

Convenient Synthesis of 3-Substituted Benzo[*b*]thiophenes by Iodine-Mediated Cyclization of α-Substituted 2-(1-Phenylethylthio)styrenes

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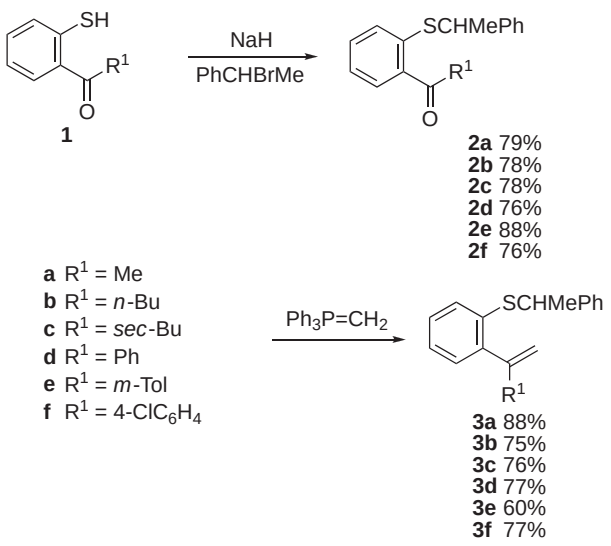
A new and convenient method for the preparation of 3-substituted benzo[*b*]thiophenes was developed. α-Substituted 2-(1-phenylethylthio)styrenes, which could easily be prepared from 2-mercaptophenyl ketones or benzenethiols in two or three steps, respectively, underwent 5-*endo* cyclization on treatment with iodine in the presence of sodium hydrogencarbonate in acetonitrile at room temperature to give 3-substituted benzo[*b*]thiophenes in fair to good yields.

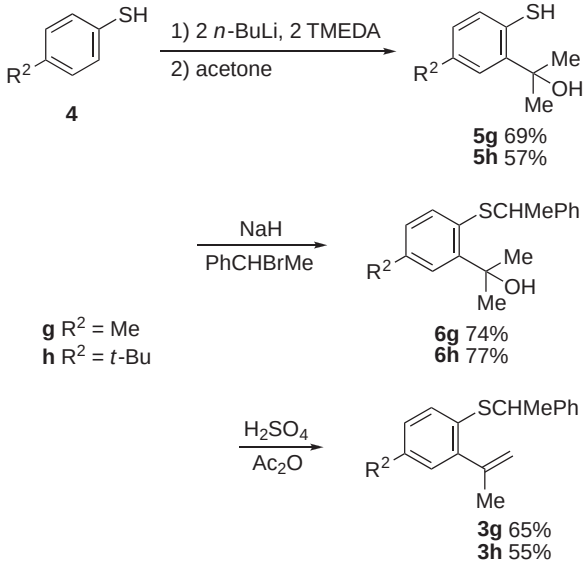
In a previous paper, we have reported an efficient synthesis of 1-aryl-1*H*-indoles by iodine-mediated cyclization of 2-(arylamino)styrene derivatives[1] and now wish to describe an application of this cyclization reaction to the synthesis of benzo[*b*]thiophenes.[2] We have found that 3-substituted benzo[*b*]thiophenes **7** are obtained in reasonable yields by treating α-substituted 2-(1-phenylethylthio)styrenes **3** with iodine.[3] Benzo[*b*]thiophene derivatives are an important class of heterocycles, because a number of molecules having this skeleton have been shown to exhibit a variety of biological activities.[4]

The starting α-substituted 2-(1-phenylethylthio)styrenes **3** were easily prepared according to the two sequences stated below. First, readily available 2-mercaptophenyl ketones **1**[5–7] were *S*-1-phenylethylated with (1-bromoethyl)benzene and sodium hydride. The resulting 2-(1-phenylethylthio)phenyl ketones **2** were subjected to a Wittig reaction with methylenetriphenylphosphorane to give **3a**–**3f** (Scheme 1). Secondly, lithiation of 4-alkylbenzenethiols **4** by butyllithium under the conditions reported by Martin et al.,[8] followed by reaction of the resultant lithium 2-lithiobenzenethiolates with acetone, afforded 2-(4-alkyl-2-mercaptophenyl)propan-2-ols **5**, which were *S*-1-phenylethylated with (1-bromoethyl)benzene and sodium hydride to afford 2-[4-alkyl-2-(1-phenylethylthio)phenyl]propan-2-ols **6**. Sequential dehydration of these 2-(2-mercaptophenyl)propan-2-ols **6** with a catalytic amount of concentrated sulfuric acid in acetic anhydride afforded 5-substituted α-methyl-2-(1-phenylethylthio)styrenes **3g** and **3h** (Scheme 2).

