

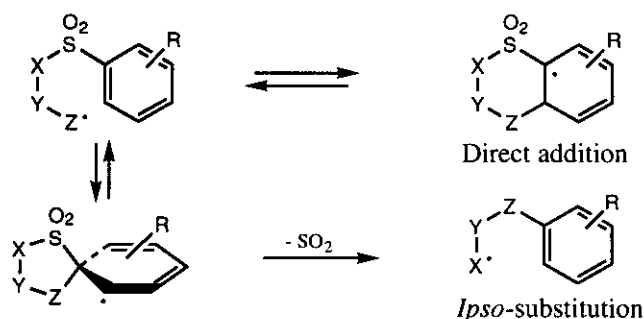
# A NOVEL ROUTE TO 4-ARYL-5,6-DIHYDRO-1,2-OXATHIIN-2,2-DIOXIDES AND RELATED HETEROCYCLIC SYSTEMS

Eric Bonfand,<sup>a</sup> William B. Motherwell,<sup>a\*</sup> Andrew M. K. Pennell,<sup>b</sup>  
 Muhammed K. Uddin,<sup>a</sup> and Feroze Ujjainwalla<sup>b</sup>

Departments of Chemistry, (a) Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1 H 0AJ, U. K. and (b) Imperial College of Science, Technology and Medicine, Exhibition Road, South Kensington, London SW7 2AY, U. K.

**Abstract**—The addition of a tri n-butylstannyl radical to arene and heteroarene sulfonate esters of homopropargyl alcohol triggers a sequence of [1,6] *ipso*-substitution followed by 6-*endo* addition and elimination to yield unusual 4-aryl-5,6-dihydro-1,2-oxathiin-2,2-dioxides and related heterocyclic systems.

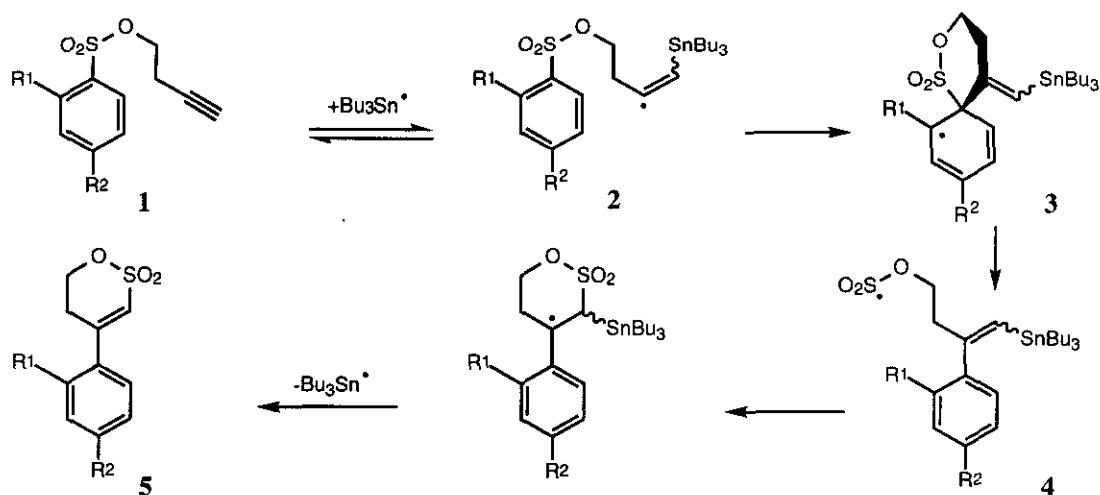
We have recently demonstrated in a series of communications<sup>1-3</sup> that intramolecular free radical *ipso*-substitution<sup>4</sup> of a suitably constituted sulfonyl substituted aromatic or heteroaromatic derivative by a second *ortho*-substituted aryl radical is a viable approach for the synthesis of biaryls and their heterocyclic congeners. As illustrated in a generalised form in Scheme 1, the successful implementation of such a strategy for biaryl synthesis ( $Z = \textit{ortho}$  substituted aryl radical) requires that the reaction pathway is directed *via* a spirocyclic intermediate capable of rearomatisation and that the alternative direct addition pathway is suppressed. As might be anticipated, the nature and number of the atoms ( $X, Y$ ) in the tethering chain and the location and electronic character of the substituents ( $R$ ) on the sulfonyl substituted acceptor ring play a vital role in determining the outcome of these reactions.



Scheme 1

Such a strategy need not of course be restricted to the formation of biaryls, and it was therefore of interest to study the behavior of vinyl radicals ( $Z = \text{vinyl radical}$ ) in such systems, with a view to assessing the potential of this approach for the construction of substituted styrene derivatives. We now report, in full detail,<sup>5</sup> on the unexpected outcome of a series of prototypical reactions of this class.

In the first instance, as shown in Scheme 2, we elected to use the elegant protocol established by Stork<sup>6</sup> for the generation of vinyl radicals **2** by reversible addition of tri-*n*-butylstannyl radicals to alkynes. Readily prepared arenesulfonate esters of homopropargyl alcohol **1** were accordingly selected as substrates in the anticipation that the [1,6] *ipso*-substitution pathway *via* spirocycles **3** would be favoured over the potentially competitive [1,7] addition process to the aromatic ring. To our initial surprise however, the subsequent extrusion of sulfur dioxide from radicals **4** to furnish functionalised vinyl stannanes was not observed, and the chosen alternative featured a 6-*endo* trig addition-elimination sequence as shown to provide  $\beta$ -aryl cyclic  $\alpha,\beta$ -unsaturated sultones **5**. From a kinetic standpoint, it is tempting to speculate that the relatively slow loss of sulfur dioxide from intermediates **4** parallels the known reluctance<sup>7</sup> of alkoxy carbonyloxy radicals ( $\text{ROCO}_2\cdot$ ) to lose carbon dioxide ( $k \leq 10^5 \text{ sec}^{-1}$ ). Further support for the mechanistic pathway outlined comes from a detailed study by Walton<sup>8</sup> who has observed preferential 6-*endo* cyclisation of the pentenesulfonyl radical.



