One-Pot Synthesis Using the Supported Reagent System Na_2CO_3/SiO_2–PPA/SiO_2: Synthesis of Benzo[*b*]thiophenes and Naphthothiophenes

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Received 19 March 2008; revised 9 April 2008

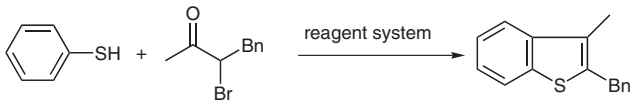
Abstract: A simple and efficient method has been developed for the synthesis of benzo[*b*]thiophenes and naphtho[2,1-*b*]thiophenes from arenethiols and α-halo ketones using Na_2CO_3/SiO_2–PPA/SiO_2. Reaction of α-halo ketones with arenethiols is promoted by Na_2CO_3/SiO_2 to afford α-sulfanyl ketones, which cyclize in the presence of PPA/SiO_2 to give the corresponding thiophene-fused arenes in one-pot. The reaction using α-bromo acetals instead of α-halo ketones also gave the corresponding naphtho[2,1-*b*]thiophenes via a three-step reaction in one-pot.

Key words: one-pot synthesis, benzothiophenes, naphthothiophenes, supported reagents, acid–base coexistence reaction

Benzo[*b*]thiophenes and naphtho[2,1-*b*]thiophenes have been of interest in recent years because of their wide range of biological and physiological effects. For example, benzo[*b*]thiophene derivatives currently in pharmaceutical use or development include selective estrogen receptor modulators,[1] angiogenesis inhibitors,[2] tubulin-binding agent,[3] site-directed thrombin inhibitors,[4] modulators of multidrug resistance,[5] and anti-inflammatory agents.[6] Naphthothiophene derivatives have been used as C_1-symmetric ligands for homogeneous stereoselective catalysts[7] and a binding compound of DNA,[8] etc.[9] Many methods for the synthesis of naphthothiophene derivatives have been developed including cross-coupling catalysis and solid-phase synthesis.[10–20] The most common method starts from arenethiols, which are reacted with α-halo ketones and this is followed by cyclization using a strong acid. We recently described a highly efficient method for the one-pot synthesis of benzo[*b*]thiophenes and naphtho[2,1-*b*]thiophenes from arenethiols and α-halo ketones by using a supported reagent system, silica gel supported sodium carbonate (Na_2CO_3/SiO_2) and silica gel supported polyphosphoric acid (PPA/SiO_2).[21]

One-pot synthesis, multistep reactions or multiple reactions performed in one pot, is very attractive in organic synthesis. In the traditional process, the reaction and the isolation of products have to be carried out more than once to synthesize the target compounds. In a one-pot process, however, the target compounds are provided in a single operation and with low cost, but also in high total yield. Much effort has been devoted to the development of one-pot reaction processes. Several different reaction stages are able to exist separately in the same vessel when several kinds of inorganic solid-supported reagents are used. Thus, the synthesis of a compound that is prepared stepwise in homogeneous solution could be possible in one pot if each step in the multistep reaction can be achieved using inorganic solid-supported reagents. Using this concept, we have demonstrated the possibility of multistep reactions in one pot by using two supported reagents.[22]

Table 1 Synthesis of 2-Benzyl-3-methylbenzo[*b*]thiophene Using Various Reagent Systems



1a 2a 4aa

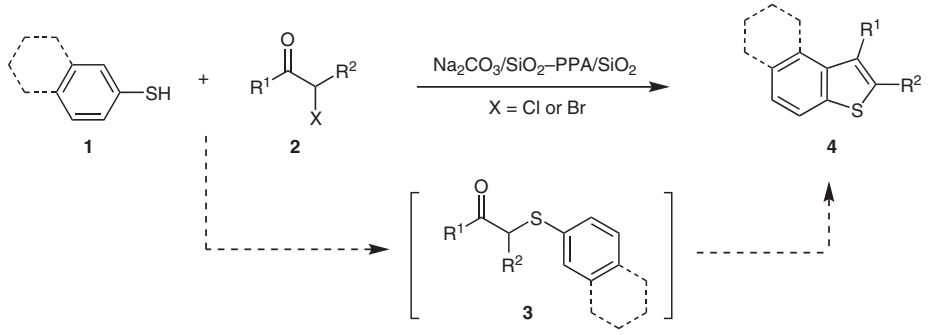
Entry	Reagent system		Yield[a] (%)
1	Na_2CO_3	PPA	0
2	–	PPA/SiO_2	44
3	Na_2CO_3	PPA/SiO_2	27
4	Na_2CO_3/SiO_2	PPA	46 (41)[b]
5	Na_2CO_3/SiO_2	PPA/SiO_2	80

[a] Isolated yield.
[b] Yield of the intermediate **3aa**.

In this paper, we report on the one-pot synthesis of benzo[*b*]thiophenes and naphthothiophenes using the supported reagent system, Na_2CO_3/SiO_2–PPA/SiO_2, in detail (Scheme 1).

First, we examined that both the acid- and base-supported reagents existing in the same vessel are able to function as an acid and a base catalyst, respectively, in the reaction of benzenethiol (**1a**) and 3-bromo-4-phenylbutan-2-one (**2a**) in chlorobenzene (Table 1). The desired product **4aa** was obtained in 80% yield when the reaction was carried out in the presence of Na_2CO_3/SiO_2 and PPA/SiO_2 (Table 1, entry 5) When unsupported sodium carbonate and polyphosphoric acid were used for the reaction, **4aa** was not detected (Table 1, entry 1). Using the reagent system Na_2CO_3–PPA/SiO_2 or only PPA/SiO_2, **4aa** was formed in moderate yields along with diphenyl disulfide as a

SYNTHESIS 2008, No. 13, pp 2089–2099
Advanced online publication: 21.05.2008
DOI: 10.1055/s-2008-1067105; Art ID: F06708SS

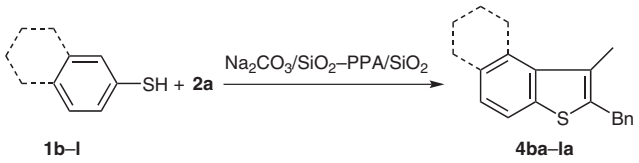


Scheme 1

byproduct (Table 1, entries 2 and 3). The reagent system, Na_2CO_3/SiO_2–PPA, gave **4aa** in 46% yield along with 4-phenyl-3-(phenylsulfanyl)butan-2-one (**3aa**) in 41% yield (Table 1, entry 4). These results suggest that large amounts of acid and base as supported reagents exist on the internal surface of the inorganic support; the acid and base could not contact each other. Therefore, acid- and base-supported reagents are available for reaction in the same vessel. Na_2CO_3/SiO_2 promotes the reaction of benzenethiol (**1a**) with **2a**, and PPA/SiO_2 catalyzes the intramolecular cyclocondensation of **3aa** to afford **4aa**.