α-Substituted 2-(1-phenylethylthio)styrene derivatives **3**, thus obtained, smoothly underwent 5-*endo* cyclization reaction on treatment with iodine in the presence of sodium hydrogen carbonate in acetonitrile at room temperature to provide the desired 3-substituted benzo[*b*]thiophenes **7** in fair to good yields, as summarized in Scheme 3. It indicates that both 3-alkyl- and 3-aryl-benzo[*b*]thiophenes can be prepared, whereas 3-arylindole derivatives can not be obtained in the indole syn-



Scheme 1.



Scheme 2.

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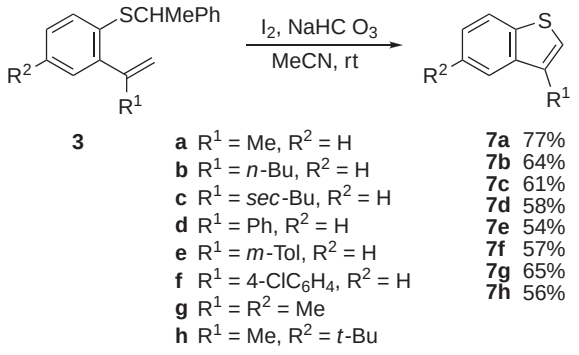
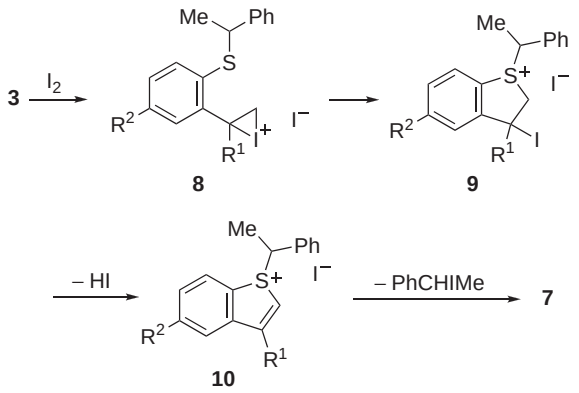


3

a R^1 = Me, R^2 = H
b R^1 = *n*-Bu, R^2 = H
c R^1 = *sec*-Bu, R^2 = H
d R^1 = Ph, R^2 = H
e R^1 = *m*-Tol, R^2 = H
f R^1 = 4-ClC_6H_4, R^2 = H
g R^1 = R^2 = Me
h R^1 = Me, R^2 = *t*-Bu

7a 77%
7b 64%
7c 61%
7d 58%
7e 54%
7f 57%
7g 65%
7h 56%

Scheme 3.



Scheme 4.

thesis previously reported by us.[1] Unfortunately, however, the possibility of the preparation of 2,3-disubstituted 3-arylbenzo[*b*]thiophenes could not be examined, because the respective α,β-disubstituted 2-(1-phenylethylthio)styrene derivatives could not be prepared by reactions of 2-(1-phenylethylthio)phenyl ketones with alkylidenetriphenylphosphoranes. It should be noted that, when α-phenyl-2-(phenylmethylthio)-styrene was subjected to the iodocyclization reaction under the same conditions as described above, a considerably smaller amount (39%) of the desired 3-phenylbenzo[*b*]thiophene (**7d**) was isolated from a rather complex reaction mixture.

The formation of the benzo[*b*]thiophenes **7** from the 2-(1-phenylethylthio)styrenes **3** is thought to proceed as illustrated in Scheme 4. Treatment of **3** with iodine generates the iodonium ion intermediates **8**. A 5-*endo* attack of the lone pair electrons of the sulfur atom on the iodonium ion moiety gives the sulfonium ion intermediate **9**. Sequential elimination of hydrogen iodide from **9** gives the benzothiophenium ion intermediate **10**, from which loss of (1-iodoethyl)benzene gives **7**.

