A general and highly regio and stereoselective method for the synthesis of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones through palladium–copper catalysis

Bidisha Nandi and Nitya G. Kundu *

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 700 032, India.; Fax: +91-33-473-2805

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A palladium–copper-catalysed procedure for the synthesis of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h** is developed. 3-[2-(Methoxycarbonyl)phenylthio]propyne **2** reacts with aryl iodides **3a–3h** in the presence of bis(triphenylphosphine)palladium(II) dichloride, copper(I) iodide and triethylamine in acetonitrile to furnish the disubstituted alkynes **4a–4h** in good yields (70–84%). These on alkaline hydrolysis and subsequent cyclisation of the carboxylic acids formed with copper(I) iodide (20 mol%) and triethylamine in tetrahydrofuran under reflux afford (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h** in 61–70% yield rather than the expected benzoxathiepinones **6**. The reactions of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones **5a** and **5g** with nucleophiles and the hydrogenation of compounds **5a**, **5b** and **5d** are also studied.

Introduction

3,1-Benzoxathiin-4-one[1] is a unique heterocyclic structure derived from 2-(hydroxymethylthio)benzoic acid. The synthesis and reactivity of benzoxathiin-4-ones have not been extensively studied so far and only a few routes are available for the synthesis of substituted or unsubstituted 3,1-benzoxathiin-4-ones.[2–10]

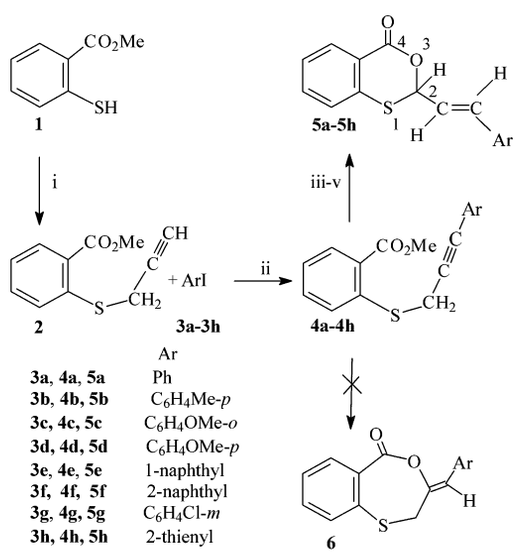
A recent trend in organic synthesis has been to develop different carbocyclic[11] and heterocyclic[12] structures through palladium-catalysed reactions.[13] The rapid development in this area has stimulated us to carry out syntheses of various benzo-fused heterocyclic compounds of biological interest. We have utilised the palladium-catalysed reactions of aryl iodides with a nucleophilic group at the *ortho* position and terminal alkynes to generate various benzofused heterocyclic structures.[14–18]

In another approach, by using prop-2-ynyloxy or prop-2-ynylamino aromatic compounds with an *ortho* nucleophilic group and aryl iodides under palladium–copper-catalysed conditions and subsequent cyclisation of the disubstituted alkynes generated, we could easily succeed in synthesising benzofused heterocyclic structures with two heteroatoms.[19–22]

In continuation of these studies, we report here a novel strategy for the synthesis of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h** starting from 3-[2-(methoxycarbonyl)phenylthio]propyne **2** and aryl iodides, **3a–3h**, using palladium- and copper-mediated reactions.[23]

Results and discussion

3-[2-(Methoxycarbonyl)phenylthio]propyne **2** reacted with aryl iodides **3a–3h**, under Sonogashira cross-coupling reaction conditions,[24] in the presence of bis(triphenylphosphine)-palladium(II) dichloride (3.5 mol%), copper(I) iodide (6 mol%) and triethylamine (4 equiv.) in acetonitrile at room temperature for 24 h in an argon atmosphere to yield the disubstituted alkynes **4a–4h**. The disubstituted alkynes **4a–4h** were then hydrolysed with 5 M methanolic KOH solution by stirring at room temperature for 2 h followed by acidification [dil. HCl (1:1)] to the carboxylic acids, which were then heated under reflux in the presence of copper(I) iodide (20 mol%) and triethylamine in THF for 24 h in an argon atmosphere. 2-(2-Arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h** were formed in a completely regio- and stereoselective manner instead of the expected seven-membered heterocyclic compounds, *i.e.* benzooxathiepinones **6**, as shown in Scheme 1 and Table 1.



Scheme 1 *Reagents and conditions*: (i) K_2CO_3, propargyl bromide, acetone, reflux, 16 h; (ii) $(PPh_3)_2PdCl_2$ (3.5 mol%), CuI (6 mol%), Et_3N; CH_3CN, rt, 24 h; (iii) 5 M methanolic KOH, rt, 2 h; (iv) HCl (1:1); (v) CuI (20 mol%), Et_3N, THF, reflux, 24 h.

Role of catalyst, co-catalyst, base and solvent

In the C-arylation step, a combination of bis(triphenyl-phosphine)palladium(II) dichloride (3.5 mol%) (catalyst) and CuI (6 mol%) (co-catalyst) was the most desired catalytic system. It was found that in the absence of bis(triphenyl-phosphine)palladium(II) dichloride, no disubstituted alkynes were formed. We have also explored other palladium catalysts, *e.g.* $(PPh_3)_4Pd$, $Pd(OAc)_2$ along with PPh_3, and found that yields were not appreciable. Copper(I) iodide was the essential co-catalyst, since in its absence very poor yields of the C-arylated

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Table 1 Palladium-catalysed arylation of **2** and the subsequent copper-catalysed cyclisation leading to (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h** (Scheme 1)[a]

Entry	Aryl iodides (Ar)	Disubstituted alkynes, **4a–4h**, yield (%)[b]	2-(2-Arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h**, yield (%)[c]
1	Ph, **3a**	**4a** (77)	**5a** (63)
2	*p*-MeC_6H_4, **3b**	**4b** (77)	**5b** (62)
3	*o*-$MeOC_6H_4$, **3c**	**4c** (81)	**5c** (67)
4	*p*-$MeOC_6H_4$, **3d**	**4d** (76)	**5d** (70)
5	1-Naphthyl, **3e**	**4e** (75)	**5e** (65)
6	2-Naphthyl, **3f**	**4f** (84)	**5f** (68)
7	*m*-ClC_6H_4, **3g**	**4g** (78)	**5g** (63)
8	2-Thienyl, **3h**	**4h** (70)	**5h** (61)

[a] Unless otherwise stated, disubstituted alkynes **4a–4h** were synthesised by stirring a mixture of an aryl halide **3a–3h** and **2** in the presence of bis(triphenylphosphine)palladium(II) dichloride (3.5 mol%), copper(I) iodide (6 mol%) and triethylamine (4 equiv.) in acetonitrile at rt for 24 h in an argon atmosphere. [b] Yields are based on **2**. [c] Yields are based on the disubstituted alkynes **4a–4h**.

products were observed. Triethylamine was the base of choice in the C-arylation reaction since the use of other bases like pyridine, potassium carbonate or sodium acetate led to very low yields of the products. Acetonitrile was the desired solvent in the C-arylation reaction. Triethylamine itself could not be used as the solvent due to the poor solubility of many compounds in it. When DMF was used as solvent, it led to formation of much polymeric material.

