**Oxaziridine-Mediated Catalytic Hydroxylation of Unactivated
3° C–H Bonds Using Hydrogen Peroxide**

Supplementary Material
(16 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 dry nitrogen. Air- and moisture-sensitive solutions were transferred via syringe. Organic solutions were concentrated under reduced pressure (ca. 20 mm Hg) by rotary evaporation. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were passed through two columns of activated alumina prior to use. *N,N*-Dimethylacetamide (DMA) and ethyl trifluoroacetate were dried over activated 3 Å molecular sieves. 1,2-Dichloroethane (DCE) was distilled from CaH_2 immediately before use. Bis(3,5-bis(trifluoromethyl)phenyl)-diselenide was prepared as described previously.¹ Chromatographic purification of products was accomplished using forced flow chromatography on Silicycle silica gel 60 (40-63 μm). Thin layer chromatography 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 Mercury 400 operating at 400, 100, and 376 MHz for ^1H , ^{13}C , and ^{19}F , respectively. ^1H and ^{13}C spectra are referenced internally according to residual solvent signals (CHCl_3 δ = 7.26 ppm, $^{13}\text{CDCl}_3$ δ = 77.23 ppm). ^{19}F NMR spectra are referenced internally using α,α,α -trifluorotoluene as a standard (−63.72 ppm). Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br broad), integration and coupling constant (Hz). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ , ppm). Infrared (IR) spectra were recorded as either thin films using NaCl plates or as KBr pellets on a Thermo-Nicolet 300 FT-IR spectrometer and are reported in frequency of absorption. High resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

Ab initio calculations were performed using the Gaussian 03 suite of programs.² Geometry optimizations and frequency calculations were carried out at the B3LYP hybrid DFT (density functional theory) level. The 6-31G* basis set was used exclusively. All stationary points were subjected to frequency analysis and characterized as a minimum on the potential energy surface (no imaginary frequencies) or as a transition state (single imaginary frequency). Transition states were further verified by imaginary frequency animation and intrinsic reaction coordinate (IRC) path analysis. Zero-point vibrational energies (ΔZPVE) were obtained from the frequency analysis and scaled by a factor of 0.9806.³ Graphical representations were generated using the program MacMolPlt.⁴

Sulfamoyl chloride ($\text{H}_2\text{NSO}_2\text{Cl}$). A 300 mL three-neck round bottom flask equipped with an addition funnel, nitrogen gas inlet, and a glass stopper was placed in an ice bath and charged with 35 mL of CH_2Cl_2 and ClSO_2NCO (19.6 g, 138.6 mmol). The contents were cooled and stirred vigorously while a solution of formic acid (6.38 g, 138.6 mmol) in 35 mL of CH_2Cl_2 was added dropwise via addition funnel over a 5–10 min period. **Caution:** the apparatus should be well vented as gas evolution ensues upon addition of $\text{H}_2\text{CO}_2\text{H}$. Following the addition, the mixture was stirred for 10 min at 0 °C. The apparatus was removed from the ice bath and the white suspension stirred for 12 h at 22 °C. The addition funnel and nitrogen gas inlet were detached, the flask sealed with polyethylene stoppers and a rubber septum and placed in a −20 °C freezer for 1 h. The cold CH_2Cl_2 supernatant was then removed with the aid of a cannula. The resulting white solid was dried in vacuo (~1 torr) to give 13.8 g (86%) of the desired product. This material was transferred to an inert atmosphere glovebox for storage and used without further purification.

Preparation and Characterization Data for Benzoxathiazine Catalysts

2-Trifluoroacetylphenol. *n*-Butyllithium (2.5 M in hexanes, 3.84 mL, 9.60 mmol, 1.1 equiv) was added dropwise to a −78 °C solution of 1-bromo-2-*tert*-butoxybenzene⁵ (2.00 g, 8.73 mmol) in 29 mL of THF. The resulting

suspension was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min, then neat ethyl trifluoroacetate (2.08 mL, 17.46 mmol, 2.0 equiv) was added via syringe. The precipitate dissipated, and the homogenous solution was stirred for 1.5 h at $-78\text{ }^{\circ}\text{C}$. The reaction was quenched at $-78\text{ }^{\circ}\text{C}$ by the addition of 20 mL of a 1/2 saturated aqueous NH_4Cl . The mixture was transferred to a separatory funnel, the organic layer was collected, and the aqueous layer was extracted with 3 x 15 mL of Et_2O . The combined organic extracts were washed with 1 x 15 mL saturated aqueous NaCl , dried over anhydrous MgSO_4 , and concentrated under reduced pressure to afford an oily residue. The unpurified material was dissolved in 35 mL of CH_2Cl_2 and to this pale yellow solution was added $\text{CF}_3\text{CO}_2\text{H}$ (3.24 mL, 43.65 mmol, 5.0 equiv). The resulting dark yellow solution was stirred for 12 h. The mixture was transferred to a separatory funnel, washed successively with 2 x 30 mL of a 1 M pH 7 $\text{KH}_2\text{PO}_4/\text{NaOH}$ aqueous buffer and 1 x 20 mL of saturated aqueous NaCl , dried over MgSO_4 , and concentrated under reduced pressure to give a brown oil. Purification by chromatography on silica gel (5% $\text{EtOAc}/\text{hexanes}$) furnished the desired trifluoroketone as a yellow oil (1.15 g, 69%). TLC R_f = 0.43 (5% $\text{EtOAc}/\text{hexanes}$); ^1H NMR (CDCl_3 , 400 MHz) δ 11.06 (s, 1H), 7.85-7.80 (m, 1H), 7.65-7.61 (m, 1H), 7.10-7.08 (m, 1H), 7.03-6.99 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 184.6 (q, J_{CF} = 35 Hz), 164.8, 139.2, 130.9 (q, J_{CF} = 4 Hz), 120.2, 119.3, 116.6 (q, J_{CF} = 288 Hz), 114.1 ppm; ^{19}F NMR (CDCl_3 , 376 MHz) δ -71.30 ppm; IR (thin film) ν 3188, 2925, 1673, 1620, 1456, 1263, 1196, 1153, 947 cm^{-1} ; HRMS (ES^-) calcd for $\text{C}_8\text{H}_5\text{F}_3\text{O}_2$ 190.0242 found 189.0157 (M^+-H).

