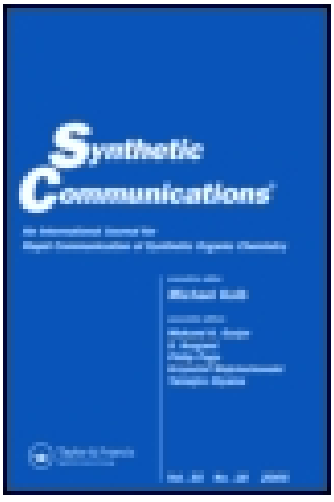

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K. C. Majumdar [a], B. Chattopadhyay [a] & S. Nath [a]
[a] Department of Chemistry, University of Kalyani, Kalyani, India
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Regioselective Synthesis of Benzofuran-Annulated Six-Membered Sulfur Heterocycles by Aryl Radical Cyclization

K. C. Majumdar, B. Chattopadhyay, and S. Nath
Department of Chemistry, University of Kalyani, Kalyani, India

Abstract: The tin hydride–mediated cyclization of a number of sulfides and sulfones under mild and neutral conditions has been investigated. The sulfides were in turn derived from 3(2*H*) benzothiofuranone and 2-bromobenzyl bromides by phase-transfer-catalyzed reaction, and the corresponding sulfones were prepared by treatment of the corresponding sulfides with *m*-CPBA at room temperature. The sulfides and sulfones were then reacted with $^{n}Bu_3SnH$-AIBN to afford regioselectively benzofuran-annulated six-membered sulfur heterocycles.

Keywords: 6-endo trig, radical cyclization, regioselective, sulfur heterocycles, tri-n-butyltin hydride

INTRODUCTION

Recently, aryl radical cyclization has been developed as a powerful method for constructucting carbon-carbon bonds in organic synthesis.[1] These radical cyclization protocols commonly have several advantages over nonradical methods; for example, radical cyclization can be carried out in neutral solutions. Previously, we synthesized several novel heterocyclic systems containing sulfur by sigmatropic rearrangement.[2] During the course of our studies, we have noted the unusual formation of [6,6]pyranothiopyrans during the second Claisen rearrangement step.[3] An examination of the

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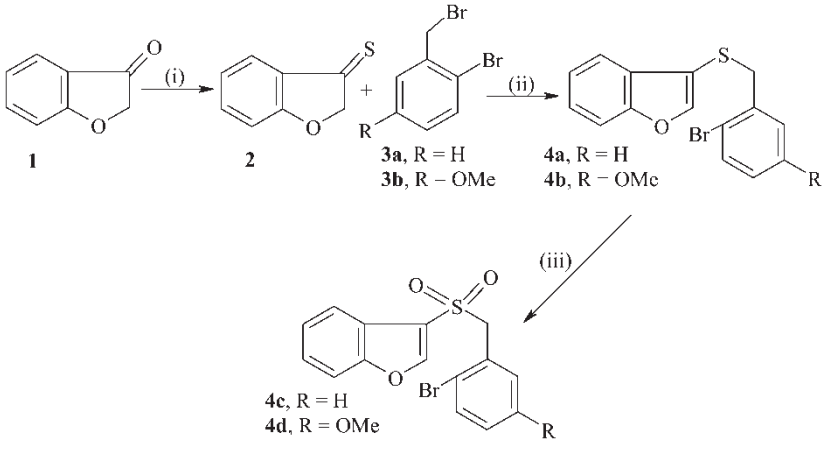
Address correspondence to K. C. Majumdar, Department of Chemistry, University of Kalyani, Kalyani, 741235, W.B., India. E-mail: kcm_ku@yahoo.co.in

literature[4] reveals only scattered examples of the synthesis of sulfur-based heterocycles via radical methods. These include cyclizations with sulfur functionality in the hexenyl chain at the 3-[5] and 4-positions[6] and an example of a sulfonylated radical in the 2-position.[7] Several useful radical cyclizations with sulfur functionality located α to the radical center have also been reported, but these yield cyclic products with the sulfur functionality external to the ring.[8] We also have recently succeeded in the regioselective synthesis of [6,6] fused cyclic sulfur heterocycles by tri-*n*-butyltin hydride–mediated cyclization.[9] In this context, we undertook a study on the radical cyclization of the sulfides (**4a**,**b**) and their corresponding sulfones (**5a**,**b**). Here we report the results.

