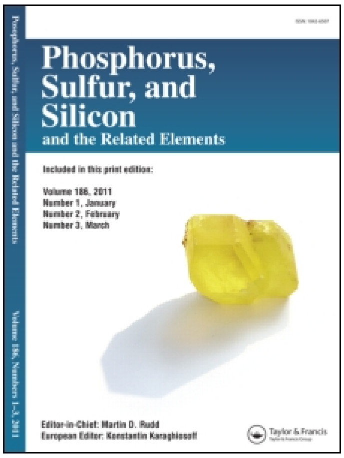

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Simple Route to Benzo[*b*]thiophenes: Sulfanylation-Acylation of *CH* Acids with 2-(Chlorosulfanyl)benzoyl Chloride

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To cite this Article Młochowski, Jacek and Potaczek, Piotr(2009) 'A Simple Route to Benzo[*b*]thiophenes: Sulfanylation-Acylation of *CH* Acids with 2-(Chlorosulfanyl)benzoyl Chloride', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 5, 1115 — 1123

To link to this Article: DOI: 10.1080/10426500902855117

URL: http://dx.doi.org/10.1080/10426500902855117

Phosphorus, Sulfur, and Silicon, 184:1115–1123, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902855117

A Simple Route to Benzo[*b*]thiophenes: Sulfanylation–Acylation of *C*–*H* Acids with 2-(Chlorosulfanyl)benzoyl Chloride

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*A convenient procedure for the preparation of 2,2-disubstituted benzo[*b*]thiophen-3(2*H*)-ones and 2-substituted 3-hydroxybenzo[*b*]thiophenes from β-diketones, β-keto- and β-cyanoesters, and β-cyanoketones, diethyl malonate, malonitrile, and anthrone has been developed. The tandem sulfanylation–acylation of these* C—H *acids resulting in the formation of a thiophene ring occurs upon treatment with 2-(chlorosulfanyl)benzoyl chloride in the presence of triethylamine.*

Keywords Acylations; cyclizations; heterocycles; sulfur; tandem reactions

INTRODUCTION

The synthesis of benzo[*b*]thiophenes has been of broad interest owing to their biological activity or application in organic materials employed in electronics.[1–6] The extensive research on chemistry and biology of benzo[*b*]thiophenes substituted in the heterocylic ring led to the drug Ralofixen, which is used for prevention and treatment of osteoporosis in postmenopausal women.[7] Other potential applications of this drug, e.g., for the treatment of Alzheimer's disease, have also been reported recently.[8] Moreover 3-(4-pyridinyl)aminobenzo[*b*]thiophenes may be useful for the treatment of central nervous system disorders,[9,10] and some 2,3-disubstituted benzo[*b*]thiophenes were found to be active as antimicrobials.[11]

Received 14 November 2007; accepted 24 February 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

The authors would like to express their thanks to Ministry of Science and Information for financial support (Grant N204022 31/0458).

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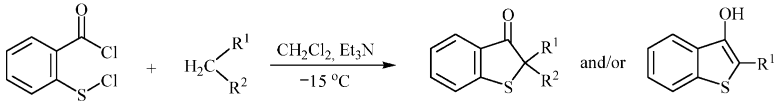
Our ongoing interest in the chemistry of organoselenium and organosulfur compounds is focused on the reactions that result in the ring closure and formation of selenium or sulfur-containing heterocycles. The well known reactions of this type are selenenylation–acylation or sulfanylation–acylation of a primary amino group with 2-(chloroselenyl)- or 2-(chlorosulfanyl)benzoyl chloride **1**. Both of these reagents can act as biselectrophiles, with the hard electrophilic center located on the carbonyl carbon atom and the soft one located on the chalcogen atom. Sulfonylation (or selenenylation) followed by acylation results in ring closure at the nitrogen atom, and benzisothiazolin-2(2*H*)-ones or benzisoselenazol-3(2*H*)-ones are produced, respectively.[12–15]Although the selenenylation–acylation of an active methylene group in ketones is reported to afford benzo[*b*]selenophenes,[16,17] the reaction of **1** with enolizable ketones and other *C—H* acids is to our knowledge still unknown.

