Supplementary Material for

The Endocyclic Restriction Test:

Oxygen Transfer from N-Sulfonyl Oxaziridines

to Alkenes

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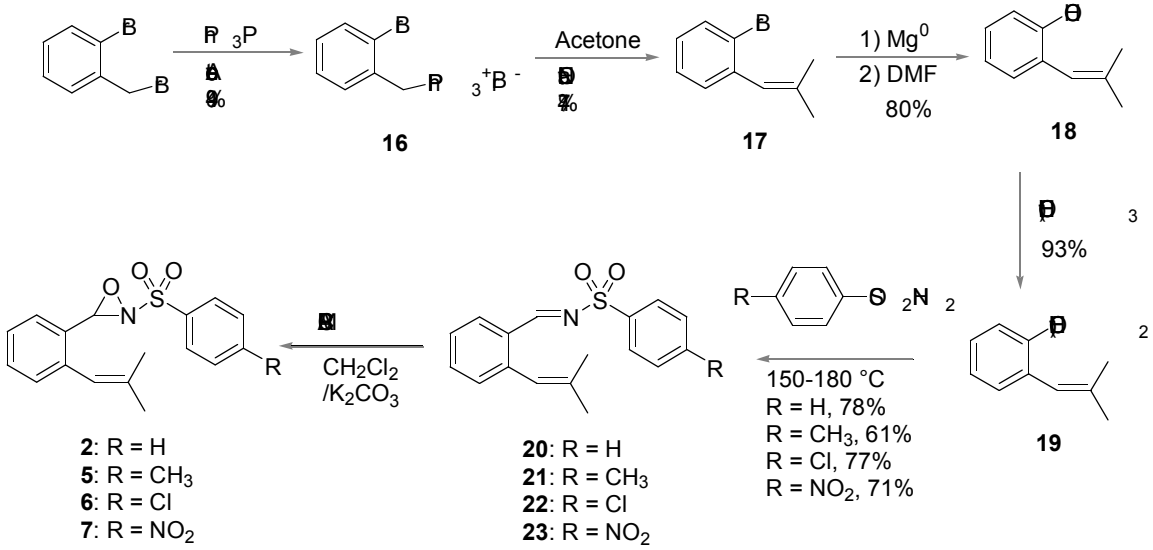
Experimental:

General Methods: All reactions were performed with flame dried or oven dried glassware under a nitrogen atmosphere unless otherwise noted. Reagents were purchased from Aldrich and used without further purification unless otherwise noted. Solvents were purified by the usual methods or purchased as spectroscopic grade prior to use. THF and ether were distilled from sodium/benzophenone under a nitrogen atmosphere immediately prior to use. Thin layer chromatography was performed on Merck silica gel plates (0.25mm) with QF-254 indicator. Visualization was accomplished by irradiation with UV light, or by exposure to $KMnO_4$ or I_2. Flash chromatography was performed using 230-400 mesh silica gel. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained using either a Varian U400 or U500 spectrometer in $CDCl_3$, with $CHCl_3$ as an internal standard unless otherwise noted. Chemical shifts are reported in ppm and coupling constants are reported in Hz. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Mass spectrometry was performed by the University of Illinois Mass Spectrometry Laboratory. Isotopic enrichments were calculated by the standard matrix method. Brine refers to a saturated aqueous solution of sodium chloride. ^{18}O-Labelled oxygen gas and N,N-dimethylform-^{13}C-amide were purchased from Isotec, Inc. Compounds **12**[S1], **18**[S2], **25**[S3] were prepared by literature procedures.

Synthesis of 1, 4-6:

The synthetic route used to obtain **2** and derivatives of **2** is depicted in Scheme S1.

Scheme S1



Oxaziridines **2**, **5-7** were not isolable species. These compounds readily rearranged to the corresponding epoxides and therefore were not completely characterized. The crude yields for the conversion of **20**-**23** to **2**, **5-7** were > 90% and the material is judged to be >90% pure by ^{1}H NMR.

Synthesis of 2-(2'-methyl-1'-propenyl)-bromobenzene (17): Triphenylphosphine (39.3 g, 150 mmol) was added to a solution of o-bromobenzyl bromide (30 g, 120 mmol) in acetone (350 mL). The resulting solution was heated to reflux for 16 hr. The crude **16** was isolated by filtration and recrystallized from EtOH/H_2O to provide **16** (58.5 g, 95% yield) as a white solid. Sodium ethoxide (1.36 g, 20 mmol) in ethanol (20 mL) was added dropwise to a solution of **16** (9.80 g, 19.1 mmol) and acetone (1.4 mL, 19 mmol) in ethanol, (20 mL) The solution was stirred for 8 hours and the solvent was removed. The residue was chromatographed on silica (pet. ether) to provide **17** (3.1 g, 74%) as a clear liquid. R_f = 0.4 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.83, 1H, ArH), δ 7.25 (m, 2H, ArH), δ 7.05 (m, 1H, ArH), δ 6.25 (bs, 1H, ArCH=C), δ 1.95 (d, J = 1.5 3H, CH=CCH3CH3), δ 1.75 (d, J = 1.2, 3H, CH=CCH3CH3) ^{13}C NMR (125.7 MHz, $CDC1_3$): δ 138.36 (Ar-CH=C), δ 136.7 (Ar-HC=C), δ 132.4 (Ar-H), δ 131.0 (Ar-H), δ 127.6 (Ar-H), δ 126.7 (Ar-H), δ 124.8 (Ar-H), δ 124.8 (Ar-HC=C), δ 124.2 (Ar-Br), δ 26.1 (CH 3), δ 19.4 (CH3) DEPT 90 (125.7 MHz, $CDC1_3$): δ 132.4 (Ar-H), δ 13 1.0 (Ar-H), δ 127.6 (Ar-H), δ 126.7 (Ar-H), δ 124.8 (Ar-H), δ 124.8 (Ar-HC=C).