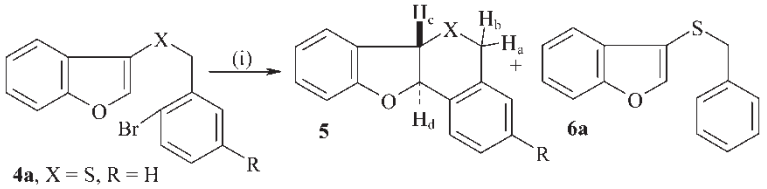
RESULTS AND DISCUSSIONS

The starting materials **4a**,**b** were synthesized in 80–95% yield by the phase-transfer-catalyzed alkylation of 3(2*H*) benzothiofuranone **2**, with either 2-bromobenzyl bromide **3a** or 2-bromo-5-methoxybenzyl bromide **3b**, in dichloromethane and 1% aq. NaOH solution in the presence of benzyltriethylammonium chloride (BTEAC) at room temperature for 30 min. The other starting materials **4c**,**d** were prepared from the corresponding sulfides **4a**,**b**, by treatment with 2 equiv. of *m*-CPBA in dry dichloromethane solution at room temperature. The compound **2**, 3(2*H*)-benzothiofuranone, was in turn prepared by the reaction of 3(2*H*) benzofuranone[10] with P_2S_5 in dry THF solution in the presence of sodium bicarbonate (Scheme 1).



Scheme 1. Reagents and conditions: (i) dry THF, P_2S_5, $NaHCO_3$, stirring, rt, 30 min; (ii) PTC, 1% NaOH(aq), CH_2Cl_2, 30 min; (iii) *m*-CPBA (2-equiv), CH_2Cl_2, stirring, rt, 3–4 h.

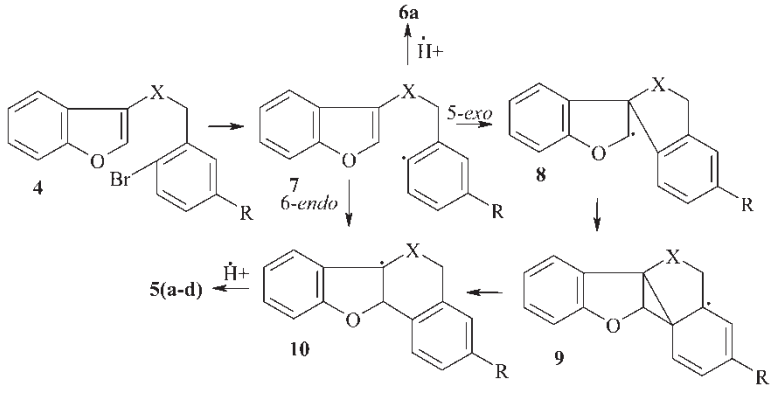
Compounds **4** were characterized from their elemental analyses and spectroscopic data. The IR spectrum of **4c** showed characteristic S═O stretching frequencies at $\nu_{max} = 1314$ (sym.) and 1125 (asym.) cm^{-1}. The two-proton singlet due to S-C**H**$_2$ protons of **4a** at $\delta_H = 4.04$ was shifted by 0.66 ppm downfield in **4c** (i.e., the two proton singlet of SO_2-C**H**$_2$ protons of **4c** appeared at $\delta_H = 4.70$). The substrate **4a** was treated at 80°C in dry degassed toluene under a nitrogen atmosphere with $^nBu_3SnH$ in the presence of AIBN as radical initiator for 4 h to afford the cyclic product **5a** (yield 90%), accompanied by a small amount of the debrominated product **6a** (10% yield). This debromination was inhibited by the conversion of the sulfides to the corresponding sulfones. Exposure of the sulfone **4c** to $^nBu_3SnH$ under the same reaction conditions as described previously afforded the cyclized heterocyclic sulfone **5c** in 96% yield. The structure of the compounds **5** (X = S, SO_2) were readily elucidated by ^{1}H NMR spectroscopy, which exhibited a one-proton doublet at $\delta_H = 4.80–4.82$ ($J = 8.0$ Hz) and another one proton doublet at $\delta_H = 5.82–5.84$ ($J = 8.0$ Hz) due to ring junction protons H_c and H_d respectively, for **5a** (X = S), whereas the same two protons resonated at $\delta_H = 4.69–4.70$ ($J = 8.8$ Hz) and 6.06–6.09 ($J = 8.8$ Hz), respectively, for **5c** (X = SO_2). The stereochemistry of the ring fusion of the cyclic system can be surmised from the molecular model (Dreiding model), which shows a *trans*-arrangement, and also from the high coupling constants of **5a** (X = S, $J = 8.0$ Hz) and **5c** (X = SO_2, $J = 8.8$ Hz). The ^{13}CNMR spectrum of **5c** (X = SO_2, R = H) also supported the proposed structure. The ^{13}C NMR chemical shift as well as the multiplicity of the signals in compound **5c** was established by a distortionless enhancement of polarization transfer (DEPT) experiment. There are 11 protonated carbons, one CH_2 and ten CH moieties. The mass spectrum of compounds **5a** and **5c** showed molecular ion peaks at $m/z = 240$ and 270 (M^+) respectively. The generality of the reaction was tested by subjecting two other substrates **4b** and **4d** under the same reaction conditions to give the products **5b** and **5d** in excellent yields (Scheme 2).