A series of arenethiols were used for similar reactions and the results obtained are shown in Table 2. In all reactions, the base-catalyzed substitution reactions were facile and intermediates **3** were produced quantitatively. Therefore, the yield of expected thiophene-fused arene depended on the ease of the acid-catalyzed cyclocondensations of **3**. In the case of the reaction with a series of methoxybenzenethiols **1e–g** (Table 2, entries 4–6), 3-methoxybenzenethiol (**1f**) was the most reactive among the three isomers and gave the isomeric benzo[*b*]thiophenes **4fa** and **4fa′**, quantitatively. These yields were determined by using ^{1}H NMR spectroscopy. The reaction of 2-methoxybenzenethiol (**1g**) and **2a** gave the desired compound **4ga** in 40% yield together with 3-[(2-methoxyphenyl)sulfanyl]-4-phenylbutan-2-one (**3ga**) in 52% yield. 4-Methoxybenzenethiol (**1e**) is much less reactive and cyclocondensation of the corresponding intermediate **3ea** was not promoted at 135 °C. When this reaction was carried out at 180 °C in 1,2-dichlorobenzene, **4ea** was obtained in 30% yield. The reactivity of a series of toluenethiols **1b–d** showed similar tendency (Table 2, entries 1–3). In the reactions with *para*-substituted benzenethiols, the yields decreased with increasing electron donation of the substituent group; 4-methoxybenzenethiol (**1e**) gave no cyclocondensed products at 135 °C, 4-*tert*-butylbenzene thiol (**1i**) and 4-toluenethiol (**1b**) gave the corresponding benzothiophenes **4ia** and **4ba** in 25 and 71% yields, respectively (Table 2, entries 1, 4, and 8). Although these substituted benzenethiols have an electron-donating group, the ease of cyclocondensation was less than that of benzenethiol. The reactions with electron-rich arenethiols, such as 2,5-dimethoxybenzenethiol (**1j**) and naphthalene-1- (**1k**) and -2-thiol (**1l**), gave the corresponding thiophene-fuse arenes **4ja**, **4ka**, and **4la**, respectively, in excellent yields (Table 2, entries 9–11).

Table 2 One-Pot Synthesis of Benzo[*b*]thiophenes and Naphthothiophenes from **1a** and Various Arenethiols



1b–l 4ba–la

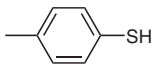
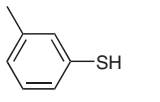
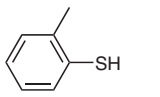
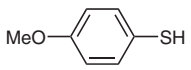
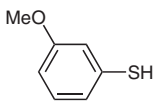
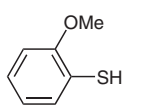
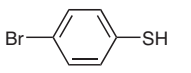
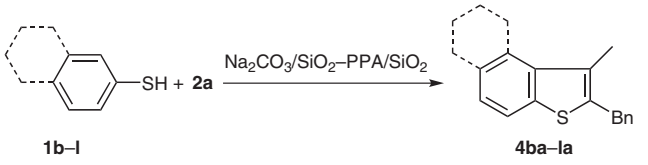
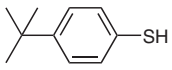
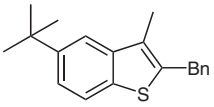
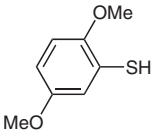
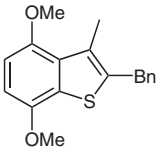
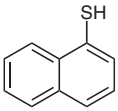
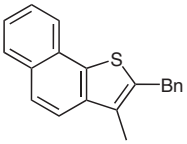
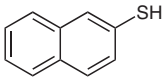
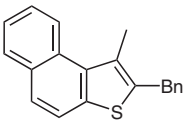
Entry	Arenethiol	Product		Yield[a] (%)
1		**1b**	**4ba**	71 (20)[b]
2		**1c**	**4ca**	34[c]
			4ca′	61[c]
3		**1d**	**4da**	94
4		**1e**	**4ea**	30[d]
5		**1f**	**4fa**	24
			4fa′	76
6		**1g**	**4ga**	40 (52)[b]
7		**1h**	**4ha**	8[d]

Table 2 One-Pot Synthesis of Benzo[*b*]thiophenes and Naphthothiophenes from **1a** and Various Arenethiols (continued)



1b–l **4ba–la**

Entry	Arenethiol	Product		Yield[a] (%)
8		**1i** 	**4ia**	25 (71)[b]
9		**1j** 	**4ja**	95
10		**1k** 	**4ka**	95
11		**1l** 	**4la**	97

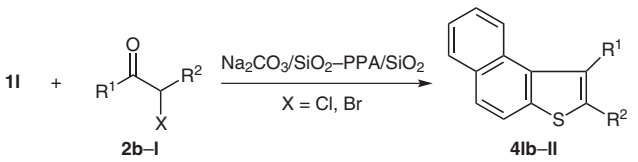
[a] Isolated yield.
[b] Yield of the intermediate **3**.
[c] Yield was determined by ^{1}H NMR.
[d] 1,2-Dichlorobenzene, 180 °C, 6 h.

The results of the reaction of naphthalene-2-thiol (**1l**) and α-halo ketones **2b–l** are summarized in Table 3. The reactions with acyclic α-halo ketones gave the corresponding naphtho[2,1-*b*]thiophenes in moderate to excellent yields. The cyclic α-halo ketone such as 2-chlorocyclohexanone (**2e**) also reacted with naphthalene-2-thiol under similar conditions to give the corresponding naphthothiophene **4le** in 87% yield (Table 3, entry 4). When ethyl 4-chloroacetoacetic acid (**2c**) was used as the starting material, unexpected side reactions occurred to afford the undesired compound **4lb** in 54% yield as the main product and the desired compound **4lc** in 39% yield (Table 3, entry 2). Stirring **4lc** in chlorobenzene at 135 °C did not give **4lb**.

Thus, we carried out the reaction of **4lc** in the presence of several catalysts in order to determine the reaction path (Table 4). The reaction using SiO_2 or Na_2CO_3/SiO_2 did not give **4lb** and **4lc** was recovered quantitatively. When the reaction was carried out using PPA/SiO_2, a small amount of **4lb** was observed in the reaction mixture. In the acid-catalyzed cyclocondensation in the one-pot reaction, water is generated. The reaction of **4lc** using PPA/SiO_2, which was pretreated with 1 mmol of water for 30 minutes, gave **4lb** in 17% yield.

From these results, a route for conversion of **4lc** into **4lb** was proposed; first hydrolysis of **4lc** occurs with PPA/SiO_2 to afford carboxylic acid derivatives **4lc′**, and then loss of carbon dioxide proceeds. Thus, we carried out the reaction of **4lc′** in the presence of several catalysts (Table 5). When the reaction was carried out in the absence of catalyst, no reaction occurred (Table 5, entry 1). Using Na_2CO_3/SiO_2 as a catalyst resulted in the absorption of **4lc′** on to the catalyst support (Table 5, entry 2). The reaction using PPA/SiO_2 and SiO_2 gave **4lb** (Table 5, entries 3 and 4). Therefore, it was proposed that the conversion of **4lc** into **4lb** was promoted by PPA/SiO_2, which existed in the reaction vessel.