Synthesis of 2-(2'-methyl-1'-propenyl) benzaldehyde (18): Approx. 20% of a solution of **17** (3.73 g 17.6 mmol) in THF (20 mL) was added to magnesium turnings (650 mg 26.4 mmol) and a crystal of iodine. A drop of 1,2 dibromoethane was added and the reaction initiated within 5 minutes. Once initiated, the remaining solution of **17** in THF was slowly added. After complete addition the solution was heated to reflux for 30 minutes. The Grignard reagent was treated with DMF (6 mL) in THF (5 mL) for 20 minutes. After cooling to 0 °C the reaction was quenched with sat. aq. NH_4Cl and diluted with ether. The layers were separated and the aqueous layer extracted with ether (3 x 30 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. Filtration and evaporation gave an oil which was purified by chromatography (5% EtOAc/Pet. Ether) to provide **18** (2.26 g, 80%) as a clear liquid. R_f = 0.28 (5% EtOAc/Pet. Ether). ^{1}H NMR (500 MHz, $CDC1_3$): δ 10.1 (s, 1H, ArC=OH), δ 7.85 (d, J = 7.41, 1H, ArH),), δ 7.50 (t, J = 7.69, 1H, ArH), δ 7.32 (t, J = 7.51, 1H, ArH), δ 7.19 (d, J = 7.95, 1H, ArH), δ 6.56 (bs, 1H, ArCH=C), δ 1.93 (d, J = 0.5 3H, CH=CCH$_3$CH$_3$), δ 1.63 (d, J = 0.4, CH=CCH$_3$CH$_3$) ^{13}C NMR (125.7 MHz, $CDC1_3$): δ 193.1 (HC=OAr), δ 142.0 (Ar-CH=C), δ 139.0 (Ar-HC=C), δ 133.5 (Ar-HC=O), δ 133.2 (Ar-H), δ 130.6 (Ar-H), δ 127.8 (Ar-H), δ 126.6 (Ar-H), δ 121.1 (Ar-HC=C), δ 25.8 (CH_3), δ 19.2 (CH_3). DEPT 90 (125.7 MHz, $CDC1_3$): δ 193.1 (HC=OAr), δ 133.5 (Ar-HC=O), δ 133.2 (Ar-H), δ 130.6 (Ar-H), δ 127.8 (Ar-H), δ 126.6 (Ar-H), δ 121.1 (Ar-HC=C).

Synthesis of 2-(2'-methyl-1'-propenyl) benzaldehyde diethyl acetal (19): A solution of **18** (664 mg, 4.14 mmol) in absolute ethanol (10 mL) was treated with 0.75 mL ethyl orthoformate and ca. 30 mg NH_4NO_3. The solution was heated to reflux for 3 hr and then concentrated. The residue was suspended in ether (25 mL) and filtered. The solids were washed with fresh ether and removal of the solvent gave an oil which was purified by kugelrhor distillation (93-95 °C bath, 0.1 mm Hg) to give **19** (907 mg, 93%) as a clear liquid. ^{1}H NMR (500 MHz, $CDC1_3$): δ 7.6 (m, 1H, ArH),), δ 7.2 (m, 2H, ArH), δ 7.12 (m, 1H,

ArH), δ 6.38 (bs, 1H, ArCH=C), δ 5.54 (s, 1H, ArCHOEt,), δ 3.56 (m, 4H, OCH_2), δ 1.9 (d, J = 1.4 3H, $CH=CCH_3CH_3$), δ 1.61 (d, J = 1. 2, $CH=CCH_3CH_3$), δ 1.21 (t, J = 7.00 3H, OCH_2CH_3). ^{13}C NMR (125.7 MHz, $CDC1_3$): δ 137.5 (Ar-CH=C), δ 136.6 (Ar-HC=C), δ 135.8 (Ar-$HCOEt_2$), δ 129.9 (Ar-H), δ 127.8 (Ar-H), δ 126.1 (Ar-H), δ 126.0 (Ar-H), δ 122.9 (Ar-HC=C), δ 99.7 ($HCOEt_2$), δ 61.4 ($HCOCH_2$), δ 26.0 (CH_3), δ 19.2 (CH_3), δ 15.2 (CH_2CH_3). DEPT 90 (125.7 MHz, $CDC1_3$): δ 129.9 (Ar-H), δ 127.8 (Ar-H), δ 126.1 (Ar-H), δ 126.0 (Ar-H), δ 122.9 (Ar- HC=C), δ 99.7 ($HCOEt_2$). Anal. Calc for $C_{15}H_{22}O_2$: C, 76.56; H, 9.42 Found: C, 76.57; H, 9.40.

General Procedure for the condensation of acetals and sulonamides to produce sulfonimines: Equimolar amounts of the diethyl acetal and sulfonamide are heated to 140-180 °C for 3 hr. The residue was dissolved in a minimal amount of CH_2Cl_2 and triturated with pentane. The sulfonimines are not stable to chromatography and hydrolyze readily, but satisfactory elemental analyses were obtained in each case.