4a, X = S, R = H
4b, X = S R = OMc
4c, X = SO_2, R = H
4d, X = SO_2, R = OMe

5	X	R	Yield (%)
a	S	H	90
b	S	OMc	95
c	SO_2	H	96
d	SO_2	OMe	93

Scheme 2. Reagents and conditions: (i) $^nBu_3SnH$, AIBN, toulene, N_2 atm, reflux, 4 h.



Scheme 3.

The mechanistic pathway for the formation of six-membered sulfur heterocycles **5** from the substrates **4** is outlined in Scheme 3. The aryl radical **7** is generated in the reaction by $^{n}Bu_3SnH$ and AIBN. The radical **7** on addition of a hydrogen radical from tri-n-butyl tin hydride afforded the debrominated product **6a**. The formation of six-membered sulfur heterocyclic ring in products **5a**–**d** from the substrates **4a**–**d** may be explained by the initial formation of the aryl radical **7** followed by a 6-*endo* trig ring closure to give a tertiary radical **10**, which may then accept a hydrogen radical to afford the final products **5a**–**d**. In an alternative route, the aryl radical **7** may undergo a 5-*exo* trig ring closure to generate a spiro heterocyclic radical **8**,[11] which may be converted to the tertiary radical **10** via radical **9** by a neophyl[12] rearrangement. The reaction pathway, whether a 6-e*ndo* or a 5-*exo* ring closure, can be predicted by the application of the frontier molecular orbital (FMO) theory. According to the theory, the aryl radicals are a high-energy species and have nucleophilic character. The presence of a high-election-withdrawing SO_2 group confers considerable electrophilic character to the C_2-position of the benzofuran moiety. In the nucliophilic radical **7**, FMO theory suggests that the mode of ring closure should largely be determined by the interaction between the radical singly occupied molecular orbital (SOMO) (i.e., highest occupied molecular orbital (HOMO)) and alkene lowest unoccupied molecular orbital (LUMO) of the acceptor (election-deficient center), and accordingly more favorable bond formation should occur between the radical center (nucleophilic) and C_2 of the benzofuran moiety, leading to 6-*endo* trig cyclization. Again, if we compare the two paths (i.e., 6-*endo* trig and 5-*exo* trig cyclization) for the resulting intermediate products radical **10** and **8**, the stability of the intermediate product radical **10** is higher than the stability of the intermediate product radical **8**. Because in intermediate **10**, the radical is at the immediate vicinity of the strong electron-withdrawing SO_2, the S group

therefore is highly stabilized[13] and expected to follow the 6-*endo* trig cyclization mode, giving the six-membered sulfur heterocyclic compounds **5**. One interesting observation is that the usual oxidation does not occur at the present instance and the dihydro compound is isolated in excellent yield. The usual course during this type of cyclization is that the initially formed dihydro products give oxidized products by aerial oxidation, i.e., an oxidation step in $^{n}Bu_3SnH$-mediated cyclization.[14]

In conclusion, we have performed the $^{n}Bu_3SnH$-mediated radical cyclization methodology to the regioselective synthesis of tetracyclic sulfur heterocyclic compounds solely by the 6-*endo* trig cyclization path. The mildness of the reaction conditions and the high degree of the chemoselectivity allow this radical cyclization to serve as a powerful synthetic tool. This methodology is a general one and is attractive by its simplicity.

