Homocouplings of Sodium Arenesulfinates: Selective Access to Symmetric Diaryl Sulfides and Diaryl Disulfides

Xin-Zhang Yu 1,2, Wen-Long Wei 2, Yu-Lan Niu 1,*, Xing Li 2, Ming Wang 3 and Wen-Chao Gao 2,3,†

1 Department of Chemistry and Chemical Engineering, Taiyuan Institute of Technology, Taiyuan 030008, China
2 Department of Biomedical Engineering, Taiyuan University of Technology, Taiyuan 030024, China
3 School of Chemistry and Molecular Engineering, East China Normal University, 3663, Shanghai 200062, China
* Correspondence: niuyulan@163.com (Y.-L.N.); gaowenchao@tyut.edu.cn (W.-C.G.)

Abstract: Symmetrical diaryl sulfides and diaryl disulfides have been efficiently and selectively constructed via the homocoupling of sodium arenesulfinates. The selectivity of products relied on the different reaction systems: symmetrical diaryl sulfides were predominately obtained under the Pd(OAc)2 catalysis, whereas symmetrical diaryl sulfides were exclusively yielded in the presence of the reductive Fe/HCl system.

Keywords: sodium arenesulfinates; homocoupling; symmetric; diaryl sulfides; diaryl disulfides

1. Introduction

Symmetrical sulfides [1–3] and disulfides [4–7] are ubiquitous structural motifs, and their corresponding derivatives have found prevalent existence in many biologically active molecules, pharmaceuticals, ligands, functional materials, and natural products. Owing to their importance, various synthetic methodologies have been developed for the preparation of these two classes of sulfur compounds [8–23]. Although the cross-coupling reactions of various sulfur surrogates with other aromatic reagents, such as aromatic halides, arenediazonium salts, and others, are generally efficient for the construction of these two symmetric structures [24–36], the homocoupling of arylsulfonyl derivatives [37,38] and thiols [39–48] has proven to be the most straightforward and convenient strategy in terms of simplicity. Despite these major advances, the utility of environmentally friendly sulfur sources for symmetric sulfides and disulfides is still highly desirable.

Due to their stable, greener, and inexpensive features, sodium sulfinates have been utilized as ideal sulfur donors and widely applied as the coupling partners in C-S cross-coupling reactions, such as sulfonylation [49,50], thiosulfonylation [51], sulfinylation [52,53], and sulfenylation [54–59]. Especially by reductive coupling, the sodium sulfinates could serve as sulfenylation reagents for the synthesis of unsymmetric sulfides under Pd, Cu, or I2 catalysts (Scheme 1a) [54–59]. However, the application of sodium sulfinates for the construction of symmetric disulfides by homocoupling reactions was still less explored. On the other hand, although several reaction systems, such as EtOP(O)H 2, TiCl4/Sm, WCl6/NaI, WCl6/Zn, MoCl6/Zn, Cp2TiCl2/Sm, and Silphos, have been reported to mediate the conversion of sodium arenesulfinates into symmetric diaryl disulfides by reductive coupling (Scheme 1b) [60–63], they generally suffered from limited substrate scope, expensive reagents, or complicated procedures. Herein, we would like to report an efficient strategy for the selective synthesis of symmetrical diaryl sulfides and diaryl disulfides using sodium sulfinates as sulfonylation reagents through homocoupling.
Previous work

a) Synthesis of unsymmetric sulfides from ArSO₂Na

\[ \text{R} \begin{array}{c} \text{SO}_2 \text{Na} \\ \text{Cat.} = \text{I}_2, \text{Pd}, \text{Cu} \end{array} \xrightarrow{\text{R} \rightarrow \text{H}} \text{R-S-R'} \]

b) Synthesis of symmetric disulfides from ArSO₂Na

\[ \text{R} \begin{array}{c} \text{SO}_2 \text{Na} \\ \text{Reductive coupling} \end{array} \rightarrow \text{R-S-S-R} \]

This work

c) Selective access of symmetric sulfides and disulfides from ArSO₂Na

\[ \begin{array}{c} \text{R} \begin{array}{c} \text{SO}_2 \text{Na} \\ \text{Pd(OAc)}_2/\text{NMP} \end{array} \xrightarrow{150 \degree \text{C}} \text{R-S-S-R} \\ \text{FeCl}_3/\text{DMF} \xrightarrow{130 \degree \text{C}} \text{R-S-S-R} \end{array} \]

Scheme 1. Sulfides and disulfides construction from sodium sulfinates.

2. Results and Discussion

Our initial study started with sodium phenylsulfinate 1a as the model substrate to explore the formation of diphenylsulfide 2a. First, by screening different solvents, NMP was proven to be the most effective out of the others, such as DMF and DMSO (Table 1, entry 3 vs. 1–2). The catalyst played a decisive role in this reaction: among the common metal catalysts, Pd(OAc)₂ was the best one to afford diphenylsulfide 2a in 47% yield (entry 3 vs. 4–6). With CuI and Ni(OAc)₂ as catalysts, the product 2a was not detected at all (entries 4 and 5). Only a trace amount of 2a was observed when FeCl₃ was employed (entry 6). The yield could be improved to 60% by increasing reaction temperature to 150 °C (entry 7 vs. 3 and 8). Most importantly, a decrease of catalyst loading to 2 mol% could further increase the yield to 89%, and no better result was observed by continuously reducing the catalyst loading (entry 10 vs. 7, 9–11). The desired 2a was not detected when sodium benzenesulfinate was replaced with benzenesulfinic acid in the presence of NaOH under the same conditions (entry 12).

Table 1. Optimization of reaction conditions for sodium benzenesulfinate to diphenylsulfide [a].

| Entry | Solvent (mL) | Catalyst (mol%) | T (°C) | Yield [b] (%) |
|-------|--------------|----------------|--------|--------------|
| 1     | DMF (1.0)    | Pd(OAc)₂ (2.5) | 130    | 28           |
| 2     | DMSO (1.0)   | Pd(OAc)₂ (2.5) | 130    | trace        |
| 3     | NMP (1.0)    | Pd(OAc)₂ (2.5) | 130    | 47           |
| 4     | NMP (1.0)    | CuI (2.5)      | 130    | N.D. [c]     |
| 5     | NMP (1.0)    | Ni(OAc)₂ (2.5) | 130    | N.D. [c]     |
| 6     | NMP (1.0)    | FeCl₃ (2.5)    | 130    | trace        |
| 7     | NMP (1.0)    | Pd(OAc)₂ (2.5) | 150    | 60           |
| 8     | NMP (1.0)    | Pd(OAc)₂ (2.5) | 170    | 52           |
| 9     | NMP (1.0)    | Pd(OAc)₂ (2.0) | 150    | 89           |
| 10    | NMP (1.0)    | Pd(OAc)₂ (1.5) | 150    | 80           |
| 11    | NMP (1.0)    | Pd(OAc)₂ (0.5) | 150    | 71           |
| 12    | NMP (1.0)    | Pd(OAc)₂ (2.0) | 150    | 0            |

[a] Reactions were performed on a 0.4 mmol scale of sodium benzenesulfinate 1a (67.0 mg) under identified conditions for 26 h; [b] isolated yield; [c] N.D. = not detected; [d] PhSO₂Na was replaced with PhSO₂H/NaOH.
Having built the optimal conditions for the construction of diphenylsulfide 2a, we turned our attention to explore the generality of sodium sulfinates. As shown in Table 2, a variety of substrates could undergo the homocoupling to afford symmetrical diaryl sulfides with high chemoselectivity. It was found that sodium benzenesulfinates with electron-donating groups such as 4-methyl, 3-methyl, 2-methyl, 4-methoxyl, 3-methoxyl, 2-methoxyl, 4-isopropyl, and 4-tert-butyl on the phenyl ring gave the corresponding products 2b–2i in good yields. Electron-withdrawing groups, such as F, Cl, Br, and NO₂, were also well-tolerated to provide the desired products 2j–2s in moderate to good yields that were somewhat lower than the electron-donating groups offered. To our delight, the intramolecular formation of sulfides was also tried, and the desired dibenzothiophene 2t was produced in a 51% yield.

