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General Information

All solvents employed in this study were reagent grade. All reagents were purchased from Sigma-Aldrich, UK and Alfa Aesar, UK and used as received unless otherwise stated. All reactions were magnetically stirred and monitored by thin layer chromatography (TLC) on pre-coated silica gel plates (254 μm). Silica plates were initially examined under UV light and then developed using aqueous basic potassium permanganate stain. Flash chromatography was carried out with silica gel (33-70 μm) supplied by Merck Co. Quoted yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, with a Bruker AMX 300 or at 400 MHz and 100 MHz, respectively, with a Bruker AMX 400 and chemical shifts (δ values) are reported in parts per million (ppm). Coupling constants are reported in Hertz (Hz). Infrared spectra were recorded on a Perkin Elmer FTIR. Mass spectra were obtained on a VG70-SE mass spectrometer. Melting points were measured in a Gallenkamp apparatus and are uncorrected.

Preparation of 1,2-dibromoethane-1-diethylsulfonamide (2)

To a solution of ethenediethylsulfonamide (5.5 g, 33.7 mmol) in CH_2Cl_2 (100 mL) was added excess bromine (107 g, 669 mmol, 34 mL) and the reaction mixture left to stir at room temperature for 1h. The reaction mixture was concentrated *in vacuo* to afford 1,2-dibromoethane-1-diethylsulfonamide **2** as a yellow oil (9.6 g, 29.7 mmol, 89 %). R_f 0.74 (Et_2O); ν_{max} (film)/cm^{-1} 2976 s, 2937 m; δ_H (300 MHz; $CDCl_3$) 1.25 (6H, t, $N(CH_2C\boldsymbol{H}_3)_2$, *J* 7.1), 3.32 (2H, dq, $(NC\boldsymbol{H}(H)CH_3)_2$, *J* 7.1, 14.3), 3.54 (2H, dq, $(NCH(\boldsymbol{H})CH_3)_2$, *J* 7.2, 14.4), 3.70 (1H, dd, $C\boldsymbol{H}CH(H)$, *J* 10.3, 11.5), 4.25 (1H, dd, $CHC\boldsymbol{H}(H)$, *J* 3.0, 11.5), 4.87 (1H, dd, $CHCH(\boldsymbol{H})$, *J* 3.0, 10.3); δ_C (300 MHz; $CDCl_3$) 14.4 (q, $NCH_2\boldsymbol{C}H_3$), 31.2 (t, $\boldsymbol{C}H_2CH$), 42.4 (t, $N\boldsymbol{C}H_2CH_3$), 63.7 (d, $CH_2\boldsymbol{C}H$). LRMS EI E^+ 323 ($[M]^+$, 4%), 310 (18%), 308 (36%), 306 (18%), 189 (25%), 187 (50%), 185 (25%), 136 (100%).

Preparation of 1-bromoethene-1-diethylsulfonamide (3)

To a solution of 1,2-dibromoethane-1-diethylsulfonamide (9.5 g, 29.4 mmol) in CH_2Cl_2 (70 mL) was added dropwise NEt_3 (3.3 g, 32.4 mmol, 4.5 mL) and the reaction mixture allowed to stir at room temperature for 3h. The reaction mixture was diluted with Et_2O (200 mL), washed with 2M HCl (3 × 80 mL) and brine (3 × 80 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with petroleum ether to 10% Et_2O in petroleum ether to afford 1-bromoethene-1-diethylsulfonamide **3** as a yellow oil (6.2 g, 25.7 mmol, 87%). R_f 0.74 (Et_2O); ν_{max} (film)/cm^{-1} 2978 s, 2937 s, 2878 m, 1600 m; δ_H (300 MHz; $CDCl_3$) 1.23 (6H, t, $N(CH_2C\boldsymbol{H}_3)_2$, *J* 6.9), 3.36 (4H, q, $(NC\boldsymbol{H}_2CH_3)_2$, *J* 6.9), 6.51 (1H, d, $C{=}C\boldsymbol{H}(H)$, *J* 2.7), 7.07 (1H, d, $C{=}CH(\boldsymbol{H})$, *J* 2.7); δ_C (300 MHz; $CDCl_3$) 14.4 (q, $NCH_2\boldsymbol{C}H_3$), 43.0 (t, $N\boldsymbol{C}H_2CH_3$), 127.6 (t, $C{=}\boldsymbol{C}H_2$), 128.0 (s, $\boldsymbol{C}{=}CH_2$). LRMS EI E^+ 243 ($[MBr^{81}]^+$, 4%), 241 ($[MBr^{79}]^+$, 4%), 228 (38%), 226 (38%), 200 (100%), 198 (100%), 164 (40%), 162 (57%), 151 (15%).

Preparation of 2-amino-1-bromoethane-1-diethylsulfonamide (4)

To a solution of 1-bromoethene-1-diethylsulfonamide **2** (0.55 g, 2.27 mmol) in *N, N*-dimethylformamide (12 mL) was added ammonium carbonate (4.36 g, 45.42 mmol) and the reaction mixture allowed to stir at 50 ºC for 4h. The reaction mixture was concentrated *in vacuo* and the crude residue purified by flash column chromatography eluting with EtOAc to afford 2-amino-1-bromoethane-1-diethylsulfonamide **4** as a viscous yellow oil (0.47 g, 1.82 mmol, 80%). R_f 0.16 (EtOAc); ν_{max} (film)/cm^{-1} 3020 s, 2980 s, 2939 s; δ_H (300 MHz; $CDCl_3$) 1.22 (6H, t, $(NCH_2C\boldsymbol{H}_3)_2$, *J* 7.2), 1.63 (2H, br s, $N\boldsymbol{H}_2$), 3.24-3.40 (4H, m), 3.49 (2H, dq, $(NC\boldsymbol{H}(H)CH_3)_2$, *J* 7.3, 14.6), 4.73 (1H, dd, $C\boldsymbol{H}CH(H)$, *J* 4.9, 6.1); δ_C (300 MHz; $CDCl_3$) 14.4 (q, $NCH_2\boldsymbol{C}H_3$), 42.8 (t, $N\boldsymbol{C}H_2CH_3$), 45.3 (t, $CH\boldsymbol{C}H_2NH_2$), 66.7 (d, $\boldsymbol{C}HCH_2$). LRMS EI E^+ 261 ($[MBr^{81}H]^+$, 50%), 259 ($[MBr^{79}H]^+$, 50%), 123 (100%), 108 (22%).

Preparation of 2-*N*-benzoyl-1-bromoethane-1-diethylsulfonamide (5a)

