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## Graphical Abstract

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# Facile synthesis of symmetric thiosulfonates by oxidation of disulfide with oxone/MX (MX = KBr, KCl, NaBr and NaCl)

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ABSTRACT

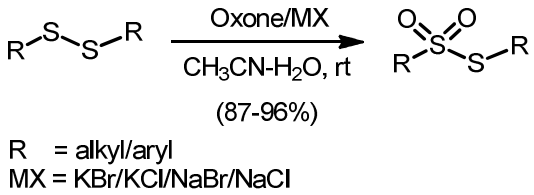
A new method is described for the oxidation of aliphatic- and aromatic disulfides containing electron-donating and electron-withdrawing groups to their corresponding thiosulfonates using oxone in combination with the MX (MX = KBr, KCl, NaBr and NaCl). No obvious electronic effects influence the yields of thiosulfonates. Avoiding the usage of toxic and unstable reagents, mild reaction conditions, short reaction times and cost-effectiveness are advantages of this methodology when likened to known methods for thiosulfonates syntheses.



Thiosulfonates have been used extensively in organic synthesis,[1] for the sulfenylation of various anions, as well as in biochemistry[2] for the evolution of antimicrobial, antiviral, bactericidal and fungicidal agents. Therefore, considerable efforts have been made in the development of both symmetric- and antisymmetric thiosulfonates.[3] Among, the most frequently employed method for the synthesis of symmetric thiosulfonates involve the direct oxidation of disulfides in the presence of various promoting reagents such as ceric ammonium nitrate/iodine,[4] chlorine/acetic anhydride,[5] 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate),[6] dibromo hydantoin,[7] dinitrogen tetroxide/charcoal,[8] dinitrogen tetroxide supported on poly(vinylpyrrolidone),[9] dichlorodioxomolybdenum,[10] 1-fluoro-2,4,6-trimethylpyridinium triflormethanesulfonate,[11] hydrogen peroxide/titanium tetrachloride,[12] 3-chloroperbenzoic acid,[13] N-bromophthalimide,[7] *N*-bromosuccinimide,[14] N-chlorophthalimide,[7] N-chlorosuccinimide,[11] scandium tris(trifluoromethanesulfonate),[15] silica sulfuric acid/sodium nitrite,[16] sodium periodate[17] and zinc dichromate trihydrate.[18] However, many of these methods have their own merits and demerits including long reaction times, drastic reaction conditions, use of volatile and toxic organic solvents, undesirable side reactions, laborious workup procedures, usage of expensive reagents, special treatment for the activation of the reagent and unsatisfactory yields. As a consequence, the exploitation of highly practical and more selective reagents is very desirable and remains a challenging area for exploration.[11]

Oxone (potassium peroxymonosulfate, $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 2:1:1 molar ratio) is a commercially available effective oxidant.[19] Due to its high stability, nontoxicity, water-solubility, ready accessibility and high efficiency, has been widely used for the oxidations of a wide range of functional groups including acetals,[19] alcohols,[19] aldehydes,[19] alkenes,[19] amines,[19] arenes,[19] imines,[19] nitroalkanes[19] and oximes.[19] But oxone has not yet been employed for the synthesis of thiosulfonates.

In continuation of our interest on the HOBr mediated oxidation of polycyclic aromatic hydrocarbons,[20] I have found that oxone combined with MX (MX = KBr, KCl, NaBr and NaCl) in aqueous $CH_3CN$ is an excellent reagent for the conversion of disulfides to thiosulfonates. Herein, I report a novel and efficient protocol (Scheme 1) for the synthesis of symmetric thiosulfonates from their disulfides by hypohalous acids (HOX) *in situ* generated by the hydrolysis of molecular halogens ($Br_2$ or $Cl_2$) produced from aqueous MX through oxone oxidation.




