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AN IMPROVED METHOD FOR THE PREPARATION OF 4,7-DIOXO-4,7-DIHYDROBENZO[*b*]THIOPHENE-2-CARBOXYLATES FROM 2-ACYL-1,4-BENZOQUINONES AND MERCAPTOACETATES

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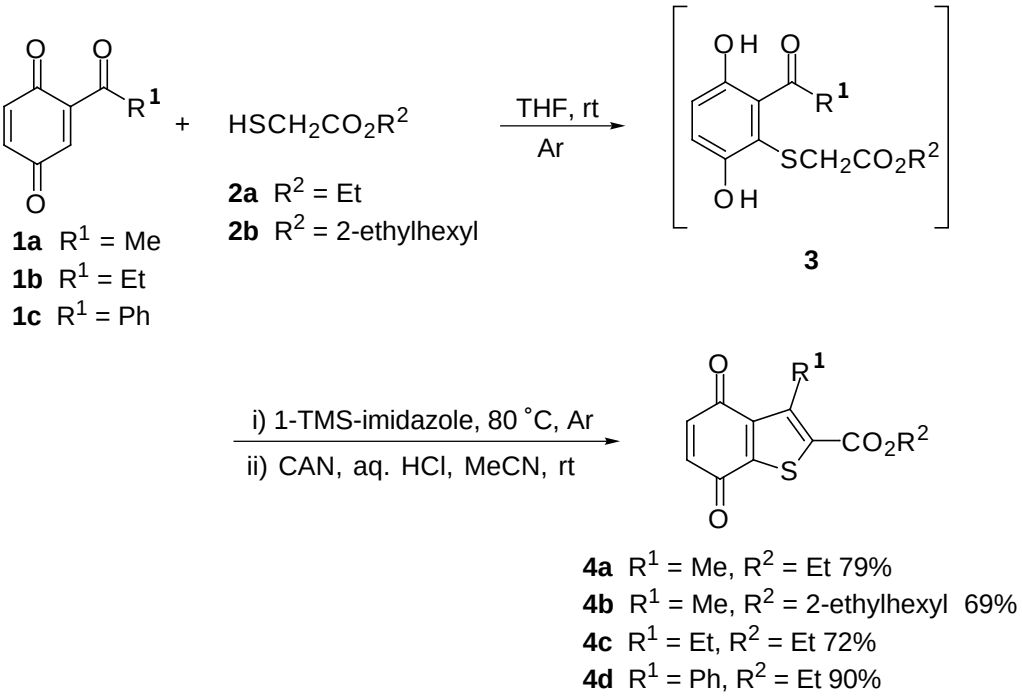
Abstract- 4,7-Dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**4**) have been synthesized in a one-pot procedure from 2-acyl-1,4-benzoquinones (**1**) and mercaptoacetates (**2**) by using 1-trimethylsilylimidazole as a protective reagent as well as a base. Thus, reaction of **1** with **2** in THF at room temperature was followed by treatment with excess of 1-trimethylsilylimidazole at 80 ˚C. Then the cooled mixture was hydrolyzed with hydrochloric acid and oxidized with cerium(IV) ammonium nitrate (CAN) to give the expected thiophenequinone derivatives (**4**). 4,9-Dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylates (**7**) were similarly prepared from 2-acyl-1,4-naphthoquinones (**5**) and mercaptoacetates, in general, by omitting the CAN oxidation procedure.

