A Unique and Highly Efficient Method for Catalytic Olefin Aziridination

Supplementary Material
(9 pages)

Kiran Guthikonda and J. Du Bois*

*Department of Chemistry
Stanford University
Stanford, CA 94305-5080*

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 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. Benzene was distilled from sodium benzophenone ketyl prior to use. Dimethyl acetamide was dried over 4 Å molecular sieves and used without further purification. All other solvents (¹PrOH, C₆H₅Cl) were used as received from commercial suppliers. Chlorosulfonyl isocyanate was obtained from Acros Chemicals, transferred via cannula to a Schlenk flask, and stored at –20 °C. Triethylamine was distilled from CaH₂ prior to use. Light magnesium oxide was flame dried under reduced pressure (15 mm Hg). (Diacetoxy)iodobenzene was recrystallized from CHCl₃ and dried *in vacuo* (1 mm Hg). Zn(Cu) couple was prepared with zinc powder (Fisher, 99.2%) by the method of Simmons and Smith.¹ The couple was heated under vacuum at 50 °C for 15 h and stored in an inert atmosphere glove box. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35–75 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 XL-400 operating at 400 and 100 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 (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; m, multiplet), integration, coupling constant (Hz). Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). ¹⁹F NMR data were acquired on a Varian Inova 300 spectrometer with a ¹H/¹⁹F/¹³C/³¹P Auto-NMR probe operating at 282 MHz. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 FTIR spectrometer using NaCl salt plates and are reported in terms of frequency of absorption. 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.

2,2,2-Trichloroethylsulfamate ester. Formic acid (2.5 mL, 65.6 mmol, 1.5 equiv) was added dropwise to neat ClSO₂NCO (5.7 mL, 65.6 mmol, 1.5 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 solid mass was then added 34 mL of CH₃CN, and the resulting solution was stirred for 1 h at 0 °C and 8 h at 25 °C. The reaction was cooled to 0 °C and a solution of 4.2 mL of Cl₃CCH₂OH (43.8 mmol) in 34 mL of DMA was added dropwise via cannula. After stirring for 3 h at 25 °C, the solution was diluted with 50 mL of Et₂O and 50 mL of H₂O. The biphasic solution was separated and the ethereal layer was washed successively with 1 x 50 mL of H₂O and 2 x 50 mL of saturated aqueous NaCl. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (gradient elution: 3:1→1:1 hexanes/EtOAc) afforded the desired product as a white solid (90%): TLC R_f = 0.35 (15:1 CH₂Cl₂/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 5.40 (br s, 2H), 4.69 (s, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 93.0, 78.6 ppm; IR (thin film) ν 3404, 3296, 3095, 1551, 1371, 1267, 1189, 1089, 1016, 932, 860, 770 cm⁻¹; HRMS (EI) calcd for C₂H₄Cl₃NO₃S 226.8977 found 227.9069 (MH⁺).

Rh₂(tfacam)₄: A 25 mL recovery flask was charged with Rh₂(OAc)₄ (140 mg, 0.32 mmol) and 18.5 mL of C₆H₅Cl, and to this suspension was added CF₃CONH₂ (512 mg, 4.5 mmol, 14 equiv). The reaction flask was equipped with a short-path distillation head fitted with a 25 mL receiving bulb. The apparatus was placed in an oil bath preheated to 155 °C. At this temperature, solvent distilled at a rate of ~1 mL/h for 36 h. Approximately every 8 h, an appropriate amount of C₆H₅Cl was added in order to restore the solvent volume of the reaction to ~18 mL. The

solution color slowly changed to a deep green and a white crystalline precipitate (CF_3CONH_2) slowly formed in the receiving flask. After 36 h, additional CF_3CONH_2 (512 mg, 4.5 mmol, 14 equiv) was added to this reaction mixture and heating at 155 °C was continued. Within 48 h, a dark blue-green solid slowly collected on the sides of the reaction vessel. Following this time, the reaction was cooled to 25 °C and the mixture was filtered. The blue-green solid was washed thoroughly with CH_2Cl_2 , and the filtrate discarded. To ensure quantitative recovery of the desired product, acetone was used to dissolve the powder. The purple filtrate was concentrated under reduced pressure and the isolated material was dried by heating at 50 °C *in vacuo* (1 mm Hg) for 1 h. For all applications, the $\text{Rh}_2(\text{tfacam})_4$ complex was used without further purification. Purification of this material by chromatography on silica gel (3:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ using ~1 mL of acetone to dissolve the product) is possible; blue-green solid, (82%): TLC R_f = 0.34 (3:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); ^{19}F NMR (282 MHz, CD_3CN , $\text{C}_6\text{H}_5\text{CF}_3$ standard at -63.7 ppm) -74.4 ppm; IR (KBr pellet) ν 3401, 1655, 1433, 1270, 1202, 1152, 854, 732 cm^{-1} ; HRMS calcd for $\text{C}_8\text{H}_4\text{F}_{12}\text{N}_4\text{O}_4\text{Rh}_2$ 653.8151 found 653.8122 (M^+).