In summary, the results detailed herein demonstrate that 3-substituted benzo[*b*]thiophenes can be conveniently prepared from readily available starting materials using simple manipulations. Work on the utilization of this and related methodologies for the syntheses of other thiophene-fused heterocycles are in progress in our laboratory and will be described at a later date.

Experimental

General. The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference in $CDCl_3$ with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. ^{13}C NMR spectra were determined using $SiMe_4$ as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz in $CDCl_3$. Low-resolution mass spectra were recorded on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). Thin-layer chromatography (TLC) was carried out using Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the solvents used were dried over the appropriate drying agents and distilled under argon prior to use.

Starting Materials. 1-(2-Mercaptophenyl)ethanone,[5] (2-mercaptophenyl)phenylmethanone,[6] (2-mercaptophenyl)(3-methylphenyl)methanone,[7] and (4-chlorophenyl)(2-mercaptophenyl)-methanone[7] were prepared according to reported procedures. All other chemicals used in this study were commercially available.

1-(2-Mercaptophenyl)pentan-1-one.[9] This compound was prepared from 2-mercaptobenzoic acid and butyllithium under same conditions as reported for the preparation of 1-(2-mercaptophenyl)ethanone[5] in 68% yield; a white solid; mp 44–45 °C (hexane–Et_2O) (lit.,[9] mp 46–47 °C).

1-(2-Mercaptophenyl)-2-methylbutan-1-one. This compound was prepared from 2-mercaptobenzoic acid and *sec*-butyllithium under same conditions as reported for the preparation of 1-(2-mercaptophenyl)ethanone[5] in 73% yield; a yellow liquid; bp 120 °C/120 Pa; IR (neat) 2550 and 1666 cm^{-1}; ^{1}H NMR δ 0.92 (3H, t, J = 7.3 Hz), 1.20 (3H, d, J = 6.9 Hz), 1.46–1.55 (1H, m), 1.79–1.88 (1H, m), 3.34–3.40 (1H, m), 4.25 (1H, s), 6.99–7.34 (3H, m), and 7.83 (1H, dd, J = 7.8 and 1.4 Hz). Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26%. Found: C, 67.88; H, 7.25%.

Typical Procedure for the Preparation of 2-(1-Phenylethylthio)phenyl Ketones 2. 1-[2-(1-Phenylethylthio)phenyl]ethanone (2a): To a stirred suspension of NaH (60% in oil; 0.12 g, 2.9 mmol) in THF (6 mL) at 0 °C was added a solution of 1-(2-mercaptophenyl)ethanone (**1a**)[5] (0.44 g, 2.9 mmol) in THF (6 mL) dropwise. After 15 min, (1-bromoethyl)benzene (0.54 g, 2.9 mmol) was added, and stirring was continued an additional 1 h at the same temperature. Saturated aqueous NH_4Cl (15 mL) was added, and the mixture was extracted with Et_2O twice (15 mL each). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was purified by column chromatography on silica gel to give the title compound (0.58 g, 79%): a pale-yellow oil; R_f 0.59 (3:1 hexane–EtOAc); IR (neat) 1663 cm^{-1}; ^{1}H NMR δ 1.65 (3H, d, J = 6.9 Hz), 2.57 (3H, s), 4.22 (1H, q, J = 6.9 Hz), 7.15–7.23 (2H, m), 7.27–7.30 (3H, m), 7.33 (1H, dd, J = 7.8 and 1.4 Hz), 7.38 (2H, d, J = 7.3 Hz), and 7.61 (1H, dd, J = 7.8 and 1.4 Hz). Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29%. Found: C, 74.91; H, 6.20%.

