Tetrahedron 65 (2009) 9633–9636

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An efficient synthesis of 3-aryl-2-aryl(or methyl)sulfanylbenzo[*b*]thiophenes via cyclization of aryl 2-aryl(or methyl)sulfanylmethylsulfanylphenyl ketones

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ARTICLE INFO

Article history:
Received 2 July 2009
Received in revised form 7 September 2009
Accepted 8 September 2009
Available online 12 September 2009

Keywords:
Benzo[*b*]thiophenes
2-Sulfanylphenyl ketones
Lithium diisopropylamide
Cyclization
Dehydration

ABSTRACT

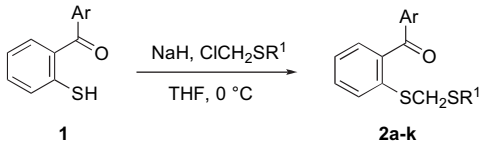
A convenient method for the preparation of 2-aryl(or methyl)sulfanylbenzo[*b*]thiophenes has been developed. Thus, aryl 2-aryl(or methyl)sulfanylmethylsulfanylphenyl ketones, easily prepared from readily available aryl 2-sulfanylphenyl ketones or 2-chloro-5-nitrophenyl phenyl ketone, are treated with LDA in 1,2-dimethoxyethane (DME) to give 3-aryl-2-aryl(or methyl)sulfanylmethylsulfanyl-2,3-dihydrobenzo[*b*]-thiophen-3-ols, which in turn were dehydrated with thionyl chloride to afford 3-aryl-2-aryl(or methyl)-sulfanylbenzo[*b*]thiophenes in reasonable overall yields.

1. Introduction

Benzo[*b*]thiophene derivatives are undoubtedly one of the most important classes of heterocycles, because some of molecules having the benzo[*b*]thiophene skeleton have been reported to exhibit wide variety of biological activities.[1] Therefore, we[2] and others[3] have recently reported efficient methods for the synthesis of benzo[*b*]thiophenes. However, there are only a few reports on the synthesis of 2-aryl(or alkyl)sulfanylbenzo[*b*]thiophenes,[4] which may also be of potential biological importance. For example, Sasaki and co-workers have synthesized 3-phenyl-2-(phenylsulfanyl)benzo[*b*]thiophene by irradiation of 1-phenyl-2,2-bis(phenylsulfanyl)ethanone.[4a] Recently, a synthesis of 2-methylsulfanylbenzo[*b*]thiophenes by cyclization of arylketene dithioacetal monoxides under Pummerer-like conditions has been reported by Yoshida et al.[4c] In this paper we wish to report a novel and facile method for the preparation of 3-aryl-2-aryl(or methyl)sulfanylbenzo[*b*]thiophenes **5** by cyclization of aryl 2-aryl(or methyl)sulfanylmethylsulfanylphenyl ketones **2**, which can be easily prepared by readily available from aryl 2-sulfanylphenyl ketones **1** or 2-chloro-5-nitrophenyl phenyl ketone (**3**), using LDA as a base and subsequent dehydration of the resulting 3-aryl-2-aryl(or methyl)-sulfanylmethylsulfanyl-2,3-dihydrobenzo[*b*]thiophen-3-ols **4** with thionyl chloride in satisfactory overall yields.

2. Results and discussion

Aryl 2-aryl(or methyl)sulfanylmethylsulfanylphenyl ketones **2a–k** were prepared by *S*-aryl(or methyl)sulfanylmethylation of aryl 2-sulfanylphenyl ketones **1**, which can be prepared by reacting 2-sulfanylbenzoic acid with aryllithiums as described previously,[5,6] with aryl chloromethyl sulfides or chloromethyl methyl sulfide using sodium hydride in THF at 0 °C as shown in Scheme 1. The yields are excellent as summarized in Table 1. Phenyl 5-Nitro-2-methyl-(or phenyl)sulfanylmethylsulfanylphenyl phenyl ketones **2l** or **2m** were prepared by treating commercially available 2-chloro-5-nitrophenyl phenyl ketone (**3**) with sodium sulfide and the subsequent *S*-methyl(or phenyl)sulfanylmethylation with chloromethyl methyl sulfide or chloromethyl phenyl sulfide as shown in Scheme 2. The yields are fair as can be seen from Table 1, entries 12 and 13.



1 **2a-k**

Scheme 1.