The compounds based on benzo[*b*]thiophene-4,7-dione or naphtho[2,3-*b*]thiophene-4,9-dione skeletons have received considerable attention because of their synthetic,[1] biological,[2] and industrial utilities.[3] Accordingly, a number of approaches to the construction of these systems have been developed.[4,5] Valderrama *et al.* have reported[6] that methyl 4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates are prepared from 2-acyl-1,4-benzoquinones and methyl mercaptoacetate in two to four step sequences. As a part of our study on the syntheses of heterocycle-fused quinone derivatives,[5,7] we investigated the possibility of modifying this method of Valderrama to a general and one-pot procedure to prepare benzo[*b*]thiophene-4,7-dione (**4**) and naphtho[2,3-*b*]thiophene-4,9-dione derivatives (**7**) as illustrated in Schemes 1 and 2, respectively. The success in our approach is attributable to the use of 1-trimethylsilylimidazole, which serves as both of a protective reagent and a base and provides easy



1a R^1 = Me
1b R^1 = Et
1c R^1 = Ph

2a R^2 = Et
2b R^2 = 2-ethylhexyl

3

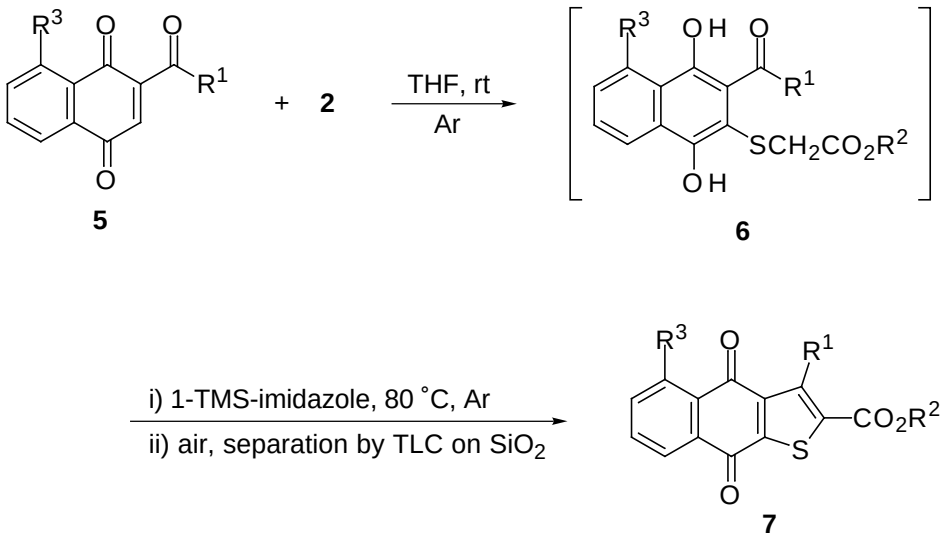
4a R^1 = Me, R^2 = Et 79%
4b R^1 = Me, R^2 = 2-ethylhexyl 69%
4c R^1 = Et, R^2 = Et 72%
4d R^1 = Ph, R^2 = Et 90%

Scheme 1.

deprotection.

The reactions for the preparation of 4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**4**) were carried out as depicted in Scheme 1. Thus, 2-acyl-1,4-benzoquinones (**1**) were treated with mercaptoacetates (**2**) in THF at room temperature. After removal of THF under reduced pressure, to the resulting 3-sulfenylated hydroquinone derivatives (**3**) was added excess 1-trimethylsilylimidazole to protect the hydroxy groups[8] and conduct thiophene ring formation, affording the 4,7-bis(trimethylsiloxy)benzo[*b*]thiophene-2-carboxylates. The reaction mixtures were then treated with aqueous HCl to deprotect the trimethylsilyl ethers and the resulting hydroquinones were exposed with CAN to give the expected thiophenequinone derivatives (**4**) in good yields. All these manipulations could be carried out in one-pot. When one of the 3-sulfenylated hydroquinone derivatives (**3**) was treated with two equivalents of 1-trimethylsilylimidazole, no thiophene ring formation occurred. This result indicates that imidazole, generated by the protection of a hydroxy group, cannot work as a base. The use of excess 1-trimethylsilylimidazole was essential for the satisfactory formation of the desired products.