To a solution of 2-amino-1-bromoethane-1-diethylsulfonamide **3** (0.30 g, 1.15 mmol) in CH_2Cl_2 (30 mL) was added benzoyl chloride (0.21 g, 1.50 mmol, 0.17 mL) and pyridine (0.27 g, 3.46 mmol, 0.28 mL) and the reaction mixture left to stir at room temperature for 6h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 2M HCl (3 × 100 mL) and 1M $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% to 50% EtOAc in petroleum ether to afford 2-*N*-benzoyl-1-bromoethane-1-diethylsulfonamide **5a** as a colourless oil (0.39 g, 1.07 mmol, 93%). R_f 0.66 (Et_2O); ν_{max} (film)/cm^{-1} 3020 s, 1666 m, 1600 w, 1580 w; δ_H (300 MHz; $CDCl_3$) 1.21 (6H, t, $(NCH_2C\boldsymbol{H}_3)_2$, *J* 7.2), 3.32 (2H, dq, $(NC\boldsymbol{H}(H)CH_3)_2$, *J* 7.3, 14.3), 3.51 (2H, dq, $(NCH(\boldsymbol{H})CH_3)_2$, *J* 7.3, 14.6), 4.08 (1H, app dt, $CHC\boldsymbol{H}(H)NH$, *J* 5.7, 14.7), 4.26 (1H, app dt, $CHCH(\boldsymbol{H})NH$, *J* 6.3, 14.7), 5.03 (1H, dd, $C\boldsymbol{H}CH(H)$, *J* 5.4, 6.4), 7.26 (1H, app br t, $CH(H)N\boldsymbol{H}$, *J* 5.4), 7.44 (3H, m, $Ar\boldsymbol{H}$), 7.81 (2H, m, $Ar\boldsymbol{H}$); δ_C (300 MHz; $CDCl_3$) 14.4 (q, $NCH_2\boldsymbol{C}H_3$), 42.4 (t, $N\boldsymbol{C}H_2CH_3$), 42.9 (t, $CH\boldsymbol{C}H(H)NH$), 60.2 (d, $\boldsymbol{C}HCH(H)$), 127.1 (d, Ar), 130.0 (d, Ar), 131.9 (s, Ar), 133.6 (d, Ar), 167.6 (s, $\boldsymbol{C}{=}O$); LRMS EI E^+ 365 ($[MBr^{81}H]^+$, 5%), 363 ($[MBr^{79}H]^+$, 5%), 292 ($[MBr^{81}\text{-}N(CH_2CH_3)_2]^+$, 5%), 290 ($[MBr^{79}\text{-}N(CH_2CH_3)_2]^+$, 5%), 229 ($[MBr^{81}\text{-}SO_2N(CH_2CH_3)_2]^+$, 30%), 227 ($[MBr^{79}\text{-}SO_2N(CH_2CH_3)_2]^+$, 30%), 148 (33%), 134 (29%), 105 ($[PhCO]^+$, 100%).

Preparation of 2-*N*-(4-nitrobenzoyl)-1-bromoethane-1-diethylsulfonamide (5b)

To a solution of 2-amino-1-bromoethane-1-diethylsulfonamide **3** (0.30 g, 1.15 mmol) in CH_2Cl_2 (50 mL) was added 4-nitrobenzoyl chloride (0.28 g, 1.50 mmol) and pyridine (0.27 g, 3.46 mmol, 0.28 mL) and the reaction mixture left to stir at room temperature for 2h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 2M HCl (3 × 100 mL) and 1M $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% to 75% Et_2O in petroleum ether to afford 2-*N*-(4-nitrobenzoyl)-1-bromoethane-1-diethylsulfonamide **5b** as a yellow oil (0.39 g, 1.07 mmol, 83 %). R_f 0.66 (Et_2O); ν_{max} (film)/cm^{-1} 2978 m, 1666 m, 1600 m,

1580 w, 1525 s, 1500 w, 1350 s; δ_H (300 MHz; $CDCl_3$) 1.26 (6H, t, $(NCH_2CH_3)_2$, *J* 7.2), 3.33 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.2, 14.3), 3.55 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.3, 14.6), 4.16-4.32 (2H, m), 4.99 (1H, dd, C*H*CH(H), *J* 4.5, 6.6), 7.26 (1H, app br t, CH(H)N*H*, *J* 5.4), 8.29 (2H, dd, Ar*H*, *J* 2.2, 9.1), 8.59 (2H, dd, Ar*H*, J 2.1, 9.1); δ_C (300 MHz; $CDCl_3$) 14.4 (q, NCH_2CH_3), 42.4 (t, NCH_2CH_3), 43.1 (t, CHCH(H)NH), 59.4 (d, CHCH(H)), 123.9 (d, Ar), 128.3 (d, Ar), 139.2 (s, Ar), 149.7 (s, Ar), 165.4 (s, C=O). LRMS EI E^+ 410 ($[MBr^{81}H]^+$, 5%), 408 ($[MBr^{79}H]^+$, 5%), 337 ($[MBr^{81}\text{-}N(CH_2CH_3)_2]^+$, 4%), 335 ($[MBr^{79}\text{-}N(CH_2CH_3)_2]^+$, 4%), 274 ($[MBr^{81}\text{-}SO_2N(CH_2CH_3)_2]^+$, 40%), 272 ($[MBr^{79}\text{-}SO_2N(CH_2CH_3)_2]^+$, 40%), 179 (70%), 150 (100%), 104 (100%).

Preparation of 2-*N*-decanoyl-1-bromoethane-1-diethylsulfonamide (5c)
To a solution of 2-amino-1-bromoethane-1-diethylsulfonamide **3** (0.50 g, 1.92 mmol) in chloroform (30 mL) was added decanoyl chloride (0.48 g, 2.50 mmol, 0.52 mL) and pyridine (0.46 g, 5.76 mmol, 0.47 mL) and the reaction mixture left to stir at room temperature for 6h. The reaction mixture was diluted with Et_2O (50 mL), washed with 2M HCl (3 × 100 mL) and 1M $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 20% to 50% Et_2O in petroleum ether to afford 2-*N*-decanoyl-1-bromoethane-1-diethylsulfonamide **5c** as a yellow oil (0.54 g, 1.30 mmol, 68 %). R_f 0.11 (40 % Et_2O in petroleum ether); ν_{max} (film)/cm^{-1} 3297 w, 2924 s, 2854 s, 1652 s; δ_H (300 MHz; $CDCl_3$) 0.86 (3H, t, CH_2CH_3, *J* 6.6), 1.20-1.27 (18H, m), 1.62 (2H, m, $CH_2CH_2CH_2C$=O), 2.21 (2H, t, CH_2CH_2C=O, *J* 7.4), 3.31 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.1, 14.3), 3.48 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.3, 14.6), 3.84 (1H, app dt, CHCH(H)NH, *J* 5.7, 14.7), 4.07 (1H, app dt, CHCH(H)NH, *J* 6.3, 14.7), 4.91 (1H, dd, CHCH-(H), *J* 4.4, 6.3), 6.20 (1H, app br t, CH(H)N*H*, *J* 5.4); δ_C (300 MHz; $CDCl_3$) 14.0 (q, CH_2CH_3), 14.4 (q, NCH_2CH_3), 22.7 (t), 25.5 (t), 29.2 (t), 29.2 (t), 29.3 (t), 29.4 (t), 31.9 (t), 36.6 (t), 41.9 (t), 42.9 (t, NCH_2CH_3), 60.3 (d, CHCH(H)), 173.5 (s, C=O). LRMS EI E^+ 415 ($[MBr^{81}H]^+$, 5%), 413 ($[MBr^{79}H]^+$, 5%), 198 (27%), 196 (25%), 167 (94%), 165 (100%).

