A metal-free approach for the synthesis of thiosulfonates from sulfonyl hydrazides

Xue Li, WeiBo Liao, Bin Huang, YuanYuan Zhang and JiangWei Wang

Abstract
Without any metal catalyst, an efficient transformation of a variety of sulfonyl hydrazides into the corresponding thiosulfonates mediated by NBS/DABCO under air is developed. The method utilizes mild reaction conditions, affords moderate to good yields of product, and tolerates a broad substrate scope. A plausible mechanism is proposed for the decomposition of the sulfonyl hydrazides and the construction of $S(O_2)–S$ bonds to form thiosulfonates.

Keywords
metal-free, NBS/DABCO, sulfonyl hydrazides, synthesis, thiosulfonates

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Introduction
Thiosulfonates play key roles in pharmaceuticals and possess rich biological activities such as antimicrobial, antiviral, and fungicidal. Owing to the wide applications of thiosulfonates, a variety of approaches have been developed for their preparation. The most common approaches for establishing the $S–S$ bonds of thiosulfonates mainly include the oxidation of disulfides/mercaptans and the sulfuration of sulfonic acid salts. To synthesize unsymmetrical thiosulfonates, sulfonyl chlorides, sulfinyl chlorides, sulfinites, or sulfonyl hydrazides are commonly reacted with disulfides or mercaptans in the presence of a metal catalyst and an oxidant. To synthesize symmetrical thiosulfonates, in the last 15 years, the direct oxidation and coupling of disulfides or mercaptans has been highly favored. However, many of these methods suffer from harsh reaction conditions involving the use of strong oxidizing agents and toxic catalysts, and give low yields with numerous byproducts. To overcome these drawbacks, we have successfully developed a procedure to prepare unsymmetrical thiosulfonates from sulfonyl hydrazides using K$_2$S$_2$O$_8$ as a stoichiometric oxidant (Scheme 1(c)). In 2020, Kim et al. reported that sulfonyl hydrazides were transformed to thiosulfonates in the absence of an oxidant at 90 °C for 15 h (Scheme 1(c)). Recently, Lv et al. described that symmetrical/unsymmetrical thiosulfonates could be prepared from sulfonyl hydrazides using versatile heteropoly acid H$_3$PMo$_{12}$O$_{40}$ as a catalyst at 90 °C for 3 h in CH$_3$NO$_2$ (Scheme 1(d)). Nevertheless, these methods suffer from environmental and economical concerns as they utilize strong oxidants, transition–metal catalysts, high reaction temperatures, and long reaction times, which impede the applicability of these methodologies. Avoiding these drawbacks, we have successfully developed a procedure to prepare symmetrical thiosulfonates from sulfonyl hydrazides in moderate to good yields (57%–88%) using NBS (N-bromosuccinimide)/DABCO (1,4-diazabicyclo[2.2.2] octane) without any metal catalyst at 80 °C for 2 h under air (Scheme 1(e)).

Obtained from sulfonyl hydrazides using K$_2$S$_2$O$_8$ as a stoichiometric oxidant (Scheme 1(c)). In 2020, Kim et al. reported that sulfonyl hydrazides were transformed to thiosulfonates in the absence of an oxidant at 90 °C for 15 h (Scheme 1(c)). Recently, Lv et al. described that symmetrical/unsymmetrical thiosulfonates could be prepared from sulfonyl hydrazides using versatile heteropoly acid H$_3$PMo$_{12}$O$_{40}$ as a catalyst at 90 °C for 3 h in CH$_3$NO$_2$ (Scheme 1(d)). Nevertheless, these methods suffer from environmental and economical concerns as they utilize strong oxidants, transition–metal catalysts, high reaction temperatures, and long reaction times, which impede the applicability of these methodologies. Avoiding these drawbacks, we have successfully developed a procedure to prepare symmetrical thiosulfonates from sulfonyl hydrazides in moderate to good yields (57%–88%) using NBS (N-bromosuccinimide)/DABCO (1,4-diazabicyclo[2.2.2] octane) without any metal catalyst at 80 °C for 2 h under air (Scheme 1(e)).

