Efficient Methods for the Synthesis of Thieno[3,2-*b*]thiophene and Thieno[3,2-*b*]furan Derivatives

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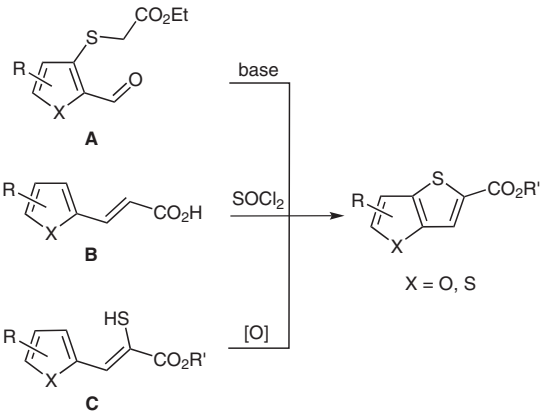
Abstract: A novel approach to the synthesis of thieno[3,2-*b*]thiophenes and thieno[3,2-*b*]furans bearing various substituents from readily accessible starting materials has been developed. The methodology is based on C- and O-alkylation of ethyl 4-hydroxy-2-methylthiophene-3-carboxylate with α-halo ketones, followed by cyclization.

Key words: alkylation, cyclization, heterocycles, thienothiophenes, thienofurans

A great interest has been concentrated on thieno[3,2-*b*]thiophene and thieno[3,2-*b*]furan derivatives, because of both their biological activity[1,2] and their potential electrooptical properties for use as molecular devices.[3–5] These compounds could be used as aryl residues for dihetarylethenes that possess good photochromic properties;[6,7] however, research in this area has been impeded by the lack of efficient synthetic routes to thieno[3,2-*b*]thiophene and thieno[3,2-*b*]furan derivatives. There are only a few basic methods for the construction of these heterocyclic systems.[8–10] The most general is intramolecular cyclization of aldehydes **A**[11,12] which can be synthesized from 3-bromothiophene (3-bromofuran) derivatives (Scheme 1). The main limitation of this method is that the starting 3-bromo-substituted thiophenes or furans are not easily accessible. Other ways for the preparation of these heterocyclic compounds are based on the cyclization of acrylic acid derivatives **B**[13–15] or **C**.[16–18] In the first case, the reaction of arylacrylic acids (compounds of type **B**) with thionyl chloride leads to formation of the substituted thienothiophene system. For compounds of type **C**, iodine or bromine can be used as the cyclizing agent. While these methods are perfectly suitable, the use of halogenous compounds for the preparation of thienothiophene and thienofuran systems often results in the formation of halogenated derivatives of the target heterocycles as side products.

In this work, we present the synthesis of thieno[3,2-*b*]thiophene and thieno[3,2-*b*]furan derivatives starting from the easily accessible 3-hydroxythiophene **1** (Scheme 2). This approach includes two stages: regioselective C- or O-alkylation of the 3-hydroxythiophene with



Scheme 1

α-halo ketones, and heterocyclization of the alkylated products **2** and **3**.

The alkylation of hydroxythiophenes, unlike phenols, is known[19] to give mixtures of O- and C-alkylated products. The direction of the reaction depends on the structure of the starting hydroxythiophene, the nature of the alkylating agent, and the base employed.[20–22] Recently, we have found that the alkylation of hydroxythiophene **1** with α-halo ketones is strongly dependent on the polarity of the solvent.[23] The C-alkylated products **2a–d** were obtained in high yields when the reaction was carried out in benzene in the presence of metallic sodium. The same reaction of hydroxythiophene **1** with α-halo ketones carried out in *N*,*N*-dimethylformamide or acetonitrile with potassium carbonate as a base exclusively gave O-alkylated compounds **3**. The synthesized alkylated products **2** and **3** are useful synthones for the preparation of thiophene-condensed heterocycles, and we have now studied in detail the cyclization process of both alkylated compound types.

The cyclization of compounds **2** to thieno[3,2-*b*]thiophene derivatives **4** was investigated in different solvents (1,4-dioxane, toluene, benzene, THF, monoglyme, diglyme, and *p*-xylene) using phosphorus pentasulfide or Lawesson's reagent as the cyclizing agent. The best results were achieved by heating ketones **2a–d** with Lawesson's reagent in *p*-xylene at 110–120 °C.

