Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 2567–2573

TETRAHEDRON

Synthesis and photochromic behaviour of new methyl induced linear and angular thieno-2*H*-chromenes

Maria-João R. P. Queiroz,[a,*] Paula M. S. Plasencia,[a] Roger Dubest,[b] Jean Aubard[b] and Robert Guglielmetti[c]

[a]*Departamento de Química, Universidade do Minho, 4710-057 Braga, Portugal*
[b]*ITODYS, UMR 7086 CNRS, Université Denis Diderot Paris 7, 75005 Paris, France*
[c]*LCMOM, UMR 6114 CNRS, Université de la Méditerranée, 13288 Marseille Cedex 9, France*

Received 11 October 2002; revised 14 January 2003; accepted 11 February 2003

Abstract—New methyl induced linear and angular thieno-2*H*-chromenes **4**, **5** and **6** were prepared by reaction of new methylated 6-hydroxybenzo[*b*]thiophenes **2** (**a**, **b** and **c**) and propargylic alcohols **3a** and **3b**, using acidic Alumina Brockmann I as catalyst and drying agent. Compounds **2** were prepared in good to excellent yields in a 'one pot' three step reaction from the corresponding bromo compounds **1**. The photochromic behaviour of compounds **4**, **5** and **6b** was evaluated with the aid of a classical set of spectrokinetic parameters, and compared to reference compounds that are benzoannellated in the 5,6 and 6,7 positions of the chromene (naphthopyrans) and also to thieno-2*H*-chromenes **7** and **8**, previously prepared, which are analogues of **5a**. The resistance to fatigue (photodegradation) under continuous irradiation was also evaluated. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Since the discovery of the photochromic behaviour of the 2*H*-chromenes (2*H*-1-benzopyrans)[1] much research has been devoted to this important class of oxygenated heterocyclic compounds.[2] They exhibit their photochromic properties by a reversible pyran ring opening, induced by light, that converts a colourless form (closed form) in a set of photoisomers where the pyran ring is open (open forms). Among the structural modifications that could be carried out on the 2*H*-chromenes, heteroannellation represents an interesting approach in promoting improvements in their photochromic properties and in their applications related to materials undergoing variable optical absorption, namely ophthalmic lenses that are coloured in the sun and colourless in the dark.[3] For application in this field, the so called heliochromic materials[4] must show highly efficient photoresponse for colouring in the near UV, a low quantum yield for bleaching with visible light and efficient thermal fading at ambient temperatures. Furthermore, the photochromic compounds must present chemical stability and resistance toward light, i.e. a large number of cycles should be possible without significant degradation of the material. This last property will determine their potential applications. In order to gain reasonable stability of the coloured forms and to prevent rapid fatigue under photoexcitation, it is required to introduce bulky substituents into the 2 position of the pyran ring especially phenyl groups.[5,6] Several five membered 5,6 heteroannellated 2*H*-chromenes have been prepared and the effect of the heteroannellation on their photochromism was determined.[7] Angular 2*H*-chromenes heteroannellated at 5,6 and 7,8 positions with a 2,3-dimethylthiophene ring were prepared by us earlier and their photochromic behaviour was studied.[8] We have thought that additional methyl groups on the benzene nucleus of the benzo[*b*]thiophene moiety could influence the photochromic behaviour of the corresponding thieno-2*H*-chromenes, by their electronic and also steric effects on the open forms.

Herein we report the synthesis and photochromic properties of new methyl induced linear and angular 5,6 and 6,7 thieno-2*H*-chromenes which were prepared from new methylated hydroxybenzo[*b*]thiophenes and two propargylic alcohols. The general representation of their photochromism and the possible open forms issued from UV irradiation are presented in Figure 1.

2. Results and discussion

2.1. Synthesis

New methylated 6-hydroxybenzo[*b*]thiophenes **2a**–**c** were prepared from the corresponding bromo compounds **1a**–**c**[9] in good to excellent yields in a 'one pot' three step reaction,

Keywords: thieno-2*H*-chromenes; hydroxybenzo[*b*]thiophenes; photochromism; flash photolysis.

