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A new synthesis of benzo[*b*]thiophenes utilizing an interrupted Pummerer reaction

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ABSTRACT

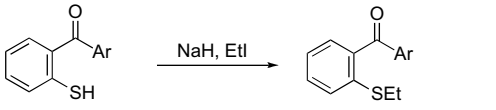
A convenient synthesis of 3-arylbenzo[*b*]thiophenes utilizing an interrupted Pummerer reaction of 2-(1-arylvinyl)phenyl ethyl sulfoxides is described. Thus, treatment of these sulfoxides, which were readily prepared from 2-sulfanylphenyl ketones or 2-fluoro-5-methoxybenzaldehyde, with acetic anhydride at 100 °C afforded 3-arylbenzo[*b*]thiophenes in reasonable yields.

1. Introduction

Literature survey has revealed that many molecules having the benzo[*b*]thiophene skeleton exhibit a wide variety of biological activities.[1] Therefore, many research groups[2] including us[3] have been developing a number of new methods for the preparation of benzo[*b*]thiophene derivatives. In this paper we wish to report a new and efficient method for the synthesis of benzo[*b*]thiophenes. We anticipated that reaction of 2-(1-arylvinyl)phenyl ethyl sulfoxides **5** with acetic anhydride would afford 3-arylbenzo[*b*]thiophenes **6**, via an interrupted Pummerer reaction,[4] because Bates et al. have reported that pyrrolo[2,1-*b*]benzothiazole is formed by treating alkyl 2-(pyrrol-1-yl)phenyl sulfoxides with trifluoroacetic anhydride.[4a] They have offered an interrupted Pummerer pathway for its formation.

2. Results and discussion

2-(1-Arylvinyl)phenyl sulfoxides **5** were readily prepared from aryl 2-ethylsulfanylphenyl ketones **2**, which were obtained by two different procedures starting with aryl 2-sulfanylphenyl ketones **1**[5] or commercially available 2-fluoro-5-methoxybenzaldehyde. In the first procedure, S-ethylation of **1** with iodoethane using sodium hydride as a base produced the corresponding 2-(ethylsulfanyl)phenyl ketones **2a**–**c** in good yields, as shown in Scheme 1. In the second procedure, aryl(2-fluoro-5-methoxyphenyl)methanones **3**, which were readily prepared from 2-fluoro-5-methoxybenzaldehyde via reaction with arylmagnesium bromide followed by the PCC oxidation in good yields (see Experimental section), were allowed to react with ethanethiol using sodium hydride as a base to give aryl 2-ethylsulfanyl-5-methoxyphenyl ketones **2d**–**i** in generally good yields, as shown in Scheme 2. A somewhat low yield was obtained with (2-fluoro-5-methoxyphenyl)(4-methoxyphenyl)methanone (**3g**). We reasoned that 4-methoxyphenyl substituent might lower the reactivity of **3g** toward sodium ethanethiolate.



1a Ar = Ph
1b Ar = *p*-Tol
1c Ar = 4-ClC$_6$H$_4$

2a Ar = Ph 79%
2b Ar = *p*-Tol 78%
2c Ar = 4-ClC$_6$H$_4$ 81%

Scheme 1.

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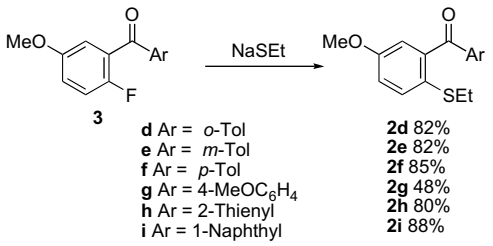
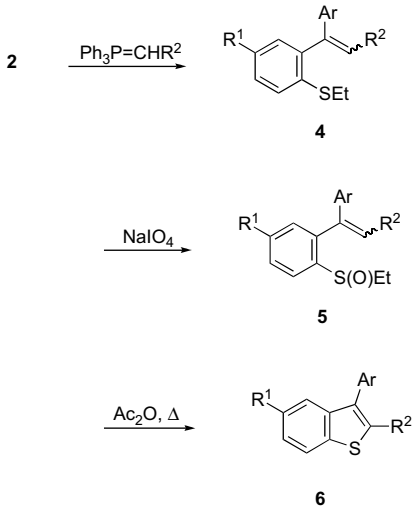


Scheme 2.

We conducted the conversion of **2**, thus obtained, into 3-arylbenzo[*b*]thiophenes **6** as outlined in Scheme 3, and the results are summarized in Table 1. Thus, the reaction of compounds **2** with methylene- or ethylene-triphenylphosphorane gave 2-(ethylsulfanyl)styrene derivatives **4**, which was then oxidized with an equimolar amount of sodium metaperiodate to give 2-(1-arylvinyl)phenyl ethyl sulfoxides **5**. As can be seen from the Table, these conversions were carried out generally in good yields.

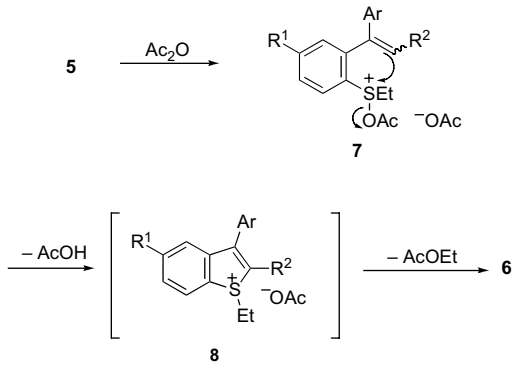


Scheme 3.

We were able to obtain 3-arylbenzo[*b*]thiophenes **6** by simply heating the sulfoxides **5** in acetic anhydride at 100 °C. We found that the reactions proceeded smoothly to give the desired products in good yields, when the α-substituents of **5** were phenyl, *p*-tolyl, 4-methoxyphenyl, 2-thienyl, or 1-naphthyl, and the β-substituent was hydrogen (entries 1, 2, 4–6, and 8–10). Poor yields were obtained, however, with ethyl (1-propenyl)phenyl sulfoxides **5c** and **5f–ii** (entries 3 and 7). Rather complicated mixtures of products were obtained, though no products arising from normal Pummerer reaction were isolated.

A limitation of the aforementioned method is that 3-alkylbenzo[*b*]thiophenes cannot be prepared. Thus, the treatment of ethyl 2-(1-methylethenyl)phenyl sulfoxide with acetic anhydride under conditions similar to those described above for the preparation of 3-arylbenzo[*b*]thiophenes **6** resulted in almost quantitative recovery of the starting sulfoxide; even the normal Pummerer product could not be formed, though we have no explanation of the reason for this.