RESULTS AND DISCUSSION

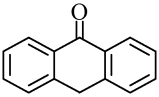
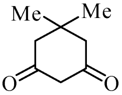
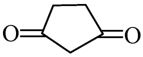
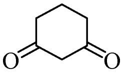
In this work, 2-(chlorosulfanyl)benzoyl chloride **1** was used as the agent for tandem sulfanylation–acylation of different compounds having an active methylene group, which results in the formation of a thiophene ring. This easy-to-prepare, stable compound, was obtained in a two-step synthesis starting from 2,2′-dithiodibenzoic acid. The acid when refluxed with thionyl chloride in benzene gave 2,2′-dithiobisbenzoyl chloride, which was dissolved in carbon tetrachloride and chlorinated with dry, gaseous chlorine to give the chloride **1**.[18] We found that this reagent easily reacted with common *C—H* acids **2** having two hydrogen atoms in an activated methylene group, such as β-diketones, β-keto- and β-cyanoesters, β-cyanoketones, diethyl cyanomethyl-phosphonate, diethyl malonate, malononitrile, and 9(10*H*)-anthracenone. The reaction, carried out at -15°C or 20°C in the presence of triethylamine as a base, was completed after 2.5 h. It resulted in a ring closure at the methylene carbon atom, and, depending on the substrate used, 2,2'-disubstituted benzo[*b*]thiophen-3(2*H*)-ones **3** and/or 3-hydroxybenzo[*b*]thiophenes **4** were produced (Table I). Monoketones, such as acetone and cyclohexanone, reacted more slowly than β-diketones, and complex mixtures of products were formed.

When *C—H* acids such as β-cyanoesters **2d–e**, malononitrile **2f**, β-cyanoacetophenone **2g**, 9(10*H*)-anthracenone (anthrone) **2h**, and 5,5dimethyl-1,3-cyclohexanedione (dimedone) **2i** were treated with 2-(chlorosulfanyl)benzoyl chloride **1**, the corresponding 2,2-disubstituted benzo[*b*]thiophen-3(2*H*)-ones **3d–i** were produced. Compounds **3d–i**

TABLE I Reaction of 2-(Chlorosulfanyl)benzoyl Chloride with *C–H* Acids



1 **2** **3** **4**

	Substrate			Method		Products	
2	R^1	R^2		**3**	Yield (%)	**4**	Yield (%)
2a	COPh	COMe	A	**3a**	84	**4a**	—
			B	**3a**	42	**4a**	23
2b	COOEt	COPh	A	**3b**	74	**4b**	—
			B	**3b**	31	**4b**	45
2c	COOEt	COOEt	A	**3c**	92	**4b**	—
			B	**3c**	36	**4b**	32
2d	COOEt	CN	A	**3d**	54	**4d**	—
			B	**3d**	46	**4d**	—
2e	CN	$P(O)(OEt)_2$	A	**3e**	97	**4e**	—
			B	**3e**	59	**4e**	—
2f	CN	CN	A	**3f**	86	**4f**	—
			B	**3f**	63	**4f**	—
2g	CN	COPh	A	**3g**	84	**4g**	—
			B	**3g**	80	**4g**	—
2h			A	**3h**	87	**4h**	—
			B	**3h**	87	**4h**	—
2i			A	**3i**	68	**4i**	—
			B	**3i**	70	**4i**	—
2j	COMe	COMe	A	**3j**	81	**4j**	—
			B	**3j**	—	**4j**	93
2k	COOEt	COMe	A	**3k**	—	**4b**	82
			B	**3k**	—	**4b**	82
2l			A	**3l**	—	**4l**[b]	98
			B	**3l**	—	**4l**[b]	74
2m			A	**3m**	—	**4m**[c]	69
			B	**3m**	—	**4m**[c]	60

[a] Isolated yield.

[b] For **4l** $R^1 = COCH_2CH_2COOH$.