* Corresponding author. Tel.: +351-253604378; fax: +351-253678983; e-mail: mjrpq@quimica.uminho.pt

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doi:10.1016/S0040-4020(03)00262-X

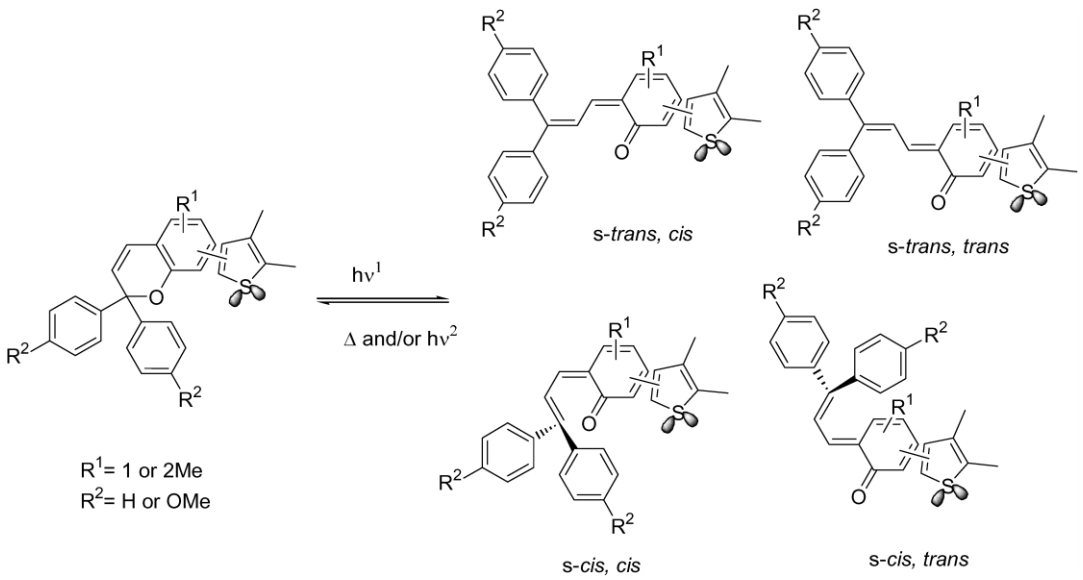
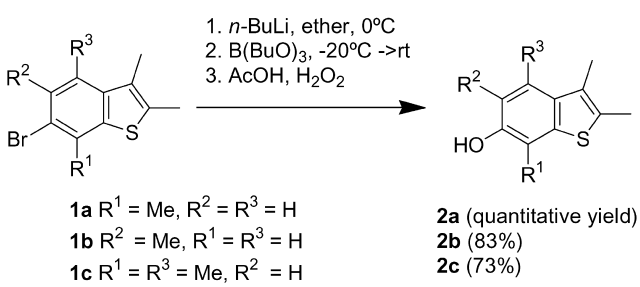


Figure 1. Photochromism and possible open forms of thieno-2*H*-chromenes.

beginning with bromine–lithium exchange followed by boron transmetalation and treatment with hydrogen peroxide in acidic medium[10] (Scheme 1).

The hydroxy compounds **2** were reacted with the propargylic alcohols **3a** and **3b** using acidic Alumina Brockmann I (Al_2O_3 ac.) to afford in low to moderate yields (10–36%) the corresponding methyl induced linear and angular thieno-2*H*-chromenes **4**, **5** and **6** (Scheme 2). The Al_2O_3 ac. (large excess) acts as an acidic catalyst and also as a water retainer decreasing the reversibility of the reaction. The synthesis of chromenes **4**–**6** involves the formation of propargyl aryl ethers by *O*-alkylation of the hydroxy compounds **2a**–**c**. Thermal cyclization of the propargyl ethers affords the chromenes in a cascade process, presumably via a Claisen-like [3,3]-sigmatropic rearrangement, followed by a [1,5]-sigmatropic shift and cyclization.[11]

From analysis of Scheme 2 it is possible to conclude that the angular compounds and the derivatives of the alcohol **3b** were obtained in better yields. More time and higher temperature were needed for linear compounds derivatives of **3a**, compound **6a** being the more difficult to obtain. Despite the low to moderate yields range, the use of Al_2O_3 ac. showed to be advantageous compared to the use of *p*-toluenesulphonic acid and Montmorinollite K10 as catalysts, used by us in the synthesis of angular thieno-



Scheme 1. Synthesis of 6-hydroxybenzo[*b*]thiophenes **2a**–**c**.