***N*-[2-(2' -methyl-l-propenyl)]benzilidinebenzenesulfonamide (20):** (78%) mp 68-70 °C ^1H NMR (500 MHz, $CDCl_3$): δ 9.19 (s, 1H, N=CArH), δ 8.12 (d, J = 7.96, 2H, ArH), δ 8.00 (d, J = 7.38, 2H, ArH), δ 7.63 (t, J = 7.27, 1H, ArH), δ 7.55 (m, 1H, ArH), δ 7.3 (t, 1H, J = 7.70, ArH), δ 7.21 (d, J = 7.6, 1H, ArH), δ 6.4 (bs, 1H, ArCH=C), δ 1.95 (d, J = 1.95, 3H, $CH=CCH_3CH_3$), δ 1.57 (d, J = 0.5, 3H, $CH=CCH_3CH_3$). ^{13}C NMR (125.7 MHz, $CDC1_3$) δ 169.9 (N=CH), δ 143.9 (Ar-SO2), δ 140.7 (Ar- CH=N), δ 138.36 (Ar-CH=C), δ 134.4 (Ar-H), δ 133.4 (Ar-H), δ 130.6 (Ar-H), δ 130.1 (Ar-HC=C), δ 129.1 (Ar-H), δ 128.5 (Ar-H), δ 128.0 (Ar-H), δ 127.0 (Ar-H), δ 126.5 (Ar-H), δ 121.0 (Ar-HC=C), δ 26.1 (CH_3)1 δ 19.5 (CH_3) DEPT 90 (125.7 MHz, $CDC1_3$): δ 169.9 (N=Cli), δ 134.4 (Ar-H), δ 133.4 (Ar-H), δ 130.6 (Ar-H), δ 129 (Ar-H), δ 128.5 (Ar-H), δ 128.0 (Ar-H), δ 127.0 (Ar-H), δ 126.5 (Ar-H), δ 121.0 (Ar-HC=C). Anal. Calc for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.02; H, 5.72; N, 4.71.

***N*-[2-(2' -methyl-l-propenyl)]benzilidine-4-methyl-benzenesulfonamide (21):** (61%) mp 108 - 109 °C. ^1H NMR (500 MHz, $CDC1_3$): δ 9.16 (s, 1H, N=CArH), δ 8.11 (d, J = 7.7, 2H, ArH), δ 7.87 (d, J = 7.78, 2H, ArH), δ 7.52 (t, J = 7.44, 1H, ArH), δ 7.3 (m, 3H, ArH), δ 6.42 (bs, 1H, ArCH=C), δ 2.43 (s, 3H, $ArCH_3$) δ 1.95 (s, 3H, $CH=CCH_3CH_3$), δ 1.56 (s, 3H, $CH=CCH_3CH_3$). ^{13}C NMR (125 MHz., $CDC1_3$): δ 169.4 (N=CH), δ 144.4 (Ar-SO2), δ 143.8 (Ar-CH=N), δ 140.5 (Ar-CH=C), δ 135.3 (Ar-H), δ 134.2 (Ar-H), δ 130.6 (Ar-H), δ 130.2 (Ar-HC=C), δ 129.7 (Ar-H), δ 128.5 (Ar-H), δ 128.1 (Ar-H), δ 127.0 (Ar-H), δ 121.0 (Ar-HC=C), δ 26.1 (CH_3), δ 21.6 (CH_3), δ 19.5 (CH_3). DEPT 90 (125.7 MHz, $CDCl_3$): δ 169.4 (N=CH), δ 134.2 (Ar-H), δ 130.6 (Ar-H), δ 129.7 (Ar-H), δ 128.5 (Ar-H), δ 128.1 (Ar-H), δ 127.0 (Ar-H), δ 121.0 (Ar-HC=C). Anal Calc for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47. Found: C, 69.10; H, 6.23; N 4.20.

***N*-[2-(2'-methyl-l-propenyl)]benzilidine-4-chloro-benzenesulfonamide (22):** (77%) mp 128 - 129 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (s, 1H, N=CArH), δ 8.11 (d, J = 7.22, 2H, ArH), δ 7.94 (d, J = 8.54, 2H, ArH), δ 7.54 (m, 2H, ArH), δ 7.52 (t, J = 7.44, 1H, ArH), δ 7.23 (d, J = 7.8, 1H, ArH), δ 6.44 (bs, 1H, ArCH=C), δ 1.97 (s, 3H, CH=C$CH_3$$CH_3$), δ 1.58 (s, 3H, CH=C$CH_3$$CH_3$).^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.2 (N=CH), δ 144.1 (Ar-SO2), δ 140.8 (Ar- CH=N), δ 140.1 (Ar-CH=C), δ 137.0 (Ar- Cl), δ 134.6 (Ar-H), δ 130.7 (Ar-H), δ 129.9 (Ar-HC=C), δ 129.5 (Ar-H), δ 129.5 (Ar-H), δ 128.6 (Ar-H), δ 127 (Ar-H), δ 121.1 (Ar-HC=C), δ 26.1 (CH_3), δ 19.5 (CH_3). DEPT 90 (125.7 MHz, $CDCl_3$): δ 170.2 (N=CH), δ 134.6 (Ar-H), δ 130.7 (Ar-H), δ 129.5 (Ar-H), δ 129.5 (Ar-H), δ 128.6 (Ar-H), δ 127.1 (Ar-H), δ 121.1 (Ar-HC=C). Anal. Calcd for $C_{17}H_{16}NClO_2S$: C, 61.16; H, 4.53; N, 4.19. Found: C, 60.79; H, 4.72; N, 4.31.

