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Synthesis of photochromic thieno-2*H*-chromene derivatives

Maria-João R.P. Queiroz [a,*], Roger Dubest [b], Jean Aubard [b], R. Faure [c], Robert Guglielmetti [d]

[a] *Departamento de Química, Universidade do Minho, Campus de Gualtar, 4700-320 Braga, Portugal*
[b] *ITODYS, ESA CNRS 7086, Université de Paris VII, rue Guy de la Brosse, F-75005 Paris, France*
[c] *ESA CNRS 6009, Université d'Aix-Marseille III, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cédex 20, France*
[d] *LCMOM, ESA CNRS 6114, Université de la Mediterranée, Faculté des Sciences de Luminy, 13288 Marseille Cédex 9, France*

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Abstract

Syntheses of photochromic thieno-2*H*-chromenes from hydroxybenzo[*b*]thiophenes and 1,1-diphenyl-2-propyn-1-ol using an acid catalyst are described. The hydroxybenzo[*b*]thiophenes were prepared by demethylation of methoxybenzo[*b*]thiophenes with pyridinium chloride or boron tribromide. The precursors were synthesized in two steps, which involved the reaction of methoxythiophenols with 3-bromobutan-2-one in an alkaline medium, to give ketoarylsulfides, followed by cyclization using phosphorus pentoxide or polyphosphoric acid. The photochromic behaviour of the target compounds was evaluated with the aid of the usual spectrokinetic parameters, and the results were compared to data from reference compounds that are benzoannellated in the 5,6 and 7,8 positions of the 2*H*-chromene system.

Keywords: Photochromism; Thieno-2*H*-chromenes; Hydroxybenzo[*b*]thiophenes; Flash photolysis; Spectrokinetic parameters

1. Introduction

In the past few decades, 2*H*-1-benzopyrans (2*H*-chromenes) have not been a target of studies involving photochromic compounds for practical applications. Instead, intensive research was devoted to the examination of their well-known spiro-heteroanalogs (spiropyrans) [1]. Indeed, Becker and coworkers established that naturally occuring or synthetic chromenes showed photochromic behaviour only at low temperatures [2,3]. Although a large number of photochromic compounds have been reported [1], the compounds that become yellow or orange upon UV irradiation are quite rare and are desirable for full-colour display applications.

A few years ago, some modified chromenes were synthesized and improved photochromic properties were obtained by using benzoannellated chromenes, namely the naphthopyrans. Moreover, several studies have shown that the alkyl groups at the sp^3 carbon should be replaced by aryl groups, to give photochromic behaviour at room temperature [4,5] and to prevent rapid fatigue under photoexcitation [6]. Among the structural modifications that could be carried out on the chromenes, heteroannellation represents an interesting approach to promoting improvements in their photochromic properties.

* Corresponding author. Tel. +351-253-604384; fax: +351-253-678983.
E-mail address: mjrpq@quimica.uminho.pt (M.-J. Queiroz).

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Various types of heteroannellated 2*H*-chromenes have been cited for their photochromic properties and for their ability to give ophthalmic lenses that are coloured in the sun and colourless in the dark [7,8]. The associated photochromic properties are based on the reversible conversion of the colourless pyran form to the coloured opened forms, when liquid solutions or polymer matrices containing the closed form are exposed to UV light or sunlight.

The thieno-2*H*-chromenes **1**, which exhibit interesting photochromic behaviour, were synthesized by the reaction of hydroxybenzo[*b*]thiophenes with 1,1-diphenyl-2-propyn-1-ol in the presence of an acid catalyst. The heterolytic scission of the sp^3 carbon–oxygen bond upon activation by UV-A light or by sunlight followed by the extremely fast (10^9–10^{12} s^{-1}) bond rotations produce the coloured opened forms (''photomerocyanines''), which may have structures and geometries of the types shown in Scheme 1 for type **1** compounds.

This present compounds could be considered as complementary to the heteroannellated compounds recently developed [9,10], in which five-membered heterocyclic rings are placed mainly in the 5–6 annellated position relative to the benzopyran nucleus.