The preparation of 3-aryl-2-aryl(or methyl)sulfanylbenzo[*b*]-thiophenes **5** from compounds **2** was conducted as illustrated in Scheme 3. Thus, compounds **2** were treated with LDA at −78 °C in DME to generate the carbanions between the two sulfur atoms. These carbanions were reactive enough to undergo ring-closure by

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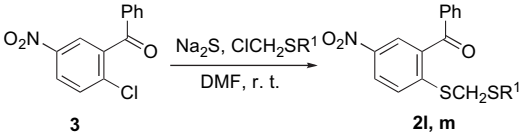
doi:10.1016/j.tet.2009.09.038

Table 1
Preparation of 3-aryl-2-aryl(or methyl)sulfanylbenzo[*b*]thiophenes **5**

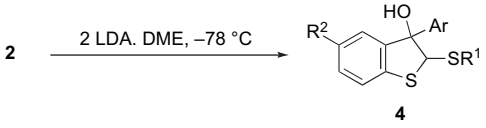
Entry	**1** or **3**	R^1	R^2	**2** (Yield/%)[a]	**5** (Yield/%)[a]
1	**1a** (Ar=Ph)	H	Me	**2a** (93)	**5a** (63)
2	**1a**	H	Ph	**2b** (98)	**5b** (60)
3	**1b** (Ar=*m*-Tol)	H	Me	**2c** (98)	**5c** (65)
4	**1b**	H	Ph	**2d** (97)	**5d** (63)
5	**1c** (Ar=4-ClC_6H_4)	H	Me	**2e** (88)	**5e** (65)
6	**1c**	H	Ph	**2f** (93)	**5f** (66)
7	**1c**	H	4-ClC_6H_4	**2g** (93)	**5g** (62)
8	**1d** (Ar=4-$MeOC_6H_4$)	H	Me	**2h** (90)	**5h** (60)
9	**1d**	H	Ph	**2i** (94)	**5i** (67)
10	**1d**	H	*p*-Tol	**2j** (86)	**5j** (65)
11	**1d**	H	4-ClC_6H_4	**2k** (85)	**5k** (67)
12	**3**	NO_2	Me	**2l** (75)	**5l** (58)
13	**3**	NO_2	Ph	**2m** (74)	**5m** (65)

[a] Isolated yields.

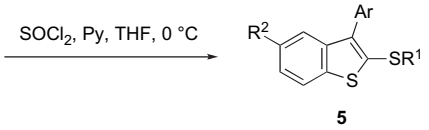


3 **2l, m**

Scheme 2.



4



5

Scheme 3.

intramolecular attack onto the carbonyl carbon at this temperature to afford, after protonation, dihydrobenzo[*b*]thiophen-3-ols **4**. It should be noted that the use of THF as a solvent gave a complex mixture of products containing a considerable amount of the starting materials in each case. Presumably, stronger activation of the amide anion by DME (compared to that by THF) due to coordination of two oxygen atoms of DME to the lithium cation is necessary for the generation of the carbanions between the two sulfur atoms. These alcohols thus obtained were then subjected to the dehydration with thionyl chloride in THF containing pyridine without purification after aqueous workup. The reaction proceeded smoothly and cleanly at 0 °C to give, after usual workup followed by purification using preparative TLC on silica gel, the desired benzothiophenes **5**.

The overall yields of **5** from **2** are also summarized in Table 1, which indicates that they are independent of the substituents on the 3-aryl groups. Initially, the somewhat lower yields of 2-methylsulfanyl derivatives **5a**, **5c**, **5e**, **5h**, and **5l** compared to those of 2-arylsulfanyl derivatives **5b**, **5d**, **5f**, **5g**, **5i**, **5j**, **5k**, and **5m** were anticipated due of the potential lower stability of the carbanions of between the two sulfur atoms from aryl 2-methylsulfanylmethylsulfanylphenyl ketones **2a**, **2c**, **2e**, **2h**, and **2l** compared to those from 2-arylsulfanylmethylsulfanylphenyl ketones **2b**, **2d**, **2f**, **2g**, **2i**, **2j**, **2k**, and **2m**. However, it can be seen from table that **2a**, **2c**, **2e**, **2h**, and **2l** also worked well to afford the corresponding 2-methylsulfanyl derivatives in the yields comparable to those of 2-arylsulfanyl derivatives.