[c] For **4m** $R^1 = COCH_2CH_2CH_2COOH$.

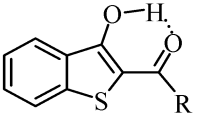
were isolated in 46–97% yield from the reaction mixture by solvent evaporation and recrystallization of the residue (Method A) or by silica gel column chromatography (Method B). When compounds **2a–c** were used as starting materials and the reaction mixture was worked up according to Method A, only benzo[*b*]thiophen-3(2*H*)-ones **3a–c** were obtained, while chromatography on silica gel (Method B) resulted in mixtures containing also 3-hydroxybenzo-[*b*]thiophenes **4a** or **4b**. The reaction of **1** with ethyl acetoacetate **2k** and the cyclic β-diketones **2l** and **2 m** gave only 2-substituted 3-hydroxybenzo[*b*]thiophenes **4b**, **4l**, and**4 m**, respectively. Most probably in these cases, the initially formed 2,2-disubstituted benzo[*b*]thiophenes underwent deacylation and conversion to 3-hydroxybenzo[*b*]thiophenes by treatment with water (Method A), or in the presence of moisture, adsorbed on silica gel during the separation by column chromatography (Method B). Similar conversion was observed when a solution of **3b** in dichloromethane and silica gel was allowed to stand with stirring at room temperature for 24 h. After this period, 65% of the substrate was converted into 2-ethoxycarbonyl-3-hydroxybenzo[*b*]thiophene **4b**.

Benzo[*b*]thiophenes **3d–g** substituted at 2-position with a cyano group as well as derivatives of 9(10*H*)-anthracenone **3h** and 5,5-dimethyl-1,3-cyclohexanedione **3i** remained resistant towards decomposition, while 2,2-diacetylbenzo[*b*]thiophen-3(2*H*)-one **3j** was converted on a silica gel column into **4j** almost quantitatively.

It should be noted that although unsubstituted benzo[*b*]thiophen-3(2*H*)-one exists preferentially as the oxo tautomer, introduction of a 2-acyl group promotes enolization, presumably by virtue of the extra stabilization conferred by intramolecular hydrogen bonding. The broad absorption band $\nu_{OH\cdots O}$, observed in the IR spectra of the compounds **4** in the range 2983–1920 cm^{-1} and bands $\nu_{C=O}$ at 1622–1537 cm^{-1} are similar to those reported for enol forms of other 1,3-diketones.[19] In addition, the signal of an acid proton present in ^{1}H NMR spectra between 10.9 and 13.5 provides good evidence that these compounds exist in the enol form as 2-substituted 3-hydroxybenzo[*b*]thiophenes, represented by formula **4** given in Figure 1. The enol form seems to be stabilized by intramolecular hydrogen bonding, similar to what was observed earlier for 3-hydroxybenzo[b]selenophenes.[16,17]

EXPERIMENTAL

Solvents were dried according to standard procedures and distilled. Silica gel 70–230 mesh (Fluka) was used for column chromatography. Melting points were measured using Digital Melting Point Apparatus



4

R = Me, Ph, OEt, $(CH_2)_nCOOH$; n = 2, 3

FIGURE 1 2-Substituted 3-hydroxybenzo[*b*]thiophenes.

Electrothermal IA 91100. IR spectra were recorded with a Perkin-Elmer 2000 FT spectrometer. ^1H and ^{13}C NMR spectra were recorded using a Bruker DRX300 spectrometer. Chemical shifts are given in ppm. The reagents were purchased from Aldrich and Fluka. 2-(Chlorosulfanyl)benzoyl chloride was prepared according to procedures given in the literature.[18]