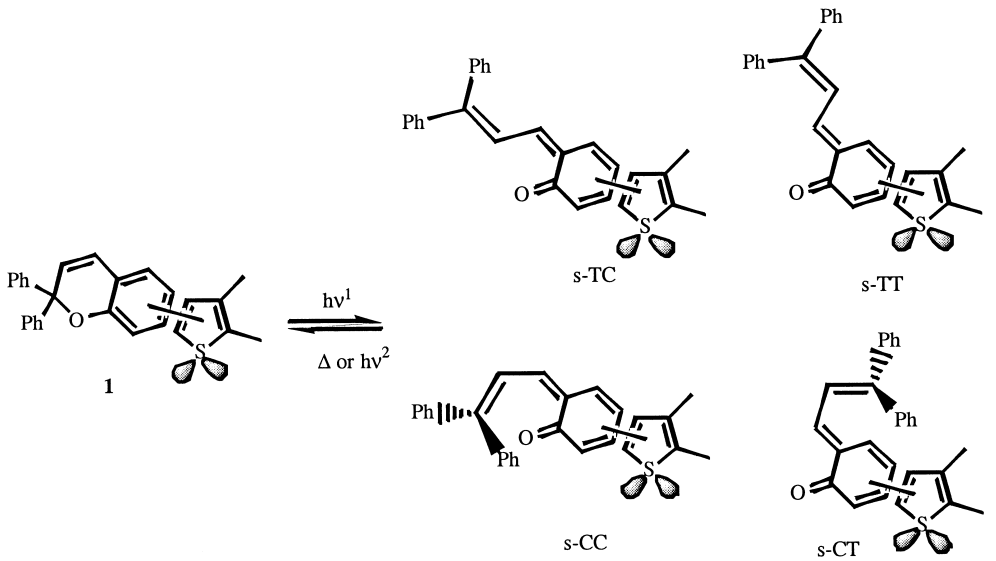
2. Results and discussion

2.1. Synthesis

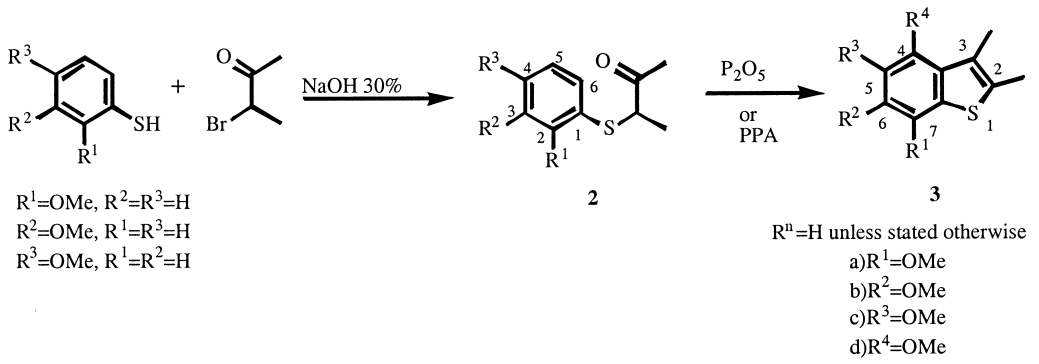
The hydroxybenzo[*b*]thiophenes were obtained by starting with the reaction of methoxythiophenols with 3-bromobutan-2-one in an alkaline medium to give ketoarylsulfides **2**, which in the presence of P_2O_5 or PPA cyclized to the methoxybenzo[*b*]thiophenes **3** [11] (Scheme 2). It was determined that better yields were obtained for the cyclisation reaction when PPA was used (Table 1).

In the prior study, compounds **3b** and **3d** were not separated, presumably because it was assumed that only compound **3b** had formed [11]. The characterization of the reaction product in that study involved only melting point determination and elemental analysis.

Pyridinium chloride [11] and boron tribromide were used, in order to compare yields in the demethylation step leading to the hydroxybenzo[*b*]thiophenes **4** (Scheme 3). The results of these experiments are shown in Table 2. Optimum reaction times were determined by TLC analysis. The BBr_3 method was not used for compound **4a** in view of satisfactory results from the pyridinium



Scheme 1.



Scheme 2.

Table 1
Comparative yields for the cyclisation reaction

	P_2O_5 (%)	PPA (%)
3a	69	100
3b[a]	19	31
3c	7	48
3d[a]	6	11

[a] These compounds were isolated from the same reaction.

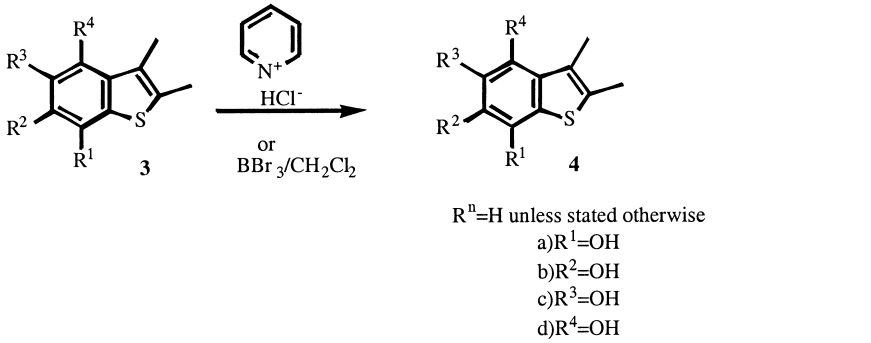
Table 2
Yields and reaction times for the demethylation of **4a–d**

	Pyridinium chloride (%)	BBr_3/CH_2Cl_2 (%)
4a	45 (15 min reflux)	–
4b	100 (30 min reflux)	54 (2h 30 min reflux)
4c	24 (30 min reflux)	79 (1 h reflux)
4d	26 (15 min reflux)	100 (2 h reflux)

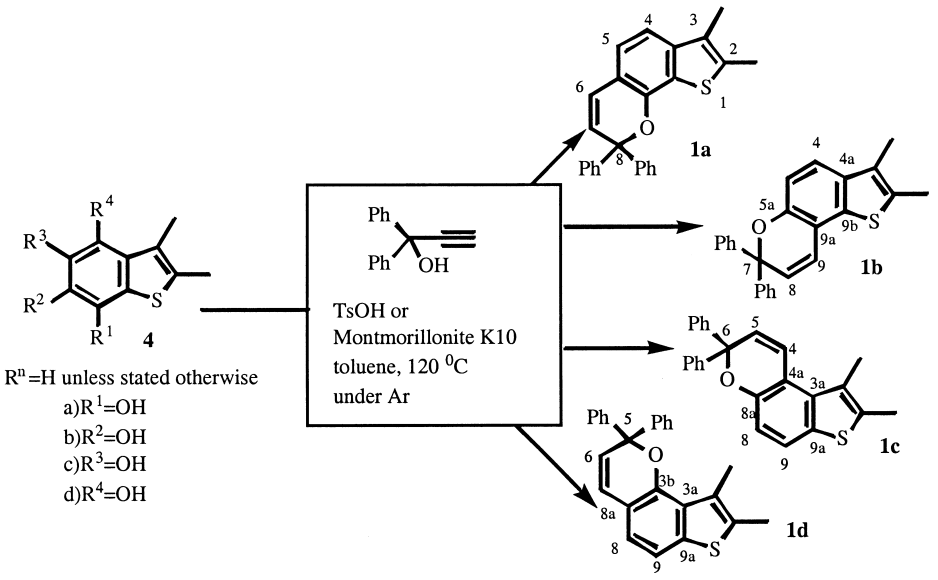
chloride method and the high yields obtained in the synthesis of its precursor **3a**.