A probable pathway leading to 3-arylbenzo[*b*]thiophenes **6** from 2-(1-arylethenyl)phenyl ethyl sulfoxides **5** is outlined in Scheme 4. This is parallel to that reported by Bates et al. for the formation of pyrrolo[2,1-*b*]benzothiazole from alkyl 2-(pyrrol-1-yl)phenyl sulfoxides.[4a] Thus, treatment of **5** with acetic anhydride generates an *S*-acetoxylated sulfonium ion intermediate **7**. The alkene π-electrons attack intramolecularly on the sulfur cation center with a loss of acetic acid to afford a benzothiophenium ion intermediate **8**. Ethyl acetate are eliminated from this intermediate to give rise to **6**. The lower yields in the reactions with ethyl (1-propenyl)phenyl sulfoxides **5c** and **5f–ii** thought to be due to unfavorable steric interaction between the methyl substituent and the ethyl group in the intermediate **8**.



Scheme 4.

In conclusion, the above-mentioned experiments have demonstrated that the treatment of 2-(1-arylethenyl)phenyl sulfoxides with acetic anhydride results in the formation of 3-arylbenzo[*b*]-thiophenes. As the present method starts with readily available materials and involves very simple manipulations, it may be of value in organic synthesis. Studies on the synthesis of sulfur-containing heterocycles utilizing this type of reaction are now under way in our laboratory.

Table 1
Preparation of benzo[*b*]thiophenes **6** from 2-(ethylsulfanyl)phenyl ketones **2**

Entry	**2**	R^2	**4** (Yield[a]/%)	**5** (Yield[a]/%)	**6** (Yield[a]/%)
1	**2a**	H	**4a** (73)	**5a** (74)	**6a** (77)
2	**2b**	H	**4b** (75)	**5b** (87)	**6b** (62)
3	**2c**	Me	**4c** (85)	**5c** (95)	**6c** (20)
4	**2d**	H	**4d** (59)	**5d** (96)	**6d** (67)
5	**2e**	H	**4e** (81)	**5e** (83)	**6e** (59)
6	**2f**	H	**4f–i** (81)	**5f–i** (93)	**6f–i** (75)
7	**2f**	Me	**4f–ii** (51)	**5f–ii** (78)	**6f–ii** (29)
8	**2g**	H	**4g** (75)	**5g** (81)	**6g** (86)
9	**2h**	H	**4h** (66)	**5h** (78)	**6h** (82)
10	**2i**	H	**4i** (76)	**5i** (92)	**6i** (78)

[a] Isolated yields.

3. Experimental

3.1. General

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400 FT NMR spectrometer operating at 400 MHz. The ^{13}C NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were measured by a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

3.2. Starting materials

Aryl(2-sulfanylphenyl)methanones **1** were prepared by a previously reported our procedure.[5] All other chemicals used in this study were commercially available.

*3.2.1. Aryl(2-fluoro-5-methoxyphenyl)methanones **3d–i***

These compounds were prepared by the reaction of 2-fluoro-5-methoxybenzaldehyde with arylmagnesium bromides in THF at 0 °C, followed by the PCC oxidation of the resulting alcohols in CH_2Cl_2 at room temperature.

3.2.1.1. (2-Fluoro-5-methoxyphenyl)(2-methylphenyl)methanol. Yield: 92%; a pale-yellow oil; R_f 0.23 (1:3 Et_2O–hexane); IR (neat) 3364 cm^{-1}; ^1H NMR (500 MHz) δ 2.17 (d, J=4.1 Hz, 1H), 2.32 (s, 3H), 3.74 (s, 3H), 6.29 (d, J=4.1 Hz, 1H), 6.77 (dd, J=8.7, 3.2 Hz, 1H), 6.87 (dd, J=3.2, 2.6 Hz, 1H), 6.96 (dd, J=9.1, 8.7 Hz, 1H), 7.15–7.23 (m, 3H), 7.45 (d, J=7.3 Hz, 1H). Anal. Calcd for $C_{15}H_{15}FO_2$: C, 73.15; H, 6.14. Found: C, 73.12; H, 6.18.

*3.2.1.2. (2-Fluoro-5-methoxyphenyl)(2-methylphenyl)methanone (**3d**).* Yield: 82%; a pale-yellow oil; R_f 0.48 (1:3 Et_2O–hexane); IR (neat) 1668 cm^{-1}; ^1H NMR (500 MHz) δ 2.49 (s, 3H), 3.82 (s, 3H), 7.00–7.07 (m, 2H), 7.13 (dd, J=7.3, 2.7 Hz, 1H), 7.23 (dd, J=7.8, 7.3 Hz, 1H), 7.29 (d, J=7.8 Hz, 1H), 7.38–7.42 (m, 2H). Anal. Calcd for $C_{15}H_{13}FO_2$: C, 73.76; H, 5.36. Found: C, 73.69; H, 5.40.

3.2.1.3. (2-Fluoro-5-methoxyphenyl)(3-methylphenyl)methanol. Yield: 68%; a pale-yellow oil; R_f 0.29 (1:3 Et_2O–hexane); IR (neat) 3408, 1607 cm^{-1}; ^1H NMR (500 MHz) δ 2.29 (d, J=4.1 Hz, 1H), 2.34 (s, 3H), 3.78 (s, 3H), 6.07 (d, J=4.1 Hz, 1H), 6.75 (dt, J=8.7, 3.7 Hz, 1H), 6.93 (dd, J=9.2, 8.7 Hz, 1H), 7.06–7.09 (m, 2H), 7.19–7.24 (m, 3H). Anal. Calcd for $C_{15}H_{15}FO_2$: C, 73.15; H, 6.14. Found: C, 72.98; H, 6.13.

*3.2.1.4. (2-Fluoro-5-methoxyphenyl)(3-methylphenyl)methanone (**3e**).* Yield: 79%; a pale-yellow oil; R_f 0.50 (1:3 Et_2O–hexane); IR (neat) 1668 cm^{-1}; ^1H NMR (500 MHz) δ 2.41 (s, 3H), 3.82 (s, 3H), 7.02–7.10 (m, 3H), 7.36 (dd, J=7.8, 7.3 Hz, 1H), 7.42 (d, J=7.3 Hz, 1H), 7.62 (d, J=7.8 Hz, 1H), 7.68 (s, 1H). Anal. Calcd for $C_{15}H_{13}FO_2$: C, 73.76; H, 5.36. Found: C, 73.81; H, 5.62.

3.2.1.5. (2-Fluoro-5-methoxyphenyl)(4-methylphenyl)methanol. Yield: 74%; a pale-yellow oil; R_f 0.26 (1:3 Et_2O–hexane); IR (neat) 3391, 1614 cm^{-1}; ^1H NMR (500 MHz) δ 2.21 (d, J=4.6 Hz, 1H), 2.33 (s, 3H), 3.78 (s, 3H), 6.07 (d, J=4.6 Hz, 1H), 6.74 (ddd, J=9.2, 3.7, 3.2 Hz, 1H), 6.92 (t, J=9.2 Hz, 1H), 7.07 (dd, J=6.0, 3.2 Hz, 1H), 7.15 (d, J=8.2 Hz, 2H), 7.29 (d, J=8.2 Hz, 2H). Anal. Calcd for $C_{15}H_{15}FO_2$: C, 73.15; H, 6.14. Found: C, 73.08; H, 5.87.