Preparation of 2-*N*-(4-methoxybenzoyl)-1-bromoethane-1-diethylsulfonamide (5d)
To a solution of 2-amino-1-bromoethane-1-diethylsulfonamide **3** (0.60 g, 2.30 mmol) in CH_2Cl_2 (50 mL) was added 4-methoxybenzoyl chloride (0.51 g, 3.00 mmol) and pyridine (0.54 g, 6.92 mmol, 0.56 mL) and the reaction mixture left to stir at room temperature for 2h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 2M HCl (3 × 100 mL) and 1M $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% Et_2O in petroleum ether to afford 2-*N*-(4-methoxybenzoyl)-1-bromoethane-1-diethylsulfonamide **5d** as a colourless oil (0.50 g, 1.27 mmol, 55 %). R_f 0.28 (50% Et_2O in petroleum ether); ν_{max} (film)/cm^{-1} 3330 w, 2974 m, 2918 m, 2849 m, 1639 s, 1606 s, 1537 m, 1503 s; δ_H (300 MHz; $CDCl_3$) 1.25 (6H, t, $(NCH_2CH_3)_2$, *J* 7.1), 3.33 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.1, 14.3), 3.55 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.3, 14.6), 3.85 (3H, s, OCH_3), 4.12 (1H, app dt, CHCH(H)NH, *J* 5.4, 14.8), 4.25 (1H, app dt, CHCH(H)NH, *J* 6.3, 14.8), 4.99 (1H, dd, CHCH(H), *J* 5.1, 6.6), 6.86 (1H, app br t, CH(H)N*H*, *J* 5.1), 6.94 (2H, dd, Ar*H*, *J* 2.0, 6.8), 7.77 (2H, dd, Ar*H*, *J* 2.0, 6.8); δ_C (300 MHz; $CDCl_3$) 14.4 (q, NCH_2CH_3), 42.3 (t, NCH_2CH_3), 43.0 (t, CHCH(H)), 55.4 (s, OCH_3), 60.3 (d, CHCH(H)), 114.0 (d, Ar), 125.9 (s, Ar), 129.0 (d, Ar), 162.5 (s), 162.9 (s). LRMS CI E^+ 423 ($[MBr^{81}NH_4]^+$, 10%), 421 ($[MBr^{81}NH_4]^+$, 6%), 395 ($[MBr^{81}H]^+$, 45%), 393 ($[MBr^{79}H]^+$, 41%), 242 (48%), 178 (50%), 135 (100%).

Preparation of 2-*N*-nicotinoyl-1-bromoethane-1-diethylsulfonamide (5e)
To a solution of 2-amino-1-bromoethane-1-diethylsulfonamide **3** (0.50 g, 1.92 mmol) in CH_2Cl_2 (30 mL) was added nicotonyl chloride hydorchloride (0.45 g, 2.50 mmol), pyridine (0.46 g, 5.77 mmol, 0.47 mL) and NEt_3 (0.59 g, 5.77 mmol, 0.81 mL) and the reaction mixture left to stir at room temperature for 3h. The reaction mixture was diluted with EtOAc (70 mL), washed with 1M $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with EtOAc afford 2-*N*-nicotonyl-1-bromoethane-1-diethylsulfonamide **5e** as a pale yellow oil (0.56 g, 1.53 mmol, 80%). R_f 0.29 (EtOAc); ν_{max} (film)/cm^{-1} 3299 w, 2976 m, 2929 m, 1654 s, 1592 s, 1534 s; δ_H (300 MHz; $CDCl_3$) 1.20 (6H, t, $(NCH_2CH_3)_2$, *J* 7.1), 3.31 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.1, 14.3), 3.51 (2H, dq, $(NCH(H)CH_3)_2$, *J* 7.3, 14.4), 4.03 (1H, app dt, CHCH(H)NH, *J* 5.7, 14.7), 4.24 (1H, app dt, CHCH(H)NH, *J* 6.2, 14.7), 5.05 (1H, app t, CHCH(H), *J* 5.9), 7.33 (1H, dd, Ar*H*, *J* 4.8, 7.8), 7.54 (1H, app br t, CH(H)N*H*, *J* 5.7), 8.10 (1H, app dt, Ar*H*, *J* 1.9, 7.9), 8.67 (1H, dd, Ar*H*, *J* 1.4, 4.8), 9.01 (1H, d, Ar*H*, *J* 1.6); δ_C (300 MHz; $CDCl_3$) 14.4 (q, NCH_2CH_3), 42.4 (t, NCH_2CH_3), 43.0 (t, CHCH(H)NH), 60.0 (d, CHCH(H)), 123.5 (d, Ar), 129.5 (s, Ar), 135.1 (d, Ar), 148.4 (d, Ar), 152.5 (d, Ar), 165.9 (s, C=O). LRMS FAB E^+ 366 ($[MBr^{81}H]^+$, 85%), 364 ($[MBr^{79}H]^+$, 85%), 154 (100%).

Preparation of 2-phenyl-4,5-dihydro-5-diethylsulfonamido-oxazole (6a)
To a solution of 2-*N*-benzoyl-1-bromoethane-1-diethylsulfonamide **5a** (0.36 g, 0.99 mmol) in *N, N*-dimethylformamide (30 mL) was added sodium tert-butoxide (0.19 g, 1.98 mmol) portionwise and the reaction mixture left to stir at room temperature for 2h. The reaction mixture was diluted with Et_2O (100 mL), washed with 10% w/v aq. LiCl (2 × 100 mL) and H_2O (100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford 2-phenyl-4,5-dihydro-5-diethylsulfonamideoxazole **6a** as a yellow oil (0.25 g, 0.88 mmol, 89%). R_f 0.70 (Et_2O); ν_{max} (film)/cm^{-1} 2978 s, , 2939 m, 2870 s, 1500 w; δ_H (300 MHz; $CDCl_3$) 1.20 (6H, t, $(NCH_2CH_3)_2$, *J* 7.2), 3.36 (4H, q, $(NCH_2CH_3)_2$, *J* 7.2), 4.32 (1H, dd, CHCH(H), *J* 9.8, 16.5), 4.48 (1H, dd, CHCH(H), *J* 5.7, 16.5), 5.37 (1H, dd, CHCH(H), *J* 5.7, 9.8), 7.37 (2H, t, Ar*H*, *J* 6.2), 7.48 (1H, m, Ar*H*) 7.91 (2H, d, Ar*H*, *J* 8.7); δ_C (300 MHz; $CDCl_3$) 14.5 (q, NCH_2CH_3), 42.1 (t, NCH_2CH_3), 57.8 (t, CHCH(H)), 89.0 (d, CHCH(H)), 126.3 (s, Ar), 128.2 (d, Ar), 128.6 (d, Ar), 132.0 (d, Ar), 162.7 (s, C=N). LRMS CI E^+ 283 ($[MH]^+$, 99%), 146 ($[M\text{-}SO_2N(CH_2CH_3)_2]^+$, 100%).

Preparation of 2-(4-nitrophenyl)-4,5-dihydro-5-diethylsulfonamideoxazole (6b)

To a solution of 2-*N*-(4-nitrobenzoyl)-1-bromoethane-1-diethylsulfonamide **5b** (0.31 g, 0.76 mmol) in *N, N*-dimethylformamide (30 mL) was added sodium tert-butoxide (0.15 g, 1.52 mmol) portionwise and the reaction mixture left to stir at room temperature for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 10% w/v aq. LiCl (2 × 100 mL) and H_2O (100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford 2-(4-nitrophenyl)-4,5-dihydro-5-diethylsulfonamideoxazole **6b** as a pale yellow oil (0.23 g, 0.70 mmol, 92%). R_f 0.59 (Et_2O); ν_{max} (film)/cm^{-1} 2978 s, 2876 s, 1600 w, 1550 s, 1500 w, 1340 s; δ_H (300 MHz; $CDCl_3$) 1.25 (6H, t, $(NCH_2CH_3)_2$, *J* 7.2), 3.42 (4H, q, $(NCH_2CH_3)_2$, *J* 7.2), 4.42 (1H, dd, CHC***H***(H), *J* 9.9, 17.0), 4.59 (1H, dd, CHCH(***H***), *J* 5.8, 17.0), 5.43 (1H, dd, C***H***CH(H), *J* 5.8, 9.9), 8.12 (2H, dd, Ar***H***, *J* 2.0, 6.9), 8.29 (2H, dd, Ar***H***, *J* 1.9, 6.9); δ_C (300 MHz; $CDCl_3$) 14.5 (q, NCH_2CH_3), 42.1 (t, N***C***H_2CH_3), 57.9 (t, CH***C***H(H)), 89.1 (d, ***C***HCH(H)), 123.8 (d, Ar), 129.3 (d, Ar), 132.0 (s, Ar), 150.2 (s, Ar)*, 160.9 (s, ***C***=N)*. LRMS EI E^+ 328 ($[MH]^+$, 9%), 234 (38%), 191 ($[M\text{-}SO_2N(CH_2CH_3)_2]^+$, 100%), 163 (82%), 117 (87%).

