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Efficient Conversion of Sulfones into β-Keto Sulfones by *N*-Acylbenzotriazoles§

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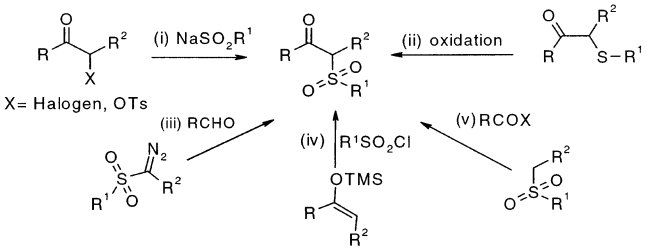
Acyclic sulfones **4a**−**f** and alicyclic sulfone **7** react with readily available *N*-acylbenzotriazoles **3a**−**g** (derived from aliphatic, aromatic, and heteroaromatic carboxylic acids) to provide the corresponding β-keto sulfones **5a**−**n** and **8a**−**c**, respectively, in good to excellent yields.

Introduction

Sulfones are of great importance in organic synthesis.[1] Among their derivatives, β-keto sulfones possess widespread synthetic applications. β-Keto sulfones are utilized as intermediates in the synthesis of, among others, disubstituted acetylenes,[2] olefins,[2d] allenes,[3] vinyl sulfones,[4] and polyfunctionalized 4*H*-pyrans.[5] β-Keto sulfones are useful intermediates for the syntheses of ketones[6] by facile reductive elimination of the sulfonyl group. In addition, β-keto sulfones are precursors for optically active β-hydroxy sulfones.[7] Certain β-keto sulfone derivatives exhibit fungicidal activity.[8]

Available routes to β-oxo-sulfones (Scheme 1) include (i) alkylation of metallic arene sulfinates with either α-halo-ketones[9] or α-tosyloxy-ketones;[10] (ii) oxidation of β-oxo-sulfides,[11] (iii) reactions of diazo sulfones with aldehydes,[12] (iv) reactions of sulfonyl chlorides with silyl enol ethers,[13] and (v) acylation of alkyl sulfones.

SCHEME 1



Method (v) is most commonly used to provide β-oxo-sulfones; it typically employs esters[14] or acid chlorides[15] as acylating agents. The methodology quoted in ref 14a−c is appropriate only when a readily available sulfone is being used: the quoted yields of 60−94% (average 77%) are based on the amount of ester utilized, whereas recalculation based on the sulfone used gives yields of 17−45% (average 31%). The methodology quoted in refs 14e and 15b is appropriate only when a readily available ester or acid chloride is being used: the quoted yields of 62−80% (average 71%) are based on the sulfone, whereas yields based on ester or acid chloride are 35−53% (average 44%). In the procedure of ref 14d, a 1:1 ratio of reagents gave yields of 71−94%; however, the use of both TMEDA and HMPA were required. Reference 15a needs the formation of sulfone dianions.

§ Dedicated to our friend Professor Ameen Farouk M. Fahmy in celebration of his 60th birthday and his 40 years of teaching and research at Ain Shams University, Egypt.

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SCHEME 2

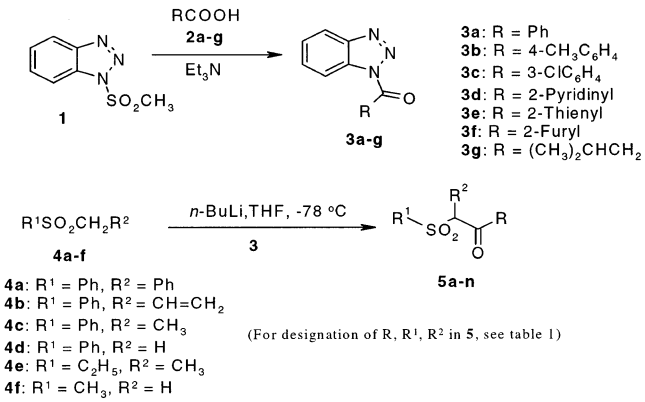


TABLE 1. Preparation of *β*-Keto Sulfones 5a−n via C-Acylation of Alkyl Sulfones with *N*-Acylbenzotriazoles