EXPERIMENTAL

General Remarks

Melting points are determined in open capillaries and are uncorrected. IR spectra were recorded on a Perkin Elmer L120-000A spectrometer (ν_{max} in cm^{-1}) using samples as neat; solid samples were recorded in KBr disks. NMR spectra were recorded on Bruker DPX-400 and Bruker DPX-500 spectrometers in $CDCl_3$ (chemical shifts in δ) with TMS as the internal standard. Silica gel (60–120 mesh, E-mark, India) was used for chromatographic separation. Silica gel G (E-mark, India) was used for thin-layer chromatography (TLC). Petroleum ether refers to the fraction boiling between 60 and 80°C.

3(2*H*)-Benzofuranone was prepared according to the published procedure.[10]

General Procedure for the Preparation of 3(2*H*)-Benzothiofuranone

To a magnetically stirred solution of 3(2*H*)-benzofuranone (**1**) (0.53 g, 4 mmol) and phosphorous pentasulfide (0.89 g, 4 mmol) in dry THF, sodium bicarbonate (2 g) was added slowly. After the addition was complete, the stirring was continued for an additional 2 h. The mixture was filtered and concentrated. This was then extracted with CH_2Cl_2 (3×20 ml). The dichloromethane solution was washed with water (2×10 ml) and dried (Na_2SO_4). Attempts to evaporate dichloromethane led to considerable decomposition of the compound **2**. Therefore, this dichloromethane solution was directly used in the next phase-transfer-catalyzed alkylation step.

General Procedure for the Preparation of the Precursors 4(a,b)

To a stirred solution of 3(2*H*)-benzothiofuranone **(2)** (0.32 g, 2 mmol) and 2-bromobenzyl bromide **3a**,**b** (2 mmol) in dichloromethane solution (20 ml), a solution of benzyltriethylammonium chloride (BTEAC) (0.33 g, 1.2 mmol) in 1% aq. NaOH solution (10 ml) was added, and the mixture was stirred for about 30 min at room temperature. It was diluted with water (20 ml). The dichloromethane layer was washed with dilute HCl followed by brine and dried (Na_2SO_4). The crude mass obtained on evaporation of CH_2Cl_2 was subjected to column chromatography over silica gel. Elution of the column with ethyl acetate–pet. ether (1%) afforded compounds **4a**,**b**.

Data

Compound **4a**

Yield 90%, viscous liquid. IR(neat): $\nu_{max} = 1460,\ 1592\ cm^{-1}$; ^1H NMR ($CDCl_3$, 400 MHz): $\delta_H = 4.04$ (s, 2H, -SC**H**$_2$), 6.88–6.90 (m, 1H, Ar**H**), 7.05–7.08 (m, 2H, Ar**H**), 7.24–7.33 (m, 2H, Ar**H**), 7.43 (s, 1H, =CC**H**), 7.46–7.48 (m, 1H, Ar**H**), 7.52–7.56 (m, 2H, Ar**H**). MS: $m/z = 318$, 320 (M^+). Anal. calcd. for $C_{15}H_{11}BrOS$: C, 56.44; H, 3.47%. Found: C, 56.51; H, 3.48%.

Compound **4b**

Yield 88%, viscous liquid. IR (neat): $\nu_{max} = 1463,\ 1593\ cm^{-1}$; ^1H NMR ($CDCl_3$, 400 MHz): $\delta_H = 3.79$ (s, 3H, -OC**H**$_3$), 3.98 (s, 2H, -SC**H**$_2$), 6.61–6.64 (dd, 1H, Ar**H**, $J = 8.76$ Hz, $J = 3.0$ Hz), 6.71–6.74 (dd, 1H, Ar**H**, $J = 8.76$ Hz, $J = 3.0$ Hz), 6.97–6.98 (d, 1H, Ar**H**, $J = 3.0$ Hz), 7.31–7.35 (m, 2H, Ar**H**), 7.46 (s, 1H, =CC**H**), 7.53–7.60 (m, 2H, Ar**H**). MS: $m/z = 348$, 350 (M^+). Anal. calcd. for $C_{16}H_{13}BrO_2S$: C, 55.03; H, 3.75%. Found: C, 55.21; H, 3.80%.

