Supporting Information for:

Anionic Halocuprate(II) Complexes as Catalysts for the Oxaziridine-Mediated Aminohydroxylation of Olefins

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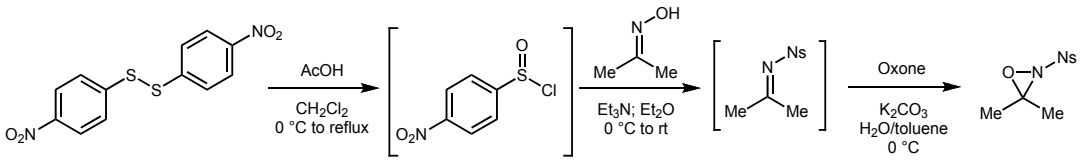
I. General Information.

Oxaziridine **1**,[1] imidazolium salts **3a–b**,[2] imidazolinium salt **4**,[3] were prepared as previously described. Anhydrous tetrabutylammonium salts were prepared by azeotropic removal of water from toluene solutions of the commercially available hydrates, and the salts were stored in an inert-atmosphere glovebox. All styrenes were distilled prior to use except for 2-vinylnaphthalene, which was purified by column chromatography on silica gel using 10:1:1 hexane:EtOAc:CH_2Cl_2 as eluent. HMPA was distilled prior to use and stored over 4Å molecular sieves. Dichloromethane, acetonitrile, and triethylamine were distilled from CaH_2 immediately prior to use. Toluene was distilled from sodium immediately prior to use. Diethyl ether was distilled from sodium metal and benzophenone immediately before use. All other chemicals were used as purchased without further purification. Silica gel chromatography was performed using 60Å silica gel (230–400 mesh). All reactions were conducted in flame-dried glassware.

Product ratios for Table 2, entries 5 and 9 were determined by ^{1}H NMR analysis of the unpurified reaction mixtures. ^{1}H and ^{13}C NMR data were obtained using 500 MHz spectrometers. ^{1}H data were internally referenced to TMS (0.0 ppm) or DMSO (2.5 ppm); ^{13}C spectra were referenced to $CDCl_3$ (77.23 ppm) or DMSO (39.50 ppm). Analytical facilities in the Chemistry Department at UW–Madison are supported by the NSF (CHE-9709005) and the University of Wisconsin.

II. Synthesis of *N*-Nosyl-3,3-dimethyloxaziridine (2)



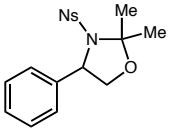
***N*-(4-Nitrobenzensulfonyl)-3,3-dimethyloxaziridine.** Synthesized using a modification of the method of Jennings.[4] In a dry 250 mL round bottom flask containing a large stir bar was placed 4-nitrophenyl disulfide (20 g, 65 mmol). The flask was charged with CH_2Cl_2 (30 mL) and anhydrous acetic acid (8.2 mL, 143 mmol), and the slurry was cooled to 0 °C under nitrogen. Sulfuryl chloride (27 mL, 320 mmol) was added dropwise over 45 minutes using a dry addition funnel. The resulting slurry was stirred for 1 h at 0 °C, 1 h at ambient temperature, and finally at reflux for an additional 7.5 h. The volatile organics were carefully removed on a rotary evaporator connected to a water aspirator, and the dense red solid was placed under vacuum overnight.

Ether (210 mL) was then added to the solid sulfinyl chloride, and the mixture was vigorously stirred under nitrogen until completely dissolved. In a separate dry 1 L round bottom flask containing a large stir bar were placed acetone oxime (9.34 g, 128 mmol), 280 mL ether, and Et_3N (18 mL, 128 mmol). The solution was cooled to 0 °C, and the dissolved sulfinyl chloride was added dropwise to the oxime solution. A second 210 mL portion of ether was used to dissolve any remaining sulfinyl chloride and to rinse the addition funnel. After the addition was complete, the flask was removed from the cooling bath, and the reaction was stirred at room temperature. After 4 h, the reaction mixture was passed through a fritted filter to remove solids. The solids were washed several times with ether and toluene and all ether was removed via rotary evaporation. The resulting yellow solution of *N*-nitrobenzenesulfonyl acetone imine in toluene was immediately subjected to oxidation.

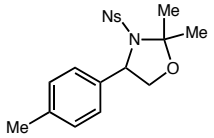
A 4 L Erlenmeyer flask, equipped with a mechanical stirrer and charged with a solution of K_2CO_3 (150 g, 1.09 mol) in water (1 L), was cooled to 0 °C. The imine solution in toluene (~0.9 L) and a solution of Oxone® (150 g, 243 mmol) in water (1 L) were added simultaneously to the reaction via addition funnel over the course of 5 min with vigorous stirring. After 15 min, the phases were separated, and the aqueous layer was extracted with toluene. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated by rotary evaporation. Purification via column chromatography (4:1 hexane:EtOAc) followed by recrystallization (1:1 hexane:EtOAc) afforded a slightly yellow crystalline product. A second crop of oxaziridine could be isolated from the mixed fractions and the mother liquor upon chromatography and crystallization under the same conditions, resulting in a total yield of 16.7 g (64.8 mmol, 49.8%). IR (neat) 3118, 1538, 1351, 1305, 1172; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dt, J = 9.2, 2.4 Hz, 2H), 8.20 (dt, J = 9.5, 2.4 Hz, 2H), 2.11 (s, 3H), 1.6 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 151.2, 143.7, 129.8, 124.6, 88.6, 77.5, 77.3, 77.2, 77.1, 77.0, 26.1, 19.5; HRMS (EI^+) calc'd for $[C_9H_{10}N_2O_5SNa]^+$ requires *m/z* 281.0203, found *m/z* 281.0208. (mp = 120–121 ºC (dec.)).

III. Aminohydroxylation Reactions (Tables 2 and 3)

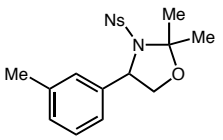
General procedure for aminohydroxylations. In a nitrogen-atmosphere glovebox, copper(II) chloride and tetrabutylammonium chloride were placed in a 2 dram vial with a stirbar. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with CH_2Cl_2 and the mixture was stirred under argon for 30 min. Styrene was then added by syringe. The septum was removed, oxaziridine (**1** or **2**) was quickly added, and the vessel was sealed and flushed with argon. The reaction progress was monitored by ^{1}H NMR or TLC. Upon completion of the reaction, the remaining oxaziridine was quenched with dimethylsulfide, the solvent was removed by rotary evaporation, and the remaining residue was loaded directly onto silica for purification by flash column chromatography.



***N*-(4-Nitrobenzensulfonyl)-2,2-dimethyl-4-phenyl-1,3-oxazolane (**Table 2, entry 1). Prepared according to the general procedure using 52.3 mg (0.502 mmol) of styrene, 3.6 mg (0.025 mmol) $CuCl_2$, 7.0 mg (0.025 mmol) TBACl, 191 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 2.5 h. The silica gel was loaded using 6:1 hexane-acetone and the product was eluted using 5:1 hexane-acetone. Isolated 134 mg (0.371 mmol, 74% yield) white solid. Yield 2: 51.2 mg (0.492 mmol) of styrene, 3.5 mg (0.025 mmol) $CuCl_2$, 7.1 mg (0.025 mmol) TBACl, 191 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Isolated 132 mg (0.365 mmol, 74% yield). IR (neat): 3005, 1535, 1346, 1155; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 9.5, 2.4 Hz, 2H), 7.48 (dt, J = 9.5, 2.4 Hz, 2H), 7.16 (m,1H), 7.10 (dt, J = 4.3 Hz, 4H), 4.94 (dd, J = 7.0, 2.7 Hz, 1H), 4.44 (dd, J = 9.1, 7.0 Hz, 1H), 3.94 (dd, J = 9.2, 2.7 Hz, 1H), 1.84 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.4, 146.9, 139.5, 128.8, 128.7, 128.4, 127.7, 123.5, 99.4, 71.7, 62.9, 27.2, 26.6; HRMS (EI^+) calc'd for $[C_{16}H_{15}N_2O_5S]^+$ $(M–CH_3)^+$ requires *m/z* 347.0697, found *m/z* 347.0700. (mp = 103–105 ºC).