***N*-[2-(2'-methyl-l-propenyl)]benzilidine-4-nitro-benzenesulfonamide (23):** (71%) mp 148 - 149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.30 (s, 1H, N=CArH), δ 8.38 (d, J = 8.22, 2H, ArH), δ 8.21 (d, J = 8.2, 2H, ArH), δ 8.10 (d, J = 8.04, 1H, ArH), δ 7.58 (t, J = 8.22, 1H, ArH), δ 7.32 (d, J = 7.63, 1H, ArH), δ 7.25 (d, J = 7.2, 1H, ArH), δ 6.47 (bs, 1H, ArCH=C), δ 1.99 (s, 3H, CH=C$CH_3$$CH_3$), δ 1.6 (s, 3H, CH=C$CH_3$$CH_3$).^{13}C NMR (125.7 MHz, $CDCl_3$): δ 171.6 (N=CH), δ 150.5 (Ar-SO2), δ 144.54 (Ar-CH=N), δ 144.49 (Ar-CH=C), δ 141.3 (Ar-Cl), δ 135.1 (Ar-H), δ 130.8 (Ar-HC=C), δ 129.7 (Ar-H), δ 129.3 (Ar-H), δ 128.7 (Ar-H), δ 127.2 (Ar-H), δ 124.3 (Ar-HC=C), δ 121.0 (Ar-H), δ 26.2 (CH_3), δ 19.5 (CH_3). DEPT 90 (125.7 MHz, $CDCl_3$): δ 171.6 (N=CH), δ 135.1 (Ar-H), δ 130.9 (Ar-H), δ 129.3 (Ar-H), δ 128.7 (Ar-H), δ 127.1 (Ar-H), δ 124.3 (Ar-H), δ 120.9 (Ar-HC=C). Anal. Calcd for $C_{17}H_{16}N_2O_4S$: C, 59.29; H, 4.68; N, 8.13. Found: C, 59.01; H, 4.62; N, 7.81.

General procedure for the oxidation of sulfonimines: A solution of 0.5 mmol of the sulfonimine in 3 mL CH_2Cl_2 was cooled in an ice bath and 0.7 mL sat. aq. K_2CO_3 were added along with 1.5 - 2.5 equivalents of mCPBA. The solution was vigorously stirred for 10 minutes at this temperature. The reaction was quenched with 5% $Na_2S_2O_5$, and diluted with CH_2Cl_2. The organic phase was washed twice with 5% $Na_2S_2O_5$, 1M NaOH, 10% aqueous sodium bisulfite, water, and brine and dried over or $MgSO_4$. Filtration and evaporation of the solvent gave the crude oxaziridine as a colorless oil which was >90% pure by ^{1}H NMR with the major contaminant being traces of **18**. The crude yields were better than 90% in all cases.

***C*-2'-(2-methyl-1-propenyl)phenyl *N*-phenylsulfonyloxaziridine (2):** ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.2 - 8.1 (m, 9H, Ar-H), δ 6.4 (s, 1H, HC=C), δ 5.6 (s, 1H, CHNO), δ 2.0 (d, J = 1.2, 3H, CH_3), δ 1.6 (d, J = 1.3, 3H, CH_3).

***C*-2'-(2-methyl-1-propenyl)phenyl *N*-4-methylphenylsulfonyloxaziridine (5):** ^{1}H NMR (500 MHz, $CDC1_3$): δ 7.9 (d, J = 7.7, 2H, ArH), δ 7.45 (d, J = 7.7, 2H, ArH), δ 7.3 (m, 4H, ArH), δ 6.42 (bs, 1H,

ArCH=C), δ 5.58 (s, 1H, CHNO), δ 2.51 (s, 1H, $ArCH_3$) δ 1.95 (s, 3H, $CH=CCH_3CH_3$), δ 1.61 (s, 3H, $CH=CCH_3CH_3$).

***C*-2'-(2-methyl-1-propenyl)phenyl *N*-4-chlorophenylsulfonyloxaziridine (6):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 7.22, 2H, ArH), δ 7.57 (d, J = 8.54, 2H, ArH), δ 7.44 (m, 4H, ArH), δ 6.37 (bs, 1H, ArCH=C), δ 5.52 (s, 1H, CHNO), δ 1.97 (s, 3H, $CH=CCH_3CH_3$), δ 1.65 (s, 3H, $CH=CCH_3CH_3$).

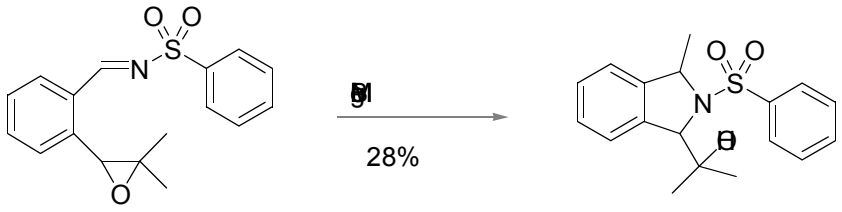
***C*-2'-(2-methyl-1-propenyl)phenyl *N*-4-nitrophenylsulfonyloxaziridine (7):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 8.22, 2H, ArH), δ 8.32 (d, J = 8.2, 2H, ArH), δ 7.90 (d, J = 8.0, 1H, ArH), δ 7.62 (t, J = 8.2, 1H, ArH), δ 7.44 (d, J = 7.6, 1H, ArH), δ 7.25 (d, J = 7.2, 1H, ArH), δ 6.47 (bs, 1H, ArCH=C), δ 5.78 (s, 1H, CHNO), δ 1.99 (s, 3H, $CH=CCH_3CH_3$), δ 1.6 (s, 3H, $CH=CCH_3CH_3$).