**Scheme 1**. Oxone/MX mediated synthesis of thiosulfonates from disulfides reported in this work.

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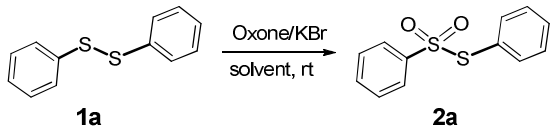
To screen the optimal reaction conditions, initial studies were conducted using 1,2-diphenyldisulfide (**1a**) as a test substrate and the outcomes are listed in Table 1. Investigations of the model reaction, under identical reaction conditions, using various solvents such as acetone, $CH_3CN$, carbon tetrachloride ($CCl_4$), chloroform ($CHCl_3$), dichloromethane (DCM), dimethyl sulfoxide (DMSO) and in combination with water ($H_2O$) suggested that a mixture of $CH_3CN$ and $H_2O$ in 1:1 ratio was the best medium for thiosulfonates formation (Table 1, entry 4). This likely reason is that water is necessary to dissolve oxone and KBr since they have limited solubility in anhydrous $CH_3CN$.

**Table 1**. Solvent effect on the oxidation of 1,2-diphenyldisulfide (**1a**) under identical reaction conditions.



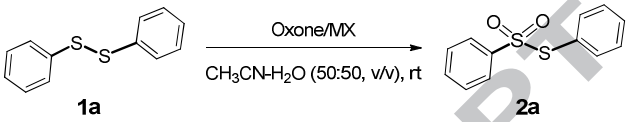

**1a** **2a**

| Entry | Solvent (v/v)[a] | Time (h) | Product Yield (%)[b] |
|---|---|---|---|
| 1 | acetone | 24 | trace |
| 2 | acetone-$H_2O$ (1:1) | 24 | 78 |
| 3 | $CH_3CN$ | 24 | trace |
| 4 | $CH_3CN$-$H_2O$ (1:1) | < 0.5 | 96 |
| 5 | $CH_3CN$-$H_2O$ (7:3) | 24 | 87 |
| 6 | $CH_3CN$-$H_2O$ (9:1) | 24 | 41 |
| 7 | $CH_3CN$-$H_2O$ (3:7) | 6 | 93 |
| 8 | $CH_3CN$-$H_2O$ (1:9) | 24 | 34 |
| 9 | $CCl_4$ | 24 | NR[c] |
| 10 | $CCl_4$-$H_2O$ (1:1) | 24 | trace |
| 11 | $CHCl_3$ | 24 | NR[c] |
| 12 | $CHCl_3$-$H_2O$ (1:1) | 24 | 18 |
| 13 | DCM | 24 | NR[c] |
| 14 | DCM-$H_2O$ (1:1) | 24 | 9 |
| 15 | DMSO | 24 | 83 |
| 16 | DMSO-$H_2O$ (1:1) | < 0.5 | 91 |
| 17 | $H_2O$ | 24 | 12 |

All reactions were run with **1a** (1.0 mmol), KBr (2.0 mmol) and oxone (2.2 mmol) in various solvent at room temperature. [a] Double distilled solvent and millipore water were employed. [b] Isolated yields. [c] No reaction (NR).

Next, was attempted to arrive at an optimum stoichiometry of the disulfide (**1a**) and the amount of KBr loading for the synthesis of thiosulfonates in aqueous $CH_3CN$ (50:50, v/v, Table 1, entry 4) at room temperature. As shown in Table 2, higher amounts of KBr neither increased the yield nor lowered the reaction time drastically and the oxone was effective only in the presence of KBr. The best result (96%, isolated yield) was obtained by carrying out the reaction with a 1:0.5 mole ratio of **1a** to KBr in the presence of oxone (2 moles) over 20 minutes. Formation of the thiosulfonate of **1a** was confirmed by the $^1$H NMR measurements as well, cf. Figure 1. The easy recognizable doublet of protons of **1a** at $\delta$ = 7.24 ppm gradually down field shifted to $\delta$ = 7.66 ppm and $\delta$ = 8.18 ppm corresponding to the formation of the thiosulfonate (**2a**)[11] within 20 minutes. It is worthy to mention that in addition to the KBr, other alkali-metal chlorides and bromides such as NaBr, KCl and NaCl also yielded **2a** in quantitative yield (Table 2). However, KI was not suitable for this transformation as the oxidation reaction with oxone/KI or oxone/NaI is sluggish. Thus, in a typical experimental procedure[21] oxone (2.0 mmol) and MX (0.5 mmol) was dissolved in mixture of $CH_3CN$-$H_2O$ (50:50, v/v) at ambient conditions. To this solution was added **1a** (1.0 mmol). Subsequently, the reaction mixture was stirred for half an hour at room temperature, diluted with water and extracted with ethyl acetate. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to obtain expected product in good to excellent yields.