General Procedure for the Synthesis of the Sulfones 4(c,d)

To a well-stirred solution of compound **3** (200 mg, 0.63 mmol) in dry dichloromethane (10 ml), a solution of *m*-CPBA (77%, 0.22 g, 1.2 mmol, 2 eq.) was added at 0°C over a period of 30 min. After complete addition of *m*-CPBA, the reaction was refluxed for 1 h to complete the oxidation. The mixture was cooled and washed with saturated sodium carbonate solution (3 × 10 ml), followed by brine, and dried (Na_2SO_4). The dichloromethane was removed, and the crude mass obtained was purified by column chromatography over silics gel and by eluting the column with 5% ethyl acetate–pet. ether to afford the sulfones as white solids **4c**,**d**.

Data

Compound **4c**

Yield 92%, white solid, mp 115°C. IR (KBr): $\nu_{max} = 1125$, 1314 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): $\delta_H = 4.70$ (s, 2H, SO_2-C**H**$_2$), 7.14–7.23 (m, 2H, Ar**H**), 7.32–7.38 (m, 4H, Ar**H**), 7.52–7.55 (m, 2H, Ar**H**), 7.94 (s, 1H, =CC**H**). ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta_C = 62.5$, 112.4, 120.6, 121.8, 123.5, 125.0, 126.3, 126.5, 128.1, 128.4, 130.9, 133.5, 133.6, 151.2, 155.7; MS: $m/z = 350$, 352 (M^+). Anal. calcd. for $C_{15}H_{11}BrO_3S$: C, 51.30; H, 3.16%. Found: C, 51.39; H, 3.11%.

Compound **4d**

Yield 92%, white solid, mp 120°C. IR (KBr): $\nu_{max} = 1129$, 1311 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): $\delta_H = 3.75$ (s, 3H, -OC**H**$_3$), 4.65 (s, 2H, SO_2-C**H**$_2$), 6.71–6.79 (dd, 2H, $J = 8.8$ Hz, $J = 3.0$ Hz, Ar**H**), 7.03–7.04 (d, 1H, $J = 3.0$ Hz, Ar**H**), 7.30–7.35 (m, 2H, Ar**H**), 7.36–7.40 (m, 2H, Ar**H**), 7.96 (s, 1H, =CC**H**); MS: $m/z = 380$, 382 (M^+). Anal. calcd. for $C_{16}H_{13}BrO_4S$: C, 50.41; H, 3.44%. Found: C, 50.30; H, 3.41%.

General Methods for the Synthesis of the Compounds 5a–d and 6a

To a magnetically stirred suspension of the compounds **4a**,**d** (0.2 mmol) and azobisisobutyronitrile (AIBN) (0.5 eq.) in dry degassed toluene (8 ml), tri-n-butyltin hydride was added slowly all at once under a nitrogen atmosphere. The reaction mixture was heated at 80°C for 4–5 h. After the complete conversion of the starting materials (TLC observation), the solvent was removed under reduced pressure. The liquid mass obtained was dissolved in CH_2Cl_2 (5 ml) and stirred with 10% aqueous potassium fluoride solution (8 ml) for 2–3 h. The white precipitate was separated by filtration, and the aqueous phase was extracted with dichloromethane (3 × 15 ml). The combined extract was washed with brine and dried (Na_2SO_4). Dichloromethane was distilled off, and the residual mass was subjected to column chromatography over silica gel. The column was eluted with ethyl acetate–pet. ether (2%) to give the products **5a–d** and **6a**.

Data

Compound **5a**

Yield 90%, white solid, mp 118°C. IR (KBr): $\nu_{max} = 2851$, 2922, 2958 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): $\delta_H = 3.45–3.49$ (d, 1H, $J = 14.8$ Hz, -SC**H**$_a$H$_b$),

3.66–3.70 (d, 1H, $J = 14.8$ Hz, -SCH$_a$**H$_b$**), 4.80–4.82 (d, 1H, $J = 8.0$ Hz, -CH$_d$C**H$_c$**), 5.82–5.84 (d, 1H, $J = 8.0$ Hz, -C**H$_d$**CH$_c$), 6.78–6.80 (d, 1H, $J = 8.0$ Hz, Ar**H**), 6.95–6.99 (m, 1H, Ar**H**), 7.17–7.21 (m, 2H, Ar**H**), 7.29–7.34 (m, 2H, Ar**H**), 7.36–7.40 (m, 1H, Ar**H**), 7.50–7.52 (d, 1H, $J = 7.05$ Hz, Ar**H**). MS: $m/z = 240$ (M^+). Anal. calcd. for $C_{15}H_{12}OS$: C, 74.97; H, 5.03%. Found: C, 75.01; H, 5.00%.