Table 2. Scope of sodium arylsulfinates to diaryl sulfides[a,b].

| Product | Yield | Conditions |
|---------|-------|------------|
| 2a      | 26%, 89% | R = H, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2b      | 28%, 86% | R = Me, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2c      | 34%, 83% | R = Me, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2d      | 35%, 78% | R = Me, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2e      | 28%, 85% | R = OMe, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2f      | 34%, 81% | R = OMe, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2g      | 34%, 73% | R = i-Pr, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2h      | 28%, 84% | R = Pr, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2i      | 28%, 81% | R = t-Bu, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2j      | 34%, 76% | R = F, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2k      | 34%, 72% | R = NO₂, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2l      | 35%, 67% | R = NO₂, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2m      | 35%, 73% | R = Cl, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2n      | 35%, 68% | R = Br, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2o      | 35%, 63% | R = Br, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2p      | 30%, 83% | R = Br, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2q      | 30%, 77% | R = Cl, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2r      | 30%, 73% | R = Cl, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2s      | 30%, 80% | R = Cl, Pd(OAc)₂ (2.0), NMP, 150 °C |
| 2t      | 24%, 51% | R = Cl, Pd(OAc)₂ (2.0), NMP, 150 °C |

[a] Reaction conditions: sodium arylsulfinate 1 (0.4 mmol), Pd(OAc)₂ (2 mg, 2 mol%), NaOH (16.0 mg), NMP (1.0 mL), and 150 °C; [b] isolated yield; [c] 4-methylbenzenesulfinic acid (0.4 mmol) was used as a starting material in the presence of Pd(OAc)₂ (2 mg, 2 mol%), NaOH (16.0 mg) in NMP (1.0 mL) at 150 °C; [d] N₂ was adopted.

During our studies on the synthesis of diphenylsulfide 2a, 1,2-diphenyldisulfide 3a was accidentally detected when using CuI as a reductant. This discovery encouraged us to search for optimal conditions for the reductive coupling of sodium benzenesulfinate for 1,2-diphenyldisulfide 3a. Fortunately, using Fe/HCl as the reductive system, diphenyldisulfide 3a was isolated as the major product. Subsequently, the investigation of the concentration of hydrochloric acid revealed that increasing the concentration led to the higher yield, and 12 mol/L of hydrochloric acid gave up to 96% yield (Table 3, entry 4 vs. 1–3). The highest yield was obtained when 4.0 equiv. of HCl was used (Table 2, entry 4). Increasing or decreasing the amount resulted in lower yields (entries 5 and 6 vs. 4). It was found that 2.0 equiv. of Fe was suitable for this transformation, and other amounts did not improve the yield further (entry 4 vs. 7 and 8). More notably, the similar high yield was
provided when the time was shortened to 9 h (entry 9). However, sodium benzenesulfinate generated in situ by the reaction of NaOH and the equivalent of 4-methylbenzenesulfinic acid only afforded the target product (3b) in a 59% yield (entry 10).

Table 3. Optimization of reaction conditions for sodium benzenesulfinate to diphenyl disulfide \([a]\).

| Entry | Concentration of HCl (mol/L) | HCl (equiv.) | Fe (equiv.) | Yield \([b]\) (%) |
|-------|-----------------------------|-------------|-------------|-----------------|
| 1     | 1                           | 4.0         | 2.0         | 34              |
| 2     | 4                           | 4.0         | 2.0         | 60              |
| 3     | 8                           | 4.0         | 2.0         | 78              |
| 4     | 12                          | 4.0         | 2.0         | 96              |
| 5     | 12                          | 2.0         | 2.0         | 71              |
| 6     | 12                          | 6.0         | 2.0         | 90              |
| 7     | 12                          | 4.0         | 1.5         | 81              |
| 8     | 12                          | 4.0         | 2.5         | 93              |
| 9     | 12                          | 4.0         | 2.0         | 96 \([c]\)       |
| 10    | 12                          | 4.0         | 2.0         | 59              |

\([a]\) Reactions were performed on a 0.2 mmol scale of sodium benzenesulfinate 1a (33.5 mg) in DMF (1.0 mL) at 130 °C for 20 h. \([b]\) Isolated yield; \([c]\) reaction time: 9 h; \([d]\) PbSO\(_4\)Na was generated in situ.

With the optimized reaction conditions in hand, we next focused on the evaluation of the scope of the coupling partner to symmetric disulfides, and the results are summarized in Table 4. To our delight, it was found that the reaction could be compatible with a broad range of functional groups, furnishing the corresponding products in good to excellent yields. Although various functional groups, including electronically diverse (3a–3u) and sterically hindered (3d, 3g, 3h, 3i, 3l, and 3r) ones are readily tolerated, some substantial influence of electronic properties and steric hindrance of the substituents was observed. The substrates possessing an electron-rich group (Me, MeO, i-2Pr, and t-Bu) showed higher yields than those bearing an electron-poor group (F, Cl, Br, and CF\(_3\)) (3b–3i vs. 3j–3l, 3p–3s, and 3u). Among substrates, sodium ortho-substituted aryl sulfinates, which are sterically hindered, gave relatively lower yields (3d vs. 3b, 3c, and 3g vs. 3e, 3f, and 3l vs. 3j, 3k, and 3r vs. 3p and 3q). In addition, an 82% yield was obtained when sodium 2-naphthalenesulfinic acid was employed as a substrate (3l). Notably, sodium 3-carboxybenzenesulfinate and sodium thiophene-2-sulfinate could not be transformed into the corresponding disulfides.

To further evaluate the utility of these two protocols, two gram-scale reactions were subsequently carried out (Scheme 2). The corresponding products 2a and 3a could be afforded in 88% and 94% yields in a 10 mmol scale, respectively, demonstrating the practicability of the present methodology.

Scheme 2. Gram-scale reactions of sodium benzenesulfinate.
To elucidate the reaction mechanism for the homocoupling of sodium arylsulfinates, several control experiments were conducted (Scheme 3). The formation of both symmetric diphenyl disulfide 3a and diphenyl sulfide 2a was not detected after the addition of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 2 equiv.) to the standard reaction systems (Scheme 3a,b), indicating that both of these two transformations underwent a free-radical process. For the synthesis of 2a, the disulfide 3a was detected by mass spectrometry. The preparation of disulfides from sodium arylsulfinates under Pd(OAc)$_2$ catalysis was also demonstrated by Xiang and co-workers [55]. In addition, the transformation from 3a to 2a could be successfully realized in the presence of a catalytic amount of Pd(OAc)$_2$ and sodium sulfinate 1a (Scheme 3c,d).