**Table 2.** The effect of molar ratio of oxone and MX on the oxidation of 1,2-diphenyldisulfide (**1a**).




**1a** **2a**

| Entry | Oxone (mmol)[a] | KBr (mmol)[a] | Time (h) | Product Yield (%)[b] |
|---|---|---|---|---|
| 1 | 2.0 | 0 | 24 | NR[c] |
| 2 | 2.0 | 0.5 | < 0.5 | 96 |
| 3 | 3.0 | 0.5 | < 0.5 | 95 |
| 4 | 1.0 | 0.5 | 24 | 21 |
| 5 | 1.0 | 1.0 | 24 | 28 |
| 6 | 1.0 | 2.0 | 24 | 26 |
| 7 | 2.0 | 1.0 | < 0.5 | 94 |
| 8 | 3.0 | 1.0 | < 0.5 | 95 |
| 9 | 0 | 1.0 | 24 | NR[c] |
| 10 | 0 | 3.0 | 24 | NR[c] |
| 11 | 2.0 | 0.5[d] | 0.5 | 94 |
| 12 | 2.0 | 0.5[e] | 0.5 | 96 |
| 13 | 2.0 | 0.5[f] | 0.5 | 95 |
| 14 | 2.0 | 0.5[g] | 24 | trace |
| 15 | 3.0 | 1.0[g] | 24 | trace |
| 16 | 2.0 | 0.5[h] | 24 | trace |
| 17 | 3.0 | 1.0[h] | 24 | trace |

All reactions were run with **1a** (1.0 mmol), MX (0-3 mmol) and oxone (0-3 mmol) in $CH_3CN$-$H_2O$ (50:50, v/v) at room temperature. [a] Oxone and MX were recrystallized before use. [b] Isolated yield. [c] No reaction (NR). [d] KCl used instead of KBr. [e] NaBr used instead of KBr. [f] NaCl used instead of KBr. [g] KI used instead of KBr. [h] NaI used instead of KBr.

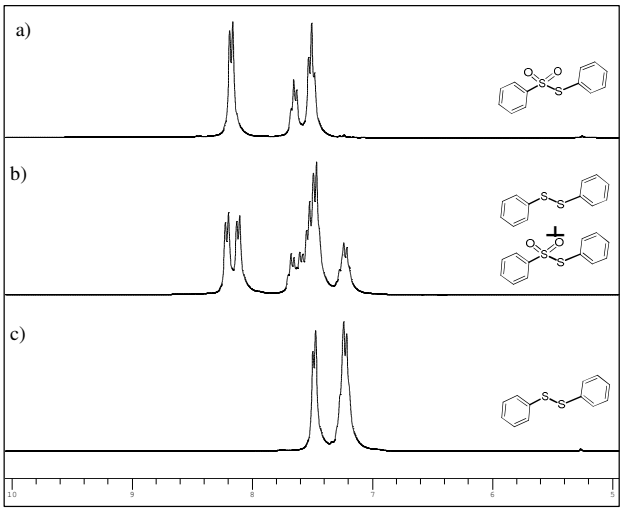
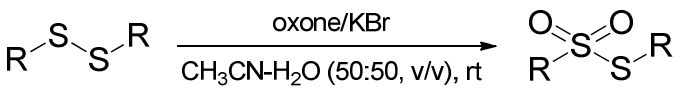
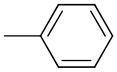
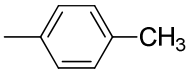
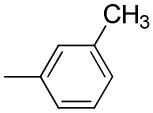
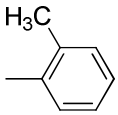
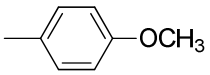
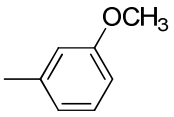
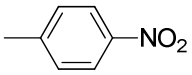
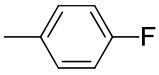
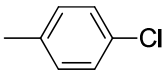
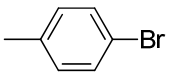
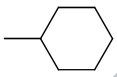
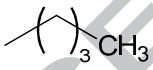
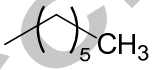
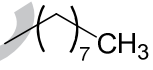
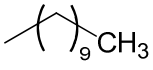



