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Methylthiolation for Electron-Rich Heteroarenes with DMSO-TsCl

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DMSO-TsCl has been developed for direct methylthiolation of various electron-rich heteroarenes (more than 40 examples) with high regioselectivity in moderate to excellent yields (up to 96%). Especially, pyrroles, furans, and thiophenes can be efficiently mono-methylthiolated. This practical method features scalable, metal-free, mild conditions and is compatible with air and moisture. Several applications of methylthiolated products were demonstrated for the first time. Based on controlled experimental results, a plausible mechanism was proposed with two key intermediates involved in the mechanism being detected by HRMS.

Introduction

Sulfides and their derivatives which are commonly found in many pharmaceuticals and agrochemicals exhibit important biological activities.[1] Especially heteroaromatic sulfides and their derivatives play significant roles in medicinal chemistry and drug development (Figure 1).[2] Additionally, heteroaromatic sulfides can be further transformed into thiols,[3] sulfoxides,[4] sulfones,[5] and applied to cross-coupling reaction.[6]

The formation of C–S bond has attracted extensive attention from chemists in recent ten years.[7] RSH,[8] RSSR,[9] sulfonates and derivatives,[10] and even sulfur-containing inorganic salts[11] have been extensively used as thioetherification reagents. Metal-catalyzed coupling of aryl halides with thiols has emerged as a popular synthetic methodology for C–S bond formation.[12] Fu's group in 2017 reported a visible-light photoredox arylation of thiols with aryl halides and heteroaromatic halides at room temperature (Scheme 1a).[13] However, thiols with smelly odors are not environmentally friendly. In addition, the Ir photocatalyst used for this reaction is expensive. Luo's group developed a catalytic synthesis of 3-thioindoles using

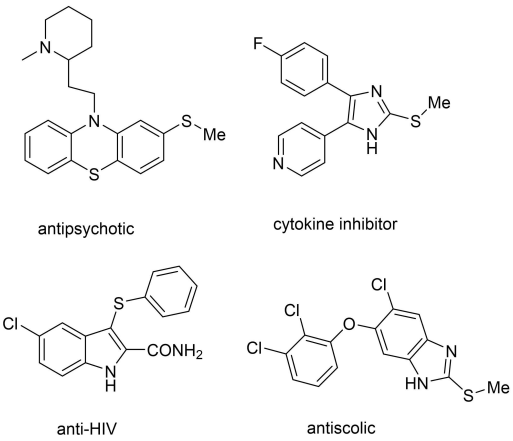

Figure 1. Bioactive Aryl Sulfides and Heteroaromatic Sulfides.

Bunte salts (R–S–SO_3Na) as sulfur sources.[14] Nevertheless, Bunte salts are not commercially available. More importantly, they could decompose into toxic gas such as SO_2 under heating. Therefore, it is highly desirable to develop more versatile and environmentally friendly reagents for C–S bond formation.

Dimethyl sulfoxide (DMSO) is a readily available and less toxic polar solvent.[15] During the past decades, it was reported as important precursors for many organic motifs such as –CH_3,[16] –CHO,[17] –CN,[18] –SMe,[19] –SOMe,[20] and –SO_2Me.[21] Cheng's group reported a Cu(I)-mediated methylthiolation of aryl iodides and aryl bromides with DMSO using ZnF_2 at 150 °C (Scheme 1b).[22] Magolan's group developed a metal-free methylthiolation of activated arenes using DMSO/Hunig's base system at 189 °C (Scheme 1c).[23] The use of excessive metal catalysts and harsh reaction temperatures limited the potential applications. Adimurthy and coworkers[24] reported a methylthiolation of imidazo[1,2-a]pyridines in the presence of *p*-Tosyl Chloride (TsCl) in the combination solvents of dichloroethane and DMSO at 100 °C. However, only 2-phenylimidazo[1,2-a] pyridine derivatives were discussed in this study. Also, the yields

