Reactions of Propargylic Bromides with Sodium Sulfinates

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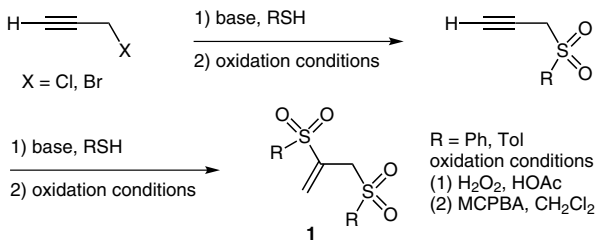
Abstract: A one-pot, palladium-catalyzed synthesis of substituted 2,3-bissulfonylpropenes starting with propargylic bromides and sodium sulfinates (RSO_2Na) in the presence of *n*-Bu_4NF under refluxing aqueous 1,4-dioxane conditions for eight hours in moderate yields is described.

Key words: cross-coupling, domino reaction, elimination, sulfones, palladium

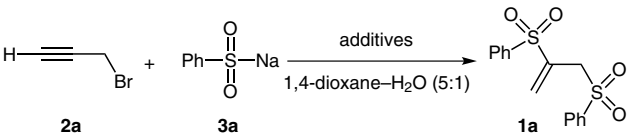
Unsaturated sulfones and their related derivatives are the versatile intermediates in the preparation of diversified and functionalized sulfone-containing frameworks due to their interesting reaction mechanism and synthetic applications.[1] Among the literature on unsaturated sulfones, substituted sulfones are the subunits in the design of multicoupling reagents.[2] Various chemical transformations from vinylic, allylic, and propargylic sulfones to useful acyclic or heterocyclic skeletons have been demonstrated by Padwa via nucleophilic substitution or radical cyclization. The three-carbon backbone of 2,3-bisarenesulfonylpropenes, including the combination of a vinylic and allylic sulfone, offers many advantages to a sulfonyl group.[3] There are a number of processes available to generate this skeleton, but generally, they are described as a nucleophilic substitution of propargylic sulfones with thiophenol and triethylamine followed by oxidation of the resulting sulfur substituent with H_2O_2 or MCPBA (Scheme 1).[3–5] Consequently, development of a one-pot protocol for constructing 2,3-bisarenesulfonylpropenes has stimulated considerable interest.[6]



Scheme 1 General route toward 2,3-bisarenesulfonylpropenes

Since the synthetic procedures of substituted 2,3-bissulfonylpropenes **1** are almost all repeated thiophenol-mediated nucleophilic substitution followed by oxidation under different reaction conditions, this work intends to explore a one-pot methodology for preparing substituted skeleton **1** using the treatment of propargylic bromides **2** with sodium sulfinates (RSO_2Na, **3**) in the presence of a different additive under refluxing aqueous 1,4-dioxane conditions. Initially, after treatment of propargyl bromide (**2a**) with one equivalent of benzenesulfinic sodium salt (**3a**) in the presence of a phase-transfer reagent propargylic benzenesulfone was isolated in 88% yield. However, when the reaction of propargyl bromide (**2a**) was treated with three equivalents of compound **3a**, compound **1a** was isolated in 43% yield. This is an interesting result. To improve the yield, some additives and reaction conditions were screened (Table 1).

Table 1 Reaction Conditions of Compounds **2a** and **3a**[a,b]



Entry	Catalyst (mmol%), PTR (equiv)	Yield (%)[b]
1	Pd/C (5), *n*-Bu_4NCl (0.1)	77
2	$CuCl_2 \cdot H_2O$ (5), *n*-Bu_4NCl (0.1)	60
3	$FeCl_3 \cdot 6H_2O$ (5), *n*-Bu_4NCl (0.1)	64
4	$CeCl_3 \cdot 6H_2O$ (5), *n*-Bu_4NCl (0.1)	60
5	$CrCl_3 \cdot 6H_2O$ (5), *n*-Bu_4NCl (0.1)	55
6	$PdCl_2 \cdot$ (5), *n*-Bu_4NCl (0.1)	70
7	10% Pd/C (5), *n*-Bu_4NF (0.1)	80
8	10% Pd/C (10), *n*-Bu_4NF (0.2)	86
9	10% Pd/C (10), *n*-Bu_4NF (0)	50

[a] The reactions were run on a 1.0 mmol scale with propargyl bromide (**2a**) (80% in toluene, 1.0 mmol), $PhSO_2Na$ (**3a**) (3.0 equiv), 1,4-dioxane (5 mL) and H_2O (1 mL), reflux temperature, 8 h.
[b] Crystalline 2,3-bisbenzenesulfonylpropene **1a** was >95% pure as determined by NMR analysis.