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**Results and discussion**

*p*-Tolylsulfonyl hydrazide (1a)\(^{20}\) was selected to optimize the reaction conditions for the selective synthesis of thiosulfonate 2a. The effects of different additives, bases, and solvents were investigated, and the results are shown in Table 1. First, various additives such as NH\(_4\)I, NBS (N-bromosuccinimide), NIS (N-iodosuccinimide), and TBAI (tetra-\(n\)-butylammonium iodide) were examined and NBS was found to be the most promising (Table 1, Entries 1–4). Only a trace amount of product was observed in the absence of an additive (Table 1, Entry 5). Second, among all the bases, DABCO proved to be the best since an 81% yield of 2a could be obtained (Table 1, Entries 6–10). Fortunately, only a trace of the byproduct 3a was detected when DABCO was used as the base. However, without any base, a 30% yield of 3a was detected (Table 1, Entry 11). Third, the solvent was optimized and CH\(_3\)CN was found to be the most promising (Table 1, Entries 10, 12–15). When the reaction was carried out under N\(_2\), the yield of 2a decreased but that of 3a increased significantly (Table 1, Entries 10 and 16). This result indicated that the reaction needs O\(_2\) or air. Subsequently, the reaction was run under O\(_2\) and the yield of the product 2a was almost equal to the yield in air (Table 1, Entries 10 and 17). No appreciable yield of 3a was obtained at room temperature, even after 10 h (Table 1, Entry 18). To further improve the yield of 2a, the amounts of NBS and DABCO were investigated (Table 1, Entries 19–22). For NBS, among Entries 10, 19, and 20, 1.5 equiv. ensured the best yield of 2a and there was no advantage gained on increasing the amount. For DABCO, among Entries 10, 21, and 22, 1.0 or 1.5 equiv. offered the same yield of 2a, but the use of 0.5 equiv. led to a decrease in the yield of 2a to 72%. Therefore, the optimum reaction conditions were established as NBS (1.5 equiv.) as the additive, DABCO (1.0 equiv.) as the base, and CH\(_3\)CN as the solvent in air at 80 °C for 2 h.
With optimized conditions in hand, we set out to explore the substrate scope. Several sulfonyl hydrazides with different substituents on the phenyl ring were investigated and the corresponding symmetrical thiosulfonates were obtained in moderate to good yields ranging from 68% to 85% (Table 2, Entries 1–14). The nature of the substituents affected the reaction yields to some degree. Compounds substituted with electron-donating groups (Table 2, Entries 1–3) gave slightly lower yields than those with electron-withdrawing groups (Table 2, Entries 6–8). When electron-donating substituents were attached to the ortho, meta, or para positions of the phenyl ring (Table 2, Entries 2, 9, and 11), the order of the product yields was para > ortho > meta, the same as with electron-withdrawing substituents (Table 2, Entries 6, 10 and 12). Multisubstituted sulfonyl hydrazides gave the corresponding thiosulfonates in good yields (75%–81%) (Table 2, Entries 13 and 14). Moreover, it was noteworthy that naphthyl and benzyl sulfonyl hydrazides also provided the desired products in 76% and 57% yields, respectively, (Table 2, Entries 15 and 16).

A scale-up experiment (20 mmol) of our synthesis provided an 82% yield of 2a and demonstrates the effectiveness of this method.

To further explore the mechanism of the decomposition of the sulfonyl hydrazides and the construction of S(O 2)–S bonds to form thiosulfonates, several control experiments were carried out. First, when adding the radical scavenger TEMPO (1.0 equiv.) to the standard reaction, only a trace amount of the target product 2a was observed (Scheme 3(a)), which suggested that the reaction proceeded through a radical intermediate. Second, when the byproduct disulfide 3a alone was subjected to the standard reaction conditions, a trace amount of product 2a was observed (Scheme 3(b)). Finally, when 1a reacted with 3a under the standard conditions, an 83% yield of thiosulfonate 2a was obtained (Scheme 3(c)), suggesting that disulfide 3a might be an intermediate in this reaction.