This one-pot procedure was extended successfully to the preparation of 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylates (**7**) from 2-acyl-1,4-naphthoquinones (**5**) and mercaptoacetates (**2**) as illustrated in Scheme 2. In principle, the CAN oxidation could be omitted in the preparation of **7**. Thus, deprotection of trimethylsilyl ethers and oxidation were accomplished during workup and separation procedure (preparative TLC on silica gel). However, attempts to obtain **7g** in pure form by separating the reaction mixture by preparative TLC as conducted for **7a–f** afforded a mixture of



Scheme 2.

Table. Preparation of 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylates (**7**)

Entry	Naphthoquinone (**5**)	Mercaptoacetate (**2**)	Product (Yield/%)[a]
1	**5a** (R^1 = R^3 = H)	**2a** (R^2 = Et)	**7a** (53)
2	**5b** (R^1 = Me, R^3 = H)	**2a**	**7b** (84)
3	**5b**	**2b** (R^2 = 2-ethylhexyl)	**7c** (81)
4	**5c** (R^1 = Et, R^3 = H)	**2a**	**7d** (77)
5	**5d** (R^1 = *n*-Pr, R^3 = H)	**2a**	**7e** (80)
6	**5e** (R^1 = Ph, R^3 = H)	**2a**	**7f** (72)
7	**5f** (R^1 = Me, R^3 = OMe)	**2a**	**7g** (71)[b]

[a]Yields after purification by preparative TLC on silica gel. [b] CAN oxidation was needed.

7g and the respective hydroquinone derivative, and CAN oxidation was carried out in this case to obtain pure expected product (**7g**) in good yield.

In the present work, it was demonstrated that the reaction between 2-acyl-1,4-benzo(or naphtho)quinones (**1** or **5**) and mercaptoacetates (**2**), followed by treatment with 1-trimethylsilylimidazole, provides a one-pot general synthesis of benzo(or naphtho)thiophenequinone derivatives (**4** or **7**). The simple operation makes the present method attractive.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Perkin-Elmer 1600 Series FT IR spectrophotometer as KBr