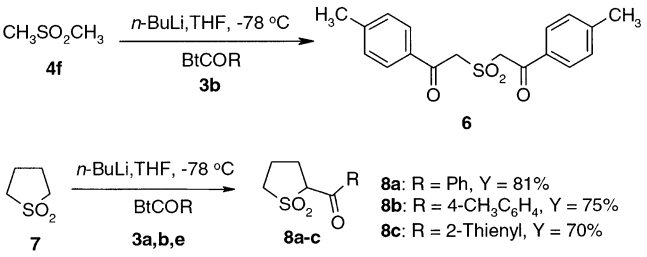
entry	R	R^1	R^2	yield (%)
5a	Ph	Ph	Ph	95
5b	3-ClC_6H_4	Ph	Ph	92
5c	2-pyridinyl	Ph	Ph	83
5d	2-furyl	Ph	Ph	89
5e	$(CH_3)_2CHCH_2$	Ph	Ph	96
5f	2-thienyl	Ph	$CH=CH_2$	85
5g	Ph	Ph	$CH=CH_2$	90
5h	4-$CH_3C_6H_4$	Ph	CH_3	87
5i	2-pyridinyl	Ph	CH_3	81
5j	2-furyl	Ph	CH_3	86
5k	$(CH_3)_2CHCH_2$	Ph	H	83
5l	2-thienyl	Ph	H	93
5m	Ph	CH_3CH_2	CH_3	79
5n	2-thienyl	CH_3	H	73

N-Acylbenzotriazoles have been used as effective reagents for the N-acylation of amines,[16] C-acylation of ketones,[17] and O-acylation of aldehydes.[18] We have recently employed *N*-acylbenzotriazoles in an efficient synthesis of *β*-keto nitriles from primary and secondary alkyl nitriles.[19] As a further application of *N*-acylbenzotriazoles, we now report a convenient preparation of *β*-keto sulfones **5a**−**n** and **8a**−**c** in yields of 70−96% (average 83%) based on using the reagent in a 1:1 ratio.

Results and Discussion

Treatment of the lithio-derivatives of sulfones **4a**−**f** (generated by the lithiation of the sulfones with *n*-BuLi) at −78 °C with *N*-acylbenzotriazoles **3a**−**g**, which were prepared from the corresponding carboxylic acids **2a**−**g** and 1-(methylsulfonyl)benzotriazole **1** as previously reported[16] (Scheme 2), gave aliphatic, aromatic, and heteroaromatic *β*-oxo-sulfones **5a**−**n** (Scheme 2 and Table 1). This synthetic route improved the previously reported[20] yield of compound **5a** from 63% to 95% and afforded previously unreported *β*-oxo-sulfones **5b**−**n** in isolated yields of 73−96%. Exceptionally, the reaction of *N*-(4-methylbenzoyl)benzotriazole **3b** with dimethyl sulfone **4f** under the same reaction conditions provided the corresponding diacylated sulfone **6** in 44% yield based on acylating agent **3b**, instead of the expected monoacylated product of type **5** (Scheme 3). The conceptually similar acylation of dimethyl sulfone with *N*-acylimidazoles reported by Ibarra et al.[21] utilized 5 molar equiv of both the starting sulfone and base to afford seven examples of *β*-keto sulfones; the average yield was 61% based on the acylating agent.

SCHEME 3



Application of our methodology to heterocyclic sulfone **7** (sulfolane) allowed the synthesis of previously unreported *β*-keto sulfones **8a**−**c** in 72−81% yields (Scheme 3).

The structures of compounds **5a**−**n**, **6**, and **8a**−**c** were supported by NMR spectrometry and elemental analyses. The ^{1}H NMR spectra of the *β*-oxo-sulfones **5a**−**n**, **6**, and **8a**−**c** each showed a characteristic signal in the region 4.52−7.36 ppm, which was assigned to the proton attached to a carbon flanked between sulfonyl and carbonyl groups. In the ^{13}C NMR spectra, the newly formed carbonyl group in compounds **5a**−**n**, **6**, and **8a**−**c** exhibited signals in the region 180.2−199.8 ppm.