Cyclisation

Copper(I) iodide and triethylamine were the essential reagents needed for the cyclisation. In the absence of any of these reagents, no benzoxathiinones were obtained. Also, 20 mol% of copper(I) iodide was found to be the optimum needed for the cyclisation reaction. Any less or more of this catalyst led to a decline in the yield. The use of other bases, *e.g.* pyridine or potassium carbonate, was not found to be satisfactory since either no product or a very poor yield of the product was then observed. THF was the best solvent for cyclisation. The use of other solvents, like acetonitrile, DMF or triethylamine, gave poor yields of the cyclised products due to either solubility problems or the formation of polymeric materials.

Nature and characterisation of the products

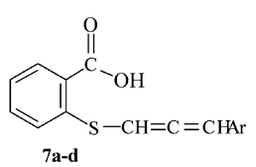
The disubstituted alkynes synthesised, **4a–4h**, were stable and could be stored at room temperature for a long time. However, a brown colour developed when they were kept in solvents like $CHCl_3$, diethyl ether, or methanol for a long time. The 3,1-benzoxathiin-4-ones **5a–5h** formed were very sensitive to light, air and heat. A pure sample of compound **5b**, on storage in air at room temperature for 2 days, developed a deep brown colour. Hence, it should preferably be stored in a brown bottle in the cold.

All the acyclic and cyclic products synthesised were well characterised by spectral (IR, ^{1}H NMR and ^{13}C NMR) evidence and elemental analysis. The structures of the disubstituted alkynes **4a–4h** were established from the following observations.

In the IR spectra of compounds **4a–4h**, the stretching frequency at ν_{max} 3247.9 cm^{-1} (≡C-H) was absent and the band corresponding to the COOMe group was in the range ν_{max} 1714–1705 cm^{-1}. In the ^{1}H NMR spectra, triplets corresponding to the acetylenic hydrogen were absent and the methylenic protons displayed a singlet at δ_H 3.73–3.96. All the other protons were at appropriate positions. In the ^{13}C NMR spectra, together with DEPT experiments, the methylenic carbons were seen in the range δ_C 21.8–22.3. The structures of the cyclic products **5a–5h** were deduced from spectral (IR, ^{1}H NMR and ^{13}C NMR) and analytical data. The IR specta revealed the C=O stretching frequency in the range ν_{max} 1732.5–1720 cm^{-1}, indicating the presence of a six-membered heterocyclic ring. In the ^{1}H NMR spectra, the two vinylic hydrogens appeared in the range δ_H 6.19–6.53 (dd, $J \approx 15.6$, 6 Hz) and δ_H 6.87–7.13 (d, $J \approx 15.6$ Hz) whereas the C-2 proton in the heterocyclic ring (SCH) displayed a doublet in the range of δ_H 6.11–6.29 ($J \approx 6$ Hz) firmly establishing the structure of 2-(2-arylvinyl)-3,1-benzoxathiin-4-ones, **5a–5h**. Furthermore, ^{13}C NMR spectra together with DEPT (135) experiments provided additional support in favour of the stuctures of **5a–5h**; the characteristic peaks for methylenic carbons were absent, thus excluding the formation of any seven-membered heterocyclic structures **6**.

The heteroannulation process was completely regio- and stereoselective. Only six-membered heterocyclic compounds were formed instead of the expected seven-membered heterocycles, *i.e.* benzoxathiepinones **6**. The stereochemistry around the double bond was assigned the *E*-configuration on the basis of the coupling constants (15 Hz) of the two vinylic protons.

The allenic intermediates **7** [25] were formed in all the cases due to the alkaline hydrolysis of compounds **4a–4h**, as was detected by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The crude allenes were used immediately for cyclisation.[26] Some of the allenic compounds, however, could be isolated, purified and characterised fully from spectral (IR, ^{1}H NMR and ^{13}C NMR) evidence and elementary analysis. In the IR spectra, the C=C=C stretching frequencies [27] were found to be in the range ν_{max} 1936.4–1932 cm^{-1}. In the ^{1}H NMR spectra, the two allenic hydrogens appeared as doublets at δ_H 6.27–6.49 (J 6 Hz) and δ_H 6.39–6.73 (J 6 Hz). Finally, in the ^{13}C NMR spectra, a characteristic peak for the central carbon of the allenic species [27] in the range δ_C 208.7–213.6 firmly established the formation of the allenic compounds **7** in the reaction sequence. The cyclisation of the isolated allenic compounds **7a–d** under the conditions described in Scheme 1 afforded the desired 3,1-benzoxathiin-4-ones **5a, 5b, 5c** and **5f**.



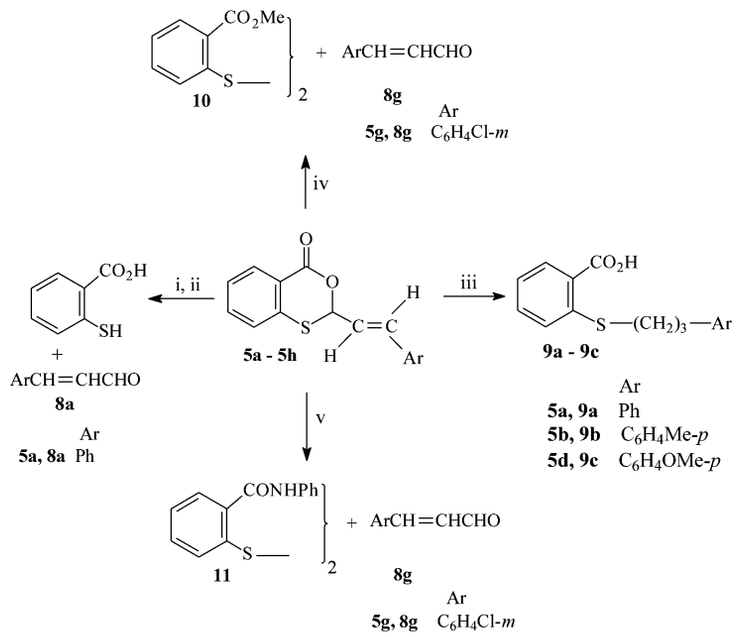
7a-d

7a, Ar = Ph
7b, Ar = C_6H_4Me-*p*
7c, Ar = C_6H_4OMe-*o*
7d, Ar = 2-naphthyl

Reactivity of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones 5a–5h

(*E*)-2-(2-Arylvinyl)-3,1-benzoxathiin-4-ones **5a–5h** are stable in neutral aq. methanolic solution at room temperature as well as at higher temperatures (60–80 °C). The heterocyclic ring remained intact when a methanolic solution of compound **5b** was refluxed under acidic conditions (6 M HCl). On alkaline hydrolysis, however, compound **5a** opened up with the formation of thiosalicylic acid and cinnamaldehyde **8a** (Scheme 2).