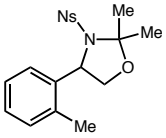


***N*-(4-Nitrobenzensulfonyl)-2,2-dimethyl-4-(4-methylphenyl)-1,3-oxazolane (**Table 2, entry 2**).** Prepared according to the general procedure using 59.5 mg (0.503 mmol) of 4-methylstyrene, 3.4 mg (0.025 mmol) $CuCl_2$, 7.1 mg (0.025 mmol) TBACl, 190 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 1.5 h. The silica gel was loaded using 10:1:1 hexane-EtOAc-CH_2Cl_2 and 2% triethylamine and the product was eluted using the same eluent. Isolated 150 mg (0.399 mmol, 79% yield) white solid. Yield 2: 60.1 mg (0.509 mmol) of 4-methylstyrene, 3.6 mg (0.025 mmol) $CuCl_2$, 6.9 mg (0.025 mmol) TBACl, 195 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Isolated 153 mg (0.403 mmol, 79% yield). IR (neat): 2992, 1528, 1351, 1165, 1148, 856; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 9.5, 2.4 Hz, 2H), 7.49 (dt, J = 9.5, 2.4 Hz, 2H), 6.96 (dt, J = 6.4 Hz, 2H), 6.89 (dt, J = 7.9 Hz, 2H), 4.88 (dd, J = 7.0, 2.8 Hz, 1H), 4.41 (dd, J = 9.2, 7.0 Hz, 1H), 3.91 (dd, J = 9.3, 3.1 Hz, 1H), 2.25 (s, 3H), 1.84 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.4, 147.0, 138.4, 136.3, 129.3, 128.7, 127.7, 123.4, 99.3, 71.7, 62.7, 27.3, 26.6, 21.2; HRMS (EI^+) calc'd for $[C_{18}H_{20}N_2O_5SNa]^+$ $(M+Na)^+$ requires *m/z* 399.0986, found *m/z* 399.0997. (mp = 103–106 ºC).

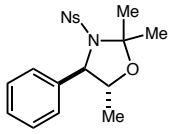


***N*-(4-Nitrobenzensulfonyl)-2,2-dimethyl-4-(3-methylphenyl)-1,3-oxazolane (**Table 2, entry 3**).** Prepared according to the general procedure using 59.9 mg (0.507 mmol) of 3-methylstyrene, 3.5 mg (0.025 mmol) $CuCl_2$, 6.8 mg (0.025 mmol) TBACl, 192 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 4 h. The silica gel was loaded using 8:1 hexane-acetone and the product was eluted using the same eluent. Isolated 147 mg (0.391 mmol, 77% yield) white solid. Yield 2: 60.0 mg (0.508 mmol) of 3-methylstyrene, 3.5 mg (0.025 mmol) $CuCl_2$, 6.9 mg (0.025 mmol) TBACl, 192 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Isolated 151 mg (0.365 mmol, 79% yield). IR (neat): 3122, 3006, 1531, 1347, 740; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 9.2, 2.4 Hz, 2H), 7.49 (dt, J = 9.5, 2.4 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.94 (dd, J = 19.5, 7.3 Hz, 2H), 6.8 (s, 1H), 4.89 (dd, J = 7.0, 2.8 Hz, 1H), 4.42 (dd, J = 8.8, 7.0 Hz, 1H), 3.91 (dd, J = 8.9, 2.8 Hz, 1H), 2.12 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H);

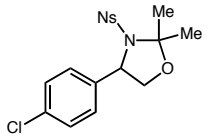
^{13}C NMR (125 MHz, $CDCl_3$) 149.4, 146.9, 139.2, 138.4, 128.9, 128.7, 128.7, 128.3, 124.9, 123.3, 99.3, 71.6, 62.8, 27.2, 26.6, 21.3; HRMS (EI^+) calc'd for $[C_{18}H_{20}N_2O_5SNa]^+$ $(M+Na)^+$ requires *m/z* 399.0986, found *m/z* 399.0980. (mp = 90–94 ºC).



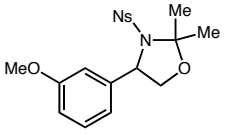
***N*-(4-Nitrobenzensulfonyl)-2,2-dimethyl-4-(2-methylphenyl)-1,3-oxazolane (**Table 2, entry 4**).** Prepared according to the general procedure using 56.3 mg (0.476 mmol) of 2-methylstyrene, 6.8 mg (0.05 mmol) $CuCl_2$, 13.9 mg (0.05 mmol) TBACl, 199 mg (0.75 mmol) oxaziridine **2** and 0.5 mL CH_2Cl_2. Reaction time was 4 h. The silica gel was loaded using 6:1 hexane-acetone and the product was eluted using 5:1 hexane-acetone. Isolated 141 mg (0.375 mmol, 79% yield) white solid. Yield 2: 58.4 mg (0.494 mmol) of 2-methylstyrene, 6.8 mg (0.05 mmol) $CuCl_2$, 14.0 mg (0.05 mmol) TBACl, 203 mg (0.75 mmol) oxaziridine **2** and 0.5 mL CH_2Cl_2. Isolated 150 mg (0.400 mmol, 81% yield). IR (neat): 3119, 2864, 1531, 1361, 1214, 856; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, J = 9.5, 2.4 Hz, 2H), 7.47 (dt, J = 9.5, 2.4 Hz, 2H), 7.00 (ddd, J = 13.7, 7.6, 1.2 Hz, 2H), 6.93 (d, J = 7.9 Hz, 1H), 6.78 (td, J = 7.9, 2.1 Hz, 1H), 5.29 (dd, J = 7.3, 2.7 Hz, 1H), 4.47 (dd, J = 8.8, 7.3 Hz, 1H), 3.85 (dd, J = 8.8, 3.1 Hz, 1H), 2.36 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.4, 146.7, 137.2, 135.6, 130.5, 128.4, 128.0, 127.5, 126.6, 123.5, 99.5, 71.3, 58.5, 27.0, 26.5, 19.5; HRMS (EI^+) calc'd for $[C_{17}H_{17}N_2O_5S]^+$ $(M—CH_3)^+$ requires *m/z* 361.0858, found *m/z* 361.0856. (mp = 144–150 ºC (dec)).