Experimental procedure and characterization data for aziridination reactions (see Table 1):

General Procedure: To a solution of $\text{Cl}_3\text{CCH}_2\text{SO}_3\text{NH}_2$ (126 mg, 0.55 mmol, 1.1 equiv) in 1.0 mL of C_6H_6 were added sequentially olefin (0.50 mmol, 1.0 equiv), MgO (46 mg, 1.15 mmol, 2.3 equiv), and $\text{Rh}_2(\text{tfacam})_4$ (3 mg, 5.0 μmol , 0.01 equiv). The resulting purple mixture was cooled to 0 °C and $\text{PhI}(\text{OAc})_2$ (209 mg, 0.65 mmol, 1.3 equiv) was added. The suspension quickly turned orange after the addition of $\text{PhI}(\text{OAc})_2$ and was allowed to warm slowly to 25 °C over 2 h. After 6 h of stirring at 25 °C, during which time the solution color faded to pale yellow, the reaction was diluted with 10 mL of CH_2Cl_2 and filtered through Celite. The filter cake was washed thoroughly with CH_2Cl_2 and the combined filtrates were concentrated under reduced pressure. The isolated material was purified by chromatography on silica gel (conditions give below) to afford the desired aziridine.

Purified by chromatography on silica gel (9:1 hexanes/ EtOAc); white solid (85%): TLC R_f = 0.58 (4:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.38-7.34 (m, 3H), 7.28 (dd, 2H, J = 7.8, 2.0 Hz), 4.81 (d, 1H, J = 10.7 Hz), 4.77 (d, 1H, J = 10.8 Hz), 3.80 (d, 1H, J = 4.5 Hz), 3.05 (dq, 1H, J = 6.0, 4.6 Hz), 1.78 (d, 3H, J = 6.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 134.2, 128.7 (2), 126.5, 92.8, 79.5, 50.7, 48.4, 13.6 ppm; IR (thin film) ν 3011, 2954, 1368, 1181, 1089, 1043, 1013, 900, 871, 777 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_3\text{NO}_3\text{S}$ 342.9603 found 307.9905 (M^+-Cl).

Purified by chromatography on silica gel (9:1 hexanes/ EtOAc); colorless oil (85%): TLC R_f = 0.58 (4:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39-7.32 (m, 5H), 4.91 (d, 1H, J = 10.8 Hz), 4.86 (d, 1H, J = 10.8 Hz), 4.07 (d, 1H, J = 7.3 Hz), 3.29 (dq, 1H, J = 7.2, 5.9 Hz), 1.15 (d, 3H, J = 5.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 131.5, 128.5, 128.4, 127.4, 92.9, 79.6, 47.6, 44.1, 11.6 ppm; IR (thin film) ν 2956, 1451, 1368, 1183, 1014, 988, 876, 786 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_3\text{NO}_3\text{S}$ 342.9603 found 196.0450 ($\text{M}^+-\text{OCH}_2\text{CCl}_3$).

Purified by chromatography on silica gel (9:1 hexanes/ EtOAc); white solid (79%): TLC R_f = 0.53 (4:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.59 (d, 1H, J = 7.7 Hz), 7.36-7.30 (m, 2H), 7.25-7.20 (m, 1H),