4-Chloro-2-trifluoroacetylphenol. Prepared according to the procedure outlined above using 1-bromo-6-*tert*-butoxy-3-chlorobenzene⁶ (5.01 g, 19.01 mmol). Purification by chromatography on silica gel (15% $\text{EtOAc}/\text{hexanes}$) afforded trifluoroketone as a yellow solid (2.98 g, 70%). TLC R_f = 0.40 (15% $\text{EtOAc}/\text{hexanes}$); ^1H NMR (CDCl_3 , 400 MHz) δ 10.98 (s, 1H), 7.78-7.76 (m, 1H), 7.58 (dd, 1H, J = 9.2, 2.4 Hz), 7.06 (d, 1H, J = 9.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 184.0 (q, J_{CF} = 36 Hz), 163.3, 139.3, 129.8 (q, J_{CF} = 4 Hz), 125.2, 121.0, 116.3 (q, J = 288 Hz), 114.5 ppm; ^{19}F NMR (CDCl_3 , 376 MHz) δ -71.51 ppm; IR (thin film) ν 3210, 1669, 1619, 1571, 1471, 1380, 1263, 1205, 1164, 1123, 962, 836, 788 cm^{-1} ; HRMS (ES^-) calcd for $\text{C}_8\text{H}_4\text{ClF}_3\text{O}_2$ 223.9852 found 222.9766 (M^+-H).

4-Trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide. To a solution of 2-trifluoroacetylphenol (300 mg, 1.58 mmol) in 3.2 mL of DMA was quickly transferred solid $\text{H}_2\text{NSO}_2\text{Cl}$ (638 mg, 5.52 mmol, 3.5 equiv). **Caution:** a mild exotherm was noted upon combining these reagents. After stirring for 12 h, the reaction was quenched by the addition of 3 mL of H_2O and transferred to a separatory funnel with 10 mL of Et_2O . The organic layer was separated, and the aqueous layer was extracted with 3 x 5 mL of Et_2O . The combined organic layers were washed successively with 2 x 3 mL of H_2O and 1 x 5 mL of saturated aqueous NaCl , dried over MgSO_4 , and concentrated under reduced pressure. Purification by chromatography on silica gel (35% $\text{EtOAc}/\text{hexanes}$) afforded the desired heterocycle as a white solid (336 mg, 85%). TLC R_f = 0.36 (30% $\text{EtOAc}/\text{hexanes}$); ^1H NMR (CDCl_3 , 400 MHz) δ 7.97-7.93 (m, 1H), 7.90-7.86 (m, 1H), 7.55-7.50 (m, 1H), 7.42 (dd, 1H, J = 8.4, 0.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.4 (q, J_{CF} = 37 Hz), 155.1, 139.2, 128.7 (q, J_{CF} = 3 Hz), 127.1, 119.8, 118.3 (q, J_{CF} = 280 Hz), 111.7 ppm; ^{19}F NMR (CDCl_3 , 376 MHz) δ -67.99 ppm; IR (thin film) ν 3111, 1604, 1562, 1451, 1407, 1363, 1299, 1216, 1166, 976, 861, 826, 783 cm^{-1} ; HRMS (ES^-) calcd for $\text{C}_8\text{H}_4\text{F}_3\text{NO}_3\text{S}$ 250.9864 found 267.9883 ($\text{M}^+-\text{H}+\text{H}_2\text{O}$).