***N*-(4-Nitrobenzensulfonyl)-2,2-dimethyl-5-methyl-4-phenyl-1,3-oxazolane (**Table 2, entry 5). Prepared according to the general procedure using 58.0 mg (0.491 mmol) of *trans*-β-methylstyrene, 6.9 mg (0.05 mmol) $CuCl_2$, 14.0 mg (0.05 mmol) TBACl, 197 mg (0.75 mmol) oxaziridine **2** and 0.5 mL CH_2Cl_2. Reaction time was 4.5 h. The silica gel was loaded using 6:1 hexane-acetone and the product was eluted using 5:1 hexane-acetone. Isolated 110 mg (0.292 mmol, 60% yield) white solid. Yield 2: 62.9 mg (0.532 mmol) of *trans*-β-methylstyrene, 7.0 mg (0.05 mmol) $CuCl_2$, 14.0 mg (0.05 mmol) TBACl, 205 mg (0.75 mmol) oxaziridine **2** and 0.5 mL CH_2Cl_2. Isolated 120 mg (0.318 mmol, 60% yield). IR (neat): 2976, 1524, 1339, 1152, 773; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.08 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 7.3 Hz, 2H), 4.17 (d, J = 8.6 Hz, 1H), 4.06 (m, 1H), 1.88 (s, 3H), 1.85 (s, 3H), 1.19 (d, J = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.5, 146.7, 135.0, 128.8, 128.7, 128.6, 128.6, 123.6, 99.6, 79.5, 70.6, 29.9, 28.8, 28.7, 16.9; HRMS (EI^+) calc'd for $[C_{17}H_{17}N_2O_5S]^+$ $(M–CH_3)^+$ requires *m/z* 361.0858, found *m/z* 361.0858. (mp = 151–156 ºC (dec.)).

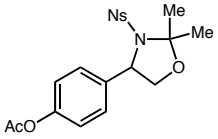


***N*-(4-Nitrobenzensulfonyl)-4-(4-chlorophenyl)-2,2-dimethyl-1,3-oxazolane** (Table 2, entry 6) Prepared according to the general procedure using 67.4 mg (0.486 mmol) of 4-chlorostyrene, 3.4 mg (0.025 mmol) $CuCl_2$, 7.0 mg (0.025 mmol) TBACl, 198 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 3 h. The silica gel was loaded using 6:1 hexane-acetone and the product was eluted using 5:1 hexane-acetone. Isolated 146 mg (0.368 mmol, 76% yield) white solid. Yield 2: 68.5 mg (0.494 mmol) of 4-chlorostyrene, 3.6 mg (0.025 mmol) $CuCl_2$, 7.0 mg (0.025 mmol) TBACl, 198 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Isolated 155 mg (0.392 mmol, 79% yield). IR (neat): 3112. 2995. 1530. 1345. 773; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.0, 1.8 Hz, 2H), 7.57 (dd, J = 7.0, 1.8 Hz, 2H), 7.11 (dd, J = 6.4, 2.1 Hz, 2H), 7.07 (dd, J = 6.7, 2.1 Hz, 2H), 4.41 (dd, J = 9.2, 7.0 Hz, 1H), 3.9 (dd, J = 9.5, 2.8 Hz, 1H), 1.83 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.6, 146.7, 138.2, 134.3, 128.9, 128.8, 128.7, 123.7, 99.4, 71.4, 62.1, 27.4, 26.3; HRMS (EI^+) calc'd for $[C_{16}H_{14}N_2O_5ClS]^+$ $(M–CH_3)^+$ requires *m/z* 381.0307, found *m/z* 381.0302. (mp = 136–139 ºC).

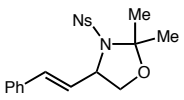


***N*-(4-Nitrobenzensulfonyl)-4-(3-methoxyphenyl)-2,2-dimethyl-1,3-oxazolane** (Table 2, entry 7). Prepared according to the general procedure using 65.3 mg (0.487 mmol) of 3-methoxystyrene, 3.4 mg (0.025 mmol) $CuCl_2$, 6.8 mg (0.025 mmol) TBACl, 189 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was

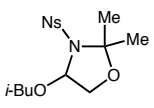
3 hours. The silica gel was loaded using 8:1 hexane-acetone and the product was eluted using the same mixture. Isolated 169 mg (0.429 mmol, 88% yield) white solid. Yield 2: 65.5 mg (0.488 mmol) of 3-methoxystyrene, 3.5 mg (0.025 mmol) $CuCl_2$, 7.0 mg (0.025 mmol) TBACl, 191 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Isolated 161 mg (0.410 mmol, 84% yield). IR (neat): 1588, 1344, 1148, 834; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, J = 9.5, 2.4 Hz, 2H), 7.53 (dt, J = 9.5, 2.4 Hz, 2H), 7.04 (t, J = 7.9 Hz, 1H), 6.71 (dt, J = 7.9 Hz, 1H), 6.68 (dd, J = 8.2, 2.8 Hz, 1H), 6.51 (t, J = 1.8 Hz, 1H), 4.88 (dd, J = 7.0, 2.4 Hz, 1H), 4.43 (dd, J = 9.2, 7.0 Hz, 1H), 3.92 (dd, J = 9.2, 2.8 Hz, 1H), 3.63 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 159.8, 149.4, 146.8, 140.9, 129.8, 128.7, 123.4, 120.0, 113.6, 113.0, 99.4, 71.6, 62.7, 55.2, 27.2, 26.6; HRMS (EI$^+$) calc'd for $[C_{18}H_{20}N_2O_6SNa]^+$ $(M+Na)^+$ requires *m/z* 415.0940, found *m/z* 415.0951. (mp = 127–130 ºC).



***N*-(4-Nitrobenzensulfonyl)-4-(4-acetoxyphenyl)-2,2-dimethyl-1,3-oxazolane** (Table 2, entry 8). Prepared according to the general procedure using 79.4 mg (0.496 mmol) of 4-acetoxystyrene, 3.4 mg (0.025 mmol) $CuCl_2$, 6.9 mg (0.025 mmol) TBACl, 191 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 2.5 h. The silica gel was loaded using 8:1 hexane-acetone and the product was eluted using the same eluent. The material obtained was re-purified using 4:1:1 hexane-EtOAc-CH_2Cl_2 and 2% triethylamine. Isolated 142 mg (0.338 mmol, 69% yield) white solid. Yield 2: 82.1 mg (0.506 mmol) of 4-acetoxystyrene, 3.5 mg (0.025 mmol) $CuCl_2$, 7.0 mg (0.025 mmol) TBACl, 194 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. The material obtained was purified using 4:1:1 hexane-EtOAc-CH_2Cl_2 and 2% triethylamine. Isolated 154 mg (0.367 mmol, 72% yield). IR (neat): 2894, 1609, 1370, 1223, 1202, 1161; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dt, J = 9.2, 2.1 Hz, 2H), 7.47 (dt, J = 9.5, 2.4 Hz, 2H), 7.12 (dt, J = 9.2, 2.4 Hz, 2H), 6.82 (dt, J = 9.2, 2.4 Hz, 2H), 4.96 (dd, J = 7.0, 2.4 Hz, 1H), 4.45 (dd, J = 9.2, 7.3 Hz, 1H), 3.95 (dd, J = 9.5, 2.8 Hz, 1H), 2.28 (s, 3H), 1.82 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 169.3, 150.7, 149.7, 146.8, 137.1, 128.8, 128.6, 123.8, 122.1, 99.3, 71.5, 62.2, 27.2, 26.5, 21.2; HRMS (EI$^+$) calc'd for $[C_{11}H_{20}N_2O_7SNa]^+$ $(M+Na)^+$ requires *m/z* 443.0885, found *m/z* 443.0871. (mp = 148–152 ºC).