In conclusion, the results mentioned above demonstrate that the cyclization–dehydration sequence starting from aryl 2-aryl(or methyl)sulfanylmethylsulfanylphenyl ketones provides an efficient approach to 3-aryl-2-aryl(or methyl)sulfanylbenzo[*b*]thiophenes. This method may be of value in organic synthesis, because the starting materials are readily available and the operations are very simple. Studies toward the synthesis of 2-aryl(or alkyl)sulfanylated thiophene-fused heterocycles as applications of the present method are now underway in our laboratory and the results will be reported shortly.

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 ^1H 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- and high-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 ketones **1a**,[6] **1b–d**,[5] chloromethyl 4-methylphenyl sulfide,[7] and chloromethyl 4-chlorophenyl sulfide[7] were prepared according to appropriate reported methods. All other chemicals used in this study were commercially available.

*3.2.1. Aryl 2-aryl(or methyl)sulfanylmethylsulfanylphenyl ketones **2a–k**.* These compounds were prepared by *S*-aryl(or methyl)-sulfanylmethylation of 2-sulfanylphenyl ketones **1** with the respective chloromethyl sulfides using NaH as a base in THF at 0 °C as described previously.[8] Compounds **2a**, **2b**, **2e** and **2f** are known.[8] The physical, spectral, and analytical data for new compounds follow.

*3.2.1.1. 3-Methylphenyl 2-methylsulfanylmethylsulfanylphenyl ketone (**2c**).* A yellow oil; R_f 0.38 (1:6 Et_2O–hexane); IR (neat) 1666 cm^{-1}; ^1H NMR (500 MHz) δ 2.08 (s, 3H), 2.40 (s, 3H), 3.93 (s, 2H), 7.32–7.40 (m, 4H), 7.48 (ddd, *J*=7.8, 7.3, 1.8 Hz, 1H), 7.55 (d, *J*=7.8 Hz, 1H), 7.62 (d, *J*=7.3 Hz, 1H), 7.64 (s, 1H). Anal. Calcd $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.47; H, 5.78.

*3.2.1.2. 3-Methylphenyl 2-phenylsulfanylmethylsulfanylphenyl ketone (**2d**).* A pale-yellow oil; R_f 0.38 (1:5 Et_2O–hexane); IR (neat) 1663, 1601 cm^{-1}; ^1H NMR (500 MHz) δ 2.38 (s, 3H), 4.27 (s, 2H), 7.18–7.27 (m, 3H), 7.30–7.36 (m, 4H), 7.39 (dd, *J*=7.8, 1.4 Hz, 2H), 7.47 (ddd, *J*=7.8, 7.3, 1.8 Hz, 1H), 7.52 (d, *J*=7.8 Hz, 1H), 7.62 (s, 1H), 7.63 (d, *J*=7.8 Hz, 1H). Anal. Calcd $C_{21}H_{18}OS_2$: C, 71.96; H, 5.18. Found: C, 71.90; H, 5.39.

*3.2.1.3. 4-Chlorophenyl 2-(4-chlorophenyl)sulfanylmethylsulfanylphenyl ketone (**2g**).* A yellow oil; R_f 0.31 (1:3 Et_2O–hexane); IR (neat) 1667 cm^{-1}; ^1H NMR (400 MHz) δ 4.24 (s, 2H), 7.21 (d, *J*=8.8 Hz, 2H), 7.24 (d, *J*=8.8 Hz, 2H), 7.36–7.50 (m, 5H), 7.60 (d, *J*=7.8 Hz, 1H), 7.68 (d, *J*=8.3 Hz, 2H). Anal. Calcd $C_{20}H_{14}Cl_2OS_2$: C, 59.26; H, 3.48. Found: C, 59.38; H, 3.55.

*3.2.1.4. 4-Methoxyphenyl 2-methylsulfanylmethylsulfanylphenyl ketone (**2h**).* A yellow oil; R_f 0.22 (1:1 Et_2O–hexane); IR (neat) 1659 cm^{-1}; ^1H NMR (400 MHz) δ 2.08 (s, 3H), 3.87 (s, 3H), 3.92 (s, 2H), 6.92 (d, J=8.8 Hz, 2H), 7.33–7.47 (m, 3H), 7.61 (d, J=7.7 Hz, 1H), 7.78 (d, J=8.8 Hz, 2H). Anal. Calcd $C_{16}H_{16}O_2S_2$: C, 63.13; H, 5.30. Found: C, 63.17; H, 5.51.