*3.2.1.6. (2-Fluoro-5-methoxyphenyl)(4-methylphenyl)methanone (**3f**).* Yield: 82%; a white solid; mp 67–70 °C (hexane–Et_2O); IR (KBr) 1668, 1607 cm^{-1}; ^1H NMR (500 MHz) δ 2.44 (s, 3H), 3.82 (s, 3H), 7.01–7.09 (m, 3H), 7.28 (d, J=8.2 Hz, 2H), 7.76 (d, J=8.2 Hz, 2H). Anal. Calcd for $C_{15}H_{13}FO_2$: C, 73.76; H, 5.36. Found: C, 73.72; H, 5.53.

3.2.1.7. (2-Fluoro-5-methoxyphenyl)(4-methoxyphenyl)methanol. Yield: 83%; a pale-yellow oil; R_f 0.18 (1:2 Et_2O–hexane); IR (neat) 3418, 1612 cm^{-1}; ^1H NMR (500 MHz) δ 2.20 (d, J=3.7 Hz, 1H), 3.78 (s, 3H), 3.79 (s, 3H), 6.06 (d, J=3.7 Hz, 1H), 6.75 (ddd, J=8.7, 3.7, 3.2 Hz, 1H), 6.87 (d, J=8.7 Hz, 2H), 6.92 (dd, J=9.2, 8.7 Hz, 1H), 7.08 (dd, J=6.0, 3.2 Hz, 1H), 7.32 (d, J=8.7 Hz, 2H). Anal. Calcd for $C_{15}H_{15}FO_3$: C, 68.69; H, 5.76. Found: C, 68.82; H, 5.90.

*3.2.1.8. (2-Fluoro-5-methoxyphenyl)(4-methoxyphenyl)methanone (**3g**).* Yield: 77%; a yellow oil; R_f 0.25 (1:2 Et_2O–hexane); IR (neat) 1661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.89 (s, 3H), 6.95 (d, J=8.7 Hz, 2H), 6.99–7.03 (m, 2H), 7.07 (t, J=8.7 Hz, 1H), 7.85 (d, J=8.7 Hz, 2H). Anal. Calcd for $C_{15}H_{13}FO_3$: C, 69.22; H, 5.03. Found: C, 68.96; H, 4.98.

3.2.1.9. (2-Fluoro-5-methoxyphenyl)(2-thienyl)methanol. Yield: 89%; a yellow oil; R_f 0.32 (1:2 Et_2O–hexane); IR (neat) 3396 cm^{-1}; ^1H NMR (500 MHz) δ 2.50 (d, J=4.6 Hz, 1H), 3.79 (s, 3H), 6.33 (d, J=4.6 Hz, 1H), 6.79 (ddd, J=8.7, 4.1, 3.7 Hz, 1H), 6.92–6.95 (m, 2H), 6.98 (dd, J=9.1, 8.7 Hz, 1H), 7.12 (dd, J=5.5, 3.2 Hz, 1H), 7.27 (d, J=1.4 Hz, 1H). Anal. Calcd for $C_{12}H_{11}FO_2S$: C, 60.49; H, 4.65. Found: C, 60.46; H, 4.81.

*3.2.1.10. (2-Fluoro-5-methoxyphenyl)(2-thienyl)methanone (**3h**).* Yield: 88%; a yellow oil; R_f 0.33 (1:3 Et_2O–hexane); IR (neat) 1645 cm^{-1}; ^1H NMR (500 MHz) δ 3.82 (s, 3H), 7.01–7.06 (m, 2H), 7.10 (dd, J=9.1, 8.7 Hz, 1H), 7.15 (dd, J=4.6, 4.1 Hz, 1H), 7.57–7.59 (m, 1H), 7.76 (dd, J=4.6, 1.4 Hz, 1H). Anal. Calcd for $C_{12}H_9FO_2S$: C, 61.00; H, 3.84. Found: C, 60.95; H, 3.95.

3.2.1.11. (2-Fluoro-5-methoxyphenyl)(naphthalen-1-yl)methanol. Yield: 89%; a colorless viscous oil; R_f 0.23 (1:3 Et_2O–hexane); IR (neat) 3381 cm^{-1}; ^1H NMR (500 MHz) δ 2.38 (d, J=4.7 Hz, 1H), 3.70 (s, 3H), 6.78 (ddd, J=8.7, 3.6, 2.7 Hz, 1H), 6.86–6.88 (m, 2H), 7.01 (dd, J=9.2, 8.7 Hz, 1H), 7.47–7.52 (m, 3H), 7.63 (d, J=7.3 Hz, 1H), 7.82 (d, J=8.2 Hz, 1H), 7.87 (dd, J=7.3, 2.3 Hz, 1H), 8.08 (dd, J=7.3, 1.8 Hz, 1H). Anal. Calcd for $C_{18}H_{15}FO_2$: C, 76.58; H, 5.36. Found: C, 76.49; H, 5.58.

*3.2.1.12. (2-Fluoro-5-methoxyphenyl)(naphthalen-1-yl)methanone (**3i**).* Yield: 81%; a white solid; mp 105–107 °C (hexane–Et_2O); IR (KBr) 1649, 1614 cm^{-1}; ^1H NMR (500 MHz) δ 3.84 (s, 3H), 7.03 (t, J=9.2 Hz, 1H), 7.07 (ddd, J=9.2, 4.1, 3.2 Hz, 1H), 7.22 (dd, J=5.5, 3.2 Hz, 1H), 7.48 (dd, J=8.2, 7.3 Hz, 1H), 7.56 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.60 (td, J=7.3, 1.4 Hz, 1H), 7.67 (d, J=7.3 Hz, 1H), 7.93 (dd, J=7.8, 1.4 Hz, 1H), 8.03 (d, J=8.2 Hz, 1H), 8.53 (d, J=8.2 Hz, 1H). Anal. Calcd for $C_{18}H_{13}FO_2$: C, 77.13; H, 4.67. Found: C, 77.02; H, 4.74.

3.3. Aryl[2-(ethylsulfanyl)phenyl]methanones 2a–c

These compounds were prepared by successive treatment of aryl(2-sulfanylphenyl)methanones **1** with sodium hydride and iodoethane in THF at 0 °C.

*3.3.1. [2-(Ethylsulfanyl)phenyl]phenylmethanone (**2a**)*

A yellow oil; R_f 0.30 (1:8 THF–hexane). The spectral data (IR and ^1H NMR) were identical to those reported previously.[6]

*3.3.2. [2-(Ethylsulfanyl)phenyl](4-methylphenyl)methanone (**2b**)*

A yellow oil; R_f 0.33 (1:8 THF–hexane); IR (neat) 1660, 1605 cm^{-1}; ^1H NMR (500 MHz) δ 1.23 (t, J=7.3 Hz, 3H), 2.42 (s, 3H), 2.88 (q, J=7.3 Hz, 2H), 7.24–7.27 (m, 3H), 7.34 (dd, J=7.3, 1.4 Hz, 1H), 7.43 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.48 (d, J=7.8 Hz, 1H), 7.69 (d, J=8.2 Hz, 2H). Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 74.80; H, 6.31.