Catalytic hydrogenation of compounds **5a**, **5b** and **5d** was carried out with palladium on activated charcoal at atmospheric pressure in ethyl acetate. Hydrogenolysis of the



Scheme 2 *Reagents and conditions*: (i) 5 M KOH, MeOH, reflux, 12 h; (ii) dil. HCl (1:1); (iii) Pd/C (10%), H_2 (1 atm), ethyl acetate, rt, 48 h; (iv) NaOMe, MeOH, reflux, 15 h; (v) $PhNH_2$, benzene, reflux, 15 h.

compounds was observed with the formation of the saturated acyclic products **9a, 9b** and **9c** respectively (Scheme 2).

On reaction of (*E*)-2-[2-(*m*-chlorophenyl)vinyl]-3,1-benzoxathiin-4-one **5g** with sodium methoxide in methanol, the disulfide **10** was formed along with *m*-chlorocinnamaldehyde **8g** (Scheme 2).

Similarly, the reaction of compound **5g** with aniline in a refluxing solution in benzene afforded the disulfide of the corresponding amide, **11** and *m*-chlorocinnamaldehyde **8g** (Scheme 2).

Conclusions

Although a number of versatile routes for synthesis of 3,1-benzoxathiin-4-ones have been devised,[2–10] most of them are either direct condensation of aldehydes with thiosalicylic acid or thermal decomposition procedures. In almost all cases, yields were not good enough. Also, the lack of a variety of functional groups in the products synthesised was observed. To the best of our knowledge, no palladium-catalysed method has so far been developed for the synthesis of 2-substituted 3,1-benzoxathiin-4-ones. We have described, for the first time, a palladium-mediated and copper-catalysed synthesis of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones from easily available starting materials. The excellent regio- and stereoselectivity exhibited by the procedure make it highly attractive. Furthermore, a vinylic functionality with a variety of aromatic substituents has been accommodated without affecting the main heteroannulation process. The method is operationally simple, does not involve any toxic reagent, and could be carried out under mild conditions. Also, 2-(2-arylvinyl)-3,1-benzoxathiin-4-ones could be of potential biological significance because of the presence of various active functionalities (*e.g.*, vinyl, lactone, sulfur moieties) in the molecular domain.

Experimental

Mps are uncorrected. Reactions were performed under argon atmosphere. Bis(triphenylphosphine)palladium(II) dichloride was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, USA, and copper(I) iodide fron Merck–Schuchardt. Light petroleum used was the fraction boiling between 60–80 °C. Column chromatography was performed on silica gel (60–120 mesh). TLC was done on 60F-254 precoated sheets. Aryl iodides were prepared according to the procedure given for the synthesis of iodobenzene.[28a] 2-Iodothiophene,[28b] 2,5-diiodothiophene,[28b] and 5-iodo-2,4-dimethoxypyrimidine[28c] were synthesised according to the known procedures. IR spectra (neat or KBr pellets) were recorded on a Shimadzu FTIR 8300. ^{1}H NMR spectra for $CDCl_3$ solution were recorded at 300 MHz on Bruker DPX 300 and Varian EM 360 spectrophotometers, respectively. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker DPX 300 spectrophotometer.

Synthesis of 3-[2-(methoxycarbonyl)phenylthio]propyne 2

Methyl thiosalicylate **1** (9.04 mmol) in acetone (20 cm^3) was stirred with K_2CO_3 (9.04 mmol) at room temperature under argon atmosphere for 4 h. Propargyl (prop-2-ynyl) bromide (9.04 mmol) was added slowly to the reaction mixture and stirring was continued for 1 h at room temperature followed by reflux for 16 h. The solvent was removed and the residue was diluted with water (10 cm^3). This was extracted with $CHCl_3$ (3 × 15 cm^3), the extract was washed with water (5 cm^3), dried (anh. Na_2SO_4), and the solvent was removed. The crude product obtained was purified by column chromatography on silica gel with the eluent being 8:1 light petroleum–$CHCl_3$ to afford compound **2** as a white solid in 84% yield, mp 95 °C (Found: C, 64.17; H, 4.95. $C_{11}H_{10}O_2S$ requres C, 64.05; H, 4.88%); ν_{max} (KBr)/cm^{-1} 3247.9, 2150.0, 1701.1, 1587.3, 1564.2; δ_H (300 MHz; $CDCl_3$) 2.2 (t, *J* 2.7 Hz, 1H, C≡CH), 3.63 (d, *J* 2.7 Hz, 2H, SCH_2), 3.9 (s, 3H, $COOCH_3$), 7.18 (td, *J* 7.2 and 1.8 Hz, 1H, ArH), 7.43–7.51 (m, 2H, ArH), 7.98 (d, *J* 8.1 Hz, 1H, ArH); δ_C ($CDCl_3$) 20.4, 52.1, 79.2, 124.2, 124.4, 125.6, 127.3, 131.2, 132.4, 140.1, 166.6; δ_C ($CDCl_3$; DEPT 135) 20.6 (inverted), 52.3, 79.4, 124.6, 125.9, 131.4, 132.7.

Typical procedure for the synthesis of 3-[2-(methoxycarbonyl)-phenylthio]-1-phenylpropyne 4a

A mixture of iodobenzene **3a** (2.42 mmol), $(PPh_3)_2PdCl_2$ (0.07 mmol, 3 mol%), CuI (0.14 mmol, 6 mol%) and Et_3N (9.68 mmol) in CH_3CN (10 cm^3) was stirred at room temperature for 0.5 h in an argon atmosphere. Compound **2** (2.42 mmol) was added slowly to the reaction mixture, which was then stirred at room temperature for 20 h. After removal of the solvent under reduced pressure, the residue was diluted with water (5 cm^3) and extracted thoroughly with $CHCl_3$ (3 × 20 cm^3). The organic

layer was washed with water (2 × 5 cm^3), dried (anh. Na_2SO_4), and the solvent was distilled off. A brown gum was obtained which was purified by column chromatography on silica gel with the eluent being 1:1 $CHCl_3$–light petroleum to furnish compound **4a** as a white solid, mp 79 °C (Found: C, 72.23; H, 5.03. $C_{17}H_{14}O_2S$ requires C, 72.31; H, 4.99%); ν_{max} (KBr)/cm^{-1} 1710.7, 1589.2, 1562.2; δ_H (300 MHz; $CDCl_3$) 3.79 (s, 2H, SCH_2), 3.81 (s, 3H, $COOCH_3$), 7.08–7.17 (m, 4H, ArH), 7.25–7.28 (m, 2H, ArH), 7.37–7.47 (m, 2H, ArH), 7.9 (d, *J* 7.8 Hz, 1H, ArH); δ_C ($CDCl_3$) 22.1, 42.5, 83.9, 85.1, 119.6, 123.3, 124.8, 126.4, 128.4, 128.6, 131.7, 132.1, 132.9, 141.1, 167.2; δ_C ($CDCl_3$; DEPT 135) 21.8 (inverted), 52.3, 124.5, 126.2, 128.1, 128.3, 131.4, 131.8, 132.6.