Double Label Crossover Experiment for 2:

Labeled **20-^{13}C** was prepared from labeled DMF by the procedures outlined above. Labeled mCPBA was prepared from oxygen by the following manner. A 3-neck flask was charged with potassium *t*-butoxide (1.7 g, 15 mmol) and evacuated. The flask was filled with labeled oxygen using a gas transfer apparatus such that the pressure of oxygen in the flask was slightly below atmospheric pressure. The flask was closed to the oxygen source and benzhydrol (3.0 g, 16 mmol) in benzene (23 mL) was added dropwise from a non-pressure equalized addition funnel. Oxygen was added continuously for 1 hr. The solution was transferred to a separatory funnel and extracted with 2 mL H_2O to provide a solution of labelled KOOH. This solution was diluted with ethanol (2 mL) and a trace of EDTA was added. 3-Chlorobenzoyl chloride (75 mg, 0.43 mmol) was added and the temperature maintained at 17-20 °C. After 10 min. a pellet of KOH (~ 100 mg) was added and the reaction stirred for another 10 minutes. The reaction mixture was poured into cold 10% HCl and extracted with $CHCl_3$. The organic layer was washed with water (x3), pH 7.2 phosphate buffer, and brine. The organic layer was dried with Na_2SO_4 and concentrated to provide labelled mCPBA (45 mg, 60%) as a white solid.

Unlabelled **20** (15 mg, 0.05 mmol) was dissolved in 1 mL CH_2Cl_2 and 0.7 mL sat. aq. K_2CO_3 was added. The mixture was treated with 80% mCPBA (15 mg, 0.07 mmol) and the reaction stirred at 25 °C for 0.5 hours. Doubly labeled **2-^{13}C, ^{18}O** was prepared simultaneously by treating **20-^{13}C** (15mg, 0.05 mmol) in 1 mL CH_2Cl_2 and 0.7 mL sat. aq. K_2CO_3 with ^{18}O labeled MCPBA (30 mg, 0.09 mmol). The reaction was stirred for 0.5 hours. The two reaction mixtures were poured together into CH_2Cl_2 and washed with 10% aq. $Na_2S_2O_5$ (x2), pH 7.2 buffer and brine. The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure. The mixture of **2** and **2-^{13}C, ^{18}O** was analyzed by FI/MS (data appears in Table 1) and dissolved in $CDCl_3$ in an NMR tube and heated to 60 °C for 0.5 hr. The progress of the reaction was measured by ^{1}H NMR by observing the appearance of the imine resonance (δ = 9.2) and the disappearance of the oxaziridine resonance (δ = 5.6). Imine **4** was not a stable species, and was converted

to isoindoline **24** by treatment of the reaction mixture with methymagnesium bromide and analyzed by FI/MS (data appears in Table 1).



4 **24**

1-(1'-Hydroxy –1'-methylethyl)-3-methyl-2-(phenylsulfonyl)-isoindoline (24): The crude **3** from the reaction of **1** (450 mg, 1.5 mmol) was dissolved in THF (15 mL) and treated with methylmagnesium bromide (2 mL of a 3.1 M solution in Et_2O) at 0 °C. The reaction was stirred at 0 °C for 1.5 hr. The reaction was quenched with sat. aq. NH_4Cl and extracted twice with Et_2O. The combined extracts were washed with sat. aq. NH_4Cl, H_2O, and brine. The organic layer was dried over $MgSO_4$ and the solvent removed to provide **24** (145 mg, 28%) as a glassy material after chromatography (20% EtOAc/pet. ether). Rf = 0.2 (25% EtOAc/pet. ether). 1H NMR (200 Mhz, CDCl3): δ 7.8 – 7.9 (m, 2H, ArH), δ 7.0 – 7.5 (m, 7H, Ar-H), δ 4.95 (q, J = 6.7, 1H, Ar-$CHCH_3$), δ 4.9 (s, 1H, OH), δ 1.7 (d, J = 6.6, 3H, CH_3CH), δ 1.4 (s, 3H, CH3), δ 1.2 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDC1_3$): δ 141.7 (Ar), δ 136.8 (Ar), δ 135.7 (Ar), δ 133.1 (Ar), δ 129.1 (Ar), δ 128.3 (Ar), δ 127.6 (Ar), δ 127.3 (Ar), δ 124.3 (Ar), δ 122.1 (Ar), δ 75.1 (COH), δ 72.6 (CH), δ 63.0 (CH), δ 27.2 (CH_3), δ 26.3 (CH_3), δ 23.3 (CH_3). IR (neat): 3500 (b), 3065(m), 2976 (s), 2933 (m), 1447 (s), 1332 (s), 1162 (s) cm^{-1}. HRMS (EI, 70 eV) Calcd for $C_{18}H_{21}NO_3S$: 331.124216. Found 331.123725. Anal. Calcd for $C_{18}H_{21}NO_3S$: C, 65.23; H, 6.39; N, 4.23. Found: C, 65.36; H, 6.51; 4.09.