Based on the results of the control experiments and literature reports [64,65], a plausible mechanism for the homocoupling of sodium arylsulfinate 1 to the selective access to symmetric sulfide 2 and disulfide 3 is shown in Scheme 4. First, in the reductive Fe/HCl system, disulfide 3a could be generated via the homocoupling of the thiyl radical A, which comes from the radical reduction of sodium phenylsulfinate 2a (Scheme 4a). Alternatively, disulfide 3a could be also formed in the presence of catalytic Pd(OAc)$_2$. After disulfide 3a was formed, the Pd(II)-insertion to the S-S bond produced the metal-intermediate B, which underwent ligand exchange to form intermediate C. The thermal extrusion of SO$_2$ of intermediate C resulted in the formation of intermediate D [66], which underwent the re-
ductive elimination to give the target sulfide 2a and regenerate Pd(0) into the next catalytic cycle (Scheme 4b).

![Scheme 3. Control experiments for the homocoupling of sodium phenylsulfinate.](image)

**a) symmetric disulfide**

![Scheme 4. Proposed mechanism for the homocoupling of sodium arylsulfinate.](image)
3. Materials and Methods

Unless otherwise indicated, all reagents and solvents were purchased from commercial sources without further purification. Deuterated solvents were purchased from Sigma–Aldrich(Shanghai, China.). Refinement of the mixed system was achieved through column chromatography, which was performed on silica gel (200–300 mesh) with petroleum ether (solvent A)/ethyl acetate (solvent B) gradients as elution. In addition, all yields were referred to the isolated yields (average of two runs) of the compounds, unless otherwise specified. The known compounds were partly characterized by melting points (for solid samples), 1H NMR, and compared to authentic samples or the literature data. Melting points were measured with an RD-II digital melting point apparatus (Henan, China) and were uncorrected. 1H NMR data were acquired on a Bruker Advance 600 MHz spectrometer (Bruker, Germany). using CDCl3 as solvent. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent CDCl3 resonance as the internal standard (CDCl3 = 7.26). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. 13C NMR data were collected at 100 MHz, with complete proton decoupling. The chemical shifts are reported in ppm downfield to the central CDCl3 resonance (δ = 77.0). High-resolution mass spectra were performed on a micrOTOF-Q II instrument (Bruker, Germany), with an ESI source.

3.1. Typical Procedure for Symmetric Diaryl Sulfides 2

The mixture of sodium arylsulfinate 1 (0.4 mmol) and Pd(OAc)2 (2 mg, 2 mol%) in NMP (1.0 mL) was stirred at 150 °C (oil bath) until the substrate was completely consumed, which was determined by TLC. Finally, the reaction mixture was purified by silica gel column chromatography (PE: EA = 40: 1) to afford the desired coupling product diarylsulfides 2.

3.2. Typical Procedure for Symmetric Diaryl Sisulfides 3

The mixture of sodium arylsulfinate 1 (0.2 mmol), Fe powder (23 mg, 2.0 equiv), and HCl (12 M, 67.0 µL) in DMF (1.0 mL) was stirred at 130 °C (oil bath), until the substrate was completely consumed, which was determined by TLC. Finally, the reaction mixture was purified by silica gel column chromatography (PE: EA = 40: 1) to afford the desired coupling product diaryldisulfides 3.

3.3. Gram-Scale Reaction of Sodium Benzenesulfinate to Diphenylsulfide

The mixture of sodium benzenesulfinate 1a (1.64 g, 10 mmol) and the catalyst, Pd(OAc)2 (45 mg, 2 mol%) in NMP (10 mL), was stirred at 150 °C (oil bath) until the substrate was completely consumed, which was determined by TLC. Finally, the reaction mixture was purified by silica gel column chromatography to afford the coupling product diphenylsulfide 2a (1.640 g, 88% yield).

3.4. Gram-Scale Reaction of Sodium Benzenesulfinate to 1,2-Diphenyldisulfane

The mixture of sodium benzenesulfinate 1a (1.640 g, 10 mmol), Fe powder (1.150 g, 2.0 equiv.), and 12 mol/L HCl (3.35 mL) in DMF (15 mL) was stirred at 130 °C (oil bath) until the substrate was completely consumed, which was determined by TLC. Finally, the reaction mixture was purified by silica gel column chromatography to afford the coupling product 1,2-diphenyldisulfane 3a (2.050 g, 94% yield).

3.5. Characterization Data for Homo-Coupling Products of Sodium Arylsulfinate

3.5.1. Characterization Data for the Products of Diaryl sulfides

Diphenyl sulfide (2a) [8]. Colorless liquid (33.1 mg, 89% yield); Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.35−7.33 (m, 4H), 7.32−7.27 (m, 4H), 7.26−7.22 (m, 2H) ppm; 13C[1H] NMR (100 MHz, CDCl3) δ 135.9, 131.2, 129.3, and 127.1; HRMS (ESI) m/z [M + H]+ calculated for C12H11S 187.0576, found 187.0579.
4,4'-Dimethyl diphenyl sulfide (2b) [67]. White solid (36.8 mg, 86% yield); mp 57–58 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.23 ($dt$, $J = 4.8$, 2.4 Hz, 4H), 7.10 ($d$, $J = 7.8$ Hz, 4H), 2.33 (s, 6H) ppm; $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 136.9, 132.7, 131.1, 129.9, and 21.0; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{14}$H$_{15}$S = 215.0889, found 215.0885.

3,3'-Dimethyl diphenyl sulfide (2e) [68]. Colorless liquid (35.5 mg, 83% yield); $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.20–7.16 (m, 4H), 7.13 ($d$, $J = 7.8$ Hz, 2H), 7.05 ($d$, $J = 7.8$ Hz, 2H), and 2.31 (s, 6H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{14}$H$_{15}$S = 215.0889, found 215.0885.

Di-o-tolyldisulfide (2d) [8]. White solid (33.4 mg, 78% yield); mp 64–65 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35–7.22 (m, 2H), 7.16 ($dd$, $J = 6.0$, 1.2 Hz, 2H), 7.11–7.08 (m, 2H), 7.05 ($dd$, $J = 6.6$, 1.2 Hz, 2H), and 2.38 (s, 6H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{14}$H$_{15}$S = 215.0889, found 215.0885.

Bis(4-methoxyphenyl)sulfide (2e) [8]. White solid (41.8 mg, 85% yield); mp 44–46 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.29–7.26 (m, 4H), 6.83 ($dt$, $J = 9.0$, 2.4 Hz, 4H), and 3.79 (s, 6H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{14}$H$_{15}$O$_2$S = 247.0787, found 247.0785.

Bis(3-methoxyphenyl)sulfide (2f) [8]. White solid (39.9 mg, 81% yield); mp 45–47 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.24–7.18 (m, 2H), 6.96–6.92 (m, 2H), 6.90–6.88 (m, 2H), 6.81–6.77 (m, 2H), and 3.76 (s, 6H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{14}$H$_{15}$O$_2$S = 247.0787, found 247.0785.

Bis(2-methoxyphenyl)sulfide (2g) [8]. White solid (35.9 mg, 73% yield); mp 73–74 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.21 (m, 2H), 7.06 ($dd$, $J = 5.6$, 2.0 Hz, 2H), 6.93–6.90 ($dd$, $J = 7.6$, 0.8 Hz, 2H), 6.87–6.85 ($dd$, $J = 6.4$, 1.2 Hz, 2H), and 3.87 (s, 6H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{14}$H$_{15}$O$_2$S = 247.0787, found 247.0785.