Compounds **4b–4h** were synthesised from aryl iodides **3b–3h** according to the procedure followed for the synthesis of compound **4a**.

3-[2-(Methoxycarbonyl)phenylthio]-1-(*p*-tolyl)propyne 4b. White solid, mp 92 °C (Found: C, 73.02; H, 5.26. $C_{18}H_{16}O_2S$ requires C, 72.94; H, 5.44%); ν_{max}(KBr)/cm^{-1} 1705.0, 1585.4, 1566.1, 1508.2; δ_H (300 MHz; $CDCl_3$) 2.30 (s, 3H, $ArCH_3$), 3.88 (s, 2H, SCH_2), 3.90 (s, 3H, $COOCH_3$), 7.05 (d, *J* 8.1 Hz, 2H, ArH), 7.18 (t, *J* 7.5 Hz, 1H, ArH), 7.24 (d, *J* 7.8 Hz, 2H, ArH), 7.48 (td, *J* 7.2 and 1.2 Hz, 1H, ArH), 7.54 (d, *J* 6.9 Hz, 1H, ArH), 7.99 (dd, *J* 7.5 and 1.2 Hz, 1H, ArH); δ_C ($CDCl_3$) 21.8, 22.2, 52.6, 84.0, 84.2, 120.2, 124.8, 126.5, 128.0, 129.4, 131.7, 132.0, 132.9, 137.7, 138.7, 167.2; δ_C ($CDCl_3$; DEPT 135) 21.5, 21.9 (inverted), 52.3, 124.5, 126.2, 129.1, 131.4, 131.7, 132.6, 137.3.

3-[2-(Methoxycarbonyl)phenylthio]-1-(2-methoxyphenyl)-propyne 4c. White solid, mp 99 °C (Found: C, 69.14; H, 5.09. $C_{18}H_{16}O_3S$ requires C, 69.2; H, 5.16%); δ_H (300 MHz; $CDCl_3$) 3.83 (s, 3H, $ArOCH_3$), 3.95 (s, 2H, SCH_2), 3.98 (s, 3H, ArH), 6.83 (d, *J* 8.1 Hz, 2H, ArH), 7.2–7.41 (m, 3H, ArH), 7.75 (d, *J* 7.5 Hz, 2H, ArH), 8.06 (dd, *J* 7.5 and 1.2 Hz, 1H, ArH).

3-[2-(Methoxycarbonyl)phenylthio]-1-(4-methoxyphenyl)-propyne 4d. White solid, mp 65 °C (Found: C, 69.04; H, 5.06. $C_{18}H_{16}O_3S$ requires C, 69.2; H, 5.16%); ν_{max} (KBr)/cm^{-1} 1705.0, 1604.7, 1585.4, 1564.2; δ_H (300 MHz; $CDCl_3$) 3.77 (s, 3H, $ArOCH_3$), 3.88 (s, 2H, SCH_2), 3.91 (s, 3H, $COOCH_3$), 6.78 (d, *J* 8.76 Hz, 2H, ArH), 7.2 (td, *J* 7.2 and 1.2 Hz, 1H, ArH), 7.29 (d, *J* 8.7 Hz, 2H, ArH), 7.47–7.57 (m, 2H, ArH), 7.99 (dd, *J* 7.7 and 1.2 Hz, 1H, ArH); δ_C ($CDCl_3$) 21.8, 52.2, 55.2, 83.0, 83.4, 113.8, 115.0, 124.3, 126.1, 129.6, 131.3, 132.5, 131.3, 132.5, 133.1, 140.7, 159.5, 166.8; δ_C ($CDCl_3$; DEPT 135) 21.9 (inverted), 52.3, 55.4, 114.0, 124.5, 126.2, 131.4, 132.6, 133.2.

3-[2-(Methoxycarbonyl)phenylthio]-1-(1-naphthyl)propyne 4e. White solid, mp 85 °C (Found: C, 75.81; H, 4.83. $C_{21}H_{16}O_2S$ requires C, 75.87; H, 4.85%); ν_{max} (KBr)/cm^{-1} 1714.6, 1585.4, 1560.0; δ_H (300 MHz; $CDCl_3$) 3.73 (s, 3H, $COOCH_3$), 3.73 (s, 2H, SCH_2), 7.02 (t, *J* 7.5 Hz, 1H, ArH), 7.18 (t, *J* 7.5 Hz, 1H, ArH), 7.27–7.35 (m, 3H, ArH), 7.42–7.48 (m, 2H, ArH), 7.57–7.62 (m, 2H, ArH), 7.85 (d, *J* 7.8 Hz, 1H, ArH), 7.98–8.01 (m, 1H, ArH); δ_C ($CDCl_3$) 22.3, 25.6, 82.0, 90.1, 120.9, 124.9, 125.6, 126.6, 126.8, 127.1, 128.0, 128.7, 129.2, 130.9, 131.8, 133.0, 133.5, 133.8, 141.0, 167.2; δ_C ($CDCl_3$; DEPT 135) 22.3, 52.65, 124.9, 125.6, 126.6, 126.8, 127.1, 128.6, 129.2, 130.9, 131.8, 133.0.

3-[2-(Methoxycarbonyl)phenylthio]-1-(2-naphthyl)propyne 4f. White solid, mp 90 °C (Found: C, 76.01; H, 4.92. $C_{21}H_{16}O_2S$ requires C, 75.87; H, 4.85%); ν_{max} (KBr)/cm^{-1} 1708.8, 1591.2, 1564.2; δ_H (300 MHz; $CDCl_3$) 3.79 (s, 3H, $COOCH_3$), 3.81 (s, 2H, SCH_2), 7.08 (td, *J* 7.2 and 1.2 Hz, 1H, ArH), 7.27–7.34 (m, 3H, ArH), 7.38 (td, *J* 8.4 and 1.5 Hz, 1H, ArH), 7.46 (d, *J* 8.1 Hz, 1H, ArH), 7.58–7.65 (m, 3H, ArH), 7.76 (s, 1H, ArH), 7.88 (dd, *J* 7.8 and 1.5 Hz, 1H, ArH); δ_C ($CDCl_3$) 22.2, 52.6, 84.3, 85.4, 120.6, 124.8, 126.4, 126.9, 127.0, 127.9, 128.1, 128.3, 128.8, 131.8, 132.0, 133.0, 133.2, 133.3, 141.1, 167.2; δ_C ($CDCl_3$; DEPT 135) 21.9, 52.3, 124.6, 126.2, 126.6, 126.8, 127.8, 128.0, 128.6, 131.5, 131.7, 132.7.