**Figure 1**. The $^1$H NMR (300 MHz) spectroscopic monitoring of conversion of **1a** into **2a** in $CD_3CN$-$D_2O$ (50:50, v/v) solution: (c) at beginning of the reaction, (b) after 10 minutes, (a) after 20 minutes.

**Table 3**. Synthesis of thiosulfonates from disulfides by oxidation with oxone/KBr in aqueous $CH_3CN$.[21]




**1** **2**

| Entry | R = | Substrate | Product[a] | Time (min) | Yield (%)[b] | mp (°C) (lit mp) | Ref. |
|---|---|---|---|---|---|---|---|
| 1 |  | **1a** | **2a** | 17 | 96 | 38-42 (38-39) | 4 |
| 2 |  | **1b** | **2b** | 15 | 97 | 69-73 (72-74) | 4 |
| 3 |  | **1c** | **2c** | 18 | 96 | 56-59 (57-58) | 8a |
| 4 |  | **1d** | **2d** | 40 | 91 | 48-53 (49-52) | 7b |
| 5 |  | **1e** | **2e** | 30 | 93 | 88-91 (89-90) | 12 |
| 6 |  | **1f** | **2f** | 22 | 92 | 68-74 (67-71) | 9 |
| 7 |  | **1g** | **2g** | 20 | 92 | 180-184 (182) | 12 |
| 8 |  | **1h** | **2h** | 18 | 94 | 70-72 (69-70) | 4 |
| 9 |  | **1i** | **2i** | 19 | 91 | 134-137 (135-136) | 4 |
| 10 |  | **1j** | **2j** | 17 | 93 | 157-160 (158-159) | 4 |
| 11 |  | **1k** | **2k** | 22 | 90 | oil (oil) | 12 |
| 12 |  | **1l** | **2l** | 20 | 94 | oil (oil) | 4 |
| 13 |  | **1m** | **2m** | 20 | 92 | oil (oil) | 9 |
| 14 |  | **1n** | **2n** | 25 | 91 | oil (oil) | 12 |
| 15 |  | **1o** | **2o** | 28 | 89 | oil (oil) | 9 |

All reactions were run with **1** (1.0 mmol), MX (0.5 mmol) and oxone (2.0 mmol) in $CH_3CN$-$H_2O$ (50:50, v/v) at room temperature. [a] The products were characterized by their comparison with known compounds. [b] Isolated yield.

With the optimized reaction conditions in hand (Tables 1 and 2),[21] the oxidation of various alkyl- and aryl disulfides was examined to explore the scope of the present protocol (Scheme 1). As shown in Table 3, a series of aromatic disulfides bearing either electron-donating or electron-withdrawing groups on the aromatic ring were investigated. The substitution groups on the aromatic ring associated with disulfides had little effect on the yields, cf. Table 3. For examples, electron-rich disulfides such as 4-tolyl disulfide (**1b**), 2-tolyl disulfide (**1d**), 4-anisyl disulfide (**1e**) and 3-anisyl disulfide (**1f**), and electron-deficient disulfides such as 4-nitrophenyl disulfide (**1g**), 4-fluorophenyl disulfide (**1h**), 4-chlorophenyl disulfide (**1i**) and 4-bromophenyl disulfide (**1j**), gave high yields of corresponding thiosulfonates[22] under optimal conditions (Tables 1, 2 and 3). Moreover, this system is also applicable to the efficient oxidation of alkyl disulfides (**1k-1o**, Table 3) into representing products in 89-94% yields (Table 3, Entries 12-15).