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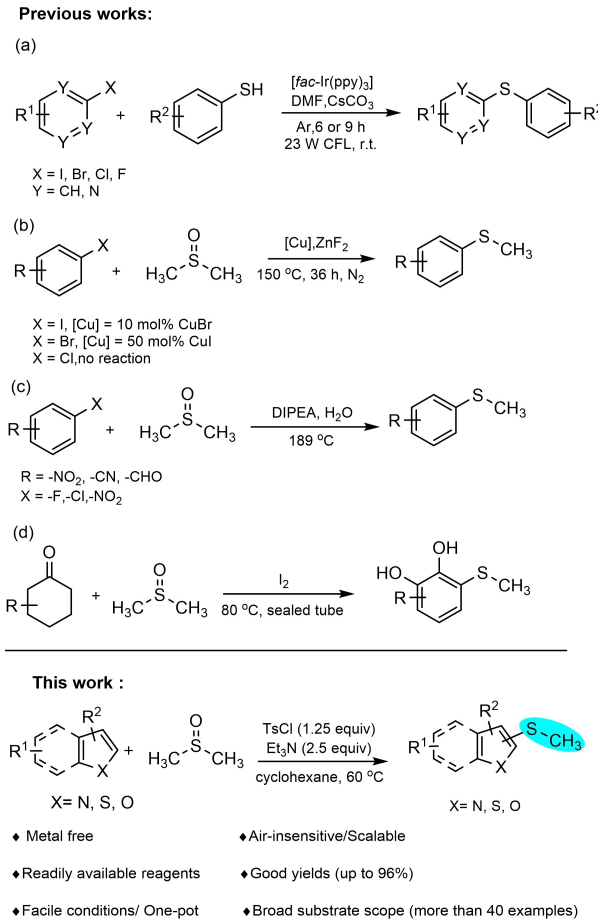


Scheme 1. Strategies for C–S Bond Coupling Reactions.

of the corresponding methylthiolated products were relatively low (23–67%) except 2-phenylimidazo[1,2-a]pyridine (91%). Additionally, Roychowdhury and co-workers[25] reported a methylthiolation of imidazo[1,2-a] pyridines and other imidazo-fused heterocycles using $POCl_3$ as the activator. Very recently, Zhao and Cao disclosed a methylthiolation of electron-rich aromatic/heteroaromatic compounds using KSCN and methanol under electrochemical redox conditions.[26] However, the methylthiolated or bismethylthiolated products of heteroaromatic compounds were obtained with low yields.

Despite the recent development of these methods for methylthiolation of heteroarenes with DMSO,[23–27] there are still challenges: 1) High catalyst loadings and harsh conditions were utilized. 2) The scope of the heteroarenes is relatively limited. 3) Direct methylthiolation of five-membered heteroarenes with low activity are less explored. Consequently, developing more general synthetic methods for methylthiolation are highly desirable.

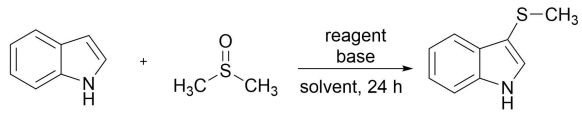
Our group has dedicated to the development of high-value transformations of bulk chemicals. We previously reported a metal-free catalytic synthesis of methylthio-substituted catechols with DMSO in one pot (Scheme 1d).[28] In order to establish a general synthetic methodology for C–S bond coupling reaction, we would like to report a methylthiolation of heteroarenes and arenes with excellent regioselectivity. Significantly, this method was successfully applied to the methylthiolation of five-membered heteroarenes such as pyrroles, furans, and thiophenes. To the best of our knowledge, this is the first report of DMSO-TsCl for the methylthiolation of pyrroles, furans and thiophenes. Compared to previous studies, this protocol features scalable conditions, general applicability of substrates, a broad functional group tolerance, and moderate to excellent yields. Moreover, a plausible mechanism was proposed. Notably, two of the key intermediates involved in the mechanism were detected by HRMS, confirming the validity of the proposed mechanism.

Results and Discussion

We initially began our investigations by using 2,4-dimethyl-1*H*-pyrrole (**1a**) with DMSO (**2a**) as model substrates for the optimization studies. The yield of **3aa** was only optimized to 75% (Table S1). The yield was higher when using a more reactive 1-*H*-indole (**1u**) with DMSO (**2a**) as model substrates for the further optimization studies (Table 1).