1-[2-(1-Phenylethylthio)phenyl]pentan-1-one (2b): A yellow solid; mp 59–60 °C (hexane–Et_2O); IR (KBr disk) 1670 cm^{-1}; ^{1}H NMR δ 0.93 (3H, t, J = 7.3 Hz), 1.39 (2H, sextet, J = 7.3 Hz), 1.63 (3H, d, J = 6.9 Hz), 1.68 (2H, quintet, J = 7.3 Hz), 2.86 (2H, t, J = 7.3 Hz), 4.38 (1H, q, J = 6.9 Hz), 7.16–7.21 (2H, m), 7.23–7.28 (3H, m), 7.31 (1H, d, J = 7.8 Hz), 7.34 (2H, d, J = 7.3 Hz), 7.51 (1H, dd, J = 7.3 and 1.4 Hz); ^{13}C NMR δ 13.94, 22.38, 22.60, 26.37, 41.53, 47.16, 125.62, 127.14, 127.25 (two overlapped C's), 128.33, 128.47 (two overlapped C's), 130.69, 131.11, 143.12, and 204.13. Calcd for $C_{19}H_{22}OS$: C, 76.46; H, 7.43%. Found: C, 76.43; H, 7.52%.

2-Methyl-1-[2-(1-phenylethylthio)phenyl]butan-1-one (2c):

A yellow oil; a mixture of diastereomers (ca. 1:1); R_f 0.45 (1:2 THF–hexane); IR (neat) 1693 cm^{-1}; ^1H NMR δ 0.91 (3H, t, $J = 7.3$ Hz), 1.15 and 1.16 (3H, 2d, $J = 6.9$ Hz each), 1.39–1.48 (1H, m), 1.61 (3H, d, $J = 6.9$ Hz), 1.73–1.83 (1H, m), 3.15–3.24 (1H, m), 4.38 (1H, q, $J = 6.9$ Hz), 7.19 (2H, dd, $J = 7.8$ and 7.3 Hz), 7.23–7.27 (3H, m), 7.29–7.33 (3H, m), and 7.43 (1H, d, $J = 7.3$ Hz). Calcd for $C_{19}H_{22}OS$: C, 76.46; H, 7.43%. Found: C, 76.31; H, 7.37%.

Phenyl[2-(1-phenylethylthio)phenyl]methanone (2d): A pale-yellow oil; R_f 0.39 (10:1 pentane–Et_2O); IR (neat) 1668 cm^{-1}; ^1H NMR δ 1.52 (3H, d, $J = 6.9$ Hz), 4.31 (1H, q, $J = 6.9$ Hz), 7.15–7.21 (4H, m), 7.26–7.37 (5H, m), 7.43 (2H, dd, $J = 8.2$ and 7.3 Hz), 7.57 (1H, tt, $J = 7.3$ and 1.4 Hz), and 7.72 (2H, dd, $J = 8.2$ and 1.4 Hz). Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70%. Found: C, 79.21; H, 5.90%.

(3-Methylphenyl)[2-(1-phenylethylthio)phenyl]methanone (2e): A yellow oil; R_f 0.75 (5:1 hexane–EtOAc); IR (neat) 1666 and 1601 cm^{-1}; ^1H NMR δ 1.52 (3H, d, $J = 6.9$ Hz), 2.38 (3H, s), 4.31 (1H, q, $J = 6.9$ Hz), 7.15–7.21 (4H, m), 7.27–7.34 (6H, m), 7.38 (1H, d, $J = 7.3$ Hz), 7.47 (1H, d, $J = 7.3$ Hz), and 7.58 (1H, s). Calcd for $C_{22}H_{20}OS$: C, 79.48; H, 6.06%. Found: C, 79.45; H, 6.19%.

(4-Chlorophenyl)[2-(1-phenylethylthio)phenyl]methanone (2f): A yellow oil; R_f 0.37 (10:1 pentane–Et_2O); IR (neat) 1667 cm^{-1}; ^1H NMR δ 1.53 (3H, d, $J = 6.9$ Hz), 4.30 (1H, q, $J = 6.9$ Hz), 7.16–7.20 (2H, m), 7.21–7.36 (5H, m), 7.39 (1H, d, $J = 8.2$ Hz), 7.42 (2H, d, $J = 8.7$ Hz), 7.63 (1H, d, $J = 8.2$ Hz), and 7.71 (2H, d, $J = 8.7$ Hz). Calcd for $C_{21}H_{17}ClOS$: C, 71.48; H, 4.86%. Found: C, 71.17; H, 5.05%.