In order to synthesize the thieno[3,2-*b*]furan derivatives **5**, we have studied the heterocyclization of compounds **2** under different conditions. The heating of ketones **2a–d** in polyphosphoric acid or in the melt, as well as using toluene or xylene as a solvent, gave low yields of thieno[3,2-

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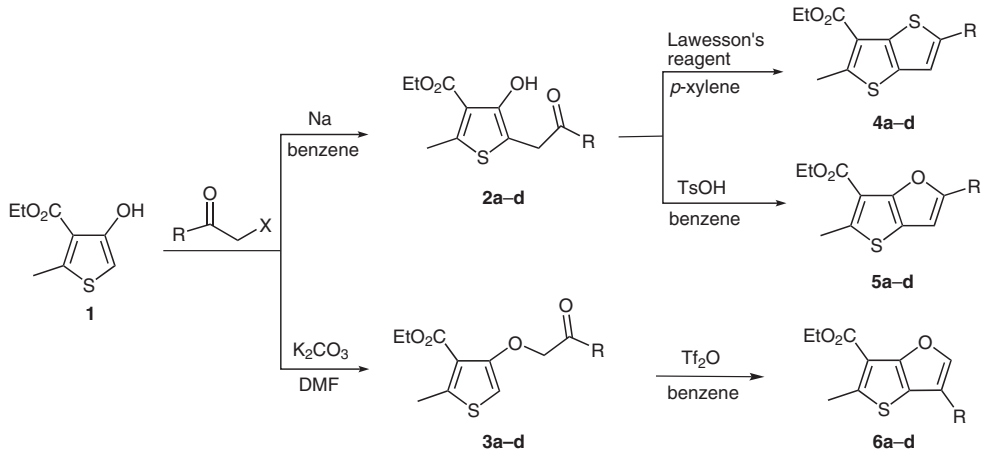

R = Me (**a**); Ph (**b**); 4-ClC_6H_4 (**c**); 4-BrC_6H_4 (**d**); X = Cl, Br

Scheme 2

b]furans **5**. It was found that *p*-toluenesulfonic acid is an efficient catalyst for this reaction; thieno[3,2-*b*]furans **5a–d** were synthesized in good yields by the heterocyclization of compounds **2a–d** in boiling benzene in the presence of catalytic amounts of *p*-toluenesulfonic acid.

For the cyclization of compounds **3** to thieno[3,2-*b*]furan derivatives **6**, we have tested various acids and anhydrides (sulfuric acid, polyphosphoric acid, and acetic, trifluoroacetic and trifluoromethanesulfonic anhydride) as cyclizing agents and anhydrous ethanol or benzene as solvent. The reaction of thiophenes **3a–d** with a catalytic amount of sulfuric acid in ethanol at 5–10 °C leads to an inseparable complex mixture. Considerably better results were obtained when the reaction was carried out in benzene in the presence of a catalytic amount of trifluoromethanesulfonic anhydride, and the thieno[3,2-*b*]furans **6a–d** were prepared in high yields.

The structures of the synthesized compounds were proved by ^{1}H NMR spectroscopy and mass spectrometry, and confirmed by elemental analysis. The signals of the thiophene and furan aromatic protons in the ^{1}H NMR spectra of the compounds containing aryl substituents, **4b**,**c**,**d**–**6b**,**c**,**d**, are shifted downfield by 0.5–0.65 ppm relative to the methyl derivatives **4a**–**6a**. The significant difference in the ^{1}H NMR chemical shifts of the furan aromatic protons (about 1 ppm) between the 2- and 3-substituted thieno[3,2-*b*]furans **5** and **6** is also noteworthy.

In summary, we have developed efficient methods for the synthesis of thieno[3,2-*b*]thiophenes and thieno[3,2-*b*]furans starting from the readily accessible ethyl 4-hydroxy-2-methylthiophene-3-carboxylate. Previously unknown thienothiophene and thienofuran derivatives bearing various substituents were synthesized, compounds that are otherwise hard to obtain.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker WM-250 and AM-300 spectrometers. Mass spectra (MS) were recorded on a Kratos instrument at 70 eV using electron impact (EI). Melting points were measured on a Boetius hot-stage apparatus and are uncorrected. The completion of the reactions was detected using TLC [Silufol UV-254, elution with petroleum ether (60–80 °C)–EtOAc]. Column chromatography was performed using Merck silica gel (0.063–0.200 mm). Hydroxythiophene derivatives **2a–d** and **3a**,**d** were prepared by the procedures reported previously.[23]