disk. The ^{1}H NMR spectra were determined in $CDCl_3$ using $SiMe_4$ as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. *J* values are given in Hz. Low-resolution MS analyses were performed on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). TLC was carried out on a Merck Kieselgel 60 PF_{254}. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 2-Acetyl-1,4-benzoquinone (**1a**),[9] 2-formyl-1,4-naphthoquinone (**5a**),[10] 2-acetyl-1,4-naphthoquinone (**5b**),[11] and 2-acetyl-8-methoxy-1,4-naphthoquinone (**5f**)[10] were prepared following appropriate methods reported previously. Other acylquinones (**1b**, **1c**, and **5c-e**) were prepared by Kraus's photoacylation[12] using appropriate quinones and aldehydes, followed by Ag_2O oxidation[13] of the resulting 2-acylhydroquinone derivatives. 1-[2-(1,4-Dihydroxyphenyl)]propanone: mp 104–105 ˚C (Et_2O–benzene); ν_{max}/cm^{-1} 3379, 1643, 1628; δ_H 1.23 (3H, t, *J* = 7.3), 2.98 (2H, q, *J* = 7.3), 4.65 (1H, s), 6.88 (1H, d, *J* = 8.9), 7.01 (1H, dd, *J* = 8.9, 3.0), 7.21 (1H, d, *J* = 3.0), 11.90 (1H, s). Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.03; H, 6.08. 2-Propanoyl-1,4-benzoquinone (**1b**)**:** mp 43–45 ˚C (Et_2O–benzene); ν_{max}/cm^{-1} 1708, 1648; δ_H 1.15 (3H, t, *J* = 7.3), 2.89 (2H, q *J* = 7.3), 6.79 (1H, d, *J* = 9.9), 6.81 (1H, dd, *J* = 9.9, 2.0), 6.94 (1H, d, *J* = 2.0). Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 66.13; H, 4.84. 2-Benzoyl-1,4-benzoquinone (**1c**)**:** mp 79–80 ˚C (Et_2O–hexane); ν_{max}/cm^{-1} 1680, 1662, 1648; δ_H 6.81 (1H, d, *J* = 2.0), 6.87 (1H, d *J* = 9.9), 6.89 (1H, d, *J* = 9.9, 2.0), 7.50 (2H, t, *J* = 7.6), 7.62 (1H, t, *J* = 7.6), 7.83 (2H, d, *J* = 7.6). Anal. Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.73; H, 4.02. 1-(1,4-Dihydroxynaphthalen-2-yl)-1-propanone: mp 186–188 ˚C (benzene–hexane); ν_{max}/cm^{-1} 3362, 1636; δ_H 1.28 (3H, t, *J* = 7.3), 3.02 (2H, q, *J* = 7.3), 4.99 (1H, s), 7.02 (1H, s), 7.56 (1H, t, *J* = 8.5), 7.67 (1H, t, *J* = 8.5), 8.09 (1H, d, *J* = 8.5), 8.46 (1H, d, *J* = 8.5), 13.69 (1H, s). Anal. Calcd for $C_{13}H_{12}O_3$: C, 77.21; H, 5.59. Found: C, 77.00; H, 5.52. 2-Propanoyl-1,4-naphthoquinone (**5c**)**:**[14] mp 84–85 ˚C (Et_2O–hexane); ν_{max}/cm^{-1} 1689, 1672; δ_H 1.20 (3H, t, *J* = 7.3), 2.97 (2H, q, *J* = 7.3), 7.09 (1H, s), 7.75-7.85 (2H, m), 8.05–8.15 (2H, m). 2-Butanoyl-1,4-naphthoquinone (**5d**)**:**[14] mp 64–65 ˚C (Et_2O–hexane); ν_{max}/cm^{-1}1684, 1670; δ_H 0.99 (3H, t, *J* = 7.3), 1.73 (2H, sextet, *J* = 7.3), 2.92 (2H, t, *J* = 7.3), 7.07 (1H, s), 7.75-7.85 (2H, m), 8.05–8.15 (2H, m). 2-Benzoyl-1,4-naphthoquinone (**5e**)**:**[15] mp 157–160 ˚C (Et_2O-hexane); ν_{max}/cm^{-1} 1664; δ_H 7.00 (1H, s), 7.50 (2H, t, *J* = 7.6), 7.64 (1H, t, *J* = 7.6), 7.8–7.85 (2H, m), 7.89 (2H, d, *J* = 7.6), 8.1–8.2 (2H, m). All other chemicals used in this study were commercially available.

One-Pot Preparation of Ethyl 3-Methyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (4a) from 2-Acetyl-1,4-benzoquinone (1a) and Ethyl Mercaptoacetate (2a). Typical Procedure for the Preparation of Thiophenequinone Derivatives (4). To a stirred solution of **1a** (0.50 g, 3.4 mmol) in THF (15 mL) at rt under argon was added **2a** (0.40 g, 3.4 mmol).

After stirring for 15 min the solvent was removed under reduced pressure. To the resulting residue was added 1-trimethylsilylimidazole (2.4 g, 17 mmol), and the mixture was stirred at 80 °C for 3 h. To the cooled mixture were added acetonitrile (10 mL) and 10 % aq. HCl (5 mL). After stirring for 5 min, CAN (1.8 g, 3.4 mmol) solution in water (10 mL) was added. The resulting mixture was stirred for an additional 30 min and acetonitrile was evaporated. The precipitate was collected and recrystallized from hexane–Et_2O to give pure **4a** (0.67 g, 79%) as yellow solid; mp 122–125 °C; ν_{max}/cm^{-1} 1717, 1661; δ_H 1.41 (3H, t, *J* = 7.3), 2.86 (3H, s), 4.40 (2H, q, *J* = 7.3), 6.79 (1H, d, *J* = 10.2), 6.85 (1H, d, *J* = 10.2); MS *m/z* 250 (M^+, 34), 222 (87), 204 (100). Anal. Calcd for $C_{12}H_{10}O_4S$: C, 57.59; H, 4.03; S, 12.81. Found: C, 57.39; H, 4.02; S, 13.00.