*3.3.3. (4-Chlorophenyl)[2-(ethylsulfanyl)phenyl]methanone (**2c**)*

A yellow oil; R_f 0.43 (1:8 THF–hexane); IR (neat) 1667 cm^{-1}; ^1H NMR (400 MHz) δ 1.23 (t, J=7.3 Hz, 3H), 2.87 (q, J=7.3 Hz, 2H), 7.27 (ddd, J=7.7, 7.3, 1.5 Hz, 1H), 7.33 (dd, J=7.7, 1.5 Hz, 1H), 7.41 (d, J=8.8 Hz, 2H), 7.44 (ddd, J=7.7, 7.3, 1.5 Hz, 1H), 7.48 (dd, J=7.7, 1.5 Hz, 1H), 7.72 (d, J=8.8 Hz, 2H). Anal. Calcd for $C_{15}H_{13}ClOS$: C, 65.09; H, 4.73. Found: C, 65.15; H, 4.73.

3.4. Aryl[2-(ethylsulfanyl)-5-methoxyphenyl]methanones 2d–i

These compounds were prepared by reacting aryl(2-fluoro-5-methoxyphenyl)methanones **3** with ethanethiol in DMF in the presence of sodium hydride at room temperature.

*3.4.1. (2-Ethylsulfanyl-5-methoxyphenyl)(2-methylphenyl)-methanone (**2d**)*

A yellow oil; R_f 0.52 (1:3 Et_2O–hexane); IR (neat) 1668 cm^{-1}; ^1H NMR (500 MHz) δ 1.17 (t, J=7.3 Hz, 3H), 2.56 (s, 3H), 2.74 (q, J=7.3 Hz, 2H), 3.79 (s, 3H), 6.92 (d, J=2.7 Hz, 1H), 6.99 (dd, J=8.7, 2.7 Hz, 1H), 7.17 (dd, J=7.8, 7.3 Hz, 1H), 7.25–7.30 (m, 2H), 7.38 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.40 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.20; H, 6.57.

*3.4.2. (2-Ethylsulfanyl-5-methoxyphenyl)(3-methylphenyl)-methanone (**2e**)*

A yellow oil; R_f 0.40 (1:3 Et_2O–hexane); IR (neat) 1668 cm^{-1}; ^1H NMR (500 MHz) δ 1.14 (t, J=7.3 Hz, 3H), 2.39 (s, 3H), 2.73 (q, J=7.3 Hz, 2H), 3.81 (s, 3H), 6.85 (d, J=2.7 Hz, 1H), 6.98 (dd, J=8.2, 2.7 Hz, 1H), 7.32 (dd, J=7.8, 7.3 Hz, 1H), 7.39 (d, J=7.3 Hz, 1H), 7.47 (d, J=8.2 Hz, 1H), 7.54 (d, J=7.8 Hz, 1H), 7.65 (s, 1H). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.28; H, 6.31.

*3.4.3. (2-Ethylsulfanyl-5-methoxyphenyl)(4-methylphenyl)-methanone (**2f**)*

A yellow oil; R_f 0.53 (1:3 Et_2O–hexane); IR (neat) 1668, 1605 cm^{-1}; ^1H NMR (500 MHz) δ 1.14 (t, J=7.3 Hz, 3H), 2.42 (s, 3H), 2.73 (q, J=7.3 Hz, 2H), 3.81 (s, 3H), 6.85 (d, J=2.7 Hz, 1H), 6.98 (dd, J=8.7, 2.7 Hz, 1H), 7.25 (d, J=8.2 Hz, 2H), 7.46 (d, J=8.7 Hz, 1H), 7.70 (d, J=8.2 Hz, 2H). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.21; H, 6.37.

*3.4.4. (2-Ethylsulfanyl-5-methoxyphenyl)(4-methoxyphenyl)-methanone (**2g**)*

A yellow oil; R_f 0.31 (1:2 Et_2O–hexane); IR (neat) 1661 cm^{-1}; ^1H NMR (500 MHz) δ 1.14 (t, J=7.3 Hz, 3H), 2.73 (q, J=7.3 Hz, 2H), 3.81 (s, 3H), 3.87 (s, 3H), 6.84 (d, J=2.7 Hz, 1H), 6.92 (d, J=9.2 Hz, 2H), 6.97 (dd, J=8.7, 2.7 Hz, 1H), 7.46 (d, J=8.7 Hz, 1H), 7.78 (d, J=9.2 Hz, 2H). Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.48; H, 6.02.

*3.4.5. (2-Ethylsulfanyl-5-methoxyphenyl)(2-thienyl)-methanone (**2h**)*

A yellow oil; R_f 0.44 (1:2 Et_2O–hexane); IR (neat) 1645 cm^{-1}; ^1H NMR (500 MHz) δ 1.17 (t, J=7.3 Hz, 3H), 2.78 (q, J=7.3 Hz, 2H), 3.82 (s, 3H), 6.96 (d, J=2.7 Hz, 1H), 6.99 (dd, J=8.7, 2.7 Hz, 1H), 7.11 (dd, J=5.0, 4.1 Hz, 1H), 7.41 (dd, J=4.1, 1.4 Hz, 1H), 7.47 (d, J=8.7 Hz, 1H), 7.73 (dd, J=5.0, 1.4 Hz, 1H). Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.36; H, 5.07.

*3.4.6. (2-Ethylsulfanyl-5-methoxyphenyl)(naphthalen-1-yl)-methanone (**2i**)*

A yellow oil; R_f 0.45 (1:3 Et_2O–hexane); IR (neat) 1661 cm^{-1}; ^1H NMR (500 MHz) δ 1.13 (t, J=7.3 Hz, 3H), 2.72 (q, J=7.3 Hz, 2H), 2.78 (s, 3H), 7.00 (d, J=2.7 Hz, 1H), 7.03 (dd, J=8.7, 2.7 Hz, 1H), 7.42 (dd, J=8.2, 7.8 Hz, 1H), 7.44 (d, J=8.7 Hz, 1H), 7.54 (dd, J=8.2, 0.9 Hz, 1H), 7.57 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.63 (ddd, J=8.2, 7.3, 1.4 Hz, 1H), 7.91 (d, J=7.8 Hz, 1H), 8.00 (d, J=8.2 Hz, 1H), 8.77 (d, J=8.2 Hz, 1H). Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63. Found: C, 74.69; H, 5.78.

3.5. 1-(1-Arylvinyl)-2-(ethylsulfanyl)benzenes 4

These compounds were prepared by treating **2** with methylene- or ethylene-triphenylphosphorane in THF at 0 °C.