Table 3 One-Pot Synthesis of Naphtho[2,1-*b*]thiophenes from Various Halo Ketones and **1l**



2b–l **4lb–ll**

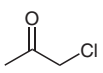
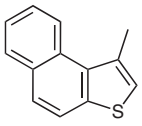
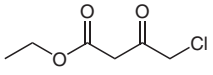
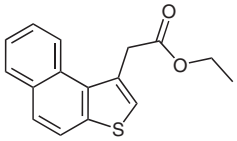
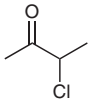
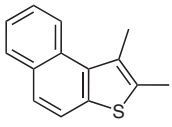
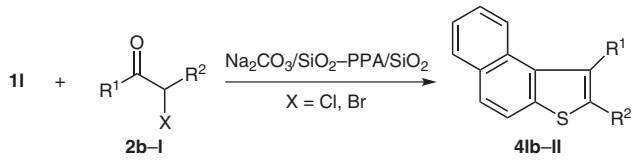
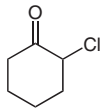
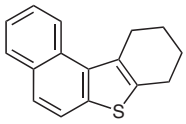
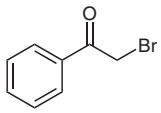
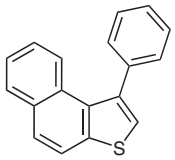
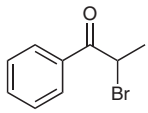
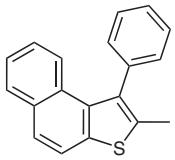
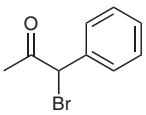
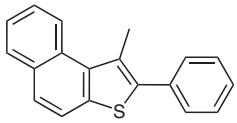
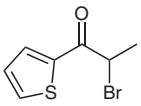
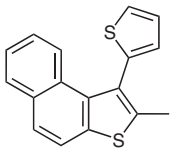
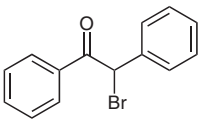
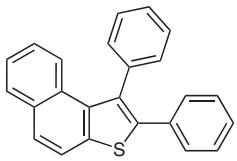
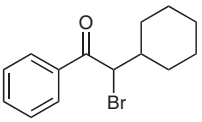
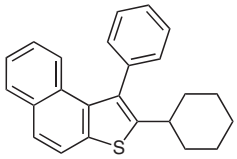
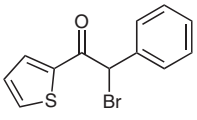
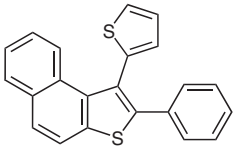
Entry	Halo ketone		Product		Yield[a] (%)
1		**2b**		**4lb**	89
2		**2c**		**4lc**	39 (54)[b]
3		**2d**		**4ld**	92

Table 3 One-Pot Synthesis of Naphtho[2,1-*b*]thiophenes from Various Halo Ketones and **1l** (continued)

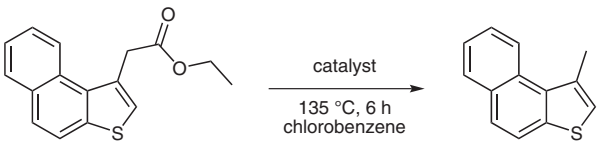


Entry	Halo ketone		Product		Yield[a] (%)
4		**2e**		**4le**	87
5		**2f**		**4lf**	94
6		**2g**		**4lg**	96
7		**2h**		**4lh**	85
8		**2i**		**4li**	quant.
9		**2j**		**4lj**	57 (19)[c]
10		**2k**		**4lk**	50 (24)[c]
11		**2l**		**4ll**	60 (18)[c]

[a] Isolated yield.
[b] Yield of **4lb**.
[c] Yield of debrominated **2j–l**.

The reaction of α-bromobenzyl phenyl ketone (**2j**) gave **4lj** in 57% yield together with the debrominated compound, benzyl phenyl ketone, in 19% yield along with di-2-naphthyl disulfide. Similar reactions using **2k** and **2l**, which have a bulky substituent, also gave the desired compounds **4lk** and **4ll** in 50% and 60% yields, and debrominated compounds in 24% and 18% yields along with di-2-naphthyl disulfide (Table 3, entries 10 and 11). These

Table 4 Reaction of **4lc** with Various Catalysts

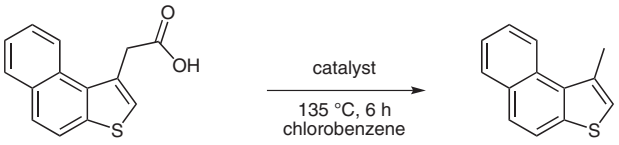


4lc **4lb**

Entry	Catalyst	Yield (%) of **4lb**
1	none	no reaction
2	Na_2CO_3/SiO_2	no reaction
3	PPA/SiO_2	2[a]
4	$PPA/SiO_2 + H_2O$[b]	17[c]
5	SiO_2	no reaction

[a] Yield was determined by GLC.
[b] 1 mmol of H_2O.
[c] Isolated yield.

Table 5 Reaction of **4lc′** with Various Catalysts

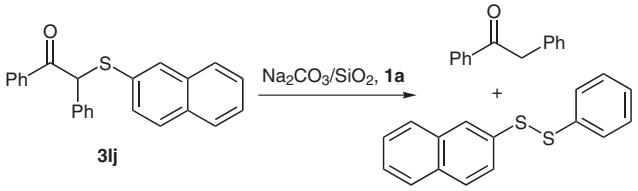


4lc′ **4lb**

Entry	Catalyst	Yield[a] (%) of **4lb**
1	none	no reaction
2	Na_2CO_3/SiO_2	no recovery[b]
3	PPA/SiO_2	30
4	SiO_2	12

[a] Isolated yield.
[b] **4lc′** was adsorbed onto Na_2CO_3/SiO_2.

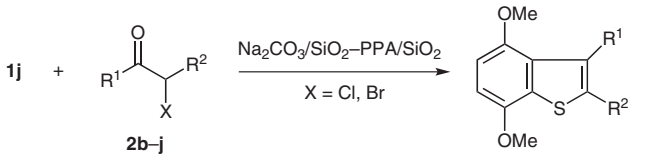
debrominated compounds were formed from the reaction of α-sulfanyl ketone **3** and **1** in the presence of Na_2CO_3/SiO_2. Stirring a mixture of **3lj** and benzenethiol (**1a**) in chlorobenzene in the presence of Na_2CO_3/SiO_2 gave benzyl phenyl ketone, as the debrominated compound, and 2-naphthyl phenyl disulfide (Scheme 2).



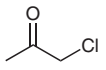
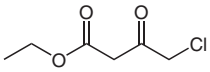
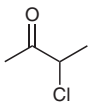
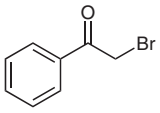
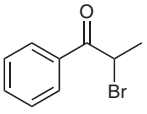
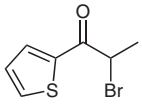
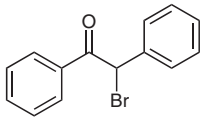
3lj

Scheme 2

Table 6 One-Pot Synthesis of 4,7-Dimethoxybenzo[*b*]thiophenes from Various Halo Ketones and **1j**



2b–j **4jb–jj**

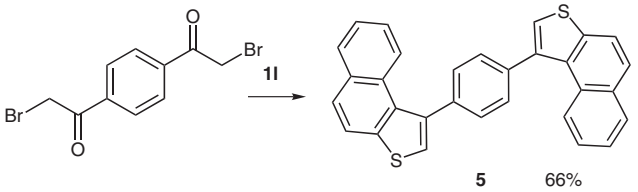
Entry	Halo ketone	Product		Yield[a] (%)
1		**2b**	**4jb**	97
2		**2c**	**4jc**	17 (70)[b]
3		**2d**	**4jd**	93
4		**2f**	**4jf**	76
5		**2g**	**4jg**	84
6		**2i**	**4ji**	90
7		**2j**	**4jj**	45 (33)[c]

[a] Isolated yield.
[b] Yield of **4jb**.
[c] Yield of debrominated **2j**.