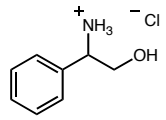


***N*-(4-Nitrobenzensulfonyl)-4-(*trans*-cinnamyl)-2,2-dimethyl-1,3-oxazolane** (Table 2, entry 9). Prepared according to the general procedure with the exception that the diene was added to a solution cooled to 0 °C, and after the addition of oxaziridine, the solution was maintained at 0 °C for 5 min. 63.8 mg (0.490 mmol) of phenylbutadiene, 1.4 mg (0.01 mmol) $CuCl_2$, 2.9 mg (0.01 mmol) TBACl, 191 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 1 h 45 min. The silica gel was loaded using 6:1:1 hexane-EtOAc-CH_2Cl_2 and the product eluted using the same eluent. Isolated 133 mg (0.343 mmol, 70% yield) white solid. Yield 2: 65.9 mg (0.506 mmol) of phenylbutadiene, 1.4 mg (0.01 mmol) $CuCl_2$, 2.9 mg (0.01 mmol) TBACl, 191 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. The silica gel was loaded using 6:1:1 hexane-EtOAc-CH_2Cl_2 and 3% triethylamine and the product eluted using the same eluent. Isolated 143 mg (0.368 mmol, 73% yield). IR (neat): 2990, 1525, 1340, 1154, 739; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dt, J = 9.2, 2.1 Hz, 2H), 7.97 (dt, J = 9.5, 2.4 Hz, 2H), 7.26 (m, 3H), 7.11 (td, J = 4.3, 2.4 Hz, 2H), 6.40 (dt, J = 15.9 Hz, 1H), 5.70 (dd, J = 15.9, 9.2 Hz, 1H), 4.50 (ddd, J = 12.8, 6.4, 3.7 Hz, 1H), 4.22 (dd, J = 9.2, 6.4 Hz, 1H), 3.83 (dd, J = 9.1, 3.7 Hz, 1H), 1.76 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.7, 147.5, 135.4, 134.0, 129.3, 128.9, 128.7, 126.5, 126.4, 124.0, 98.9, 69.5, 62.1, 28.2, 26.7; HRMS (EI$^+$) calc'd for $[C_{19}H_{20}N_2O_5SNa]^+$ $(M+Na)^+$ requires *m/z* 411.0986, found *m/z* 411.0997. (mp = 109–114 ºC).



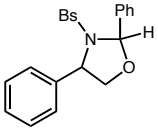
***N*-(4-Nitrobenzenesulfonyl)-3-isobutoxy-2,2-dimethyl-1,3-oxazolane (**Table 2, entry 10). Prepared according to the general procedure using 50.2 mg (0.501 mmol) of isobutyl vinyl ether, 3.5 mg (0.025 mmol) $CuCl_2$, 7.1 mg (0.025 mmol) TBACl, 189 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Reaction time was 2 h. The silica gel was loaded using 10:1:1 hexane-EtOAc-CH_2Cl_2 and 1% triethylamine and the product was eluted using the same eluent. Isolated 112 mg (0.314 mmol, 63% yield) white solid. Yield 2: 48.4 mg (0.483 mmol) of

isobutyl vinyl ether, 3.2 mg (0.025 mmol) $CuCl_2$, 6.6 mg (0.025 mmol) TBACl, 188 mg (0.75 mmol) oxaziridine **2** and 0.25 mL CH_2Cl_2. Isolated 107 mg (0.297 mmol, 62% yield). IR (neat): 2961, 1533, 1348, 742; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dt, J = .2, 2.1 Hz, 2H), 8.20 (dt, J = 9.1, 2.1 Hz, 2H), 5.41 (t, J = 2.4 Hz, 1H), 4.01 (s, 1H), 4.00 (d, J = 0.9 Hz, 1H), 3.31 (dd, J = 9.2, 6.7 Hz, 1H), 3.06 (dd, J = 8.8, 6.4 Hz, 1H), 1.72 (m, 1H), 1.59 (s, 3H), 1.52 (s, 3H), 0.84 (dd, J = 18.0, 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 150.1, 148.2, 129.1, 124.1, 98.1, 88.8, 74.2, 68.8, 28.7, 27.4, 26.2, 19.5; HRMS (EI^+) calc'd for $[C_{15}H_{22}N_2O_6SNa]^+$ $(M+Na)^+$ requires *m/z* 381.1091, found *m/z* 381.1101. (mp = 72–75 ºC).

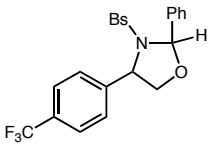


2-Phenylglycinol, HCl salt (Scheme 2). *N*-(4-Nitrobenzensulfonyl)-2,2-dimethyl-4-phenyl-1,3-oxazolane (2.90 g, 8 mmol) was dissolved in 1,2-dimethoxyethane (27 mL) in a 100 mL round-bottomed flask and treated with trifluoroacetic acid (1.3 mL, 17 mmol) and 13.2 mL of H_2O. The yellow reaction mixture was heated to reflux at 80 °C. After 6 h, the reaction was quenched with sat. aq. $NaHCO_3$ (18 mL) and extracted with ether (70 mL). The aqueous layer was extracted with EtOAc (3 x 30 mL), and the combined organics were dried with Na_2SO_4 and concentrated by rotary evaporation to yield the product as a pale yellow solid. The crude *N*-nosyl aminoalcohol was carried on to the next step without further purification.

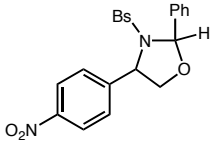
The nosyl moiety was removed using a variation of the method described by Maligres et al.[5] The unpurified *N*-nosyl aminoalcohol was placed in a 500 mL round-bottomed flask. Thiophenol (0.85 mL, 8 mmol), K_2CO_3, and CH_3CN (180 mL) were added, and the mixture was heated to reflux at 50 °C for 24 h. The K_2CO_3 was removed by filtration through a layer of Celite, and the filtrate was concentrated to yield an orange residue. The residue was dissolved in a minimal amount of CH_3CN. The product was precipitated by addition of 2 M HCl in Et_2O (5.0 mL, 10 mmol) to furnish 1.3 g of a white-gray solid (0.726 mmol, 91%). The free base of this compound exhibited spectral data identical to those reported for phenylglycinol.[6]



***N*-(4-Benzenesulfonyl)-2,4-diphenyl-1,3-oxazolane (**Table 3, entries 1-2). Prepared according to the general procedure using 50.1 mg (0.481 mmol) of styrene, 1.4 mg (0.010 mmol) $CuCl_2$, 2.8 mg (0.010 mmol) TBACl, 194 mg (0.74 mmol) oxaziridine **1** and 1.0 mL CH_2Cl_2. Reaction time was 2 h. The crude residue was loaded directly onto silica for purification by flash column chromatography using 5:1 hexane: EtOAc with 2% triethylamine as an eluent. Isolated 166.9 mg clear oil (0.457 mmoles, 95% yield) as mixture of diastereomers (dr = 1:1). The spectral properties of the aminals were found to be identical to those previously reported.[7] Yield 2: 50.0 mg (0.480 mmol) of styrene, 1.4 mg (0.010 mmol) $CuCl_2$, 2.9 mg (0.010 mmol) TBACl, 194 mg (0.74 mmol) oxaziridine **1** and 1.0 mL CH_2Cl_2. Isolated 158 mg (0.432 mmol, 90% yield).