For optimum yields, the reactions of *N*-acylbenzotriazoles **3** with sulfones required 2 molar equiv of *n*-BuLi, since the *β*-keto sulfones formed are rapidly deprotonated by unreacted carbanions under the reaction conditions. For **4a**, the use of 1.2 equiv of base under the same reaction conditions provided the acylated sulfone **5a** in 62% yield. The generality of this method has been tested by using *N*-acylbenzotriazoles **3** derived from aliphatic, aromatic, and heteroaromatic acids and a variety of sulfones.

In summary, we have developed a convenient and general method for the synthesis of aliphatic, aromatic, and heteroaromatic ketones of type **5** and **8** via *N*-acylbenzotriazoles **3**. This approach uses sulfone and readily available *N*-acylbenzotriazole in a 1:1 ratio and affords yields that range from 70% to 96% (Schemes 2 and 3 and Table 1), thus demonstrating the potential of *N*-acylbenzotriazoles **3** as effective C-acylation reagents, particularly when it is advantageous to use sulfone and acylating reagent in stochiometic ratio.

Experimental Section

General. Melting points were determined on a hot stage apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as internal standard for ^{1}H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Microanalyses were performed on elemental analyzer. Anhydrous THF was obtained by distillation immediately prior to

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use. Column chromatography was conducted with silica gel 200−425 mesh. $BtSO_2CH_3$ (**1**) and *N*-acylbenzotriazoles **3a**−**g** were prepared according to literature procedures.[16]

General Procedures for the Preparation of β-Keto Sulfones 5a−**l.** A solution of the alkyl sulfone **4** (2 mmol) in anhydrous THF (15 mL) was cooled to −40 °C under nitrogen and thereafter treated dropwise with *n*-BuLi (2.6 mL of 1.55 M in hexane, 4 mmol) to afford a yellow mixture, which was stirred at this temperature for 1 h. After the mixture cooled to −78 °C, a solution of *N*-acylbenzotriazole **3** (2 mmol) in THF (10 mL) was slowly added. The reaction was allowed to warm to room temperature while stirring overnight, quenched by the addition of saturated NH_4Cl, and extracted with EtOAc. The organic extracts were combined, washed with brine and water, and dried over $MgSO_4$. After evaporation under vacuum, the residue was purified by flash chromatography (hexanes/EtOAc, 5:1) to afford the desired product **5**.

1,2-Diphenyl-2-(phenylsulfonyl)-1-ethanone (5a). Colorless microcrystals (95%), mp 118−120 °C, (lit.[20] 138−140 °C). ^{1}H NMR δ 7.87 (d, J = 7.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.61−7.51 (m, 2H), 7.43−7.28 (m, 9H), 6.15 (s, 1H). ^{13}C NMR δ 190.7, 136.9, 136.0, 134.0, 133.9, 130.4, 130.3, 129.7, 128.9, 128.8, 128.7, 128.5, 128.4, 76.2. Anal. Calcd for $C_{20}H_{16}O_3S$: C, 71.41; H, 4.79. Found: C, 71.07; H, 4.92.

1-(3-Chlorophenyl)-2-phenyl-2-(phenylsulfonyl)-1-ethanone (5b). Colorless microcrystals (92%), mp 127−129 °C. ^{1}H NMR δ 7.84 (t, J = 1.9 Hz, 1H), 7.73 (dt, J = 1.2, 7.8 Hz, 1H), 7.65−7.57 (m, 3H), 7.51−7.28 (m, 9H), 6.08 (s, 1H). ^{13}C NMR δ 189.5, 137.5, 136.5, 135.2, 134.1, 133.9, 130.3, 130.2, 130.1, 129.8, 129.0, 128.7, 128.4, 128.1, 126.8, 76.1. Anal. Calcd for $C_{20}H_{15}ClO_3S$: C, 64.77; H, 4.08. Found: C, 64.65; H, 4.03.