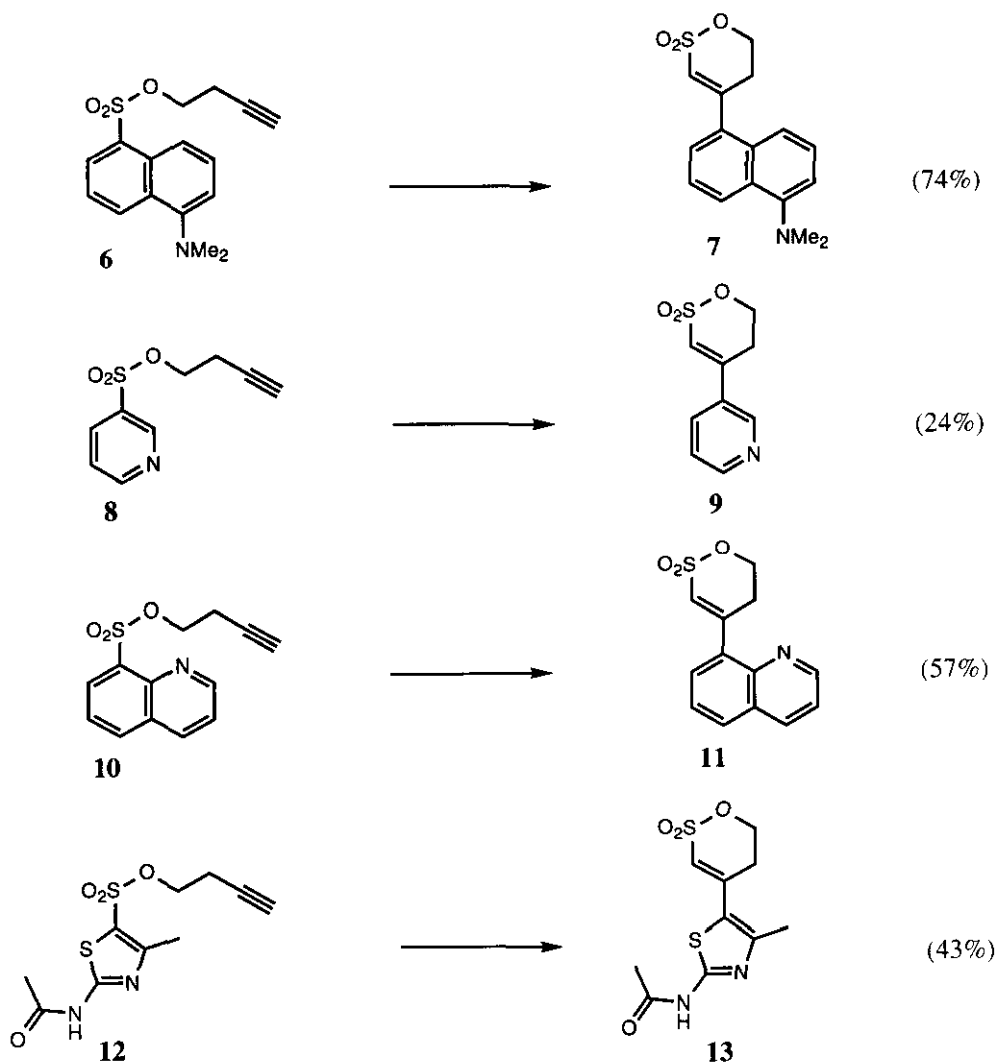
Scheme 2

The results for a variety of aromatic substrates are shown in Table 1, and reveal that the above process constitutes a general route to the 5,6-dihydro-1,2-oxathiin-2,2-dioxide unit. To the best of our knowledge, only two isolated examples<sup>9,10</sup> of this unusual class of heterocycle at such an oxidation level are known, and neither of these possess the  $\beta$ -aryl functionality present in **5**. From a practical viewpoint, although reactions were carried out by slow motor-driven syringe addition of tri-*n*-butylstannane containing AIBN as initiator to the substrate, simple hydrostannylation of the alkyne was, in all cases, the major competing reaction. Thus, although the overall transformation of **1** to **5** may be considered as a tri-*n*-butylstannyl radical catalysed rearrangement, the relative inefficiency of the chain propagation sequence and the competitive hydrostannylation reaction combine to thwart this idealised picture. Moreover, efforts to induce the rearrangement using hexabutylditin under photochemical conditions proved to be impractical since, although the reaction of **1** ( $\text{R}^1 = \text{CO}_2\text{Me}$ ,  $\text{R}^2 = \text{H}$ ) proceeded cleanly at low conversion (**5** 18% : **1** 75%), prolonged irradiation led to photodecomposition of the desired product **5**. In similar fashion, the use of tris(trimethylsilyl)silane in place of tri-*n*-butylstannane did not offer any improvement, with

reaction of **1** yielding only 28% of cyclic sultone **5** and hydrosilylation as the dominant process (45%). The present reaction can also be applied to heterocyclic arenesulfonates, as shown by the additional examples in Scheme 3. In all the examples listed in Table 1 and Scheme 3, the steric and electronic effects of substituents sited around the sulfonyl substituted acceptor ring parallel those which we have

**Table 1** Tri *n*-butylstannyl Radical Rearrangement of But-3-ynyl Arenesulfonates

| Substrate | R <sup>1</sup>     | R <sup>2</sup> | Product   | Yield (%) |
|-----------|--------------------|----------------|-----------|-----------|
| <b>1a</b> | H                  | Me             | <b>5a</b> | 35        |
| <b>1b</b> | CO <sub>2</sub> Me | H              | <b>5b</b> | 61        |
| <b>1c</b> | F                  | F              | <b>5c</b> | 39        |
| <b>1d</b> | H                  | OMe            | <b>5d</b> | 8         |
| <b>1e</b> | H                  | N(Me)COMe      | <b>5e</b> | 19        |
| <b>6</b>  |                    |                | <b>7</b>  | 74        |

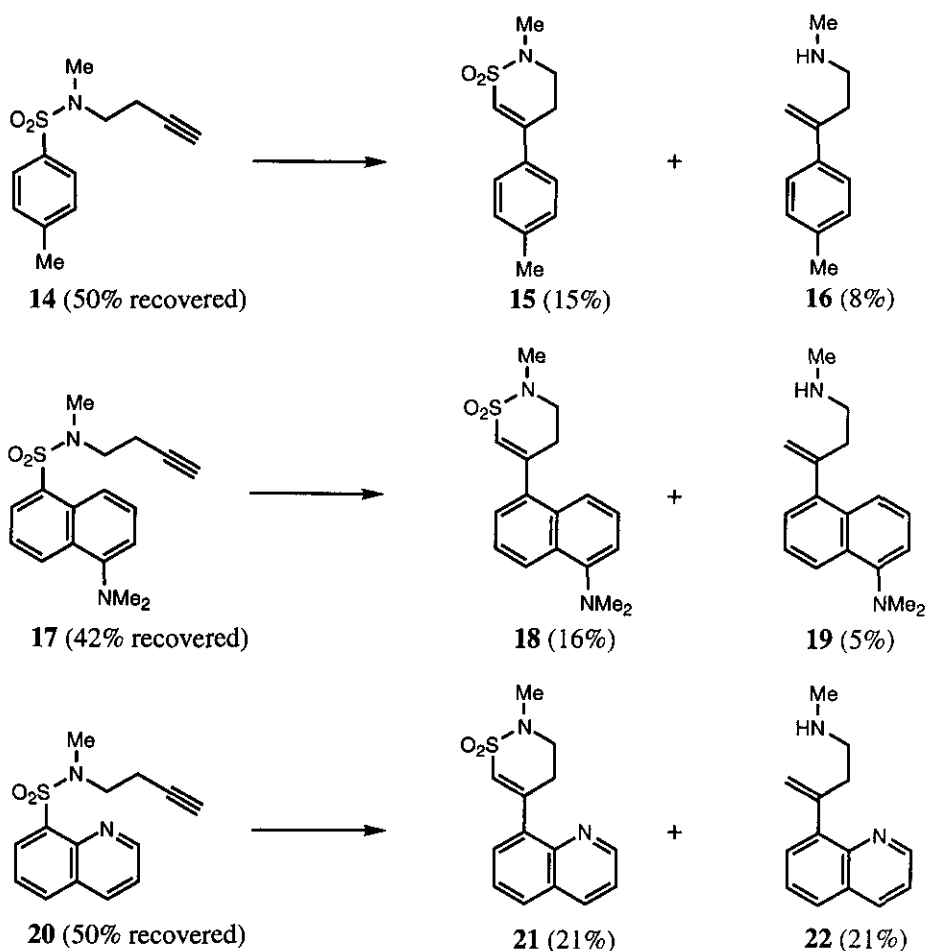


Reagents: <sup>n</sup>Bu<sub>3</sub>SnH, AIBN, benzene, reflux.

**Scheme 3**

previously outlined in the synthesis of biaryls and heterobiaryls,<sup>2</sup> with flanking *ortho* substituents being demonstrably powerful directors of *ipso*-substitution.

Our attention was then directed towards the behaviour of the analogous *N*-methylsulfonamide derivatives. Although the replacement of the oxygen atom by the *N*-methyl group is, at first sight, a trivial one, our experience in biaryl synthesis<sup>3</sup> has shown that the consequences may be profound. In the event, as shown by some representative examples in Scheme 4, the preparation of the corresponding cyclic sultams by this approach is of limited synthetic use, and, to our surprise, reactions proved to be extremely sluggish, even with continual additions of AIBN as initiator. Thus, for example, in sharp contrast to the efficient reaction of the arenesulfonate **1** ( $R^1 = \text{CO}_2\text{Me}$ ,  $R^2 = \text{H}$ ) (Table 1), which possesses a favourably located *ortho*-carbomethoxyl group, several attempts to induce reaction of the corresponding *N*-methylsulfonamide led only to substantial recovery of starting material, accompanied by trace amounts of the hydrostannylation product. The sulfonamide series is further complicated by the fact that the formation of amines,



Reagents :  $n\text{Bu}_3\text{SnH}$ , AIBN, benzene, reflux.

Amines (**16**) (**19**) and (**22**) were isolated following protodestannylation on work up.

Scheme 4

which also form part of the *ipso*-substitution manifold, is a significant competing process. These products arise, either as a result of tri-*n*-butylstannyl radical induced cleavage of the heterocyclic sulfonamide linkage in the product sultam,<sup>11</sup> or at the intermediate stage following *ipso*-substitution and rearomatisation where radicals  $R_2NSO_2\cdot$  may well lose sulfur dioxide at an appreciate rate.<sup>7</sup>

In summary, the present sequence of reactions has demonstrated the viability of the intramolecular [1,6] *ipso*-substitution reaction of vinylic radicals to suitably constituted aromatic and heteroaromatic sulfonyl acceptors and also led to the discovery of a novel route to 4-aryl-5,6-dihydro-1,2-oxathiin-2,2-dioxides.

## EXPERIMENTAL

**General:** <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> unless otherwise stated at 250, 270, 300, 400 and 500 MHz on spectrometers Bruker WM 250, Jeol GSX 270, Bruker AC 300, VarianVXR 400 and Bruker AM 500 respectively. Residual protic solvent was used as internal reference. Coupling constants were measured in hertz. <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> unless otherwise stated at 68, 100 and 126 MHz on spectrometers Jeol GSX 270, Jeol GX 400 and Bruker AM 500 respectively, using the resonances of the solvent as internal reference. IR spectra were recorded on Perkin Elmer 983G, Perkin Elmer 881, and Perkin Elmer 1600 FT-IR instruments. MS spectra were recorded using VG-7070B, VG 12-253, VG ZAB-E, Jeol DX303, VG TRIO-1 and VG-Autospec instruments University. Melting points were determined on Reichert and Gallenkamp hot stage instruments and are uncorrected.

**Materials:** Flash column chromatography was performed on Merck Kieselgel 60 (230-400 mesh) at low positive pressure. THF and benzene solvents were distilled from sodium-benzophenone ketyl; CH<sub>2</sub>Cl<sub>2</sub> from phosphorous pentoxide. Petrol refers to petroleum ether (bp 40-60°C). Tri-*n*-butylstannane was distilled prior to use.