Preparation of 2-nonanayl-4,5-dihydro-5-diethylsulfonamideoxazole (6c)

To a solution of 2-*N*-decanoyl-1-bromoethane-1-diethylsulfonamide **5c** (0.54 g, 1.30 mmol) in *N, N*-dimethylformamide (30 mL) was added sodium tert-butoxide (0.25 g, 2.60 mmol) portionwise and the reaction mixture left to stir at room temperature for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 10% w/v aq. LiCl (2 × 100 mL) and H_2O (100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford 2-nonanayl-4,5-dihydro-5-diethylsulfonamideoxazole **6c** as a clear oil (0.27 g, 0.81 mmol, 62%). R_f 0.19 (50% Et_2O in petroleum ether); ν_{max} (film)/cm^{-1} 2924 s, 2854 s, 1685 s; δ_H (300 MHz; $CDCl_3$) 0.82 (3H, t, CH_2CH_3, *J* 6.6), 1.16-1.28 (18H, m), 1.58 (2H, m, $CH_2CH_2CH_2C$=O), 2.28 (2H, t, CH_2CH_2C=O, *J* 7.4), 3.28-3.44 (4H, m), 4.10 (1H, dd, CHC***H***(H), *J* 9.8, 15.8), 4.22 (1H, dd, CHCH(***H***), *J* 5.7, 15.8), 5.14 (1H, dd, C***H***CH(H), *J* 5.7, 9.8); δ_C (300 MHz; $CDCl_3$) 14.0 (q, CH_2CH_3), 14.4 (q, NCH_2CH_3), 22.7 (t), 25.7 (t), 27.7 (t), 29.0 (t), 29.3 (t), 29.3 (t), 29.4 (t), 31.9 (t), 42.0 (t), 57.0 (t, CH***C***H(H)), 88.4 (d, ***C***HCH(H)) 166.8 (s, ***C***=N). LRMS EI E^+ 333 ($[MH]^+$, 85%), 214 (55%), 196 ($[M\text{-}SO_2N(CH_2CH_3)_2]^+$, 100%). HRMS (CI) $[MH]^+$, $C_{16}H_{33}N_2SO_3$ Requires 333.22119. Found 333.22264.

Preparation of 2-(4-methoxyphenyl)-4,5-dihydro-5-diethylsulfonamideoxazole (6d)

To a solution of 2-*N*-(4-methoxybenzoyl)-1-bromoethane-1-diethylsulfonamide **5d** (0.40 g, 1.01 mmol) in *N, N*-dimethylformamide (30 mL) was added sodium *tert*-butoxide (0.20 g, 2.02 mmol) portionwise and the reaction mixture left to stir at room temperature for 2h. The reaction mixture was diluted with Et_2O (100 mL), washed with 10% w/v aq. LiCl (2 × 100 mL) and H_2O (100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% to 75% Et_2O in petroleum ether to afford 2-(4-methoxyphenyl)-4,5-dihydro-5-diethylsulfonamideoxazole **6d** as a pale yellow oil (0.18 g, 0.58 mmol, 57%). R_f 0.45 (Et_2O); ν_{max} (film)/cm^{-1} 2975 s, 2939 s, 2876 m, 1660 s, 1609 s, 1578 m, 1513 s; δ_H (300 MHz; $CDCl_3$) 1.23 (6H, t, $(NCH_2CH_3)_2$, *J* 7.8), 3.36 (4H, q, $(NCH_2CH_3)_2$, *J* 7.8), 3.83 (3H, s, O***C***H_3), 4.32 (1H, dd, CHC***H***(H), *J* 9.8, 16.4), 4.47 (1H, dd, CHCH(***H***), *J* 5.7, 16.4), 5.36 (1H, dd, C***H***CH(H), *J* 5.7, 9.8), 6.91 (2H, app dt, Ar***H***, *J* 2.7, 9.7), 7.84 (2H, app dt, Ar***H***, *J* 2.7, 9.7); δ_C (300 MHz; $CDCl_3$) 14.5 (q, NCH_2CH_3), 42.1 (t, N***C***H_2CH_3), 55.4 (s, O***C***H_3), 57.5 (t, CH***C***H(H)), 89.1 (d, ***C***HCH(H)), 114.0 (d, Ar), 118.8 (s, Ar), 130.0 (d, Ar), 162.5 (s, Ar), 162.5 (s, ***C***=N). LRMS FAB E^+ 313 ($[MH]^+$, 100%), 176 ($[M\text{-}SO_2N(CH_2CH_3)_2]^+$, 77%).

Preparation of 2-(nicotinoyl)-4,5-dihydro-5-diethylsulfonamideoxazole (6e)

To a solution of 2-*N*-nicotonyl-1-bromoethane-1-diethylsulfonamide **5e** (0.36 g, 0.99 mmol) in *N, N*-dimethylformamide (30 mL) was added sodium tert-butoxide (0.19 g, 1.98 mmol) portionwise and the reaction mixture left to stir at room temperature for 2h. The reaction mixture was diluted with EtOAc (100 mL), washed with H_2O (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% to 80% EtOAc in petroleum ether to afford 2-(nicotanyl)-4,5-dihydro-5-diethylsulfonamideoxazole **6e** as a yellow oil (0.14 g, 0.44 mmol, 50%). R_f 0.29 (EtOAc); ν_{max} (film)/cm^{-1} 2976 m, 1667 s, 1592 m; δ_H (300 MHz; $CDCl_3$) 1.23 (6H, t, $(NCH_2CH_3)_2$, *J* 7.2), 3.36 (4H, q, $(NCH_2CH_3)_2$, *J* 7.2), 4.32 (1H, dd, CHC***H***(H), *J* 9.8, 16.7), 4.47 (1H, dd, CHCH(***H***), *J* 5.8, 16.7), 5.36 (1H, dd, C***H***CH(H), *J* 5.8, 9.8), 7.37 (1H, dd, Ar***H***, *J* 4.8, 7.8), 8.19 (1H, app dt, Ar***H***, *J* 1.9, 7.8), 8.71 (1H, dd, Ar***H***, *J* 1.4, 4.8), 9.08 (1H, d, Ar***H***, *J* 1.6); δ_C (300 MHz; $CDCl_3$) 14.5 (q, NCH_2CH_3), 42.1 (t, N***C***H_2CH_3), 57.6 (t, CH***C***H(H)), 88.8 (d, ***C***HCH(H)), 122.6 (d, Ar), 123.5 (s, Ar), 135.6 (d, Ar), 149.2 (d, Ar), 152.6 (d, Ar), 160.7 (s, ***C***=N). LRMS CI E^+ 284 ($[MH]^+$, 49%), 147 (100%), 119 (26%), 92 (16%).

Preparation of 2-phenyloxazole (7a)[1]

To a solution of 2-phenyl-4,5-dihydro-5-diethylsulfonamideoxazole **6a** (0.15 g, 0.53 mmol) in *N*-methyl-2-pyrrolidinone (20 mL) was added excess 2M NaOH (5 mL) and the reaction mixture left to stir at 140 ºC for 1h. The reaction mixture was diluted with Et_2O (80 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to yield. The crude residue was purified by flash column chromatography eluting with CH_2Cl_2 to afford 2-phenyloxazole **7a** as a colourless oil (0.052 g, 0.36 mmol, 68 %). R_f 0.30 (CH_2Cl_2); ν_{max} (film)/cm^{-1} 2923 m, 2853 m, 1558 m; δ_H (300 MHz; $CDCl_3$) 7.24 (1H, s, OHC=C***H***N), 7.45 (3H, m, Ar***H***), 7.70 (1H, s, O***H***C=CHN), 8.04 (2H, m, Ar***H***); δ_C (300 MHz; $CDCl_3$) 126.4 (d, Ar), 127.5 (s, Ar), 128.4 (d, Ar), 128.8 (s, Ar), 130.3 (d, OHC=***C***HN), 138.6 (d, OH***C***=CHN), 162.0 (s, ***C***=N). LRMS CI E^+ 146 ($[MH]^+$, 100%), 145 ($[M]^+$, 35%), 90 (12%). Data in agreement with literature values.