Based on these observations and relevant references, a mechanism can be proposed in Scheme 4.

| Entry | Additive (equiv.) | Base (equiv.) | Solvent | Yield of 2a (%)b | Yield of 3a (%)b |
|-------|------------------|--------------|---------|-----------------|-----------------|
| 1     | NH4I (1.5)       | K2CO3 (1.0)  | CH3CN   | Trace           | Trace           |
| 2     | NBS (1.5)        | K2CO3 (1.0)  | CH3CN   | 62              | 10              |
| 3     | NIS (1.5)        | K2CO3 (1.0)  | CH3CN   | 40              | 13              |
| 4     | TBAI (1.5)       | K2CO3 (1.0)  | CH3CN   | Trace           | Trace           |
| 5     | none (1.5)       | K2CO3 (1.0)  | CH3CN   | Trace           | Trace           |
| 6     | NBS (1.5)        | NaOH (1.0)   | CH3CN   | 67              | 10              |
| 7     | NBS (1.5)        | Cs2CO3 (1.0) | CH3CN   | 71              | 12              |
| 8     | NBS (1.5)        | Et3N (1.0)   | CH3CN   | 60              | 11              |
| 9     | NBS (1.5)        | Pyridine (1.0)| CH3CN  | 65              | 10              |
| 10    | NBS (1.5)        | DABCO (1.0)  | CH3CN   | 81              | Trace           |
| 11    | NBS (1.5)        | None (1.0)   | CH3CN   | 20              | 30              |
| 12    | NBS (1.5)        | DABCO (1.0)  | THF     | 74              | Trace           |
| 13    | NBS (1.5)        | DABCO (1.0)  | Toluene | 70              | Trace           |
| 14    | NBS (1.5)        | DABCO (1.0)  | 1,4-dioxane| 63              | Trace           |
| 15    | NBS (1.5)        | DABCO (1.0)  | H2O     | Trace           | Trace           |
| 16a   | NBS (1.5)        | DABCO (1.0)  | CH3CN   | 40              | 17              |
| 17a   | NBS (1.5)        | DABCO (1.0)  | CH3CN   | 81              | Trace           |
| 18a   | NBS (1.5)        | DABCO (1.0)  | CH3CN   | 60              | Trace           |
| 19a   | NBS (1.0)        | DABCO (1.0)  | CH3CN   | 70              | Trace           |
| 20a   | NBS (2.0)        | DABCO (1.0)  | CH3CN   | 80              | Trace           |
| 21h   | NBS (1.5)        | DABCO (0.5)  | CH3CN   | 72              | 6               |
| 22h   | NBS (1.5)        | DABCO (1.5)  | CH3CN   | 80              | Trace           |

aReaction conditions: 1a (1.0 mmol), additive (1.5 equiv), base (1.0 equiv), solvent (2 mL), air, 80 °C, 2 h.
bIsolated yield.
cUnder N2.
dUnder O2.
eAt room temperature for 10 h.
NBS (1.0 equiv).
NBS (2.0 equiv).
DABCO (0.5 equiv).
DABCO (1.5 equiv).
acid B in the presence of NBS/DABCO via expulsion of HBr and N₂. Next, B can be oxidized to an oxygen-centered radical C by air upon heating.¹⁴

Table 2. Synthesis of thiosulfonates 2 from sulfonyl hydrazides under the optimized conditions.

| Entry | Reactant R       | Producta | Yield (%)b |
|-------|------------------|----------|------------|
| 1     | 4-MeC₆H₄         | 2a        | 81         |
| 2     | 4-MeOC₆H₄        | 2b        | 79         |
| 3     | 4-EtOC₆H₄        | 2c        | 76         |
| 4     | C₆H₅             | 2d        | 80         |
| 5     | 4-FC₆H₄          | 2e        | 82         |
| 6     | 4-ClC₆H₄         | 2f        | 84         |
| 7     | 4-BrC₆H₄         | 2g        | 85         |
| 8     | 4-O₂NC₆H₄        | 2h        | 80         |
| 9     | 2-MeC₆H₄         | 2i        | 77         |
| 10    | 2-ClC₆H₄         | 2j        | 75         |
| 11    | 3-MeC₆H₄         | 2k        | 72         |
| 12    | 3-ClC₆H₄         | 2l        | 68         |
| 13    | 2-Me-3-ClC₆H₃    | 2m        | 75         |
| 14    | 2,4,6-MeC₆H₂     | 2n        | 81         |
| 15    | o               | 2o        | 76         |
| 16    | C₆H₅CH₂          | 2p        | 57         |

Self-coupling of the radical C can offer the intermediate disulfone D. Subsequently, D can be reduced by B to give the disulfoxide E and sulfonic acid F.¹⁴ The unstable intermediate E takes place homolytic cleavage under heating to generate radical G. Finally, G may disproportionate into radicals I and H, which can easily be combined into the target thiosulfonate 2.