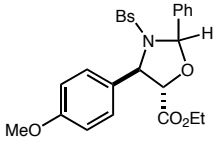


***N*-(4-Benzenesulfonyl)-2-phenyl-4-(4-trifluoromethylphenyl)-1,3-oxazolane (**Table 3, entries 3-4). Prepared according to the general procedure using 82.7 mg (0.480 mmol) of 4-trifluoromethylstyrene, 1.5 mg (0.011 mmol) $CuCl_2$, 2.9 mg (0.010 mmol) TBACl, 195 mg (0.75 mmol) oxaziridine **1** and 1.0 mL CH_2Cl_2. Reaction time was 3 h. The crude residue was loaded directly onto silica for purification by flash column chromatography using 10:1:1 hexane: EtOAc: CH_2Cl_2 with 1% triethylamine as an eluent. Isolated 167.4 mg white solid (0.386 mmoles, 80% yield) as mixture of diastereomers (dr = 3:1). The spectral properties of the aminals were found to be identical to those previously reported.[7]

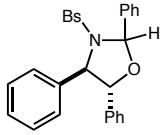


***N*-(4-Benzenesulfonyl)-2-phenyl-4-(4-nitrophenyl)-1,3-oxazolane (**Table 3, entries 5-6). The $Cu(TFA)_2$-HMPA procedure was set up as reported earlier[7] using 76.4 mg (0.512 mmol) of 4-nitrostyrene, 2.9 mg (0.010 mmol) $Cu(TFA)_2$, 9 μL (0.050 mmol) HMPA, 202 mg (0.77 mmol) oxaziridine **1** and 1.0 mL CH_2Cl_2. Reaction time was 24 h, then the oxaziridine was quenched using Me_2S. The crude residue was loaded directly onto silica for purification by flash column chromatography using 10:1:1

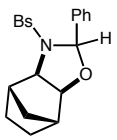
hexane: EtOAc: CH_2Cl_2 with 1% triethylamine as an eluent.. Isolated 96.3 mg white solids (0.235 mmoles, 46% yield) as mixture of diastereomers (dr = 3:1). Yield 2 (Table 3, entry 6): Prepared according to the general procedure using 73.8 mg (0.495 mmol) of 4-nitrostyrene, 1.5 mg (0.011 mmol) $CuCl_2$, 2.9 mg (0.010 mmol) TBACl, 197 mg (0.75 mmol) oxaziridine **1** and 1.0 mL CH_2Cl_2. Reaction time was 4.5 h. Isolated 153.6 mg (0.374 mmol, 76% yield). Major isomer (2*R**,4*S**): IR (neat): 2941, 1514, 1349, 1314; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.040 (d, J = 8.0 Hz, 2H), 7.453 (m, 4H), 7.375 (m, 4H), 7.233 (d, J = 7.5 Hz, 2H), 7.162 (t, J = 7.5 Hz, 2H), 6.435 (s, 1H), 5.181 (dd, J = 6.0, 2.4 Hz, 1H), 4.466 (dd, J = 9.0, 6.0 Hz, 1H), 3.959 (dd, J = 9.0, 2.4 Hz, 1H),; ^{13}C NMR (125 MHz, $CDCl_3$) 147.8, 146.5, 140.5, 137.5, 132.7, 129.6, 128.7, 128.7, 127.6, 127.0, 123.9, 92.9, 72.8, 62.1; HRMS (EI^+) calc'd for $[C_{21}H_{19}N_2O_5S]^+$ $(M+H)^+$ requires *m/z* 411.1010, found *m/z* 411.1016. (mp = 220–222 ºC). Minor isomer (2*S**,4*S**): IR (neat): 2941, 1527, 1350; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.122 (d, J = 8.5 Hz, 2H), 7.797 (d, J = 7.7 Hz, 2H), 7.647 (t, J = 7.7 Hz, 1H), 7.547 (m, 4H), 7.401 (m, 5H), 6.373 (s, 1H), 4.969 (dd, J = 7.5, 7.0 Hz, 1H), 4.233 (dd, J = 9.0, 7.5 Hz, 1H), 3.892 (dd, J = 9.0, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 147.8, 146.2, 137.4, 137.1, 133.9, 129.6, 129.4, 128.9, 128.2, 128.2, 127.1, 124.1, 92.9, 72.9, 62.6; HRMS (EI^+) calc'd for $[C_{21}H_{19}N_2O_5S]^+$ $(M+H)^+$ requires *m/z* 411.1010, found *m/z* 411.1008. (mp = 115–117 ºC).



***N*-(4-Benzenesulfonyl)-5-ethoxycarbonyl-4-(4-methoxyphenyl)-2-phenyl-1,3-oxazolane (**Table 3, entries 7-8). The $Cu(TFA)_2$-HMPA procedure was set up as reported earlier[7] using 51.3 mg (0.249 mmol) of 4-methoxyphenyl ethyl cinnamate, 1.5 mg (0.005 mmol) $Cu(TFA)_2$, 4.5 μL (0.025 mmol) HMPA, 97.7 mg (0.374 mmol) oxaziridine **1** and 0.5 mL CH_2Cl_2. Reaction time was 24 h, then the oxaziridine was quenched using Me_2S. The crude residue was loaded directly onto silica for purification by flash column chromatography using 4:1 hexane: EtOAc with 1% triethylamine as an eluent.. Isolated 26.0 mg colorless oil (0.056 mmoles, 22% yield) as mixture of diastereomers (>10:1 trans isomers, dr = 5:2). Yield 2 (Table 3, entry 8): Prepared according to the general procedure using 50.3 mg (0.244 mmol) of 4-methoxyphenyl ethyl cinnamate, 1.5 mg (0.006 mmol) $CuCl_2$, 2.9 mg (0.006 mmol) TBACl, 99.9 mg (0.382 mmol) oxaziridine **1** and 0.5 mL CH_2Cl_2. Reaction time was 24 h. Isolated 84.2 mg (0.180 mmol, 74% yield). Major isomer (2*S**,4*R**,5*R**): IR (neat): 2991, 2940, 1720, 1514, 1251; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.472 (d, J = 7.0 Hz, 2H), 7.355 (m, 4H), 7.308 (t, J = 7.0 Hz, 1H), 7.243 (m, 2H), 7.135 (m, 4H), 6.826 (d, J = 8.7 Hz, 2H), 6.279 (s, 1H), 5.475 (d, J = 5.0 Hz, 1H), 4.692 (d, J = 5.0 Hz, 1H), 4.125 (m, 2H), 3.823 (s, 3H), 1.182 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 169.8, 160.0, 140.4, 135.9, 132.2, 129.7, 129.5, 129.4, 129.0, 128.5, 128.2, 127.3, 114.3, 93.1, 82.8, 65.8, 62.1, 55.6, 14.2; HRMS (EI^+) calc'd for $[C_{25}H_{26}NO_6S]^+$ $(M+H)^+$ requires *m/z* 468.1476, found *m/z* 468.1479. (mp = 143–145 ºC). Minor isomer (2*R**,4*R**,5*R**): IR (neat): 2922, 1754, 1514, 1357; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.724 (d, J = 7.5 Hz, 2H), 7.572 (m, 3H), 7.469 (t, J = 7.5 Hz, 2H), 7.362 (m, 3H), 7.210 (d, J = 8.7 Hz, 2H), 6.805 (d, J = 8.7 Hz, 2H), 6.516 (s, 1H), 5.078 (d, J = 5.0 Hz, 1H), 4.626 (d, J = 5.0 Hz, 1H), 4.059 (m, 2H), 3.782 (s, 3H), 1.213 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 169.0, 159.7, 137.7, 137.4, 133.4, 130.7, 129.9, 129.3, 128.7, 128.7, 128.3, 127.6, 114.2, 93.2, 82.5, 65.5, 62.0, 55.4, 14.3; HRMS (EI^+) calc'd for $[C_{25}H_{26}NO_6S]^+$ $(M+H)^+$ requires *m/z* 468.1476, found *m/z* 468.1475.