Sulfanylation-Acylation of *C—H* Acids: General Procedure

To a stirred solution of the *C—H* acid **2a–m** (3.3 mmol) and triethylamine (0.668 g, 6.6 mmol) in dry dichloromethane (30 mL), a solution of 2-(chlorosulfanyl)benzoyl chloride (**1**) (0.621 g, 3.0 mmol) in dry dichloromethane (20 mL) was added dropwise at room temperature (for **2i**, **2l**: acetone and cyclohexanone, −15°C) during 30 min, and the reaction was continued for an additional 2 h. The reaction mixture was washed with acidified water (50 mL H_2O and 1 mL HCl) and then with water (2 × 50 mL). The organic layer was dried with anhydrous Na_2SO_4, the solvent was evaporated in vacuo, and the residue was recrystallized from a suitable solvent (Method A). Alternatively (Method B), from the reaction mixture the solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography using ethyl acetate (for **3e–f**, **4l–m**), chloroform (for **4j**), ethyl acetate:hexane 1:3 (for **4k**), and dichloromethane (in all other cases) as eluent.

2-Acetyl-2-benzoylbenzo[b]thiophen-3(2H)-one (3a)

White needles from ethyl acetate, mp 146–148°C. IR (KBr): $\nu = 1729$, 1663, 1249 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.59$ (s, 3H, CH_3), 7.38–7.43 (m, 1H, arom-H), 7.49–7.54 (m, 1H, arom-H), 7.58–7.67 (m, 3H, arom-H), 7.72–7.77 (m, 1H, arom-H), 7.84 (d, $J = 8.1$ Hz, 1H, arom-H), 8.32 (d, $J = 7.2$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 29.4$, 122.9; 123.4; 125.2, 128.3, 129.0, 130.6, 133.0, 134.5, 138.4, 164.0, 190.7. Anal. Calcd for $C_{17}H_{12}O_3S$: C, 68.89; H, 4.09; S, 10.82%. Found: C, 68.95; H, 4.18; S, 10.90%.

2-Benzoyl-2-ethoxycarbonylbenzo[b]thiophen-3(2H)-one (3b)

White prisms from hexane, mp 90–93°C. IR (KBr): $\nu = 1742, 1702, 1378, 1292, 1255, 1088\ \mathrm{cm}^{-1}$. ^{1}H NMR ($CDCl_3$): $\delta = 1.19$ (t, $J = 7.1$ Hz, 3H, CH_3), 4.29 (q, $J = 7.1$ Hz, 2H, CH_2), 7.42 (t, $J = 7.1$ Hz, 1H, arom-H), 7.49–7.59 (m, 3H, arom-H), 7.66–7.72 (m, 1H, arom-H), 7.75 (d, $J = 8.1$ Hz, 1H, arom-H), 7.80 (d, $J = 8.1$ Hz, 1H, arom-H), 8.31 (d, $J = 8.5$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 61.5, 122.3, 123.1, 125.1, 128.0, 128.9, 130.6, 133.1, 134.0, 138.1, 145.1, 161.4, 164.1$. Anal. Calcd. for $C_{18}H_{14}O_4S$: C, 66.24; H, 4.33; S, 9.82%. Found: C, 66.44; H, 4.34; S, 9.95%.

2,2-Diethoxycarbonylbenzo[b]thiophen-3(2H)-one (3c)

Yellow oil. IR (KBr): $\nu = 2984, 1737, 1247\ \mathrm{cm}^{-1}$.^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (t, $J = 7.1$ Hz, 6H, CH_3), 4.29 (q, $J = 7.1$ Hz, 4H, CH_2), 7.25 (t, $J = 7.8$ Hz, 1H, arom-H), 7.38 (d, $J = 7.8$ Hz, 1H, arom-H), 7.58 (t, $J = 7.1$ Hz, 1H, arom-H), 7.78–7.81 (m, 1H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 13.8, 63.4, 123.8, 125.8, 128.0, 136.6, 150.5, 164.4, 190.2$. Anal. Calcd. for $C_{14}H_{14}O_5S$: C, 57.12; H, 4.80; S, 10.89%. Found: C, 57.21; H, 4.92; S, 10.92%.