*3.2.1.5. 4-Methoxyphenyl 2-phenylsulfanylmethylsulfanylphenyl ketone (**2i**).* A yellow oil; R_f 0.29 (1:2 Et_2O–hexane); IR (neat) 1653 cm^{-1}; ^1H NMR (400 MHz) δ 3.86 (s, 3H), 4.27 (s, 2H), 6.90 (d, J=8.8 Hz, 2H), 7.19–7.26 (m, 3H), 7.31–7.46 (m, 5H), 7.61 (d, J=7.7 Hz, 1H), 7.75 (d, J=8.8 Hz, 2H). Anal. Calcd $C_{21}H_{18}O_2S_2$: C, 68.82; H, 4.95. Found: C, 68.52; H, 5.02.

*3.2.1.6. 4-Methoxyphenyl 2-(4-methylphenyl)sulfanylmethylsulfanylphenyl ketone (**2j**).* A yellow oil; R_f 0.36 (1:2 Et_2O–hexane); IR (neat) 1659 cm^{-1}; ^1H NMR (500 MHz) δ 2.30 (s, 3H), 3.87 (s, 3H), 4.22 (s, 2H), 6.90 (d, J=8.7 Hz, 2H), 7.05 (d, J=8.2 Hz, 2H), 7.24 (d, J=8.2 Hz, 2H), 7.34–7.46 (m, 3H), 7.61 (d, J=7.8 Hz, 1H), 7.76 (d, J=8.7 Hz, 2H). Anal. Calcd $C_{22}H_{20}O_2S_2$: C, 69.44; H, 5.30. Found: C, 69.21; H, 5.37.

*3.2.1.7. 2-(4-Chlorophenyl)sulfanylmethylsulfanylphenyl 4-methoxyphenyl ketone (**2k**).* A yellow oil; R_f 0.28 (1:4 Et_2O–hexane); IR (neat) 1653 cm^{-1}; ^1H NMR (500 MHz) δ 3.88 (s, 3H), 4.24 (s, 2H), 6.91 (d, J=9.2 Hz, 2H), 7.19 (d, J=8.7 Hz, 2H), 7.24 (d, J=8.7 Hz, 2H), 7.35–7.46 (m, 3H), 7.59 (d, J=7.8 Hz, 1H), 7.74 (d, J=9.2 Hz, 2H). Anal. Calcd $C_{21}H_{17}ClO_2S_2$: C, 62.91; H, 4.27. Found: C, 62.91; H, 4.31.

*3.2.2. 2-Methyl(or phenyl)sulfanylmethylsulfanylphenyl phenyl ketones **2l** or **2m**.* These compounds were prepared by treating (2-chloro-5-nitrophenyl)phenylmethanone (**3**) with sodium sulfide nonahydrate in DMF at room temperature and subsequent *S*-methyl(or phenyl)sulfanylmethylation with the respective chloromethyl sulfides at the same temperature.

*3.2.2.1. 2-Methylsulfanylmethylsulfanyl-5-nitrophenyl phenyl ketone (**2l**).* A yellow oil; R_f 0.31 (1:3 Et_2O–hexane); IR (neat) 1661, 1516, 1344 cm^{-1}; ^1H NMR (500 MHz) δ 2.15 (s, 3H), 4.06 (s, 2H), 7.51 (dd, J=7.8, 7.3 Hz, 2H), 7.66 (t, J=7.3 Hz, 1H), 7.69 (d, J=8.7 Hz, 1H), 7.80 (d, J=7.8 Hz, 2H), 8.26 (d, J=2.3 Hz, 1H), 8.32 (dd, J=8.7, 2.3 Hz, 1H). Anal. Calcd for $C_{15}H_{13}NO_3S_2$: C, 56.45; H, 4.08; N, 4.38. Found: C, 56.39; H, 4.16; N, 4.25.