1-(3-Chlorophenyl)-3-[2-(methoxycarbonyl)phenylthio]propyne 4g. White solid, mp 80 °C (Found: C, 64.39; H, 4.09. $C_{17}H_{13}ClO_2S$ requires C, 64.44; H, 4.13%); ν_{max} (KBr)/cm^{-1} 1710.7, 1591.2, 1562.2; δ_H (300 MHz; $CDCl_3$) 3.88 (s, 2H, SCH_2), 3.91 (s, 3H, $COOCH_3$), 7.15–7.27 (m, 4H, ArH), 7.33 (s, 1H, ArH), 7.51 (d, *J* 7 Hz, 2H, ArH), 8.00 (d, *J* 7.5 Hz, 1H, ArH); δ_C ($CDCl_3$) 21.9, 52.6, 82.5, 86.4, 124.9, 126.4, 127.9, 128.9, 129.9, 130.2, 131.8, 131.9, 133.0, 134.4, 140.8, 167.2; δ_C ($CDCl_3$; DEPT 135) 21.7, 52.3, 124.6, 126.1, 128.6, 129.6, 130.0, 131.5, 131.7, 132.7.

3-[2-(Methoxycarbonyl)phenylthio]-1-(2-thienyl)propyne 4h. White solid, mp 86 °C (Found: C, 70.19; H, 4.73. $C_{15}H_{12}O_2S$ requires C, 70.28; H, 4.72%); ν_{max} (KBr)/cm^{-1} 1706.9, 1585.4, 1564.2; δ_H (300 MHz; $CDCl_3$) 3.93 (s, 3H, $COOCH_3$), 3.96 (s, 2H, SCH_2), 7.23 (td, *J* 7.8 and 1.2 Hz, 1H, ArH), 7.41 (dd, *J* 8.4 and 1.5 Hz, 1H, ArH), 7.45–7.48 (m, 2H, ArH), 7.54 (td, *J* 8.1 and 1.5 Hz, 1H, ArH), 7.61 (d, *J* 7.8 Hz, 1H, ArH), 8.03 (dd, *J* 7.8 and 1.2 Hz, 1H, ArH); δ_C ($CDCl_3$) 22.2, 52.6, 84.2, 85.4, 120.5, 124.8, 126.4, 127.1, 127.9, 128.1, 128.8, 131.8, 133.0, 141.1, 167.3; δ_C ($CDCl_3$; DEPT 135) 21.9 (inverted), 52.3, 124.5, 126.1, 126.6, 127.8, 128.6, 131.5, 132.7.

Typical procedure for the synthesis of (*E*)-2-styryl-3,1-benzoxathiin-4-one 5a

3-[2-(Methoxycarbonyl)phenylthio]-1-phenylpropyne **4a** (1.4 mmol) was stirred with a methanolic solution of potassium hydroxide (5 M; 25 cm^3) at room temperature for 2 h in an argon atmosphere. After the removal of methanol under reduced pressure, the residue was diluted with water (5 cm^3), acidified with dil. HCl (1:1) and extracted with diethyl ether (3 × 30 cm^3). The combined organic layer was washed with water (5 cm^3) and dried (anh. Na_2SO_4). The crude product obtained was then heated under reflux with CuI (0.28 mmol; 20 mol%) and Et_3N (2.86 mmol) in THF (20 cm^3) in an argon atmosphere for 24 h. After removal of the solvent and Et_3N, the residue was purified by column chromatography on silica gel (60–120 mesh) with the eluent being 1:1 $CHCl_3$–light petroleum to furnish **5a** as a light yellow solid, mp 96 °C (Found: C, 71.59; H, 4.54. $C_{16}H_{12}O_2S$ requires C, 71.61; H, 4.50%); ν_{max} (KBr)/cm^{-1} 1726.2, 1593.1, 1541.0; δ_H (300 MHz; $CDCl_3$) 6.14 (d, *J* 6 Hz, 1H, SCH), 6.32 (dd, *J* 15.6 and 6 Hz, 1H, C*H*=CHPh), 6.87 (d, *J* 15.6 Hz, 1H, CH=C*H*Ph), 7.22–7.27 (m, 5H, ArH), 7.34 (d, *J* 7.2 Hz, 2H, ArH), 7.41 (t, *J* 7.2 Hz, 1H, ArH), 8.12 (d, *J* 7.8 Hz, 1H, ArH); δ_C ($CDCl_3$) 82.4, 122.0, 124.7, 127.2, 127.4, 128.0, 129.2, 129.4, 133.1, 134.2, 135.4, 135.81, 138.6, 164.2; δ_C ($CDCl_3$; DEPT 135) 82.1, 121.7, 126.9, 127.2, 127.7, 128.9, 129.1, 132.8, 133.9, 135.5.

Compounds **5b–5h** were synthesised from **4b–4h** following the procedure for the synthesis of **5a**.

(*E*)-2-[2-(*p*-Tolyl)vinyl]-3,1-benzoxathiin-4-one 5b. Light yellow solid, mp 89 °C (Found: C, 72.35; H, 5.01. $C_{17}H_{14}O_2S$ requires C, 72.31; H, 4.99%); ν_{max} (KBr)/cm^{-1} 1728.1, 1589.2, 1512.2; δ_H (300 MHz; $CDCl_3$) 2.35 (s, 3H, $ArCH_3$), 6.22 (d, *J* 6.3 Hz, 1H, SCH), 6.36 (dd, *J* 15.9 and 6.3 Hz, 1H, C*H*=CHAr), 6.92 (d, *J* 15.9 Hz, 1H, CH=C*H*Ar), 7.16 (d, *J* 7.8 Hz, 2H, ArH), 7.31–7.37 (m, 4H, ArH), 7.5 (td, *J* 9 and 1.2 Hz, 1H, ArH), 8.2 (d, *J* 8.1 Hz, 1H, ArH); δ_C ($CDCl_3$) 20.3, 81.2, 119.5, 124.8, 125.7, 125.9, 126.5, 128.4, 129.0, 131.6, 132.6, 134.4, 137.3, 138.0, 162.8; δ_C ($CDCl_3$; DEPT 135) 20.3, 81.2, 119.5, 125.7, 125.9, 126.5, 128.4, 131.6, 132.6, 134.3.