After screening six additives (10% Pd/C, $CuCl_2 \cdot H_2O$, $FeCl_3 \cdot 6H_2O$, $CeCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $PdCl_2$) and two phase-transfer reagents (PTR, *n*-Bu_4NCl, or *n*-Bu_4NF), we found that entry 8 (Table 1) provided the optimized conditions and best yield. Therefore, this reaction must be controlled by 10% Pd/C (10 mmol%) in the presence of *n*-Bu_4NF (0.2 equiv) under refluxing conditions for eight hours; otherwise, compound **1a** will be isolated in lower yields (Table 1, entries 2–6). Without the addition of

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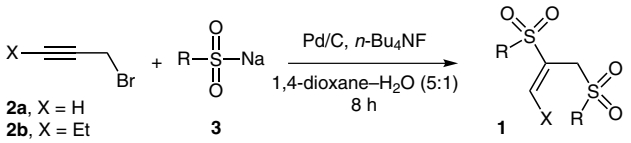
n-Bu_4NF, compound **1a** provided an only 50% yield (Table 1, entry 9). Recently, there have been a number of investigations for a one-pot reaction of a reactive intermediate with RSO_2Na using palladium-mediated cross-coupling reactions.[7,8] Based on the above-mentioned phenomenon, compounds **1b**–**m** were obtained by a one-pot palladium-catalyzed synthetic protocol; the results are summarized in Table 2.[9,10]

Compounds **1a**–**m**, with different bisarenesulfonyl groups were also synthesized in 65–90% yields via palladium-mediated reaction of propargylic bromides **2a**,**b** (X = H, Et) and sodium sulfinates (RSO_2Na) **3a**–**k** in the presence of *n*-Bu_4NF under the refluxing aqueous 1,4-dioxane conditions for eight hours. Furthermore, the structures of compounds **1e** and **1m** were determined by single-crystal X-ray crystallography (Figure 1).[11] Compared with the isolated yields of products with different arene substituents, it was found that skeleton **1**, with the electron-withdrawing substituent **1b** (4-fluorophenyl), was slightly poorer than the other analogues. Compound **1g**, with an electron-donating group, provided a better yield (90%). From this phenomenon, we believe that the electron-rich group delocalized to the benzylic position easily and favored a palladium-mediated double nucleophilic attack of compound **2a**. The Pd/C catalyst plays the key promoter to increase the yields of skeleton **1**.

Table 2 Synthesis of Skeleton **1**[a]



2a, X = H
2b, X = Et
3
1

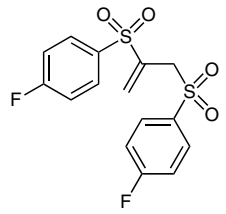
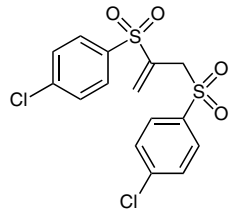
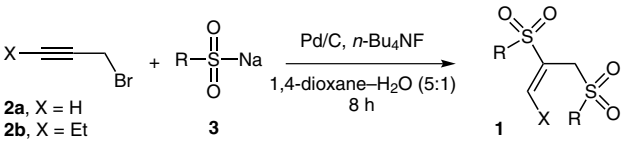
Entry	Skeleton **1**	Yield (%)
1	 **1b**	65
2	 **1c**	77

Table 2 Synthesis of Skeleton **1**[a] (continued)