*3.2.2.2. Phenyl 2-phenylsulfanylmethylsulfanyl-5-nitrophenyl ketone (**2m**).* A pale-yellow solid; mp 65–67 °C (hexane–CH_2Cl_2); IR (KBr) 1651, 1504, 1341 cm^{-1}; ^1H NMR (500 MHz) δ 4.38 (s, 2H), 7.25–7.28 (m, 3H), 7.38 (dd, J=7.8, 1.8 Hz, 2H), 7.50 (d, J=7.8, 7.3 Hz, 2H), 7.64 (t, J=7.3 Hz, 1H), 7.69 (d, J=9.2 Hz, 1H), 7.76 (d, J=7.8 Hz, 2H), 8.26 (d, J=2.3 Hz, 1H), 8.30 (dd, J=8.7, 2.3 Hz, 1H). Anal. Calcd $C_{20}H_{15}NO_3S_2$: C, 62.97; H, 3.96; N, 3.67. Found: C, 62.73; H, 4.12; N, 3.42.

3.3. Typical procedure for the preparation of 3-aryl-2-aryl(or methyl)sulfanylbenzo[*b*]thiophenes 5

*3.3.1. 2-Methylsulfanyl-3-phenylbenzo[b]thiophene (**5a**).* To a stirred solution of LDA (1.5 mmol) in DME (3 mL) at −78 °C, generated from *i*-Pr_2NH and *n*-BuLi by the standard method, was added a solution of **2a** (0.20 g, 0.73 mmol) in DME (2 mL) dropwise; the mixture was stirred for 1 h at the same temperature. Saturated aqueous NH_4Cl (10 mL) was added, and the organic materials were extracted with Et_2O twice (10 mL each). The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated by evaporation to give the crude 2-methylsulfanyl-3-phenyl-2,3-dihydrobenzo[*b*]thiophene-3-ol (**4a**). This was used in the next dehydration reaction without any purification. Thus, the crude **4a** was dissolved in THF (5 mL) containing pyridine (0.58 g, 7.3 mmol). To this solution at 0 °C was added $SOCl_2$ (0.17 g, 1.5 mmol) under stirring, and the stirring was continued for 30 min. Water (15 mL) was added, and the mixture was extracted with Et_2O twice (10 mL each). The combined extracts were washed successively with saturated aqueous $NaHCO_3$, 1% hydrochloric acid, and brine, and then dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by preparative TLC on silica gel (hexane) to give **5a** (0.12 g, 63%); a pale-yellow oil; R_f 0.57 (hexane). The spectral (IR, ^1H NMR, and ^{13}C NMR) data for this compound were identical to those reported previously.[4c]

*3.3.2. 3-Phenyl-2-phenylsufanylbenzo[b]thiophene (**5b**).* A white solid; mp 125–126 °C (hexane–Et_2O). The spectral (IR and ^1H NMR) data for this compound were identical to those reported previously.[4a]

*3.3.3. 3-(3-Methylphenyl)-2-methylsulfanylbenzo[b]thiophene (**5c**).* A pale-yellow oil; R_f 0.39 (hexane); IR (neat) 1605, 1425 cm^{-1}; ^1H NMR (500 MHz) δ 2.44 (s, 3H), 2.48 (s, 3H), 7.24–7.33 (m, 5H), 7.40 (dd, J=7.8, 7.3 Hz, 1H), 7.53 (dd, J=6.9, 2.3 Hz, 1H), 7.78 (dd, J=7.3, 1.8 Hz, 1H); MS m/z 270 (M^+, 100). Anal. Calcd $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 70.99; H, 5.27.

*3.3.4. 3-(3-Methylphenyl)-2-phenylsulfanylbenzo[b]thiophene (**5d**).* A yellow oil; R_f 0.64 (1:4 Et_2O–hexane); IR (neat) 1605, 1477 cm^{-1}; ^1H NMR (500 MHz) δ 2.40 (s, 3H), 7.19 (tt, J=7.3, 1.4 Hz, 1H), 7.22–7.29 (m, 7H), 7.34–7.38 (m, 3H), 7.60 (dd, J=7.8, 1.8 Hz, 1H), 7.77 (dd, J=7.8, 1.4 Hz, 1H); MS m/z 332 (M^+, 100). Anal. Calcd $C_{21}H_{16}S_2$: C, 75.86; H, 4.85. Found: C, 75.63; H, 5.02.

*3.3.5. 3-(4-Chlorophenyl)-2-methylsulfanylbenzo[b]thiophene (**5e**).* A yellow oil; R_f 0.23 (hexane); IR (neat) 1424 cm^{-1}; ^1H NMR (400 MHz) δ 2.48 (s, 3H), 7.29–7.34 (m, 2H), 7.41 (d, J=8.7 Hz, 2H), 7.47–7.50 (m, 3H), 7.79 (dd, J=6.4, 2.4 Hz, 1H); ^{13}C NMR δ 19.90, 121.83, 122.37, 124.38, 124.67, 128.73, 131.35, 132.97, 133.68, 135.80, 135.90, 139.53, 139.63; MS m/z 290 (M^+, 100). Anal. Calcd $C_{15}H_{11}ClS_2$: C, 61.95; H, 3.81. Found: C, 61.72; H, 4.02.