(*E*)-2-[2-(2-Methoxyphenyl)vinyl]-3,1-benzoxathiin-4-one 5c. White solid, mp 99 °C (Found: C, 68.4; H, 4.71. $C_{17}H_{14}O_3S$ requires C, 68.43; H, 4.73%); ν_{max} (KBr)/cm^{-1} 1728.1, 1596.9; δ_H (300 MHz; $CDCl_3$) 3.78 (s, 3H, ArOC*H*$_3$), 6.16 (dd, *J* 6.6 and 1.2 Hz, 1H, SCH), 6.42 (dd, *J* 15.9 and 6.6 Hz, 1H, C*H*=CHAr), 6.81–6.9 (m, 2H, CH=C*H*Ar, ArH), 7.18–7.29 (m, 4H, ArH), 7.35–7.45 (m, 2H, ArH), 8.13 (dd, *J* 7.8 and 1.2 Hz, 1H, ArH); δ_C ($CDCl_3$) 55.8, 83.2, 111.4, 121.0, 122.6, 124.3, 124.7, 127.1, 128.2, 130.5, 131.3, 133.0, 134.0, 138.9, 157.8, 164.4; δ_C ($CDCl_3$; DEPT 135) 55.5, 82.9, 111.1, 120.8, 122.3, 126.8, 127.7, 127.9, 128.4, 130.2, 131.0, 132.7, 133.8.

(*E*)-2-[2-(4-Methoxyphenyl)vinyl]-3,1-benzoxathiin-4-one 5d. Light yellow solid, mp 91 °C (Found: C, 68.45; H, 4.72. $C_{17}H_{14}O_3S$ requires C, 68.43; H, 4.73%); ν_{max} (KBr)/cm^{-1} 1724.2, 1602.7, 1571.9; δ_H (300 MHz; $CDCl_3$) 3.73 (s, 3H, ArOC*H*$_3$), 6.11 (d, *J* 6.6 Hz, 1H, SCH), 6.19 (dd, *J* 15.6 and 6.6 Hz, 1H, C*H*=CHAr), 6.78–6.84 (m, 3H, CH=C*H*Ar, ArH), 7.22–7.29 (m, 4H, ArH), 7.42 (t, *J* 7.8 Hz, 1H, ArH), 8.11 (d, *J* 7.5 Hz, 1H, ArH); δ_C ($CDCl_3$) 55.7, 82.8, 114.6, 119.6, 124.7, 127.2, 128.0, 128.1, 128.8, 133.0, 134.1, 135.5, 138.8, 160.7, 164.4; δ_C ($CDCl_3$; DEPT 135) 55.4, 82.5, 114.3, 119.3, 126.7, 127.7, 128.5, 132.2, 132.7, 133.8.

(*E*)-2-[2-(1-Naphthyl)vinyl]-3,1-benzoxathiin-4-one 5e. White solid, mp 120 °C (Found: C, 75.39; H, 4.41. $C_{20}H_{14}O_2S$ requires C, 75.44; H, 4.43%); ν_{max} (KBr)/cm^{-1} 1730.0, 1585.3; δ_H (300 MHz; $CDCl_3$) 6.26 (d, *J* 6 Hz, 1H, SCH), 6.51 (dd, *J* 15.6 and 6 Hz, 1H, C*H*=CHAr), 7.11 (d, *J* 15.6 Hz, 1H, CH=C*H*Ar), 7.31–7.42 (m, 5H, ArH), 7.5–7.67 (m, 4H, ArH), 7.87 (d, *J* 7.8 Hz, 1H, ArH), 8.24 (d, *J* 7.8 Hz, 1H, ArH).

(*E*)-2-[2-(2-Naphthyl)vinyl]-3,1-benzoxathiin-4-one 5f. White solid, mp 137 °C (Found: C, 75.41; H, 4.44. $C_{20}H_{14}O_2S$ requires C, 75.44; H, 4.43%); ν_{max} (KBr)/cm^{-1} 1732.0, 1589.2; δ_H (300 MHz; DMSO-d_6 + $CDCl_3$) 6.29 (d, *J* 6 Hz, 1H, SCH), 6.53 (dd, *J* 15.6 and 6 Hz, 1H, C*H*=CHAr), 7.13 (d, *J* 15.6 Hz, 1H, CH=C*H*Ar), 7.33–7.39 (m, 2H, ArH), 7.47–7.55 (m, 3H, ArH), 7.61 (d, *J* 8.7 Hz, 1H, ArH), 7.82 (d, *J* 7.8 Hz, 4H, ArH), 8.22 (d, *J* 7.8 Hz, 1H, ArH); δ_C (DMSO-d_6 + $CDCl_3$) 32.5, 122.2, 123.7, 124.7, 126.9, 127.0, 127.2, 128.0, 128.1, 128.3, 128.6, 128.9, 132.8, 133.1, 133.8, 134.0, 134.1, 135.9, 138.7, 164.1; δ_C (DMSO-d_6 + $CDCl_3$; DEPT 135) 82.2, 121.9, 123.4, 126.6, 126.7, 126.9, 127.7, 127.8, 128.0, 128.3, 128.6, 132.8, 133.8, 135.6.

(*E*)-2-[2-(3-Chlorophenyl)vinyl]-3,1-benzoxathiin-4-one 5g. Light yellow solid, mp 101 °C (Found: C, 71.92; H, 4.14. $C_{16}H_{11}ClO_2S$ requires C, 71.88; H, 4.15%); ν_{max} (KBr)/cm^{-1} 1728.2, 1595.7; δ_H (300 MHz; $CDCl_3$) 6.16 (d, *J* 6 Hz, 1H, SCH), 6.35 (dd, *J* 15.6 and 6 Hz, 1H, C*H*=CHAr), 6.91 (d, *J* 15.6 Hz, 1H, CH=C*H*Ar), 7.31–7.39 (m, 4H, ArH), 7.43 (s, 1H, ArH), 7.65 (d, *J* 7.2 Hz, 2H, ArH), 8.22 (d, *J* 7.5 Hz, 1H, ArH).

(*E*)-2-[2-(2-Thienyl)vinyl]-3,1-benzoxathiin-4-one 5h. White solid, mp 128 °C (Found: C, 61.18; H, 3.61. $C_{14}H_{10}O_2S_2$ requires C, 61.28; H, 3.67%); ν_{max} (KBr)/cm^{-1} 1720.4, 1585.4, 1564.2; δ_H (300 MHz; $CDCl_3$) 6.18 (d, *J* 6 Hz, 1H, SCH), 6.23 (dd, *J* 15.6 Hz, 1H, C*H*=CHAr), 6.99–7.01 (m, 1H, ArH), 7.07–7.12 (m, 2H, CH=C*H*Ar, ArH), 7.27 (d, *J* 4.5 Hz, 1H, ArH), 7.36 (d, *J* 7.5 Hz, 2H, ArH), 7.51 (td, *J* 7.8 and 1.2 Hz, 1H, ArH), 8.2 (dd, *J* 7.5 and 0.9 Hz, 1H, ArH).