6-Chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide. Prepared according to the procedure described above using 619 mg of 4-chloro-2-trifluoroacetylphenol (2.76 mmol) and 957 mg of ClSO_2NH_2 (8.28 mmol, 3.0 equiv) in 5.5 mL of DMA. Purification by chromatography on silica gel (45% EtOAc/hexanes) afforded the desired product as a pale yellow oil which slowly solidified under vacuum (720 mg, 91%). TLC R_f = 0.18 (50% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.91-7.88 (m, 1H), 7.82 (dd, 1H, J = 8.8, 2.4 Hz), 7.40 (d, 1H, J = 8.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.4 (q, J_{CF} = 38 Hz), 153.6, 138.9, 132.8, 128.1 (q, J_{CF} = 4 Hz), 121.3, 118.3 (q, J_{CF} = 280 Hz), 112.6 ppm; ^{19}F NMR (CDCl_3 , 376 MHz) δ -68.09 ppm; IR (thin film) ν 3114, 1621, 1560, 1419, 1357, 1206, 1103, 986, 868, 836, 800, 766 cm^{-1} ; HRMS (ES^-) calcd for $\text{C}_8\text{H}_3\text{ClF}_3\text{NO}_3\text{S}$ 284.9474 found 301.9510 ($\text{M}^+ - \text{H} + \text{H}_2\text{O}$).

Preparation and Characterization Data for Oxaziridines

To a solution of 4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide (600 mg, 2.39 mmol) in 15.9 mL of DCE was added freshly purified *m*-CPBA (453 mg, 2.63 mmol, 1.1 equiv). The mixture was stirred for 75 min and then concentrated under reduced pressure to a volume of ~2 mL. The resulting white suspension was applied directly to a column of silica gel and the product was eluted with 12% EtOAc/hexanes. The desired oxaziridine was obtained as a white solid (582 mg, 91%). TLC R_f = 0.41 (15% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.97-7.93 (m, 1H), 7.71 (dt, 1H, J = 7.8, 1.5 Hz), 7.51 (dt, 1H, J = 7.8, 1.2 Hz), 7.32 (dd, 1H, J = 8.2, 1.1 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.4, 134.9, 130.8 (q, J_{CF} = 4 Hz), 128.0, 120.5, 119.4 (q, J_{CF} = 281 Hz), 111.4, 80.0 (q, J_{CF} = 40 Hz) ppm; ^{19}F NMR (CDCl_3 , 376 MHz) δ -74.33 ppm; IR (thin film) ν 3131, 1619, 1496, 1463, 1432, 1352, 1272, 1218, 1154, 1112, 968, 924, 877, 823, 790 cm^{-1} ; HRMS (ES^-) calcd for $\text{C}_8\text{H}_4\text{F}_3\text{NO}_4\text{S}$ 266.9813 found 267.9894 ($\text{M}^+ - \text{OH} + \text{H}_2\text{O}$).

Prepared according to the procedure described above using 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide (290 mg, 1.01 mmol). Purification by chromatography on silica gel (10% EtOAc/hexanes) yielded the desired product as a white solid (194 mg, 71%). TLC R_f = 0.40 (10% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.91-7.89 (m, 1H), 7.68 (dd, 1H, J = 8.9, 2.4 Hz), 7.28 (d, 1H, J = 8.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.8, 134.9, 133.9, 130.8 (q, J_{CF} = 4 Hz), 121.8, 119.2 (q, J_{CF} = 282 Hz), 113.0, 79.4 (q, J_{CF} = 40 Hz) ppm; ^{19}F NMR (CDCl_3 , 376 MHz) δ -74.30 ppm; IR (thin film) ν 3124, 1487, 1438, 1352, 1269, 1196, 1158, 1118, 1102, 979, 875, 816 cm^{-1} ; HRMS (ES^-) calcd for $\text{C}_8\text{H}_3\text{ClF}_3\text{NO}_4\text{S}$ 300.9423 found 301.9492 ($\text{M}^+ - \text{OH} + \text{H}_2\text{O}$).

General Procedure for 3° C–H Oxidation Reactions

Substrate (1.00 mmol), 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide (57 mg, 0.20 mmol, 0.20 equiv), and bis(3,5-bis(trifluoromethyl)phenyl)diselenide (5.8 mg, 10 μmol , 0.01 equiv) were dissolved in 1 mL

DCE. To this yellow solution was added urea hydrogen peroxide (376 mg, 4.00 mmol, 4.0 equiv). The reaction flask was fitted with a reflux condenser and placed in an oil bath preheated to the desired reaction temperature (as indicated below). The initial yellow suspension became essentially colorless within several minutes and was stirred for the prescribed amount of time as indicated below (48–96 h). After cooling to 22 °C, the reaction was quenched by slow addition of 3 mL of a 1M aqueous solution of Na₂S₂O₃. The biphasic mixture was transferred to a separatory funnel and diluted with 10 mL of EtOAc and 2 mL of 1M aqueous Na₂S₂O₃. The organic layer was collected, and the aqueous phase was extracted with 3 x 5 mL of EtOAc. The combined organic extracts were washed with 1 x 3 mL of saturated aqueous NaCl, dried over anhydrous MgSO₄, and concentrated under reduced pressure. Purification of this material by chromatography on silica gel (conditions given below) furnished the desired product.