Preparation of 2-(4-nitrophenyl)oxazole (7b)[2]

To a solution of 2-(4-nitrophenyl)-4,5-dihydro-5-diethylsulfonamideoxazole **6b** (0.22 g, 0.67 mmol) in *N, N*-dimethylformamide (20 mL) was added excess 2M NaOH (3 mL) and the reaction mixture left to stir at 120 ºC for 3h. The reaction mixture was diluted with Et_2O (80 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and

concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with CH_2Cl_2 to afford 2-(4-nitrophenyl)oxazole **7b** as a white solid (0.089 g, 0.47 mmol, 70%). R_f 0.75 (Et_2O); m.p. 161-164 ºC ; ν_{max} (solid)/cm^{-1} 3104 m, 2924 m, 2844 m, 1604 s, 1558 s, 1516 s, 1507 s, 1334 s; δ_H (300 MHz; $CDCl_3$) 7.31 (1H, s, OHC=C***H***N), 7.80 (1H, s, O***H***C=CHN), 8.18 (2H, d, Ar***H***, *J* 9.0), 8.29 (2H, d, Ar***H***, *J* 9.0); δ_C (300 MHz; $CDCl_3$) 124.2 (d, Ar), 127.1 (d, Ar), 129.4 (d, OHC=***C***HN), 132.8 (s, Ar), 140.0 (d, OH***C***=CHN), 148.7 (s, Ar), 159.8 (s, ***C***=N). LRMS EI E^+ 190 ($[M]^+$, 100%), 160 (50%), 116 (47%), 104 (68%). HRMS (CI) M^+, $C_9H_6N_2O_3$ Requires 190.03729. Found 190.03754. Data in agreement with literature values.

Preparation of 2-nonoyloxazole (7c)
To a solution of 2-nonanayl-4,5-dihydro-5-diethylsulfonamideoxazole **6c** (0.085 g, 0.26 mmol) in *N, N*-dimethylformamide (20 mL) was added excess 2M NaOH (5 mL) and the reaction mixture left to stir at 140 ºC for 3h. The reaction mixture was diluted with Et_2O (80 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% Et_2O in petroleum ether to afford 2-nonoyloxazole **7c** as a colourless oil (0.031 g, 0.16 mmol, 62 %). R_f 0.47 (50% Et_2O in petroleum ether); ν_{max} (film)/cm^{-1} 2923 s, 2854 s, 1575 m, 1466 m; δ_H (300 MHz; $CDCl_3$) 0.87 (3H, t, CH_2CH_3, *J* 6.6), 1.16-1.28 (12H, m), 1.75 (2H, m, $CH_2CH_2CH_2C$=O), 2.76 (2H, t, CH_2CH_2C=O, *J* 7.7), 7.02 (1H, s, OHC=C***H***N), 7.54 (1H, s, O***H***C=CHN); δ_C (300 MHz; $CDCl_3$) 14.0 (q, CH_2CH_3), 22.6 (t), 27.0 (t), 28.1 (t), 29.1 (t), 29.2 (t), 29.4 (t), 29.7 (t), 31.9 (t), 126.8 (d), 138.0 (d), 165.5 (s). LRMS CI E^+ 196 ($[MH]^+$, 100%), 172 (8%), 155 (8%). HRMS (CI) $[MH]^+$, $C_{12}H_{22}NO$ Requires 196.17014. Found 196.17088.

Preparation of 2-(4-methoxyphenyl)oxazole (7d)[3]
To a solution of 2-(4-methoxyphenyl)-4,5-dihydro-5-diethylsulfonamideoxazole **6d** (0.13 g, 0.42 mmol) in *N, N*-dimethylformamide (20 mL) was added excess 2M NaOH (5 mL) and the reaction mixture left to stir at 120 ºC for 2h. The reaction mixture was diluted with Et_2O (80 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% Et_2O in petroleum ether to afford 2-(4-methoxyphenyl)oxazole **7d** as a pale yellow oil (0.067 g, 0.38 mmol, 92%). R_f 0.80 (Et_2O); ν_{max} (film)/cm^{-1} 3127 w, 3003 w, 2940 m, 2837 m, 1610 s, 1587 m, 1494 s; δ_H (300 MHz; $CDCl_3$) 3.86 (3H, s, OC***H***$_3$)6.94 (2H, d, Ar***H***, *J* 8.6), 7.12 (1H, s, OHC=C***H***N), 7.60 (1H, s, O***H***C=CHN), 7.95 (2H, d, Ar***H***, *J* 8.6); δ_C (300 MHz; $CDCl_3$) 55.4 (q, O***C***H_3), 114.2 (d, Ar), 120.4 (s, Ar), 128.0 (d), 128.2 (d), 138.0 (d, OH***C***=CHN), 161.3 (s), 162.1 (s). LRMS EI E^+ 175 ($[M]^+$, 100%), 135 (63%), 120 (36%). Data in agreement with literature values.

Preparation of 2-(nicotanyl)oxazole (7e)[4]
To a solution of 2-(nicotanyl)-4,5-dihydro-5-diethylsulfonamideoxazole **6e** (0.10 g, 0.37 mmol) in *N, N*-dimethylformamide (20 mL) was added excess 2M NaOH (5 mL) and the reaction mixture left to stir at 100 ºC for 1h. The reaction mixture was diluted with Et_2O (80 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with Et_2O to afford 2-(nicotanyl)oxazole **7e** as a yellow oil (0.054 g, 0.31 mmol, 83%). R_f 0.30 (Et_2O); ν_{max} (film)/cm^{-1} 3113 s, 2923 s, 1600 s, 1582 s; δ_H (300 MHz; $CDCl_3$) 7.27 (1H, s, OHC=C***H***N), 7.38 (1H, dd, Ar***H***, *J* 4.9, 7.9), 7.76 (1H, s, O***H***C=CHN), 8.28 (1H, app dt, Ar***H***, *J* 1.8, 7.9), 8.67 (1H, d, Ar***H***, *J* 4.9), 9.27 (1H, s, Ar***H***); δ_C (300 MHz; $CDCl_3$) 123.6 (d), 123.7 (s, Ar), 128.8 (d), 133.5 (d), 139.3 (d), 147.7 (d), 151.1 (d), 159.7 (s, ***C***=N). LRMS CI E^+ 147 ($[MH]^+$, 100%), 146 ($[M]^+$, 35%). HRMS (EI) M^+, $C_8H_6N_2O$ Requires 146.04746. Found 146.04756. Data in agreement with literature values.