4,4'-Disopropyl diphenyl sulfide (2h). White solid (45.4 mg, 84% yield); mp 73–75 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.28–7.25 (m, 4H), 7.17–7.14 (m, 4H), 2.92–2.82 (m, 2H), and 1.24 ($d$, $J = 6.6$ Hz, 12H) ppm; $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 147.8, 132.8, 131.0, 127.3, 33.7, and 23.9; HRMS (ESI) m/z [M + K]$^+$ calculated for C$_{18}$H$_{22}$SK = 309.1074, found 309.1073.

4,4'-Di-tert-butyl diphenyl sulfide (2i) [69]. White solid (48.3 mg, 81% yield); mp 83–84 °C; $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.34–7.30 (m, 4H), 7.28 ($t$, $J = 1.8$ Hz, 2H), 7.26 ($t$, $J = 2.4$ Hz, 2H), and 1.30 (s, 18H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{20}$H$_{27}$S = 299.1828, found 299.1821.

4,4'-Difluorodiphenyl sulfide (2j) [8]. Colorless liquid (33.7 mg, 76% yield); $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33–7.28 (m, 4H), 7.03–6.98 (m, 4H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{12}$H$_8$F$_2$S = 223.0388, found 223.0393; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.3 ppm.

3,3'-Difluorodiphenyl sulfide (2k) [68]. Colorless liquid (32.0 mg, 72% yield); $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33–7.26 (m, 2H), 7.16–7.11 (m, 2H), 7.06–7.01 (m, 2H), 6.99–6.94 (m, 2H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{12}$H$_8$F$_2$S = 223.0388, found 223.0393; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -111.5 ppm.

Bis(2-fluorophenyl)sulfide (2l) [70]. Colorless liquid (29.8 mg, 67% yield); $R_f = 0.6$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31–7.22 (m, 4H) and 7.14–7.06 (m, 4H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{12}$H$_8$F$_2$S = 233.0598, found 233.0593; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -108.7 ppm.

Bis(4-nitrophenyl)sulfide (2m) [8]. White solid (40.3 mg, 73% yield); mp 156–158 °C; $R_f = 0.5$ (petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.06 ($dt$, $J = 9.0$, 2.4 Hz, 2H), 7.58–7.52 (m, 2H), 7.48–7.44 (m, 2H), and 7.17 ($dt$, $J = 9.0$, 2.4 Hz, 2H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{12}$H$_8$N$_2$O$_2$S = 277.0278, found 277.0281.

Bis(3-nitrophenyl)sulfide (2n) [71]. White solid (37.5 mg, 68% yield); mp 42–44 °C; $R_f = 0.5$ (petroleum ether); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 ($t$, $J = 4.0$ Hz, 2H), 8.15–8.06 (m, 2H), 7.86–7.77 (m, 2H), and 7.53 (t, $J = 12.0$ Hz, 2H) ppm; HRMS (ESI) m/z [M + H]$^+$ calculated for C$_{12}$H$_8$N$_2$O$_2$S = 277.0278, found 277.0282.
Bis(2-nitrophenyl)sulfide (2o) [8]. Yellow solid (34.8 mg, 63% yield); mp 123–124 °C; Rf = 0.5 (petroleum ether); 1H NMR (400 MHz, CDCl3) δ 8.41 (dd, J = 8.4, 1.2 Hz, 2H), 8.07 (dd, J = 8.4, 1.2 Hz, 2H), 7.84–7.77 (m, 2H), and 7.61–7.54 (m, 2H) ppm; HRMS (ESI) m/z [M + H]+ calculated for C12H8N2O2S 277.0278, found 277.0281.

4,4′-Dichlorodiphenyl sulfide (2p) [8]. White solid (42.2 mg, 83% yield); mp 88–89 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.30–7.27 (m, 4H) and 7.26–7.23 (m, 4H) ppm; HRMS (ESI) m/z [M + H]+ calculated for C12H8Cl2S 254.9797, found 254.9792.

Bis(3-clorophenyl)sulfide (2q) [71]. Colorless liquid (39.1 mg, 77% yield); Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.32–7.31 (m, 2H), 7.26–7.23 (m, 4H), and 7.22–7.19 (m, 2H) ppm; HRMS (ESI) m/z [M + H]+ calculated for C12H8Cl2S 254.9797, found 254.9792.

Bis(2-clorophenyl)sulfide (2r) [68]. White solid (37.1 mg, 73% yield); mp 68–70 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.47 (dd, J = 7.8, 1.2 Hz, 2H), 7.24 (td, J = 7.8, 1.8 Hz, 2H), 7.19 (td, J = 7.8, 1.2 Hz, 2H), and 7.14 (dd, J = 7.8, 1.8 Hz, 2H) ppm; HRMS (ESI) m/z [M + H]+ calculated for C12H8Cl2S 254.9797, found 254.9792.

Bis(4-bromophenyl)sulfide (2s) [8]. White solid (54.7 mg, 80% yield); mp 110–111 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.45–7.40 (m, 4H) and 7.21–7.16 (m, 4H) ppm; HRMS (ESI) m/z [M + H]+ calculated for C12H8Br2S 342.8786, found 342.8784.

Dibenz[o,b,d]thiophene (2t) [72]. White solid (38 mg, 51% yield); m.p. 95–96 °C. Rf = 0.8 (PE/EA = 20:1); 1H NMR (400 MHz, CDCl3) δ 8.17 (m, 2H), 7.87 (dd, 2 H, J = 8.0, 4.0 Hz), and 7.47 (m, 4 H). The NMR data were consistent with the previous report (see spectra at Supplementary Materials).

3.5.2. Characterization Data for the Products of Diaryl Disulfides

Diphenyl disulfide (3a) [73]. White solid (21.0 mg, 96% yield); mp 61–62 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.54–7.45 (m, 4H), 7.33–7.26 (m, 4H), and 7.25–7.19 (m, 2H) ppm; 13C{1H} NMR (100 MHz, CDCl3) δ 137.0, 129.0, 127.5, and 127.1; HRMS (ESI) m/z [M]+ calculated for C12H10S2 218.0224, found 218.0217.

4-Methylphenyl disulfide (3b) [73]. White solid (22.9 mg, 93% yield); mp 47–48 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.39 (d, J = 8.4 Hz, 4H), 7.11 (d, J = 7.8 Hz, 4H), and 2.32 (s, 6H) ppm; 13C{1H} NMR (100 MHz, CDCl3) δ 137.4, 133.9, 129.8, 128.6, and 21.0; HRMS (ESI) m/z [M]+ calculated for C14H12S2 246.0537, found 246.0517.

3-Methylphenyl disulfide (3c) [73]. White solid (22.1 mg, 90% yield); mp 112–114 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.31 (d, J = 7.2 Hz, 4H), 7.19 (t, J = 7.4 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), and 2.32 (s, 6H) ppm; HRMS (ESI) m/z [M]+ calculated for C14H12S2 246.0537, found 246.0519.