Reaction performed at 22 °C for 95 h. Purified by chromatography on silica gel using 20% EtOAc/hexanes as eluent (white solid, 80%): TLC R_f = 0.26 (20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 2.16-2.10 (br s, 3H), 1.70 (br d, 6H, J = 2.4 Hz), 1.65-1.55 (m, 6H), 1.49-1.42 (m, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 68.4, 45.5, 36.3, 30.9 ppm; IR (KBr) ν 3292, 2916, 2848, 1452, 1353, 1301, 1227, 1116, 1087, 981, 926, 812 cm⁻¹.⁷

Reaction performed at 35 °C for 48 h. Purified by chromatography on silica gel using 15% EtOAc/hexanes as eluent (white solid, 63%): TLC R_f = 0.34 (15% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz, 50 °C) δ 1.80-1.24 (m, 17H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 71.8, 42.8, 28.0 (br), 22.7 (br) ppm; IR (KBr) ν 3359, 2927, 2859, 1446, 1363, 1347, 1264, 1157, 1137, 1028, 996, 951, 932 cm⁻¹.⁸

Reaction performed at 50 °C for 72 h. Purified by chromatography on silica gel using 25% EtOAc/hexanes as eluent (white solid, 36%): TLC R_f = 0.17 (20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 4.94-4.89 (m, 1H), 1.92-1.84 (m, 2H), 1.70-1.60 (m, 4H), 1.52-1.46 (m, 2H), 1.26 (s, 3H), 1.18 (s, 9H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 178.1, 69.5, 69.4, 39.1, 34.6, 30.5, 27.4, 26.5 ppm; IR (thin film) ν 3426, 2961, 2933, 1727, 1481, 1398, 1371, 1286, 1174, 1136, 1011, 968, 907 cm⁻¹; HRMS (ES⁺) calcd for C₁₂H₂₂O₃ 214.1569 found 237.1472 (MNa⁺).

Reaction performed at 50 °C for 96 h. Purified by chromatography on silica gel using 20% EtOAc/hexanes as eluent (colorless oil, 43%): TLC R_f = 0.29 (20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 8.04-8.00 (m, 2H), 7.55-7.50 (m, 1H), 7.44-7.39 (m, 2H), 4.39-4.29 (m, 2H), 1.84-1.76 (m, 1H), 1.69-1.52 (m, 3H), 1.46-1.30 (m, 5H), 1.19 (s, 6H), 0.95 (d, 3H, J = 6.4 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 166.8, 133.0, 130.6, 129.7, 128.5, 71.0, 63.6, 44.2, 37.5, 35.7, 30.1, 29.4, 21.7, 19.7 ppm; IR (thin film) ν 3418, 2965, 2936, 1720, 1453, 1379, 1315, 1277, 1176, 1115, 1070, 1027, 939 cm⁻¹; HRMS (ES⁺) calcd for C₁₇H₂₆O₃ 278.1882 found 301.1775 (MNa⁺).

Reaction performed at 50 °C for 72 h. Purified by chromatography on silica gel using 40% EtOAc/hexanes as eluent (colorless oil, 39%): TLC R_f = 0.48 (50% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 6.33 (br s, 1H), 4.08-3.98 (m, 1H), 1.58-1.35 (m, 6H), 1.22 (d, 3H, J = 6.4 Hz), 1.20 (s, 6H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ

156.8 (q, $J_{\text{CF}} = 36$ Hz), 116.1 (q, $J_{\text{CF}} = 287$ Hz), 71.0, 46.6, 43.2, 36.8, 29.5, 29.4, 20.7, 20.6 ppm; ^{19}F NMR(CDCl_3 , 376 MHz) δ -77.07 ppm; IR (thin film) ν 3295, 3090, 2975, 2942, 1703, 1561, 1462, 1378, 1189, 1161 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{18}\text{F}_3\text{NO}_2$ 241.129 found 264.1180 (MNa^+).

Reaction performed at 22 °C for 72 h. Purified by chromatography on silica gel using 30% EtOAc/hexanes as eluent (colorless oil, 70%): TLC $R_f = 0.24$ (30% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 4.24-4.20 (m, 2H), 2.65-2.61 (m, 2H), 1.88-1.82 (m, 2H), 1.79-1.70 (m, 4H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.4, 69.5, 34.7, 29.5, 29.2, 23.1 ppm; IR (thin film) ν 2935, 1730, 1439, 1393, 1292, 1252, 1089, 1055, 1016 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_6\text{H}_{10}\text{O}_2$ 114.0681 found 137.0573 (MNa^+).

General Procedure for Olefin Epoxidation Reactions

Olefin (1.00 mmol), 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide (catalyst loading given below), and bis(3,5-bis(trifluoromethyl)phenyl)diselenide (5.8 mg, 10 μmol , 0.01 equiv) were dissolved in DCE (volume given below). To this yellow solution was added urea hydrogen peroxide (188 mg, 2.00 mmol, 2.0 equiv). The resulting suspension became essentially colorless within several minutes and was stirred until TLC indicated the complete consumption of starting material (12-46 h). The reaction was quenched by the slow addition of 3 mL of a 1 M aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The biphasic mixture was transferred to a separatory funnel and diluted with 10 mL of EtOAc and 2 mL of 1 M aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The organic layer was collected, and the aqueous phase was extracted with 3 x 5 mL of EtOAc. The combined organic extracts were washed with 1 x 3 mL of saturated aqueous NaCl, dried over anhydrous MgSO_4 , and concentrated under reduced pressure. Purification of this material by chromatography on silica gel (conditions given below) furnished the desired epoxide product.