Typical Procedure for the Preparation of 2-(1-Phenylethylthio)styrenes 3a–3f. 1-(1-Methylethenyl)-2-(1-phenylethylthio)benzene (3a): To a stirred suspension of methyltriphenylphosphonium iodide (0.77 g, 1.9 mmol) in THF (5 mL) at 0 °C was added *n*-BuLi (1.5 M in hexane; 1.9 mmol) (1 M = 1 mol dm^{-3}) dropwise. After 15 min, a solution of **2a** (0.33 g, 1.3 mmol) in THF (6 mL) was added, and stirring was continued for an additional 4 h at the same temperature. The resulting mixture was worked up in a manner similar to that described above, and the crude product was purified by preparative TLC on silica gel to give **3a** (0.29 g, 88%): a pale-yellow oil; R_f 0.73 (5:1 hexane–EtOAc); IR (neat) 1639 and 1601 cm^{-1}; ^1H NMR δ 1.60 (3H, d, $J = 7.3$ Hz), 2.09 (3H, d, $J = 0.9$ Hz), 4.38 (1H, q, $J = 7.3$ Hz), 4.85 (1H, quint, $J = 0.9$ Hz), 5.20 (1H, quint, $J = 0.9$ Hz), 7.08–7.16 (4H, m), 7.19 (1H, tt, $J = 7.3$ and 1.4 Hz), 7.26 (2H, dd, $J = 7.8$ and 7.3 Hz), and 7.30 (2H, dd, $J = 7.8$ and 1.4 Hz); ^{13}C NMR δ 22.30, 24.20, 47.38, 115.68, 126.62, 127.05, 127.18, 127.23, 128.34, 128.66, 131.96, 132.90, 143.26, 145.88, and 146.38. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13%. Found: C, 79.99; H, 7.18%.

1-(1-Butylethenyl)-2-(1-phenylethylthio)benzene (3b): A yellow oil; R_f 0.80 (1:3 AcOEt–hexane); IR (neat) 1636 cm^{-1}; ^1H NMR δ 0.88 (3H, t, $J = 7.3$ Hz), 1.31–1.34 (4H, m), 1.59 (3H, d, $J = 6.9$ Hz), 2.43 (2H, t, $J = 6.9$ Hz), 4.38 (1H, q, $J = 6.9$ Hz), 4.85 (1H, s), 5.17 (1H, d, $J = 1.4$ Hz), 7.05 (1H, dd, $J = 6.9$ and 1.8 Hz), 7.08–7.13 (2H, m), 7.18 (1H, t, $J = 7.3$ Hz), 7.24–7.27 (3H, m), and 7.30 (2H, d, $J = 7.3$ Hz). Calcd for $C_{20}H_{24}S$: C, 81.02; H, 8.16%. Found: C, 80.80; H, 8.16%.

1-[1-(1-Methylpropyl)ethenyl]-2-(1-phenylethylthio)benzene (3c): A yellow oil; a mixture of diastereomers (ca. 1:1); R_f 0.83 (1:3 AcOEt–hexane); IR (neat) 1631 and 1603 cm^{-1}; ^1H NMR δ 0.88 and 0.90 (combined 3H, 2t, $J = 7.3$ Hz each), 1.07 and 1.09 (combined 3H, 2d, $J = 6.9$ Hz each), 1.20–1.30 (1H, m), 1.52–1.62 (combined 4H, m including 2d at 1.58 and 1.59, $J = 6.9$ Hz each), 2.45–2.54 (1H, m), 4.37 (1H, q, $J = 6.9$ Hz), 4.88 (1H, t, $J = 1.4$ Hz), 5.15 (1H, t, $J = 1.4$ Hz), 7.02–7.05 (1H, m), 7.08–7.14 (2H, m), 7.16–7.21 (1H, m), 7.23–7.31 (5H, m). Calcd for $C_{20}H_{24}S$: C, 81.02; H, 8.16%. Found: C, 80.75; H, 8.13%.