Similar reactions have been reported by Suzuki et al. for the reaction of α-halo ketone and diphenyl disulfide in the presence of sodium telluride.[23] Furthermore Oki et al. have described this reaction mechanism for the reaction of α-carbonyl sulfides with thiolates.[24]

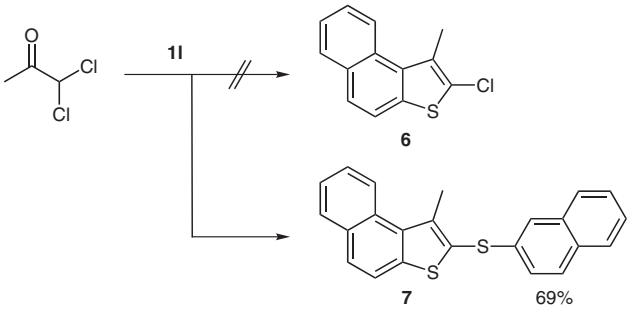
The reaction of 2,5-dimethoxybenzenethiol (**1j**) and a series of α-halo ketones **2b–d**,**f**,**g**,**i**,**j** was also carried out (Table 6). Its reactivity was similar to that of naphthalene-2-thiol. The reaction using ethyl 4-chloroacetoacetate (**2c**) gave the desired **4jc** in 17% yield along with 70% of **4jb**, formed from hydrolysis and decarboxylation of **4jc**. α-Bromobenzyl phenyl ketone (**2j**) gave debrominated ketone, benzyl phenyl ketone in 33% yield.

Dihalogenated compounds were used for the reactions in order to synthesize bis(thiophenes) and halogen-substituted thiophenes. The reaction of 1,4-bis(bromoacetyl)benzene gave the corresponding bis(naphthothiophene) **5** in 66% yield when twice the amount of naphthalene-2-thiol (**1l**), Na_2CO_3/SiO_2 and PPA/SiO_2 were used (Scheme 3).



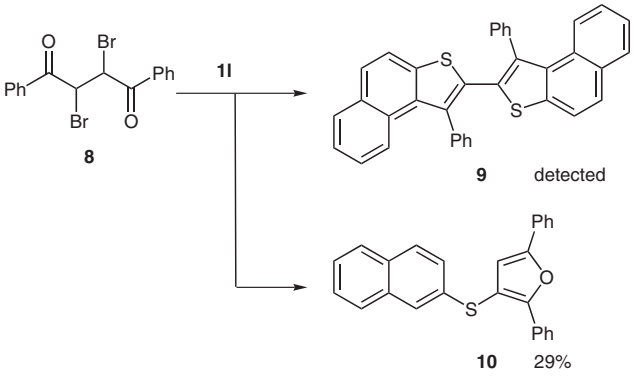
Scheme 3

α,α-Dichloroacetone afforded 1-methyl-2-(2-naphthylsulfanyl)naphtho[2,1-*b*]thiophene (**7**) and **4lb** in 69% and 10% yields. The expected product, 2-chloro-1-methylnaphtho[2,1-*b*]thiophene (**6**), was not observed in the reaction mixture (Scheme 4).

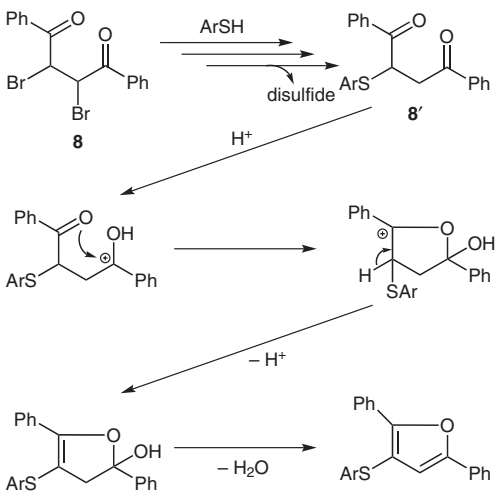


Scheme 4

When 2,3-dibromo-1,4-diphenylbutane-1,4-dione (**8**) was used, many kinds of products were observed in the reaction mixture. The expected bithiophene **9** was detected by mass spectrometry, but could not be isolated. 3-(2-Naphthylsulfanyl)-2,5-diphenylfuran (**10**) was isolated as the main product in 29% yield along with disulfide (Scheme 5). The proposed reaction path is shown in Scheme 6. Compound **8** reacted with three equivalents of naphthalene-2-thiol (**1l**) to afford **8′** as an intermediate. Then acid-catalyzed cyclization of **8′** proceeded to afford



Scheme 5

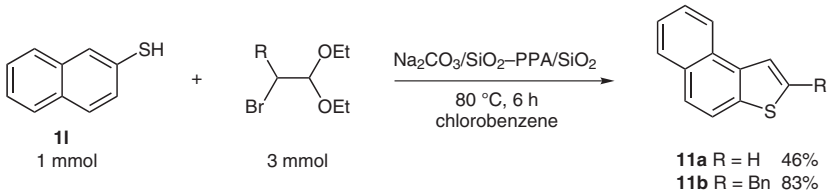


Scheme 6

the furan ring. The naphthothiophene, which is formed from **8′**, could not be observed in the reaction mixture.

We tried to synthesize naphthothiophenes from α-bromo acetals via three-step reactions since acetals easily undergo deprotection with acid and are converted into aldehydes. α-Bromoaldehydes are formed from the reaction of α-bromo acetals with PPA/SiO_2. Three equivalents of α-bromo acetal were needed against **1l** to obtain naphthothiophenes in moderate to good yield (Scheme 7). For example, when (2-bromo-3,3-diethoxypropyl)benzene was used, 83% yield of the corresponding naphthothiophene **11b** was obtained.

In conclusion, we have developed a simple and efficient method for the synthesis of benzo[*b*]thiophenes and naphthothiophenes from various α-halo ketones and α-bromo acetals in one pot using the supported reagent systems Na_2CO_3/SiO_2–PPA/SiO_2. Arenethiols, α-halo ketones, and α-bromo acetals are commercially available, and some of α-bromo ketones are easily synthesized by using our reported methods.[22d] It is particularly noteworthy that (a) this method does not require the isolation of the intermediates, (b) all supported reagents were uneventfully removed from the crude products by simple filtration, and (c) a reaction process using coexisting base and acid was possible. Other one-pot chemical transformations using



Scheme 7

coexisting base and acid catalyts are now under investigation.

Melting points were determined on Yanako Micro melting point apparatus or were uncorrected. Elemental analysis were performed on a Yanako CHN corder MT-5. NMR spectra were recorded on a JEOL JNM-GX400 spectrometer; TMS (δ = 0) was used as an internal standard for ^{1}H NMR and $CDCl_3$ (δ = 77.0) for ^{13}C NMR. Mass analysis were performed on a Agilent G1969 LC/MDS TOF. IR spectra were recorded on a Thermo Electron Nicolet 380 spectrophotometer.