Preparation of (*E*)-Phenyl-2-(4-methylphenyl)vinylsulfonate (15a)
To a solution of phenyl vinylsulfonate **14** (0.2 g, 1.08 mmol) in *N, N*-dimethylformamide (10 mL) was added *N*-methyl-dicyclohexylamine (0.42 g, 2.17 mmol, 0.46 mL), palladium(II) acetate (12 mg, 0.05 mmol) and 4-iodotoluene (0.36 g, 1.63 mmol) and the reaction mixture left to stir at 80 ºC for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 2M HCl (3 × 100 mL) and 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% Et_2O in petroleum ether and recrystallised from CH_2Cl_2/hexane to afford (*E*)-Phenyl-2-(4-Methylphenyl)vinylsulfonate **15a** (0.11 g, 0.40 mmol, 37%) as a white crystals. R_f 0.54 (40% Et_2O in petroleum ether); m.p. 95-97 ºC; ν_{max} (solid)/cm^{-1} 3057 m, 2918 s, 2849 m, 1616 s, 1606 s, 1587 s, 1486 s; δ_H (300 MHz; $CDCl_3$) 2.34 (3H, s, C***H***$_3$), 6.83 (1H, d, HC=C***H***SO_3Ph, *J* 15.5), 7.21-7.31 (5H, m, Ar***H***), 7.34-7.40 (4H, m, Ar***H***), 7.48 (1H, d, ***H***C=CHSO_3Ph, *J* 15.5); δ_C (300 MHz; $CDCl_3$) 21.6 (q, ***C***H_3), 119.4 (d), 122.5 (d), 127.2 (d), 128.7 (d), 129.0 (s, Ar), 129.9 (d), 130.0 (d), 142.6 (s, Ar), 146.3 (d), 149.6 (s, Ar). LRMS CI E^+ 275 ($[MH]^+$, 100%), 181 (42%), 95 (34%).

Preparation of (*E*)-Phenyl-2-(4-chlorophenyl)vinylsulfonate (15b)
To a solution of phenyl vinylsulfonate **14** (0.5 g, 2.71 mmol) in *N, N*-dimethylformamide (10 mL) was added *N*-methyl-dicyclohexylamine (1.06 g, 5.42 mmol, 1.15 mL), palladium (II) acetate (30 mg, 0.14 mmol) and 4-chloro-1-iodobenzene (0.97 g, 4.07 mmol) and the reaction mixture left to stir at 80 ºC for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 2M HCl (3 × 100 mL) and 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% to 20% Et_2O in petroleum ether and recrystallised from CH_2Cl_2/hexane to afford (*E*)-Phenyl-2-(4-chlorophenyl)vinylsulfonate **15b** (0.38 g, 1.28 mmol, 48%) as a white crystals. R_f 0.51 (20% Et_2O in petroleum ether); m.p. 103-106 ºC; ν_{max} (solid)/cm^{-1} 3058 m, 1621 s, 1586 s, 1487 s; δ_H (300 MHz; $CDCl_3$) 6.85 (1H, d, HC=C***H***SO_3Ph, *J* 15.5), 7.23-7.40 (8H, m, Ar***H***), 7.47 (1H, d, ***H***C=CHSO_3Ph, *J* 15.5); δ_C (300 MHz; $CDCl_3$) 121.3 (d), 122.4 (d), 127.3 (d), 129.6 (d), 129.8 (d), 129.9 (d), 130.2 (s, Ar), 137.9 (s, Ar), 144.7 (d),

149.5 (s, Ar); LRMS EI E^+ 297 ([MCl^{37}]$^+$, 15%), 295 ([MCl^{35}]$^+$, 33%), 230 (75%), 201 (68%), 137 (100%). HRMS (CI) [MH]$^+$, $C_{14}H_{11}SO_3Cl$ Requires 295.01957. Found 295.01938.

Preparation of (*E*)-Phenyl-2-(4-nitrophenyl)vinylsulfonate (15c)
To a solution of phenyl vinylsulfonate **14** (0.5 g, 2.71 mmol) in *N, N*-dimethylformamide (10 mL) was added *N*-methyl-dicyclohexylamine (1.06 g, 5.42 mmol, 1.15 mL), palladium (II) acetate (30 mg, 0.14 mmol) and 4-iodonitrobenzene (1.01 g, 4.07 mmol) and the reaction mixture left to stir at 80 ºC for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 2M HCl (3 × 100 mL) and 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% to 20% Et_2O in petroleum ether and recrystallised from CH_2Cl_2/hexane to afford (*E*)-Phenyl-2-(4-nitrophenyl)vinylsulfonate **15c** (0.21 g, 0.67 mmol, 26%) as yellow crystals. R_f 0.29 (20% Et_2O in petroleum ether); m.p. 136-140 ºC; ν_{max} (solid)/cm^{-1} 3052 m, 1594 m, 1584 m, 1511 s, 1486 s, 1350 s; δ_H (300 MHz; $CDCl_3$) 7.03 (1H, d, HC=C***H***SO_3Ph, *J* 15.3), 7.23-7.40 (4H, m, Ar***H***), 7.57 (1H, d, ***H***C=CHSO$_3$Ph, *J* 15.5), 7.65 (2H, d, Ar***H***, *J* 8.7), 8.28 (2H, d, Ar***H***, *J* 8.7); δ_C (300 MHz; $CDCl_3$) 122.3 (d), 124.5 (d), 125.1 (d), 127.6 (d), 129.3 (d), 130.0 (d), 137.6 (s, Ar), 143.0 (d), 149.3 (s, Ar), 149.3 (s, Ar); LRMS CI E^+ 306 ([MH]$^+$, 35%), 276 (36%), 182 (50%), 150 (43%), 120 (52%), 95 (100%). HRMS (EI) M$^+$, $C_{14}H_{11}NO_5S$ Requires 305.03524. Found 305.03655.

Preparation of (*E*)-Phenyl-2-(4-methoxyphenyl)vinylsulfonate (15d)
To a solution of phenyl vinylsulfonate **14** (0.5 g, 2.71 mmol) in *N, N*-dimethylformamide (10 mL) was added *N*-methyl-dicyclohexylamine (1.06 g, 5.42 mmol, 1.15 mL), palladium (II) acetate (30 mg, 0.14 mmol) and 4-iodoanisole (0.95 g, 4.07 mmol) and the reaction mixture left to stir at 80 ºC for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 2M HCl (3 × 100 mL) and 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% to 20% Et_2O in petroleum ether and recrystallised from CH_2Cl_2/hexane to afford (*E*)-Phenyl-2-(4-methoxyphenyl)vinylsulfonate **15d** (0.38 g, 1.31 mmol, 48%) as white crystals; R_f 0.40 (20% Et_2O in petroleum ether); m.p. 76-80 ºC; ν_{max} (solid)/cm^{-1} 3060 m, 2942 m, 2849 m, 1599 s, 1570 s, 1511 s, 1486 s; δ_H (300 MHz; $CDCl_3$) 3.82 (3H, s, OC***H***$_3$), 6.73 (1H, d, HC=C***H***SO_3Ph, *J* 15.5), 6.91 (2H, d, Ar***H***, *J* 8.8), 7.24-7.40 (7H, m, Ar***H***), 7.44 (1H, d, ***H***C=CHSO$_3$Ph, *J* 15.5); δ_C (300 MHz; $CDCl_3$) 55.5 (q, ***C***H3), 114.7 (d), 117.6 (d), 122.5 (d), 124.3 (s, Ar), 127.2 (d), 129.8 (d), 130.6 (d), 146.0 (s, Ar), 149.7 (d), 162.6 (s, Ar). LRMS EI E^+ 290 ([M]$^+$, 18%), 226 (72%), 197 (86%), 133 (100%).