### Preparation of 3-butyryl arene sulfonates and sulfonamides

**3-Butyryl 4-methylbenzenesulfonate (1a).** To a stirred solution of 3-butyryl-1-ol (1.04 g, 14.8 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (14.5 mL) and pyridine (2.7 mL) at 0°C, was added 4-methylbenzenesulfonyl chloride (4.08 g, 21.4 mmol) in small portions over 5 min. After a further 18 h, the reaction mixture was warmed to rt, Et<sub>2</sub>O (45 mL) and water (10 mL) were added and the organic layer was washed thoroughly with 10% aq. HCl (2 mL), sat. aq. NaHCO<sub>3</sub> (2 mL), water (2 mL) and was then dried (MgSO<sub>4</sub>). The solvent was removed *in vacuo* and the residue was purified by column chromatography (30% Et<sub>2</sub>O/petrol) to yield (1a) (2.71 g, 82%) as a colourless oil; IR (neat) 3306 (≡CH), 1597, 1353 (SO<sub>2</sub>), 1181 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 7.78 (2H, d, *J* 7.5, ArH), 7.34 (2H, d, *J* 7.5, ArH), 4.08 (2H, t, *J* 7.2, OCH<sub>2</sub>), 2.53 (2H, dt, *J* 2.6, 7.2, ≡CCH<sub>2</sub>), 2.40 (3H, s, ArCH<sub>3</sub>), 1.97 (1H, t, *J* 2.6, ≡CH); MS *m/z* (EI) 224 (M<sup>+</sup>), 185, 172, 91; Anal. Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>S: C, 58.91, H, 5.39. Found C, 58.81; H, 5.15.

**Methyl 2-(3-butyryloxysulfonyl)benzoate (1b).** Methyl 2-(chlorosulfonyl)benzoate (4.69 g, 20.0 mmol) was added portionwise, over *ca.* 10 min, *via* a solid addition tube, to a stirred mixture of 3-butyryl-1-ol (1.00 g, 14.3 mmol), DMAP (0.17 g, 1.4 mmol) and pyridine (2.60 mL, 32.1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (14 mL) at 0°C. After allowing to warm to 25°C, the resulting solution was left to stand overnight. The reaction mixture was then poured into water and extracted with Et<sub>2</sub>O. The combined extract was washed successively with sat. aq. CuSO<sub>4</sub>, water, aq. 1N HCl, sat. aq. NaHCO<sub>3</sub> and brine. The organic layer was dried (MgSO<sub>4</sub>) and evaporated *in vacuo*. Purification of the residue by flash chromatography (40-60% Et<sub>2</sub>O/petrol) afforded (1b) (3.06 g, 80%) as a colourless oil; IR (neat) 3291 (≡CH), 1740 (C=O), 1366 (SO<sub>2</sub>), 1263, 1186 (SO<sub>2</sub>), 976 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 8.05 (1H, dd *J* 1.4, 7.0, ArH), 7.68 (3H, m, ArH), 4.25 (2H, t, *J* 7.1, OCH<sub>2</sub>), 4.25 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.63 (2H, dt, *J* 2.6, 7.1, ≡CCH<sub>2</sub>), 1.99 (1H, t, *J* 2.6, ≡CH); MS *m/z* (EI) 267 (M<sup>+</sup>, 15), 199 (100), 195 (7).

185 (15), 174 (5), 135 (32), 121 (7), 104 (9), 92 (12), 77 (33); Anal. Calcd for  $C_{12}H_{12}O_5S$ : C, 53.72; H, 4.51. Found: C, 53.58; H, 4.23.

**3-Butynyl 2,4-difluorobenzenesulfonate (1c).** A solution of 2,4-difluorobenzenesulfonyl chloride (1.97 g, 7.13 mmol) in dry  $CH_2Cl_2$  (5 mL) was added dropwise, over ca. 10 min, to a stirred mixture of 3-butyne-1-ol (0.50 g, 7.1 mmol), DMAP (87 mg, 0.71 mmol) and DIPEA (2.80 mL, 16.1 mmol) in dry  $CH_2Cl_2$  (5 mL) at  $-10^\circ C$ . After 1 d, the reaction mixture was poured into water and extracted with  $CH_2Cl_2$ . The combined extract was washed with brine, dried ( $MgSO_4$ ) and evaporated *in vacuo*. Purification of the residue by chromatography (30-40%  $Et_2O$ /petrol) gave (1c) (0.84 g, 48%) as a colourless oil, IR (neat) 3295 ( $\equiv CH$ ), 1605, 1482, 1433, 1371 ( $SO_2$ ), 1279, 1187 ( $SO_2$ ), 1151, 1125, 1078, 972, 908, 860  $cm^{-1}$ ;  $^1H$  NMR (500 MHz)  $\delta$  7.96 (1H, dt,  $J$  8.0, 6.0, ArH), 7.03 (2H, m, ArH), 4.27 (2H, t,  $J$  7.0,  $OCH_2$ ), 2.63 (2H, dt,  $J$  2.7, 6.8,  $\equiv CCH_2$ ), 1.98 (1H, t,  $J$  2.6,  $\equiv CH$ );  $^{13}C$  NMR (126 MHz)  $\delta$  166.6 (dd,  $J$  11.1, 259.5), 160.3 (dd,  $J$  13.1, 261.7), 132.7 (d,  $J$  11.0), 120.7 (dd,  $J$  11.8), 112.1 (dd,  $J$  3.3, 22.8), 106.1 (t,  $J$  25.4), 78.0 (d), 70.9 (s), 68.5 (t), 19.5 (t); MS  $m/z$  (EI) 246 ( $M^+$ , 0.1), 207 (8), 177 (100), 129 (24), 113 (40), 101 (3), 93 (3), 63 (22), 55 (19), 52 (20); Anal. Calcd for  $C_{10}H_8O_3F_2S$ : C, 48.78, H, 3.28. Found: C, 48.71; H, 3.15.

**3-Butynyl 4-methoxybenzenesulfonate (1d).** Following a similar procedure as that described for 1c, 4-methoxybenzenesulfonyl chloride (1.92 g, 9.27 mmol) reacted with 3-butyne-1-ol (0.50 g, 7.1 mmol) for 2.5 d to give, after chromatography (30-40%  $Et_2O$ /petrol), the title compound (1d) (1.00 g, 58%) as a colourless oil; IR (neat) 3287 ( $\equiv CH$ ), 1595, 1576, 1496, 1357 ( $SO_2$ ), 1311, 1264, 1190, 1168 ( $SO_2$ ), 1099, 1024, 982, 904, 835, 809, 769, 666  $cm^{-1}$ ;  $^1H$  NMR (270 MHz)  $\delta$  7.86 (2H, d,  $J$  9.0, ArH), 7.01 (2H, d,  $J$  9.0, ArH), 4.09 (2H, t,  $J$  7.1,  $OCH_2$ ), 2.55 (2H, dt,  $J$  2.7, 7.1,  $\equiv CCH_2$ ), 1.97 (1H, t,  $J$  2.7,  $\equiv CH$ ); MS  $m/z$  (EI) 240 ( $M^+$ , 12), 188 (14), 171 (100), 146 (13), 123 (16), 107 (36), 92 (14), 77 (20); Anal. Calcd for  $C_{11}H_{12}O_4S$ : C, 54.99; H, 5.03. Found: C, 54.95; H, 4.93.