2-Phenyl-2-(phenylsulfonyl)-1-(2-pyridinyl)-1-ethanone (5c). Colorless plates (83%), mp 92−94 °C. ^{1}H NMR δ 8.61 (d, J = 4.3 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.65 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.47−7.36 (m, 6H), 7.32−7.24 (m, 3H). ^{13}C NMR δ 191.5, 151.6, 148.9, 137.3, 137.1, 133.7, 130.7, 129.7, 129.2, 128.5, 128.4, 128.3, 127.9, 122.7, 71.8. Anal. Calcd for $C_{19}H_{15}NO_3S$: C, 67.64; H, 4.48; N, 4.15. Found: C, 67.88; H, 4.63; N, 4.00.

1-(2-Furyl)-2-phenyl-2-(phenylsulfonyl)-1-ethanone (5d). Colorless needles (89%), mp 133−135 °C. ^{1}H NMR δ 7.63 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.0 Hz, 2H), 7.43−7.25 (m, 8H), 6.54−6.52 (m, 1H), 6.05 (s, 1H). ^{13}C NMR δ 178.7, 151.7, 147.6, 136.6, 134.0, 130.5, 130.1, 129.5, 128.6, 128.4, 128.1, 119.6, 113.2, 75.1. Anal. Calcd for $C_{18}H_{14}O_4S$: C, 66.24; H, 4.32. Found: C, 65.88; H, 4.35.

4-Methyl-1-phenyl-1-(phenylsulfonyl)-2-pentanone (5e). Colorless plates (96%), mp 103−105 °C. ^{1}H NMR δ 7.61−7.56 (m, 3H), 7.43−7.23 (m, 7H), 5.24 (s, 1H), 2.58 (dd, J = 17.2, 6.6 Hz, 1H), 2.43 (dd, J = 17.2, 6.9 Hz, 1H), 2.19−2.06 (m, 1H), 0.87 (d J = 6.7 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H). ^{13}C NMR δ 199.8, 136.6, 133.9, 130.3, 129.8, 129.5, 128.6, 128.4, 127.7, 79.5, 53.4, 24.0, 22.2, 22.1. Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37. Found: C, 68.36; H, 6.51.

1-(2-Thienyl)-2-(phenylsulfonyl)-3-buten-1-one (5f). Colorless plates (85%), mp 88−90 °C. ^{1}H NMR δ 7.85−7.81 (m, 3H), 7.75 (dd, J = 5.0, 1.1 Hz, 1H), 7.69−7.63 (m, 1H), 7.56−7.51 (m, 2H), 7.18−7.15 (m, 1H), 6.04−5.92 (m, 1H), 5.51−5.37 (m, 3H). ^{13}C NMR δ 182.6, 143.2, 136.4, 136.3, 134.4, 134.3, 130.1, 128.7, 128.6, 126.5, 125.2, 76.0. Anal. Calcd for $C_{14}H1_2O_3S_2$: C, 57.51; H, 4.14. Found: C, 57.13; H, 4.10.

1-Phenyl-2-(phenylsulfonyl)-3-buten-1-one (5g). Colorless prisms (90%), mp 99−101 °C. ^{1}H NMR δ 7.98 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.69−7.47 (m, 6H), 6.05−5.93 (m, 1H), 5.64 (d, J = 8.9 Hz, 1H), 5.50−5.41 (m, 2H). ^{13}C NMR δ 190.6, 136.6, 136.1, 134.2, 134.1, 130.1, 129.0, 128.8, 128.7, 127.1, 125.1, 74.4. Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found: C, 66.76; H, 5.13.

1-(4-Methylphenyl)-2-(phenylsulfonyl)-1-propanone (5h). Colorless plates (87%), mp 87−89 °C. ^{1}H NMR δ 7.87 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 7.9 Hz, 2H), 7.67−7.62 (m, 1H), 7.54−7.49 (m, 2H), 7.27 (d, J = 7.6 Hz, 2H), 5.15 (q, J = 6.9 Hz, 1H), 2.42 (s, 3H), 1.56 (d, J = 6.9 Hz, 3H). ^{13}C NMR δ 191.9, 145.3, 136.0, 134.1, 133.7, 129.8, 129.5, 129.3, 128.8, 64.8, 21.7, 13.2. Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.71; H, 5.78.