***N*-(4-Benzenesulfonyl)-2,4,5-triphenyl-1,3-oxazolane (**Table 3, entries 9-10). Prepared according to the general procedure using 87.0 mg (0.483 mmol) of *cis*-stilbene, 1.4 mg (0.010 mmol) $CuCl_2$, 2.9 mg (0.010 mmol) TBACl, 199 mg (0.76 mmol) oxaziridine **1** and 0.5 mL CH_2Cl_2. Reaction time was 12 h. The crude residue was loaded directly onto silica for purification by flash column chromatography using 10:1 hexane: EtOAc and eluted using 8:1 hexane: EtOAc. Isolated 170.9 mg white solids (0.387 mmoles, 80% yield) as mixture of diastereomers (dr = 2:1). The spectral properties of the aminals were found to be identical to those previously reported.[7]



***N*-Benzenesulfonyl-4-phenyl-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decane** (Table 3, entries 11-12). The $Cu(TFA)_2$-HMPA procedure was set up as reported earlier[7] using 48.9 mg (0.519 mmol) of norbornene, 3.0 mg (0.010 mmol) $Cu(TFA)_2$, 9 μL (0.050 mmol) HMPA, 196 mg (0.75 mmol) oxaziridine **1** and 1.0 mL CH_2Cl_2. Reaction time was 6 h, then the oxaziridine was quenched using Me_2S. The crude residue was loaded directly onto silica for purification by flash column chromatography using 10:1 hexane: EtOAc with 1% triethylamine as an eluent.. Isolated 99.0 mg white semi-solids (0.279 mmoles, 54% yield) as mixture of diastereomers (dr = 4:1). Yield 2 (Table 3, entry 12): Prepared according to the general procedure using 49.0 mg (0.520 mmol) of 4-nitrostyrene, 1.3 mg (0.010 mmol) $CuCl_2$, 2.9 mg (0.010 mmol) TBACl, 204 mg (0.78 mmol) oxaziridine and 1.0 mL CH_2Cl_2. Reaction time was 6 h. Isolated 133 mg (0.374 mmol, 72% yield, dr = 8:1) white semi-solids. Major isomer (2*S**,4*R**,6*R**): IR (neat): 2967, 1447, 1356; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.569 (d, J = 7.9 Hz, 2H), 7.499 (t, J = 7.3 Hz, 1H), 7.388 (m, 4H), 7.292 (t, J = 6.6 Hz, 1H), 7.241 (t, J = 7.3 Hz, 2H), 5.334 (s, 1H), 3.993 (d, J = 6.6 Hz, 1H), 3.653 (d, J = 6.6 Hz, 1H), 2.703 (d, J = 3.3 Hz, 1H), 2.392 (d, J = 3.3 Hz, 1H), 2.010 (d, J = 10.3 Hz, 1H), 1.558 (m, 2H), 1.213 (d, J = 10.3 Hz, 1H), 1.136 (t, J = 9.1 Hz, 1H), 0.975 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 138.0, 136.0, 132.9, 129.8, 128.9, 128.8, 128.5, 128.3, 128.0, 92.4, 83.9, 66.4, 41.2, 40.9, 32.2, 25.1, 22.7; HRMS (EI^+) calc'd for $[C_{20}H_{22}NO_3S]^+$ $(M+H)^+$ requires *m/z* 356.1315, found *m/z* 356.1306. (mp = 133–135 ºC). Minor isomer (2*S**,4*S**,6*R**): IR (neat): 2960, 1447, 1350; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.461 (m, 3H), 7.284 (m, 3H), 7.207 (m, 4H), 6.208 (s, 1H), 4.245 (d, J = 3.9 Hz, 1H), 3.610 (d, J = 3.9 Hz, 1H), 2.864 (m, 1H), 2.311 (m, 1H), 1.514 (m, 3H), 1.049 (m, 1H), 0.950 (m, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) 140.6, 139.0, 132.4, 128.9, 128.8, 128.6, 127.2, 127.2, 93.8, 86.2, 65.7, 41.0, 39.8, 32.0, 25.0, 22.8; HRMS (EI^+) calc'd for $[C_{20}H_{22}NO_3S]^+$ $(M+H)^+$ requires *m/z* 356.1315, found *m/z* 356.1322. (mp = 127–128 ºC).

NOE correlations. The stereochemistry of the major and minor isomers of the 4-nitrostyrene product were assigned based on analogy to the already characterized 4-trifluorostyrene product.[7] The stereochemistry of other new products were assigned using the following NOE correlations:

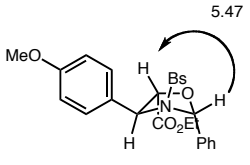


Table 3, entries 7-8

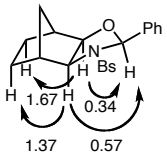
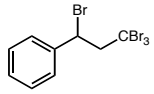


Table 3, entries 11-12

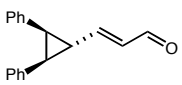
IV. Mechanistic Studies

Stoichiometric aminohydroxylation using $Cu(OTf)_2$ (eq 4). Anhydrous $Cu(OTf)_2$ (91.5 mg, 0.253 mmoles) was placed in an argon-flushed 2 dram vial. The vessel was charged with 1 mL acetonitrile and the mixture was stirred under argon for 30 min to afford a homogenous blue solution. Styrene (27.6 mg, 0.265 mmol) was then added by syringe. The septum was removed, oxaziridine **1** (101 mg, 0390 mmol) was quickly added, and the vessel was sealed and flushed with argon. Upon addition of the oxaziridine, no change in color was observed. After 12 h, the reaction mixture was washed with saturated sodium bicarbonate, and the aqueous phase was extracted twice with dichloromethane, dried over $MgSO_4$ and the volatiles were removed by rotary evaporation. The residue was loaded directly onto silica for purification by flash column chromatography using 5:1 hexane: EtOAc with 2% triethylamine as an eluent. Isolated 41.7 mg clear oil (0.114 mmoles, 41% yield, d.r. > 10:1). The spectral properties of the aminal were found to be identical to those previously reported.[7]

Stoichiometric aminohydroxylation using Cu(OTf) (eq 5). In a nitrogen-atmosphere glovebox, Cu(OTf) tetraacetonitrile complex (96.1 mg, 0.255 mmol) was placed in a 2 dram vial. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with 1 mL acetonitrile and the mixture was stirred under argon for 30 min resulting in a colorless homogenous solution. Styrene (28.9 mg, 0.277 mmol) was then added by syringe. The septum was removed, oxaziridine **1** (102 mg, 0390 mmoles) was quickly added, and the vessel was sealed and flushed with argon. Upon addition of the oxaziridine, the colorless reaction mixture quickly turned blue then green. After 12 h, an aliquot was removed and analyzed by ^{1}H NMR, and the spectrum showed no aminal product or oxaziridine. The reaction mixture then was washed with saturated sodium bicarbonate, the aqueous phase was extracted twice with dichloromethane, dried over $MgSO_4$, and the volatiles were removed by rotary evaporation. ^{1}H NMR analysis of the crude reaction mixture once again showed neither the aminal product nor oxaziridine.

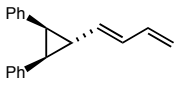


Carbon tetrabromide radical trap experiment (eq 6). In a nitrogen-atmosphere glovebox, a 2 dram vial was charged with copper(II) chloride (3.3 mg, 0.025 mmol) and tetrabutylammonium chloride (7.0 mg, 0.025 mmol). The vial was capped with a septum and transferred out of the glovebox. 0.25 mL of CH_2Cl_2 was added and the reaction mixture allowed to stir under argon for 30 min. Styrene (48.7 mg, 0.47 mmol) was then added via syringe and the septum was removed quickly to add *N*-nitrobenzenesulfonyl 3,3-dimethyloxaziridine (199 mg, 0.77 mmol) and carbon tetrabromide (1.32 g, 3.98 mmol) along with 0.75 mL of CH_2Cl_2. The vial was flushed with argon, sealed, and allowed to stir for 6 h. Upon completion of the reaction, the remaining oxaziridine was quenched with dimethyl sulfide, the solvent removed by rotary evaporation, and the resulting residue loaded directly onto silica for purification by flash column chromatography with 20:1 hexanes:EtOAc as the eluent to yield (1,3,3,3-tetrabromopropyl)benzene[8] as a white solid (84 mg, 0.20 mmol, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.34 (m, 3H), 5.32 (dd, J = 7.5, 4.3 Hz, 1H), 4.08 (AB, J = 7.5, 4.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.1, 129.3, 129.2, 128.5, 66.8, 50.4, 35.4 HRMS (EI^+) calc'd for $[C_9H_8Br_4]^+$ requires *m/z* 431.7354, found *m/z* 431.7344.