Compound **5b**

Yield 95%, white solid, mp 120°C. IR (KBr): $\nu_{max} = 2853, 2923, 2958$ cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 3.38–3.42$ (d, 1H, $J = 14.8$ Hz, -SC**H$_a$**H$_b$), 3.64–3.68 (d, 1H, $J = 14.8$ Hz, -SCH$_a$**H$_b$**), 3.81 (s, 3H, -OC**H$_3$**), 4.77–4.79 (d, 1H, $J = 8.0$ Hz, -CH$_d$C**H$_c$**), 5.82–5.84 (d, 1H, $J = 8.0$ Hz, -C**H$_d$**CH$_c$), 6.75–6.78 (m, 2H, Ar**H**), 6.84–6.87 (m, 1H, Ar**H**), 6.94–6.98 (m, 1H, Ar**H**), 7.15–7.17 (m, 1H, Ar**H**), 7.37–7.42 (m, 2H, Ar**H**). MS: $m/z = 270$ (M^+). Anal. calcd. for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22%. Found: C, 71.19; H, 5.22%.

Compound **5c**

Yield 95%, white solid, mp. 195°C. IR (KBr): $\nu_{max} = 2849, 2920, 2955$ cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 3.93–3.97$ (d, 1H, $J = 15.0$ Hz, -SC**H$_a$**H$_b$), 4.18–4.22 (d, 1H, $J = 15.0$ Hz, -SCH$_a$**H$_b$**), 4.67–4.70 (d, 1H, $J = 8.8$ Hz, -CH$_d$C**H$_c$**), 6.06–6.09 (d, 1H, $J = 8.8$ Hz, -C**H$_d$**CH$_c$), 6.84–6.86 (d, 1H, $J = 8.11$ Hz, Ar**H**), 7.04–7.07 (t, 1H, $J = 7.4$ Hz, Ar**H**), 7.24–7.26 (d, 1H, $J = 5.94$ Hz, Ar**H**), 7.29–7.33 (m, 1H, Ar**H**), 7.46–7.50 (m, 2H, Ar**H**), 7.54–7.57 (m, 1H, Ar**H**), 7.61–7.63 (d, 1H, $J = 7.57$ Hz, Ar**H**). ^{13}CNMR ($CDCl_3$, 125 MHz): $\delta_C = 51.7, 63.2, 85.1, 109.9, 120.0, 122.0, 128.3, 129.3, 130.0, 130.3, 130.4, 130.7, 131.0, 131.2, 160.7$; DEPT ($CDCl_3$, 125 MHz): $\delta_C = 51.7, 63.2, 85.0, 109.9, 122.0, 128.3, 129.3, 130.3, 130.4, 131.0, 131.2$; MS: $m/z = 272$ (M^+). Anal. calcd. for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44%. Found: C, 66.29; H, 4.37%.

Compound **5d**

Yield 93%, white solid, mp. 190°C. IR (KBr): $\nu_{max} = 2850, 2921, 2954$ cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 3.83$ (s, 3H, -OC**H$_3$**), 3.86–3.90 (dd, 1H, $J = 15.04$ Hz, $J = 2.76$ Hz, -SC**H$_a$**H$_b$), 4.17–4.20 (d, 1H, $J = 15.04$ Hz, -SCH$_a$**H$_b$**), 4.63–4.66 (dd, 1H, $J = 8.92$ Hz, $J = 2.44$ Hz, -CH$_d$C**H$_c$**), 6.03–6.05 (d, 1H, $J = 8.92$ Hz, -C**H$_d$**CH$_c$), 6.77 (d, 1H, $J = 2.2$ Hz, Ar**H**), 6.82–6.84 (d, 1H, $J = 8.12$ Hz, Ar**H**), 6.94–6.97 (dd, 1H, $J = 8.32$ Hz, $J = 2.4$ Hz, Ar**H**), 7.02–7.06 (t, 1H, $J = 7.56$ Hz, Ar**H**), 7.29–7.32 (t, 1H, $J = 7.52$ Hz, Ar**H**), 7.45–7.47 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.59–7.61 (d, 1H, $J = 7.52$ Hz, Ar**H**). MS: $m/z = 302$ (M^+). Anal. calcd. for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67%. Found: C, 63.61; H, 4.66%.

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