4.92 (d, 1H, $J = 10.9$ Hz), 4.87 (d, 1H, $J = 10.9$ Hz), 4.16 (dd, 1H, $J = 7.3, 4.6$ Hz), 3.14 (d, 1H, $J = 7.3$ Hz), 2.51 (d, 1H, $J = 4.6$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 133.6, 132.7, 130.1, 127.7, 127.5, 123.4, 92.8, 79.7, 42.8, 37.4 ppm; IR (thin film) ν 2956, 1384, 1184, 1088, 1011, 1014, 922, 859, 786 cm^{-1} ; calcd for $\text{C}_{10}\text{H}_9\text{BrCl}_3\text{NO}_3\text{S}$ 406.8552 found 259.9385 ($\text{M}^+ - \text{OCH}_2\text{CCl}_3$).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); white solid (95%): TLC $R_f = 0.56$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.35-7.39 (m, 3H), 7.29-7.32 (m, 2H), 4.88 (d, 1H, $J = 10.9$ Hz), 4.81 (d, 1H, $J = 10.9$ Hz), 3.88 (dd, 1H, $J = 7.2, 4.6$ Hz), 3.09 (d, 1H, $J = 7.2$ Hz), 2.63 (d, 1H, $J = 4.7$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 133.8, 128.9, 128.8, 126.5, 92.8, 79.6, 42.7, 37.5 ppm; IR (thin film) ν 1389, 1385, 1182, 1088, 1010, 922, 872, 787 cm^{-1} ; calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{NO}_3\text{S}$ 328.9447 found 182.0284 ($\text{M}^+ - \text{OCH}_2\text{CCl}_3$).

Purified by chromatography on silica gel (5:1 hexanes/EtOAc); off-white solid (95%): TLC $R_f = 0.25$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (ddd, 1H, $J = 8.1, 2.2, 1.2$ Hz), 8.17 (t, 1H, $J = 1.8$ Hz), 7.68 (d, 1H, $J = 7.6$ Hz), 7.58 (t, 1H, $J = 7.9$ Hz), 4.90 (d, 1H, $J = 11.0$ Hz), 4.85 (d, 1H, $J = 10.8$ Hz), 3.97 (dd, 1H, $J = 7.2, 4.6$ Hz), 3.17 (d, 1H, $J = 7.2$ Hz), 2.65 (d, 1H, $J = 4.4$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.5, 136.2, 132.7, 129.9, 123.8, 121.4, 92.6, 79.8, 41.4, 37.7 ppm; IR (thin film) ν 1532, 1383, 1352, 1184, 1088, 1009, 936, 878, 784 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_9\text{Cl}_3\text{N}_2\text{O}_5\text{S}$ 373.9298 found 227.0126 ($\text{M}^+ - \text{OCH}_2\text{CCl}_3$).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); white solid (91%): TLC $R_f = 0.62$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.18 (s, 4H), 4.87 (d, 1H, $J = 10.9$ Hz), 4.80 (d, 1H, $J = 10.9$ Hz), 3.84 (dd, 1H, $J = 7.2, 4.6$ Hz), 3.07 (d, 1H, $J = 7.3$ Hz), 2.62 (d, 1H, $J = 4.6$ Hz), 2.36 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 138.8, 130.7, 129.4, 126.4, 92.8, 79.6, 42.8, 37.4, 21.2 ppm; IR (thin film) ν 2956, 2923, 1519, 1460, 1390, 1382, 1181, 1089, 1012, 923, 873, 783 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_3\text{NO}_3\text{S}$ 342.9603 found 196.0450 ($\text{M}^+ - \text{OCH}_2\text{CCl}_3$).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); white solid (88%): TLC $R_f = 0.56$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.35 (dd, 2H, $J = 6.6, 1.9$ Hz), 7.24 (dd, 2H, $J = 6.7, 1.8$ Hz), 4.87 (d, 1H, $J = 10.8$ Hz), 4.81 (d, 1H, $J = 10.9$ Hz), 3.84 (dd, 1H, $J = 7.2, 4.6$ Hz), 3.09 (d, 1H, $J = 7.2$ Hz), 2.58 (d, 1H, $J = 4.6$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 133.8, 131.4, 128.0, 126.8, 91.7, 78.7, 41.0, 36.5 ppm; IR (thin film) ν 2958, 1496, 1390, 1382, 1184, 1091, 1013, 921, 875, 826, 784 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_9\text{Cl}_4\text{NO}_3\text{S}$ 362.9057 found 362.9058 (M^+).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); off-white solid (71%): TLC R_f = 0.28 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 8.24 (d, 2H, J = 8.7 Hz), 7.50 (d, 2H, J = 8.8 Hz), 4.90 (d, 1H, J = 10.8 Hz), 4.84 (d, 1H, J = 10.9 Hz), 3.95 (dd, 1H, J = 7.2, 4.5 Hz), 3.17 (d, 1H, J = 7.3 Hz), 2.62 (d, 1H, J = 4.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.2, 141.1, 127.4, 124.0, 92.6, 79.8, 41.4, 37.9 ppm; IR (thin film) ν 1605, 1523, 1371, 1348, 1184, 1088, 1008, 918, 859, 786 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_9\text{Cl}_3\text{N}_2\text{O}_5\text{S}$ 373.9298 found 373.9420 (M^+).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); off-white solid (65%): TLC R_f = 0.58 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.42 (d, 1H, J = 7.3 Hz), 7.32-7.27 (m, 1H), 7.23 (t, 1H, J = 7.6 Hz), 7.11 (d, 1H, J = 7.3 Hz), 4.78 (d, 1H, J = 10.9 Hz), 4.72 (d, 1H, J = 11.0 Hz), 3.90 (d, 1H, J = 7.1 Hz), 3.68 (br d, 1H, J = 7.0 Hz), 2.87-2.76 (m, 1H), 2.65 (dd, 1H, J = 15.8, 5.5), 2.45 (ddt, 1H, J = 14.3, 6.2, 2.0 Hz), 1.77 (tdd, 1H, J = 13.8, 5.6, 1.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 136.3, 129.8, 129.0, 128.8, 128.7, 126.6, 92.9, 79.5, 44.0, 43.6, 24.6, 19.9 ppm; IR (thin film) ν 2951, 1434, 1366, 1179, 1088, 1012, 989, 950, 913, 868, 775 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{NO}_3\text{S}$ 354.9603 found 225.0405 ($\text{MH}^+ - \text{CH}_2\text{CCl}_3$).