Reaction performed for 18 h using 0.1 equiv of 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide and 2 mL of DCE. Purified by chromatography on silica gel using 5% EtOAc/hexanes as eluent (colorless oil, 89%): TLC $R_f = 0.30$ (5% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 2.92-2.87 (m, 1H), 2.74 (dd, 1H, $J = 5.2, 4.0$ Hz), 2.46 (dd, 1H, $J = 4.8, 2.8$ Hz), 1.55-1.38 (m, 4H), 1.38-1.22 (m, 10H), 0.88 (t, 3H, $J = 6.8$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 52.7, 47.4, 32.7, 32.1, 29.7 (2), 29.4, 26.2, 22.9, 14.3 ppm; IR (thin film) ν 2927, 2856, 1466, 1410, 1260, 916, 834 cm^{-1} .⁷

Reaction performed for 36 h using 0.1 equiv of 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide and 1 mL of DCE. Purified by chromatography on silica gel using 15% EtOAc/hexanes as eluent (colorless oil, 92%): TLC $R_f = 0.33$ (15% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 8.07-8.03 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.42 (m, 2H), 4.53-4.44 (m, 2H), 3.14-3.09 (m, 1H), 2.82 (dd, 1H, $J = 4.8, 4.0$ Hz), 2.57 (dd, 1H, $J = 4.8, 2.4$ Hz), 2.12-2.04 (m, 1H), 2.00-1.92 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.7, 133.2, 130.3, 129.8, 128.6, 62.1, 49.9, 47.1, 32.3 ppm; IR (thin film) ν 2995, 2926, 1719, 1602, 1453, 1276, 1177, 1115, 1071, 1027 cm^{-1} .

Reaction performed for 12 h using 0.1 equiv of 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide and 2 mL of DCE. Purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (white solid, 94%): TLC $R_f = 0.26$ (10% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 8.08-8.05 (m, 2H), 7.57-7.54 (m, 1H), 7.45-7.40 (m,

2H), 4.55 (dd, 1H, $J = 12.0, 4.4$ Hz), 4.29 (dd, 1H, $J = 12.0, 6.8$ Hz), 3.29 (dt, 1H, $J = 6.8, 4.4$ Hz), 3.17 (dq, 1H, $J = 5.6, 4.4$ Hz), 1.37 (d, 3H, $J = 5.6$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.5, 133.3, 129.9, 128.5, 63.3, 53.9, 52.3, 13.6 ppm; IR (thin film) ν 2999, 1722, 1601, 1452, 1339, 1315, 1273, 1115, 1071, 1027 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$ 192.0786 found 215.0688 (MNa^+).

Reaction performed for 46 h using 0.2 equiv of 6-chloro-4-trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide and 2 mL of DCE. Purified by chromatography on silica gel using 7.5% EtOAc/hexanes as eluent (colorless oil, 96%): TLC $R_f = 0.31$ (10% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 4.24-4.16 (m, 2H), 3.33 (s, 1H), 1.68-1.61 (m, 2H), 1.44-1.34 (m, 2H), 1.42 (s, 3H), 1.37 (s, 3H), 0.94 (t, 3H, $J = 7.3$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.9, 65.4, 60.4, 59.7, 30.8, 24.5, 19.3, 18.5, 13.9 ppm; IR (thin film) ν 2963, 2876, 1753, 1728, 1413, 1381, 1314, 1286, 1195, 1121, 1091 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_9\text{H}_{16}\text{O}_3$ 172.1099 found 195.0989 (MNa^+).

Table of Energies and Zero-point Vibrational Energies (ΔZPVE):

Substrate	Energy (Hartree)	ΔZPVE (Hartree)
ethylene	-78.587458	0.050229
methane	-40.518389	0.044345
oxaziridine 1	-1115.638869	0.115011
TS_E^1	-1194.191281	0.166203
TS_M^1	-1156.073309	0.156429

TS_E^1

TS_M^1

$\text{TS}_\text{M}^{\text{DMDO}}$

Comparative Table of Selected Bond Lengths and Angles for TS_M^1 and $\text{TS}_\text{M}^{\text{DMDO}}$:⁹

Bond Lengths ($\text{\AA}$)				Bond Angles ($^\circ$)			
TS_M^1		$\text{TS}_\text{M}^{\text{DMDO}}$		TS_M^1		$\text{TS}_\text{M}^{\text{DMDO}}$	
C2-H1	1.48	C2-H1	1.41	C2-H1-O1	116.97	C2-H1-O1	114.56
C2-O1	2.18	C2-O1	2.11	C2-O1-N1	164.09	C2-O1-O2	168.67
O1-H1	1.07	O1-H1	1.09	C1-O1-C2	123.17	C1-O1-C2	128.67
O1-N1	2.11	O1-O2	2.01	H1-O1-N1	141.98	H1-O1-O2	142.64
O1-C1	1.53	O1-C1	1.59	H1-O1-C1	115.19	H1-O1-C1	118.04

Table of Cartesian Coordinates for TS_E¹:

<u>Center</u>	<u>Atom</u>	<u>X (Å)</u>	<u>Y (Å)</u>	<u>Z (Å)</u>
1	C	-0.501603	2.662280	0.729486
2	C	-0.033109	1.388669	0.425639
3	C	-0.814733	0.474809	-0.296196
4	C	-2.083790	0.871176	-0.731307
5	C	-2.567154	2.143816	-0.426215
6	C	-1.778492	3.033066	0.307380
7	O	1.208525	1.010499	0.898363
8	S	2.162447	0.124763	-0.183290
9	N	1.146406	-1.067600	-0.763659
10	C	-0.231758	-0.894682	-0.554829
11	O	-0.044343	-1.698478	0.681982
12	C	-1.020195	-1.681325	-1.527879
13	N	-1.680255	-2.296308	-2.257161
14	O	2.486695	1.003537	-1.298284
15	O	3.191525	-0.450336	0.654874
16	C	-1.374384	-1.626683	2.189930
17	C	-1.507079	-2.785342	1.458768
18	H	-2.150788	4.026423	0.540241
19	H	-2.691546	0.183933	-1.312336
20	H	0.140505	3.339675	1.282254
21	H	-3.554060	2.440518	-0.767220
22	H	-0.950371	-3.679598	1.714912
23	H	-2.235132	-2.871785	0.658721
24	H	-0.700130	-1.568608	3.036916
25	H	-1.986125	-0.755889	1.980760

Table of Cartesian Coordinates for TS_M¹:

<u>Center</u>	<u>Atom</u>	<u>X (Å)</u>	<u>Y (Å)</u>	<u>Z (Å)</u>
1	C	0.091084	1.089146	-0.359797
2	C	0.883125	-0.191773	-0.254626
3	C	0.258530	-1.289030	0.354996
4	O	-1.025031	-1.163019	0.849935
5	S	-2.105190	-0.316583	-0.138552
6	N	-1.284853	1.062347	-0.568568
7	C	2.195415	-0.333748	-0.717995
8	C	2.872396	-1.542060	-0.551764
9	C	2.236986	-2.618505	0.071980
10	C	0.921883	-2.499954	0.521311
11	O	-2.303316	-1.107573	-1.346141
12	O	-3.206155	0.002070	0.743993

13	O	-0.067384	1.721544	1.028732
14	C	0.736059	2.102480	-1.221843
15	N	1.277425	2.896841	-1.870830
16	H	2.761007	-3.561598	0.196644
17	H	2.683758	0.499400	-1.214963
18	H	0.397790	-3.325647	0.990549
19	H	3.890359	-1.643139	-0.914843
20	C	1.615483	2.113229	2.361383
21	H	1.009052	1.923939	3.239334
22	H	2.222678	1.289277	2.003419
23	H	2.053913	3.109963	2.278475
24	H	0.665781	2.455932	1.279984

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Crystallographic Data for Oxaziridine 3

Experimental

Data Collection

A colorless plate crystal of C₈ H₄ F₃ N O₄ S having approximate dimensions of 0.30 x 0.26 x 0.08 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART¹ CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 2139 centered reflections with $I > 10\sigma(I)$ in the range $2.75^\circ < \theta < 24.59^\circ$, corresponded to a primitive monoclinic cell with dimensions:

$$\begin{array}{ll} a = 8.298(2) \text{ \AA} & \alpha = 90^\circ \\ b = 14.819(4) \text{ \AA} & \beta = 110.067(4)^\circ \\ c = 8.293(2) \text{ \AA} & \gamma = 90^\circ \\ V = 957.8(4) \text{ \AA}^3 \end{array}$$

For $Z = 4$ and $F.W. = 267.18$, the calculated density is 1.853 g/cm^3 .

Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P 2_1/n$ (#14)

The data were collected at a temperature of 118 K. 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 $1.6 \times 1.6 \times 1.0^\circ$ to a maximum θ value of 24.68° . The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ , for 0.71073 Å radiation is 0.389 mm^{-1} . Data were analyzed for agreement and possible absorption using XPREP³. A semi-empirical absorption correction based on 1989 reflections with $I > 10\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.82 to 0.97. Of the 4043 reflections that were collected, 1562 were unique ($R_{\text{int}} = 0.0588$); equivalent reflections were merged. No decay correction was deemed necessary.

Structure Solution and Refinement

The structure was solved by direct methods (SIR-97)⁴ and expanded using Fourier techniques⁵. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on the difference Fourier map, but were positioned using the HFIX command (idealized positions via a riding refinement). The final cycle of full-matrix least-squares refinement⁶ was based on 1562 reflections (all data) and 154 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0312 \text{ for 1258 data with } F_o > 4\sigma(F_o)$$

$$wR_2 = [(\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w |F_o|^2)]^{1/2} = 0.0804$$

The standard deviation of an observation of unit weight (S)⁷ was 0.957. Sheldrick weights⁶ were used; where applicable, weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.28 and -0.47 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁸. Anomalous dispersion effects were included in F_{calc} ⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley¹⁰. The values for the mass attenuation coefficients were those of Creagh and Hubbel¹¹. All calculations were performed using the Crystal Structure¹² crystallographic software package.