Alkylated Thiophenes 3; General Procedure

To a stirred mixture of ethyl 4-hydroxy-2-methylthiophene-3-carboxylate (**1**; 1.86 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) in DMF (10 mL), a soln of a 2-bromoacetophenone (10.5 mmol) in DMF (3 mL) was added dropwise at 5–10 °C. The reaction mixture was stirred at 20–25 °C until the starting hydroxythiophene **1** completely disappeared; the progress of the reaction was monitored by TLC (petroleum ether–EtOAc, 6:1). The mixture was poured onto ice, the product was extracted with EtOAc (3 × 50 mL), and the extract was washed with brine (30 mL) and dried (anhyd $MgSO_4$). The solvent was removed, and the residue was purified by column chromatography (petroleum ether–EtOAc, 6:1).

Ethyl 2-Methyl-4-(2-oxo-2-phenylethoxy)thiophene-3-carboxylate (3b)

Yield: 1.21 g (40%); yellowish powder; mp 56–57 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 2.61 (s, 3 H, CH_3), 4.32 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.21 (s, 2 H, OCH_2CO), 6.06 (s, 1 H, H^{thioph}), 7.42–7.63 (m, 3 H, H^{arom}), 8.02 (d, *J* = 7.3 Hz, 2 H, H^{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.21, 16.86, 60.33, 73.63 (OCH_2CO), 96.48 (CH^{thioph}), 120.57, 128.45 (CH^{arom}), 128.67 (CH^{arom}), 133.79 (CH^{arom}), 134.58, 148.06, 155.04, 162.94, 194.65 (OCH_2CO).

MS (EI, 70 eV): *m*/*z* (%) = 304 (34) [M^+], 105 (100).

Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; S, 10.54. Found: C, 63.23; H, 5.40; S, 10.46.

Ethyl 4-[2-(4-Chlorophenyl)-2-oxoethoxy]-2-methylthiophene-3-carboxylate (3c)

Yield: 2.16 g (64%); yellowish powder; mp 81–82 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.36 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 2.62 (s, 3 H, CH_3), 4.33 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.14 (s, 2 H, OCH_2CO), 6.09 (s, 1 H, H^{thioph}), 7.45 (d, *J* = 7.3 Hz, 2 H, H^{arom}), 8.08 (d, *J* = 7.3 Hz, 2 H, H^{arom}).

MS (EI, 70 eV): *m*/*z* (%) = 338/340 (20/10) [M^+], 139/141 (100/53).

Anal. Calcd for $C_{16}H_{15}ClO_4S$: C, 56.72; H, 4.46; S, 9.46. Found: C, 56.62; H, 4.53; S, 9.30.

Thieno[3,2-*b*]thiophenes 4; General Procedure

To a hot soln (70–80 °C) of a hydroxythiophene **2** (8.2 mmol) in *p*-xylene (20 mL), Lawesson's reagent (6.63 g, 16.4 mmol) was added in several portions with stirring. The reaction mixture was heated at 110–120 °C until the starting compound completely disappeared; the progress of the reaction was monitored by TLC (petroleum ether–EtOAc, 5:1). The reaction mixture was cooled, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography (petroleum ether–EtOAc, 5:1).

Ethyl 2,5-Dimethylthieno[3,2-*b*]thiophene-3-carboxylate (4a)

Yield: 1.06 g (56%); mp 85–87 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.55 (s, 3 H, CH_3), 2.82 (s, 3 H, CH_3), 4.39 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 6.81 (s, 1 H, H^{thioph}).

MS (EI, 70 eV): *m*/*z* (%) = 240 (83) [M^+], 211 (100) [M^+ – Et].

Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03; S, 26.68. Found: C, 54.78; H, 5.08; S, 26.40.

Ethyl 2-Methyl-5-phenylthieno[3,2-*b*]thiophene-3-carboxylate (4b)

Yield: 1.33 g (54%); mp 69–71 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.49 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.86 (s, 3 H, CH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 7.27–7.45 (m, 4 H, 3 × H^{arom} and H^{thioph}), 7.65 (d, *J* = 7.1 Hz, 2 H, H^{arom}).