Preparation of Na_2CO_3/SiO_2

Silica gel [Wakogel C-200 (Wako Pure Chemical Ind. Ltd), 16.82 g] was added to a soln of Na_2CO_3 (3.18 g, 30 mmol) in distilled H_2O, and the mixture was stirred at r.t. for 0.5 h. H_2O was removed on a rotary evaporator under reduced pressure and the resulting reagent was dried in vacuo (13 mbar) at 160 °C for 5 h.

Preparation of PPA/SiO_2

PPA (2.0 g) and $CHCl_3$ (100 mL) were placed in a round-bottom flask and the mixture was stirred at 50 °C for 1 h. SiO_2 [Wakogel C-200 (Wako Pure Chemical Ind. Ltd.), 18.0 g], which was dried in vacuo at 160 °C for 2 h, was added to the mixture and the mixture was stirred for a further 1 h. The $CHCl_3$ was removed on a rotary evaporator and the resulting solid was dried in vacuo at r.t. for 3 h.

Benzo[*b*]thiophenes and Naphthothiophenes; General Procedure

A mixture of α-halo ketone (1 mmol) or α-bromo acetal (3 mmol), arenethiol (1 mmol), Na_2CO_3/SiO_2 (1.0 g, 1.5 mmol), and PPA/SiO_2 (3.5 g, 10 wt%) in PhCl (15 mL) was stirred at 135 °C for 6 h. The supported reagents were then removed by filtration and the filtrate was evaporated to leave the crude product, which was purified by flash column chromatography (hexane–EtOAc) to give the desired product.

2-Benzyl-3-methylbenzo[*b*]thiophene (4aa)

Light yellow oil.

IR (neat): 1602, 1583, 1494, 1459, 1453, 1436, 754, 729, 712, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H), 4.20 (s, 2 H), 7.19–7.37 (m, 7 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.7, 34.4, 121.4, 122.2, 123.7, 123.8, 126.5, 127.6, 128.5, 128.6, 137.7, 138.6, 139.7, 140.9.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}S$: 239.0894; found: 239.0899.

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92. Found: C, 80.44; H, 5.71.

2-Benzyl-3,5-dimethylbenzo[*b*]thiophene (4ba)

White solid; mp 46–47 °C (hexane–EtOAc).

IR (neat): 1602, 1492, 1451, 1445, 868, 801, 756, 727, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H), 2.46 (s, 3 H), 4.17 (s, 2 H), 7.09 (d, *J* = 8.3 Hz, 1 H), 7.18–7.29 (m, 5 H), 7.42 (s, 1 H), 7.59 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.7, 21.5, 34.4, 121.5, 121.8, 125.4, 126.4, 127.3, 128.4, 128.5, 133.5, 135.7, 137.7, 139.8, 141.1.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}S$: 253.1050; found: 253.1056.

Anal. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.39. Found: C, 80.90; H, 6.26.

2-Benzyl-3,4-dimethylbenzo[*b*]thiophene (4ca) and 2-Benzyl-3,6-dimethylbenzo[*b*]thiophene (4ca′)

Oil.

IR (neat): 1602, 1494, 1473, 1452, 866, 808, 764, 745, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 1.9 H), 2.43 (s, 1.9 H), 2.56 (s, 1.1 H), 2.76 (s, 1.1 H), 4.16 (s, 2 H), 7.03 (d, *J* = 6.8 Hz, 0.4 H), 7.10 (t, *J* = 7.6 Hz, 0.4 H), 7.15–7.30 (m, 5.6 H), 7.49–7.51 (m, 1.2 H), 7.55 (d, *J* = 7.6 Hz, 0.4 H).

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}S$: 253.1050; found: 253.1058.

2-Benzyl-3,7-dimethylbenzo[*b*]thiophene (4da)

White solid; mp 60–61 °C (hexane–EtOAc).

IR (neat): 1601, 1493, 1471, 1450, 1434, 775, 760, 725, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3 H), 2.47 (s, 3 H), 4.20 (s, 2 H), 7.07 (d, *J* = 7.3 Hz, 1 H), 7.18–7.30 (m, 6 H), 7.48 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.9, 20.2, 34.4, 119.1, 124.1, 124.3, 126.4, 128.3, 128.5, 128.5, 131.6, 137.2, 138.7, 139.8, 140.7.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}S$: 253.1050; found: 253.1044.

Anal. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.39. Found: C, 80.88; H, 6.28.

2-Benzyl-5-methoxy-3-methylbenzo[*b*]thiophene (4ea)

Light yellow oil.

IR (neat): 1604, 1456, 1430, 1143, 849, 794, 755, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H), 3.88 (s, 3 H), 4.18 (s, 2 H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.08 (d, *J* = 2.4 Hz, 1 H), 7.21–7.31 (m, 5 H), 7.59 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.8, 34.5, 55.6, 104.3, 113.4, 122.8, 126.5, 127.4, 128.4, 128.5, 130.9, 139.1, 139.7, 141.9, 157.4.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}OS$: 269.1000; found: 269.1001.

Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 75.76; H, 5.97.

2-Benzyl-4-methoxy-3-methylbenzo[*b*]thiophene (4fa) and 2-Benzyl-6-methoxy-3-methylbenzo[*b*]thiophene (4fa′)

IR (neat): 1601, 1494, 1478, 1452, 1233, 1048, 818, 725 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 2.28 H), 2.55 (s, 0.72 H), 3.82 (s, 2.88 H), 3.88 (s, 0.72 H), 4.14 (s, 0.48 H), 4.15 (s, 1.52 H), 6.07 (d, *J* = 8.0 Hz, 0.24 H), 6.97 (d, *J* = 8.8 Hz, 0.76 H), 7.15 (t, *J* = 8.0 Hz, 0.24 H), 7.17–7.30 (m, 6 H), 7.50 (d, *J* = 8.8 Hz, 0.76 H).

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}OS$: 269.1000; found: 269.1005.

Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.18; H, 6.03.

2-Benzyl-7-methoxy-3-methylbenzo[*b*]thiophene (4ga)
White solid; mp 76–77 °C (hexane–EtOAc).

IR (neat): 1556, 1493, 1416, 1264, 1046, 779, 734 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 3 H), 3.94 (s, 3 H), 4.19 (s, 2 H), 6.73 (dd, *J* = 7.6, 1.0 Hz, 1 H), 7.17–7.33 (m, 7 H).

^{13}C NMR ($CDCl_3$): δ = 11.9, 34.4, 55.6, 103.9, 114.3, 125.2, 126.4, 127.0, 128.0, 128.5, 128.5, 138.0, 139.7, 142.7, 154.2.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}OS$: 269.1000; found: 269.0993.

Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.20; H, 6.04.

2-Benzyl-5-bromo-3-methylbenzo[*b*]thiophene (4ha)
Light brown oil.

IR (neat): 1601, 1580, 1570, 1494, 1453, 1433, 863, 798, 758, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H), 4.19 (s, 2 H), 7.21–7.32 (m, 5 H), 7.36 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.56 (d, *J* = 8.5 Hz, 1 H), 7.76 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.7, 34.4, 118.0, 123.5, 124.3, 126.6, 126.6, 127.0, 128.5, 128.6, 137.2, 139.3, 139.9, 142.6.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{16}H_{13}SBr$: 315.9921; found: 315.9922.