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Function minimized: $\sum w (|F_o|^2 - |F_c|^2)^2$
 $w = 1 / [\sigma^2(F_o^2) + (0.0516P)^2]$ where $P = (F_o^2 + 2F_c^2) / 3$
- Sheldrick weights: G. M. Sheldrick (1997)
- (7) Standard deviation of an observation of unit weight:
$$S = [\sum w (|F_o|^2 - |F_c|^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations
 N_v = number of variables
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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C ₈ H ₄ F ₃ N O ₄ S
Formula Weight	267.18
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.30 x 0.26 x 0.08 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	$a = 8.298(2) \text{ \AA}$ $b = 14.819(4) \text{ \AA}$ $c = 8.293(2) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 110.067(4)^\circ$ $\gamma = 90^\circ$ $V = 957.8(4) \text{ \AA}^3$
Space Group	P 2 ₁ /n (#14)
Z value	4
d_{calc}	1.853 g/cm ³
F_{000}	536
$\mu(0.71073 \text{ \AA radiation})$	0.39 cm ⁻¹

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	$\lambda = 0.71073 \text{ \AA}$ graphite monochromated
Exposure Time	10 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	24.68°
Data Collection Temperature	118 K
No. of Reflections Measured	Total: 4043 Unique: 1562 ($R_{\text{int}} = 0.0588$)
Corrections	Lorentz-polarization Absorption: $T_{\text{max}} = 0.97$ $T_{\text{min}} = 0.82$

C. Structure Solution and Refinement

Structure Solution	Direct (SIR-97)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(F_o ^2 - F_c ^2)^2$
Least Squares Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	1258
No. Variables	154
Reflection/Parameter Ratio	10.14
Residuals: R_1 ; wR_2	0.0312; 0.0804
Goodness of Fit Indicator (S)	0.957
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.28 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.47 e ⁻ /Å ³

Table 1. Atomic coordinates, $U_{\text{iso}}/U_{\text{eq}}$, and occupancy

atom	x	y	z	U_{eq}	occ
S1	0.4193(1)	0.3717(1)	0.3982(1)	0.017(1)	1
F1	0.0640(2)	0.1662(1)	0.4303(2)	0.024(1)	1
F2	-0.0328(2)	0.2822(1)	0.5245(2)	0.024(1)	1
F3	-0.1628(2)	0.2341(1)	0.2668(2)	0.022(1)	1
O1	0.3174(2)	0.4342(1)	0.2431(2)	0.017(1)	1
O2	0.4415(2)	0.4131(1)	0.5585(2)	0.021(1)	1
O3	0.5580(2)	0.3361(1)	0.3560(2)	0.025(1)	1
O4	0.1734(2)	0.2640(1)	0.2092(2)	0.020(1)	1
N1	0.2811(2)	0.2853(1)	0.3908(2)	0.018(1)	1
C1	0.1548(3)	0.4654(1)	0.2412(3)	0.016(1)	1
C2	0.0437(3)	0.4046(1)	0.2773(2)	0.016(1)	1
C3	-0.1178(3)	0.4368(2)	0.2679(3)	0.020(1)	1
C4	-0.1630(3)	0.5254(2)	0.2209(3)	0.024(1)	1
C5	-0.0484(3)	0.5834(2)	0.1856(3)	0.021(1)	1
C6	0.1136(3)	0.5538(2)	0.1978(3)	0.019(1)	1
C7	0.1008(3)	0.3095(1)	0.3201(3)	0.016(1)	1
C8	-0.0089(3)	0.2467(1)	0.3872(3)	0.018(1)	1
H3	-0.1948	0.3987	0.2934	0.024	1
H4	-0.2712	0.5462	0.2129	0.028	1
H5	-0.0805	0.6427	0.1534	0.025	1
H6	0.1922	0.5928	0.1771	0.023	1

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.014(1)	0.018(1)	0.019(1)	0.001(1)	0.006(1)	-0.002(1)
F1	0.025(1)	0.016(1)	0.032(1)	0.004(1)	0.012(1)	-0.001(1)
F2	0.031(1)	0.026(1)	0.019(1)	-0.003(1)	0.014(1)	-0.004(1)
F3	0.017(1)	0.024(1)	0.023(1)	-0.003(1)	0.006(1)	-0.006(1)
O1	0.014(1)	0.021(1)	0.016(1)	0.002(1)	0.007(1)	-0.001(1)
O2	0.022(1)	0.021(1)	0.018(1)	-0.002(1)	0.005(1)	-0.005(1)
O3	0.016(1)	0.029(1)	0.033(1)	0.001(1)	0.013(1)	0.003(1)
O4	0.020(1)	0.022(1)	0.020(1)	-0.006(1)	0.007(1)	-0.002(1)
N1	0.016(1)	0.019(1)	0.017(1)	-0.002(1)	0.005(1)	-0.001(1)
C1	0.014(1)	0.019(1)	0.013(1)	-0.002(1)	0.004(1)	0.000(1)
C2	0.016(1)	0.016(1)	0.014(1)	-0.001(1)	0.004(1)	-0.001(1)
C3	0.018(1)	0.023(1)	0.021(1)	-0.002(1)	0.008(1)	-0.002(1)
C4	0.021(1)	0.025(1)	0.024(1)	-0.003(1)	0.008(1)	0.006(1)
C5	0.029(1)	0.015(1)	0.017(1)	-0.001(1)	0.005(1)	0.005(1)
C6	0.025(1)	0.018(1)	0.014(1)	-0.002(1)	0.007(1)	-0.004(1)
C7	0.013(1)	0.020(1)	0.016(1)	-0.002(1)	0.006(1)	0.000(1)
C8	0.019(1)	0.017(1)	0.018(1)	-0.002(1)	0.005(1)	-0.002(1)