Isolation of the allenic intermediates 7a–d

Allenic acids were formed by the hydrolysis of the disubstituted alkynes **4** with methanolic KOH, acidification with dil. HCl and extraction with diethyl ether (see under **5a**). Some of them were isolated as pure compounds by crystallisation (diethyl ether–light petroleum) of the crude products formed.

1-(2-Carboxyphenylthio)-3-phenylpropa-1,2-diene 7a. White solid, mp 156 °C (Found: C, 71.51; H, 4.43. $C_{16}H_{12}O_2S$ requires C, 71.61; H, 4.50%); ν_{max} (KBr)/cm^{-1} 1936.4, 1681.8, 1593.1, 1573.8; δ_H (300 MHz; $CDCl_3$) 6.36 (d, *J* 6 Hz, 1H, C*H*=C=CHAr), 6.39 (d, *J* 6 Hz, 1H,CH=C=C*H*Ar), 7.12–7.2 (m, 2H, ArH), 7.26–7.3 (m, 4H, ArH), 7.46–7.48 (m, 1H, ArH), 7.57 (d, *J* 7.8 Hz, 1H, ArH), 7.98 (d, *J* 7.8 Hz, 1H, ArH); δ_C ($CDCl_3$) 94.0, 120.3, 129.7, 131.7, 132.5, 132.7, 133.4, 133.9, 136.8, 137.6, 137.9, 146.2, 173.3, 213.6.

1-(2-Carboxyphenylthio)-3-(*p*-tolyl)propa-1,2-diene 7b. White solid, mp 149 °C (Found: C, 72.19; H, 4.85. $C_{17}H_{14}O_2S$ requires C, 72.31; H, 4.99%); ν_{max} (KBr)/cm^{-1} 1932.5, 1678.0, 1585.4, 1562.2; δ_H (300 MHz; $CDCl_3$) 2.33 (s, 3H, ArC*H*$_3$), 6.38 (d, *J* 6 Hz, 1H, C*H*= C=CHAr), 6.41 (d, *J* 6 Hz, 1H, CH=C=C*H*Ar), 7.07 (d, *J* 8.1 Hz, 1H, ArH), 7.13 (d, *J* 8.1 Hz, 1H, ArH), 7.2–7.24 (m, 3H, ArH), 7.5 (t, *J* 7.2 Hz, 1H, ArH), 7.63 (d, *J* 7.8 Hz, 1H, ArH), 8.06 (d, *J* 7.8 Hz, 1H, ArH); δ_C ($CDCl_3$) 21.7, 88.9, 124.4, 124.7, 125.7, 126.8, 127.5, 129.2, 129.7, 130.0, 132.0, 132.6, 137.9, 168.6, 208.7; δ_C ($CDCl_3$; DEPT 135) 21.9, 89.0, 124.9, 127.0, 127.7, 129.4, 129.9, 132.2, 132.8.

1-(2-Carboxyphenylthio)-3-(2-methoxyphenyl)propa-1,2-diene 7c. White solid, mp 132 °C (Found: C, 68.31; H, 4.69. $C_{17}H_{14}O_3S$ requires C, 68.43; H, 4.73%); ν_{max} (KBr)/cm^{-1} 1932.0, 1670.0, 1585.5; δ_H (300 MHz; $CDCl_3$) 3.78 (s, 3H, ArOC*H*$_3$), 6.27 (d, *J* 6 Hz, 1H, C*H*=C=CHAr), 6.73 (d, *J* 6 Hz, 1H, CH=C=C*H*Ar), 6.79–6.89 (m, 2H, ArH), 7.12–7.17 (m, 2H, ArH), 7.3–7.32 (m, 1H, ArH), 7.43 (t, *J* 7.2 Hz, 1H, ArH), 7.58 (d, *J* 7.8 Hz, 1H, ArH), 8.00 (d, *J* 7.5 Hz, 1H, ArH).

1-(2-Carboxyphenylthio)-3-(2-naphthyl)propa-1,2-diene 7d. White solid, mp 154 °C (Found: C, 75.4; H, 4.41. $C_{20}H_{14}O_2S$ requires C, 75.44; H, 4.43%); ν_{max} (KBr)/cm^{-1} 1932.5, 1678.0, 1596.9, 1585.4; δ_H (300 MHz; $CDCl_3$) 6.49 (d, *J* 6 Hz, 1H, C*H*=C=CHAr), 6.62 (d, *J* 6 Hz, 1H, CH=C=C*H*Ar), 7.24 (td, *J* 7.2 and 1.2 Hz, 1H, ArH), 7.44–7.53 (m, 4H, ArH), 7.66–7.71 (m, 2H, ArH), 7.77–7.81 (m, 3H, ArH), 8.08 (dd, *J* 7.6 and 1.5 Hz, 1H, ArH); δ_C ($CDCl_3$) 89.6, 98.0, 125.0, 125.2, 126.4, 126.7, 126.9, 127.3, 128.1, 128.2, 128.8, 130.7, 132.1, 132.8, 133.3, 133.9, 141.6, 168.7, 209.3; δ_C ($CDCl_3$; DEPT 135) 89.3, 97.7, 124.7, 124.9, 126.1, 126.5, 126.6, 126.7, 127.8, 127.9, 128.5, 131.9, 132.5.

Reaction of compound 5a with alkali

Compound **5a** (0.25 mmol) was refluxed with 5 M methanolic KOH solution (7 cm^3) for 12 h in an argon atmosphere. After removal of the solvent under reduced pressure the residue was diluted with water (2 cm^3) followed by extraction with $CHCl_3$ (3 × 5 cm^3). The organic layer was dried (anh. Na_2SO_4) and the solvent was distilled off. Cinnamaldehyde **8a** was obtained as a light yellow oil which was identical with an authentic sample. The aqueous part was then acidified with dil. HCl (1:1) and the precipitate was filtered off and dried *in vacuo*; a white solid was obtained which was identified as thiosalicylic acid, mp 163 °C (mp of an authentic sample was 165 °C).