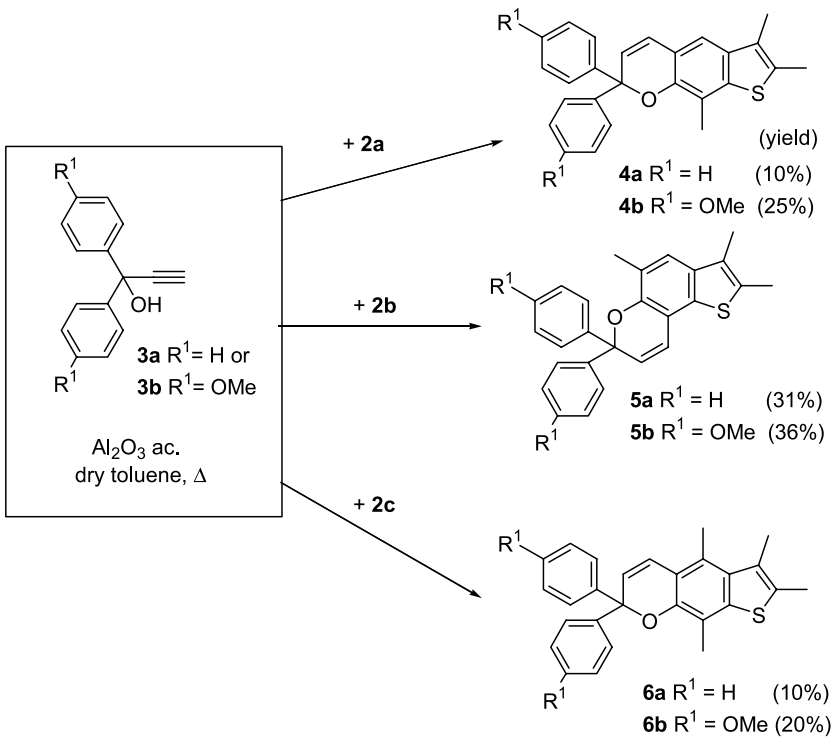
2*H*-chromenes unmethylated on the benzene ring (9–11% yield).[8] The presence of a methyl group in compound **2b** can also contribute to increase the yield of compound **5a** when compared with the yield of compound **7** (9%) in our earlier work. The formation of the corresponding β-phenylcinnamaldehydes by the Meyer–Schuster rearrangement[12] of **3a** and **3b** was evident from the ^{1}H NMR spectra of the crude reaction mixtures and can explain in part the range of yields obtained. But despite these drawbacks, the merit of the reaction is its simplicity of implementation.

The thieno-2*H*-chromenes **4**–**6** were isolated in their closed forms and were characterized by ^{1}H, ^{13}C NMR, UV spectroscopy and high resolution mass spectrometry or elemental analysis. In their ^{1}H NMR spectra it is observed a one proton doublet centred at δ 6.14–6.25 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 81.03–82.75 ppm) of the pyran is also a characteristic signal in the ^{13}C NMR spectrum.[8,13] In the UV spectra of the angular compounds **5a** and **5b** a low intensity band at 335 nm and two moderate intensity absorption bands differing from 12 nm are present (300 and 312 nm), which is in agreement with other angular thieno-2*H*-chromenes.[8] For the linear compounds **4** and **6** two shoulders of moderate intensity are present differing from 15 nm (285 and 300 nm). High intensity absorption bands are present for all compounds at 259–265 nm.

2.2. Photochromic properties

The photochromic behaviour of thieno-2*H*-chromenes **4**, **5** and **6b** was evaluated and compared with reference 2*H*-chromene compounds benzoannellated **A** and **B** in the same positions (5,6 and 6,7) and also with a thieno-2*H*-chromene **7** synthesized by us earlier,[8] which corresponds to 5-demethylated compound **5a** (Table 1). Compound **6a** was not studied due to the difficulty of its synthesis.

The thieno-2*H*-chromenes prepared are either the result of



Scheme 2. Synthesis of the linear and angular thieno-2*H*-chromenes **4**, **5** and **6.4a** (2.5 h, 110°C); **4b** (20 min, 80°C); **5a** (2 h, 110°C); **5b** (0.5 h, 80°C); **6a** (26 h, 110°C); **6b** (40 min, 80°C).

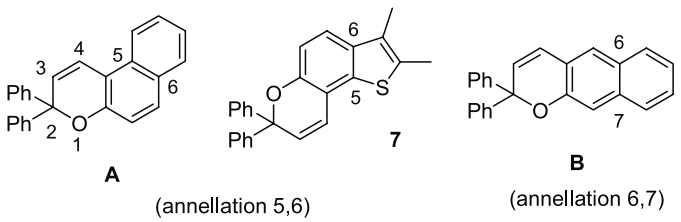
6,7 or 5,6 thiophene annellations on the 2*H*-chromene moiety. All the compounds studied exhibit photochromic behaviour at room temperature in toluene solutions (Table 1), which was quantified by three spectrokinetic parameters:—absorption maxima of the coloured forms (λ_{max}); —thermal bleaching (ring closure) rate (k_Δ) and 'colourability' (A_0). The latter parameter which has been defined for photochromic compounds,[14] 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 the following equation:

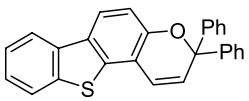
$$A_0 = \varepsilon_{MC} \varnothing_{col} k C_{CF} \text{ (for low concentration)}$$

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

Table 1. Spectrokinetic parameters for chromenes **4**, **5** and **6b**, and reference compounds **A** and **7** (2.5×10^{-5} M in toluene, 25°C) and resistance to fatigue ($t_{A0/2}$)

Chromenes (annellation)	λ_1 (nm)	A_{01}	λ_2 (nm)	A_{02}	k_Δ (s^{-1})	$t_{A0/2}$
4a (6,7)	449	0.36	610	0.08	k_1=0.42, (A_1=0.29)(91.5%) k_2=0.010, (A_1=0.03)(8.5%)	13 min 50 s
4b (6,7)	456 sh, 477	0.36, 0.48	639	0.07	k_1=1.85, (A_1=0.356)(95.4%) k_2=0.014, (A_1=0.017)(4.6%)	18 min 50 s
5a (5,6)	456	0.39	552	0.31	k=0.038	61 min
5b (5,6)	474	0.47	567	0.47	k_1=0.20 $k_2<5\times10^{-3}$	126 min
6b (6,7)	457 sh, 474	0.40, 0.53	638	0.07	k_1=14.6, (A_1=0.447)(97.4%) k_2=0.24, (A_1=0.012)(2.6%)	100 min
7[8] (5,6)	452	0.29	542	0.29	k_1=0.17 (540 nm) k_2=0.058	Not determined
A[6] (5,6)	432	0.84	–	–	k=0.1 (432 nm)	456 min





8[16]

Figure 2. Structure of benzothieno-2*H*-chromene **8**.

Furthermore, photochromic compounds must satisfy the following performance criteria: a minimal fatigue or chemical instability upon repetitive cycling or continuous irradiation; a highly efficient photoresponse in near-UV; a relative fast thermal fading rate at room temperature and a minimum quantum yield for bleaching with visible light, thus preserving colouration.

The resistance to fatigue (photodegradation) under continuous irradiation was also evaluated, using the 'Degraphot' apparatus.[15] We found that the values for the time required to reach 50% of the initial value ($t_{A0/2}$) are much lower than the value for the reference compound **A** (Table 1) but they are in agreement with heteroannellated chromene derivatives containing five membered rings such as furan and pyrrole as reported previously.[7]

The open forms of the 2*H*-chromenes annellated in positions 5,6 and 6,7 with a dimethylthiophene ring gave broad visible spectra with an absorption maxima at high wavelength (λ_2) compared with reference compound **A** (Table 1). Comparing the spectra of the open forms of the angular compounds **5a** and **5b** (annellation 5,6) with compound **7** it is possible to conclude that the methyl group of the benzene ring increases the bathochromic effect for λ_2 of 10 nm and the colourability in both wavelengths is slightly increased. A comparison could also be done between compound **5a** and the corresponding benzothieno-2*H*-chromene **8** prepared and studied by some of us[16] (Fig. 2), having the same type of annellation (5,6) and the same regio-isomery (S–C_5): the spectroscopic data are quite similar but the thermal bleaching kinetic constant is slower for **5a** (0.038 s^{-1} vs 0.68 s^{-1} for compound **8**).

The presence of the methoxy groups in the benzene rings of the sp^3 carbon of compound **5b** had a bathochromic effect in both wavelengths and the colourability increases significantly in both cases comparing to **5a** (Table 1).

For the 6,7-annellation the corresponding naphthopyran is compound **B**. Its poor photochromic behaviour (photochromic only at very low temperatures)[2] is the result of the loss of aromaticity of both rings in the naphthalene nucleus present in the open form. As already shown[17] the heteroannellation in these positions (6,7) represents a structural modification that leads to an important improvement of the photochromic properties of this type of compounds.

For the open forms of the linear compounds **4** and **6b** a bathochromic effect is observed on λ_2, this effect being stronger in the derivatives of the dimethoxylated propargylic alcohol, **4b** and **6b**, presenting a second absorption band at λ_{max} 638 and 639 nm but the corresponding colourability values are very low (A_{02}=0.07). In the same spectra a shoulder at 456–457 is observed and the colourability is identical. For the same compounds (**4b** and **6b**) it is possible to conclude that the additional methyl group of **6b**, involving supplementary non-bonding interactions, destabilizes the photogenerated open forms (Fig. 1). This affects highly the value of the thermal bleaching kinetic constant being much faster for **6b** than for **4b** (14.6 s^{-1} vs 1.85 s^{-1}).