2-Cyano-2-ethoxycarbonylbenzo[b]thiophen-3(2H)-one (3d)

White needles from hexane, mp 97–98°C. IR (KBr): $\nu = 2979, 2252, 1744, 1713, 1576, 1452, 1238\ \mathrm{cm}^{-1}$. ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (t, $J = 7.1$ Hz, 3H, CH_3), 4.35 (q, $J = 7.1$ Hz, 2H, CH_2), 7.38 (t, $J = 7.5$ Hz, 1H, arom-H), 7.45 (d, $J = 8.0$ Hz, 1H, arom-H), 7.68–7.74 (m, 1H, arom-H), 7.90 (d, $J = 7.5$ Hz, 1H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 13.8, 65.0, 113.1, 124.2, 126.5, 126.9, 129.1, 137.6, 149.9$. Anal. Calcd. for $C_{12}H_9NO_3S$: C, 58.28; H, 3.67; N, 5.66; S, 12.96%. Found: C, 58.39; H, 3.73; N, 5.70; S, 13.03%.

2-Cyano-2-diethylphosphonylbenzo[b]thiophen-3(2H)-one (3e)

Orange oil. IR (KBr): $\nu = 2986, 2222, 1529, 1366, 1284, 1038\ \mathrm{cm}^{-1}$.^{1}H NMR ($CDCl_3$): $\delta = 1.40$ (t, $J = 6.1$ Hz, 6H, CH_3), 4.39 (q, $J = 6.1$ Hz, 4H, CH_2), 7.46–7.58 (m, 2H, arom-H), 7.74 (d, $J = 8.0$ Hz, 1H, arom-H), 8.03 (d, $J = 7.7$ Hz, 1H, arom-H).^{13}C NMR ($CDCl_3$): $\delta = 16.1, 16.2, 66.0, 66.1, 112.1, 122.9, 123.1, 126.0, 128.4, 129.0, 158.5$. Anal. Calcd. for $C_{13}H_{14}NO_4PS$: C, 50.15; H, 4.54; N, 4.50; S, 10.30%. Found: C, 50.23; H, 4.62; N, 4.59; S, 10.42%.

2,2-Dicyanobenzo[b]thiophen-3(2H)-one (3f)

Yellow needles from hexane-ethyl acetate, mp 224–227°C. IR (KBr): $\nu = 2975, 2256, 1671, 1410, 1266\ \mathrm{cm}^{-1}$. ^{1}H NMR (DMSO): $\delta = 7.30–7.38$

(m, 1H, arom-H), 7.44–7.57 (m, 1H, arom-H), 7.60–7.65 (m, 1H, arom-H), 7.93–8.02 (m, 1H, arom-H).^{13}C NMR (DMSO): $\delta = 112.2$, 124.2, 125.9, 126.8, 127.2, 129.2, 136.6, 152.2. Anal. Calcd. for $C_{10}H_4N_2OS$: C, 59.99; H, 2.02; N, 13.99; S, 16.01%. Found: C, 60.11; H, 2.18; N, 14.12 S, 16.15%.

2-Benzoyl-2-cyanobenzo[b]thiophen-3(2H)-one (3g)

Yellow prisms from ethyl acetate, mp 118°C. IR (KBr): $\nu = 2220$, 1754, 1231, 1057 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.46$–7.51 (m, 1H, arom-H), 7.59 (t, $J = 7.7$ Hz, 3H, arom-H), 7.71–7.76 (m, 2H, arom-H), 7.83 (d, $J = 8.2$ Hz, 1H, arom-H), 8.30 (d, $J = 7.1$ Hz, 2H, arom-H).^{13}C NMR ($CDCl_3$): $\delta = 112.0$, 122.5, 123.1, 125.9, 127.6, 128.8, 129.0, 130.8, 134.7, 138.5, 149.9, 163.1. Anal. Calcd. for $C_{16}H_9NO_2S$: C, 68.80; H, 3.25; N, 5.02 S, 11.48%. Found: C, 68.98; H, 3.34; N, 5.13 S, 11.55%.