**3-Butynyl 4-(*N*-methylacetamido)benzenesulfonate (1e).** Following a similar procedure as that described for 1c, *N*-acetyl-sulfanilyl chloride (2.17 g, 9.27 mmol) reacted with 3-butyne-1-ol (0.50 g, 7.1 mmol) for 1 d to give, after chromatography (3-4%  $MeOH/CH_2Cl_2$ ), 3-butynyl 4-(acetamido)benzenesulfonate (1.39 g, 73%) as colourless crystals; mp  $89^\circ C$  ( $CH_2Cl_2$ /petrol); IR (neat) 3289 (NH,  $\equiv CH$ ), 1681 (C=O), 1592, 1359 ( $SO_2$ ), 1317, 1190, 1171 ( $SO_2$ ), 979  $cm^{-1}$ ;  $^1H$  NMR (270 MHz)  $\delta$  7.86 (1H, s, NH), 7.84 (2H, d,  $J$  9.0, ArH), 7.72 (2H, d,  $J$  9.0, ArH), 4.10 (2H, t,  $J$  6.8,  $OCH_2$ ), 2.55 (2H, dt,  $J$  2.7, 6.8,  $\equiv CCH_2$ ), 2.22 (3H, s,  $CH_3$ ), 1.97 (1H, t,  $J$  2.7,  $\equiv CH$ ); MS  $m/z$  (EI) 267 ( $M^+$ , 24), 225 (42), 198 (41), 173 (31), 156 (49), 134 (19), 131 (22), 108 (30), 93 (28), 92 (37), 65 (30), 43 (100); Anal. Calcd for  $C_{12}H_{13}NO_4S$ : C, 53.92; H, 4.90, N, 5.24. Found: C, 54.05; H, 4.86; N, 5.16. A solution of 3-butynyl 4-(acetamido)benzenesulfonate (0.44 g, 1.7 mmol) in THF (6 mL) was added dropwise to a stirred suspension of freshly washed sodium hydride (0.12 g of a 60% dispersion in mineral oil, 3.0 mmol) in THF (1 mL) at  $25^\circ C$ . After ca. 1 h, iodomethane (1.03 mL, 16.5 mmol) was added and the resulting solution maintained at  $25^\circ C$  overnight. The reaction mixture was then poured into water and extracted with  $CH_2Cl_2$ . The combined extract was washed with brine, dried ( $MgSO_4$ ) and concentrated *in vacuo*. Purification of the residue by flash chromatography (75-85%  $AcOEt$ /petrol) provided (1e) (0.26 g, 57%) as colourless crystals; mp  $64.5-65.5^\circ C$  ( $CH_2Cl_2$ /petrol); IR (neat) 3287 ( $\equiv CH$ ), 1684 (C=O), 1593, 1496, 1360 ( $SO_2$ ), 1178 ( $SO_2$ ), 977  $cm^{-1}$ ;  $^1H$  NMR (270 MHz)  $\delta$  7.97 (2H, d,  $J$  8.8, ArH), 7.41 (2H, d,  $J$  8.6, ArH), 4.18 (2H, t,  $J$  7.1,  $OCH_2$ ), 3.33 (3H, s, NMe), 2.60 (2H, dt,  $J$  2.7, 6.9,  $\equiv CCH_2$ ), 2.00 (3H, s, Me), 1.98 (1H, t,  $J$  2.7,  $\equiv CH$ );  $^{13}C$  NMR (68 MHz)  $\delta$  169.9 (s), 149.3 (s), 134.5 (s), 129.4 (d), 127.4 (d), 78.2 (d), 70.9 (s), 67.8 (t), 37.3 (q), 22.6 (q), 19.5 (t); MS  $m/z$  (EI) 281 ( $M^+$ , 71), 239 (74), 212 (41), 187 (68), 170 (30), 148 (30), 145 (32), 122 (49), 107 (45), 106 (35), 105 (27), 77 (25), 43 (100); Anal. Calcd for  $C_{13}H_{15}NO_4S$ : C, 55.50; H, 5.37; N, 4.98. Found: C, 55.75; H, 5.48, N, 4.97.

**3-Butynyl 5-(dimethylamino)-1-naphthalenesulphonate (6).** Following a similar procedure as that described for **1c**, 5-(dimethylamino)naphthalenesulphonyl chloride (2.69 g, 9.99 mmol) reacted with 3-butyne-1-ol (0.50 g, 7.1 mmol) for 1.5 d to give, after chromatography on silica gel (50-70% Et<sub>2</sub>O/petrol), the title compound (**6**) (1.94 g, 90%) as a bright green oil; IR (neat) 3294 ( $\equiv$ CH), 1460, 1410, 1351 (SO<sub>2</sub>), 1205, 1174 (SO<sub>2</sub>), 1070, 983 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz)  $\delta$  8.61 (1H, dd, *J* 1.1, 8.6, ArH), 8.28 (1H, dd, *J* 1.2, 7.3, ArH), 8.26 (1H, d, *J* 8.7, ArH), 7.59 (1H, t, *J* 7.7, ArH), 7.55 (1H, t, *J* 8.7, ArH), 7.21 (1H, d, *J* 7.6, ArH), 4.08 (2H, t, *J* 7.0, OCH<sub>2</sub>), 2.89 (6H, s, NMe<sub>2</sub>), 2.52 (2H, dt, *J* 2.7, 7.1,  $\equiv$ CCH<sub>2</sub>), 1.87 (1H, t, *J* 2.8,  $\equiv$ CH). MS *m/z* (EI) 303 (M<sup>+</sup>, 100), 251 (55), 234 (11), 170 (54), 155 (12), 154 (18), 127 (16), 126 (8); HRMS Calcd for C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>S: 303.0929. Found: 303.0933; Anal. Calcd for C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>S: C, 63.35; H, 5.65; N, 4.62. Found: C, 63.31; H, 5.61, N, 4.51.

**3-Butynyl 3-pyridinesulfonate (8).** Following a similar procedure as that described for **1c**, 3-pyridinesulphonyl chloride (1.77 g, 9.99 mmol) reacted with 3-butyne-1-ol (0.50 g, 7.1 mmol) for 18 h to give, after chromatography (50-70% Et<sub>2</sub>O/petrol), the title compound (**8**) (1.10 g, 73%) as unstable colourless crystals; mp 32.5-34°C (Et<sub>2</sub>O); IR (neat) 3294 ( $\equiv$ CH), 1346 (SO<sub>2</sub>), 1204, 1141 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz)  $\delta$  9.14 (1H, dd, *J* 0.8, 2.4, ArH), 8.89 (1H, dd, *J* 1.6, 4.9, ArH), 8.21 (1H, ddd, *J* 1.6, 2.2, 8.1, ArH), 7.52 (1H, ddd, *J* 0.8, 4.9, 8.1, ArH), 4.21 (2H, t, *J* 6.7, OCH<sub>2</sub>), 2.60 (2H, dt, *J* 2.7, 6.9,  $\equiv$ CCH<sub>2</sub>), 1.96 (1H, t, *J* 2.6,  $\equiv$ CH); MS *m/z* (EI) 211 (M<sup>+</sup>, 13), 172 (14), 168 (14), 142 (47), 78 (100); Anal. Calcd for C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub>S: C, 51.17; H, 4.29; N, 6.63. Found: C, 50.98; H, 4.37; N, 6.48.

**3-Butynyl 8-quinolinesulfonate (10).** Following a similar procedure as that described for **1c**, 8-quinolinesulphonyl chloride (2.27 g, 9.99 mmol) reacted with 3-butyne-1-ol (0.50 g, 7.1 mmol) for 3.5 d to give, after chromatography (3-5% Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>), the title compound (**10**) (1.02 g, 55%) as colourless crystals; mp 80°C (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 3288 ( $\equiv$ CH), 1354 (SO<sub>2</sub>), 1175 (SO<sub>2</sub>), 977, 790 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz)  $\delta$  9.15 (1H, dd, *J* 1.8, 4.2, ArH), 8.52 (1H, dd, *J* 1.5, 7.4, ArH), 8.28 (1H, dd, *J* 1.8, 8.4, ArH), 8.13 (1H, dd, *J* 1.4, 8.2, ArH), 7.66 (1H, dd, *J* 7.4, 8.0, ArH), 7.57 (1H, dd, *J* 4.3, 8.4, ArH), 4.51 (2H, t, *J* 7.3, OCH<sub>2</sub>), 2.62 (2H, dt, *J* 2.6, 7.3,  $\equiv$ CCH<sub>2</sub>), 1.89 (1H, t, *J* 2.7,  $\equiv$ CH); MS *m/z* (EI) 261 (M<sup>+</sup>, 0.2), 192 (26), 167 (51), 129 (100), 128 (99), 102 (16), 101 (27); Anal. Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>3</sub>S: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.68, H, 4.22, N, 5.39.

**3-Butynyl 2-acetamido-4-methylthiazol-5-sulfonate (12).** To a suspension of 2-acetamido-4-methylthiazol-5-sulphonyl chloride (480 mg, 1.86 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 0°C were added 3-butyne-1-ol (465  $\mu$ L, 6 mmol) and pyridine (0.5 mL) over 5 min. The mixture was then stirred for 7 h at rt and allowed to stand for 2 d. Water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extract was washed with sat. aq. CuSO<sub>4</sub> and water, dried (MgSO<sub>4</sub>) and concentrated *in vacuo* to give the title compound (**12**) (320 mg, 44%) as a pale yellow solid; mp 141-143°C; IR (KBr) 3280 ( $\equiv$ CH), 3144 (NH), 1361 (SO<sub>2</sub>), 1175 (SO<sub>2</sub>), 910, 785 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz)  $\delta$  9.24 (1H, br s, NH), 4.21 (2H, t, *J* 6.8, OCH<sub>2</sub>), 2.61 (2H, dt, *J* 2.6, 6.8,  $\equiv$ CCH<sub>2</sub>), 2.58 (3H, s), 2.31 (3H, s), 1.99 (1H, t, *J* 2.7,  $\equiv$ CH); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 100 MHz)  $\delta$  16.9, 19.7, 22.9, 69.9, 71.5, 80.3, 117.9, 156.6, 161.4, 170.5; MS *m/z* (FAB) 289 (MH<sup>+</sup>, 100), 237 (10), 195 (18), 155 (16), 154 (40), 137 (31), 136 (41), 107 (19); HRMS Calcd for C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub>S: 289.0317. Found: 289.0330.

**N-(3-Butynyl)-N,4-dimethyl-benzenesulfonamide (14).** Following a similar procedure as that described for **1c**, 4-methylbenzenesulphonyl chloride (8.0 g, 42 mmol) reacted with 3-butyne-1-amine<sup>12</sup> (2.4 g, 35 mmol) to give, after chromatography (Et<sub>2</sub>O/petrol), *N*-(3-butyne-1-yl)-4-methylbenzenesulfonamide (70%) as white needles; mp 89-93°C; IR (neat) 3286 ( $\equiv$ CH, NH), 1337 (SO<sub>2</sub>), 1158 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz)  $\delta$  7.78 (2H, d, *J* 8.0, ArH), 7.35 (2H, d, *J* 8.0, ArH), 4.82 (1H, br s, NH), 3.13 (2H, dt, *J* 7.6, 2.7, NCH<sub>2</sub>), 2.45 (3H, s, ArCH<sub>3</sub>), 2.37 (2H, dt, *J* 7.5, 2.6,  $\equiv$ CCH<sub>2</sub>), 2.02 (1H, t, *J* 2.6,  $\equiv$ CH), MS *m/z* (FAB) 223 (M<sup>+</sup>, 24), 185 (100). As described in the preparation of **1e**, the *N*-methylation of *N*-(3-butyne-1-yl)-4-methylbenzenesulfonamide afforded, after chromatography (Et<sub>2</sub>O/petrol), the title compound (**14**) (98%) as a yellow oil.