Generally two values for the thermal bleaching kinetics (with their respective amplitude) are observed, corresponding to the more stable stereoisomers of the open form. When we observe, only one value it corresponds to the most stable, the other one being negligible, taking into account the type of annellation, the relative positions of sulfur atom and the positions of the substituents.

3. Conclusion

It has been shown that the methyl groups on the benzene nucleus of the benzo[*b*]thiophene induce a bathochromic effect on the absorption of the photogenerated open forms and the methoxy groups in the *para* positions of the phenyl substituents on the sp^3 carbon have a tendency to enhance this effect.

Concerning the 6,7 annellation type, the methyl thieno-2*H*-chromene compounds present a measurable photochromic behaviour contrarily to the corresponding 2,2-diphenyl-2*H*-naphtho[2,3-*b*]pyran **B**, but their resistance to fatigue is not very high. It was interesting to prepare such 6,7-annellated compounds because very few compounds of this type are found in the literature.

In spite of the difficulty in synthesis of such molecules, the spectrokinetic results show that by using judicious substitutions, the photochromic properties could be adjusted to convenient values. Nevertheless the resistance to fatigue is not at the level of our expectations.

4. Experimental

4.1. Materials and methods

Melting points (°C) were determined in a Gallenkamp apparatus and are uncorrected. UV spectra were recorded in EtOH using a Varian Cary Win 50 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus at 300 and 75.4 MHz respectively, unless stated on a Bruker AMX at 400 and 100.6 MHz. ^1H–^1H spin–spin decoupling and DEPT θ 45° were used. Chemical shifts are given in ppm and coupling constants in Hz. The mass spectra were obtained on a Unicam GC/MS 120 spectrometer or on a Micromass Autospec 3F by an electronic impact (70 eV) direct injection method. Elemental analysis was performed on a LECO CHNS 932 elemental analyser.

Chloroform and carbon tetrachloride were used in the work up but were manipulated in the hotte.

The reactions were monitored by thin layer chromatography (TLC). Column chromatography was performed on

Macherey–Nagel silica gel 230–400 mesh. Preparative Layer Chromatography was performed in 20×20 cm plates Macherey–Nagel, Layer 2 mm SIL G-200 UV_{254}. Petroleum ether refers to the boiling range 40–60°C. When solvent gradient was used, the increase of polarity was made from neat petroleum ether to mixtures of ether/petroleum ether, increasing 5% of ether each time until the isolation of the product.

Compound **3a** is commercially available (Lancaster) and **3b** was prepared following a literature procedure.[18]

4.2. General method for the synthesis of 6-hydroxybenzo[*b*]thiophenes 2a, 2b or 2c

To a solution of 6-bromobenzo[*b*]thiophenes **1a**,**b** or **c** (3.7 mmol) in dry ether (25 mL) under Ar a solution of *n*-BuLi (4.8 mmol, 1.6 M in hexane) was added dropwise at 0°C. After 10 min a precipitate came out and the mixture was left stirring for another 10 min. The mixture was cooled to −20°C, tributylborate (4.1 mmol) was added dropwise and it was left stirring for 2 h reaching room temperature. After that, the mixture was cooled to 10°C, treated with glacial acetic acid (1.5 mL) in one portion, cooled to 0°C, treated dropwise with a 30% hydrogen peroxide solution (1.5 mL) in H_2O (5 mL) and it was left stirring for 2 h reaching room temperature. The mixture was poured in an aqueous saturated solution of ammonium sulfate containing ferrous ammonium sulfate (50 mL) and ether was added (25 mL). The phases were separated and the organic phase was washed with water, dried ($MgSO_4$), filtered and the solvent is removed to give colourless oil. Carbon tetrachloride was added to remove *n*-butanol formed during the reaction and compounds **2** were obtained as colourless solids in good to excellent yields after the removal of solvents.

4.2.1. 6-Hydroxy-2,3,7-trimethylbenzo[*b*]thiophene (2a). Following the general procedure compound **2a** was obtained in quantitative yield (0.70 g). Crystallization from ether/petroleum ether afforded colourless crystals mp 124–125°C. ^{1}H NMR ($CDCl_3$): 2.26 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.46 (3H, s, CH_3), 4.65 (1H, s, OH, exchangeable with D_2O), 6.86 (1H, d, J=8 Hz, H-5), 7.30 (1H, d, J=8 Hz, H-4). ^{13}C NMR ($CDCl_3$): 11.41 (CH_3), 13.71 (2×CH_3), 113.44 (CH), 116.21 (C), 119.12 (CH), 127.36 (C), 130.90 (C), 135.06 (C), 140.07 (C), 149.76 (C). Anal. calcd for $C_{11}H_{12}OS$: C 68.71; H 6.29; S 16.67; found C 68.51; H 6.60; S 16.30.