*3.5.1. 1-Ethylsulfanyl-2-(1-phenylethenyl)benzene (**4a**)*

A pale-yellow oil; R_f 0.31 (1:5 CH_2Cl_2–hexane); IR (neat) 1615 cm^{-1}; ^1H NMR (400 MHz) δ 1.19 (t, J=7.3 Hz, 3H), 2.81 (q, J=7.3 Hz, 2H), 5.26 (d, J=1.0 Hz, 1H), 5.82 (d, J=1.0 Hz, 1H), 7.17–7.34 (m, 9H). Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71. Found: C, 79.83; H, 6.75.

*3.5.2. 1-Ethylsulfanyl-2-[1-(4-methylphenyl)ethenyl]benzene (**4b**)*

A pale-yellow oil; R_f 0.53 (1:2 CH_2Cl_2–hexane); IR (neat) 1611 cm^{-1}; ^1H NMR (500 MHz) δ 1.20 (t, J=7.3 Hz, 3H), 2.33 (s, 3H), 2.82 (q, J=7.3 Hz, 2H), 5.20 (s, 1H), 5.79 (d, J=0.9 Hz, 1H), 7.09 (d, J=7.8 Hz, 2H), 7.17–7.21 (m, 4H), 7.28–7.33 (m, 2H). Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13. Found: C, 80.05; H, 7.36.

*3.5.3. 1-[1-(4-Chlorophenyl)prop-1-enyl]-2-(ethylsulfanyl)-benzene (**4c**)*

A pale-yellow oil; a mixture of stereoisomers (E/Z=ca. 6:4); R_f 0.57 (1:3 CH_2Cl_2–hexane); IR (neat) 1635 cm^{-1}; ^1H NMR (400 MHz) δ 1.20 (t, J=7.3 Hz, 1.8H), 1.22 (t, J=7.3 Hz, 1.2H), 1.62 (d, J=6.9 Hz, 1.2H), 1.89 (d, J=6.9 Hz, 1.8H), 2.78 (q, J=7.3 Hz, 1.2H), 2.84 (q, J=7.3 Hz, 0.8H), 5.83 (q, J=6.9 Hz, 0.6H), 6.30 (q, J=6.9 Hz, 0.4H), 7.06–7.34 (m, 8H). Anal. Calcd for $C_{17}H_{17}ClS$: C, 70.69; H, 5.93. Found: C, 70.54; H, 5.77.

*3.5.4. 1-Ethylsulfanyl-4-methoxy-2-[1-(2-methylphenyl)ethenyl]-benzene (**4d**)*

A pale-yellow oil; R_f 0.41 (1:3 CH_2Cl_2–hexane); IR (neat) 1591 cm^{-1}; ^1H NMR (500 MHz) δ 1.10 (t, J=7.3 Hz, 3H), 2.25 (s, 3H), 2.61 (q, J=7.3 Hz, 2H), 3.78 (s, 3H), 5.46 (d, J=1.8 Hz, 1H), 5.51 (d, J=1.8 Hz, 1H), 6.79 (d, J=2.7 Hz, 1H), 6.81 (dd, J=8.2, 2.7 Hz, 1H), 7.09–7.18 (m, 4H), 7.30 (d, J=8.2 Hz, 1H). Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09. Found: C, 75.80; H, 7.12.

*3.5.5. 1-Ethylsulfanyl-4-methoxy-2-[1-(3-methylphenyl)-ethenyl]benzene (**4e**)*

A pale-yellow oil; R_f 0.40 (1:3 CH_2Cl_2–hexane); IR (neat) 1593 cm^{-1}; ^1H NMR (500 MHz) δ 1.10 (t, J=7.3 Hz, 3H), 2.31 (s, 3H), 2.67 (q, J=7.3 Hz, 2H), 3.81 (s, 3H), 5.21 (d, J=0.9 Hz, 1H), 5.79 (d, J=0.9 Hz, 1H), 6.82 (d, J=3.2 Hz, 1H), 6.87 (dd, J=8.7, 3.2 Hz, 1H), 7.06–7.07 (m, 2H), 7.11 (s, 1H), 7.17 (dd, J=7.8, 7.3 Hz, 1H), 7.35 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09. Found: C, 75.76; H, 7.20.

*3.5.6. 1-Ethylsulfanyl-4-methoxy-2-[1-(4-methylphenyl)-ethenyl]benzene (**4f–i**)*

A colorless oil; R_f 0.28 (1:3 CH_2Cl_2–hexane); IR (neat) 1591 cm^{-1}; ^1H NMR (400 MHz) δ 1.11 (t, J=7.3 Hz, 3H), 2.33 (s, 3H), 2.67 (q, J=7.3 Hz, 2H), 3.80 (s, 3H), 5.17 (s, 1H), 5.76 (s, 1H), 6.82 (d, J=2.9 Hz, 1H), 6.86 (dd, J=8.4, 2.9 Hz, 1H), 7.09 (d, J=8.0 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H), 7.34 (d, J=8.4 Hz, 1H). Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09. Found: C, 75.76; H, 7.36.

*3.5.7. 1-Ethylsulfanyl-4-methoxy-2-[1-(4-methylphenyl)prop-1-enyl]benzene (**4f–ii**)*

A colorless oil; a mixture of stereoisomers (E/Z=ca. 6:4); R_f 0.28 (1:3 CH_2Cl_2–hexane); IR (neat) 1591 cm^{-1}; ^1H NMR (400 MHz) δ 1.10 (t, J=7.3 Hz, 1.2H), 1.15 (t, J=7.3 Hz 1.8H), 1.62 (d, J=6.9 Hz, 1.8H), 1.90 (d, J=6.9 Hz, 1.2H), 2.30 (s, 1.8H), 2.33 (s, 1.2H), 2.61 (q, J=7.3 Hz, 1.2H), 2.71 (q, J=7.3 Hz, 0.8H), 3.789 (s, 1.2H), 3.794 (s, 1.8H), 5.77 (q, J=6.9 Hz, 0.4H), 6.28 (q, J=6.9 Hz, 0.6H), 6.69 (d, J=2.7 Hz, 0.4H), 6.77–6.80 (m, 1.2H), 6.87 (dd, J=8.7, 2.7 Hz, 0.4H), 7.05 (d, J=7.8 Hz, 2H), 7.11 (d, J=7.8 Hz, 2H), 7.24 (d, J=8.7 Hz, 0.4H), 7.34 (d, J=8.2 Hz, 0.6H). Anal. Calcd for $C_{19}H_{22}OS$: C, 76.46; H, 7.43. Found: C, 76.22; H, 7.31.

*3.5.8. 1-Ethylsulfanyl-4-methoxy-2-[1-(4-methoxyphenyl)-ethenyl]benzene (**4g**)*

A pale-yellow oil; R_f 0.21 (1:3 CH_2Cl_2–hexane); IR (neat) 1606 cm^{-1}; ^1H NMR (500 MHz) δ 1.12 (t, J=7.3 Hz, 3H), 2.70 (q, J=7.3 Hz, 2H), 3.80 (s, 3H), 3.81 (s, 3H), 5.12 (d, J=0.9 Hz, 1H),

5.71 (d, J=0.9 Hz, 1H), 6.81–6.84 (m, 3H), 6.87 (dd, J=8.7, 2.7 Hz, 1H), 7.21 (d, J=9.2 Hz, 2H), 7.34 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71. Found: C, 71.91; H, 6.62.