2a, X = H
2b, X = Et
3
1

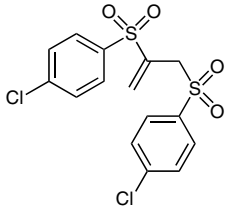
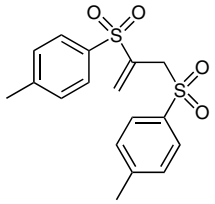
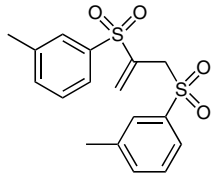
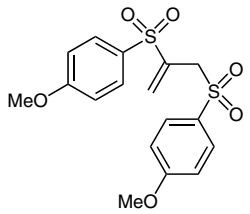
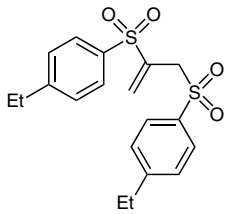
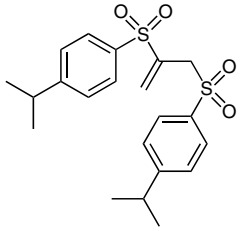
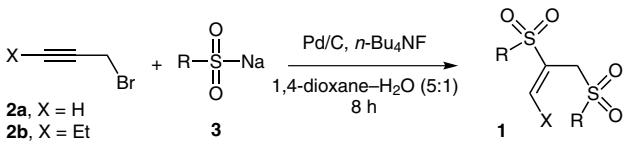
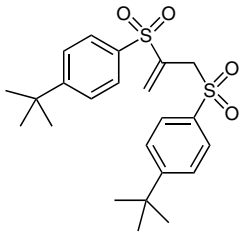
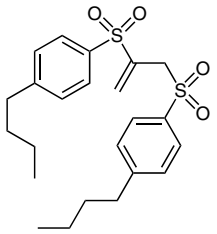
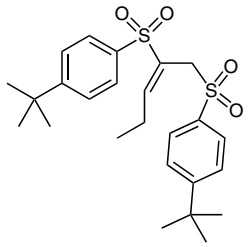
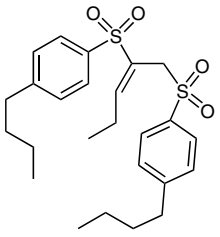
Entry	Skeleton **1**	Yield (%)
3	 **1d**	73
4	 **1e**	82
5	 **1f**	84
6	 **1g**	90
7	 **1h**	80
8	 **1i**	82

Table 2 Synthesis of Skeleton **1**[a] (continued)



Entry	Skeleton **1**	Yield (%)
9	 **1j**	83
10	 **1k**	82
11	 **1l**	80
12	 **1m**	82

[a] Isolated compounds **1a**–**m** were >95% pure as determined by ^{1}H NMR analysis.

To further examine the palladium-catalyzed cross-coupling reaction of propargyl bromide (**2a**), an aryl group (R = Ar) of sodium sulfinates **3** was changed to a methyl group (**3l**, R = Me). Under the above-mentioned reaction conditions, only a trace of compound **1n** (ca. 10%) was yielded. The major 2,3-bismethylsulfonylpropan-1-ol (**4**) was isolated in 66% yield via a palladium-mediated 1,4-addition of compound **1n** with water (Scheme 2). The structure of compound **4** was determined by single-crystal X-ray crystallography (Figure 2).[11]

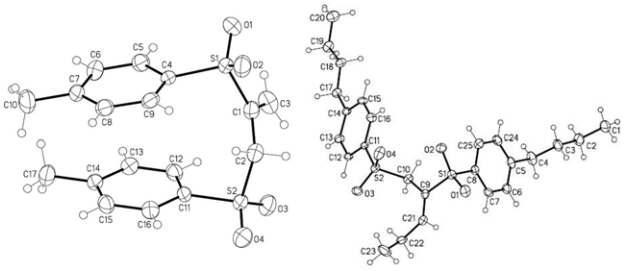


Figure 1 X-ray crystal structures of compounds **1e** and **1m**

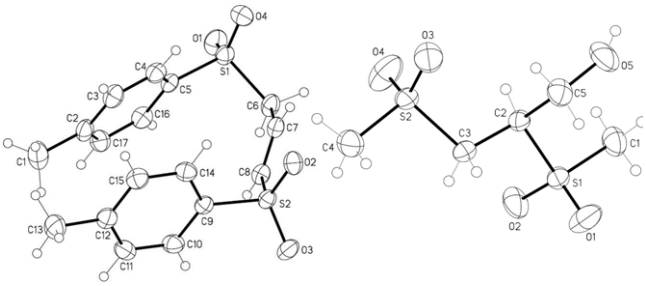
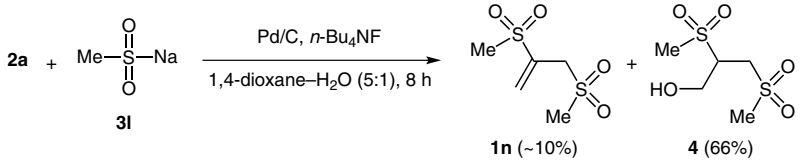