4.2.2. 6-Hydroxy-2,3,5-trimethylbenzo[*b*]thiophene (2b). Following the general procedure compound **2b** was obtained in 83% yield (0.59 g). Crystallization from ether/petroleum ether afforded colourless crystals mp 115–116°C. ^{1}H NMR ($CDCl_3$): 2.24 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.43 (3H, s, CH_3), 4.74 (1H, s, OH, exchangeable with D_2O), 7.14 (1H, s, H-7), 7.31 (1H, s, H-4). ^{13}C NMR ($CDCl_3$): 11.40 (CH_3), 13.62 (CH_3), 16.32 (CH_3), 107.18 (CH), 121.54 (C), 122.65 (CH), 126.23 (C), 130.68 (C), 135.36 (C), 136.56 (C), 151.20 (C). Anal. calcd for $C_{11}H_{12}OS$: C 68.71; H 6.29; S 16.67; found C 68.67; H 6.41; S 16.33.

4.2.3. 6-Hydroxy-2,3,4,7-tetramethylbenzo[*b*]thiophene (2c). Following the general procedure compound **2c** was obtained in 73% yield (0.56 g). Crystallization from ether/petroleum ether afforded colourless crystals mp 136–138°C. ^{1}H NMR ($CDCl_3$): 2.34 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.46 (3H, s, CH_3), 2.67 (3H, s, CH_3), 4.58 (1H, s, OH, exchangeable with D_2O), 6.59 (1H, s, H-5). ^{13}C NMR ($CDCl_3$): 13.17 (CH_3), 13.93 (CH_3), 15.20 (CH_3), 21.20 (CH_3), 113.34 (C), 116.31 (CH), 128.85 (C), 130.26 (C), 131.27 (C), 133.22 (C), 140.75 (C), 148.83 (C). Anal. calcd for $C_{12}H_{14}OS$: C 69.86; H 6.84; S 15.54; found C 69.52; H 7.15; S 15.35.

4.3. General method for the synthesis of thieno-2*H*-chromenes 4, 5 and 6

A mixture of 6-hydroxybenzo[*b*]thiophenes **2a**, **b** or **c** (0.78 mmol) and the propargylic alcohols **3a** or **3b** (0.86 mmol) in dry toluene (15 mL) under Ar was heated at 60°C for 5 min. Then dry acidic alumina Brockmann I (10× the weight of compound **2**) was added and the mixture was heated at different temperatures with stirrer (Scheme 2). The reaction was followed by TLC and was stopped when no more product seemed to be formed. The mixture was filtered, the solid retained was washed with chloroform and the solvent removal gave an orange oil which was submitted to chromatography.

4.3.1. 2,3,9-Trimethyl-7,7-diphenyl-[7*H*]-chromene[7,6-*b*]thiophene (4a). Heating at 110°C for 2 h 30 min, compound **4a** was obtained in 10% yield (0.030 g) after column chromatography using as gradient of eluents from neat petroleum ether to 20% ether/petroleum ether. Crystallization from petroleum ether gave colourless crystals, mp 200–202°C. UV (closed form): λ_{max} EtOH (ε $dm^3\ mol^{-1}\ cm^{-1}$) 300 (9800, sh), 285 (19590, sh), 264 (41460), 202 (26180) nm. ^{1}H NMR ($CDCl_3$): 2.21 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.44 (3H, s, CH_3), 6.21 (1H, d, J=10 Hz, H-6), 6.77 (1H, d, J=10 Hz, H-5), 7.08 (1H, s, H-4), 7.23–7.49 (10H, m, Ar-H). ^{13}C NMR ($CDCl_3$): 11.39 (CH_3), 13.70 (CH_3), 13.72 (CH_3), 82.62 (Csp^3), 116.33 (CH), 117.94 (C), 119.17 (C), 124.79 (CH), 126.85 (CH), 127.30 (CH), 127.37 (C), 128.04 (CH), 128.72 (CH), 131.08 (C), 134.78 (C), 139.85 (C), 145.26 (C), 146.77 (C). Anal. calcd for $C_{26}H_{22}OS$: C 81.64; H 5.80; S 8.38; found C 81.44; H 6.15; S 8.28.