MS (EI, 70 eV): *m*/*z* (%) = 302 (97) [M^+], 273 (100) [M^+ – Et].

Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.67; S, 21.21. Found: C, 63.59; H, 4.76; S, 20.86.

Ethyl 5-(4-Chlorophenyl)-2-methylthieno[3,2-*b*]thiophene-3-carboxylate (4c)

Yield: 0.91 g (33%); mp 86–88 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 2.87 (s, 3 H, CH_3), 4.44 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 7.35–7.45 (m, 3 H, 2 × H^{arom} and H^{thioph}), 7.57 (d, *J* = 7.4 Hz, 2 H, H^{arom}).

MS (EI, 70 eV): *m*/*z* (%) = 336/338 (97/52) [M^+], 307/309 (100/40) [M^+ – Et].

Anal. Calcd for $C_{16}H_{13}ClO_2S_2$: C, 57.05; H, 3.89; S, 19.04. Found: C, 57.09; H, 4.01; S, 18.86.

Ethyl 5-(4-Bromophenyl)-2-methylthieno[3,2-*b*]thiophene-3-carboxylate (4d)

Yield: 1.72 g (55%); mp 112–114 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.47 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 2.85 (s, 3 H, CH_3), 4.44 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 7.33 (s, 1 H, H^{thioph}), 7.42–7.55 (m, 4 H, H^{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.51, 16.80, 60.93, 114.92, 115.02 (CH^{thioph}), 121.56, 127.16 (CH^{arom}), 132.07 (CH^{arom}), 133.69, 134.41, 139.21, 144.62, 151.94, 162.93.

MS (EI, 70 eV): *m*/*z* (%) = 380/382 (100/97) [M^+].

Anal. Calcd for $C_{16}H_{13}BrO_2S_2$: C, 50.40; H, 3.44; S, 16.82. Found: C, 50.45; H, 3.49; S, 16.52.

2-Substituted Thieno[3,2-*b*]furans 5; General Procedure

To a soln of a hydroxythiophene **2** (8.2 mmol) in benzene (15 mL), *p*-toluenesulfonic acid (0.16 g, 0.82 mmol) was added, and the reaction mixture was refluxed until the starting compound completely disappeared. The progress of the reaction was monitored by TLC (petroleum ether–EtOAc, 5:1). After the reaction mixture was cooled, the solvent was evaporated, and the residue was purified by column chromatography (petroleum ether–EtOAc, 5:1).

Ethyl 2,5-Dimethylthieno[3,2-*b*]furan-6-carboxylate (5a)

Yield: 0.55 g (30%); mp 66–68 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.46 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 4.41 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 6.27 (s, 1 H, H^{furan}).

MS (EI, 70 eV): *m*/*z* (%) = 224 (69) [M^+], 195 (100) [M^+ – Et].

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.51; H, 5.29.

Ethyl 5-Methyl-2-phenylthieno[3,2-*b*]furan-6-carboxylate (5b)

Yield: 1.36 g (58%); mp 83–85 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 2.83 (s, 3 H, CH_3), 4.45 (q, *J* = 7.4 Hz, 2 H, CH_2CH_3), 6.92 (s, 1 H, H^{furan}), 7.29 (t, *J* = 7.4 Hz, 1 H, H^{arom}), 7.42 (t, *J* = 7.4 Hz, 2 H, H^{arom}), 7.76 (d, *J* = 7.4 Hz, 2 H, H^{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.49, 17.16, 60.59, 100.48 (CH^{furan}), 114.25, 120.83, 123.96 (CH^{arom}), 127.83 (CH^{arom}), 128.83 (CH^{arom}), 130.92, 149.91, 155.12, 156.89, 162.24 (CO_2Et).

MS (EI, 70 eV): *m*/*z* (%) = 286 (59) [M^+], 257 (100) [M^+ – Et].

Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93; S, 11.20. Found: C, 67.31; H, 5.01; S, 10.96.

Ethyl 2-(4-Chlorophenyl)-5-methylthieno[3,2-*b*]furan-6-carboxylate (5c)

Yield: 1.62 g (62%); mp 77–79 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.82 (s, 3 H, CH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 6.90 (s, 1 H, H^{furan}), 7.37 (d, *J* = 8.5 Hz, 2 H, H^{arom}), 7.67 (d, *J* = 8.5 Hz, 2 H, H^{arom}).