The general temperature factor expression:

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

Table 3. Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O3	1.4144(16)	S1	O2	1.4172(15)
S1	O1	1.5749(15)	S1	N1	1.7055(18)
F1	C8	1.331(2)	F2	C8	1.330(2)
F3	C8	1.338(2)	O1	C1	1.421(2)
O4	C7	1.430(2)	O4	N1	1.498(2)
N1	C7	1.452(3)	C1	C6	1.371(3)
C1	C2	1.393(3)	C2	C3	1.399(3)
C2	C7	1.491(3)	C3	C4	1.384(3)
C3	H3	0.9300	C4	C5	1.386(3)
C4	H4	0.9300	C5	C6	1.384(3)
C5	H5	0.9300	C6	H6	0.9300
C7	C8	1.532(3)			

Table 4. Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O3	S1	O2	122.58(9)	O3	S1	O1	105.75(8)
O2	S1	O1	111.85(9)	O3	S1	N1	107.80(9)
O2	S1	N1	103.17(9)	O1	S1	N1	104.20(8)
C1	O1	S1	116.25(11)	C7	O4	N1	59.43(12)
C7	N1	O4	57.95(12)	C7	N1	S1	114.64(14)
O4	N1	S1	110.89(12)	C6	C1	C2	123.43(19)
C6	C1	O1	117.68(18)	C2	C1	O1	118.85(18)
C1	C2	C3	117.32(19)	C1	C2	C7	118.91(18)
C3	C2	C7	123.76(18)	C4	C3	C2	120.1(2)
C4	C3	H3	120.0	C2	C3	H3	120.0
C3	C4	C5	120.6(2)	C3	C4	H4	119.7
C5	C4	H4	119.7	C6	C5	C4	120.5(2)
C6	C5	H5	119.7	C4	C5	H5	119.7
C1	C6	C5	118.1(2)	C1	C6	H6	121.0
C5	C6	H6	121.0	O4	C7	N1	62.62(12)
O4	C7	C2	117.51(16)	N1	C7	C2	121.86(18)
O4	C7	C8	112.42(17)	N1	C7	C8	111.23(17)
C2	C7	C8	118.73(17)	F2	C8	F1	108.19(16)
F2	C8	F3	108.05(16)	F1	C8	F3	107.68(16)
F2	C8	C7	110.65(17)	F1	C8	C7	111.75(17)
F3	C8	C7	110.40(17)				

Table 5. Torsion Angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O3	S1	O1	C1	169.33(13)	O2	S1	O1	C1	-54.96(15)
N1	S1	O1	C1	55.82(15)	C7	O4	N1	S1	-106.71(15)
O3	S1	N1	C7	-141.53(14)	O2	S1	N1	C7	87.49(15)
O1	S1	N1	C7	-29.48(15)	O3	S1	N1	O4	-78.26(14)
O2	S1	N1	O4	150.76(12)	O1	S1	N1	O4	33.79(13)
S1	O1	C1	C6	137.61(16)	S1	O1	C1	C2	-44.6(2)
C6	C1	C2	C3	0.0(3)	O1	C1	C2	C3	-177.62(16)
C6	C1	C2	C7	178.90(19)	O1	C1	C2	C7	1.2(3)
C1	C2	C3	C4	1.3(3)	C7	C2	C3	C4	-177.5(2)

C2	C3	C4	C5	-1.1(3)	C3	C4	C5	C6	-0.4(3)
C2	C1	C6	C5	-1.5(3)	O1	C1	C6	C5	176.19(17)
C4	C5	C6	C1	1.7(3)	N1	O4	C7	C2	113.6(2)
N1	O4	C7	C8	-103.15(19)	S1	N1	C7	O4	100.12(14)
O4	N1	C7	C2	-106.9(2)	S1	N1	C7	C2	-6.8(2)
O4	N1	C7	C8	105.04(18)	S1	N1	C7	C8	-154.83(14)
C1	C2	C7	O4	-48.6(3)	C3	C2	C7	O4	130.1(2)
C1	C2	C7	N1	24.7(3)	C3	C2	C7	N1	-156.53(19)
C1	C2	C7	C8	170.47(19)	C3	C2	C7	C8	-10.7(3)
O4	C7	C8	F2	162.03(15)	N1	C7	C8	F2	93.95(19)
C2	C7	C8	F2	-55.2(2)	O4	C7	C8	F1	41.4(2)
N1	C7	C8	F1	-26.7(2)	C2	C7	C8	F1	-175.85(16)
O4	C7	C8	F3	-78.4(2)	N1	C7	C8	F3	-146.49(17)
C2	C7	C8	F3	64.3(2)					

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure is given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

x, y, z -x+1/2, y+1/2, -z+1/2 -x, -y, -z x-1/2, -y-1/2, z-1/2