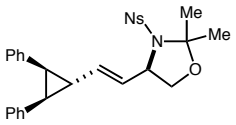
***trans*-2, *trans*-3-Diphenylcyclopropane vinyl aldehyde.** A dry round-bottomed flask was charged with *trans*-2, *trans*-3-diphenylcyclopropane carboxaldehyde[9] (710 mg, 3.2 mmol), (triphenylphosphoranylidene) acetaldehyde (922 mg, 3.0 mmol), and benzene (19 mL). The orange suspension was heated to reflux for 8 h, concentrated and purified by flash column chromatography on silica gel with 4:1 hexanes:EtOAc as the eluent to yield 675 mg of the product as a yellow solid (2.72 mmol, 90% yield). IR (neat): 3030, 2829, 1678, 1632, 1496; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, J = 8.2 Hz, 1H), 7.14 (m, 6H), 6.93 (dd, J = 7.9, 2.1 Hz, 4H), 6.71 (dd, J = 15.5, 9.6 Hz, 1H), 6.36 (dd, J = 15.2, 7.6 Hz, 1H), 2.84 (d, J = 5 Hz, 2H), 2.60 (dt, J = 9.8, 5.6 Hz, 1H); ^{13}C NMR (125

MHz, $CDCl_3$) 193.2, 160.6, 135.9, 131.2, 129.0, 128.3, 126.8, 35.4, 30.4; HRMS (EI^+) calc'd for $[C_{18}H_{16}O]^+$ requires *m/z* 248.1196, found *m/z* 248.1198. (mp = 105–107 ºC)

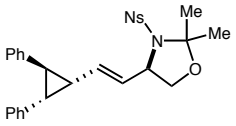


***Trans*-2, *trans*-3-Diphenylcyclopropane 1-butadiene (7).** A dry round-bottomed flask was charged with methyltriphenylphosphonium bromide (267 mg, 0.75 mmol) and THF (2.6 mL) and cooled to 0 ºC. *n*-Butyllithium (0.75 mL, 0.87 mmol) was then added dropwise. To the resulting yellow suspension was added *trans*-2, *trans*-3-diphenylcyclopropane carboxaldehyde (186 mg, 0.75 mmol) in THF (5.3 mL) dropwise and the reaction was allowed to warm to room temperature. After 2 h, the reaction mixture was concentrated and purified by flash column chromatography on silica gel with 9:1 hexanes:EtOAc as the eluent to yield 150 mg of the product as a yellow oil (0.61 mmol, 81% yield). IR (thin film): 3085, 3026, 1648, 1603, 1496, 1446; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.1 (m, 6H), 6.92 (dt, J = 6.7, 1.4 Hz, 4H), 6.35 (m, 2H), 5.67 (dd, J = 14.8, 8.3 Hz, 1H), 5.15 (dd, J = 16.0, 1.9 Hz, 1H), 5.00 (dd, J = 9.8, 2.3 Hz, 1H), 2.56 (d, J = 5.6 Hz, 2H), 2.33 (dt, J = 8.3, 5.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 137.6, 137.0, 136.6, 130.2, 129.1, 128.0, 126.1, 115.3, 33.5, 29.6; HRMS (EI^+) calc'd for $[C_{19}H_{18}]^+$ requires *m/z* 246.1404, found *m/z* 246.1405.

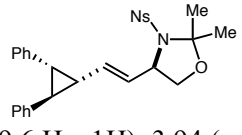
Aminohydroxylation of *trans*-2, *trans*-3-Diphenylcyclopropane 1-butadiene. Prepared according to the general procedure using 115 mg (0.47 mmol) *trans*-2, *trans*-3-diphenylcyclopropane 1-butadiene, 3.0 mg (0.22 mmol) $CuCl_2$, 7.0 mg (0.25 mmol) TBACl, 182 mg (0.70 mmol) oxaziridine, and 0.92 mL CH_2Cl_2. Upon completion of the reaction at 5 h, the remaining oxaziridine was quenched with dimethyl sulfide, the reaction mixture concentrated, and the resulting residue purified by flash column chromatography on silica gel with 9:1:1 hexanes:EtOAc:acetone as the eluent to yield 103.5 mg (0.21 mmol, 44% yield) of mixture of diastereomers (2:3:3 8a:8b:8c) as an off-white oil. Multiple purification attempts resulted in isolation of the three diastereomers, with full characterization of each given below.



***N*-(4-Nitrobenzensulfonyl)-4-[*cis*-(*trans*-2,*trans*-3-diphenylcyclopropylvinyl)]-2,2-dimethyl-1,3-oxazolane (8a).** Isolated as a yellow semi-solid. IR (thin film): 3027, 2986, 1530, 1329, 1162; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 22.9, 9.1 Hz, 4H), 7.11 (m, 6H), 6.83 (dd, J = 25.3, 6.4 Hz, 4H), 5.53 (dd, J = 14.9, 8.5 Hz, 1H), 5.29 (dd, J = 15.5, 9.4 Hz, 1H), 4.44 (m, 1H), 4.19 (dd, J = 9.2, 6.4 Hz, 1H), 3.78 (dd, J = 8.8, 3.3 Hz, 1H), 2.43 (m, 2H), 2.07 (m, 1H), 1.72 (d, J = 3.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.9, 148.0, 137.7, 136.7, 136.6, 129.3, 129.1, 128.6, 128.3, 128.2, 126.6, 126.5, 126.4, 124.1, 98.8, 69.6, 62.0, 33.1, 33.1, 28.3, 28.1, 26.9; HRMS (EI^+) calc'd for $[C_{28}H_{28}N_2O_5SNa]^+$ $(M+Na)^+$ requires *m/z* 527.1612, found *m/z* 527.1600.



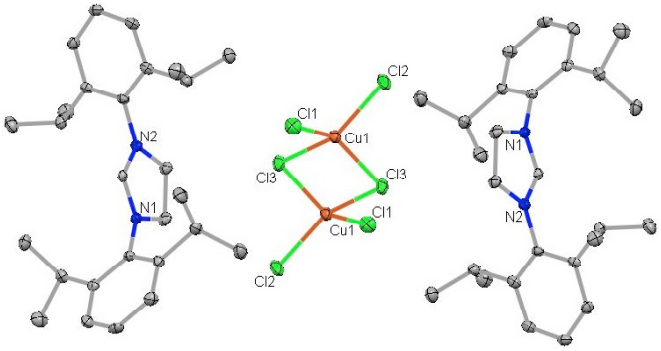
***N*-(4-Nitrobenzensulfonyl)-4-[*trans*-(*trans*-2,*cis*-3-diphenylcyclopropylvinyl)]-2,2-dimethyl-1,3-oxazolane (8b).** IR (thin film): 1529, 1349, 1161; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 4H), 7.38 (t, J = 7.1 Hz, 2H), 7.29 (m, 6H), 7.15 (d, J = 7.1 Hz, 2H), 5.22 (dd, J = 15.2, 9.0 Hz, 1H), 5.14 (dd, J = 15.3, 9.3 Hz, 1H), 4.24 (m, 1H), 4.05 (dd, J = 9.0, 6.3 Hz, 1H), 3.64 (dd, J = 8.8, 3.4 Hz, 1H), 2.71 (dd, J = 9.0, 5.9 Hz, 1H), 2.47 (t, J = 5.7 Hz, 1H), 1.94 (td, J = 9.0, 4.7 Hz, 1H), 1.63 (d, J = 9.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.3, 136.6, 131.6, 131.5, 131.0, 130.5, 129.3, 128.2, 126.4, 100.9, 97.4, 71.9, 64.4, 36.3, 35.3, 33.2, 30.4, 29.3; HRMS (EI^+) calc'd for $[C_{28}H_{28}N_2O_5SNa]^+$ $(M+Na)^+$ requires *m/z* 527.1612, found *m/z* 527.1590. mp = 123–127 ºC. The structure was confirmed by X-ray crystallographic analysis.