4.3.2. 2,3,9-Trimethyl-7,7-bis(4-methoxyphenyl)-[7*H*]-chromene[7,6-*b*]thiophene (4b). Heating at 80°C for 20 min, compound **4b** was obtained in 25% yield (0.086 g), after column chromatography using as eluents from petroleum ether to 15% ether/petroleum ether. Crystallization from petroleum ether gave colourless crystals, mp 128–130°C. UV (closed form): λ_{max} EtOH (ε $dm^3\ mol^{-1}\ cm^{-1}$) 300 (7340, sh), 285 (15000, sh), 263 (48040), 230 (20730) nm. ^{1}H NMR ($CDCl_3$): 2.21 (3H, s, CH_3), 2.41 (6H, s, 2×CH_3), 3.78 (6H, s, 2×OCH_3), 6.15 (1H, d, J=10 Hz, H-6), 6.73 (1H, d, J=10 Hz, H-5), 6.83 (4H, d, J=9 Hz, H-3′, 5′, 3″ and 5″), 7.07 (1H, s, H-4), 7.37 (4H, d, J=9 Hz, H-2′, 6′, 2″ and 6″). ^{13}C NMR ($CDCl_3$): 11.42 (CH_3), 13.72 (CH_3), 13.73 (CH_3), 55.20 (OCH_3), 82.20 (Csp^3), 113.29 (CH), 116.23 (CH), 117.90 (C), 119.22 (C), 124.41 (CH), 127.36 (C), 128.15 (CH), 129.19 (CH), 130.96 (C), 134.66 (C), 137.58 (C), 139.71 (C), 146.82 (C), 158.65 (C). MS: *m*/*z* (%) 444 (12, M^++2), 443 (45, M^++1), 442

(100, M^+), 335 (40). Anal. calcd for $C_{28}H_{26}O_3S$: C 75.99; H 5.92; S 7.24; found C 75.59; H 6.20; S 7.31.

4.3.3. 2,3,5-Trimethyl-7,7-diphenyl-[7*H*]-chromene[5,6-*b*]thiophene (5a). Heating at 110°C for 2 h, compound **5a** was obtained as a white solid in 31% yield (0.092 g) after column chromatography using as eluent petroleum ether. Crystallization from petroleum ether gave colourless crystals, mp 143–144°C. UV (closed form): λ_{max} EtOH (ε $dm^3\ mol^{-1}\ cm^{-1}$) 335 (1840), 313 (6570), 301 (5360), 259 (31740) nm. ^1H NMR ($CDCl_3$, 400 MHz): 2.18 (3H, s, CH_3), 2.40 (6H, s, 2×CH_3), 6.22 (1H, d, J=9.7 Hz, H-8), 6.78 (1H, d, J=9.7 Hz, H-9), 7.18 (1H, s, H-4), 7.24 (2H, t, H-4′ and 4″), 7.29 (4H, t, H-3′, 5′, 3″ and 5″), 7.47 (4H, d, H-2′, 6′, 2″ and 6″). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 11.49 (CH_3), 13.83 (CH_3), 16.54 (CH_3), 82.75 (Csp^3), 114.36 (C), 121.65 (CH), 122.61 (CH), 123.27 (C), 126.93 (CH and C), 127.47 (CH), 128.16 (CH), 128.61 (CH), 130.52 (C), 133.25 (C), 135.39 (C), 145.31 (C), 147.73 (C). MS: *m/z* (%) 384 (15, M^++2), 383 (45, M^++1), 382 (100, M^+), 305 (40), 191 (20). Anal. calcd for $C_{26}H_{22}OS$: C 81.64; H 5.80; S 8.38; found C 81.49; H 6.12; S 8.27.

4.3.4. 2,3,5-Trimethyl-7,7-bis(4-methoxyphenyl)-[7*H*]-chromene[5,6-*b*]thiophene (5b). Heating at 80°C for 30 min, compound **5b** was obtained as a white solid in 36% yield (0.124 g) after column chromatography using as eluents from petroleum ether to 20% ether/petroleum ether. Crystallization from petroleum ether afforded colourless crystals mp 154–155.5°C. UV (closed form): λ_{max} EtOH (ε $dm^3\ mol^{-1}\ cm^{-1}$): 335 (693), 312 (3680), 300 (2740, sh), 267 (37390), 234 (37370) nm. ^1H NMR ($CDCl_3$, 400 MHz): 2.18 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.41 (3H, s, CH_3), 3.75 (6H, s, OCH_3), 6.14 (1H, d, J=9.7 Hz, H-8), 6.75 (1H, d, J=9.7 Hz, H-9), 6.82 (4H, d, J=8.9 Hz, H-3′, 5′, 3″ and 5″), 7.16 (1H, s, H-4), 7.37 (4H, d, J=8.8 Hz, H-2′, 6′, 2″ and 6″). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 11.45 (CH_3), 13.83 (CH_3), 16.54 (CH_3), 55.30 (OCH_3), 82.39 (Csp^3), 113.45 (CH), 114.38 (C), 121.25 (CH), 122.50 (CH), 123.27 (C), 126.96 (C), 128.25 (CH), 129.04 (CH), 130.41 (C), 133.20 (C), 135.29 (C), 137.66 (C), 147.76 (C), 158.86 (C). MS: *m/z* (%) 444 (30, M^++2), 443 (70, M^++1), 442 (100, M^+), 335 (55), 251 (25). Anal. calcd for $C_{28}H_{26}O_3S$: C 75.99; H 5.92; S 7.24; found C 75.86; H 6.18; S 6.92.