2-(Phenylsulfonyl)-1-(2-pyridinyl)-1-propanone (5i). Colorless plates (81%), mp 79−81 °C. ^{1}H NMR δ 8.60 (d, J = 4.3 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.86−7.80 (m, 3H), 7.62−7.46 (m, 4H), 6.27 (q, J = 7.0 Hz, 1H), 1.60 (d, J = 7.0 Hz, 3H). ^{13}C NMR δ 193.9, 151.9, 148.9, 137.4, 137.1, 133.8, 129.4, 128.8, 127.7, 122.6, 61.8, 12.1. Anal. Calcd for $C_{14}H_{13}O_3S$: C, 61.07; H, 4.76; N, 5.09. Found: C, 60.86; H, 4.84; N, 4.79.

1-(2-Furyl)-2-(phenylsulfonyl)-1-propanone (5j). Colorless needles (86%), mp 93−95 °C. ^{1}H NMR δ 7.81 (d, J = 7.8 Hz, 2H), 7.67−7.50 (m, 4H), 7.32 (d, J = 3.6 Hz, 1H), 6.57 (d, J = 3.3 Hz, 1H), 4.97 (q, J = 7.0 Hz, 1H), 1.56 (d, J = 7.0 Hz, 3H). ^{13}C NMR δ 180.2, 151.9, 147.8, 136.2, 134.1, 129.6, 128.9, 119.9, 113.1, 65.5, 12.0. Anal. Calcd for $C_{13}H_{12}O_4S$: C, 59.08; H, 4.58. Found: C, 59.03; H, 4.73.

4-Methyl-1-(phenylsulfonyl)-2-pentanone (5k). Colorless plates (83%), mp 44−46 °C. ^{1}H NMR δ 7.89 (d, J = 7.4 Hz, 2H), 7.71−7.56 (m, 3H), 4.14 (s, 2H), 2.58 (d, J = 6.7 Hz, 2H), 2.18−2.05 (m, 1H), 0.91 (d, J = 6.7 Hz, 6H). ^{13}C NMR δ 197.7, 138.6, 134.2, 129.3, 128.2, 66.9, 53.1, 23.9, 22.2. Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.98; H, 6.71. Found: C, 60.03; H, 7.03.

2-(Phenylsulfonyl)-1-(2-thienyl)-1-ethanone (5l). Colorless plates (92%), mp 79−80 °C. ^{1}H NMR δ 7.90 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 3.9 Hz, 1H), 7.76 (d, J = 4.9 Hz, 1H), 7.70−7.65 (m, 1H), 7.59−7.54 (m, 2H), 7.17 (dd, J = 3.9, 4.9 Hz, 1H), 4.63 (s, 2H). ^{13}C NMR δ 180.1, 143.1, 138.4, 136.4, 135.2, 134.3, 129.2, 128.7, 128.5, 64.4. Anal. Calcd for $C_{12}H_{10}O_3S_2$: C, 54.12; H, 3.78. Found: C, 53.91; H, 3.60.

General Procedures for the Preparation of β-Keto Sulfones 5m,n, 6, and 8a−**c.** A solution of the alkyl sulfone (2 mmol) in anhydrous THF (15 mL) was cooled to 0 °C under nitrogen and thereafter treated dropwise with *n*-BuLi (2.6 mL of 1.55 M in hexane, 4 mmol) to afford a yellow mixture, which was warmed to room temperature and stirred at this temperature for 1 h. After the mixture cooled to −78 °C, a solution of *N*-acylbenzotriazole **3** (2 mmol) in THF (10 mL) was slowly added. The reaction was allowed to warm to room temperature while stirring overnight, quenched by the addition of saturated NH_4Cl, and extracted with EtOAc. The organic extracts were combined, washed with brine and water, and dried over $MgSO_4$. After evaporation under vacuum, the residue was purified by flash chromatography (hexanes/EtOAc, 5:1) to afford the desired product.