Preparation of (*E*)-Phenyl-(2-(3-methoxyphenyl))vinylsulfonate (15e)
To a solution of phenyl vinylsulfonate **14** (0.5 g, 2.71 mmol) in *N, N*-dimethylformamide (10 mL) was added *N*-methyl-dicyclohexylamine (1.06 g, 5.42 mmol, 1.15 mL), palladium (II) acetate (30 mg, 0.14 mmol) and 3-iodoanisole (0.95 g, 4.07 mmol) and the reaction mixture left to stir at 80 ºC for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 2M HCl (3 × 100 mL) and 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 40% to 60% $CHCl_3$ in petroleum ether to afford (*E*)-Phenyl-2-(3-methoxyphenyl)vinylsulfonate **15e** as a pale yellow oil (0.29 g, 1.00 mmol, 37%). R_f 0.31 (40% $CHCl_3$ in petroleum ether); ν_{max} (solid)/cm^{-1} 3065 m, 2940 m, 2838 m, 1617 s, 1597 s, 1579 s, 1486 s; δ_H (300 MHz; $CDCl_3$) 3.82 (3H, s, OC***H***$_3$), 6.88 (1H, d, HC=C***H***SO_3Ph, *J* 15.5), 6.98-7.06 (3H, m, Ar***H***), 7.24-7.37 (6H, m, Ar***H***), 7.47 (1H, d, ***H***C=CHSO$_3$Ph, *J* 15.5); δ_C (300 MHz; $CDCl_3$) 55.4 (q, ***C***H3), 113.6 (d), 117.5 (d), 121.0 (d), 121.2 (d), 122.5 (d), 127.3 (d), 129.9 (d), 130.3 (d), 133.0 (s, Ar), 146.2 (d), 149.6 (s, Ar), 160.1 (s, Ar). LRMS EI E^+ 290 ([M]$^+$, 10%), 226 (100%), 197 (98%), 148 (93%).

Preparation of (*Z*)-Phenyl (1-bromo-2-phenyl)vinylsulfonate (17)
To a solution of 2-phenylethene-1-phenylsulfonate ester **16** (0.50 g, 1.91 mmol) in acetic acid (20 mL) was added bromine (4.6 g, 28.7 mmol, 1.5 mL) and the reaction mixture left to stir for 1h. The reaction was concentrated *in vacuo* to afford crude 2-phenylethane-1,2-dibromo-1-phenylsulfonate ester. To a solution of crude 2-phenylethane-1,2-dibromo-1-phenylsulfonate ester in CH_2Cl_2 (20 mL) was added NEt_3 (0.25 g, 2.47 mmol, 0.34 mL) and the reaction mixture left to stir for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 2M HCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% Et_2O in petroleum ether and recrystallised from CH_2Cl_2/hexane to afford 2-phenylethene-1-bromo-1-phenylsulfonate ester **17** (0.55 g, 1.62 mmol, 85%) as a white solid. R_f 0.40 (20% Et_2O in petroleum ether); m.p. 127-130 ºC; ν_{max} (solid)/cm^{-1} 3061 m, 3024 m, 1599 s, 1586 s, 1487 s; δ_H (300 MHz; $CDCl_3$) 7.13-7.47 (8H, m, Ar***H***), 7.31 (2H, dd, Ar***H***, *J* 0.9, 7.2), 7.96 (1H, s, ***H***C=C); δ_C (300 MHz; $CDCl_3$) 113.0 (s), 122.2 (d), 127.7 (d), 128.9 (d), 130.0 (d), 130.2 (d), 131.3 (s), 131.6 (d), 149.7 (s); LRMS FAB E^+ 341 ([$MBr^{81}H$]$^+$, 97%), 339 ([$MBr^{79}H$]$^+$, 100%), 195 (35%), 181 (38%), 165 (46%), 157 (99%), 155 (100%).

Preparation of 2-amino-2-phenylethane-1-bromo-1-phenylsulfonate ester (18)
To a solution of 2-phenylethene-1-bromo-1-phenylsulfonate ester **17** (0.9 g, 2.65 mmol) in dimethyl sulfoxide (25 mL) was added concentrated ammonia (3 mL) and the reaction mixture left to stir at room temperature for 2h. The reaction mixture was diluted with Et_2O (250 ml) and washed with H_2O (3 × 100 mL) and brine (2 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 1% MeOH in $CHCl_3$ to afford 2-amino-2-phenyl-ethane-1-bromo-1-phenylsulfonate ester **18a-b** as a pale yellow oil (0.51 g, 1.43 mmol, 54%) and as a mixture of diastereomers in a 2:1 ratio (Diastereomer A: Diastereomer B). Diastereomer A: R_f 0.08 (20% Et_2O in petroleum ether); ν_{max} (film)/cm^{-1} 3401 w, 3371 w, 2922 m, 1624 m, 1586 m, 1551 m, 1486 s; δ_H (300 MHz; $CDCl_3$) 2.02 (2H, app br s, CH(Ar)N***H***$_2$), 4.93 (1H, d, C***H***CH(Ar)NH$_2$, *J* 1.4), 5.17 (1H, d, CHC***H***(Ar)NH$_2$, *J* 1.4), 7.26-7.46 (10H, m, Ar***H***); δ_C (300 MHz; $CDCl_3$) 55.0 (d), 68.7 (d), 121.9 (d, Ar), 126.7 (d, Ar), 127.8 (d, Ar), 128.5 (d, Ar), 128.8 (d, Ar), 130.2 (d, Ar),

139.5 (s, Ar), 149.4 (s, Ar); LRMS EI E^+ 358 ($[MBr^{81}H]^+$, 5%), 356 ($[MBr^{79}H]^+$, 5%), 119 (37%), 106 (100%), 95 (62%). Diastereomer B: R_f 0.05 (20% Et_2O in petroleum ether); ν_{max} (film)/cm^{-1} 3392 w, 3371 w, 2924 m, 1600 m, 1586 m, 1487 s; δ_H (300 MHz; $CDCl_3$) 2.09 (2H, app br s, CH(Ph)N***H***$_2$), 4.72 (1H, d, C***H***CH(Ph)NH_2, *J* 7.5), 5.15 (1H, d, CHC***H***(Ph)NH_2, *J* 7.5), 7.26-7.45 (10H, m, Ar***H***); δ_C (300 MHz; $CDCl_3$) 58.6 (d), 64.9 (d), 122.0 (d, Ar), 127.7 (d, Ar), 128.6 (d, Ar), 128.7 (d, Ar), 128.8 (d, Ar), 130.1 (d, Ar), 140.1 (s, Ar), 149.5 (s, Ar); LRMS CI E^+ 358 ($[MBr^{81}H]^+$, 20%), 356 ($[MBr^{79}H]^+$, 20%), 261 (40%), 196 (55%), 195 (64%), 120 (82%), 106 (64%), 95 (100%).

Preparation of 2-*N*-(4-nitrobenzoyl)-2-phenylethane-1-bromo-1-phenylsulfonate ester (19a)
To a solution of 2-amino-2-phenylethane-1-bromo-1-phenylsulfonate ester **18a** (diasteromer A, 0.50 g, 1.40 mmol) in CH_2Cl_2 (30 ml) was added 4-nitrobenzoyl chloride (0.34 g, 1.83 mmol) and pyridine (0.33 g, 4.21 mmol, 0.35 mL) and the reaction mixture left to stir at room temperature for 1h. The reaction mixture was diluted with Et_2O (250 ml) and washed with 2M HCl (3 × 100 mL) and brine (2 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 20% Et_2O in pertroleum ether and recrystallised from CH_2Cl_2/hexane to afford 2-*N*-(4-nitrobenzoyl)-2-phenylethane-1-bromo-1-phenylsulfonate ester **19a** (0.54 g, 1.07 mmol, 77%) as a white crystals. R_f 0.32 (40% Et_2O in petroleum ether); m.p. 137-138 ºC; ν_{max} (solid)/cm^{-1} 3236 m, 3066 m, 2983 w, 1651 s, 1600 m, 1586 m, 1519 s, 1485 s, 1344 s; δ_H (300 MHz; $CDCl_3$) 5.37 (1H, d, CHCH(Ar)N***H***, *J* 3.3), 6.30 (1H, dd, CHC***H***(Ar)NH, *J* 3.3, 8.4), 7.23 (1H, d, C***H***CH(Ar), *J* 8.4), 7.32-7.46 (10H, m, Ar***H***), 7.97 (2H, d, Ar***H***, *J* 8.7), 8.24 (2H, d, Ar***H***, *J* 8.7); δ_C (300 MHz; $CDCl_3$) 53.0 (d), 64.0 (d), 121.8 (d), 124.0 (d), 126.6 (d), 128.0 (d), 128.6 (d), 129.1 (d), 129.1 (d), 130.3 (d), 136.1 (s), 139.3 (s), 149.0 (s), 149.9 (s), 165.0 (s); LRMS CI E^+ 507 ($[MBr^{81}H]^+$, 10%), 505 ($[MBr^{79}H]^+$, 10%), 269 (60%), 167 (40%), 120 (89%), 95 (100%). HRMS (CI) $[MH]^+$, $C_{21}H_{18}BrN_2O_6S$ Requires 505.00689. Found 505.00617.