*3.5.9. 1-Ethylsulfanyl-4-methoxy-2-[1-(2-thienyl)ethenyl]-benzene (**4h**)*

A pale-yellow oil; R_f 0.42 (1:3 CH_2Cl_2–hexane); IR (neat) 1593 cm^{-1}; ^1H NMR (500 MHz) δ 1.15 (t, J=7.3 Hz, 3H), 2.74 (q, J=7.3 Hz, 2H), 3.81 (s, 3H), 5.08 (s, 1H), 5.77 (s, 1H), 6.66 (dd, J=3.7, 1.4 Hz, 1H), 6.85 (d, J=2.7 Hz, 1H), 6.88 (dd, J=8.7, 2.7 Hz, 1H), 6.91 (dd, J=5.0, 3.7 Hz, 1H), 7.20 (dd, J=5.0, 1.4 Hz, 1H), 7.37 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{15}H_{16}OS_2$: C, 65.18; H, 5.83. Found: C, 64.87; H, 6.02.

*3.5.10. 1-Ethylsulfanyl-4-methoxy-2-[1-(naphthalen-1-yl)-ethenyl]benzene (**4i**)*

A pale-yellow oil; R_f 0.41 (1:3 CH_2Cl_2–hexane); IR (neat) 1591 cm^{-1}; ^1H NMR (500 MHz) δ 1.06 (t, J=7.3 Hz, 3H), 2.62 (q, J=7.3 Hz, 2H), 3.75 (s, 3H), 5.69 (d, J=0.9 Hz, 1H), 5.71 (d, J=0.9 Hz, 1H), 6.82 (dd, J=8.7, 2.7 Hz, 1H), 6.86 (d, J=2.7 Hz, 1H), 7.30 (d, J=7.3 Hz, 1H), 7.33 (d, J=8.7 Hz, 1H), 7.38 (d, J=7.8 Hz, 1H), 7.40–7.46 (m, 2H), 7.76 (d, J=8.2 Hz, 1H), 7.83 (d, J=7.8 Hz, 1H), 8.26 (d, J=8.2 Hz, 1H). Anal. Calcd for $C_{21}H_{20}OS$: C, 78.71; H, 6.29. Found: C, 78.50; H, 6.33.

3.6. Ethyl 2-(1-arylvinyl)phenyl sulfoxides 5

These compounds were prepared by treating **4** with $NaIO_4$ in aqueous MeOH at room temperature.

*3.6.1. Ethyl 2-(1-phenylethenyl)phenyl sulfoxide (**5a**)*

A pale-yellow oil; R_f 0.29 (1:2 THF–hexane); IR (KBr) 1614, 1034 cm^{-1}; ^1H NMR (400 MHz) δ 1.08 (t, J=7.3 Hz, 3H), 2.49–2.58 (m, 1H), 2.65–2.74 (m, 1H), 5.33 (s, 1H), 5.83 (s, 1H), 7.22–7.25 (m, 2H), 7.30–7.32 (m, 4H), 7.50 (ddd, J=7.7, 7.3, 1.1 Hz, 1H), 7.59 (ddd, J=7.7, 7.3, 1.1 Hz, 1H), 8.01 (1H, d, J=7.7 Hz, 1H). Anal. Calcd for $C_{18}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 75.06; H, 6.41.

*3.6.2. Ethyl 2-[1-(4-methylphenyl)ethenyl]phenyl sulfoxide (**5b**)*

A pale-yellow oil; R_f 0.30 (1:3 THF–hexane); IR (neat) 1609, 1334 cm^{-1}; ^1H NMR (500 MHz) δ 1.08 (t, J=7.3 Hz, 3H), 2.34 (s, 3H), 2.55 (dq, J=14.7, 7.3 Hz, 1H), 2.72 (dq, J=14.7, 7.3 Hz, 1H), 5.27 (d, J=0.9 Hz, 1H), 5.79 (d, J=0.9 Hz, 1H), 7.11 (d, J=8.7 Hz, 2H), 7.13 (d, J=8.7 Hz, 2H), 7.30 (dd, J=7.8, 1.4 Hz, 1H), 7.49 (td, J=7.3, 1.4 Hz, 1H), 7.58 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.80 (dd, J=7.8, 1.4 Hz, 1H). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71. Found: C, 75.60; H, 6.80.

*3.6.3. 2-[1-(4-Chlorophenyl)prop-1-enyl]phenyl ethyl sulfoxide (**5c**)*

A pale-yellow oil; a mixture of stereoisomers (E/Z=ca. 6:4); R_f 0.31 (1:2 THF–hexane); IR (neat) 1634, 1035 cm^{-1}; ^1H NMR (500 MHz) δ 1.09 (t, J=7.3 Hz, 3H), 1.68 (d, J=6.4 Hz, 1.2H), 1.91 (d, J=7.3 Hz, 1.8H), 2.44–2.58 (m, 2H), 5.93 (q, J=7.3 Hz, 0.6H), 6.35 (br, 0.4H), 7.08 (d, J=8.7 Hz, 2H), 7.25–7.29 (m, 1H), 7.30 (d, J=8.7 Hz, 2H), 7.46 (ddd, J=7.8, 7.3, 1.4 Hz, 0.6H), 7.52 (ddd, J=7.8, 7.3, 1.4 Hz, 0.6H), 7.55 (ddd, J=7.8, 7.3, 1.4 Hz, 0.4H), 7.61 (ddd, J=7.8, 7.3, 1.4 Hz, 0.4H), 7.93 (dd, J=7.8, 1.4 Hz, 0.6H), 8.03 (dd, J=7.8, 1.4 Hz, 0.4H). Anal. Calcd for $C_{17}H_{17}ClOS$: C, 66.98; H, 5.62. Found: C, 66.80; H, 5.61.

*3.6.4. Ethyl 4-methoxy-2-[1-(2-methylphenyl)ethenyl]phenyl sulfoxide (**5d**)*

A pale-yellow oil; R_f 0.48 (1:1 THF–hexane); IR (neat) 1589, 1045 cm^{-1}; ^1H NMR (500 MHz) δ 1.03 (t, J=7.3 Hz, 3H), 2.18 (s, 3H), 2.24–2.37 (m, 2H), 3.88 (s, 3H), 5.48 (d, J=1.4 Hz, 1H), 5.56 (d, J=1.4 Hz, 1H), 6.95 (d, J=2.7 Hz, 1H), 7.04 (dd, J=8.7, 2.7 Hz, 1H), 7.12 (td, J=7.3, 1.4 Hz, 1H), 7.15 (d, J=7.3 Hz, 2H), 7.21 (td, J=7.3, 1.4 Hz, 1H), 7.86 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71. Found: C, 72.04; H, 6.75.

