Product 4 twin crystal x-ray data

Single crystal x-ray structure model incomplete due to weak data.

4. Spectral Data of New Compounds

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

^{19}F NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

^{13}C NMR Spectrum

^1H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum

¹H NMR Spectrum

¹³C NMR Spectrum