2,2-[10,10-(9-Anthacenonyl)]benzo[b]thiophen-3(2*H*)-one (3h)

White needles from acetonitrile, mp 205–208°C. IR (KBr): $\nu = 1703$, 1657, 1586, 1245, 1317, 1271 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.35$ (t, $J = 7.0$ Hz, 1H, arom-H), 7.49–7.54 (m, 6H, arom-H), 7.61 (d, $J = 8.0$ Hz, 1H, arom-H), 7.70–7.76 (m, 1H, arom-H), 7.78–7.80 (m, 1H, arom-H), 8.38–8.44 (m, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 123.9$, 126.0, 126.9, 127.4, 128.1, 129.0, 129.1, 131.9, 133.7, 136.7, 139.7, 153.3, 182.8, 198.5. Anal. Calcd. for $C_{21}H_{12}O_2S$: C, 76.80; H, 3.69; S, 9.76%. Found: C, 76.95; H, 3.78; S, 9.90%.

2,2-[(3,3-Dimethyl)glutaryl]benzo[b]thiophen-3(2H)-one (3i)

White needles from hexane, mp 137–139°C. IR (KBr): $\nu = 2936$, 1742, 1699, 1288, 1219 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.97$ (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 2.67 (d, $J = 14.2$ Hz, 2H, CH_2), 3.32 (d, $J = 14.2$ Hz, 2H, CH_2), 7.21 (t, $J = 7.9$ Hz, 1H, arom-H), 7.43 (d, $J = 7.9$ Hz, 1H, arom-H), 7.54–7.59 (m, 1H, arom-H), 7.64–7.67 (m, 1H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 27.8$, 30.0, 51.5, 124.2, 126.2, 128.2, 135.0, 136.8, 152.6, 190.5, 196.2. Anal. Calcd. for $C_{15}H_{14}O_3S$: C, 65.66; H, 5.15; S, 11.68%. Found: C, 65.79; H, 5.22; S, 11.70%.

2,2-Diacetylbenzo[b]thiophen-3(2H)-one (3j)

Yellow needles from hexane, mp 75–77°C. IR (KBr): $\nu = 1730$, 1667, 1253 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.35$ (s, 6H, CH_3), 7.28–7.33 (m, 1H, arom-H), 7.46 (d, $J = 8.0$ Hz, 1H, arom-H), 7.60–7.65 (m, 1H, arom-H), 7.82 (d, $J = 7.8$ Hz, 1H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 27.3$, 124.3, 126.2, 128.0, 129.6, 136.8, 150.6, 192.4, 196.2. Anal. Calcd. for

$C_{12}H_{10}O_3S$: C, 61.52; H, 4.30; S, 13.69%. Found: C, 61.79; H, 4.32; S, 13.70%.

2-Benzoyl-3-hydroxybenzo[b]thiophene (4a)

Yellow needles from ethyl acetate, mp 116–118°C. IR (KBr): $\nu =$ 2940–1980, 1593, 1517, 1342, 1294, 1227 cm^{-1}.^{1}H NMR ($CDCl_3$): $\delta = 7.44$ (t, $J = 7.5$ Hz, 1H, arom-H), 7.53–7.65 (m, 4H, arom-H), 7.74 (d, $J = 8.1$ Hz, 1H, arom-H), 8.07 (t, $J = 6.4$ Hz, 3H, arom-H), 13.45 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): $\delta = 123.0$, 124.0, 124.8, 128.4, 128.7, 130.4, 132.6, 138.3, 140.8, 165.5, 191.8. Anal. Calcd. for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.97; S, 12.61%. Found: C, 70.96; H, 4.04; S, 12.69%.