2-(Ethylsulfonyl)-1-phenyl-1-propanone (5m). Colorless microcrystals (79%), mp 35−37 °C. ^{1}H NMR δ 8.06−8.02 (m, 2H), 7.68−7.62 (m, 1H), 7.56−7.50 (m, 2H), 5.03 (q, J = 7.1 Hz, 1H), 3.21−3.10 (m, 2H), 1.74 (d, J = 7.1 Hz, 3H), 1.39 (t, J = 7.6 Hz, 3H). ^{13}C NMR δ 193.8, 135.7, 134.4, 129.2, 128.9, 63.5, 43.6, 13.3, 5.0. Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.23; H, 6.31.

2-(Methylsulfonyl)-1-(2-thienyl)-1-ethanone (5n). Colorless plates (73%), mp 98−100 °C. ^{1}H NMR δ 7.85 (d, J = 3.9 Hz, 1H), 7.82 (d, J = 4.9 Hz, 1H), 7.20−7.23 (m, 1H), 4.52 (s, 2H), 3.16 (s, 3H). ^{13}C NMR δ 181.3, 142.9, 137.1, 135.4, 128.9, 62.2, 41.7. Anal. Calcd for $C_{11}H_{14}O_3S$: C, 41.16; H, 3.95. Found: 41.55; H, 3.71.

1-(4-Methylphenyl)-2-{[2-(4-methylphenyl)-2-oxoethyl]-sulfonyl}-1-ethanone (6). Colorless needles (44%), mp 137−139 °C. ^{1}H NMR δ 7.86 (d, J = 8.1 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 4.98 (s, 4H), 2.43 (s, 6H). ^{13}C NMR δ 188.9, 145.9, 133.2, 129.7, 128.9, 59.7, 21.8. Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49. Found: C, 65.41; H, 5.77.

2-Benzoyltetrahydrothiophene-1,1-dione (8a). Colorless plates (81%), mp 83−85 °C. ^{1}H NMR δ 8.09 (d, J = 7.6 Hz, 2H), 7.66−7.61 (m, 1H), 7.55−7.50 (m, 2H), 4.90 (t, J = 7.6 Hz, 1H), 3.24−3.11 (m, 2H), 2.90−2.82 (m, 1H), 2.43−2.21 (m, 3H). ^{13}C NMR δ 190.0, 136.2, 134.3, 129.0, 128.9, 65.3, 52.6,

26.0, 20.6. Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.95; H, 5.38.

2-(4-Methylbenzoyl)tetrahydrothiophene-1,1-dione (8b). Colorless plates (77%), mp 94−96 °C. ^{1}H NMR δ 7.98 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.87 (t, J = 7.5 Hz, 1H), 3.23−3.08 (m, 2H), 2.89−2.81 (m, 1H), 2.43 (s, 3H), 2.40−2.17 (m, 3H). ^{13}C NMR δ 189.5, 145.5, 133.9, 129.7, 129.1, 65.2, 52.6, 25.9, 21.8, 20.6. Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.38; H, 6.14.

2-(2-Thienylcarbonyl)tetrahydrothiophene-1,1-dione (8c). Colorless plates (72%), mp 100−102 °C. ^{1}H NMR δ 7.94 (d, J = 3.8 Hz, 1H), 7.78 (d, J = 5.0 Hz, 1H), 7.21 (dd, J = 3.8, 5.0 Hz, 1H), 4.71 (t, J = 7.6 Hz, 1H), 3.27−3.09 (m, 2H), 2.87−2.77 (m, 1H), 2.46−2.33 (m, 2H), 2.30−2.17 (m, 1H). ^{13}C NMR δ 182.4, 143.8, 136.1, 134.3, 128.8, 66.6, 52.3, 25.6, 20.5. Anal. Calcd for $C_9H_{10}O_3S_2$: C, 46.94; H, 4.38. Found: C, 47.22; H, 4.3

Supporting Information Available: General procedure and characterization data for compounds **5a**−**n**, **6**, and **8a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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