1-(1-Phenylethenyl)-2-(1-phenylethylthio)benzene (3d): A pale-yellow oil; R_f 0.72 (5:1 hexane–EtOAc); IR (neat) 1614 and 1601 cm^{-1}; ^1H NMR δ 1.44 (3H, d, $J = 6.9$ Hz), 4.19 (1H, q, $J = 6.9$ Hz), 5.16 (1H, d, $J = 1.4$ Hz), 5.78 (1H, d, $J = 1.4$ Hz), 7.16–7.24 (10H, m), and 7.26–7.30 (4H, m); ^{13}C NMR δ 22.27, 47.11, 115.74, 126.60, 126.68, 126.95, 127.28, 127.49, 127.74, 128.14, 128.23, 130.56, 132.29, 134.58, 140.70, 143.28, 144.21, and 148.67. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37%. Found: C, 83.37; H, 6.62%.

1-[1-(3-Methylphenyl)ethenyl]-2-(1-phenylethylthio)benzene (3e): A yellow oil; R_f 0.83 (4:1 hexane–CH_2Cl_2); IR (neat) 1614 and 1601 cm^{-1}; ^1H NMR δ 1.44 (3H, d, $J = 6.9$ Hz), 2.31 (3H, s), 4.18 (1H, q, $J = 6.9$ Hz), 5.14 (1H, d, $J = 0.9$ Hz), 5.77 (1H, d, $J = 0.9$ Hz), 7.01 (1H, d, $J = 7.8$ Hz), 7.08 (2H, d, $J = 7.8$ Hz), 7.15–7.22 (9H, m), and 7.27 (1H, ddd, $J = 7.8$, 6.9, and 1.8 Hz). Calcd for $C_{23}H_{22}S$: C, 83.59; H, 6.71%. Found: C, 83.54; H, 6.43%.

1-[1-(4-Chlorophenyl)ethenyl]-2-(1-phenylethylthio)benzene (3f): A pale-yellow oil; R_f 0.70 (10:1 hexane–Et_2O); IR (neat) 1614 cm^{-1}; ^1H NMR δ 1.47 (3H, d, $J = 7.3$ Hz), 4.23 (1H, q, $J = 7.3$ Hz), 5.22 (1H, s), 5.73 (1H, s), 7.09 (2H, d, $J = 8.2$ Hz), and 7.11–7.32 (11H, m). Calcd for $C_{22}H_{19}ClS$: C, 75.30; H, 5.46%. Found: C, 75.06; H, 5.54%.

2-(2-Mercapto-5-methylphenyl)propan-2-ol (5g). This compound was prepared by the reaction of lithium 2-lithio-4-methylbenzenethiolate, which was generated from 4-methylbenzenethiol (**4g**) by the method of Martin et al.,[8] with acetone; a white solid; mp 40–42 °C (hexane–Et_2O); IR (KBr disk) 3290 and 2544 cm^{-1}; ^1H NMR δ 1.70 (6H, s), 2.30 (3H, s), 2.53 (1H, s), 3.96 (1H, s), 6.92 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.18 (1H, d, $J = 7.8$ Hz), and 7.19 (1H, d, $J = 1.4$ Hz). Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74%. Found: C, 65.85; H, 7.78%.

2-[5-Methyl-2-(1-phenylethylthio)phenyl]propan-2-ol. (6g). This compound was prepared by 1-phenylethylation of **5g** as described for the preparation of **2a**. **6g**: R_f 0.31 (8:1 hexane–AcOEt); IR (neat) 3435 cm^{-1}; ^1H NMR δ 1.60 (3H, s), 1.648 (3H, d, $J = 6.9$ Hz), 1.649 (3H, s), 2.32 (3H, s), 4.33 (1H, q, $J = 6.9$ Hz), 4.98 (1H, s), 6.93 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.17 (1H, d, $J = 7.8$ Hz), and 7.23–7.33 (6H, m). Calcd for $C_{18}H_{22}OS$: C, 75.48; H, 7.74%. Found: C, 75.33; H, 7.79%.

4-Methyl-2-(1-methylethenyl)-1-(1-phenylethylthio)benzene (3g). This compound was prepared by the treatment of **6g** with a catalytic amount of sulfuric acid in Ac_2O at 0 °C; a yellow oil; R_f 0.80 (8:1 hexane–AcOEt); IR (neat) 1638 cm^{-1}; ^1H NMR δ 1.58 (3H, d, $J = 6.9$ Hz), 2.08 (3H, s), 2.28 (3H, s), 4.32 (1H, q, $J = 6.9$ Hz), 4.83 (1H, d, $J = 1.4$ Hz), 5.17 (1H, d, $J = 1.4$ Hz), 6.93–6.94 (2H, m), 7.16–7.20 (2H, m), and 7.24–7.30 (4H, m). Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51%. Found: C, 80.40; H, 7.59%.