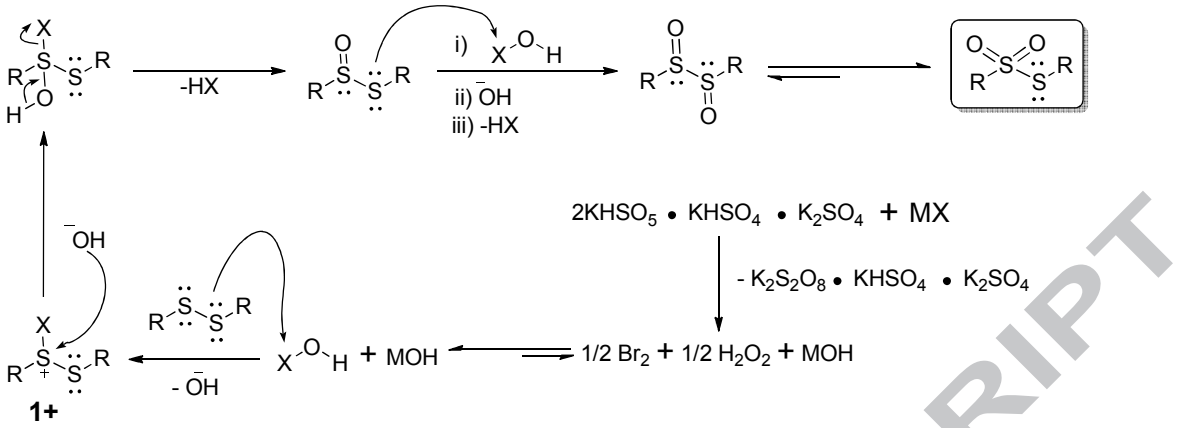
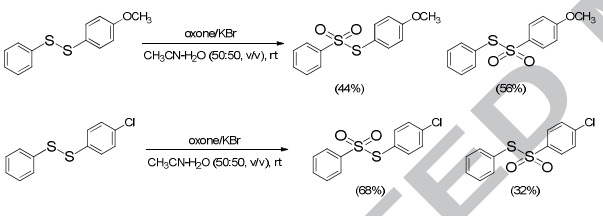



**Figure 2**. The proposed reaction mechanism for the synthesis of thiosulfonates from disulfides.

Next, was attempted to synthesis unsymmetric thiosulfonates from unsymmetrical disulfides under standard conditions described in Tables 1 and 2 for the preparation of symmetric thiosulfonates (**2a-2o**, Table 3). However, this procedure cannot be suitable for the synthesis of unsymmetric thiosulfonates as a mixture of products (Scheme 2) were noticed. It is believed that the oxidation proceeds via the formation of hypohalous acid,[11] which has higher instability due to pronounced ionic nature and thus more reactivity towards the disulfides leading to a mixture of products.[7]




**Scheme 2**. Oxone/KBr mediated synthesis of unsymmetric thiosulfonates from unsymmetric disulfides. Reaction conditions: disulfide (1.0 mmol), KBr (0.5 mmol) and oxone (2.0 mmol) in $CH_3CN$-$H_2O$ (50:50, v/v), rt. Yields given in parenthesis were determined by GC analysis.

The plausible reaction mechanism for the preparation of thiosulfonates from disulfides is outlined in Figure 2 on the basis of blank experiments and an earlier proposed mechanism. To understand the role of MX and oxone in the synthesis of thiosulfonates, I carried out blank experiments with disulfides and MX (in the absence of oxone, Table 2, entries 9 and 10) as well as disulfides and oxone (in the absence of MX, Table 2, entry 2), and the reactions did not succeed. Therefore, both MX and oxone played an important role in the product formation. It is well-known that oxidation of halide ion ($X^-$) by oxone affords the molecular halogens ($X_2$),[19,23] which can react with either hydroxyl ion or water to form HOX (Figure 2).[19,20] Eventually, HOX will react with the disulfide to give a cationic intermediate (**1+**) that further undergo nucleophile attack by hydroxyl ion/water to produce a thiosulfonate, cf. Figure 2.

In summary, a novel method is described for the synthesis of thiosulfonates from disulfides by oxidation using oxone in combination with the alkali-metal chlorides and bromides. Reactions proceed smoothly in environmentally benign solvents yielding expected product in good to excellent yields. Mild and simple reaction conditions, inexpensive reagents and non-polluting byproducts make this method valuable from a preparative point of perspectives.