***N*-(4-Nitrobenzensulfonyl)-4-[*trans*-(*cis*-2,*trans*-3-diphenylcyclopropylvinyl)]-2,2-dimethyl-1,3-oxazolane (8c).** Isolated as a white solid. IR (thin film): 2253, 907; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 9.1 Hz, 2H), 7.73 (d, J = 8.9 Hz, 2H), 7.35 (m, 6H), 7.19 (m, 4H), 5.41 (dd, J = 15.0, 8.1 Hz, 1H), 5.18 (dd, J = 15.4, 9.6 Hz, 1H), 3.94 (m, J = Hz, 2H), 3.60 (dd, J = 8.6, 4.6 Hz, 1H), 2.76 (dd, J = 9.5, 6.5 Hz, 1H), 2.45 (t, J = 5.5 Hz, 1H), 2.10 (td, J = 9.3, 5.1 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

146.5, 141.0, 137.8, 132.8, 129.2, 129.1, 128.8, 128.7, 128.1, 126.9, 126.5, 126.2, 124.1, 98.9, 69.6, 61.8, 33.9, 32.7, 30.4, 29.9, 28.6, 26.2, 0.2; HRMS (EI^+) calc'd for $[C_{28}H_{28}N_2O_5SNa]^+$ $(M+Na)^+$ requires *m/z* 527.1612, found *m/z* 527.1590. mp = 128–133 ºC.

Crystal structure of (SIMes•H)$_2$(Cu$_2$Cl$_6$). CIF data for this complex are included in the file cu2cl6.cif.



V. C–H Oxidation Studies

Oxidation of *sec*-phenylethanol to acetophenone (eq 7). In a nitrogen-atmosphere glovebox, 3.5 mg (0.026 mmol) copper(II) chloride and 7.0 mg (0.025 mmol) tetrabutylammonium chloride were placed in a 2 dram vial with a stirbar. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with CH_2Cl_2 and the mixture was stirred under argon for 30 min. *sec*-Phenylethanol (62.5 mg, 0.512 mmol) was then added by syringe, followed by 18.4 mg 1,4-bis(trimethylsilyl)benzene as the internal standard. The septum was removed, oxaziridine **2** was quickly added, and the vessel was sealed and flushed with argon. The reaction progress was monitored by ^{1}H NMR. After 4 h, quantitative NMR analysis of the crude reaction mixture in CD_2Cl_2 showed 97% NMR yield per internal standard.

A control reaction using the $Cu(TFA)_2$/HMPA system was also performed, using 63.7 mg (0.521 mmol) of *sec*-phenylethanol, 7.3 mg (0.025 mmol) $Cu(TFA)_2$, 9 μL (0.050 mmol) HMPA, and 18.2 mg 1,4-bis(trimethylsilyl)benzene as the internal standard, 203 mg (0.77 mmol) oxaziridine **2** and 1.0 mL CH_2Cl_2. After 4 h, quantitative NMR analysis of the crude reaction mixture in CD_2Cl_2 showed 2% percent conversion to acetophenone.

A control reaction with no catalyst was also performed, using 59.4 mg (0.486 mmol) of *sec*-phenylethanol, 1.0 mL CH_2Cl_2, 18.0 mg 1,4-bis(trimethylsilyl)benzene and 193 mg (0.75 mmol) oxaziridine **2**. After 4 h, quantitative NMR analysis of the crude reaction mixture in CD_2Cl_2 showed no detectable product.

Oxidation of 1,4-cyclohexadiene to benzene (eq 8). In a nitrogen-atmosphere glovebox, 3.4 mg (0.025 mmol) copper(II) chloride and 7.1 mg (0.026 mmol) tetrabutylammonium chloride were placed in a 2 dram vial with a stirbar. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with CH_2Cl_2 and the mixture was stirred under argon for 30 min. 1,4-Cyclohexadiene (38.4 mg 0.479 mmol) was then added by syringe, followed by 24 mg 1,4-bis(trimethylsilyl)benzene as the internal standard. The septum was removed, oxaziridine **2** was quickly added, and the vessel was sealed and flushed with argon. The reaction progress was monitored by ^{1}H NMR. After 20 min, quantitative NMR analysis of the crude reaction mixture in CD_2Cl_2 95% NMR yield per internal standard.

A control reaction using the $Cu(TFA)_2$/HMPA system was also performed, using 39.9 mg (0.498 mmol) of 1,4-cyclohexadiene, 7.2 mg (0.025 mmol) $Cu(TFA)_2$, 9 μL (0.050 mmol) HMPA, and 29.7 mg 1,4-bis(trimethylsilyl)benzene as the internal standard, 194 mg (0.75 mmol) oxaziridine **2** and 1.0 mL CH_2Cl_2. After 4 h, quantitative NMR analysis of the crude reaction mixture in CD_2Cl_2 gave 8% percent conversion.

A control reaction with no catalyst was also performed, using 38.9 mg (0.485 mmol) of 1,4-cyclohexadiene, 1.0 mL CH_2Cl_2, 29.7 mg 1,4-bis(trimethylsilyl)benzene and 197 mg (0.76 mmol) oxaziridine **2**. After 4 h, quantitative NMR analysis of the crude reaction mixture in CD_2Cl_2 gave 3% product. A ^{1}H NMR spectrum of the starting material showed 3% of benzene as a contaminant, accounting for the product in the reaction mixture.

References

(1) Davis, F. A.; Jenkins, R.; Yocklovich, S. G. *Tetrahedron Lett*. **1978**, *19*, 5171–5174.

(2) (a) **3a**: Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49. (b) **3b**: Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem. Int. Ed. Engl*. **2001**, *40*, 3387–3389.

(3) Arduengo III, A. J.; Krafczyk, R.; Schmutzer, R. *Tetrahedron* **1999**, *55*, 14523–14534.

(4) Jennings, W. B.; Watson, S. P.; Boyd, D. R. *J. Chem. Soc., Chem. Commun.* **1988**, 931–932.

(5) Maligres, P. E.; See, M. M.; D. Askin, D.; Reider, P. J. *Tetrahedron Lett.* **1997**, *38*, 5253–5256.

(6) Periasamy, M.; Sivakumar, S.; Reddy, M. N. *Synthesis*, **2003**, *13*, 1965–1967.

(7) Michaelis, D. J.; Shaffer, C. J.; Yoon, T. P. *J. Am. Chem. Soc*. **2007**, *129*, 1866–1867.

(8) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc*. **1946**, *68*, 154–155.

(9) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, 110, 7512–7519.