2 mol% $\text{Rh}_2(\text{tfacam})_4$ employed. Purified by chromatography on silica gel (9:1 hexanes/EtOAc); white solid (82%): TLC R_f = 0.66 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.79 (s, 2H), 2.93-2.85 (m, 2H), 2.26-2.18 (m, 2H), 1.72-1.30 (m, 10H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 92.1, 78.4, 44.8, 25.1 (2), 24.1 ppm; IR (thin film) ν 2931, 2857, 1368, 1180, 1090, 1008, 938, 877, 781 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{16}\text{Cl}_3\text{NO}_3\text{S}$ 334.9916 found 335.9998 (MH^+).

2 mol% $\text{Rh}_2(\text{tfacam})_4$ employed. Purified by chromatography on silica gel (24:1 hexanes/EtOAc); colorless oil (72%, 1:1 mixture of diastereomers): TLC R_f = 0.78 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.77 (d, 2H, J = 10.9 Hz), 4.74 (d, 2H, J = 10.9 Hz), 3.70-3.57 (m, 4H), 2.89-2.83 (m, 2H), 1.64 (s, 6H), 1.63-1.22 (m, 14H), 1.34 (s, 3H), 0.92-0.85 (m, 24H), 0.04 (s, 12H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 93.2, 79.2, 61.0, 55.1, 55.0, 51.8, 39.6, 44.0, 39.6, 34.2, 29.3, 29.2, 25.9, 25.4, 25.3, 21.1, 20.5, 19.4, 18.3, -5.3 ppm; IR (thin film) ν 2956, 2929, 2857, 1463, 1377, 1367, 1254, 1180, 1093, 1018, 868, 837, 776 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{36}\text{Cl}_3\text{NO}_4\text{SSi}$ 495.1200 found 438.0483 ($\text{M}^+ - \text{tBu}$).

2 mol% $\text{Rh}_2(\text{tfacam})_4$ employed. Purified by chromatography on silica gel (gradient elution: 15:1 $\rightarrow$ 9:1 hexanes/EtOAc); colorless oil (72%, 1:1 mixture of diastereomers): TLC R_f = 0.44 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.78 (d, 2H, J = 11.0 Hz), 4.74 (d, 2H, J = 10.7 Hz), 4.16-4.04 (m, 4H), 2.89-2.84 (m, 2H),

2.052 (s, 3H), 2.050 (s, 3H), 1.70-1.25 (m, 14H), 1.65 (s, 6H), 1.35 (s, 6H), 0.93 (d, 3H, $J = 6.4$ Hz), 0.92 (d, 3H, $J = 6.5$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.0, 93.1, 79.1, 62.4, 54.83, 54.78, 51.7, 51.6, 35.2, 33.9, 29.4, 25.13, 25.08, 25.4, 21.0, 20.9, 20.4, 19.1 ppm; IR (thin film) ν 2960, 2930, 1740, 1461, 1366, 1243, 1178, 1090, 1017, 940, 869, 777 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{24}\text{Cl}_3\text{NO}_5\text{S}$ 423.0441 found 424.0517 (MH^+).