MS (EI, 70 eV): *m*/*z* (%) = 320/322 (52/19) [M^+], 291/293 (100/33) [M^+ – Et].

Anal. Calcd for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08; S, 10.00. Found: C, 60.06; H, 4.15; S, 9.69.

Ethyl 2-(4-Bromophenyl)-5-methylthieno[3,2-*b*]furan-6-carboxylate (5d)

Yield: 1.61 g (54%); mp 79–81 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.81 (s, 3 H, CH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 6.90 (s, 1 H, H^{furan}), 7.47–7.65 (m, 4 H, H^{arom}).

MS (EI, 70 eV): *m*/*z* (%) = 364/366 (100/98) [M^+].

Anal. Calcd for $C_{16}H_{13}BrO_3S$: C, 52.62; H, 3.59; S, 8.78. Found: C, 52.21; H, 3.66; S, 8.54.

3-Substituted Thieno[3,2-*b*]furans 6; General Procedure

To a stirred soln of an alkylated thiophene **3** (8.2 mmol) in benzene (20 mL), trifluoromethanesulfonic anhydride (5 drops) was added at r.t. After 5–10 min, the reaction mixture was poured into H_2O (100 mL) and extracted with EtOAc (3 × 50 mL). The extract was washed with dilute $NaHCO_3$ soln (50 mL) and brine (50 mL), and dried (anhyd $MgSO_4$). The solvent was removed, and the residue was purified by column chromatography (petroleum ether–EtOAc, 5:1).

Ethyl 3,5-Dimethylthieno[3,2-*b*]furan-6-carboxylate (6a)

Yield: 1.56 g (85%); viscous oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.17 (s, 3 H, CH_3), 2.80 (s, 3 H, CH_3), 4.41 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 7.34 (s, 1 H, H^{furan}).

MS (EI, 70 eV): *m*/*z* (%) = 224 (58) [M^+], 195 (100) [M^+ – Et].

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.65; H, 5.31.

Ethyl 5-Methyl-3-phenylthieno[3,2-*b*]furan-6-carboxylate (6b)
Yield: 2.20 g (94%); mp 84–86 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.85 (s, 3 H, CH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 7.32 (t, *J* = 7.2 Hz, 1 H, H^{arom}), 7.44 (t, *J* = 7.2 Hz, 2 H, H^{arom}), 7.56 (d, *J* = 7.2 Hz, 2 H, H^{arom}), 7.89 (s, 1 H, H^{furan}).

MS (EI, 70 eV): *m*/*z* (%) = 286 (77) [M^+], 257 (100) [M^+ – Et].

Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found: C, 66.78; H, 5.01.

Ethyl 3-(4-Chlorophenyl)-5-methylthieno[3,2-*b*]furan-6-carboxylate (6c)
Yield: 2.36 g (90%); mp 130–132 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.84 (s, 3 H, CH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 7.36–7.53 (m, 4 H, H^{arom}), 7.86 (s, 1 H, H^{furan}).

MS (EI, 70 eV): *m*/*z* (%) = 320/322 (81/38) [M^+], 291/293 (100/40) [M^+ – Et].

Anal. Calcd for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08; S, 10.00. Found: C, 60.16; H, 4.15; S, 9.44.

Ethyl 3-(4-Bromophenyl)-5-methylthieno[3,2-*b*]furan-6-carboxylate (6d)
Yield: 2.42 g (81%); mp 171–173 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.84 (s, 3 H, CH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 7.40 (d, *J* = 8.5 Hz, 2 H, H^{arom}), 7.55 (d, *J* = 8.5 Hz, 2 H, H^{arom}), 7.87 (s, 1 H, H^{furan}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.40, 17.21, 60.68, 114.50, 117.27, 121.24, 121.62, 127.17, 127.18 (CH^{arom}), 129.86, 132.16 (CH^{arom}), 140.98 (CH^{furan}), 150.73, 161.99.

MS (EI, 70 eV): *m*/*z* (%) = 364/366 (31/37) [M^+], 335/337 (97/100) [M^+ – Et].

Anal. Calcd for $C_{16}H_{13}BrO_3S$: C, 52.61; H, 3.59; S, 8.78. Found: C, 52.93; H, 3.65; S, 8.56.

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