Conclusion

In summary, we have developed an efficient approach for the transformation of a variety of sulfonyl hydrazides into the corresponding thiosulfonates mediated by NBS/DABCO under air without any metal catalyst. The approach provides mild reaction conditions, moderate to good yields of products, and a broad substrate scope. A plausible mechanism has been proposed for the decomposition of the sulfonyl hydrazides and the construction of S(O₂)–S bonds to form the target thiosulfonates. The reaction is limited to only symmetrical thiosulfonates, which should be as a limitation of the methodology.

Experimental

Infrared spectra were determined on a Nicolet Avatar-370 spectrometer in KBr (ν in cm⁻¹). Melting points were measured on a Büchi B-540 capillary melting point apparatus and were uncorrected. Mass spectra (electrospray ionization mass spectrometry (ESI-MS)) were recorded on a Thermo Finnigan LCQ-Advantage. High-resolution mass spectra (ESI-HRMS) were obtained using an Agilent 6210 TOF instrument.¹ H NMR and ¹³C NMR spectra were recorded on a Varian Mercury Plus-400 spectrometer (400 and 100 MHz), δ in parts per million, J in Hertz, using TMS as the internal standard. Signal multiplicity was assigned as singlet (s), doublet (d), and multiplet (m). All analytical reagents were commercially available and used directly without further purification.
A mixture of p-tolylsulfonyl hydrazide (1a) (0.37 g, 2 mmol), NBS (0.53 g, 3.0 mmol), and DABCO (0.22 g, 2 mmol) in CH₂CN (5 mL) was stirred at 80 °C for about 2 h until total consumption of the starting material, as monitored by TLC (petroleum ether/EtOAc = 20:1). The reaction mixture was then washed with brine (20 mL) and extracted with CH₂Cl₂ (2 × 20 mL). The combined organic extract was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to afford the product 2a (white solid, 81%, 0.23 g).

S-(p-Toly) 4-methylbenzenesulfonothioate²⁰ (2a): White solid; 81%, 0.23 g; m.p. 76–78 °C (lit.²⁰ m.p. 76–77 °C). IR (KBr, cm⁻¹): ν = 1344, 1151. ¹H NMR (400 MHz, DMSO-d₆): δ 7.47 (d, J = 8.2 Hz, 2H), 7.26-7.21 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H), 2.36 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆): δ 144.6, 142.1, 140.5, 136.3, 130.3, 129.2, 127.5, 124.6, 21.5, 21.6. MS (ESI): m/z (%) = 279.1 ([M⁺], 100). HRMS (ESI): m/z [M⁺] calcd for C₁₂H₁₁O₂S₂: 279.0513; found: 279.0520.

S-(4-Methoxyphenyl) 4-methylbenzenesulfonothioate²⁰ (2b): White solid; 79%, 0.25 g; m.p. 84–85 °C (lit.¹¹ m.p. 84–85 °C). IR (KBr, cm⁻¹): ν = 1341, 1152. ¹H NMR (400 MHz, DMSO-d₆): δ 7.51 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.88-6.84 (m, 4H), 3.88 (s, 3H), 3.86 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆): δ 163.4, 162.3, 138.2, 134.8, 129.9, 118.8, 114.9, 113.8, 55.8, 55.5. MS (ESI): m/z (%) = 311.0 ([M⁺], 100). HRMS (ESI): m/z [M⁺] calcd for C₁₄H₁₃O₄S₂: 311.0411; found: 311.0419.

S-(4-Ethoxyphenyl) 4-ethylbenzenesulfonothioate²⁰ (2c): White solid; 76%, 0.26 g; m.p. 89–90 °C (lit.²⁰ m.p. 89 °C). IR (KBr, cm⁻¹): ν = 1344, 1153. ¹H NMR (400 MHz, DMSO-d₆): δ 7.68 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 4.09-4.05 (m, 4H), 1.34-1.29 (m, 6H). ¹³C NMR (100 MHz, DMSO-d₆): δ 163.7, 158.3, 131.2, 130.1, 129.0, 124.1, 115.8, 114.9, 64.8, 64.7, 14.5, 14.4. MS (ESI): m/z (%) = 339.1 ([M⁺], 100). HRMS (ESI): m/z [M⁺] calcd for C₁₆H₁₆O₂S₂: 339.0725; found: 339.0734.