*3.3.6. 3-(4-Chlorophenyl)-2-phenylsulfanylbenzo[b]thiophene (**5f**).* A pale-yellow solid; mp 108–110 °C (hexane); IR (KBr) 1482 cm^{-1}; ^1H NMR (400 MHz) δ 7.18–7.28 (m, 5H), 7.32–7.40 (m, 4H), 7.44 (d, J=8.4 Hz, 2H), 7.56 (dd, J=7.3, 1.8 Hz, 1H), 7.78 (dd, J=7.3, 1.8 Hz, 1H); ^{13}C NMR δ 122.12, 123.40, 124.70, 125.40, 126.89, 128.69, 128.93, 129.11, 131.11, 131.37, 132.64, 133.99, 136.63, 139.21, 140.70, 141.23; MS m/z 352 (M^+, 100). Anal. Calcd $C_{20}H_{13}ClS_2$: C, 68.07; H, 3.71. Found: C, 68.08; H, 3.74.

*3.3.7. 3-(4-Chlorophenyl)-2-(4-chlorophenyl)sulfanylbenzo[b]thiophene (**5g**).* A white solid; mp 100–102 °C (hexane); IR (KBr) 1476 cm^{-1}; ^1H NMR (400 MHz) δ 7.15 (d, J=8.8 Hz, 2H), 7.21 (d, J=8.8 Hz, 2H), 7.34–7.42 (m, 4H), 7.45 (d, J=8.8 Hz, 2H), 7.57 (d, J=7.8, 1.4 Hz, 1H), 7.79 (d, J=7.3 Hz, 1H); ^{13}C NMR δ 122.17, 123.54, 124.83, 125.64, 128.76 (2C), 129.24, 129.98, 131.31 (2C), 132.45, 132.91, 134.15, 135.24, 139.12, 141.28; MS m/z 386 (M^+, 100). Anal. Calcd $C_{20}H_{12}Cl_2S_2$: C, 62.02; H, 3.12. Found: C, 61.83; H, 3.17.

*3.3.8. 3-(4-Methoxyphenyl)-2-methylsulfanylbenzo[b]thiophene (**5h**).* A white solid; mp 84–85 °C (hexane–Et_2O); IR (KBr) 1611, 1526 cm^{-1}; ^1H NMR (400 MHz) δ 2.47 (s, 3H), 3.88 (s, 3H), 7.04 (d, J=8.8 Hz, 2H), 7.29–7.31 (m, 2H), 7.40 (d, J=8.8 Hz, 2H), 7.53 (dd, J=6.6, 2.6 Hz, 1H), 7.77 (dd, J=7.3, 1.8 Hz, 1H); MS m/z 286 (M^+, 100). Anal. Calcd $C_{16}H_{14}OS_2$: C, 67.10; H, 4.90. Found: C, 66.94; H, 5.16.

*3.3.9. 3-(4-Methoxyphenyl)-2-phenylsulfanylbenzo[b]thiophene (**5i**).* A pale-yellow solid; mp 106–107 °C (hexane–Et_2O); IR (KBr) 1611,

1526 cm^{-1}; ^1H NMR (500 MHz) δ 3.87 (s, 3H), 7.00 (d, J=9.2 Hz, 2H), 7.19–7.26 (m, 5H), 7.32–7.35 (m, 2H), 7.38 (d, J=9.2 Hz, 2H), 7.62 (d, J=7.8 Hz, 1H), 7.78 (d, J=7.3 Hz, 1H); ^{13}C NMR δ 55.27, 113.87, 122.07, 123.80, 124.48, 125.25, 126.48, 126.60, 128.68, 129.02, 129.79, 131.22, 137.18, 139.62, 141.28, 142.07, 159.35; MS m/z 348 (M^+, 100). Anal. Calcd $C_{21}H_{16}OS_2$: C, 72.38; H, 4.63. Found: C, 72.42; H, 4.64.