Hydrogenation of (*E*)-2-(2-arylvinyl)-3,1-benzoxathiin-4-ones. A typical procedure

Styryl-3,1-benzoxathiin-4-one **5a** (0.18 mmol) in dry ethyl acetate (5 cm^3) was hydrogenated in the presence of palladium on activated charcoal (10%; 0.06 mmol) at room temperature under atmospheric pressure for 48 h. After completion of the reaction, the catalyst was removed by filtration, washed with ethyl acetate (20 cm^3), and the solvent was distilled off. The residue was purified by preparative TLC, using light petroleum–ethyl acetate (1:2) as the eluent, to yield 1-(2-carboxyphenylthio)-3-phenylpropane **9a** as a pale yellow solid (90%), mp

121 °C (Found: C, 70.59; H, 5.91. $C_{16}H_{16}O_2S$ requires C, 70.55; H, 5.92%); ν_{max} (KBr)/cm^{-1} 1681.8, 1585.4, 1562.2; δ_H (300 MHz; $CDCl_3$) 1.94–2.04 (m, 2H, SCH_2CH_2), 2.73 (t, *J* 7.2 Hz, 2H, CH_2Ar), 2.85 (t, *J* 7.2 Hz, 2H, SCH_2), 7.06–7.24 (m, 7H, ArH), 7.35 (t, *J* 7.5 Hz, 1H, ArH), 8.04 (d, *J* 7.8 Hz, 1H, ArH), 8.88 (br s, 1H, COOH).

Compounds **9b** and **9c** were synthesised from **5b** and **5d** following the procedure for **9a**.

1-(2-Carboxyphenylthio)-3-(*p*-tolyl)propane 9b. Light yellow solid, mp 118 °C (Found: C, 71.41; H, 6.38. $C_{17}H_{18}O_2S$ requires C, 71.29; H, 6.33%); ν_{max} (KBr)/cm^{-1} 1689.5, 1585.4, 1560.3; δ_H (300 MHz; $CDCl_3$) 1.92–2.02 (m, 2H, SCH_2CH_2), 2.25 (s, 3H, $ArCH_3$), 2.7 (t, *J* 7.5 Hz, 2H, CH_2Ar), 2.85 (t, *J* 7.5 Hz, 2H, SCH_2), 7.00–7.03 (m, 3H, ArH), 7.12 (t, *J* 8.1 Hz, 1H, ArH), 7.17–7.2 (m, 2H, ArH), 7.37 (td, *J* 7.5 and 1.5 Hz, 1H, ArH), 8.05 (dd, *J* 7.8 and 1.5 Hz, 1H, ArH); δ_C ($CDCl_3$) 20.0, 28.3, 30.6, 33.5, 123.1, 125.3, 127.2, 127.4, 128.1, 131.5, 132.0, 134.5, 136.9, 141.3, 169.1; δ_C ($CDCl_3$; DEPT 135) 20, 28.7 (inverted), 30.5 (inverted), 33.5 (inverted), 123, 125.1, 127.5, 128.1, 131.5, 132.1

1-(2-Carboxyphenylthio)-3-(4-methoxyphenyl)propane 9c. White solid, mp 113 °C (Found: C, 67.61; H, 5.97. $C_{17}H_{18}O_3S$ requires C, 67.52; H, 6.00%); ν_{max} (KBr)/cm^{-1} 1679.9, 1585.4, 1564.2; δ_H (300 MHz; $CDCl_3$) 1.91–2.00 (m, 2H, SCH_2CH_2), 2.68 (t, *J* 7.2 Hz, 2H, CH_2Ar), 2.84 (t, *J* 7.2 Hz, 2H, SCH_2), 3.72 (s, 3H, $ArOCH_3$), 6.76 (d, *J* 8.4 Hz, 2H, ArH), 7.03–7.18 (m, 4H, ArH), 7.36 (td, *J* 7.5 and 1.2 Hz, 1H, ArH), 8.04 (dd, *J* 7.8 and 1.2 Hz, 1H, ArH); δ_C ($CDCl_3$) 30.2, 31.7, 34.4, 55.6, 114.3, 124.3, 126.3, 126.9, 129.8, 132.9, 133.5, 134.1, 143.0, 158.4, 171.4; δ_C ($CDCl_3$; DEPT 135) 30.2 (inverted), 31.6 (inverted), 34.4 (inverted), 55.6, 114.3, 124.3, 126.2, 129.8, 132.9, 133.5.

Synthesis of 10

A solution of **5g** (0.33 mmol) in methanol was heated under reflux with sodium methoxide (0.82 mmol) in an argon atmosphere for 15 h. After usual work-up, the residue was purified by column chromatography on silica gel with the eluent being 1:1 $CHCl_3$–light petroleum to furnish the disulfide **10** as a white solid in 82% yield, mp 128 °C (Found: C, 57.58; H, 4.18. $C_{16}H_{14}O_4S_2$ requires C, 57.46; H, 4.22%); ν_{max} (KBr)/cm^{-1} 1710.7, 1587.3, 1562.2; δ_H (300 MHz; $CDCl_3$) 3.88 (s, 6H, $ArCOOCH_3$), 7.2 (td, *J* 7.5 and 1.5 Hz, 2H, ArH), 7.44–7.53 (m, 4H, ArH), 7.95 (dd, *J* 7.8 and 1.2 Hz, 2H, ArH); δ_C ($CDCl_3$) 35.8, 52.6, 125.2, 127.0, 128.5, 131.7, 133.0, 140.6, 167.0; δ_C ($CDCl_3$; DEPT 135) 35.4, 52.3, 124.8, 126.6, 131.4, 132.7.

Synthesis of the disulfide 11

A mixture of compound **5g** (0.25 mmol) and aniline (0.75 mmol) in benzene (5 cm^3) was heated under reflux for 15 h in an argon atmosphere. The resulting reaction mixture was then diluted with water (5 cm^3) and the benzene layer was separated. This was washed successively with dil. HCl (2 × 3 cm^3) and with water (2 × 5 cm^3) and dried (anh. Na_2SO_4). After removal of the solvent, a brown residue was obtained which was purified by column chromatography on silica gel (60–120 mesh) with the eluent being 1:1 $CHCl_3$–light petroleum to afford *m*-chlorocinnamaldehyde **8g** and compound **11** as a white solid, mp 246 °C (lit.,[29] 248 °C) (Found: C, 68.25; H, 4.37; N, 6.18. Calc. for $C_{26}H_{20}N_2O_2S_2$: C, 68.39; H, 4.41; N, 6.13%); ν_{max} (KBr)/cm^{-1} 3288.4, 1849.0, 1598.9; δ_H (300 MHz; DMSO-d_6) 7.11 (t, *J* 7.2 Hz, 2H, ArH), 7.33–7.38 (m, 6H, ArH), 7.49 (t, *J* 7.8 Hz, 2H, ArH), 7.13–7.77 (m, 8H, ArH), 10.53 (s, 2H, NH); δ_C (DMSO-d_6) 120.9, 121.0, 124.8, 127.1, 129.3, 129.5, 132.2, 135.5, 137.4, 139.7, 166.5; δ_C (DMSO-d_6; DEPT 135) 120.7, 124.5, 126.8, 129.0, 129.2, 131.9.

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