The hydroxybenzo[*b*]thiophenes **4** were subsequently reacted with 1,1-diphenyl-2-propyn-1-ol in the presence of acid catalysis, TsOH or montmorillonite K10, to give the thieno-2*H*-chromenes **1** in 9–11% yields after chromatography (Scheme 4). The angular isomers **1b** and **1c** were the only products obtained when the compounds **4b** and **4c** were the starting materials.

Mechanistically, the synthesis of chromenes **1** involves the formation of propargyl aryl ethers by *O*-alkylation of the phenols. Thermal cyclisation of the propargyl aryl ethers affords the chromenes directly, presumably via a Claisen-like [3,3]-sigmatropic rearrangement, followed by a [1,5]-sigmatropic shift and cyclisation [12]. The formation of β-phenylcinnamaldehyde by Meyer–Schuster rearrangement [13] of 1,1-diphenyl-2-propyn-1-ol was evident from the ^{1}H NMR spectra of the



Scheme 3.



Scheme 4.

reaction mixtures after work-up, and helps explain the low yields of type **1** compounds and the presence of various by-products.

Thieno-2*H*-chromenes **1** were isolated in their closed *leuco* forms and were fully characterized by ^{1}H, ^{13}C NMR, heteronuclear correlations and electronic spectroscopy. As previously described for other types of heteroannellated chromenes [14], the ^{1}H NMR spectra of these compounds showed a one-proton doublet centered at δ 6–6.2 ppm with a coupling constant of 10 Hz, which is typical for the proton that is α to the quaternary carbon of the pyran ring. The presence of the sp^3 carbon (δ 80–83 ppm) of the pyran ring is a characteristic signal in the ^{13}C NMR spectrum.

In the UV–Vis spectra of the closed forms of compounds **1**, bands in three distinct absorption zones are observed: (1) low intensity absorption bands near 400 nm, (2) moderate absorption intensity absorption bands at 350–290 nm that normally have shoulders, and (3) high intensity absorption bands at 270–200 nm. These results are consistent with those reported previously [9,14].

2.2. Photochromic properties

Since photochromic behaviour is quantified by three main spectrokinetic parameters, compounds are normally compared in terms of absorption maxima for the coloured forms (λ_{max}), thermal bleaching (ring closure) rate (K_{Δ}), and "colourability" (A_0). Furthermore, photochromic compounds must satisfy the following performance criteria: (1) minimal fatigue or chemical instability upon repetitive cycling or continuous irradiation, (2) a highly efficient photoresponse in the near-UV, (3) a relatively fast thermal fading rate at room temperature, and (4) a minimum quantum yield for bleaching with visible light, thus preserving colour.

The spectra of the opened forms were determined in 2.5×10^{-5} M toluene solutions at 25°C, under flash photolysis (flashes of ca. 60 J, duration of ca. 50 μs), with the aid of a Warner–Swasey fast scanning spectrometer that was able to record the entire transient absorption spectrum in the visible region in 1.25 ms [15]. The kinetics for thermal bleaching of the coloured forms K_{Δ} were investigated by following the fading of colour at the wavelength of maximum absorption. The "colourability" that has been defined for photochromic compounds [16], is directly connected to the molar absorptivity of coloured species and to the quantum yield of colouration, and was evaluated by monitoring the absorbance (A_0) at λ_{max} immediately after the flashgun was fired. A_0 is the experimental value corresponding to Eq. (1):

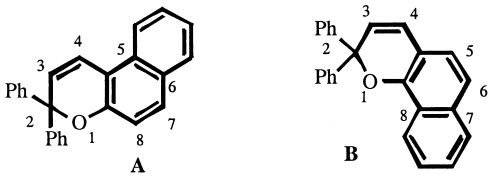
$$A_0 = \varepsilon_{MC}.\phi_{col}.k.C_{CF} \quad \text{(for low concentration)} \tag{1}$$

ε_{MC}, molar absorptivity of coloured forms
ϕ_{col}, quantum yield for photocolouration
k, constant including photolysis conditions
C_{CF}, initial concentration of the colourless form

The spectrokinetic properties of compounds **1** and of reference compounds [17] **A** and **B** (Fig. 1) are given in Table 3.

The opened forms of the diphenylbenzopyrans annellated in positions 5–6 or 7–8 with a dimethylthiophene nucleus (**1a**–**1d**) gave broad visible spectra with a shoulder or absorption maxima at high wavelength (520–540 nm). The sulfur atom had a bathochromic effect on the absorption maxima (or shoulders), as evident from a comparison with the opened forms of compounds **A** and **B** (Table 3).

For the dimethylthiophene or benzo-7,8-annellated compounds (**1a**, **1d** and **B**), we observed a very slow bleaching kinetic constant (ca. 10^{-3} s^{-1}).



(annnellation 5-6) (annnellation 7-8)

Fig. 1.

Table 3
Spectrokinetic parameters for chromenes **1** and reference compounds **A** and **B** (2.5×10^{-5} M in toluene, 25°C)

Chromenes	λ_1 (nm)	A_{01}	λ_2 (nm)	A_{02}	K_Δ (s^{-1})
1a	431	1.19	sh 520	0.31	$K=9.10^{-3}$ (460 nm)
1b	452	0.29	542	0.29	$K_1=0.17$ (540 nm) $K_2=0.058$
1c	432	0.71	sh 519	0.33	$K_1=0.31$ (432 nm) $K_2=0.037$
1d	405	0.79	528	0.34	$K=5.10^{-3}$ (530 nm)
A [17]	432	0.84	–	–	$K=0.1$ (432 nm)
B [17]	403	1.08	482	1.62	$K=2.10^{-3}$ (482 nm)

On the other hand, dimethylthiophene-5,6-annellated compounds (**1b** and **1c**) gave two rapid bleaching kinetic constants (around 10^{-1} and 10^{-2} s^{-1}), with only one observed for reference compound A (10^{-1} s^{-1}) (Table 3). These differences in the thermal bleaching constants are thought to be related to (i) the geometry of the photomerocyanine opened forms, in the case of the two types of annellations (5–6) and (7–8), and (ii) the nature of the non-bonding interactions arising from the methyl groups and the positions of the sulfur atom.