2-Benzyl-5-*tert*-butyl-3-methylbenzo[*b*]thiophene (4ia)
Light yellow oil.

IR (neat): 1601, 1494, 1452, 810, 731, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 9 H), 2.36 (s, 3 H), 4.18 (s, 2 H), 7.17–7.29 (m, 5 H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.61 (d, *J* = 2.0 Hz, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.7, 31.7, 34.4, 34.8, 117.6, 121.7, 122.1, 126.4, 127.7, 128.4, 128.5, 135.8, 137.7, 139.8, 140.7, 147.1.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}S$: 295.1520; found: 295.1513.

2-Benzyl-4,7-dimethoxy-3-methylbenzo[*b*]thiophene (4ja)
White solid; mp 100–101 °C (hexane–EtOAc).

IR (neat): 1598, 1485, 1453, 1433, 1257, 1167, 1047, 795, 730, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.54 (s, 3 H), 3.85 (s, 3 H), 3.88 (s, 3 H), 4.14 (s, 2 H), 6.58 (d, *J* = 8.5 Hz, 1 H), 6.63 (d, *J* = 8.5 Hz, 1 H), 7.17–7.29 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 34.2, 55.8, 55.9, 103.3, 105.3, 126.3, 128.5, 128.5, 129.0, 129.1, 131.8, 136.2, 139.8, 148.4, 150.8.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}O_2S$: 299.1105; found: 299.1113.

Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.57; H, 6.06.

2-Benzyl-3-methylnaphtho[1,2-*b*]thiophene (4ka)
Light yellow solid; mp 108–109 °C (hexane–EtOAc).

IR (neat): 1601, 1507, 1493, 1453, 1256, 806, 747, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 3 H), 4.27 (s, 2 H), 7.20–7.33 (m, 5 H), 7.42–7.52 (m, 2 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.73 (d, *J* = 8.7 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 8.00 (dd, *J* = 8.0, 0.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.9, 34.4, 120.3, 123.5, 124.9, 125.2, 126.4, 126.5, 128.5, 128.6, 128.7, 128.9, 129.0, 130.7, 135.7, 136.9, 138.2, 139.9.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}S$: 289.1050; found: 289.1055.

Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.47; H, 5.48.

2-Benzyl-1-methylnaphtho[2,1-*b*]thiophene (4la)
Light brown solid; mp 98–100 °C (hexane–EtOAc).

IR (neat): 1602, 1508, 1493, 1454, 802, 781, 746, 716, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.80 (s, 3 H), 4.30 (s, 2 H), 7.20–7.32 (m, 5 H), 7.48–7.59 (m, 2 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.93 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.71 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 16.9, 34.5, 120.7, 123.3, 124.5, 124.7, 125.8, 126.5, 128.4, 128.6, 129.0, 130.4, 130.5, 132.1, 134.7, 136.5, 137.5, 139.8.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}S$: 289.1050; found: 289.1049.

Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.25; H, 5.57.

1-Methylnaphtho[2,1-*b*]thiophene (4lb)
White solid; mp 60–61 °C (hexane–EtOAc) (Lit.[25] 60 °C).

IR (neat): 1615, 1511, 1438, 860, 797, 756, 679 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.90 (d, *J* = 1.2 Hz, 3 H), 7.20 (s, 1 H), 7.45–7.54 (m, 1 H), 7.57–7.61 (m, 1 H), 7.70 (d, *J* = 8.8 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.95 (dd, *J* = 7.8, 1.5 Hz, 1 H), 8.67 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 19.9, 121.3, 122.5, 123.4, 124.7, 125.3, 126.0, 128.9, 130.7, 131.9, 133.5, 134.8, 139.2.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}S$: 199.0581; found: 199.0583.

Anal. Calcd for $C_{13}H_{10}S$: C, 78.75; H, 5.08. Found: C, 78.76; H, 4.91.

Ethyl Naphtho[2,1-*b*]thiophene-1-acetate (4lc)
Light brown solid; mp 103–104 °C (hexane–EtOAc).

IR (neat): 1725, 1368, 859, 798, 750, 736 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 4.29 (s, 2 H), 7.41 (s, 1 H), 7.50–7.62 (m, 2 H), 7.72 (d, *J* = 8.7 Hz, 1 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.95 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.43 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.1, 38.4, 61.1, 121.1, 122.9, 124.9, 125.3, 125.7, 126.2, 129.0, 129.9, 130.8, 131.9, 132.8, 139.4, 170.9.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_2S$: 271.0792; found: 271.0798.

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 71.22; H, 5.15.

1,2-Dimethylnaphtho[2,1-*b*]thiophene (4ld)
White solid; mp 108–109 °C (hexane–EtOAc) (Lit.[26] 102.5–103.5 °C).

IR (neat): 1613, 1522, 1433, 804, 780, 742, 680, 516 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.55 (s, 3 H), 2.74 (s, 3 H), 7.46–7.50 (m, 1 H), 7.53–7.57 (m, 1 H), 7.63 (d, *J* = 8.5 Hz, 1 H), 7.75 (d, *J* = 8.5 Hz, 1 H), 7.92 (d, *J* = 7.8 Hz, 1 H), 8.69 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.2, 16.5, 120.6, 123.3, 124.3, 124.4, 125.7, 128.9, 129.8, 130.3, 132.1, 133.5, 134.7, 135.6.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}S$: 213.0737; found: 213.0731.

Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 78.93; H, 5.68.

8,9,10,11-Tetrahydrobenzo[*b*]naphtho[1,2-*d*]thiophene (4le)
Light yellow solid; mp 80–82 °C (hexane–EtOAc) (Lit.[27] 80–81 °C).

IR (neat): 1525, 1507, 1435, 1370, 802, 779, 745, 680 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.92–2.03 (m, 4 H), 2.98 (t, *J* = 5.9 Hz, 2 H), 3.32 (t, *J* = 6.0 Hz, 2 H), 7.46–7.56 (m, 2 H), 7.64 (d, *J* = 8.8 Hz, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.92 (d, *J* = 7.8 Hz, 1 H), 8.59 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 22.8, 23.2, 26.4, 28.8, 120.8, 123.8, 124.3, 124.4, 125.6, 128.8, 130.3, 131.8, 132.0, 134.1, 136.0, 137.0.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}S$: 239.0894; found: 239.0891.

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92. Found: C, 80.77; H, 5.81.

1-Phenylnaphtho[2,1-*b*]thiophene (4lf)
White solid; mp 87–88 °C (hexane–EtOAc) (Lit.[28] 83–84).

IR (neat): 1600, 1512, 1474, 1443, 1367, 808, 779, 765, 747, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.20–7.24 (m, 1 H), 7.33 (s, 1 H), 7.39–7.43 (m, 1 H), 7.47–7.51 (m, 5 H), 7.74 (d, *J* = 8.8 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 121.0, 123.9, 124.6, 125.0, 125.7, 125.8, 127.8, 128.6, 128.7, 129.7, 129.9, 131.9, 132.8, 138.8, 139.1, 140.4.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{13}S$: 261.0737; found: 261.0734.