*3.3.10. 3-(4-Methoxyphenyl)-2-(4-methylphenyl)sulfanylbenzo[b]-thiophene (**5j**).* A pale-yellow solid; mp 89–91 °C (hexane–Et_2O); IR (KBr) 1611, 1526 cm^{-1}; ^1H NMR (500 MHz) δ 2.31 (s, 3H), 3.87 (s, 3H), 7.02 (d, J=8.7 Hz, 2H), 7.07 (d, J=8.2 Hz, 2H), 7.21 (d, J=8.2 Hz, 2H), 7.30–7.35 (m, 2H), 7.40 (d, J=8.7 Hz, 2H), 7.60 (dd, J=6.9, 1.8 Hz, 1H), 7.74 (dd, J=6.9, 1.8 Hz, 1H); MS m/z 362 (M^+, 100). Anal. Calcd $C_{22}H_{18}OS_2$: C, 72.89; H, 5.00. Found: C, 72.89; H, 5.02.

*3.3.11. 2-(4-Chlorophenyl)sulfanyl-3-(4-methoxyphenyl)benzo[b]-thiophene (**5k**).* A pale-yellow solid; mp 135–136 °C (hexane–CH_2Cl_2); IR (KBr) 1609, 1526 cm^{-1}; ^1H NMR (500 MHz) δ 3.87 (s, 3H), 7.00 (d, J=8.7 Hz, 2H), 7.15 (d, J=8.7 Hz, 2H), 7.20 (d, J=8.7 Hz, 2H), 7.33–7.37 (m, 3H), 7.39 (td, J=7.3, 1.4 Hz, 1H), 7.63 (dd, J=7.3, 0.9 Hz, 1H), 7.79 (d, J=7.3 Hz, 1H); MS m/z 382 (M^+, 100). Anal. Calcd $C_{21}H_{15}ClOS_2$: C, 65.87; H, 3.95. Found: C, 65.63; H, 4.00.

*3.3.12. 2-Methylsulfanyl-5-nitro-3-phenylbenzo[b]thiophene (**5l**).* A yellow solid; mp 185–187 °C (hexane–CH_2Cl_2); IR (KBr) 1504, 1333 cm^{-1}; ^1H NMR (500 MHz) δ 2.54 (s, 3H), 7.46 (dd, J=7.8, 1.4 Hz, 2H), 7.49 (td, J=7.3, 1.4 Hz, 1H), 7.56 (dd, J=7.8, 7.3 Hz, 2H), 7.89 (d, J=8.7 Hz, 1H), 8.16 (dd, J=8.7, 2.3 Hz, 1H), 8.38 (d, J=2.3 Hz, 1H); ^{13}C NMR δ 19.37, 118.01, 118.33, 122.27, 128.51, 128.94, 129.80, 133.15, 136.82, 139.95, 140.01, 145.12, 145.87; MS m/z 301 (M^+, 100). Anal. Calcd $C_{15}H_{11}NO_2S_2$: C, 59.78; H, 3.68; N, 4.65. Found: C, 59.81; H, 3.93; N, 4.40.

*3.3.13. 5-Nitro-3-phenyl-2-phenylsulfanylbenzo[b]thiophene (**5m**).* A pale-yellow solid; mp 107–110 °C (hexane–Et_2O); IR (KBr) 1508, 1339 cm^{-1}; ^1H NMR (500 MHz) δ 7.29–7.33 (m, 3H), 7.37 (dd, J=7.8, 1.4 Hz, 2H), 7.47 (dd, J=7.8, 1.4 Hz, 2H), 7.49 (t, J=7.3 Hz, 1H), 7.55 (dd, J=7.8, 7.3 Hz, 2H), 7.83 (d, J=8.7 Hz, 1H), 8.18 (dd, J=8.7, 2.3 Hz, 1H), 8.43 (d, J=2.3 Hz, 1H); ^{13}C NMR δ 118.85, 119.11, 122.50, 128.04, 128.68, 128.90, 129.37, 129.87, 130.89, 132.88, 134.81, 136.94, 139.68, 140.36, 145.77, 146.32; MS m/z 363 (M^+, 100). Anal. Calcd $C_{20}H_{13}NO_2S_2$: C, 66.09; H, 3.61; N, 3.85. Found: C, 66.13; H, 3.61; N, 3.73.

Acknowledgements

We are indebted to Mrs. Miyuki Tanmatsu of Tottori University for determination of mass spectra and performance of combustion analyses.

References and notes

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