Figure 2 X-ray crystal structures of compounds **4** and **5a**

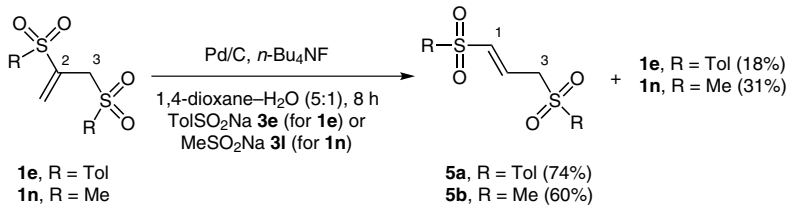
For treatment of compound **1e** (R = Tol) or **1n** (R = Ms) with three equivalents of 4-$TsSO_2Na$ (**3e**) or $MeSO_2Na$ (**3l**), 1,3-bistoluenesulfonylpropene (**5a**) or 1,3-bistoluenesulfonylpropene (**5b**) was provided in 74% or 60% yield and compound **1e** or **1n** was recovered in 18% or 31% yield via one-pot palladium-catalyzed 1,2-shift rearrangement of the 4-tosyl or methyl group (Scheme 3). This is a novel cascade route to conversion from the skeleton of 2,3-bissulfonylpropene **1** to 1,3-bissulfonylpropene **5**. The structure of compound **5a** was determined by single-crystal X-ray crystallography (Figure 2).[11] For the palladium-catalyzed cross-coupling reaction of propargyl bromide (**2a**) with *n*-$BuSO_2Na$ (**3m**), when the reaction solvent was changed from aqueous 1,4-dioxane to water, compounds **6** (56%) and **7** (22%) were observed and no products with the bissulfonyl group were generated.[12] A plausible mechanism was proposed as shown in Scheme



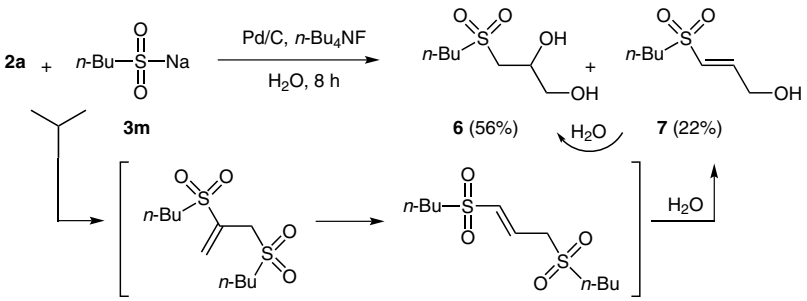
Scheme 2 Reaction of compound **2a** with **3l**

4. The initial event may be considered as the generation of 2,3-bissulfonylpropene via double nucleophilic addition of compound **2a** with **3m**. 1,2-Sulfonyl migration affords 1,3-bissulfonylpropene. Two structures in brackets are the reasonable intermediates. Under the basic aqueous conditions, compound **7** should be formed via water-mediated allylic desulfonation. Followed by 1,4-addition of water, product **6** was generated. To demonstrate this 1,4-addition from compound **6** to compound **7**, treatment of sole compound **7** with the above reaction conditions provided compound **6** with 76% yield.