*3.6.5. Ethyl 4-methoxy-2-[1-(3-methylphenyl)ethenyl]phenyl sulfoxide (**5e**)*

A pale-yellow oil; R_f 0.20 (1:2 THF–hexane); IR (neat) 1589, 1047 cm^{-1}; ^1H NMR (500 MHz) δ 1.07 (t, J=7.3 Hz, 3H), 2.32 (s, 3H), 2.52 (dq, J=13.3, 7.3 Hz, 1H), 2.63 (dq, J=13.3, 7.3 Hz, 1H), 3.86 (s, 3H), 5.28 (d, J=0.9 Hz, 1H), 5.80 (d, J=0.9 Hz, 1H), 6.84 (d, J=2.7 Hz, 1H), 6.98–7.12 (m, 4H), 7.20 (t, J=7.8 Hz, 1H), 7.90 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71. Found: C, 72.02; H, 6.62.

*3.6.6. Ethyl 4-methoxy-2-[1-(4-methylphenyl)ethenyl]phenyl sulfoxide (**5f–i**)*

A pale-yellow oil; R_f 0.44 (1:1 THF–hexane); IR (neat) 1587, 1040 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, J=7.3 Hz, 3H), 2.34 (s, 3H), 2.52 (dq, J=14.7, 7.3 Hz, 1H), 2.65 (dq, J=14.7, 7.3 Hz, 1H), 3.86 (s, 3H), 5.25 (s, 1H), 5.78 (s, 1H), 6.83 (d, J=2.7 Hz, 1H), 7.09 (dd, J=8.7, 2.7 Hz, 1H), 7.11 (d, J=8.7 Hz, 2H), 7.15 (d, J=8.7 Hz, 2H), 7.90 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71. Found: C, 71.93; H, 6.63.

*3.6.7. Ethyl 4-methoxy-2-[1-(4-methylphenyl)prop-1-enyl]phenyl sulfoxide (**5f–ii**)*

A pale-yellow oil; a mixture of stereoisomers (E/Z=ca. 6:4); R_f 0.41 (1:1 THF–hexane); IR (neat) 1589, 1065 cm^{-1}; ^1H NMR (500 MHz) δ 1.04 (t, J=7.3 Hz, 3H), 1.68 (br s, 1.2H), 1.91 (d, J=6.9 Hz, 1.8H), 2.31 (s, 1.2H), 2.34 (s, 1.8H), 2.36–2.40 (m, 2H), 3.86 (s, 1.8H), 3.87 (s, 1.2H), 5.87 (q, J=6.9 Hz, 0.6H), 6.32 (br s, 0.4H), 6.73 (br s, 0.4H), 6.82 (d, J=2.3 Hz, 0.6H), 6.98–7.13 (m, 5H), 7.80 (d, J=8.7 Hz, 0.6H), 7.92 (d, J=8.7 Hz, 0.4H). Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.56; H, 7.28.

*3.6.8. Ethyl 4-methoxy-2-[1-(4-methoxyphenyl)ethenyl]phenyl sulfoxide (**5g**)*

A pale-yellow oil; R_f 0.33 (1:1 THF–hexane); IR (neat) 1589, 1034 cm^{-1}; ^1H NMR (500 MHz) δ 1.08 (t, J=7.3 Hz, 3H), 2.53 (dq, J=14.7, 7.3 Hz, 1H), 2.66 (dq, J=14.7, 7.3 Hz, 1H), 3.81 (s, 3H), 3.86 (s, 3H), 5.19 (s, 1H), 5.72 (s, 1H), 6.83–6.84 (m, 3H), 7.09 (dd, J=8.7, 2.7 Hz, 1H), 7.19 (d, J=8.7 Hz, 2H), 7.90 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37. Found: C, 68.20; H, 6.45.

*3.6.9. Ethyl 4-methoxy-2-[1-(thienyl)ethenyl]phenyl sulfoxide (**5h**)*

A pale-yellow oil; R_f 0.17 (1:2 THF–hexane); IR (neat) 1591, 1045 cm^{-1}; ^1H NMR (500 MHz) δ 1.10 (t, J=7.3 Hz, 3H), 2.57 (dq, J=14.7, 7.3 Hz, 1H), 2.74 (dq, J=14.7, 7.3 Hz, 1H), 3.86 (s, 3H), 5.15 (s, 1H), 5.79 (s, 1H), 6.70 (dd, J=3.7, 0.9 Hz, 1H), 6.87 (d, J=2.7 Hz, 1H), 6.93 (dd, J=5.0, 3.7 Hz, 1H), 7.11 (dd, J=8.7, 2.7 Hz, 1H), 7.25 (dd, J=5.0, 0.9 Hz, 2H), 7.92 (d, J=8.7 Hz, 1H). Anal. Calcd for $C_{15}H_{16}O_2S_2$: C, 61.61; H, 5.52. Found: C, 61.53; H, 5.49.

*3.6.10. Ethyl 4-methoxy-2-[1-(naphthalen-1-yl)ethenyl]phenyl sulfoxide (**5i**)*

A pale-yellow viscous oil; R_f 0.46 (1:1 THF–hexane); IR (neat) 1589, 1045 cm^{-1}; ^1H NMR (500 MHz) δ 0.87 (t, J=7.3 Hz, 3H), 2.20 (dq, J=14.7, 7.3 Hz, 1H), 2.30 (dq, J=14.7, 7.3 Hz, 1H), 3.90 (s, 3H), 5.71 (d, J=0.9 Hz, 1H), 5.80 (d, J=0.9 Hz, 1H), 7.06 (dd, J=8.7, 2.3 Hz, 1H), 7.09 (d, J=2.3 Hz, 1H), 7.28 (dd, J=7.3, 1.4 Hz, 1H), 7.40 (dd, J=8.2, 7.3 Hz, 1H), 7.43 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.47 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.82 (d, J=8.2 Hz, 1H), 7.84 (d, J=8.7 Hz, 1H), 7.86 (d, J=7.8 Hz, 1H), 8.08 (d, J=7.8 Hz, 1H). Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99. Found: C, 74.83; H, 6.17.