Anal. Calcd for $C_{18}H_{12}S$: C, 83.04; H, 4.65. Found: C, 83.16; H, 4.54.

2-Methyl-1-phenylnaphtho[2,1-*b*]thiophene (4lg)
Colorless oil.

IR (neat): 1600, 1487, 1442, 1369, 803, 783, 742, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 7.35–7.39 (m, 3 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.50–7.56 (m, 3 H), 7.68 (d, *J* = 8.8 Hz, 1 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.87 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.4, 120.4, 123.6, 124.6, 124.6, 125.4, 127.7, 128.6, 129.0, 129.5, 130.2, 131.9, 134.2, 135.7, 136.2, 136.4, 138.6.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}S$: 275.0888; found: 275.0894.

1-Methyl-2-phenylnaphtho[2,1-*b*]thiophene (4lh)
White solid; mp 125–127 °C (hexane–EtOAc).

IR (neat): 1482, 1444, 1375, 1222, 796, 762, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.88 (s, 3 H), 7.38–7.62 (m, 7 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 8.77 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 17.9, 120.6, 123.4, 124.7, 125.3, 125.9, 127.8, 128.5, 129.1, 130.2, 130.4, 130.8, 132.2, 134.9, 134.9, 137.3, 138.7.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}S$: 275.0894; found: 275.0893.

Anal. Calcd for $C_{19}H_{14}S$: C, 83.17; H, 5.14. Found: C, 82.92; H, 5.02.

2-Methyl-1-(2-thienyl)naphtho[2,1-*b*]thiophene (4li)
White solid; mp 85 °C (hexane–EtOAc).

IR (neat): 1614, 1506, 1439, 847, 803, 780, 742, 723, 706, 697 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3 H), 7.07 (dd, *J* = 3.5, 1.2 Hz, 1 H), 7.23–7.27 (m, 1 H), 7.23 (dd, *J* = 5.3, 3.5 Hz, 1 H), 7.38–7.42 (m, 1 H), 7.53 (dd, *J* = 5.3, 1.2 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.68 (d, *J* = 8.8 Hz, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.87, (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 120.3, 123.2, 124.8, 124.9, 125.7, 127.0, 127.7, 127.8, 128.1, 128.6, 129.3, 132.0, 134.6, 135.4, 138.5, 140.0.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{13}S_2$: 281.0458; found: 281.0457.

Anal. Calcd for $C_{17}H_{12}S_2$: C, 72.82; H, 4.31. Found: C, 72.94; H, 4.04.

1,2-Diphenylnaphtho[2,1-*b*]thiophene (4lj)
White solid; mp 166–168 °C (hexane–EtOAc).

IR (neat): 1600, 1497, 1475, 1441, 804, 781, 758, 726, 709, 700, 692 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.15–7.29 (m, 6 H), 7.36–7.45 (m, 6 H), 7.51 (d, *J* = 8.5 Hz, 1 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.89 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 120.4, 123.7, 124.8, 125.6, 125.7, 127.4, 127.8, 128.2, 128.8, 128.9, 129.7, 130.1, 130.8, 132.2, 134.5, 134.5, 135.7, 137.1, 138.3, 139.9.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{17}S$: 337.1050; found: 337.1045.

Anal. Calcd for $C_{24}H_{16}S$: C, 85.68; H, 4.79. Found: C, 85.68; H, 4.66.

2-Cyclohexyl-1-phenylnaphtho[2,1-*b*]thiophene (4lk)
White solid; mp 157–158 °C (hexane–EtOAc).

IR (neat): 1602, 1487, 1444, 1373, 1168, 804, 778, 743, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.14–1.30 (m, 3 H), 1.47–1.57 (m, 2 H), 1.65–1.68 (m, 1 H), 1.73–1.77 (m, 2 H), 1.92–1.95 (m, 2 H), 2.67–2.74 (m, 1 H), 7.12 (t, *J* = 7.3 Hz, 1 H), 7.33–7.39 (m, 4 H), 7.50–7.55 (m, 2 H), 7.52 (d, *J* = 7.3 Hz, 1 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 7.85 (d, *J* = 7.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 25.8, 26.5, 35.9, 38.4, 120.7, 123.8, 124.4, 124.6, 125.4, 127.6, 128.6, 128.9, 129.7, 130.2, 131.9, 134.0, 134.2, 135.5, 138.8, 149.4.

HRMS (TOF-CI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}S$: 343.1514; found: 343.1507.

Anal. Calcd for $C_{24}H_{22}S$: C, 84.16; H, 6.47. Found: C, 84.22; H, 6.39.

2-Phenyl-1-(2-thienyl)naphtho[2,1-*b*]thiophene (4ll)
White solid; mp 186–187 °C (hexane–EtOAc).

IR (neat): 1597, 1476, 1442, 1371, 1221, 1032, 804, 745, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.11 (dd, *J* = 3.4, 1.2 Hz, 1 H), 7.16 (dd, *J* = 5.1, 3.4 Hz, 1 H), 7.24–7.45 (m, 7 H), 7.48 (dd, *J* = 5.1, 1.2 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.86 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 120.2, 123.4, 125.0, 125.9, 125.9, 127.2, 127.6, 127.8, 128.2, 128.3, 128.8, 129.1, 129.4, 129.9, 132.2, 134.2, 134.9, 136.6, 138.5, 142.9.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{22}H_{15}S_2$: 343.0615; found: 343.0622.

Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12. Found: C, 77.18; H, 3.97.

4,7-Dimethoxy-3-methylbenzo[*b*]thiophene (4jb)
White solid; mp 89–91 °C (hexane–EtOAc).

IR (neat): 1594, 1581, 1527, 1481, 1456, 1432, 1371, 1333, 1254, 1041, 793, 765, 710 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.59 (s, 3 H), 3.86 (s, 3 H), 3.94 (s, 3 H), 6.63 (d, *J* = 8.5 Hz, 1 H), 6.65 (d, *J* = 8.5 Hz, 1 H), 6.88 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 17.4, 55.8, 55.9, 103.9, 104.9, 120.7, 130.8, 131.5, 133.9, 148.7, 151.3.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{11}H_{13}O_2S$: 209.0636; found: 209.0646.

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.58; H, 5.64.

Ethyl 4,7-Dimethoxybenzo[*b*]thiophene-3-acetate (4jc)
Light brown oil.

IR (neat): 1738, 1597, 1584, 1487, 1463, 1383, 1259, 1179, 1054, 796, 714 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H), 3.82 (s, 3 H), 3.94 (s, 3 H), 3.98 (s, 2 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 6.63 (d, *J* = 8.5 Hz, 1 H), 6.66 (d, *J* = 8.5 Hz, 1 H), 7.10 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.3, 36.8, 55.4, 55.9, 60.5, 104.2, 104.8, 111.7, 112.5, 113.5, 123.8, 129.8, 148.7, 150.5, 171.6.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{14}H_{17}O_4S$: 281.0847; found: 281.0853.

Anal. Calcd for $C_{14}H_{17}O_4S$: C, 59.98; H, 5.75. Found: C, 59.96; H, 5.75.

4,7-Dimethoxy-2,3-dimethylbenzo[*b*]thiophene (4jd)
White solid; mp 109–111 °C (hexane–EtOAc).