IR (neat) 1598, 1457, 1340 (SO<sub>2</sub>), 1161 (SO<sub>2</sub>), 959 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz) δ 7.65 (2H, d, *J* 8.0, ArH), 7.30 (2H, d, *J* 8.0, ArH), 3.19 (2H, t, *J* 7.3, NCH<sub>2</sub>), 2.79 (3H, s, NCH<sub>3</sub>), 2.44 (2H, dt, *J* 2.6, 7.5, NCH<sub>2</sub>), 2.41 (3H, s, ArCH<sub>3</sub>), 1.97 (1H, t, *J* 2.6, ≡CH); Anal. Calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub>S: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.82; H, 6.34; N, 5.93.

***N*-(3-Butynyl)-*N*-methyl-5-dimethylamino-1-naphthalenesulfonamide (17).** Following a similar procedure as that described for **1c**, 5-(dimethylamino)naphthalenesulphonyl chloride (1.95 g, 7.21 mmol) reacted with 3-butyn-1-amine<sup>12</sup> (0.50 g, 7.2 mmol) for 1 d to give, after chromatography (40-50% Et<sub>2</sub>O/petrol), *N*-(3-butynyl)-5-dimethylamino-1-naphthalenesulfonamide (2.18 g, 100%) as bright yellow crystals; mp 123-124°C (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 3280 (≡CH, NH), 1312 (SO<sub>2</sub>), 1142 (SO<sub>2</sub>), 789 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 8.56 (1H, d, *J* 8.6, ArH), 8.28 (1H, d, *J* 8.6, ArH), 8.26 (1H, dd, *J* 1.2, 7.1, ArH), 7.57 (1H, t, *J* 7.6, ArH), 7.53 (1H, t, *J* 7.6, ArH), 7.19 (1H, d, *J* 7.6, ArH), 4.98 (1H, t, *J* 6.4, NH), 3.06 (2H, q, *J* 6.6, NCH<sub>2</sub>), 2.89 (6H, s, NMe<sub>2</sub>), 2.29 (2H, dt, *J* 2.7, 6.6, ≡CCH<sub>2</sub>), 1.90 (1H, t, *J* 2.7, ≡CH); MS *m/z* (EI) 302 (M<sup>+</sup>, 80), 171 (98), 170 (100), 154 (23), 127 (21), 85 (9); Anal. Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.22; H, 6.03; N, 9.12. As described in the preparation of **1e**, the *N*-methylation of *N*-(3-butynyl)-5-dimethylamino-1-naphthalenesulfonamide (0.50 g, 1.7 mmol) afforded, after chromatography (50% Et<sub>2</sub>O/petrol), the title compound (**17**) (0.52 g, 100%) as a bright green oil; IR (neat) 3288, 1328 (SO<sub>2</sub>), 1143 (SO<sub>2</sub>), 794, 622 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 8.55 (1H, dd, *J* 1.0, 8.5, ArH), 8.33 (1H, d, *J* 8.8, ArH), 8.18 (1H, dd, *J* 1.2, 7.3, ArH), 7.55 (1H, t, *J* 7.7, ArH), 7.52 (1H, t, *J* 7.9, ArH), 7.18 (1H, d, *J* 7.6, ArH), 3.42 (2H, t, *J* 7.1, NCH<sub>2</sub>), 2.93 (3H, s, NMe), 2.88 (6H, s, NMe<sub>2</sub>), 2.47 (2H, dt, *J* 2.7, 7.3, ≡CCH<sub>2</sub>), 1.94 (1H, t, *J* 2.7, ≡CH); MS *m/z* (EI) 316 (M<sup>+</sup>, 34), 277 (9), 171 (53), 170 (100), 168 (18), 155 (11), 154 (14), 127 (13); HRMS Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: 316.1245. Found: 316.1237.

***N*-But-3-ynyl-*N*-methyl-8-quinolinesulphonamide (20).** Following a similar procedure as that described for **1c**, 8-quinolinesulphonyl chloride (2.31 g, 10.1 mmol) reacted with 3-butyn-1-amine<sup>12</sup> (0.50 g, 7.2 mmol) for 2 d to give, after chromatography on silica gel (gradient elution; 90-100% Et<sub>2</sub>O/petrol), *N*-(3-butynyl)-8-quinolinesulphonamide (1.37 g, 73%) as beige needles; mp 121.5-122.5°C (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 3292 (≡C-H, NH), 1321 (SO<sub>2</sub>), 1165, 1146 (SO<sub>2</sub>), 1080, 835, 790 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 9.03 (1H, dd, *J* 1.7, 4.4, ArH), 8.43 (1H, dd, *J* 1.5, 7.3, ArH), 8.29 (1H, dd, *J* 1.7, 8.3, ArH), 8.07 (1H, dd, *J* 1.2, 8.1, ArH), 7.66 (1H, t, *J* 7.3, ArH), 7.57 (1H, dd, *J* 4.2, 8.3, ArH), 6.71 (1H, t, *J* 6.4, NH), 3.07 (2H, q, *J* 6.6, NCH<sub>2</sub>), 2.33 (2H, dt, *J* 2.7, 6.6, ≡CCH<sub>2</sub>), 1.83 (1H, t, *J* 2.7, ≡CH); <sup>13</sup>C NMR (68 MHz) δ 151.3 (d), 143.3 (s), 137.1 (d), 136.1 (s), 133.4 (d), 131.1 (d), 128.8 (s), 125.8 (d), 122.4 (d), 80.7 (s), 70.3 (d), 42.4 (t), 19.7 (t); MS *m/z* (EI) 259 (M<sup>+</sup>, 0.2), 221 (100), 192 (42), 129 (62), 128 (79), 102 (14), 101 (16), 77 (10); Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.76; H, 4.60; N, 10.72. As described for the preparation of **1e**, the *N*-methylation of *N*-(3-butynyl)-8-quinolinesulfonamide (0.43 g, 1.7 mmol) afforded, after chromatography (70-90% Et<sub>2</sub>O/petrol), the title compound (**20**) (0.45 g, 100%) as a colourless oil; IR (neat) 3270 (≡C-H), 1328 (SO<sub>2</sub>), 1160, 1140 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 9.06 (1H, dd, *J* 2.0, 4.4, ArH), 8.50 (1H, dd, *J* 1.5, 7.3, ArH), 8.24 (1H, dd, *J* 1.7, 8.3, ArH), 8.03 (1H, dd, *J* 1.2, 8.3, ArH), 7.62 (1H, t, *J* 7.3, ArH), 7.52 (1H, dd, *J* 4.4, 8.5, ArH), 3.63 (2H, t, *J* 7.1, NCH<sub>2</sub>), 3.03 (3H, s, NMe), 2.51 (2H, dt, *J* 2.7, 7.6, ≡CCH<sub>2</sub>), 1.94 (1H, t, *J* 2.7, ≡CH); MS *m/z* (EI) 275 (MH<sup>+</sup>, 0.1), 235 (20), 192 (39), 129 (100), 128 (67), 101 (14); Anal. Calcd for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S: C, 61.29; H, 5.14; N, 10.21. Found: C, 61.51; H, 4.97; N, 9.91.

#### Isomerisation of arene sulfonates and sulfonamides; General procedure:

A solution of AIBN (0.15 g, 0.9 mmol) and tri-*n*-butylstannane (0.24 mL, 0.9 mmol) in benzene (9 mL) was introduced over 15 h, *via* uniform motor-driven syringe addition, to a rapidly stirred solution of the sulfonate (0.9 mmol) in benzene (18 mL) at 80°C. After a further 1-6 h, the reaction mixture was allowed to cool to 25°C. **Procedure A:** The reaction mixture was concentrated *in vacuo*. **Procedure B:** Carbon tetrachloride (5 mL) and a few crystals of iodine were added until a persistent

faint colouration was observed. The reaction mixture was then evaporated *in vacuo*, diluted with AcOEt (20 mL) and stirred vigorously with sat. aq. KF (10 mL) for 0.5 h. After filtration, the organic layer was separated and the aqueous phase re-extracted with AcOEt. The combined organic layer was washed with brine, dried (MgSO<sub>4</sub>) and evaporated *in vacuo*.

**Procedure C:** The solvent was removed *in vacuo* and the residue was dissolved in 10% AcOH in MeOH (20 mL). After refluxing for 35 min, the mixture was cooled to rt, neutralised by addition of sat. aq. NaHCO<sub>3</sub> (40 mL) and then extracted with Et<sub>2</sub>O, and then procedure B.