Preparation of 2-*N*-(4-nitrobenzoyl)-2-phenylethane-1-bromo-1-phenylsulfonate ester (19b)
To a solution of 2-amino-2-phenyl-ethane-1-bromo-1-phenylsulfonate ester **18b** (diasteromer B, 0.27 g, 0.76 mmol) in CH_2Cl_2 (30 ml) was added 4-nitrobenzoyl chloride (0.18 g, 0.99 mmol) and pyridine (0.18 g, 2.28 mmol, 0.18 mL) and the reaction mixture left to stir at room temperature for 1h. To work up, the reaction mixture was diluted with Et_2O (250 ml) and washed with 2M HCl (3 × 100 mL) and brine (2 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 40% to 60% Et_2O in pertroleum ether and recrystallised from CH_2Cl_2/hexane to afford 2-*N*-(4-nitrobenzoyl)-2-phenylethane-1-bromo-1-phenylsulfonate ester **19b** (0.30 g, 0.59 mmol, 78%) as white crystals. R_f 0.27 (40% Et_2O in petroleum ether); m.p. 157-160 ºC; ν_{max} (solid)/cm^{-1} 3257 m, 2077 m, 2982 m, 1639 s, 1601 s, 1585 m, 1550 m, 1527 s, 1347 s; δ_H (300 MHz; 1% MeOD in $CDCl_3$) 5.73 (1H, d, CHC***H***(Ar), *J* 12.1), 6.24 (1H, d, C***H***CH(Ar), *J* 12.1), 7.12 (2H, d, Ar***H***, *J* 8.1), 7.23-7.38 (6H, m, Ar***H***), 7.50 (2H, d, Ar***H***, *J* 6.7), 7.94 (2H, d, Ar***H***, *J* 8.1), 8.21 (2H, d, Ar***H***, *J* 8.1); δ_C (300 MHz; 1% MeOD in $CDCl_3$) 56.1 (d), 60.9 (d), 121.6 (d), 123.8 (d), 127.7 (d), 127.8 (d), 128.6 (d), 128.9 (d), 129.2 (d), 130.0 (d), 135.9 (s), 139.1 (s), 149.1 (s), 149.8 (s), 165.3 (s); LRMS CI E^+ 507 ($[MBr^{81}H]^+$, 7%), 505 ($[MBr^{79}H]^+$, 7%), 269 (44%), 239 (41%), 167 (37%), 120 (85%), 95 (100%).

Preparation of 2-(4-nitrophenyl)-4-phenyloxazole (20)
To a solution of 2-*N*-(4-nitrobenzoyl)-2-phenylethane-1-bromo-1-phenylsulfonate ester **19a** (0.20 g, 0.41 mmol) in *N, N*-dimethylformamide (10 mL) was added sodium *tert*-butoxide (0.08 g, 0.82 mmol) portionwise and the reaction mixture left to stir at room temperature for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 10% to 30% Et_2O in petroleum ether and recrystallised from CH_2Cl_2/hexane to afford 2-(4-nitrophenyl)-4-phenyloxazole **20a** (0.06 g, 0.23 mmol, 55%) as white crystals. R_f 0.75 (20% Et_2O in petroleum ether); m.p. 174-176 ºC; ν_{max} (solid)/cm^{-1} 3104 m, 2925 m, 2855 m, 1723 m, 1603 m, 1584 m, 1558 m, 1515 s, 1344 s; δ_H (300 MHz; $CDCl_3$) 7.38 (1H, d, Ar***H***, *J* 8.5), 7.43-7.48 (2H, m, Ar***H***), 7.83 (2H, d, Ar***H***, *J* 8.5), 8.05 (1H, s, O***H***C=C(Ar)N), 8.28 (2H, d, Ar***H***, *J* 8.7), 8.34 (2H, d, Ar***H***, *J* 8.7; δ_C (300 MHz; $CDCl_3$) 124.2 (d), 125.7 (d), 127.2 (d), 128.6 (d), 128.9 (d), 130.5 (s), 132.9 (s), 134.8 (d), 143.0 (s), 148.7 (s), 159.8 (s). LRMS CI E^+ 267 ($[MH]^+$, 55%), 266 ($[M]^+$, 45%), 265 (60%), 237 (100%), 192 (26%), 165 (25%), 104 (48%). HRMS (EI) M^+, $C_{15}H_{10}N_2O_3$ Requires 266.06859. Found 266.06753

Preparation of 2-(4-nitrophenyl)-4-phenyloxazole (20)
To a solution of 2-(4-nitrobenzoyl)-2-phenylethane-1-bromo-1-phenylsulfonate ester **19b** (0.30 g, 0.59 mmol) in *N, N*-dimethylformamide (20 mL) was added sodium *tert*-butoxide (0.11 g, 1.18) portionwise and the reaction mixture left to stir at room temperature for 1h. The reaction mixture was diluted with Et_2O (100 mL), washed with 10% w/v aq. LiCl (3 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography eluting with 50% $CHCl_3$ in hexane and recrystallised from CH_2Cl_2/hexane to afford 2-(4-nitrophenyl)-4-phenyloxazole **20b** (0.10 g, 0.37 mmol, 62%) as white crystals. R_f 0.75 (20% Et_2O in petroleum ether); m.p. 174-176 ºC; ν_{max} (solid)/cm^{-1} 3104 m, 2923 m, 2855 m, 1723 m, 1603 m, 1584 m, 1557 m, 1516 s, 1343 s; δ_H (300 MHz; $CDCl_3$) 7.38 (1H, d, Ar***H***, *J* 8.5), 7.43-7.48 (2H, m, Ar***H***), 7.82 (2H, d, Ar***H***, *J* 8.5), 8.05 (1H, s, O***H***C=C(Ar)N), 8.28 (2H, d, Ar***H***, *J* 8.7), 8.34 (2H, d, Ar***H***, *J* 8.7); δ_C (300 MHz; $CDCl_3$) 124.2 (d), 125.7 (d), 127.2 (d), 128.6 (d), 128.9 (d), 130.5 (s), 132.9 (s), 134.8 (d), 143.0 (s), 148.7 (s), 159.8 (s); LRMS EI E^+ 267 ($[MH]^+$, 20%), 266 ($[M]^+$, 100%), 238 (20%), 192 (40%), 191 (22%), 165 (34%).

[1] A. Y. Berlin, V. I. Maimind, *Zh. Obshch. Khim*. 1951, **21**, 132
[2] E. V. Brown, *J. Org. Chem.* 1977, **42**, 3208-3209
[3] O. Ottoni, R. Cruz, R. Alves, *Tetrahedron* 1998, **54**, 13915-13928
[4] M. Dadkhad, B. Prijs, *Helv. Chim. Acta.* 1962, **45**, 375-81