Reaction performed in 0.5 mL of C_6H_6 (1.0 M in [olefin]). Purified by chromatography on silica gel (19:1 hexanes/EtOAc); colorless oil (57%): TLC $R_f = 0.70$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.79 (s, 2H), 2.79-2.70 (m, 2H), 1.78-1.57 (m, 2H), 1.56-1.39 (m, 2H), 1.54 (d, 3H, $J = 5.6$ Hz), 1.39-1.20 (m, 8H), 0.88 (t, 3H, $J = 6.8$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 93.1, 79.3, 50.9, 45.8, 30.8, 30.0, 29.0 (2), 26.8, 22.6, 14.6, 14.0 ppm; IR (thin film) ν 2929, 2858, 1454, 1378, 1367, 1180, 1091, 1017, 869, 778, 726 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{Cl}_3\text{NO}_3\text{S}$ 365.0386 found 366.0474 (MH^+).

Purified by chromatography on silica gel (19:1 hexanes/EtOAc); colorless oil (72%): TLC $R_f = 0.70$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.81 (d, 1H, $J = 10.8$ Hz), 4.77 (d, 1H, $J = 11.0$ Hz), 3.05-2.97 (m, 1H), 2.92-2.85 (m, 1H), 1.61-1.40 (m, 4H), 1.40-1.22 (m, 8H), 1.32 (d, 3H, $J = 5.9$ Hz), 0.88 (t, 3H, $J = 6.7$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 93.1, 79.3, 47.1, 42.4, 31.7, 29.13, 29.07, 26.9, 26.2, 22.6, 14.0, 11.8 ppm; IR (thin film) ν 2929, 2858, 1456, 1380, 1368, 1181, 1090, 1017, 872, 783, 727 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{Cl}_3\text{NO}_3\text{S}$ 365.0386 found 154.1595 ($\text{M}^+ - \text{SO}_3\text{CH}_2\text{CCl}_3$).

2 mol% $\text{Rh}_2(\text{tfacam})_4$ employed. Purified by chromatography on silica gel (19:1 hexanes/EtOAc); colorless oil (72%): TLC $R_f = 0.59$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.49 (d, 1H, $J = 10.9$ Hz), 4.77 (d, 1H, $J = 10.9$ Hz), 2.63 (s, 1H), 2.47 (s, 1H), 1.66-1.59 (m, 2H), 1.57 (s, 3H), 1.51-1.41 (m, 2H), 0.95 (t, 3H, $J = 7.3$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 93.2, 79.2, 50.4, 42.9, 39.2, 18.8, 18.3, 13.8 ppm; IR (thin film) ν 2962, 2938, 2876, 1467, 1366, 1269, 1181, 1090, 1011, 960, 865, 778 cm^{-1} ; HRMS calcd for $\text{C}_8\text{H}_{14}\text{Cl}_3\text{NO}_3\text{S}$ 308.9759 found 308.9769 (M^+).

Purified by chromatography on silica gel (gradient elution: 1:1→1:2 hexanes/EtOAc); pale yellow oil (84%): TLC $R_f = 0.17$ (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.61 (dt, 1H, $J = 12.0, 6.3$ Hz), 4.45-4.37 (m, 1H), 3.24-3.17 (m, 1H), 2.70 (dd, 1H, $J = 4.9, 1.4$ Hz), 2.61 (dd, 1H, $J = 4.9, 1.3$ Hz), 2.52-2.41 (m, 1H), 2.27-2.17 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 68.5, 41.5, 34.2, 18.2 ppm; IR (thin film) ν 2922, 2850, 1460, 1365, 1184, 1035, 931, 781 cm^{-1} ; HRMS calcd for $\text{C}_4\text{H}_7\text{NO}_3\text{S}$ 149.0147 found 150.0222 (MH^+).