Kinetic studies for 2, 5-7:

For the kinetic runs, a solution of 0.15 mmol of the appropriate sulfonimine was dissolved in 3 ml $CDCl_3$ and cooled in an ice bath. 0.5 ml sat. aqueous K_2CO_3 were added along with 1.5 - 2.5 equivalents of MCPBA and the resulting suspension stirred vigorously for 5 minutes. The reaction was quenched with sat. $Na_2S_2O_5$, and diluted with 1 mL $CDCl_3$. The organic phase was washed with sat. $Na_2S_2O_5$, and dried with Na_2SO_4. The organic phase was filtered into a 5 ml volumetric flask containing diphenylmethane (30 mg, 0.17 mmol) as an internal standard and diluted to the mark. The measured concentrations were between 0.01 and 0.03 M. The reaction was immediately monitored by ^1H NMR at 25 °C until there was no longer a trace of oxaziridine (peak at 5.5 ppm). The peaks corresponding to the oxaziridine (~ 6.5, 5.5, 1.9, 1.6 ppm) were integrated with respect to the internal standard and the log of their integration values were plotted versus time. At least 3 half-lives were measured by this method. The error reported in Table 2 represents one standard deviation of the rate constants measured from each NMR resonance from multiple experiments. The large error associated with **7** results from its rapid isomerization and our

difficulty in measuring this rapid rate reproducibly. Linear fits were calculated by the least squares method and the error calculated to the 99% confidence level.

Sample kinetic data is shown below. This data is typical of that which was obtained for the systems examined. Good linear fits were obtained in all cases except when impurities or traces of decomposition products were present close to or beneath the peaks of interest. The data depicted are for the isomerization of **6**.

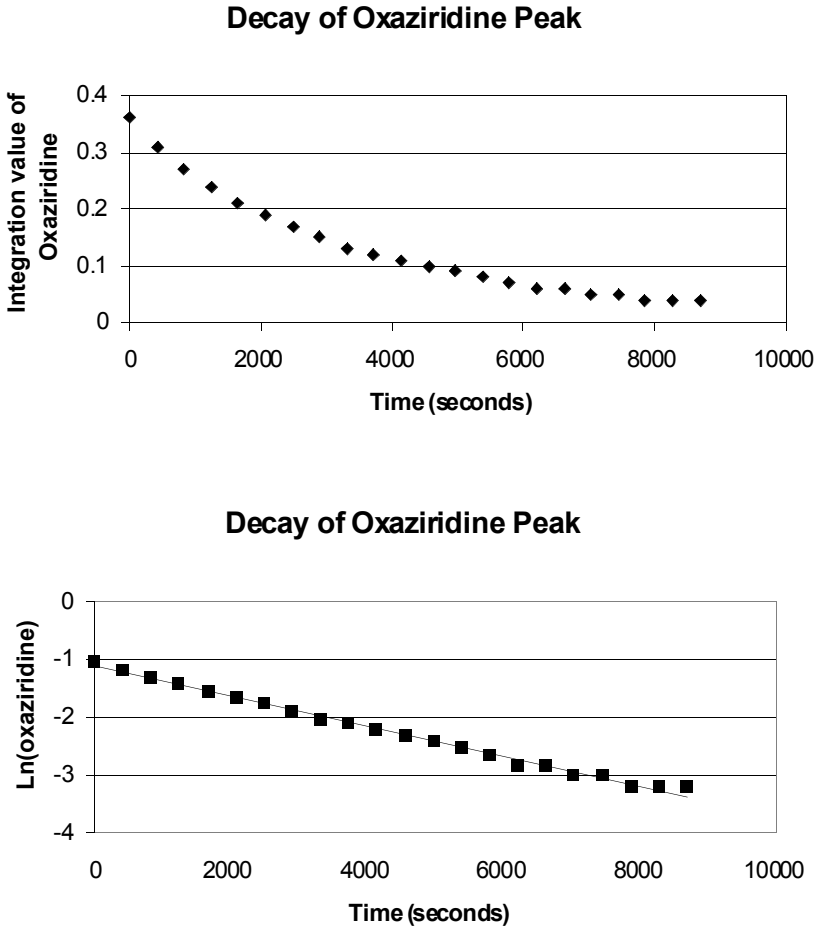


Figure S1: Sample kinetic data for the isomerizaiton of **6**.

The Hammett plot for the kinetic data is given below.

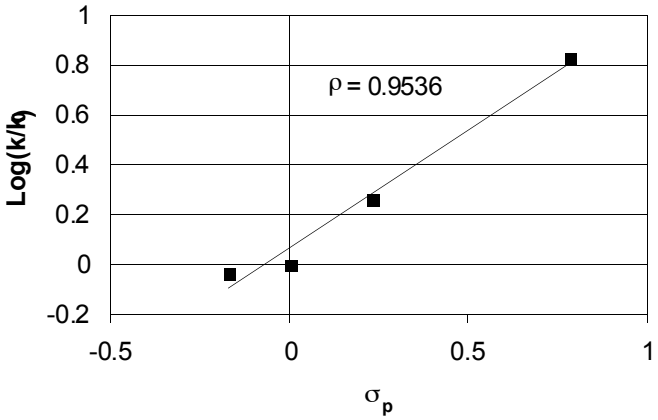
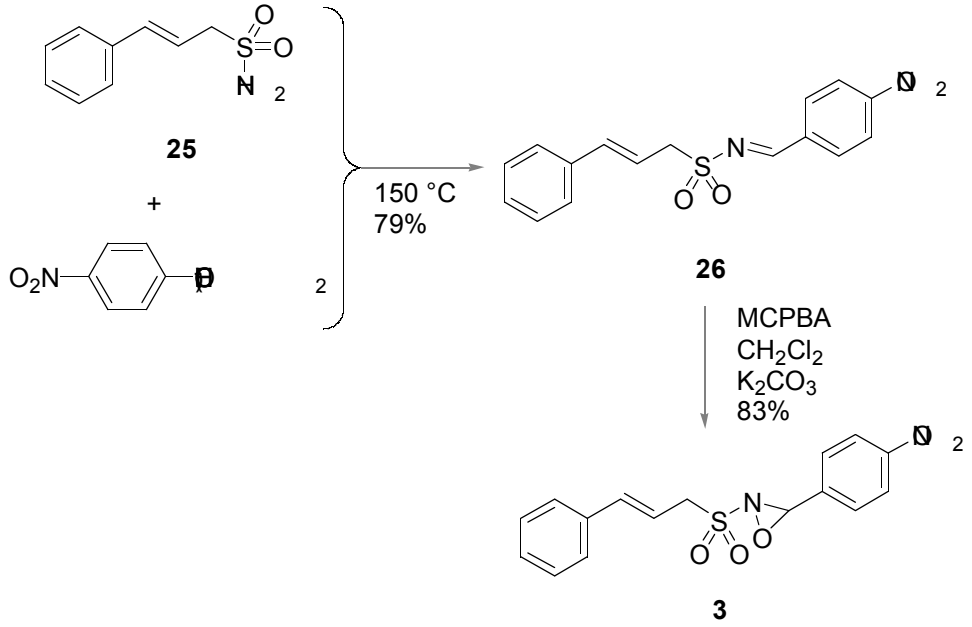