S-Phenyl benzenesulfonothioate¹² (2d): White solid; 80%, 0.20 g; m.p. 39–41 °C (lit.¹² m.p. 39–41 °C). IR (KBr, cm⁻¹): ν = 1342, 1151. ¹H NMR (400 MHz, DMSO-d₆): δ 7.76-7.73 (m, 1H), 7.61-7.55 (m, 5H), 7.46-7.41 (m, 2H), 7.36-7.32 (m, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 142.7, 136.6, 134.6, 132.2, 129.8, 129.6, 127.8, 127.4. MS (ESI): m/z (%) = 251.0 ([M⁺], 100). HRMS (ESI): m/z [M⁺] calcd for C₁₃H₁₁O₄S₂: 251.0200; found: 251.0207.

S-(4-Fluorophenyl) 4-fluorobenzenesulfonothioate¹² (2e): White solid; 82%, 0.22 g; m.p. 70–71 °C (lit.¹² m.p. 70 °C). IR (KBr, cm⁻¹): ν = 1341, 1153. ¹H NMR (400 MHz, DMSO-d₆): δ 7.67-7.62 (m, 2H), 7.47-7.38 (m, 4H), 7.30-7.25 (m, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 166.6 (d, J = 84.2 Hz), 163.4 (d, J = 81.2 Hz), 138.4 (d, J = 9.4 Hz), 138.0 (d, J = 2.8 Hz), 131.1 (d, J = 10.1 Hz), 123.4 (d, J = 3.2 Hz), 117.5 (d, J = 22.3 Hz), 117.2 (d, J = 23.1 Hz). ¹⁹F NMR (375 MHz, DMSO-d₆): δ (d, J = 102.6, −106.9). MS (ESI): m/z (%) = 287.0 ([M⁺], 100). HRMS (ESI): m/z [M⁺] calcd for C₁₃H₁₁F₂O₂S₂: 287.0012; found: 287.0019.

S-(4-Chlorophenyl) 4-chlorobenzenesulfonothioate¹² (2f): White solid; 84%, 0.28 g; m.p. 134–136 °C (lit.¹² m.p. 134–136 °C). IR (KBr, cm⁻¹): ν = 1345, 1153. ¹H NMR (400 MHz, DMSO-d₆): δ 6.72 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.36-7.30 (m, 4H). ¹³C NMR (100 MHz, DMSO-d₆): δ 141.2, 140.4, 138.6, 137.7, 129.8, 129.2, 128.9, 126.1. MS (ESI): m/z (%) = 318.9 ([M⁺], 75), 322.9 ([M⁺], 25). HRMS (ESI): m/z [M⁺] calcd for C₁₃H₁₁Cl₂O₂S₂: 318.9421; found: 318.9429; C₁₃H₁₁Cl₂O₂S₂: 322.9362; found: 322.9369.

S-(4-Bromophenyl) 4-bromobenzenesulfonothioate¹² (2g): White solid; 85%, 0.36 g; m.p. 160–161 °C (lit.¹⁶ m.p. 160–161 °C). IR (KBr, cm⁻¹): ν = 1343, 1152. ¹H NMR (400 MHz, DMSO-d₆): δ 7.78 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 141.7, 137.7, 132.9, 132.2, 129.2, 128.9, 127.1, 126.5. MS (ESI): m/z (%) = 406.8 ([M⁺], 51), 410.8 ([M⁺], 49). HRMS (ESI): m/z [M⁺] calcd for C₁₃H₁₁Br₂O₂S₂: 406.8411; found: 406.8418; C₁₃H₁₁Br₂O₂S₂: 410.8370; found: 410.8377.