This reaction was performed in $\text{C}_6\text{H}_5\text{Cl}$ at 1.0 M in substrate using 4 mol% $\text{Rh}_2(\text{tfacam})_4$. The reaction was initiated at -40 $^\circ\text{C}$ and stirred at this temperature for 1 h. The viscous reaction mixture was warmed to -30 $^\circ\text{C}$ and stirred for 2 h, then warmed to -20 $^\circ\text{C}$ and stirred for 2 h. Following this period, the reaction bath temperature was slowly

raised to 25 °C and the reaction quenched. Purified by chromatography on silica gel (gradient elution: 6:1→1:1 hexanes/EtOAc); white solid (54%): TLC R_f = 0.38 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.35 (m, 5H), 4.83 (d, 1H, J = 10.8 Hz), 4.77 (d, 1H, J = 10.8 Hz), 4.38 (d, 1H, J = 4.0 Hz), 3.87 (s, 3H), 3.72 (d, 1H, J = 4.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.5, 130.9, 129.6, 128.8, 127.6, 92.7, 79.5, 53.4, 49.3, 46.3 ppm; IR (thin film) ν 3037, 2956, 1751, 1441, 1392, 1183, 1012, 871, 780 cm^{-1} .

2 mol% $\text{Rh}_2(\text{tfacam})_4$ employed. Purified by chromatography on silica gel (9:1 hexanes/EtOAc); white solid, (91%): TLC R_f = 0.56 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (d, 2H, J = 8.2 Hz), 7.44 (d, 2H, J = 8.2 Hz), 7.14 (d, 2H, J = 7.9 Hz), 7.08 (d, 2H, J = 7.9 Hz), 5.41 (s, 2H), 3.71 (dd, 1H, J = 7.0, 4.6 Hz), 2.99 (d, 1H, J = 7.2 Hz), 2.50 (d, 1H, J = 4.6 Hz), 2.35 (s, 3H) ppm; ^{13}C NMR (d_6 -acetone, 100 MHz) δ 139.4, 139.2, 132.8, 131.2 ($J_{\text{C-F}}$ = 32 Hz), 130.1, 129.9, 127.5, 126.4 ($J_{\text{C-F}}$ = 350 Hz), 126.3, 73.9, 42.6, 37.5, 21.2 ppm; IR (thin film) ν 1359, 1320, 1172, 1134, 1066, 941, 922, 822, 740 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{NO}_3\text{S}$ 371.0803 found 372.0872 (MH^+).

The reaction was performed with 3 equiv of olefin and 2 mol% $\text{Rh}_2(\text{tfacam})_4$. Purified by column chromatography on silica gel (4:1 hexanes/EtOAc); colorless oil, (33%): TLC R_f = 0.48 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.55-7.49 (m, 2H), 7.40-7.35 (m, 2H), 7.25-7.18 (m, 2H), 7.18-7.07 (m, 6H), 3.89 (ddd, 1H, J = 16.8, 6.1, 3.6 Hz), 3.08 (ddd, 1H, J = 19.8, 6.1, 1.1 Hz), 2.41 (ddd, 1H, J = 15.6, 3.6, 1.1 Hz), 2.34 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 146.6, 137.9, 133.0 ($J_{\text{C-P}}$ = 10 Hz), 130.6, 129.1, 127.8, 126.1, 126.0, 125.6, 121.8, 39.6, 35.5 (d, $J_{\text{C-P}}$ = 7 Hz), 21.2 ppm; IR ν 3728, 3626, 2923, 1584, 1479, 1294, 1217, 1061, 947, 779 cm^{-1} HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{NO}_3\text{P}$ 433.0401 found 434.0483 (MH^+).

Experimental procedure and characterization data for aziridine ring openings (see Figure 2):

To a solution of aziridine **2** (100 mg, 0.29 mmol) in 0.5 mL of MeOH were added Et_3N (230 μL , 1.6 mmol, 5.6 equiv) and PhSH (85 μL , 0.81 mmol, 2.8 equiv). The solution was stirred for 12 h and then concentrated under reduced pressure. Purification of the resulting oily residue by chromatography on silica gel (9:1 hexanes/EtOAc) afforded the desired sulfide as a white solid (95%): TLC R_f = 0.48 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.48-7.44 (m, 2H), 7.39-7.33 (m, 2H), 7.33-7.27 (m, 3H), 7.25-7.16 (m, 3H), 5.16 (d, 1H, J = 9.1 Hz), 4.61 (d, 1H, J = 10.8 Hz), 4.57 (d, 1H, J = 4.2 Hz), 4.54 (d, 1H, J = 10.8 Hz), 4.09-4.00 (m, 1H), 1.31 (d, 3H, J = 6.7 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 138.1, 134.0, 131.1, 129.1, 128.8, 128.5, 127.9, 127.3, 93.3, 78.0, 60.0, 55.5, 17.4 ppm; IR (thin film) ν 3300, 3061, 2979, 2930, 1583, 1439, 1366, 1183, 1088, 993, 855, 754 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{Cl}_3\text{NO}_3\text{S}_2$ 452.9794 found 452.9784 (M^+).