**5,6-Dihydro-4-(4-methylphenyl)-1,2-oxathiin-S,S-dioxide (5a).** Following the procedure C from 1a, purification of the residue by chromatography (10-60% Et<sub>2</sub>O/petrol) furnished, in order of elution, 3-butenyl 4-methylphenylsulfonate (50%) as a colourless oil; IR (neat) 3082, 2982, 1639, 1598, 1357, 1307, 1291, 1189, 1176, 1096, 1011, 964, 878, 814 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 7.79 (2H, d, *J* 8.7, ArH), 7.34 (2H, d, *J* 8.7, ArH), 5.68 (1H, m, =CH), 5.07 (2H, m, =CH<sub>2</sub>), 4.06 (2H, t, *J* 7.6, OCH<sub>2</sub>), 2.45 (3H, s, ArCH<sub>3</sub>), 2.37 (2H, m, =CCH<sub>2</sub>); MS *m/z* (EI) 226 (M<sup>+</sup>), 185, 172, 155, 91; HRMS Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>S: 226.0664. Found: 226.0667; Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>S: C, 58.39; H, 6.24. Found: C, 58.42; H, 6.19; and the sultone (5a) (35%) as a colourless oil; IR (neat) 1065, 1510, 1460, 1342, 1162 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 7.34 (2H, d, *J* 8.9, ArH), 7.25 (2H, d, *J* 8.9, ArH), 6.73 (1H, t, *J* 1.4, =CH), 4.87 (2H, t, *J* 6.2, OCH<sub>2</sub>), 2.90 (2H, dt, *J* 5.8, 1.8, =CCH<sub>2</sub>), 2.39 (3H, s, ArCH<sub>3</sub>); MS *m/z* (EI) 224 (M<sup>+</sup>), 160, 142, 128, 115; HRMS Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>S: 224.0507. Found: 224.0512.

**Methyl 2-(5,6-dihydro-1,2-oxathiin-4-yl)benzoate-S,S-dioxide (5b).** Following the procedure A from 1b, purification of the residue by chromatography (40-50% Et<sub>2</sub>O/petrol) provided, in order of elution, the methyl 2-[(4-tributylstannyl)-3-butenyloxy]sulphonylbenzoate (22%) as a colourless oil; IR (neat) 2955, 2923, 1739 (C=O), 1366 (SO<sub>2</sub>), 1294, 1183 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz) δ 8.02 (1H, dd, *J* 0.8, 7.8, ArH), 7.66 (3H, m, ArH), 6.03 (1H, dt, *J* 19.0, 1.3, =CHSn), 5.84 (1H, dt, *J* 19.0, 6.1, =CH), 4.20 (2H, t, *J* 7.0, OCH<sub>2</sub>), 3.96 (3H, s, CO<sub>2</sub>Me), 2.54 (2H, m, =CCH<sub>2</sub>), 1.46 (6H, m), 1.28 (6H, m), 0.88 (15H); MS *m/z* (CI, NH<sub>3</sub>) 578 (M+NH<sub>3</sub><sup>+</sup> (<sup>120</sup>Sn), 19), 576 (M+NH<sub>3</sub><sup>+</sup> (<sup>118</sup>Sn), 23), 561 (MH<sup>+</sup> (<sup>120</sup>Sn), 82), 559 (MH<sup>+</sup> (<sup>118</sup>Sn), 64), 503 (28), 501 (22), 308 (90), 306 (72), 299 (49), 288 (100). HRMS Calcd for C<sub>23</sub>H<sub>41</sub>O<sub>4</sub>S(<sup>120</sup>Sn): 561.1697. Found: 561.1700; Calcd for C<sub>23</sub>H<sub>41</sub>O<sub>4</sub>S(<sup>118</sup>Sn): 559.1691. Found: 559.1690; and the sultone (5b) (61%) as colourless needles; mp 130.5-131.5°C (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O); IR (neat) 1712 (C=O), 1345 (SO<sub>2</sub>), 1304, 1280, 1250, 1167 (SO<sub>2</sub>), 969, 885 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 8.05 (1H, dd, *J* 1.4, 7.6, ArH), 7.57 (1H, dt, *J* 1.4, 7.6, ArH), 7.50 (1H, dt, *J* 1.4, 7.6, ArH), 7.23 (1H, dd, *J* 1.4, 7.6, ArH), 6.30 (1H, t, *J* 1.7, =CH), 4.90 (2H, t, *J* 5.5, OCH<sub>2</sub>), 3.91 (3H, s, CO<sub>2</sub>Me), 2.72 (2H, dt, *J* 1.7, 5.5, =CCH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz) δ 166.0 (s), 152.1 (s), 139.4 (s), 132.9 (s), 131.1 (s), 129.3 (s), 128.5 (s), 128.0 (s), 121.3 (s), 69.6 (t), 52.5 (q), 30.7 (t); MS *m/z* (EI) 237 (M<sup>+</sup>-OMe, 0.6), 174 (100), 159 (27), 131 (19), 115 (22), 77 (8). Anal. Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>5</sub>S: C, 53.72; H, 4.51. Found: C, 53.79; H, 4.49.

**4-(2,4-Difluorophenyl)-5,6-dihydro-1,2-oxathiin-S,S-dioxide (5c).** Following the procedure A from 1c, purification of the residue by chromatography (55% Et<sub>2</sub>O/petrol) afforded the sultone (5c) (39%) as colourless crystals, mp 120.5-122.5°C (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O); IR (neat) 1725, 1618, 1505, 1348 (SO<sub>2</sub>), 1288, 1167 (SO<sub>2</sub>), 1144, 974, 889, 855 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 7.30 (1H, m, ArH), 6.93 (2H, m, ArH), 6.68 (1H, t, *J* 1.8, =CH), 4.85 (2H, t, *J* 5.6, OCH<sub>2</sub>), 2.89 (2H, dt, *J* 1.0, 5.6, =CCH<sub>2</sub>). MS *m/z* (EI) 246 (M<sup>+</sup>, 69), 182 (16), 165 (33), 164 (50), 153 (38), 152 (24), 151 (100), 149 (18), 139 (23), 138 (18), 133 (17), 127 (21), 75 (11); HRMS Calcd for C<sub>10</sub>H<sub>8</sub>O<sub>3</sub>F<sub>2</sub>S: 246.0162. Found: 246.0166.

**5,6-Dihydro-4-(4-methoxyphenyl)-1,2-oxathiin-S,S-dioxide (5d).** Following the procedure A from 1d, purification of the residue by chromatography (15-30% Et<sub>2</sub>O/petrol) gave, in order of elution, the [4-tributylstannyl-3-butenyl] 4-methoxybenzenesulfonate (40%) as a colourless oil; IR (neat) 2957, 2925, 1598, 1363 (SO<sub>2</sub>), 1263, 1170 (SO<sub>2</sub>), 970 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz) δ 7.85 (2H, d, *J* 8.9, ArH), 7.00 (2H, d, *J* 8.9, ArH), 5.99 (1H, d, *J* 19.0, =CHSn), 5.79 (1H, dt, *J* 19.0, 6.1, =CH), 4.06 (2H, t, *J* 6.9, OCH<sub>2</sub>), 3.88 (3H, s, OMe), 2.47 (2H, d, *J* 7.1, =CCH<sub>2</sub>), 1.45 (6H, m), 1.28 (6H, m), 0.88 (15H, m); MS *m/z*

(EI) 475 ( $M^+$ -C<sub>4</sub>H<sub>9</sub>, 100), 421 (50), 307 (69), 227 (45), 161 (42), 107 (20), 92 (20), 77 (25); HRMS Calcd for C<sub>23</sub>H<sub>41</sub>O<sub>4</sub>S<sup>(119)</sup>Sn: 533.1748. Found: 533.1750; Anal. Calcd for C<sub>23</sub>H<sub>40</sub>OSSn: C, 51.99; H, 7.59. Found: C, 51.74; H, 7.88, the starting sulfonate (**1d**) (15%); and the sultone (**5d**) (8%) as colourless needles; mp 109-109.5°C (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O), IR (neat) 1339 (SO<sub>2</sub>), 1160 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 7.39 (2H, d, *J* 8.8, ArH), 6.94 (2H, d, *J* 8.8, ArH), 6.67 (1H, t, *J* 1.7, =CH), 4.85 (2H, t, *J* 5.8, OCH<sub>2</sub>), 3.85 (3H, s, OMe), 2.88 (2H, dt, *J* 1.7, 5.9, =CCH<sub>2</sub>), MS *m/z* (EI) 240 ( $M^+$ , 81), 176 (13), 159 (24), 148 (23), 147 (23), 133 (29), 115 (37), 103 (43), 91 (18), 77 (38); HRMS Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>S: 240.0456. Found: 240.0456; Anal. Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>S: C, 54.99; H, 5.03. Found: C, 54.76; H, 4.98.