S-(4-Nitrophenyl) 4-nitrobenzenesulfonothioate¹² (2h): White solid; 80%, 0.29 g; m.p. 181–183 °C (lit.¹² m.p.
181–183 °C). IR (KBr, cm⁻¹): ν = 1345, 1152. ¹H NMR (400 MHz, DMSO-d₆): δ 8.37 (d, J = 8.8 Hz, 2H), 8.28 (t, J = 9.2 Hz, 2H), 7.88–7.80 (m, 2H), 7.66 (t, J = 8.8 Hz, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 151.2, 149.8, 137.9, 134.3, 129.4, 129.1, 127.5, 126.2, 125.2. MS (ESI): m/z (%) = 341.0 ([M⁺]¹⁰⁰), 100. HRMS (ESI): m/z [M⁺] calculated for C₉H₇N₃O₈S₂: 340.9902; found: 340.9900.

S-(2-Methylphenyl) 2-methoxybenzenesulfonothioate¹¹

(2i): Yellowish solid; 77%; 0.24 g; mp 39–40 °C (lit.¹² m.p. 39–40 °C). IR (KBr, cm⁻¹): ν = 1351, 1342, 1153. ¹H NMR (400 MHz, DMSO-d₆): δ 8.74-8.70 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 2H), 7.14-7.06 (m, 2H), 2.68 (s, 3H), 2.17 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆): δ 139.0, 138.6, 138.1, 133.6, 132.8, 131.7, 131.0, 130.8, 130.6, 128.9, 127.6, 126.3. MS (ESI): m/z (%) = 279.1 ([M⁺]¹⁰⁰), 100. HRMS (ESI): m/z [M⁺] calculated for C₉H₇ClO₂S₂: 279.0513; found: 279.0521.

S-(2-Chlorophenyl) 2-chlorobenzenesulfonothioate

(2j): White solid; 75%; 0.24 g; mp 81–83 °C (lit.¹³ m.p. 81–83 °C). IR (KBr, cm⁻¹): ν = 1343, 1150. ¹H NMR (400 MHz, DMSO-d₆): δ 6.71-6.76 (m, 2H), 7.61 (m, 1H), 7.38 (m, 1H), 7.24-7.19 (m, 3H), 7.01 (m, 1H), 2.34 (s, 3H), 2.32 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆): δ 140.7, 139.4, 138.4, 134.0, 132.4, 129.6, 128.9, 127.7, 126.7, 126.4, 125.8, 125.3, 20.9. MS (ESI): m/z (%) = 279.1 ([M⁺]¹⁰⁰), 100. HRMS (ESI): m/z [M⁺] calculated for C₉H₇ClO₂S₂: 279.0513; found: 279.0520.

S-(3-Methylphenyl) 3-methoxybenzenesulfonothioate

(2k): Yellowish solid; 72%; 0.22 g; mp 56–58 °C (lit.¹⁴ m.p. 56–58 °C). IR (KBr, cm⁻¹): ν = 1343, 1152. ¹H NMR (400 MHz, DMSO-d₆): δ 7.77-7.69 (m, 2H), 7.61 (m, 1H), 7.38 (m, 1H), 7.24-7.19 (m, 3H), 7.01 (m, 1H), 2.34 (s, 3H), 2.32 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆): δ 140.7, 139.4, 138.4, 134.0, 132.4, 129.6, 128.9, 127.7, 126.7, 126.4, 125.8, 125.3, 20.9. MS (ESI): m/z (%) = 279.1 ([M⁺]¹⁰⁰), 100. HRMS (ESI): m/z [M⁺] calculated for C₉H₇ClO₂S₂: 279.0513; found: 279.0520.

S-(3-Chlorophenyl) 3-chlorobenzenesulfonothioate

(2l): White solid; 76%; 0.22 g; mp 105–107 °C (lit.¹⁵ m.p. 105–107 °C). IR (KBr, cm⁻¹): ν = 1343, 1153. ¹H NMR (400 MHz, DMSO-d₆): δ 7.41-7.35 (m, 4H), 7.33-7.26 (m, 6H), 4.67 (s, 2H), 3.83 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 139.6, 133.2, 130.8, 128.7, 126.9, 126.7, 125.7, 125.1, 125.0, 20.2. MS (ESI): m/z (%) = 279.1 ([M⁺]¹⁰⁰), 100. HRMS (ESI): m/z [M⁺] calculated for C₁₂H₁₃ClO₂S₂: 279.0513; found: 279.0519.

Declaration of conflicting interests

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