To a solution of aziridine **2** (50 mg, 0.14 mmol) in 0.5 mL of ⁱPrOH was added NaN₃ (20 mg, 0.29 mmol, 2.0 equiv) and 0.5 mL of H₂O. The solution was stirred for 17 h after which time the volatiles were removed under reduced pressure. The resulting oily suspension was diluted with 5 mL of EtOAc and poured into 20 mL of 1:1 EtOAc/1.0 M aqueous NaH₂PO₄. The biphasic solution was separated and the aqueous layer was washed with 3 x 10 mL of EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (9:1 hexanes/EtOAc) afforded the product as a colorless oil (89%): TLC R_f = 0.46 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.46-7.32 (m, 5H), 5.06-5.00 (m, 2H), 4.64 (d, 1H, *J* = 10.8 Hz), 4.60 (d, 1H, *J* = 10.8 Hz), 3.88-3.78 (m, 1H), 1.15 (d, 3H, *J* = 6.7 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) 135.7, 129.0, 128.7, 127.0, 93.3, 78.1, 69.0, 55.2, 15.0 ppm; IR (thin film) ν 3300, 2925, 2108, 1431, 1366, 1184, 1088, 997, 854 cm⁻¹; HRMS calcd for C₁₁H₁₃Cl₃N₄O₃S 385.9774 found 404.0111 (MNH₄⁺).

To a solution of aziridine **2** (50 mg, 0.14 mmol) in 2.0 mL of THF was added C₆H₅CH₂NH₂ (50 μL, 0.44 mmol, 3.0 equiv). The reaction was stirred at 35 °C for 20 h. After this time, the solution was transferred to a separatory funnel with 10 mL of EtOAc and washed with 10 mL of saturated aqueous NaCl. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (gradient elution: 6:1→4:1 hexanes/EtOAc) afforded the desired product as an opaque oil (83%): TLC R_f = 0.34 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.41 (t, 1H, *J* = 7.2 Hz), 7.38-7.24 (m, 4H), 4.56 (d, 1H, *J* = 10.8 Hz), 4.47 (d, 1H, *J* = 10.9 Hz), 3.94 (d, 1H, *J* = 4.0 Hz), 3.87-3.78 (m, 2H), 3.61 (d, 1H, *J* = 13.0 Hz), 2.10-1.45 (br s, 1H), 1.07 (d, 3H, *J* = 6.7 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 139.5, 138.2, 128.9, 128.6, 128.3, 128.0, 127.4, 127.3, 93.5, 77.9, 64.5, 54.5, 51.3, 16.0 ppm; IR (thin film) ν 3319, 3028, 2925, 2850, 1456, 1364, 1182, 1087, 996, 853, 753 cm⁻¹; HRMS calcd for C₁₈H₂₁Cl₃N₂O₃S 450.0338 found 451.0432 (MH⁺).

To a solution of aziridine **3** (81 mg, 0.24 mmol) in 0.5 mL of ⁱPrOH were added NaN₃ (102 mg, 0.96 mmols, 4.0 equiv) and 0.5 mL of H₂O. The solution was stirred for 15 h after which time the volatiles were removed under reduced pressure. The resulting oily suspension was diluted with 5 mL of EtOAc and poured into 20 mL of 1:1 EtOAc/1.0 M aqueous NaH₂PO₄. The organic layer was isolated and the aqueous portion was washed with 3 x 10 mL of EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (gradient elution: 9:1→4:1 hexanes/EtOAc) afforded the desired product as a white solid (82%): TLC R_f = 0.61 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 4.84 (d, 1H, *J* = 9.4 Hz), 4.67 (s, 2H), 3.34 (td, 1H, *J* = 9.5, 3.0 Hz), 1.77-1.52 (m, 2H), 1.48-1.20 (m, 4H), 1.43 (s, 3H), 1.38 (s, 3H), 0.91 (t, 3H, *J* = 7.3 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 93.5, 78.0, 64.2, 63.4, 30.6, 28.3, 24.3, 23.7, 22.6, 13.9 ppm; IR (thin film) ν 3299, 2960, 2874, 2107, 1450, 1361, 1262, 1182, 1004, 854, 759 cm⁻¹; HRMS calcd for C₁₀H₁₉Cl₃N₄O₃S 380.0243 found 398.0585 (MNH₄⁺).