Also from an analysis of data in Table 3, it is observed that the "colourability" generally lies in the same range. The exception is compound **1b**, which has lower values.

The resistance to fatigue (photodegradation) under continuous irradiation was evaluated only for compound **1c**, using the Degraphot apparatus [18]. We found that the time required to reach 50% of the initial absorbance value ($tA_0/2$) was 182 min, which compares favorably with the value for reference compound **A** ($tA_0/2=456$ min) and that heteroannellated chromenes derivatives containing five membered rings such as furan and pyrrole have much lower $tA_0/2$ values than compound **1c** [8].

3. Experimental

Melting points were determined in a Gallenkamp apparatus and are uncorrected. IR spectra were recorded as nujol mulls, unless stated otherwise, on a Perkin–Elmer 1600-FTIR spectrophotometer, and UV–Vis spectra were recorded in EtOH on a Hitachi U-2000 spectrophotometer. ^{1}H NMR were measured on a Varian Unity Plus spectrometer (300 MHz) or a Bruker AMX (400 MHz), in $CDCl_3$, unless stated otherwise, using the signals of the undeuterated solvents ($CHCl_3$ or DMSO of $CDCl_3$ and DMSO-d_6) as internal references. J values are given in Hz. COSY experiments were conducted on the Bruker instrument at 400 MHz. ^{13}C NMR spectra were measured on the same instruments at 75.4 MHz (using DEPT θ 45°) or at 100.6 MHz. ^{1}H, ^{13}C heteronuclear correlation experiments were conducted,

using HMBC and HMQC gradient techniques, on the Bruker AMX 400 instrument. Mass spectra were obtained on a Unicam GC/MS 120 spectrometer using the electron impact (EI, 70 ev) direct probe method. High-resolution mass spectra (HR-MS) were measured using the spectrometry service of Butterworth Company (UK), and elemental analyses were determined on a LECO CHNS 932 elemental analyser.

Chemical reactions were followed by thin layer chromatography (TLC), which was carried out on Merck silica gel 60 F_{254}, 0.2 mm. Preparative layer chromatography (PLC) was carried out on Merck silica gel 60 F_{254}, 2 mm, and flash chromatography was carried out on Merck silica gel 230–400 mesh.

The light petroleum that was used for purifications refers to the boiling range of 40–60°C.

3.1. 2,3-Dimethyl-7-methoxybenzo[b]thiophene (**3a**)

2-Methoxythiophenol (5.2 g, 0.037 mol) was added to NaOH (30%, 15 ml) with stirring and external cooling. To this mixture 3-bromobutan-2-one (5.6 g, 0.037 mol) was added dropwise, and the reaction mixture was stirred for 30 min. At that point, the reaction was allowed to reach ambient temperature. Extraction with Et_2O gave, after drying ($MgSO_4$) and solvent removal, ketoarylsulfide **2a** as a colourless oil (5.2 g, 68%).

ν_{max} cm^{-1} (oil): 3399, 3063, 2971, 2938, 2837, 2348, 2040, 1709 (C=O), 1582, 1552, 1502, 1478, 1450, 1432, 1354, 1295, 1246, 1182, 1162, 1130, 1070, 1042, 1024, 967, 850, 798, 754, 684;

^{1}H NMR, δ (300 MHz): 1.40 (3H, d $J=7$ Hz, SCH*Me*), 2.27 (3H, s, COMe), 3.80 (1H, q $J=7$ Hz, SCH*Me*), 3.87 (3H, s, OMe), 6.85–6.94 (2H, m, Ar–H), 7.27–7.42 (2H, m, Ar–H).

EI-MS, *m*/*z* (rel. int.): 210 (M^+, 57%), 167 (M^+ − COMe, 100), 139 (60) 108 (60).

3.2. Cyclisation using P_2O_5

Compound **2a** (5 g, 0.025 mol) was mixed with one-third its weight of P_2O_5 (1.7 g) and the mixture was heated for 40 min at 170°C. After cooling, water was added and this was followed by Et_2O extractions. The organic phase was washed with water, dried ($MgSO_4$) and filtered. Activated carbon was added to the filtrate, and the mixture was heated briefly. Filtration and removal of solvent gave **3a** as a crystalline yellow solid (3.3 g, 69%), mp 88–90°C (lit. [11] 108°C, from light petroleum).

^{1}H NMR, δ (300 MHz) 2.32 (3H, s, Me), 2.52 (3H, s, Me), 4.00 (3H, s, OMe), 6.74 (1H, br d $J=8$ Hz, H-6), 7.23 (1H, br d $J=8$ Hz, H-4), 7.32 (1H, t $J=8$ Hz, H-5).

EI-MS, *m*/*z* (rel. int.): 192 (M^+, 100%), 177 (50), 149 (65), 134 (40), 115 (20).

3.3. Cyclisation using PPA

Commercial PPA (6.5 g) was heated for 15 min at 150°C to remove water. Compound **2a** (2.7 g, 0.013 mol) was added and the mixture was stirred for 15 min at 150°C and then for 15 min without heating. After cooling to ambient temperature, crushed ice (11 g) was added and stirring was continued for a few min. The aqueous mixture was extracted with $CHCl_3$ (4×100 ml). Drying the organic phase and removal of solvent gave **3a** (2.5 g, 100%), for which the analytical data were identical to that recorded above for P_2O_5 cyclisation.