2-[5-(1,1-Dimethylethyl)-2-mercaptophenyl]propan-2-ol (5h). This compound was prepared by reacting acetone with lithium 4-(1,1-dimethylethyl)-2-lithiobenzenethiolate, which was generated from 4-(1,1-dimethylethyl)benzenethiol (**4h**) by the method of Martin et al.;[8] a yellow solid; mp 54–57 °C (hexane–Et_2O); IR (neat) 3400 and 2557 cm^{-1}; ^1H NMR δ 1.30 (9H, s), 1.55 (1H, br s), 1.72 (6H, s), 3.96 (1H, s), 7.12 (1H, dd, $J = 8.2$ and 1.8 Hz), 7.21 (1H, d, $J = 8.2$ Hz), and 7.42 (1H, d, $J = 1.8$ Hz). Calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98%. Found: C, 69.52; H, 9.01%.

2-[5-(1,1-Dimethylethyl)-2-(1-phenylethylthio)phenyl]pro-

pan-2-ol (6h). This compound was prepared by 1-phenylethylation of **5h** as described for the preparation of **3a**. **6h**: a yellow oil; R_f 0.38 (2:1 hexane–Et_2O); IR (neat) 3440 cm^{-1}; ^1H NMR δ 1.30 (9H, s), 1.63 (3H, s), 1.66 (3H, d, $J = 6.9$ Hz), 1.67 (3H, s), 4.35 (1H, q, $J = 6.9$ Hz), 4.94 (1H, s), 7.14 (1H, dd, $J = 8.2$ and 2.3 Hz), 7.23–7.27 (2H, m), 7.29–7.33 (4H, m), and 7.45 (1H, d, $J = 2.3$ Hz). Calcd for $C_{21}H_{28}OS$: C, 76.78; H, 8.59%. Found: C, 76.50; H, 8.80%.

4-(1,1-Dimethylethyl)-2-(1-methylethenyl)-1-(1-phenylethylthio)benzene (3h). This compound was prepared from **6h** as described for the preparation of **3g**. **3h**: a pale-yellow oil; R_f 0.81 (10:1 hexane–THF); IR (neat) 1639 cm^{-1}; ^1H NMR δ 1.28 (9H, s), 1.59 (3H, d, $J = 7.3$ Hz), 2.10 (3H, d, $J = 1.4$ Hz), 4.34 (1H, q, $J = 7.3$ Hz), 4.86 (1H, d, $J = 0.9$ Hz), 5.19 (1H, d, $J = 0.9$ Hz), 7.11 (1H, d, $J = 2.3$ Hz), 7.14 (1H, dd, $J = 8.2$ and 2.3 Hz), 7.18–7.21 (2H, m), 7.26 (2H, dd, $J = 7.8$ and 7.3 Hz), and 7.31 (2H, d, $J = 7.8$ Hz). Calcd for $C_{21}H_{26}S$: C, 81.23; H, 8.44%. Found: C, 80.99; H, 8.67%.

Typical Procedure for the Preparation of Benzo[*b*]thiophenes 7. 3-Methylbenzo[*b*]thiophene (7a):[10] To a stirring mixture of **3a** (0.12 g, 0.48 mmol) and $NaHCO_3$ (0.12 g, 1.4 mmol) in MeCN (2 mL) at 0 °C was added iodine (0.37 g, 1.4 mmol) portionwise; the mixture was then stirred for 4 h at room temperature. Ten percent aqueous $Na_2S_2O_3$ was added until the color of iodine disappeared and the mixture was extracted with Et_2O twice (10 mL each). The combined extracts was washed with saturated aqueous $NaHCO_3$ and then brine, and dried over anhydrous K_2CO_3. After evaporation of the solvent, the residue was purified by preparative TLC on silica gel to give **7a** (55 mg, 77%): a pale-yellow liquid; R_f 0.76 (8:1 hexane–EtOAc); the ^1H NMR spectrum of this product was identical to that reported previously.[10]