IR (neat): 1596, 1584, 1553, 1485, 1449, 1435, 1390, 1256, 1175, 1045, 793, 733, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H), 2.47 (s, 3 H), 3.85 (s, 3 H), 3.92 (s, 3 H), 6.57 (d, *J* = 8.5 Hz, 1 H), 6.64 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 13.7, 14.1, 55.9, 56.0, 103.1, 105.4, 128.5, 128.5, 132.0, 132.2, 148.4, 150.5.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{12}H_{15}O_2S$: 223.0792; found: 223.0797.

Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: C, 64.75; H, 6.36.

4,7-Dimethoxy-3-phenylbenzo[*b*]thiophene (4jf)
White solid; mp 108–109 °C (hexane–EtOAc).

IR (neat): 1597, 1490, 1462, 1367, 1261, 1073, 1051, 978, 794, 766, 704 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.60 (s, 3 H), 3.98 (s, 3 H), 6.70 (d, *J* = 8.5 Hz, 1 H), 6.72 (d, *J* = 8.5 Hz, 1 H), 7.19 (s, 1 H), 7.31–7.39 (m, 3 H), 7.47–7.50 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 56.0, 56.0, 104.2, 106.4, 124.2, 126.8, 127.1, 129.2, 129.7, 131.6, 137.7, 138.8, 148.8, 150.6.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{16}H_{15}O_2S$: 271.0792; found: 271.0801.

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 71.31; H, 5.10.

4,7-Dimethoxy-2-methyl-3-phenylbenzo[*b*]thiophene (4jg)
White solid; mp 117–118 °C (hexane–EtOAc).

IR (neat): 1582, 1489, 1479, 1449, 1434, 1385, 1257, 1088, 1048, 980, 787, 735, 706, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 3 H), 3.46 (s, 3 H), 3.95 (s, 3 H), 6.63 (d, *J* = 8.5 Hz, 1 H), 6.65 (d, *J* = 8.5 Hz, 1 H), 7.28–7.40 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 56.0, 56.4, 103.6, 107.1, 126.5, 127.1, 128.4, 130.2, 131.3, 133.9, 135.8, 137.3, 148.5, 149.9.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{17}O_2S$: 285.0949; found: 285.0952.

Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.79; H, 5.67.

4,7-Dimethoxy-2-methyl-3-(2-thienyl)benzo[*b*]thiophene (4ji)
White solid; mp 98–99 °C (hexane–EtOAc).

IR (neat): 1579, 1480, 1448, 1256, 1191, 1176, 1086, 1048, 804, 789, 704, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3 H), 3.57 (s, 3 H), 3.94 (s, 3 H), 6.63 (d, *J* = 8.5 Hz, 1 H), 6.66 (d, *J* = 8.5 Hz, 1 H), 6.95 (dd, *J* = 1.2, 3.4 Hz, 1 H), 7.06 (dd, *J* = 3.4, 5.1 Hz, 1 H), 7.36 (dd, *J* = 1.2, 5.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.7, 56.0, 56.5, 103.8, 107.1, 125.3, 125.9, 125.9, 127.6, 128.0, 131.3, 137.8, 139.1, 148.4, 149.8.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{15}H_{15}O_2S_2$: 291.0513; found: 291.0519.

Anal. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.04; H, 4.86. Found: C, 62.05; H, 4.78.

4,7-Dimethoxy-2,3-diphenylbenzo[*b*]thiophene (4jj)
White solid; mp 171–174 °C (hexane–EtOAc).

IR (neat): 1597, 1578, 1489, 1462, 1387, 1260, 1090, 1054, 797, 788, 727, 708, 697 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.48 (s, 3 H), 3.99 (s, 3 H), 6.68 (d, *J* = 8.5 Hz, 1 H), 6.71 (d, *J* = 8.5 Hz, 1 H), 7.18–7.27 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 56.0, 56.3, 104.2, 107.2, 126.6, 127.1, 127.4, 128.1, 129.3, 129.7, 130.8, 131.6, 133.5, 134.5, 137.2, 139.4, 148.5, 150.8.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{22}H_{19}O_2S$: 347.1105; found: 347.1101.

Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24. Found: C, 76.45; H, 5.13.

1,4-Bis(naphtho[2,1-*b*]thiophen-1-yl)benzene (5)
White solid; mp 290–292 °C (hexane–EtOAc).

IR (neat): 1583, 1529, 1363, 1145, 833, 812, 781, 750, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.40 (br s, 2 H), 7.51 (br s, 4 H), 7.68 (s, 4 H), 7.81 (d, *J* = 8.5 Hz, 2 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 7.98 (br s, 2 H), 8.17 (br s, 2 H).

^{13}C NMR ($CDCl_3$): δ 121.1, 123.9, 125.1, 125.7, 125.9, 128.9, 129.9, 129.9, 129.9, 132.0, 132.8, 138.6, 138.9, 139.9.

HRMS (TOF-CI): *m/z* [M + H]$^+$ calcd for $C_{30}H_{19}S_2$: 443.0928; found: 443.0938.

Anal. Calcd for $C_{30}H_{18}S_2$: C, 81.41; H, 4.10. Found: C, 81.00; H, 3.85.

1-Methyl-2-(2-naphthylsulfanyl)naphtho[2,1-*b*]thiophene (7)
White solid; mp 115–116 °C (hexane–EtOAc).

IR (neat): 1622, 1586, 1500, 817, 805, 775 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.02 (s, 3 H), 7.29 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.36–7.46 (m, 3 H), 7.55–7.58 (m, 2 H), 7.63–7.67 (m, 2 H), 7.71 (d, *J* = 8.8 Hz, 1 H), 7.74–7.77 (m, 1 H), 7.79 (d, *J* = 3.4 Hz, 1 H), 7.98 (dd, *J* = 8.1, 1.2 Hz, 1 H), 8.76 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 18.0, 120.5, 123.3, 124.8, 125.1, 125.1, 125.7, 126.5, 126.5, 126.6, 127.1, 127.7, 128.7, 129.1, 130.6, 131.7, 132.0, 133.7, 134.0, 135.3, 140.4, 141.4.

HRMS (TOF-CI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{17}S_2$: 357.0771; found: 357.0775.

Anal. Calcd for $C_{23}H_{16}S_2$: C, 77.49; H, 4.52. Found: C, 77.25; H, 4.48.

3-(2-Naphthylsulfanyl)-2,5-diphenylfuran (10)
White solid; mp 146–147 °C (hexane–EtOAc).

IR (neat): 3056, 1623, 1586, 1500, 1487, 1479, 799, 767, 688, 675 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.75 (s, 1 H), 7.25–7.33 (m, 2 H), 7.39–7.46 (m, 7 H), 7.67–7.78 (m, 6 H), 8.10–8.12 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 111.5, 112.6, 123.9, 125.3, 125.6, 125.7, 126.0, 126.6, 127.1, 127.7, 128.0, 128.2, 128.5, 128.8, 128.8, 129.9, 130.0, 131.7, 133.8, 134.1, 134.2, 152.9.

HRMS (TOF-CI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{19}OS$: 379.1156; found: 379.1155.

Anal. Calcd for $C_{26}H_{18}OS$: C, 82.51; H, 4.79. Found: C, 82.68; H, 4.50.

Acknowledgment

This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientists (B), 18710066, 2006.

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