3.4. 2,3-Dimethyl-6-methoxybenzo[b]thiophene (**3b**), and 2,3-dimethyl-4-methoxybenzo[b] thiophene (**3d**)

By the methods described for compound **3a**, 3-methoxythiophenol (10 g, 0.071 mol), NaOH (30%, 25 ml), and 3-bromobutan-2-one (10.8 g, 0.071 mol) gave ketoarylsulfide **2b** as a colourless oil (13.3 g, 89%).

ν_{max} cm^{-1} (oil): 3401, 3065, 2970, 2933, 2836, 2361, 2075, 1710 (C=O), 1590, 1575, 1480, 1423, 1355, 1312, 1283, 1249, 1231, 1183, 1159, 1098, 1041, 993, 968, 862, 847, 777, 689.

^{1}H NMR, δ (300 MHz): 1.44 (3H, d $J=7$ Hz, SCH*Me*), 2.27 (3H, s, COMe), 3.80 (4H, m, OMe and SCH*Me*), 6.82 (1H, m, Ar–H), 6.91–6.99 (2H, m, Ar–H), 7.22 (1H, t $J=8$ Hz, H-5).

EI-MS, *m*/*z* (rel. int.): 210 (M^+, 55%), 167 (M^+ − COMe, 100), 139 (62).

3.5. Cyclisation using P_2O_5

Compound **2b** (4.3 g, 0.021 mol) was heated with P_2O_5 (1.4 g) as described for **3a**. Work-up gave a yellow oil that was shown by ^{1}H NMR to be a mixture of two products. Flash chromatography using light petroleum gave colourless crystals of **3d** (0.3 g, 6%), as the less polar product, mp 44–45.5°C.

CHS anal. $C_{11}H_{12}OS$ requires: C, 68.7; H, 6.3; S, 16.7; found: C, 68.8; H, 6.45; S, 16.4. ν_{max}/cm^{-1}: 1577, 1544, 1469, 1437, 1416, 1386, 1333, 1260, 1236, 1199, 1185, 1156, 1051, 929, 879, 857, 805, 769, 734, 695.

^{1}H NMR, δ (300 MHz): 2.45 (3H, s, Me), 2.52 (3H, s, Me), 3.92 (3H, s, OMe), 6.71 (1H, br d $J=8$ Hz, H-5), 7.18 (1H, t $J=8$ Hz, H-6), 7.35 (1H, br d $J=8$ Hz, H-7).

EI-MS, m/z (rel. int.): 192 (M^+, 100%), 177 (67), 149 (54), 134 (30).

Also obtained was compound **3b** as colourless crystals (0.94 g, 19%) m.p. 69–70.5°C (lit. [11] 69°C).

CHS anal. $C_{11}H_{12}OS$ requires: C, 68.7; H, 6.3; S, 16.7; found: C, 68.5; H, 6.5; S, 16.3. ν_{max}/cm^{-1}: 1666, 1605, 1549, 1538, 1514, 1462, 1377, 1321, 1267, 1235, 1171, 1054, 878, 827, 810, 762, 722.

^{1}H NMR, δ (300 MHz) 2.25 (3H, s, Me), 2.45 (3H, s, Me), 3.85 (3H, s, OMe), 6.97 (1H, dd $J=9$ Hz and 2.4 Hz, H-5), 7.25 (1H, d $J=2.4$ Hz, H-7), 7.47 (1H, d $J=9$ Hz, H-4).

EI-MS, m/z (rel. int.) 192 (M^+, 100%), 177 (93), 149 (74), 134 (40).

3.6. Cyclisation using PPA

PPA (33.5 g) and compound **2b** (13.3 g, 0.063 mol) were mixed and heated as described for **3a**. After cooling, crushed ice (50 g) was added. Extractions with $CHCl_3$ (4×100 ml) gave a brown oil (7.2 g) that was purified by flash chromatography using light petroleum to give colourless crystals of **3d** (11%) and of **3b** (31%). The analytical data for the two compounds were identical to that obtained following P_2O_5 cyclisation.

3.7. 2,3-Dimethyl-5-methoxybenzo[b]thiophene (**3c**)

By the methods described for compound **3a**, 4-methoxythiophenol (10 g, 0.071 mol), NaOH (30%, 15 ml), and 3-bromobutan-2-one (10.8 g, 0.071 mol) gave ketoarylsulfide **2c** as a colourless oil (12.2 g, 82%).

ν_{max} cm^{-1} (oil): 3399, 2970, 2930, 2837, 2534, 2044, 1890, 1708 (C=O), 1653, 1592, 1570, 1540, 1494, 1463, 1406, 1374, 1364, 1284, 1248, 1206, 1174, 1105, 1062, 966, 874, 830, 799, 780, 640, 626, 602.

^{1}H NMR, δ (300 MHz) 1.35 (3H, d $J=7$ Hz, SCH*Me*), 2.30 (3H, s, COMe), 3.65 (1H, q, $J=7$ Hz, SC*H*Me), 3.80 (3H, s, OMe), 6.86 (2H, d $J=9$ Hz, Ar–H *ortho* to OMe), 7.35 (2H, d $J=9$ Hz, Ar–H *meta* to OMe).

EI-MS, m/z (rel. int.): 210 (M^+, 55%), 167 (M^+ − COMe, 100), 139 (62).

3.8. Cyclisation using P_2O_5

Compound **2c** (5.4 g, 0.026 mol) was mixed and heated with P_2O_5 (1.8 g) as described for **3a**. Extractions with Et_2O gave a brown oil (1 g) that was purified by PLC (ether/light petroleum 1:1) to give **3c** as an amber oil (0.49 g, 7%) (lit. [11] amber oil).

CHS anal. $C_{11}H_{12}OS$ requires: C, 68.7; H, 6.3; S, 16.7; found: C, 68.6; H, 6.5; S, 16.6.