To a solution of aziridine **3** (81 mg, 0.24 mmol) in 2.0 mL of dioxane was added 3.0 mL of distilled H₂O. The reaction was heated at 60 °C for 24 h, then cooled to 25 °C and the volatiles removed under reduced pressure. The resulting oily suspension was diluted with 5 mL of EtOAc and poured into 20 mL of 1:1 EtOAc/1.0 M aqueous NaH₂PO₄. The biphasic solution was separated and the aqueous layer was washed with 3 x 10 mL of EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 hexanes/EtOAc) afforded the desired product as a colorless oil (80%): TLC R_f = 0.20 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 5.37 (d, 1H, *J* = 9.2 Hz), 4.66 (s, 2H), 3.33 (td, 1H, *J* = 9.2, 3.1 Hz), 2.11 (br s, 1H), 1.73-1.53 (m, 2H), 1.48-1.24 (m, 4H), 1.34 (s, 3H), 1.23 (s, 3H), 0.90 (t, 3H, *J* = 7.2) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 93.5, 78.0, 73.0, 64.5, 30.6, 28.6, 27.8, 25.8, 22.6, 13.9 ppm; IR (thin film) ν 3529, 3294, 2958, 1460, 1451, 1356, 1182, 1081, 1002, 853, 757 cm⁻¹; HRMS calcd for C₁₀H₂₀Cl₃NO₄S 355.0179 found 373.0517 (MNH₄⁺).

Experimental procedure and characterization data for sulfamate ester deprotection (see eq 1):

A solution of sulfamate **4** (100 mg, 0.26 mmol) in 2.0 mL of 1:1 MeOH/AcOH was transferred via cannula into a flask containing Zn(Cu) couple (88 mg, 1.35 mmol, 5.0 equiv). Transfer of **4** was made quantitative with an additional 2.0 mL of 1:1 MeOH/AcOH. The resulting suspension was stirred vigorously for 16 h at 25 °C. After this time, the reaction contents were filtered and the filter cake was rinsed with MeOH. The combined filtrates were concentrated under reduced pressure to afford a white solid, which was redissolved in a solution of anhydrous HCl in MeOH (140 μL of CH₃COCl in 2.0 mL of MeOH). The solution was heated at 45 °C for 6 h and then concentrated under reduced pressure. The resulting viscous oil was dissolved in 2.0 mL of CH₂Cl₂ and 2.0 mL of saturated aqueous K₂CO₃ was then added. To this biphasic solution was added dropwise BnO₂CCl (65 μL, 0.46 mmol, 1.7 equiv). The reaction was stirred vigorously for 5 h, then diluted with 5 mL of CH₂Cl₂ and 5 mL of 5 wt.% aqueous NaHCO₃. The organic phase was collected and the aqueous layer was extracted with 3 x 5 mL of CH₂Cl₂. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (gradient elution: 11.5:1→4:1 hexanes/EtOAc) afforded a colorless oil (84%): TLC R_f = 0.48 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.37-7.28 (m, 5H), 5.11 (s, 2H), 4.87 (d, 1H, *J* = 10.2 Hz), 3.57 (m, 1H), 3.17 (s, 3H), 1.68-1.56 (m, 1H), 1.42-1.21 (m, 5H), 1.17 (s, 3H), 1.13 (s, 3H), 0.88 (t, 3H, *J* = 5.8 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 157.0, 137.1, 128.7, 128.24, 128.17, 76.8, 67.4, 59.4, 50.1, 29.7, 28.9, 23.0, 22.3, 22.2, 14.3 ppm; IR (thin film) ν 3339, 2956, 2872, 1702, 1421, 1365, 1333, 1161, 1075, 1049 cm⁻¹; HRMS calcd for C₁₇H₂₇NO₃ 293.1991 found 294.2064 (M⁺).

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