Figure S2: Hammett plot for systems **2, 5-7**.

Synthesis and Reactions of 3:

System **3** was prepared by the route outlined in Scheme S2.

Scheme S2



***N*-4-nitrobenzylidene-3-phenyl-2-propene-1-sulfonamide (26):** This compound was prepared by the general procedure outlined above. (79%) mp 152-153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ9.06 (s, 1H, N=CArH), δ 8.36 (d, J = 8.8, 2H, NO_2ArH), δ 8.12 (d, J = 8.8, 2H, NO_2ArH), δ 7.4 (m, 5H, ArH), δ 6.71 (d, 1H, J = 15.7 ArCH=CH), δ 6.2 (dt, J = 15.6, 7.61 1H, ArCH=CH), δ 4.15 (dd, J = 7.56, 1.1 2H, $CH=CHCH_2$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.5 (N=CH), δ 151.4 (Ar-NO_2), δ 139.9 (HC=CH), δ 137.1 (Ar-CH=N), δ 135.5 (Ar-C=C), δ 131.92 (Ar-H), δ 128.8 (Ar-H), δ 128.7 (Ar-H), δ 126.7 (Ar-H), δ 124.3 (Ar-H), δ 114.1 (HC=CH), δ 56.4 ($HC=CHCH_2$). DEPT 90 (125.7 MHz, $CDCl_3$): δ 170.5

(N=CH), δ 139.9 (Ar-H), δ 131.92 (Ar-H), δ 128.8 (HC=CH), δ 128.7 (ArH), δ 126.7 (Ar-H), δ 124.3 (Ar-H), δ 114.1 (HC=CH). Anal. Calcd for $C_{16}H_{14}N_2O_4S$: C, 58.17; H, 4.27; N, 8.48. Found: C, 58.00; H, 4.31; N, 8.42. FI/MS: M^+ 330.

***C*-4-nitrophenyl *N*-3-phenyl-2-propene-1-sulfonyloxaziridine (3):** This compound was prepared by the general procedure outlined above and was estimated to be >90% pure with the major contaminant being traces of p-NO_2 benzaldehyde. (83%). mp 109 - 112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 9.6, 2H, ArH), δ 7.55 (d, J = 9.3, 2H, ArH), δ 7.3 (m, 5H, ArH), δ 6.82 (d, J = 16.0, 1H, C=CHAr), δ 6.29 (dt, J = 15.8, 7.65, 1H, C=CHAr), δ 5.53 (s, 1H, NOCHAr), δ 4.27 (ABX, J_{ab} = 14.16, J_{ax} = 7.8, 1H, CH_2SO_2), δ 4.23 (ABX, J_{ab} = 14.16, J_{bx} = 7.4, 1H, CH_2SO_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 149.9 (Ar-NO_2), δ 140.8 (Ar-H), δ 137.0 (Ar-CHON), δ 135.3 (Ar-C=C), δ 129.4 (Ar-H), δ 129.0 (HC=CH), δ 128.8 (ArH), δ 126.9 (Ar-H), δ 123.9 (Ar-H), δ 112.4 (HC=CH), δ 73.4 (Ar-CHON), δ 56.4 (HC=$CHCH_2$). DEPT 90 (125.7 MHz, $CDCl_3$): δ 140.8 (Ar-H), δ 129.4 (Ar-H), δ 129.0 (HC=CH), δ 128.8 (ArH), δ 126.9 (Ar-H), δ 123.9 (Ar-H), δ 112.4 (HC=CH), δ 73.4 (Ar-CHON). FI/MS: M^+ 346.