ν_{max} cm^{-1} (oil): 2956, 2858, 2832, 1872, 1600, 1550, 1511, 1496, 1456, 1381, 1346, 1309, 1264, 1247, 1179, 1153, 1093, 1050, 1029, 942, 875, 832, 803, 755, 724, 685, 654, 638.

^{1}H NMR, δ (300 MHz): 2.28 (3H, s, Me), 2.49 (3H, s, Me), 3.90 (3H, s, OMe), 6.94 (1H, dd $J=9$ Hz and 2.4 Hz, H-6), 7.06 (1H, d $J=2.4$ Hz, H-4), 7.62 (1H, d $J=9$ Hz, H-7).

3.9. Cyclisation using PPA

PPA (25 g) and compound **2c** (12 g, 0.057 mol) were mixed and heated as described for **3a**. After cooling, crushed ice (50 g) was added. Extractions with $CHCl_3$ (4×100 ml) gave a brown oil (8.15 g) that was purified by flash chromatography (light

petroleum to ether/light petroleum, 1:3) to give **3c** as an amber oil (5.3 g, 48%). The analytical data were identical to that reported above following P_2O_5 cyclisation.

3.10. 2,3-Dimethyl-7-hydroxybenzo[b]thiophene (**4a**)

Pyridinium chloride (7.9 g) was added to compound **3a** (2.2 g, 0.012 mol) and the mixture was heated under reflux for 15 min. After cooling, HCl (6N, 0.5 ml) and Et_2O were added. The organic phase was separated, dried ($MgSO_4$) and filtered. The filtrate was heated briefly with activated carbon followed by filtration and removal of solvent. Compound **4a** was obtained as a white solid (0.95 g, 45%), m.p. 134–136°C (lit. [11] 137°C).

ν_{max} cm^{-1}: 3362 (OH), 1596, 1558, 1472, 1443, 1379, 1350, 1251, 1190, 1113, 1085, 1049, 1006, 975, 888, 778, 749, 718, 700.

^1H NMR, δ (300 MHz, $CDCl_3$) 2.31 (3H, s, Me), 2.49 (3H, s, Me), 5.11 (1H, s, OH, exchanges with D_2O), 6.66–6.73 (1H, m, Ar–H), 7.20–7.25 (2H, m, Ar–H).

EI-MS, *m/z* (rel. int.): 178 (M^+, 100%), 163 (98), 134 (25), 115 (55).

The ^1H NMR spectrum of **4a** was also recorded in DMSO-d_6 to clarify the overlapped signals present in the $CDCl_3$ spectrum. δ_H (300 MHz, DMSO-d_6) 2.21 (3H, s, Me), 2.41 (3H, s, Me), 6.68 (1H, dd $J=7.5$ Hz and 1 Hz, H-6), 7.09 (1H, dd $J=7.5$ Hz and 1 Hz, H-4), 7.15 (1H, t $J=7.5$ Hz, H-5), 10.1 (1H, br s, OH).

3.11. 2,3-Dimethyl-6-hydroxybenzo[b]thiophene (**4b**)

3.11.1. Demethylation using pyridinium chloride

By the method described for compound **4a**, pyridinium chloride (1 g) and compound **3b** (0.5 g, 2.6 mmol) were heated at reflux for 30 min to give, after acidifying and extracting with Et_2O, compound **4b** as a pale yellow solid in a quantitative yield, mp 99–100.5°C (lit. [11] 103°C).

ν_{max} cm^{-1}: 3186 (OH) 1603, 1557, 1466, 1377, 1287, 1242, 1218, 1172, 1072, 1040, 928, 893, 832, 804, 766, 722, 672, 600.

^1H NMR, δ (300 MHz): 2.23 (3H, s, Me), 2.43 (3H, s, Me), 4.70 (1H, br s, OH, exchanges with D_2O), 6.88 (1H, dd $J=8.5$ Hz and 2.4 Hz, H-5), 7.20 (1H, d $J=2.4$ Hz, H-7), 7.44 (1H, d $J=8.5$ Hz, H-4).

EI-MS, *m/z* (rel. int.): 178 (M^+, 100%), 163 (97), 134 (20), 115 (25).

3.11.2. Demethylation using BBr_3

A solution of compound **3b** (0.5 g, 2.6 mmol) in CH_2Cl_2 (15 ml) was cooled to 0°C under Ar. A BBr_3 in CH_2Cl_2 (1M, 3 ml, 2.8 mmol) was added dropwise and after the addition was complete, the mixture was heated at reflux for 2 h 30 min. After cooling, water was added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated to give a green solid that was purified by PLC (ether: light petroleum, 1:1). This gave compound **4b** as a colourless solid (0.25 g, 54%), for which the analytical data were identical to that rep-orted above following pyridinium chloride treatment.

3.12. 2,3-Dimethyl-5-hydroxybenzo[b]thiophene (**4c**)

3.12.1. Demethylation using pyridinium chloride

By the method described for compound **4a**, pyridinium chloride (4 g) and compound **3c** (2 g, 0.0104 mol) afforded a brown oil that was purified by flash chromatography (light petroleum to ether:light petroleum, 1:3) to give compound 4c as a white solid (0.45 g, 24%), mp 100–101°C (lit. [11] 100.5°C).

CHS anal. for $C_{10}H_{10}OS$ requires: C, 67.4; H, 5.65; S, 18.0; found: C, 67.2; H, 5.70; S, 18.0%. ν_{max} cm^{-1}: 3251 (OH) 1602, 1557, 1514, 1442, 1378, 1269, 1238, 1210, 1151, 949, 882, 842, 798, 748, 726, 648, 659, 631.

^1H NMR, δ (300 MHz): 2.24 (3H, s, Me), 2.47 (3H, s, Me), 4.92 (1H, s, OH, exchanges with D_2O), 6.83 (1H, dd $J=8.5$ Hz and 2.4 Hz, H-6), 7.02 (1H, d $J=2.4$ Hz, H-4), 7.58 (1H, d $J=8.5$ Hz, H-7).