Di(o-methylphenyl)disulfide (3d) [73]. White solid (20.9 mg, 85% yield); mp 40–42 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.24–7.21 (m, 2H), 7.19–7.15 (m, 2H), 7.11–7.07 (m, 2H), 7.06 (dd, J = 7.8, 1.8 Hz, 2H), and 2.37 (s, 6H) ppm; HRMS (ESI) m/z [M]+ calculated for C14H14S2 246.0537, found 246.0517.

Di(4-methoxyphenyl)disulfide (3e) [34]. White solid (25.6 mg, 92% yield); mp 45–47 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.31–7.27 (m, 4H), 6.87–6.81 (m, 4H), and 3.79 (s, 6H) ppm; HRMS (ESI) m/z [M]+ calculated for C14H14O2S2 278.0435, found 278.0423.

Di(3-methoxyphenyl)disulfide (3f) [34]. White solid (24.5 mg, 88% yield); mp 106–108 °C; Rf = 0.6 (petroleum ether); 1H NMR (400 MHz, CDCl3) δ 7.18–7.11 (m, 2H), 7.03–6.99 (m, 2H), 6.88–6.81 (m, 2H), 6.73–6.67 (m, 2H), and 3.69 (s, 6H) ppm; HRMS (ESI) m/z [M]+ calculated for C14H14O2S2 278.0435, found 278.0423.

Di(2-methoxyphenyl)disulfide (3g) [34]. White solid (23.4 mg, 84% yield); mp 120–121 °C; Rf = 0.6 (petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.53 (dd, J = 6.6, 12.2 Hz, 2H), 7.21–7.16 (m, 2H), 6.93–6.88 (m, 2H), 6.86 (d, J = 7.8 Hz, 2H), and 3.90 (s, 6H) ppm; HRMS (ESI) m/z [M]+ calculated for C14H14O2S2 278.0435, found 278.0427.

1,2-bis(4-isopropylphenyl)disulfane (3h) [73]. White solid (27.5 mg, 91% yield); mp 79–81 °C; Rf = 0.6 (Petroleum ether); 1H NMR (600 MHz, CDCl3) δ 7.44 (dt, J = 8.4, 4.8 Hz, 4H), 7.23–7.16 (m, 4H), 7.11–7.07 (m, 4H), 6.88–6.81 (m, 4H), and 3.79 (s, 6H) ppm; HRMS (ESI) m/z [M]+ calculated for C14H14O2S2 278.0435, found 278.0427.
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4H), 7.17 (dt, J = 7.8, 4.2 Hz, 4H), 2.93−2.86 (m, 2H), and 1.24 (d, J = 7.2 Hz, 12H) ppm; HRMS (ESI) m/z [M + H]+ calculated for C_{18}H_{25}S_{2} 303.1236, found 303.1226.

**Bis(4-tert-butylphenyl) disulfide (3i) [74].** White solid (28.7 mg, 87% yield); mp 88−89 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.46 (d, J = 9.0 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), and 1.31 (s, 18H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{20}H_{26}S_{2} 330.1476, found 330.1462.

**Bis(4-fluorophenyl) disulfide (3j) [34].** White solid (21.8 mg, 86% yield); mp 112−114 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.48−7.41 (m, 4H), and 7.05−6.98 (m, 4H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}F_{2}S_{2} 254.0035, found 254.0029; ^19^F NMR (376 MHz, CDCl_3) δ -113.4 ppm.

**Bis(3-fluorophenyl) disulfide (3k) [75].** White solid (20.6 mg, 81% yield); mp 93−94 °C; Rf = 0.6 (Petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.31−7.27 (m, 2H), 7.26 (s, 1H), 7.25−7.23 (m, 2H), 7.22 (t, J = 1.8 Hz, 1H), and 6.96−6.91 (m, 2H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}F_{2}S_{2} 254.0035, found 254.0030; ^19^F NMR (376 MHz, CDCl_3) δ -111.1 ppm.

**Bis(2-fluorophenyl)disulfide (3l) [75].** Slight yellow oil (19.9 mg, 75% yield); mp 119 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.40 (td, J = 7.8, 1.8 Hz, 2H), 7.28−7.25 (m, 2H), 7.12 (td, J = 7.8, 1.2 Hz, 2H), and 7.08−7.04 (m, 2H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}F_{2}S_{2} 254.0035, found 254.0029; ^19^F NMR (376 MHz, CDCl_3) δ -109.9 ppm.

**4,4′-Dichlorodiphenyl disulfide (3p) [73].** White solid (26.0 mg, 91% yield); mp 68−70 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.40 (dt, J = 8.4, 4.8 Hz, 4H) and 7.28 (dt, J = 8.4, 4.8 Hz, 4H) ppm; ^13^C(^1^H) NMR (100 MHz, CDCl_3) δ 135.1, 133.7, 129.4, and 129.3; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}Cl_{2}S_{2} 285.9444, found 285.9421.

**Bis(3-chlorophenyl)disulfide (3q) [73].** White solid (25.2 mg, 88% yield); mp 80−82 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 2.4 Hz, 1H), 7.37−7.32 (m, 2H), 7.26 (d, J = 2.4 Hz, 1H), and 7.24−7.20 (m, 4H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}Cl_{2}S_{2} 285.9444, found 285.9425.

**Bis(2-chlorophenyl)disulfide (3r) [76].** White solid (24.0 mg, 84% yield); mp 90−91 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (400 MHz, CDCl_3) δ 7.48 (dd, J = 8.0, 1.6 Hz, 2H), 7.30 (dd, J = 7.2, 1.6 Hz, 2H), 7.14 (td, J = 7.6, 1.2 Hz, 2H), and 7.09 (td, J = 7.6, 1.6 Hz, 2H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}Cl_{2}S_{2} 285.9444, found 285.9421.

**Bis(4-bromoophenyl)disulfide (3s) [75].** White solid (33.3 mg, 89% yield); mp 110−112 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.44−7.41 (m, 4H), and 7.35−7.32 (m, 4H) ppm; HRMS (ESI) m/z [M]^+ calculated for C_{12}H_{8}Br_{2}S_{2} 373.8434, found 373.8414.

**2,2′-Dinaphthyl disulfide (3t) [77].** White solid (26.1 mg, 82% yield); mp 139−141 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.99 (d, J = 1.8 Hz, 2H), 7.82−7.76 (m, 4H), 7.75−7.71 (m, 2H), 7.62 (dd, J = 9.0, 6.6 Hz, 2H), and 7.49−7.44 (m, 4H) ppm; HRMS (ESI) m/z [M + H]^+ calculated for C_{20}H_{15}S_{2} 319.0610, found 319.0614.

**Bis(4-trifluoromethylphenyl)disulfide (3u) [42].** White solid (28.3 mg, 80% yield); mp 119−120 °C; Rf = 0.6 (petroleum ether); ^1^H NMR (600 MHz, CDCl_3) δ 7.60−7.55 (m, 8H) ppm; HRMS (ESI) m/z [M + H]^+ calculated for C_{14}H_{8}F_{2}S_{2} 355.0044, found 355.0039; ^19^F NMR (376 MHz, CDCl_3) δ -62.5 ppm.