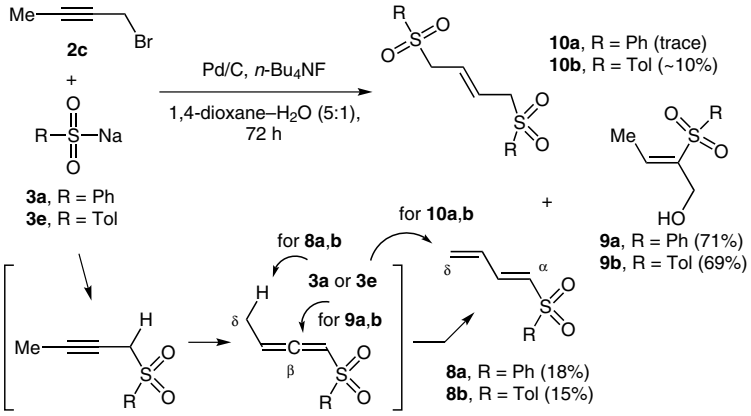
Next, a one-pot, palladium-catalyzed reaction of 1-bromobut-2-yne (**2c**) with compound $PhSO_2Na$ (**3a**) or 4-$TsSO_2Na$ (**3e**) in refluxing water for 72 hours was examined, as shown in Scheme 5. However, three skeletons of 1-sulfonylbutadienes **8a** or **8b**, (*Z*)-2-sulfonylbut-2-en-1-ols **9a** or **9b**, and (*E*)-1,4-bissulfonylbut-2-enes **10a** or **10b** were isolated in different yields.[13–15] The two shown intermediates with monosulfonyl alkyne and allene should be the key intermediates (in brackets) for providing skeletons **8**–**10**. When sodium sulfinate **3a** or **3e** played the role of base to deprotonate the δ-proton, compound **8a** or **8b** was formed by protonation of the δ-carbanion under basic conditions. For the formation of compound (*Z*)-**9a** or **9b**, we believe that sodium sulfinate **3a** or **3e** should serve as the nucleophile and the δ-carbon of sulfonyl allene was attacked from the less hindering face to produce the skeleton of 2,3-bissulfonyl butene followed by nucleophilic substitution of the allylic sulfone with water. Furthermore, compound **10a** or **10b** was isolated via the δ-attack of compound **8a** or **8b** with sodium sulfinate **3a** or **3e** followed by α-protonation. To examine this δ-attack (1,6-addition) from skeleton **8** to **10**, treatment of sole compound **8b** with the above conditions provided compound **10b** with only 32% yield. And, an unknown complex mixture was isolated as the major product. The structure **10b** was determined by single-crystal X-ray crystallography (Figure 3).[11] Among the isolated products, skeleton **9** was observed in good yield.



Scheme 3 Formation of compound **5a** or **5b**



Scheme 4 Reaction of compound **2a** with **3m**



Scheme 5 Reaction of compound **2c** with **3a** or **3e**

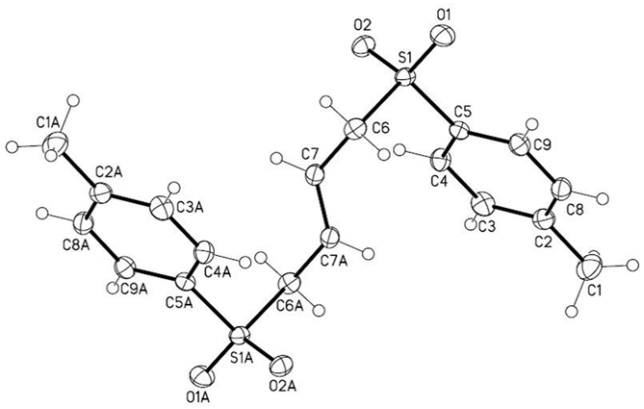
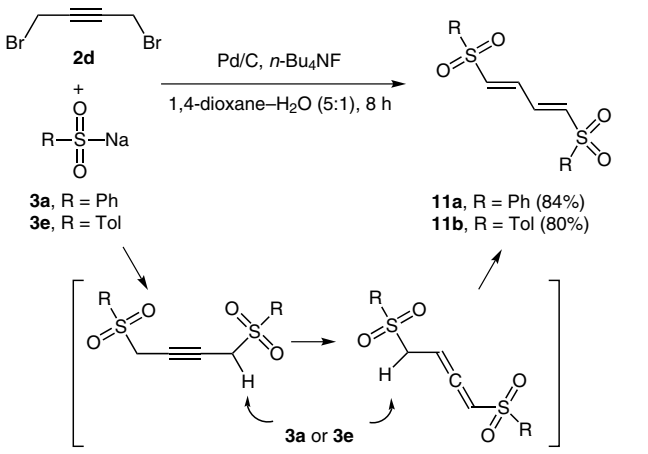


Figure 3 X-ray crystal structure of compound **10b**

To extend this one-pot domino protocol for the application of 1,4-dibromobut-2-yne (**2d**), we found that compounds **11a** or **11b** with the symmetrical bis-(*E*,*E*)-vinylsulfonyl group was observed for the above palladium-mediated reaction of compounds **2d** with sodium sulfinates **3a** or **3e**, as shown in Scheme 6.[16] From the experimental results, we envisioned that two intermediates with bissulfonyl alkyne and allene (in brackets) must be formed. After deprotonation of the allenic proton with sodium sulfinates **3a** or **3e**, compound **11a** or **11b** could be separated in high yield via the sequential protonation.