EI-MS, *m/z* (rel. int.): 178 (M^+, 100%), 163 (95), 134 (20), 115 (25).

3.12.2. Demethylation using BBr_3

By the method described above for compound **4b**, **3c** (2.24 g, 0.017 mol) in CH_2Cl_2 (40 ml) was treated with BBr_3 in CH_2Cl_2 (1M, 12 ml, 0.017 mol). Following a 1-h reflux and then work up, a white solid (1.63 g, 79%) m.p. 93–94°C was obtained. ^{1}H NMR spectrum showed the compound to be **4c**. Crystallization from light petroleum afforded colourless crystals m.p. 99–100.6°C.

3.13. 2,3-Dimethyl-4-hydroxybenzo[b]thiophene (**4d**)

3.13.1. Demethylation using pyridinium chloride

By the method described above for compound **4a**, pyridinium chloride (0.75 g) and compound **3d** (0.25 g, 1.3 mmol) gave, after reflux for 15 min and work up, compound **4d** as a white solid (0.06 g, 26%), m.p. 80–82°C.

CHS anal. $C_{10}H_{10}OS$ requires: C, 67.4; H, 5.65; S, 18.0%; found: C, 67.2; H, 5.7; S, 17.8.

ν_{max} cm^{-1}: 3320 (OH) 1601, 1576, 1547, 1432, 1378, 1327, 1294, 1244, 1176, 1153, 1078, 1042, 929, 916, 869, 766, 732, 694.

^{1}H NMR, δ (300 MHz): 2.31 (3H, s, Me), 2.49 (3H, s, Me), 5.00 (1H, s, OH, exchanges with D_2O), 6.60 (1H, dd $J=8$ Hz and 1Hz, H-5), 7.08 (1H, t $J=8$Hz, H-6), 7.31 (1H, dd $J=8$ Hz and 1 Hz, H-7).

EI-MS, *m/z* (rel. int.): 178 (M^+, 100%), 163 (95), 134 (22), 115 (25).

3.13.2. Demethylation using BBr_3

By the method described above for **4b**, compound **3d** (0.26 g, 1.4 mmol) in CH_2Cl_2 (5 ml) and BBr_3 (1.5 ml, 1 M in CH_2Cl_2, 1.4 mmol) gave, after reflux for 2 h and work up, compound **4d** as a white solid (0.24 g, 100%).

3.14. 2,3-Dimethyl-8,8-diphenyl-[8H]-chromene[7,8-d]thiophene (**1a**)

Compound **4a** (0. 5 g, 2.8 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.53 g, 2.5 mmol) were dissolved with stirring in dry toluene (6 ml) at 60°C. TsOH (1 mol%) was added under Ar and the mixture was heated for 40 min at 120°C. After cooling, NaOH (5%, 60 ml) was added and the phases were separated. The aqueous phase was extracted several times with CH_2Cl_2 and the combined organic extracts were dried ($MgSO_4$) and concentrated to an orange oil. This oil was purified by flash chromatography (ether:-light petroleum, 1:1) to give compound **1a** as a light yellow oil. Crystallization from MeOH gave colourless crystals (0.1 g, 11%), mp 140–142°C.

CHS anal. $C_{25}H_{20}OS$ requires: C, 81.5; H, 5.5; S, 8.7; found: C, 81.25, H, 5.7; S 8.6.

λ_{max} (ε dm^3 mol^{-1} cm^{-1}): 404 (9175), 341 (15,575) 333 (14,750), 304 (20,475), 290 (20,825), 257 (55,550), 252 (sh, 53,350), 204 (96,000);

ν_{max} cm^{-1} 1655, 1628, 1606, 1578, 1542, 1492, 1468, 1449, 1415, 1380, 1219, 1187, 1162, 1132, 1088, 1050, 1010, 955, 925, 911, 909, 808, 788, 770, 753, 716, 694, 648.

^{1}H NMR, δ (300 MHz): 2.23 (3H, s, Me), 2.46 (3H, s, Me), 6.16 (1H, d $J=10$ Hz, H-7), 6.72 (1H, d $J=10$ Hz, H-6), 7.03 (1H, d $J=8$ Hz, H-5), 7.10 (1 H, d $J=8$ Hz, H-4), 7.20–7.40 (6H, m, Ar–H), 7.50 (4H, m, Ar–H).

^{13}C NMR, δ (75.4 MHz): 11.45 (Me), 14.00 (Me), 83.19 (C-8), 114.04, 115.32 (Cq), 123.06, 123.66, 125.41 (Cq), 126.76, 127.07, 127.42, 127.63 (Cq), 128.10, 135.03 (Cq), 143.33 (Cq), 145.03 (Cq), 146.80 (Cq).

EI-MS, *m/z* (rel. int.) 368 (M^+, 100), 291 (M^+-Ph, 76), 191 (32).

3.15. 2,3-Dimethyl-7,7-diphenyl-[7H]-chromene[6,5-d]thiophene (**1b**)

Using a slight variation on the method described for compound **1a**, compound **4b** (0.33 g, 1.9 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.35 g, 1.7 mmol) were heated together with TsOH for 5 min at 100°C. After CH_2Cl_2 extractions, an orange oil was obtained that was purified by PLC (ether:light petroleum, 1:1) to give a yellow solid. Washing this solid with light petroleum gave colourless crystals of **1b** (0.06 g, 9%), mp 197–199°C.

λ_{max} (ε dm^3 mol^{-1} cm^{-1}): 403 (690), 341 (2593), 309 (6955), 295 (8110), 285 (sh, 8218), 258 (38,425), 211 (28,627).