**4. Conclusions**

In summary, we have developed an efficient protocol for the selective access to symmetrical diaryl sulfides and disulfides using sodium sulfinites as sulfenylation reagents via homocoupling reaction. The utilization of readily available sodium sulfinites as coupling partners and good functional group tolerance with modest to excellent yields for most substrates enable these two types of novel transformations to become attractive alternatives for the preparation of the corresponding sulfur compounds. More importantly, sodium sulfinites were used for the first time to access symmetrical diaryl sulfides. The convinced mechanism, selectivity, and synthetic application of this transformation are still under investigation.
**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/molecules27196232/s1](https://www.mdpi.com/article/10.3390/molecules27196232/s1), 1H, 13C, 19F NMR, IR and HPLC spectra.

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**References**

1. Pasquini, S.; Mugnaini, C.; Tintori, C.; Botta, M.; Trejos, A.; Arvela, R.K.; Larhed, M.; Witvrouw, M.; Michiels, M.; Christ, F.; et al. Investigations on the 4-Quinolone-3-carboxylic Acid Motif. 1. Synthesis and Structure—Activity Relationship of a Class of Human Immunodeficiency Virus type 1 Integrase Inhibitors. *J. Med. Chem.* 2008, 51, 5125. [CrossRef] [PubMed]

2. Beletskaya, I.P.; Ananikov, V.P. Transition-Metal-Catalyzed C–S, C–Se, and C–Te Bond Formation via Cross-Coupling and Atom-Economic Addition Reactions. *Chem. Rev.* 2011, 111, 1596. [CrossRef] [PubMed]

3. Brigg, S.; Pribut, N.; Basson, A.E.; Avgenikos, M.; Venter, R.; Blackie, M.A.; van Otterlo, W.A.L.; Pelly, S.C. Novel indole sulfides as potent HIV-1 NNRTIs. *Bioorg. Med. Chem. Lett.* 2016, 26, 1580. [CrossRef] [PubMed]

4. Feng, M.; Tang, B.; Liang, S.; Jiang, X. Sulfur Containing Scaffolds in Drugs: Synthesis and Application in Medicinal Chemistry. *Curr. Top. Med. Chem.* 2016, 16, 1200. [CrossRef] [PubMed]

5. Ke, F.; Qu, Y.; Jiang, Z.; Li, Z.; Wu, D.; Zhou, X. An Efficient Copper-Catalyzed Carbon–Sulfur Bond Formation Protocol in Water. *Org. Lett.* 2011, 13, 454. [CrossRef]

6. García, N.; García-Garcia, P.; Fernández-Rodriguez, M.A.; Rubio, R.; Pedrosa, M.R.; Arnaíz, F.J.; Sanz, R. Pinacol as a New Green Reducing Agent: Molybdenum-Catalyzed Chemoselective Reduction of Sulfoxides and Nitroaromatics. *Adv. Synth. Catal.* 2012, 354, 321. [CrossRef]

7. Jang, Y.; Kim, K.T.; Jeon, H.B. Deoxygenation of Sulfoxides to Sulfides with Thionyl Chloride and Triphenylphosphine: Competition with the Pummerer Reaction. *J. Org. Chem.* 2013, 78, 6328. [CrossRef]

8. Garcia, N.; García-Garcia, P.; Fernández-Rodriguez, M.A.; García, D.; Pedrosa, M.R.; Arnaíz, F.J.; Sanz, R. An unprecedented use for glycerol: Chemoselective reducing agent for sulfoxides. *Green Chem.* 2013, 15, 999. [CrossRef]

9. Mitsuodome, T.; Takahashi, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Hydrogenation of Sulfoxides to Sulfides under Mild Conditions Using Ruthenium Nanoparticle Catalysts. *Angew. Chem. Int. Ed.* 2014, 53, 8348. [CrossRef]

10. Touchy, A.S.; Siddiki, S.M.A.H.; Onodera, W.; Kon, K.; Shimizu, K. Hydrodeoxygenation of sulfoxides to sulfides by a Pt and MoOx co-loaded TiO2 catalyst. *Green Chem.* 2016, 18, 2554. [CrossRef]

11. Wu, R.; Huang, K.; Qiu, G.; Liu, J.-B. Synthesis of Thioethers from Sulfonyl Chlorides, Sodium Sulfinates, and Sulfonyl Hydrazides. *Synthesis* 2019, 51, 3567. [CrossRef]

12. Tanimoto, K.; Aras, T.; Goto, M. Copper-catalyzed chalcogenation of aryl iodides via reduction of chalcogen elements by aluminum or magnesium. *Tetrahedron* 2012, 68, 10510. [CrossRef]

13. Taniguchi, N. Copper-catalyzed chalcogenation of aryl iodides via reduction of chalcogen elements by aluminum or magnesium. *Tetrahedron* 2012, 68, 10510. [CrossRef]
19. Abbasi, M.; Nowrouzi, N.; Borazjani, S.G. Conversion of organic halides to disulfanes using KCN and CS₂. *Tetrahedron Lett.* 2017, **58**, 4251. [CrossRef]

20. Xiao, X.; Xue, J.; Jiang, X. Polysulphurating reagent design for unsymmetrical polysulfide construction. *Nat. Commun.* 2018, **9**, 2191. [CrossRef] [PubMed]

21. Xue, J.; Jiang, X. Unsymmetrical polysulphidation via designed bilateral disulfurating reagents. *Nat. Commun.* 2020, **11**, 4170. [CrossRef] [PubMed]

22. Wu, Z.; Pratt, D.A. A Divergent Strategy for Site-Selective Radical Disulfuration of Carboxylic Acids with Trisulfide-1,1-Dioxides. *Angew. Chem. Int. Ed.* 2021, **60**, 15598. [CrossRef] [PubMed]

23. Wang, F.; Chen, Y.; Rao, W.; Ackermann, L.; Wang, S.-Y. Efficient preparation of unsymmetrical disulfides by nickel-catalyzed reductive coupling strategy. *Nat. Commun.* 2022, **13**, 2588. [CrossRef] [PubMed]

24. Chen, H.-Y.; Peng, W.-T.; Lee, Y.-H.; Chang, Y.-L.; Chen, Y.-J.; Lai, Y.-C.; Jheng, N.-Y.; Chen, H.-Y. Use of Base Control to Provide High Selectivity between Diaryl Thiourea and Diaryl Disulfide for C–S Coupling Reactions of Aryl Halides and Sulfur and a Mechanistic Study. *Organometallics* 2015, **32**, 5514. [CrossRef]

25. Kamal, A.; Sirivivasulu, V.; Murty, J.N.S.R.C.; Shankaraiah, N.; Nagesh, N.; Reddy, T.S.; Rao, A.V.S. Copper Oxide Nanoparticles Supported on Graphene Oxide-Catalyzed S-Arylation: An Efficient and Ligand-Free Synthesis of Aryl Sulfinides. *Adv. Synth. Catal.* 2013, **355**, 2297. [CrossRef]

26. Cai, M.; Yao, R.; Chen, L.; Zhao, H. A simple, efficient and recyclable catalytic system for carbon–sulfur coupling of aryl halides with thiaoacetamide. *J. Mol. Catal. A Chem.* 2014, **395**, 349. [CrossRef]

27. Firouzabadi, H.; Iranpoor, N.; Gorginpour, F.; Samadi, A. Dithiooxamide as an Effective Sulfur Surrogate for Odorless High-Yielding Carbon–Sulfur Bond Formation in Wet PEG200 as an Eco-Friendly, Safe, and Recoverable Solvent. *Eur. J. Org. Chem.* 2015, **2914**. [CrossRef]