2-Ethoxycarbonyl-3-hydroxybenzo[b]thiophene (4b)

White needles from hexane, mp 73–75°C. IR (KBr): $\nu = 3487$, 2983, 2950–1920, 1532, 1304, 1227 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.43$ (t, $J =$ 7.1 Hz, 3H, CH_3), 4.43 (q, $J = 7.1$ Hz, 2H, CH_2), 7.38–7.43 (m, 1H, arom-H), 7.48–7.53 (m, 1H, arom-H), 7.74 (d, $J = 8.1$ Hz, 1H, arom-H), 7.95 (d, $J = 7.8$ Hz, 1H, arom-H), 10.19 (s, 1H, OH). ^{13}C NMR ($CDCl_3$,): $\delta = 14.4$, 61.4, 123.0, 123.1, 124.4, 128.8, 130.5, 138.9, 159.5, 167.4. Anal. Calcd. for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.54; S, 14.42%. Found: C, 59.53; H, 4.56; S, 14.50%.

2-Acetyl-3-hydroxybenzo[b]thiophene (4j)

White needles from hexane, mp 79–80°C. IR (KBr): $\nu =$ 2920–1905, 1622, 1520, 1357, 1298, 1221 cm^{-1}.^{1}H NMR ($CDCl_3$): $\delta = 2.51$ (s, 3H, CH_3), 7.40–7.45 (m, 1H, arom-H), 7.52–7.57 (m, 1H, arom-H), 7.74 (d, $J = 8.2$ Hz, 1H, arom-H), 8.00 (d, $J = 8.0$ Hz, 1H, arom-H), 12.27 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): $\delta = 28.2$, 111.5, 123.3, 123.8, 124.8, 129.8, 139.1, 161.7, 196.7. Anal. Calcd. for $C_{10}H_8O_2S$: C, 62.47; H, 4.20; S, 16.68%. Found: C, 62.59; H, 4.34; S, 16.75%.

2-(3-Carboxypropionyl)-3-hydroxybenzo[b]thiophene (4l)

White needles from acetonitrile, mp 189–192°C. IR (KBr): $\nu =$ 3325–2165, 1710, 1617, 1521, 1402, 1247 cm^{-1}. ^{1}H NMR (DMSO): $\delta = 2.59$ (t, $J = 6.4$ Hz, 2H, CH_2), 3.22 (t, $J = 6.4$ Hz, 2H, CH_2), 7.43 (t, $J = 7.1$ Hz, 1H, arom-H), 7.53 (t, $J = 7.1$ Hz, 1H, arom-H), 7.88 (d, $J = 8.0$ Hz, 1H, arom-H), 8.10 (d, $J = 8.0$ Hz, 1H, arom-H), 11.91 (s, 2H, OH, COOH). ^{13}C NMR (DMSO): $\delta = 28.2$, 36.5, 117.0, 123.9, 124.0, 125.0, 129.3, 132.4, 138.7, 155.5, 174.3, 194.0. Anal. Calcd. for $C_{12}H_{10}O_4S$: C, 57.58; H, 4.03; S, 12.81%. Found: C, 57.70; H, 4.14; S, 12.90%.

2-(4-Carboxybutyl)-3-hydroxybenzo[b]thiophene (4m)

White needles from acetonitrile, mp 154–156°C. IR (KBr): $\nu = 3057$, 2946–2005, 1708, 1587 cm^{-1}. ^{1}H NMR (DMSO): $\delta = 1.90$ (quintet, $J = 7.3$ Hz, 2H, CH_2), 2.34 (t, $J = 7.3$ Hz, 2H, CH_2), 3.04 (t, $J = 7.3$ Hz, 2H, CH_2), 7.45 (t, $J = 7.6$ Hz, 1H, arom-H), 7.56 (t, $J = 7.6$ Hz, 1H, arom-H), 7.91 (d, $J = 8.1$ Hz, 1H, arom-H), 8.11 (d, $J = 8.1$ Hz, 1H, arom-H), 12.09 (s, 2H, OH, COOH). ^{13}C NMR (DMSO): $\delta = 29.3$, 37.2, 117.3, 123.9, 124.7, 125.0, 129.9, 133.4, 139.1, 156.5, 175.9, 195.6. Anal. Calcd. for $C_{13}H_{12}O_4S$: C, 59.08; H, 4.58; S, 12.13%. Found: C, 59.20; H, 4.54; S, 12.10%.

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