***N*-[4-(5,6-Dihydro-1,2-oxathiin-4-yl)phenyl]-*N*-methylacetamide-*S,S*-dioxide (**5e**).** Following the procedure A from **1e**, purification of the residue by chromatography (80-100% AcOEt/petrol) furnished, in order of elution, the [4-tributylstannyl-3-butenyl] 4-(*N*-methylacetamido)benzenesulfonate (34%) as a colourless oil; IR (neat) 2926, 1672 (C=O), 1595, 1496, 1461, 1369 (SO<sub>2</sub>), 1185 (SO<sub>2</sub>), 967, 917, 658 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 7.95 (2H, d, *J* 8.8, ArH), 7.39 (2H, d, *J* 8.5, ArH), 6.04 (1H, d, *J* 19.0, =CHSn), 5.82 (1H, dt, *J* 18.8, 6.0, =CH), 4.15 (2H, t, *J* 7.1, OCH<sub>2</sub>), 3.33 (3H, s, NMe), 2.52 (2H, q, *J* 7.1, =CCH<sub>2</sub>), 2.00 (3H, s, Me), 1.45 (6H, m), 1.30 (6H, m), 0.88 (15H, m); <sup>13</sup>C NMR (126 MHz) δ 169.9 (s), 149.0 (s), 141.5 (d), 133.6 (d), 133.2 (d), 129.2 (d), 127.3 (d), 69.9 (t), 36.8 (q), 28.9 (t), 27.1 (t), 22.5 (q), 13.6 (q), 9.3 (t); MS *m/z* (CI, NH<sub>3</sub>) 574 ( $MH^+$ , 100), 516 (33), 440 (12), 308 (31), 284 (26), 150 (30); HRMS Calcd for C<sub>25</sub>H<sub>43</sub>NO<sub>4</sub>S<sup>(119)</sup>Sn: 574.2013. Found: 574.2010; Anal. Calcd for C<sub>25</sub>H<sub>43</sub>NO<sub>4</sub>SSn: C, 52.46; H, 7.57; N, 2.45. Found: C, 52.43; H, 7.79; N, 2.68; the starting sulfonate (**1e**) (6%); and the sultone (**5e**) (19%) as a low melting solid; mp ~51-61°C; IR (neat) 1656 (C=O), 1346 (SO<sub>2</sub>), 1165 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz) δ 7.49 (2H, d, *J* 8.6, ArH), 7.28 (2H, d, *J* 8.5, ArH), 6.77 (1H, t, *J* 1.5, =CH), 4.89 (2H, t, *J* 5.6, OCH<sub>2</sub>), 3.29 (3H, s, NMe), 2.91 (2H, dt, *J* 1.7, 5.6, =CCH<sub>2</sub>), 1.93 (3H, s, Me); MS *m/z* (EI) 281 ( $M^+$ , 44), 239 (100), 158 (22), 144 (27), 130 (21), 115 (30), 77 (16), 56 (72); HRMS Calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>S: 281.0722. Found: 281.0722; Anal. Calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>S: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.33; H, 5.66; N, 5.30.

**5-(5,6-Dihydro-1,2-oxathiin-4-yl)-*N,N*-dimethyl-1-naphthaleneamine-*S,S*-dioxide (**7**).** Following the procedure B from **6**, purification of the residue by chromatography (35-60% Et<sub>2</sub>O/petrol) furnished the sultone (**7**) (74%) as pale green needles; mp 144°C (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O); IR (neat) 1583, 1348 (SO<sub>2</sub>), 1164 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 8.32 (1H, dd, *J* 1.1, 8.6, ArH), 7.47 (3H, m, ArH), 7.30 (1H, dd, *J* 1.3, 7.1, ArH), 7.13 (1H, dd, *J* 3.1, 5.4, ArH), 6.62 (1H, t, *J* 1.9, =CH), 4.94 (2H, t, *J* 5.7, OCH<sub>2</sub>), 2.90 (8H, m, =CCH<sub>2</sub>, NMe<sub>2</sub>); <sup>13</sup>C NMR (126 MHz) δ 151.6 (s), 150.1 (s), 135.5 (s), 131.1 (s), 129.2 (s), 127.2 (d), 125.9 (d), 124.7 (d), 124.6 (d), 124.3 (d), 118.7 (d), 114.7 (d), 68.9 (t), 45.2 (t), 30.7 (t); MS *m/z* (EI) 303 ( $M^+$ , 23), 209 (83), 208 (100), 194 (16), 165 (83); Anal. Calcd for C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>S: C, 63.35; H, 5.65; N, 4.93. Found: C, 63.63; H, 5.58; N, 4.93.

**3-(5,6-Dihydro-1,2-oxathiin-4-yl)pyridine-*S,S*-dioxide (**9**).** Following the procedure A from **8**, purification of the residue by chromatography (15% Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>) furnished, in order of elution, the starting sulfonate (**8**) (26%); and the sultone (**9**) (24%); mp >230°C (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 1329, 1198, 1159, 745 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 8.71 (2H, m, 2-H, ArH), 7.75 (1H, ddd, *J* 1.5, 2.3, 8.0, ArH), 7.40 (1H, ddd, *J* 0.7, 4.8, 8.1, ArH), 6.80 (1H, t, *J* 1.8, =CH), 4.90 (2H, t, *J* 5.8, OCH<sub>2</sub>), 2.92 (2H, dt, *J* 1.8, 5.7, =CCH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz) δ 151.6 (d), 147.0 (d), 145.2 (s), 133.3 (d), 131.8 (s), 123.8 (d), 122.2 (d), 68.4 (t), 27.1 (t); MS *m/z* (EI) 211 ( $M^+$ , 100), 149 (11), 130 (49), 129 (47), 118 (29), 117 (29), 104 (19), 103 (11); Anal. Calcd for C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub>S: C, 51.17; H, 4.37; N, 6.40. Found: C, 51.03; H, 4.37; N, 6.40.

**8-(5,6-Dihydro-1,2-oxathiin-4-yl)quinoline-*S,S*-dioxide (**11**).** Following the procedure A from **10**, purification of the residue by chromatography (90% Et<sub>2</sub>O/petrol) afforded the sultone (**11**) (57%) as colourless plates, mp 170°C (decomp) (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 1338 (SO<sub>2</sub>), 1159 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz) δ 8.90 (1H, dd, *J* 1.8, 4.2, ArH), 8.20 (1H, dd, *J* 1.8, 8.4, ArH), 7.89 (1H, dd, *J* 1.8, 8.0, ArH), 7.63 (1H, dd, *J* 1.7, 7.1, ArH), 7.55 (1H, t, *J* 7.9, ArH), 7.46 (1H, dd, *J* 4.2,

8.3, ArH), 6.73 (1H, t,  $J$  1.8, =CH), 4.96 (2H, t,  $J$  5.7, OCH<sub>2</sub>), 3.31 (2H, dt,  $J$  1.8, 5.7, =CCH<sub>2</sub>), <sup>13</sup>C NMR (126 MHz)  $\delta$  151.3 (s), 150.3 (d), 145.7 (s), 136.8 (s), 136.3 (d), 130.0 (d), 128.7 (d), 128.4 (s), 126.2 (d), 123.3 (d), 121.7 (d), 69.5 (t), 29.9 (t); MS  $m/z$  (EI) 261 (M<sup>+</sup>, 0.9), 167 (100), 154 (11); Anal. Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>3</sub>S: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.75; H, 4.04; N, 5.28.

**2-Acetamido-5-(5,6-dihydro-1,2-oxathiin-4-yl)-4-methylthiazole-S,S-dioxide (13).** Following the procedure B from **12**, purification of the residue by chromatography (30-100% AcOEt/petrol) furnished, in order of elution, the starting sulfonate (**12**) (35%); and the sultone (**13**) (43%); mp >250°C (decomp); IR (KBr) 3140 (NH), 1562, 1342 (SO<sub>2</sub>), 1166 (SO<sub>2</sub>), 839 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  6.98 (1H, s, =CH), 4.77 (2H, t,  $J$  5.6, OCH<sub>2</sub>), 2.88 (2H, t,  $J$  5.6, =CCH<sub>2</sub>), 2.40 (3H, s), 2.15 (3H, s); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  17.6, 22.6, 29.4, 69.1, 118.2, 120.1, 141.8, 147.6, 157.4, 170.0; MS  $m/z$  (FAB) 289 (MH<sup>+</sup>, 100), 282 (53), 179 (32), 177 (35), 137 (41), 91 (30), 77 (35), 55 (50), 43 (47), 41 (42).