Following the procedure described above for the preparation of **4a**, benzothiophenequinone derivatives (**4b**–**d**) were prepared. The physical and spectral data of these products are as follows.

2-Ethylhexyl 3-Methyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (4b): yellow solid; mp 83–85 °C (hexane–Et_2O); ν_{max}/cm^{-1} 1716, 1660; δ_H 0.85–1.0 (6H, m), 1.3–1.7 (9H, m), 2.87 (3H, s), 4.25–4.3 (2H, m), 6.79 (1H, d, *J* = 10.2), 6.87 (1H, d, *J* = 10.2); MS *m/z* 334 (M^+, 0.25), 70 (100). Anal. Calcd for $C_{18}H_{12}O_4S$: C, 64.64; H, 6.63. Found: C, 53.48; H, 6.62.

Ethyl 3-Ethyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (4c): yellow solid; mp 105–107 °C (hexane–Et_2O); ν_{max}/cm^{-1} 1716, 1664; δ_H 1.21 (3H, t, *J* = 7.4), 1.41 (3H, t, *J* = 7.1), 3.40 (2H, q, *J* = 7.4), 4.40 (2H, q, *J* = 7.1), 6.80 (1H, d, *J* = 10.2), 6.86 (1H, d, *J* = 10.2); MS *m/z* 264 (M^+, 47), 236 (44), 218 (100). Anal. Calcd for $C_{13}H_{12}O_4S$: C, 59.08; H, 4.58. Found: C, 59.11; H, 4.53.

Ethyl 3-Phenyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (4d): orange solid: mp 114–116 °C (hexane–Et_2O); ν_{max}/cm^{-1} 1727, 1669, 1658; δ_H 1.14 (3H, t, *J* = 7.3), 4.19 (2H, q, *J* = 7.3), 6.72 (1H, d, *J* = 10.2), 6.88 (1H, d, *J* = 10.2), 7.27.3 (2H, m), 7.35–7.5 (3H, m); MS *m/z* 312 (M^+, 14), 283 (100). Anal. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87. Found: C, 65.56; H, 4.01.

Ethyl 3-Methyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7b). Typical Procedure for the Preparation of the Naphthothiophenequinone Derivatives (7). To a stirred solution of 2-acetyl-1,4-naphthoquinone (**5b**) (0.13g, 0.67 mmol) in THF (2.7 mL) at rt under argon was added ethyl mercaptoacetate (**2a**) (81 mg, 0.67 mmol). After stirring for 15 min, the solvent was removed under reduced pressure. To the resulting residue was added 1-trimethylsilylimidazole (0.98 g, 6.7 mmol), and the mixture was heated at 80 °C for 3 h. The cooled resulting mixture was diluted by Et_2O (20 mL), washed successively with 10% aq. HCl and then brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was subjected to preparative TLC on silica gel (1 : 7 EtOAc-hexane) to give **7b** (0.17 g, 84%): yellow solid; mp 152–154 °C (hexane–Et_2O); ν_{max}/cm^{-1} 1720, 1670; δ_H 1.42 (3H, t, *J* = 7.3), 2.98 (3H, s), 4.41 (2H, q, *J* = 7.3), 7.7–7.85 (2H, m), 8.15–8.3 (2H, m); MS *m/z* 300

(M^+, 100). Anal. Calcd for $C_{16}H_{12}O_4S$: C, 63.99; H, 4.03; S, 10.68. Found: C, 64.16; H, 4.02; S, 10.69.

Naphthothiophenequinone derivatives (**7a**, **7c–f**) were prepared by the above-mentioned procedure for the preparation of **7b**.