4.3.5. 2,3,4,9-Tetramethyl-7,7-diphenyl-[7*H*]-chromene[7,6-*b*]thiophene (6a). Heating at 110°C for 26 h, compound **6a** was obtained as a white solid in 10% yield (0.035 g) after column chromatography using as a gradient of eluents from neat petroleum ether to 10% ether/petroleum ether. Crystallization from petroleum ether afforded colourless crystals, mp 232–233°C. UV (closed form): λ_{max} EtOH (ε $dm^3\ mol^{-1}\ cm^{-1}$) 300 (6733, sh), 283 (11871, sh), 265 (31045), 205 (26772) nm. ^1H NMR ($CDCl_3$): 2.39 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.45 (3H, s, CH_3), 2.67 (3H, s, CH_3), 6.25 (1H, d, J=10 Hz, H-6), 7.05 (1H, d, J=10 Hz, H-5), 7.18–7.34 (6H, m, Ar-H), 7.44–7.50 (4H, m, Ar-H). ^{13}C NMR ($CDCl_3$): 13.64 (CH_3), 14.11 (CH_3), 15.12 (CH_3), 16.14 (CH_3), 81.38 (Csp^3), 115.56 (C), 118.32 (C), 122.01 (CH), 126.36 (C), 126.81 (CH), 127.23 (CH), 128.01 (CH), 128.59 (CH), 129.01 (C), 130.45 (C), 133.21 (C), 140.24 (C), 145.26 (C), 146.40 (C). MS: *m/z* (%) 398 (9, M^++2), 397 (31, M^++1), 396 (100, M^+), 382 (17). HRMS $C_{27}H_{24}OS$ requires M 396.154787. M^+ found 396.155081.

4.3.6. 2,3,4,9-Tetramethyl-7,7-bis(4-methoxyphenyl)-[7*H*]-chromene[7,6-*b*]thiophene (6b). Heating at 80°C for 40 min, compound **6b** was obtained in 20% yield (0.071 g) after column chromatography using as eluents from petroleum ether to 15% ether/petroleum ether. Crystallization from petroleum ether afforded colourless crystals, mp 177–179°C. UV (closed form): λ_{max} EtOH (ε $dm^3\ mol^{-1}\ cm^{-1}$) 300 (7240, sh), 285 (14760, sh), 266 (36610), 229 (17680), 208 (37160) nm. ^1H NMR ($CDCl_3$): 2.38 (6H, s, 2×CH_3), 2.45 (3H, s, CH_3), 2.67 (3H, s, CH_3), 3.77 (6H, s, 2×OCH_3), 6.18 (1H, d, J=10 Hz, H-6), 6.82 (4H, d, J=9 Hz, H-3′, 5′, 3″ and 5″), 7.01 (1H, d, J=10 Hz, H-5), 7.36 (4H, d, J=9 Hz, H-2′, 6′, 2″ and 6″). ^{13}C NMR ($CDCl_3$): 13.61 (CH_3), 14.05 (CH_3), 15.08 (CH_3), 16.08 (CH_3), 55.15 (OCH_3), 81.03 (Csp^3), 113.29 (CH), 115.49 (C), 118.39 (C), 121.60 (CH), 126.23 (C), 128.11 (CH), 128.98 (C), 129.04 (CH), 130.33 (C), 133.13 (C), 137.64 (C), 140.19 (C), 146.50 (C), 158.64 (C). Anal. calcd for $C_{29}H_{28}O_3S$: C 76.29; H 6.18; S 7.02; found C 76.32; H 6.36; S 7.09.

Acknowledgements

The Foundation for Science and Technology (Portugal) is thanked for the financial support through IBQF-Univ. of Minho and Escola Superior de Tecnologia e Gestão of IPBragança for financial support to P. M. S. Plasencia.

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