**5,6-Dihydro-4-(4-methylphenyl)-1,2-thiazin-S,S-dioxide (15).** A solution of AIBN (0.362 g, 2.2 mmol) and tri-*n*-butylstannane (0.592 mL, 2.2 mmol) in benzene (6 mL) was introduced over 13 h, *via* uniform motor-driven syringe addition, to a rapidly stirred solution of **15** (0.475 g, 2.0 mmol) in benzene (19 mL) at 80°C. After a further 3 h, the reaction mixture was allowed to cool to 25°C. The reaction mixture was concentrated *in vacuo*. The residue was dissolved in ether and treated with 2M HCl. After neutralisation with 10% aq. NaOH, the aqueous layer was extracted with ether. The combined extract was washed with water and carbon tetrachloride was added. After 3 h, the solvents were removed *in vacuo*, and the residue was dissolved in AcOEt and stirred vigorously with sat. aq. KF for 12 h. After filtration, the organic layer was separated and the aqueous phase re-extracted with AcOEt. The combined organic layer was washed with brine, dried (MgSO<sub>4</sub>) and evaporated *in vacuo*. Purification of the residue by chromatography (Et<sub>2</sub>O/petrol) furnished, in order of elution, the sultam (**15**) (15%) as a brown oil; IR (neat) 1453, 1342 (SO<sub>2</sub>), 1156 (SO<sub>2</sub>), 1022 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz)  $\delta$  7.79 (2H, d,  $J$  7.5, ArH), 7.12 (2H, d,  $J$  7.5, ArH), 7.11 (1H, s, =CH), 3.01 (2H, m, NCH<sub>2</sub>), 2.71 (3H, s, NMe), 2.37 (3H, s, ArCH<sub>3</sub>), 2.25 (2H, m, =CCH<sub>2</sub>), the starting sulfonamide (**14**) (50%), and the amine (**16**) (8%) as a bright yellow oil; IR (neat) 3371 (NH), 1654, 1332, 1083, cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz)  $\delta$  7.66 (2H, d,  $J$  8.0, ArH), 7.16 (2H, d,  $J$  8.0, ArH), 6.86 (1H, s, NH), 5.32 (1H, s, =CH), 5.09 (1H, s, =CH), 2.92 (3H, s, NMe), 2.87 (2H, t,  $J$  6.2, NCH<sub>2</sub>), 2.65 (2H, t,  $J$  5.9, =CCH<sub>2</sub>), 2.28 (3H, s, ArCH<sub>3</sub>).

**5-(3,4-Dihydro-2-methyl-1,2-thiazin-5-yl)-N,N-dimethyl-1-naphthaleneamine-S,S-dioxide (18)** Following the same procedure as that described for **15**, purification of the residue by chromatography (10-35% Et<sub>2</sub>O/petrol) furnished, in order of elution, the starting sulfonamide (**17**) (42%), the sultam (**18**) (16%) as pale green crystals, mp 145.5-151.5°C (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 1325 (SO<sub>2</sub>), 1145 (SO<sub>2</sub>), 790 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz)  $\delta$  8.29 (1H, d,  $J$  8.6, ArH), 7.49 (1H, t,  $J$  8.4, ArH), 7.46 (1H, d,  $J$  8.6, ArH), 7.44 (1H, t,  $J$  7.4, ArH), 7.29 (1H, dd,  $J$  1.0, 7.0, ArH), 7.12 (1H, d,  $J$  7.3, ArH), 6.59 (1H, t,  $J$  2.1, =CH), 3.91 (2H, t,  $J$  5.9, NCH<sub>2</sub>), 3.02 (3H, s, NMe), 2.90 (6H, s, NMe<sub>2</sub>), 2.66 (2H, dt,  $J$  2.0, 5.9, =CCH<sub>2</sub>); MS  $m/z$  (EI) 316 (M<sup>+</sup>, 29), 209 (51), 208 (100), 194 (21), 165 (21); HRMS Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: 316.1245. Found: 316.1240; and the amine (**19**) (5%) as a brown oil; IR (neat) 3378 (NH), 1452, 1581 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz)  $\delta$  8.17 (1H, d,  $J$  8.6, ArH), 7.63 (1H, d,  $J$  7.9, ArH), 7.40 (1H, t,  $J$  7.0, ArH), 7.36 (1H, t,  $J$  7.9, ArH), 7.22 (1H, d,  $J$  6.0, ArH), 7.05 (1H, d,  $J$  7.3, ArH), 5.42 (1H, d,  $J$  1.1, =CH), 5.13 (1H, d,  $J$  1.7, =CH), 3.75 (2H, t,  $J$  4.5), 3.61 (2H, t,  $J$  4.5), 2.87 (6H, s, NMe<sub>2</sub>), 2.41 (3H, s, NMe), MS  $m/z$  (FAB) 255 (MH<sup>+</sup>, 82), 212 (76), 149 (52), 95 (42), 81 (46), 69 (70), 44 (100); HRMS Calcd for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>: 255.1850. Found: 255.1861.

**8-(3,4-Dihydro-2-methyl-1,2-thiazin-5-yl)quinoline-S,S-dioxide (21).** Following the same procedure as that described for **15**, purification of the residue by chromatography (10-50% Et<sub>2</sub>O/petrol) provided, in order of elution, the starting sulfonate (**20**) (50%), the sultam (**21**) (21%) as colourless crystals; mp 153-154°C (CH<sub>2</sub>Cl<sub>2</sub>/petrol); IR (neat) 1321 (SO<sub>2</sub>), 1148 (SO<sub>2</sub>).

1036, 961, 796  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz)  $\delta$  8.87 (1H, dd,  $J$  1.7, 4.2, ArH), 8.16 (1H, dd,  $J$  1.7, 8.3, ArH), 7.84 (1H, dd,  $J$  1.7, 7.6, ArH), 7.55 (2H, m, ArH), 7.43 (1H, dd,  $J$  4.2, 8.3, ArH), 6.63 (1H, t,  $J$  2.0, =CH), 3.91 (2H, t,  $J$  5.9,  $\text{NCH}_2$ ), 3.03 (5H, m, =CCH<sub>2</sub>, NMe); MS  $m/z$  (EI) 274 ( $\text{M}^+$ , 0.9), 167 (100), 154 (12); HRMS Calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ : 274.0776. Found: 274.0780; and the amine (**22**) (21%) as a pale yellow oil; IR (neat) 3274 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz)  $\delta$  8.92 (1H, dd,  $J$  1.6, 4.3, ArH), 7.75 (1H, dd,  $J$  2.0, 7.53, ArH), 7.58 (1H, d,  $J$  1.6, ArH), 7.49 (1H,  $J$  4.2, ArH), 7.39 (2H, m, ArH), 5.49 (1H, d,  $J$  0.9, =CH), 5.19 (1H, d,  $J$  1.7, =CH), 3.69 (2H, m,  $\text{NCH}_2$ ), 3.05 (3H, d,  $J$  2.9, NMe), 2.97 (2H, t,  $J$  6.8, =CCH<sub>2</sub>); HRMS Calcd for  $\text{C}_{14}\text{H}_{17}\text{N}_2$ : 213.1380. Found: 213.1392

## ACKNOWLEDGEMENTS

We thank Dr C. R. A. Godfrey for helpfull discussions and the EPSRC for the Award of a CASE studentship (to F. U.). We are also grateful to the European Community for the Award of a Fellowship under the MRT Programme (to E. B.).

## REFERENCES

1. W. B. Motherwell and A. M. K. Pennell, *J. Chem. Soc., Chem. Commun.*, 1991, 877.
2. M. L. E. N. da Mata, W. B. Motherwell, and F. Ujjainwalla, *Tetrahedron Lett.*, 1997, **38**, 137.
3. M. L. E. N. da Mata, W. B. Motherwell, and F. Ujjainwalla, *Tetrahedron Lett.*, 1997, **38**, 141.
4. (a) L. Benati, P. Spagnolo, A. Tundo, and G. Zanardi, *J. Chem. Soc., Chem. Commun.*, 1979, 141; (b) J. L. Huppertz and W. H. F. Sasse, *Aust. J. Chem.*, 1963, **16**, 417; (c) N. S. Narsimhan and I. S. Aidhen, *Tetrahedron Lett.*, 1988, **29**, 2987. (d) For particular cases involving sulfonyl substituted aromatic derivatives see, *inter alia*: J. J. Kohler and W. N. Speckamp, *Tetrahedron Lett.*, 1977, **18**, 631; *ibid.*, 1977, **18**, 635; R. Loven and W. N. Speckamp, *Tetrahedron Lett.*, 1972, 1567; J. J. Kohler and W. N. Speckamp, *J. Chem. Soc., Chem. Commun.*, 1978, 166; *ibid.*, 1980, 142 and references therein; D. L. J. Clive and T. L. Boivin, *J. Org. Chem.*, 1989, **54**, 1997; A. Feigenbaum, J. P. Pete, and D. Scholler, *J. Org. Chem.*, 1984, **49**, 2355; J. Grimshaw and J. Trocha, *J. Chem. Soc., Perkin Trans. 1*, 1979, 799.
5. W. B. Motherwell, A. M. K. Pennell, and F. Ujjainwalla, *J. Chem. Soc., Chem. Commun.*, 1992, 1067.
6. G. Stork and R. Mook, Jr., *J. Am. Chem. Soc.*, 1987, **109**, 2829.
7. J. Chateaneuf, J. Luszyk, B. Maillard, and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 6727; A. L. J. Beckwith and I. G. E. Davidson, *Tetrahedron Lett.*, 1991, **32**, 49; M. Newcomb, M. Uday Kumar, J. Boivin, E. Crepon, and S. Z. Zard, *Tetrahedron Lett.*, 1991, **32**, 45 and references therein.
8. P. N. Culshaw and J. C. Walton, *Tetrahedron Lett.*, 1990, **31**, 6433.
9. T. Akiyama, M. Sugihara, T. Imagawa, and M. Kawanisi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1251.
10. T. Beetz, R. M. Kellogg, C. Th. Kiers, and A. Piepenbrook, *J. Org. Chem.*, 1975, **40**, 3309.
11. S. Caddick and S. Joshi, *Synlett*, 1992, 805.
12. E. C. Taylor, J. E. Macor, and J. L. Pont, *Tetrahedron*, 1987, **43**, 5145.

Received, 31st March, 1997