3-Butylbenzo[*b*]thiophene (7b):[10] A pale-yellow oil; R_f 0.69 (8:1 hexane–EtOAc); the ^1H NMR spectrum of this product was identical to that reported previously.[10]

3-(1-Methylpropyl)benzo[*b*]thiophene (7c):[11] A pale-yellow oil; R_f 0.71 (pentane); IR (neat) 3067, 2963, 1456, 1427, 762, and 733 cm^{-1}; ^1H NMR δ 0.93 (3H, t, $J = 7.3$ Hz), 1.35 (3H, d, $J = 6.9$ Hz), 1.62–1.71 (1H, m), 1.80–1.89 (1H, m), 3.10 (1H, sextet, $J = 7.3$ Hz), 7.07 (1H, s), 7.33 (1H, ddd, $J = 8.2$, 7.3, and 1.4 Hz), 7.37 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.78 (1H, d, $J = 7.8$ Hz), and 7.86 (1H, dd, $J = 8.2$ and 1.4 Hz); MS m/z (%) 190 (M^+, 100).

3-Phenylbenzo[*b*]thiophene (7d):[10] A pale-yellow oil; R_f 0.69 (8:1 hexane–EtOAc); the ^1H NMR spectrum of this product was identical to that reported previously.[10]

3-(3-Methylphenyl)benzo[*b*]thiophene (7e): A colorless oil; R_f 0.57 (pentane); IR (neat) 3048, 2920, 1605, 1427, 777, 760, 732, and 698 cm^{-1}; ^1H NMR δ 2.44 (3H, s), 7.23 (1H, d, $J = 6.9$ Hz), 7.36–7.41 (6H, m), and 7.91–7.93 (2H, m); ^{13}C NMR δ 21.51, 122.88, 122.99, 123.22, 124.25, 124.35, 125.78, 128.30, 128.59, 129.41, 135.94, 137.96, 138.20, 138.36, and 140.67; MS m/z (%) 224 (M^+, 100). Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39%. Found: C, 80.27; H, 5.67%.

3-(4-Chlorophenyl)benzo[*b*]thiophene (7f): A pale-yellow oil; R_f 0.62 (10:1 hexane–EtOAc); IR (neat) 3059, 1585, 1521, 1481, 1090, 1014, 825, 762, and 734 cm^{-1}; ^1H NMR δ 7.38–7.41 (3H, m), 7.46 (2H, d, $J = 8.7$ Hz), 7.52 (2H, d, $J = 8.7$ Hz), 7.85 (1H, dd, $J = 7.3$ and 0.9 Hz), and 7.92 (1H, dd, $J = 7.8$ and 1.4 Hz); MS m/z (%) 244 (M^+, 100). Calcd for $C_{14}H_9ClS$: C, 68.71; H, 3.71%. Found: C, 68.69; H, 3.89%.

3,5-Dimethylbenzo[*b*]thiophene (7g):[12] A colorless oil; R_f 0.67 (pentane); IR (neat) 3062, 2918, 1445, 1290, 835, 800, and 768 cm^{-1}; ^1H NMR δ 2.42 (3H, d, $J = 0.9$ Hz), 2.50 (3H, s), 7.04 (1H, s), 7.18 (1H, d, $J = 8.2$ Hz), 7.51 (1H, s), 7.72 (1H, d, $J = 8.2$ Hz); MS m/z (%) 162 (M^+, 100).

5-(1,1-Dimethylethyl)-3-methylbenzo[*b*]thiophene (7h):[13] A colorless oil; R_f 0.71 (pentane); IR (neat) 3076, 2962, 1448, 1363, 1256, 877, 835, 812, 768, and 656 cm^{-1}; ^1H NMR δ 1.41 (9H, s), 2.45 (3H, d, $J = 0.9$ Hz), 7.05 (1H, q, $J = 0.9$ Hz), 7.43 (1H, dd, $J = 8.2$ and 1.8 Hz), 7.68 (1H, d, $J = 1.8$ Hz), and 7.78 (1H, d, $J = 8.2$ Hz); MS m/z (%) 204 (M^+, 100).

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