Ethyl 4,9-Dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7a): yellow solid: mp 165–167 ˚C (hexane–Et_2O); ν_{max}/cm^{-1} 1728, 1672; δ_H 1.43 (3H, t, *J* = 7.3), 4.43 (2H, q, *J* = 7.3), 7.75–7.85 (2H, m), 8.2–8.3 (3H, m); MS *m/z* 286 (M^+, 16), 258 (34), 241 (100). Anal. Calcd for $C_{15}H_{10}O_4S$: C, 62.93; H, 3.52. Found: C, 62.92; H, 3.70.

2-Ethylhexyl 3-Methyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7c): yellow solid; mp 67–69 ˚C (hexane–Et_2O); ν_{max}/cm^{-1} 1717, 1670; δ_H 0.85–1.0 (6H, m), 1.35–1.55 (9H, m), 2.98 (3H, s), 4.28 (2H, d, *J* = 5.6), 7.7–8.0 (2H, m), 8.2–8.3 (2H, m); MS *m/z* 384 (M^+, 1.9), 272 (100). Anal. Calcd for $C_{22}H_{24}O_4S$: C, 68.72; H, 6.29. Found: C, 69.00; H, 6.29.

Ethyl 3-Ethyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7d): yellow solid; mp 148–149 ˚C (hexane–Et_2O); ν_{max}/cm^{-1} 1717, 1671, 1654; δ_H 1.28 (3H, t, *J* = 7.3), 1.43 (3H, t, *J* = 7.3), 3.52 (2H, q, *J* = 7.3), 4.41 (2H, q, *J* = 7.3), 7.7–7.85 (2H, m), 8.15–8.3 (2H, m); MS *m/z* 314 (M^+, 100). Anal. Calcd for $C_{17}H_{14}O_4S$: C, 64.95; H, 4.49. Found: C, 64.81; H, 4.48.

Ethyl 3-Propyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7e): yellow solid; mp 112–115 ˚C (hexane–Et_2O); ν_{max}/cm^{-1} 1722, 1670; δ_H 1.06 (3H, t, *J* = 7.3), 1.42 (3H, t, *J* = 7.3), 1.55–1.75 (2H, m), 3.47 (2H, t, *J* = 7.6), 4.41 (2H, q, *J* = 7.3), 7.7–7.85 (2H, m), 8.15–8.3 (2H, m); MS *m/z* 328 (M^+, 100). Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.84; H, 4.91. Found: C, 66.03; 4.90.

Ethyl 3-phenyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7f): yellow solid; mp 255–260 ˚C (hexane–Et_2O); ν_{max}/cm^{-1} 1727, 1673, 1658; δ_H 1.14 (3H, t, *J* = 7.3), 4.20 (2H, q, *J* = 7.3), 7.25–7.4 (2H, m), 7.45–7.5 (3H, m), 7.7–7.8 (2H, m), 8.0–8.15, 8.2–8.25 (2H, m); MS *m/z* 362 (M^+, 17), 333 (100). Anal. Calcd for $C_{21}H_{14}O_4S$: C, 69.60; H, 3.89. Found: C, 69.52; H, 3.90.

5-Methoxy-3-methyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-2-carboxylate (7g): This compound was prepared according to the procedure described above for the preparation of **4a**: yellow solid; mp 168–169 ˚C (hexane–Et_2O); ν_{max}/cm^{-1} 1720, 1668; δ_H 1.41 (3H, t, *J* = 7.3), 2.95 (3H, s), 4.05 (3H, s), 4.40 (2H, q, *J* = 7.3), 7.35 (1H, d, *J* = 8.2), 7.68 (1H, t, *J* = 8.2), 8.88 (1H, d, *J* = 8.2); MS *m/z* 330 (M^+, 100). Anal. Calcd for $C_{17}H_{14}O_5S$: C, 61.81; H, 4.27. Found: C, 61.94; H, 4.34.

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