3.7. Typical procedure for the preparation of benzo[*b*]thiophenes 6

*3.7.1. 3-Phenylbenzo[b]thiophene (**6a**)*[7]

A solution of **5a** (0.16 g, 0.64 mmol) in Ac_2O (1 mL) was heated at 100 °C until the spot of the starting material had disappeared by TLC analyses (1:3 THF–hexane; 9 h). After removal of Ac_2O under

reduced pressure, the residue was purified by preparative TLC on silica gel to give **6a** (0.10 g, 77%); a pale-yellow oil; R_f 0.72 (1:10 THF–hexane). The spectral (IR and ^{1}H NMR) data of this product were identical to those reported previously.[7]

*3.7.2. 3-(4-Methylphenyl)benzo[b]thiophene (**6b**)*[7]

A pale-yellow oil; R_f 0.65 (1:20 THF–hexane). The spectral (IR and ^{1}H NMR) data of this product were identical to those reported previously.[7]

*3.7.3. 3-(4-Chlorophenyl)-2-methylbenzo[b]thiophene (**6c**)*

A pale-yellow oil; R_f 0.59 (1:30 THF–hexane); IR (neat) 3057, 1589, 1435, 1090, 833, 760, 733 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.48 (s, 3H), 2.88–7.31 (m, 2H), 7.33 (d, J=8.7 Hz, 2H), 7.44–7.49 (m, 3H), 7.79–7.81 (m, 1H); ^{13}C NMR δ 14.47, 122.00, 122.14, 123.91, 124.25, 128.79, 131.33, 132.53, 133.24, 133.70, 136.52, 138.18, 140.02; MS m/z 258 (M$^+$, 100). Anal. Calcd for $C_{15}H_{11}ClS$: C, 69.62; H, 4.28. Found: C, 69.50; H, 4.09.

*3.7.4. 5-Methoxy-3-(2-methylphenyl)benzo[b]thiophene (**6d**)*

A pale-yellow oil; R_f 0.69 (1:40 THF–hexane); IR (neat) 3060, 1599, 1456, 1261, 1229, 1028, 790 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.19 (s, 3H), 3.76 (s, 3H), 6.86 (d, J=2.3 Hz, 1H), 7.03 (dd, J=8.7, 2.3 Hz, 1H), 7.27–7.36 (m, 5H), 7.77 (d, J=8.7 Hz, 1H); MS m/z 254 (M$^+$, 100). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.30; H, 5.69.

*3.7.5. 5-Methoxy-3-(3-methylphenyl)benzo[b]thiophene (**6e**)*

A yellow oil; R_f 0.57 (1:10 THF–hexane); IR (neat) 3091, 1601, 1454, 1435, 1267, 1221, 1029, 847, 775 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.44 (s, 3H), 3.84 (s, 3H), 7.04 (dd, J=8.7, 2.3 Hz, 1H), 7.23 (dd, J=7.8, 1.8 Hz, 1H), 7.36 (d, J=2.3 Hz, 1H), 7.38–7.40 (m, 4H), 7.77 (d, J=8.7 Hz, 1H); MS m/z 254 (M$^+$, 100). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.49; H, 5.59.

*3.7.6. 5-Methoxy-3-(4-methylphenyl)benzo[b]thiophene (**6f–i**)*

A pale-yellow solid mp 73–75 °C (hexane–CH_2Cl_2); IR (KBr) 3088, 1601, 1497, 1454, 1427, 1263, 1235, 1028, 820, 779 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.44 (s, 3H), 3.83 (s, 3H), 7.04 (dd, J=8.7, 2.7 Hz, 1H), 7.30 (d, J=8.7 Hz, 2H), 7.35 (d, J=2.7 Hz, 1H), 7.37 (s, 1H), 7.48 (d, J=8.7 Hz, 2H), 7.76 (d, J=8.7 Hz, 1H); MS m/z 254 (M$^+$, 100). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.58; H, 5.79.

*3.7.7. 5-Methoxy-2-methyl-3-(4-methylphenyl)benzo[b]thiophene (**6f–ii**)*

A pale-yellow oil; R_f 0.37 (1:10 THF–hexane); IR (neat) 1597, 1456, 1441, 1269, 1231, 1151, 1030, 826 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.44 (s, 3H), 2.47 (s, 3H), 3.77 (s, 3H), 6.93 (dd, J=8.7, 2.3 Hz, 1H), 6.97 (d, J=2.7 Hz, 1H), 7.28 (d, J=8.2 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 7.64 (d, J=8.7 Hz, 1H); MS m/z 268 (M$^+$, 100). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.02; H, 6.12.

*3.7.8. 5-Methoxy-3-(4-methoxyphenyl)benzo[b]thiophene (**6g**)*

A pale-yellow solid; mp 118–120 °C (hexane–CH_2Cl_2); IR (KBr) 3086, 1609, 1497, 1454, 1425, 1247, 1177, 1031 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.84 (s, 3H), 3.88 (s, 3H), 7.02–7.05 (m, 3H), 7.330 (d, J=1.8 Hz, 1H), 7.331 (s, 1H), 7.51 (d, J=8.7 Hz, 2H), 7.76 (d, J=8.7 Hz, 1H); ^{13}C NMR δ 55.35, 55.57, 105.19, 114.20, 114.53, 123.49, 123.92, 128.63, 129.65, 132.97, 137.39, 139.17, 157.67, 159.08; MS m/z 270 (M$^+$, 100). Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 70.84; H, 5.41.

*3.7.9. 5-Methoxy-3-(2-thienyl)benzo[b]thiophene (**6h**)*

A pale-yellow oil; R_f 0.25 (hexane); IR (neat) 3090, 1599, 1456, 1434, 1261, 1232, 1026, 777, 698 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.88 (s, 3H), 7.05 (dd, J=8.7, 2.3 Hz, 1H), 7.17 (dd, J=5.0, 3.7 Hz, 1H), 7.32 (d, J=3.7 Hz, 1H), 7.36 (d, J=5.0 Hz, 1H), 7.51 (s, 1H), 7.57 (d, J=2.3 Hz, 1H), 7.75 (d, J=8.7 Hz, 1H); ^{13}C NMR δ 55.57, 105.17, 114.98, 123.50, 124.76, 125.00, 125.25, 127.58, 130.22, 132.84, 137.46, 138.44, 157.90; MS m/z 246 (M$^+$, 100). Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09. Found: C, 63.24; H, 4.09.

*3.7.10. 5-Methoxy-3-(naphthalen-2-yl)benzo[b]thiophene (**6i**)*

A pale-yellow oil; R_f 0.30 (hexane); IR (neat) 3055, 1599, 1454, 1435, 1269, 1219, 1024, 779 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.64 (s, 3H), 6.83 (d, J=2.3 Hz, 1H), 7.04 (dd, J=8.7, 2.3 Hz, 1H), 7.38 (dd, J=7.8, 7.3 Hz, 1H), 7.48 (s, 1H), 7.49 (ddd, J=7.8, 7.3, 1.4 Hz, 1H), 7.54 (dd, J=7.3, 1.4 Hz, 1H), 7.58 (dd, J=8.2, 7.3 Hz, 1H), 7.73 (d, J=8.2 Hz, 1H), 7.82 (d, J=8.7 Hz, 1H), 7.94 (d, J=7.8 Hz, 2H); ^{13}C NMR δ 55.47, 105.47, 114.86, 123.31, 125.46, 125.98, 126.04, 126.21, 126.31, 127.73, 128.24 (two overlapped C's), 132.32, 132.35, 133.71, 133.78, 136.05, 140.57, 157.57; MS m/z 290 (M$^+$, 100). Anal. Calcd for $C_{19}H_{14}OS$: C, 78.59; H, 4.86. Found: C, 78.47; H, 5.13.

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