^{1}H NMR, δ (400 MHz, using COSY): 2.19 (3H, s, 3-Me), 2.40 (3H, s, 2-Me), 6.25 (1H, d J = 10 Hz, H-8), 6.77 (1H, d J = 10 Hz, H-9), 6.97 (1 H, d J = 8.4 Hz, H-5), 7.22 (2H, m, H-4′), 7.29 (4H, m, H-3′ and H-5′) 7.30 (1H, d J = 8.4 Hz, H-4), 7.44 (4H, m, H-2′ and H-6′).

^{13}C NMR, δ (100.6 MHz): 11.43 (3-Me), 13.82 (2-Me), 82.87 (C-7), 114.49 (CH-5), 114.76 (C-9a), 121.11 (CH-9), 121.60 (CH-4), 127.12 (CH-2′ and 6′), 127.23 (C-3), 127.58 (CH-4′), 128.17 (CH-3′ and 5′), 129.13 (CH-8), 130.79 (C-2), 135.62 (C-9b), 135.99 (C-4a), 144.84 (C-1′), 149.25 (C-5a).

EI-MS, m/z (rel. int.): 368 (M^+, 100%), 291 ($M^+ - Ph$, 90), 191 (25). (HR-MS Found: M^+ 368.124. $C_{25}H_{20}OS$ requires M^+ 368.1235).

3.16. 2,3-Dimethyl-6,6-diphenyl-[6H]-chromene[5,6-d]thiophene (**1c**)

Using a slight variation on the method described for compound **1a**, compound **4c** (0.23 g, 1.3 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.25 g, 1.2 mmol) were heated with TsOH for 60 min at 120°C. After extractions with $CHCl_3$, an orange oil obtained was purified by PLC (ether:light petroleum, 1:1) to give compound 1c as a light yellow oil. Washing with ether gave colourless crystals (0.036 g, 9%), m.p. 171–173°C.

CHS analysis for $C_{25}H_{20}OS$. Requires: C, 81.5; H, 5.5; S, 8.7; found: C, 81.3.; H, 5.6; S, 8.5%.

λ_{max} (ε dm^3 mol^{-1} cm^{-1}): 404 (3440), 341 (8700), 301 (15,190), 295 (15,610), 273 (32,110), 265 (30,980), 235 (sh, 32,470), 210 (54,780), 204 (63,680);

^{1}H NMR, δ (400 MHz, using COSY): 2.40 (3H, s, 3-Me), 2.44 (3H, s, 2-Me), 6.17 (1H, d J = 10 Hz, H-5) 6.93 (1H, d J = 8.5 Hz, H-8) 7.22 (2H, m, 2×H-4′), 7.29 (4H, m, 2×H-3′ and H-5′) 7.43 (1H, d J = 8.5 Hz, H-9), 7.45 (1H, d J = 10 Hz, H-4) 7.46 (4H, m, 2×H-2′ and H-6′).

^{13}C NMR, δ (100.6 MHz) 14.30 (2-Me), 15.64 (3-Me), 81.45 (C-6), 114.39 (CH-8), 116.38 (C-4a), 121.32 (CH-4) 122.78 (CH-9), 127.12 (CH-2′ and CH-6′), 127.48 (CH-4′), 127.73 (C-2), 127.85 (CH-5), 128.11 (CH-3′ and CH-5′), 131.56 (C-9a), 135.93 (C-3), 136.60 (C-3a), 144.94 (C-1′), 150.59 (C-8a).

EI-MS, m/z rel. int.): 368 (M^+, 85), 291 ($M^+ - Ph$, 100), 191 (15).

3.17. Catalysis using montmorillonite K10

Compound **1c** was isolated in the same yield (9%) and gave analytical data that were identical to that reported above following TsOH catalysis.

3.17.1. 2,3-Dimethyl-5,5-diphenyl-[5H]-chromene[8,7-d]thiophene (**1d**)

Using a slight variation on the method described for compound **1a**, compound **4d** (0.2 g, 1.2 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.25 g, 1.2 mmol) were heated together with TsOH for 45 min at 110°C. After extractions with $CHCl_3$, the oil obtained was purified by PLC (light petroleum) to give compound **1d** as a light yellow oil. Washing with MeOH gave colourless crystals (0.050 g, 11%), mp 139–141°C.

λ_{max} (ε dm^3 mol^{-1} cm^{-1}): 403 (520), 349 (3020), 335 (3282), 320 (2544), 313 (2214), 290 (sh 3182), 270 (sh, 20,090), 258 (23,530), 211 (22,291).

^{1}H NMR, δ (400 MHz): 2.37 (3H, s, 2-Me), 2.56 (3H, s, 3-Me), 5.97 (1H, d J = 10 Hz, H-6) 6.67 (1H, d J = 10 Hz, H-7), 6.88 (1H, d J = 8 Hz, H-8), 7.16 (1H, d J = 8 Hz, H-9), 7.23 (2H, m, H-4′) 7.31 (4H, m, H-3′ and H-5′) 7.46 (4H, m, H-2′ and H-6′).

^{13}C NMR, δ (100.6 MHz) 13.73 (2-Me), 14.75 (3-Me), 83.46 (C-5), 114.76 (CH-9), 115.88 (C-8a), 122.62 (CH-8), 124.23 (CH-7), 125.89 (CH-6), 127.22 (CH-2′ and CH-6′), 127.45 (CH-4′ and C-3), 128.20 (CH-3′ and CH-5′), 129.71 (C-3a), 132.20 (C-2), 140.24 (C-9a), 145.19 (C-1′), 148.05 (C-3b).

EI-MS, m/z (rel. int.): 368 (M^+, 100), 291 ($M^+ - Ph$, 77) (HR-MS found: M^+ 368.123. $C_{25}H_{20}OS$ requires M^+ 368.1235).

3.18. Catalysis using montmorillonite K10

Compound **1d** was isolated in 11% yield, a sample of which gave analytical data that were identical to that obtained following TsOH catalysis.

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