28. Ghorbani-Choghamarani, A.; Taherinia, Z. The first report on the preparation of peptide nanofibers decorated with zirconium oxide nanoparticles applied as versatile catalyst for the amination of aryl halides and synthesis of biaryl and symmetrical sulfides. *New. J. Chem.* 2017, **41**, 9414. [CrossRef]

29. Liu, X.; Cao, Q.; Xu, W.; Zeng, M.-T.; Dong, Z.-B. Nickel-Catalyzed C–S Coupling: Synthesis of Diaryl Sulfinides Starting from Phenylthiolyliodocarbamates and Iodobenzenes. *Eur. J. Org. Chem.* 2017, **5795**. [CrossRef]

30. Cheng, Y.; Liu, X.; Dong, Z.-B. Phenylthiolyliodocarbamates: Efficient Sulfuration Reagents in the Chan–Lam Coupling Reaction. *Eur. J. Org. Chem.* 2018, **815**. [CrossRef]

31. Dong, Z.-B.; Balkenhohl, M.; Tan, E.; Knochel, P. Synthesis of Functionalized Diaryl Sulfinides by Cobalt-Catalyzed Coupling between Arylzinc Pivalates and Diaryl Disulfides. *Org. Lett.* 2018, **20**, 7581. [CrossRef] [PubMed]

32. Arguello, J.E.; Schmidt, L.C.; Penenory, A.B. “One-Pot” Two-Step Synthesis of Aryl Sulfur Compounds by Photoinduced Reactions of Thiourea Anion with Aryl Halides. *Org. Lett.* 2003, **5**, 4133. [CrossRef] [PubMed]

33. Soleiman-Beigi, M.; Mohammadi, F. A novel copper-catalyzed, one-pot synthesis of symmetrical organic disulfides from alkyl and aryl halides: Potassium 5-methyl-1,3,4-oxadiazole-2-thiolate as a novel sulfur transfer reagent. *Tetrahedron Lett.* 2012, **53**, 7028. [CrossRef]

34. Li, Z.K.; Ke, F.; Deng, H.; Xu, H.L.; Xiang, H.F.; Zhou, X.G. Synthesis of disulfides and diselenides by copper-catalyzed coupling reactions in water. *Org. Biomol. Chem.* 2011, **9**, 2943. [CrossRef]

35. Soleiman-Beigi, M.; Hemmati, M. An efficient, one-pot and CuCl-catalyzed route to the synthesis of symmetric organic disulfides via domino reactions of thiaoacetamide and aryl (alkyl) halides. *Appl. Organometal. Chem.* 2013, **27**, 734. [CrossRef]

36. Li, X.; Du, J.; Zhang, Y.; Chang, H.; Gao, W.; Wei, W. Synthesis and nano-Pd catalyzed chemoselective oxidation of symmetrical and unsymmetrical sulfides. *Org. Biomol. Chem.* 2019, **17**, 3048. [CrossRef]

37. Olah, G.A.; Narang, S.C.; Field, L.D.; Karpeles, R. Synthetic methods and reactions. 101. Reduction of sulfonic acids and sulfonyl derivatives to disulfides with iodide in the presence of boron halides. *J. Org. Chem.* 1981, **46**, 2408. [CrossRef]

38. Zheng, Y.; Qing, F.-L.; Huang, Y.; Xu, X.-H. Tunable and Practical Synthesis of Thiosulfonates and Disulfides from Sulfonyl Chlorides in the Presence of Tetrabutylammonium Iodide. *Adv. Synth. Catal.* 2016, **358**, 3477. [CrossRef]

39. Haipour, A.R.; Mallakpour, S.E.; Adibi, H. Selective and Efficient Oxidation of Sulfinides and Thiols with Benzyltriphenylphosphonium Peroxymonoacetate in Aprotic Solvent. *J. Org. Chem.* 2002, **67**, 8666. [CrossRef]

40. Banfield, S.C.; Omori, A.T.; Leisch, H.; Hudlicky, T. Unexpected Reactivity of the Burgess Reagent with Thiols: Synthesis of Symmetrical Disulfides. *J. Org. Chem.* 2007, **72**, 4989. [CrossRef]

41. Dhakashinamorthy, A.; Alvaro, M.; Garcia, H. Aerobic oxidation of thiols to disulfides using iron metal–organic frameworks as solid redoxcatalysts. *Chem. Commun.* 2010, **46**, 6476. [CrossRef] [PubMed]

42. Oba, M.; Tanaka, K.; Nishiyama, K.; Ando, W. Aerobic Oxidation of Thiols to Disulfides Catalyzed by Diaryl Tellurides under Photosensitized Conditions. *J. Org. Chem.* 2011, **76**, 4173. [CrossRef] [PubMed]

43. Corma, A.; Rodenas, T.; Sabater, M.J. Aerobic oxidative oxidation of thiols to disulfinides by heterogeneous gold catalysts. *Chem. Sci.* 2012, **3**, 398. [CrossRef]

44. Li, X.-B.; Li, Z.-J.; Gao, Y.-J.; Meng, Q.-Y.; Yu, S.; Weiss, R.G.; Tung, C.-H.; Wu, L.-Z. Mechanistic Insights into the Interface-Directed Transformation of Thiols into Disulfides and Molecular Hydrogen by Visible-Light Irradiation of Quantum Dots. *Angew. Chem. Int. Ed.* 2014, **53**, 2085. [CrossRef]