Scheme 6 Reaction of compound **2d** with **3a** or **3e**

In summary, a synthetic methodology for producing several substituted 2,3-bissulfonylpropenes **1** has been successfully presented using the one-pot facile palladium-catalyzed coupling of propargylic bromides **2** with sodium sulfinates **3** in good yields in the presence of *n*-Bu_4NF conditions. The one-pot synthesis of functionalized sulfonyl skeletons **6**–**10** was investigated under aqueous conditions. The structures of the key products were confirmed by X-ray crystal analysis. The one-pot synthetic approach begins with simple starting materials and provides a potential methodology for the synthetic research of vinylic or allylic sulfonyl derivatives. Further investigation of skeleton **1** regarding a one-pot synthesis of multifunctionalized biphenyls will be conducted and published in due course.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(9) **Representative Synthetic Procedure of Skeleton 1**
n-Bu_4NF (1.0 M in THF, 0.2 mL, 0.2 mmol) was added to a solution of propargyl bromide (**2a**) (80% in toluene, 150 mg, 1.0 mmol) or 1-bromopent-2-yne (**2b**, 150 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at r.t. Then, RSO_2Na **3** (3.0 mmol) in hot H_2O (1 mL) was slowly added to the reaction mixture. The reaction mixture was stirred at r.t. for 10 min. Next, Pd/C (10% in carbon, 11 mg, 0.1 mmol) was added to the stirred solution at r.t. The reaction mixture was stirred at reflux for 8 h. The reaction mixture was cooled, filtered, washed, and concentrated under reduced pressure. The residue was diluted with H_2O (10 mL), and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product. Purification on silica gel (hexanes–EtOAc, 6:1 to 2:1) afforded skeleton **1**.
Compound **1e**: yield 82% (287 mg); colorless solid; mp 154–155 °C. ESI-HRMS: *m/z* calcd for $C_{17}H_{19}O_4S_2$ [M^+ + 1]: 351.0725; found: 351.0726. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 4 H), 7.28–7.25 (m, 4 H), 6.64 (d, *J* = 0.8 Hz, 1 H), 6.49 (d, *J* = 0.8, 1.6 Hz, 1 H), 4.02 (d, *J* = 1.2 Hz, 2 H), 2.43 (s, 3 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.29, 145.09, 139.67, 134.74, 134.69, 130.43, 129.95 (2×), 129.79 (2×), 128.48 (2×), 128.39 (2×), 54.05, 21.66, 21.64.
Single-crystal X-ray diagram: Crystal of **1e** was grown by slow diffusion of EtOAc into a solution of **1e** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*121/*c*1, *a* = 15.6737(5) Å, *b* = 11.2694(4) Å, *c* = 19.6400(6) Å, *V* = 3298.69(19) Å^3, *Z* = 8, d_{calcd} = 1.411 g/cm^3, *F*(000) = 1472, 2*θ* range 2.11–26.39°; *R* indices (all data): *R*1 = 0.1105, *wR*2 = 0.2077.
Compound **1m**: yield 82% (379 mg); colorless solid; mp 106–108 °C. ESI-HRMS: *m/z* calcd for $C_{25}H_{35}O_4S_2$ [M^+ + 1]: 463.1977; found: 463.1974. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.32 (*J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 4.17 (s, 2 H), 2.71–2.65 (m, 4 H), 2.37–2.30 (m, 2 H), 1.65–1.57 (m, 4 H), 1.38–1.30 (m, 4 H), 1.09 (t, *J* = 7.6 Hz, 3 H), 0.93 (t, *J* = 7.6 Hz, 3 H), 0.92 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.91, 150.03, 149.35, 136.65, 136.25, 131.20, 129.20 (2×), 129.11 (2×), 128.43 (2×), 128.40 (2×), 53.93, 35.62, 35.59, 33.10 (2×), 23.69, 22.23, 22.19, 13.82 (2×), 12.49.Single-crystal X-ray diagram: Crystal of **1m** was grown by slow diffusion of EtOAc into a solution of **1m** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*121/*c*1, *a* = 29.984 (3) Å, *b* = 5.2734(5) Å, *c* = 15.4864(17) Å, *V* = 2408.6(4) Å^3, *Z* = 4, d_{calcd} = 1.276 g/cm^3, *F*(000) = 992, 2*θ* range 0.69–26.40°; *R* indices (all data): *R*1 = 0.1069, *wR*2 = 0.1900.

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This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk].

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