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**Supplementary data**

Supplementary data (NMR and IR spectra of some selected products) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.0000.00. 000.

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21. **General Aspects**: Solvents were distilled prior to use and millipore water was used for preparing aqueous solutions. All commercial chemicals were used as received. All reactions were carried out in an open atmosphere. Reactions were monitored by analytical thin layer chromatography (TLC) on silica gel (Merck). NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer in deuterated solvents. Melting points were determined on a FEC hotplate apparatus.
**General Procedure for Synthesis of Thiosulfonates from Disulfides**: Oxone (2.0 mmol) was added to a well-stirred solution of MX (KBr, KCl, NaBr and NaCl, 0.5 mmol) in aqueous acetonitrile (50:50, v/v), followed by substrate (1.0 mmol) was added. Resulting mixture was stirred for the appropriate period of time (Table 3) at room temperature. After complete consumption of the starting material as observed by TLC, water (50 mL) was added and the mixture was extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous sodium sulfate and evaporated to afford the corresponding thiosulfonate as the sole product. It was further recrystallized using mixture of ethyl acetate and petroleum ether to remove color impurities. All of the products are known compounds and were characterized by comparison with authentic samples (NMR spectra and melting points).
22. Some of the products obtained in this study were characterized by NMR, IR and elemental analysis:
**Diphenyl thiosulfonate** (**2a**):[4] Yield (96%), mp 38-42 °C (lit. mp 38-39 ºC). IR (KBr, $cm^{-1}$): 3054, 1620, 1381, 1310, 1131, 1142, 1000, 820, 750, 690. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.31-7.82 (10H, m). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 127.49, 128.01, 128.54, 129.37, 131.31, 134.01, 136.54, 142.83. Anal. calcd for $C_{12}H_{10}O_2S_2$: C, 57.57; H, 4.03. Found: C, 57.33; H, 4.04.
**4,4′-Dimethylphenyl thiosulfonate** (**2b**):[4] Yield (97%), mp 69-73 °C (lit. mp 71-72 °C). IR (KBr, $cm^{-1}$): 3031, 2918, 1614, 1379, 1319, 1141, 1003, 817, 754. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.37 (3H, s), 2.43 (3H, s), 7.14-7.16 (2H, m), 7.21-7.29 (4H, m), 7.49-7.82 (2H, m). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 21.52, 21.64, 125.04, 127.61, 129.37, 130.09, 136.54, 140.42, 145.02. Anal. calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.29; H, 5.11.
**4,4′-Dimethoxyphenyl thiosulfonate** (**2e**):[12] Yield (93%), mp 88-91 °C (lit. mp 89-90 °C). IR (KBr, $cm^{-1}$): 3043, 1632, 1382, 1320, 1132, 1008, 814, 752. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 3.78 (3H, s), 3.83 (3H, s), 6.76-6.83 (4H, m), 7.20 (2H, d, $J$ = 8.9 Hz), 7.46 (2H, d, $J$ = 8.9 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 55.61, 55.64, 113.78, 114.90, 118.91, 129.89, 134.88, 138.37, 162.19, 163.48. Anal. calcd for $C_{14}H_{14}O_4S_2$: C, 54.17; H, 4.55. Found: C, 54.19; H, 4.51.
**4,4′-Dichlorophenyl thiosulfonate** (**2i**):[4] Yield (91%), mp 134-137 °C (lit. mp 135-136 °C). IR (KBr, $cm^{-1}$): 3032, 2984, 1631, 1572, 1454, 1133, 1141, 1084, 1002, 810, 753. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.28 (2H, d, $J$ = 8.4 Hz), 7.37 (2H, d, $J$ = 8.4 Hz), 7.44 (2H, d, $J$ = 8.6 Hz), 7.51 (2H, d, $J$ = 8.6 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 125.96, 129.02, 129.24, 129.86, 137.71, 138.49, 140.51, 141.32. Anal. calcd for $C_{12}H_8Cl_2O_2S_2$: C, 45.15; H, 2.53. Found: C, 45.12; H, 2.53.
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