---

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45. Tabrizian, E.; Amoozadeh, A.; Rahmani, S. Sulfamic acid-functionalized nano-titanium dioxide as an efficient, mild and highly recyclable solid acid catalyst for chemoselective oxidation of sulfides and thiols. RSC Adv. 2016, 6, 21854. [CrossRef]
46. Samanta, S.; Ray, S.; Ghosh, A.B.; Biswas, P. 3,6-Di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) mediated metal-free mild oxidation of thiols to disulfides in aqueous medium. RSC Adv. 2016, 6, 39356. [CrossRef]
47. Paul, S.; Islam, S.M. Oxidative dehydrogenation of thiols to disulfides at room temperature using silica supported iron oxide as an efficient solid catalyst. RSC Adv. 2016, 6, 95753. [CrossRef]
48. Laudat, G.; Straathof, N.J.W.; Lanting, M.D.; Knoops, B.; Hessel, V.; Noël, T. An environmentally benign and selective electrochemical oxidation of thiols to disulfides in a continuous-flow microreactor. Green Chem. 2017, 19, 4061. [CrossRef]
49. Ning, Y.; Ji, Q.; Liao, P.; Anderson, E.A.; Bi, X. Silver-Catalyzed Stereoselective Aminosulfenylation of Alkynes. Angew. Chem. Int. Ed. 2017, 56, 13805. [CrossRef]
50. Yue, H.; Zhu, C.; Rueping, M. Cross-Coupling of Sodium Sulfinates with Aryl, Heteroaryl, and Vinyl Halides by Nickel/Photoredox Dual Catalysis. Angew. Chem. Int. Ed. 2018, 57, 1371. [CrossRef]
51. Cao, L.; Luo, S.-H.; Jiang, K.; Hao, Z.-F.; Wang, B.-W.; Pang, C.-M.; Wang, Z.-Y. Disproportionate Coupling Reaction of Sodium Sulfinates Mediated by BF3·OEt2: An Approach to Symmetrical/Unsymmetrical Thiosulfonate. Org. Lett. 2018, 20, 4754. [CrossRef] [PubMed]
52. Miao, T.; Li, P.; Zhang, Y.; Wang, L. A Sulfinylation Reaction: Direct Synthesis of 3-Arylsulfinylindoles from Arylsulfinic Acids and Indoles in Water. Org. Lett. 2015, 17, 832. [CrossRef] [PubMed]
53. Ji, Y.-Z.; Li, H.-J.; Yang, H.-R.; Zhang, Z.-Y.; Xie, L.-J.; Wu, Y.-C. TMSOTf-Promoted Sulfinylation of Electron-Rich Aromatics with Sodium Arylsulfinates. Synlett 2020, 31, 349.
54. Xiao, F.; Xie, H.; Liu, S.; Deng, G.-J. Iodine-Catalyzed Regioselective Sulfinylation of Indoles with Sodium Sulfinates. Adv. Synth. Catal. 2014, 356, 364. [CrossRef]
55. Guo, S.; He, W.; Xiang, J.; Yuan, Y. Palladium-catalyzed direct thiolation of ethers with sodium sulfinates. Tetrahedron Lett. 2014, 55, 6407. [CrossRef]
56. Lin, Y.-M.; Lu, G.-P.; Cai, C.; Yi, W.-B. Odorless, One-Pot Regio- and Stereoselective Iodothiolation of Alkynes with Sodium Arylsulfinates. Synlett 2020, 59, 2338. [CrossRef]
57. Liu, Y.; Lam, L.Y.; Ye, J.; Blanchard, N.; Ma, C. DABCO-promoted Diaryl Thioether Formation by Metal-catalyzed Coupling of Sodium Sulfinates and Aryl Iodides. Org. Synth. Catal. 2020, 362, 2326. [CrossRef]
58. Lam, L.Y.; Ma, C. Chan–Lam-Type C–S Coupling Reaction by Metal-catalyzed Coupling of Sodium Sulfinates and Aryl Iodides. Org. Lett. 2021, 23, 6164. [CrossRef]
59. Pinnick, H.W.; Reynolds, M.A.; McDonald, R.T., Jr.; Brewster, W.D. Reductive coupling of aromatic sulfinate salts to disulfides. J. Org. Chem. 1980, 45, 930. [CrossRef]
60. Wang, J.Q.; Zhang, Y.M. The Reduction of Arylsulfonyl Chlorides and Sodium Arylsulfinates with TiCl4/Sm System. J. Org. Chem. 2014, 85, 10204. [CrossRef] [PubMed]
61. Wang, Y.; Deng, J.; Chen, J.; Cao, F.; Hou, Y.; Yang, Y.; Deng, X.; Yang, J.; Wu, L.; Shao, X.; et al. Dechalcogenization of Aryl Dichalcogenides to Synthesize Aryl Chalcogenides via Copper Catalysis. ACS Catal. 2020, 10, 2707. [CrossRef]
62. Li, Y.-M.; Nie, C.-P.; Wang, H.-P.; Verpoort, F.; Duan, C.-Y. A Highly Efficient Method for the Copper-Catalyzed Selective Synthesis of Diaryl Chalcogenides from Easily Available Chalcogen Sources. Eur. J. Org. Chem. 2011, 2011, 7331–7338. [CrossRef]
63. Still, I.W.; Watson, I.D.G. An efficient solid-state route to aryl thiocyanates from aren sulfinates. Synth. Commun. 2001, 31, 1355. [CrossRef]
64. Emmett, E.J.; Hayter, B.R.; Willis, M.C. Palladium-Catalyzed Synthesis of Ammonium Sulfinates from Aryl Halides and a Sulfur Dioxide Surrogate: A Gas- and Reductant-Free Process. Angew. Chem. Int. Ed. 2014, 53, 10204. [CrossRef] [PubMed]
65. Wang, Y.; Deng, J.; Chen, J.; Cao, F.; Hou, Y.; Yang, Y.; Deng, X.; Yang, J.; Wu, L.; Shao, X.; et al. Dechalcogenization of Aryl Dichalcogenides to Synthesize Aryl Chalcogenides via Copper Catalysis. ACS Catal. 2020, 10, 2707. [CrossRef]
66. Li, Y.-M.; Nie, C.-P.; Wang, H.-P.; Verpoort, F.; Duan, C.-Y. A Highly Efficient Method for the Copper-Catalyzed Selective Synthesis of Diaryl Chalcogenides from Easily Available Chalcogen Sources. Eur. J. Org. Chem. 2011, 2011, 7331–7338. [CrossRef]
67. Still, I.W.; Watson, I.D.G. An efficient solid-state route to aryl thiocyanates from aren sulfinates. Synth. Commun. 2001, 31, 1355. [CrossRef] [PubMed]
68. Carpino, L.A.; Gao, H.S.; Ti, G.S.; Segev, D. Thioxanthene Dioxide Based Amino-Protecting Groups Sensitive to Pyridine Bases and Dipolar Aprotic Solvents. J. Org. Chem. 1999, 54, 5887–5897. [CrossRef]
69. Zhu, Y.-C.; Li, Y.; Zhang, B.-C.; Yang, Y.-N.; Wang, X.-S. Palladium-Catalyzed Enantioselective C-H Olefination of Diaryl Sulfoxides via Parallel Kinetic Resolution and Desymmetrization. Angew. Chem. Int. Ed. 2015, 57, 5129–5133. [CrossRef] [PubMed]
70. Hajipour, A.-R.; Karimzadeh, M.; Azizi, G. Highly Efficient and Magnetically Separable Nano-CuFe2O4 Catalyzed S-Arylation of Thiourea by Aryl/Heteroaryl Halides. Chin. Chem. Lett. 2014, 25, 1382–1386. [CrossRef]
71. García-López, J.-A.; Çetin, M.; Greaney, M.F. Synthesis of Hindered Biaryls via Aryne Addition and in Situ Dimerization. Org. Lett. 2015, 17, 2649–2651. [CrossRef]
73. Liu, Y.-Y.; Wang, H.; Wang, C.-P.; Wan, J.-P.; Wen, C.-P. Bio-Based Green Solvent Mediated Disulfide Synthesis via Thiol Couplings Free of Catalyst and Additive. *RSC Adv.* **2013**, *3*, 21369–21372. [CrossRef]

74. Murahashi, S.I.; Zhang, D.Z.; Iida, H.; Miyawaki, T.; Uenaka, M.; Uenaka, K.; Meguro, K. Flavin-Catalyzed Aerobic Oxidation of Sulfides and Thiols with Formic Acid/Triethylamine. *Chem. Commun.* **2014**, *50*, 10295–10298. [CrossRef] [PubMed]

75. Ruano, J.L.G.; Parra, A.; Alemán, J. Efficient Synthesis of Disulfides by Air Oxidation of Thiols under Sonication. *Green Chem.* **2008**, *10*, 706–711. [CrossRef]

76. Chai, P.J.; Li, Y.S.; Tan, C.X. An Efficient and Convenient Method for Preparation of Disulfides from Thiols Using Air as Oxidant Catalyzed by Co-Salophen. *Chin. Chem. Lett.* **2011**, *22*, 1403–1406. [CrossRef]

77. Wang, L.; Clive, D.L. [(tert-Butyl)dimethylsilyloxy)methyl Group for Sulfur Protection. *Org. Lett.* **2011**, *12*, 1734–1737. [CrossRef]