3-phenyl-2-propene-1-sulfonamide oxide (13): mCPBA (700 mg, 80%, 3.56 mmol, 7.4 equiv.) was added to a solution of **25** (95 mg, 0.48 mmol) in CH_2Cl_2 (3 mL). The solution was stirred for 10 hr and the reaction quenched with sat. aq. $Na_2S_2O_5$. The solution was diluted with CH_2Cl_2 and washed with water (pH 7.2; x5 10 mL) dried over Na_2SO_4 filtered and evaporated. The residue was purified by chromatography to give **30** (43 mg, 44%) as a white solid. It is noteworthy that **8** can also be prepared from **25** and **11**, although purification is more difficult. Rf = 0.28 (30% EtOAc/Pet ether) mp 107 - 108 °C (benzene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.7 (m, 5H, ArH), δ 4.9 (bs, 2H, NH_2), δ 3.86 (d, J = 2, 1H, COCHAr), δ 3.61 (dd, J = 14.28, 3.84, 1H, $COCHCH_2$), δ 3.47 (ddd, J = 7.42, 3.73, 1.94, 1H, $COCHCH_2$), δ 3.33 (dd, J = 14.21, 7.43, 1H, $COCHCH_2$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 135.3 (ArCOC), δ 128.9 (ArH), δ 128.7 (ArH), δ 125.7 (ArH), δ 58.0 (CHOCH), δ 57.2 ($CHOCHCH_2$), δ 56.7 (CHOCH). DEPT 90 (125.7 MHz, $CDCl_3$): δ 128.9 (ArH), δ 128.7 (ArH), δ 125.7 (ArH), δ 58.0 (CHOCH), δ 56.7 (CHOCH). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.31; H, 4.99; N, 6.35. FI/MS: M^+ 213

***N*-4-nitrobenzyl-3-phenyl-2-propene-1-sulfonamide (14):** A solution of **26** (161 mg, 0.48 mmol) in EtOH (15 mL) was treated with $NaBH_4$ (28 mg, 1.5 equiv.). The heterogeneous solution was stirred for 20 minutes before the solvent was removed and the residue was partitioned between 2N HCl and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was crystallized from EtOH to give **14** (160 mg, 98%) as a white solid. mp 148-149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.7, 2H, NO_2ArH), δ 7.50 (d, J = 8.7, 2H, NO_2ArH), δ 7.3 (m, 5H, ArH), δ 6.57 (dt, J = 16.0, 1.0 1H, ArCH=CH), δ 6.2 (dt, J = 16.0, 7.5 1H, ArCH=CH), δ 4.81 (t, J = 6.6 1H, NH), δ 4.42 (d, J = 6.3, 2H, CH_2) δ 3.90 (dd, J = 7.54, 1.2, 2H, N-CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.4 (Ar-NO_2), δ 144.4 (Ar-C), δ 138.7 (HC=CH), δ 135.3 (Ar-CH=C), δ 128.87 (Ar-H), δ 128.85 (Ar-H), δ 128.5 (Ar-H), δ 126.4 (ArH), δ 124.0 (Ar-H), δ 115.8 (HC=CH), δ 57.6 (HC=$CHCH_2$), δ 46.7 (N-CH_2) . DEPT 90 (125.7 MHz, $CDCl_3$): δ 138.7 (Ar-H), δ 128.87 (Ar-H), δ 128.85 (HC=CH), δ 128.5 (ArH), δ 126.6 Ar-H), δ 124.0(Ar-H), δ 115.1 (HC=CH). Anal. Calcd for $C_{16}H_{16}N_2O_4S$: C, 57.82; H, 4.82; N, 8.43. Found: C, 57.49; H, 4.77; N, 8.30.

***N*-4-nitrobenzyl-3-phenyl-2-propene-1-sulfonamide oxide (15):** This compound was prepared by the procedure described for **13**. (40%) mp 148-149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.0, 2H, NO_2ArH), δ 7.56 (d, J = 8.0, 2H, NO_2ArH), δ 7.3 (m, 5H, ArH), δ 4.81 (t, J = 6.6 1H, NH), δ 4.47 (m, 2H, N-CH_2), δ 3.81 (d, J = 1.7, 1H, COCHAr), δ 3.62 (dd, J = 14.8, 2.9, 1H, $COCHCH_2$), δ 3.47 (ddd, J = 8.2, 3.0, 1.9, 1H, $COCHCH_2$), δ 3.33 (dd, J = 14.51, 8.2, 1H, $COCHCH_2$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.7 (Ar-NO_2), δ 144.0 (Ar-C), δ 135.0 (Ar-CHOC), δ 129.0 (Ar-H), δ 128.8 (Ar-H), δ 128.7 (Ar-H), δ 125.7 (ArH), δ 124.0 (Ar-H), δ 57.96 (CHOCH), δ 55.96 (CHOCH), δ 55.24 ($CHCH_2$), δ 46.5 (N-CH_2) . DEPT 90 (125.7 MHz, $CDCl_3$): δ 129.07 (Ar-H), δ 128.8 (Ar-H), δ 128.7 (HC=CH), δ 125.7 (ArH), δ 124.0 Ar-H), δ 57.9 (CHOCH), δ 55.9 (CHOCH). Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63; N, 8.04. Found: C, 55.13; H, 4.51; N, 7.78.

Reactions of 3: Measured quantities of **3** with or without **14** were dissolved in 0.7 mL $CDCl_3$ containing toluene as an internal standard (0.01 M). $CDCl_3$ was distilled from calcium hydride prior to use. The solutions were transferred to an NMR tube, cooled to –78 °C under N_2 and sealed with an oxygen torch. The resulting solutions were heated to 56 °C in a drying pistol using acetone as the solvent. The reaction was monitored periodically by ^{1}H NMR. After the oxaziridine peak could no longer be detected, the mixture was hydrolyzed on silica and the presence or absence of **13** and/or **15** was established by ^{1}H NMR comparison with authentic materials and by the addition of authentic materials to the reaction mixture.

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(S2) Munro, D. P.; Sharp, J. T. *J. Chem. Soc. Perkin Trans. I* **1984**, 849.
(S3) Kuroda, S.; Hirooka, S.; Tanbo, Y.; Takemura, K.; Nakahashi, H.; Matsuoka, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1431.