According to our previous work,[28] DMSO/I_2 system worked well as a methylthiolation reagent. Unfortunately, there was no desired product observed when DMSO/I_2 was used (entry 1). To our delight, 22% yield of the desired product was obtained in the presence of 1.0 equiv. of NH_4I (entry 4). A series of acidic

Table 1. Optimization of the Reaction Conditions of Methylthiolation of Indole.[a]



1u 2a 3au

Entry	Activator [equiv]	Base	Solvent	Temp. [°C]	Yield[b][%]
1	I_2(1.0)	–	DMSO	60	0
2	KI(1.0)	–	DMSO	60	0
3	TBAI(1.0)	–	DMSO	60	0
4	NH_4I(1.0)	–	DMSO	60	22
5	H_2SO_4(1.0)	Et_3N	DMSO	60	0
6	TsOH(1.0)	Et_3N	DMSO	60	0
7	TFAA(1.0)	Et_3N	DMSO	60	26
8	TsCl(1.0)	Et_3N	DMSO	60	64
9	TsCl(1.0)	Et_3N	CH_3CN	60	34
10	TsCl(1.0)	Et_3N	toluene	60	59
11	TsCl(1.0)	Et_3N	cyclohexane	60	74
12	TsCl(1.0)	Et_3N	dioxane	60	47
13	TsCl(0.75)	Et_3N	cyclohexane	60	54
14	TsCl(1.25)	Et_3N	cyclohexane	60	82
15	TsCl(1.5)	Et_3N	cyclohexane	60	89
16	TsCl(1.5)	K_2CO_3	cyclohexane	60	41
17	TsCl(1.5)	*t*-BuOK	cyclohexane	60	53
18	TsCl(1.5)	DBU	cyclohexane	60	81
19	TsCl(1.5)	Et_3N	cyclohexane	50	56
20	TsCl(1.5)	Et_3N	cyclohexane	70	92
21	TsCl(1.5)	Et_3N	cyclohexane	80	82
22	–	Et_3N	cyclohexane	70	0
23	TsCl(1.5)	–	cyclohexane	70	0

[a] Reaction conditions: indole (**1u**, 0.4 mmol 1.0 equiv), base (2.5 equiv), DMSO (**2a**, 0.5 mL) and 0.5 mL solvent in sealed tube for 24 h, unless otherwise noted. [b] Isolated yield.

substances in the presence of Et_3N were then screened. It was found that 64% yield of the product was achieved when 1.0 equiv. of TsCl was utilized (entries 5–8). The effects of different solvents in the reaction were then investigated and cyclohexane was selected as the most suitable solvent for this transformation (entries 9–12). Subsequently, the amount of TsCl was screened. 89% yield was achieved when the amount of TsCl was increased to 1.5 equiv. (entries 13–15). To further improve the yield, several bases were also examined and Et_3N was found to give the best result (entries 16–18). The investigation of the effect of reaction temperature revealed that 70 °C was the optimal temperature (entries 19–21). Notably, there was no product formed in the absence of TsCl or Et_3N (entries 22–23), which indicated that DMSO-TsCl and Et_3N were crucial for this methylthiolation reaction.

With the optimal conditions in hand, a wide range of substrates were converted to the corresponding products (Scheme 2). First, various five-membered heteroarenes were investigated, including pyrroles, furans, and thiophenes. Numerous pyrrole derivatives participated in this coupling reaction, affording the desired sulfides in moderate to good yields (**3 aa**–**3 ai**). We found that pyrroles bearing electron-withdrawing groups (Ac, COOMe and COOH) were unfavorable for this reaction (**3 ag**–**3 ai**). In addition, disubstituted and monosubstituted furan and thiophene derivatives gave the corresponding sulfides with lower yields (**3 aj**–**3 at**). Unfortunately, there were no desired products obtained with furan derivatives bearing strong electron-withdrawing groups (**3 am**–**3 an**). It is noteworthy that thiophene and furan derivatives with strong electron-donating groups are advantageous to this transformation (**3 at** *Vs* **3 ao**).

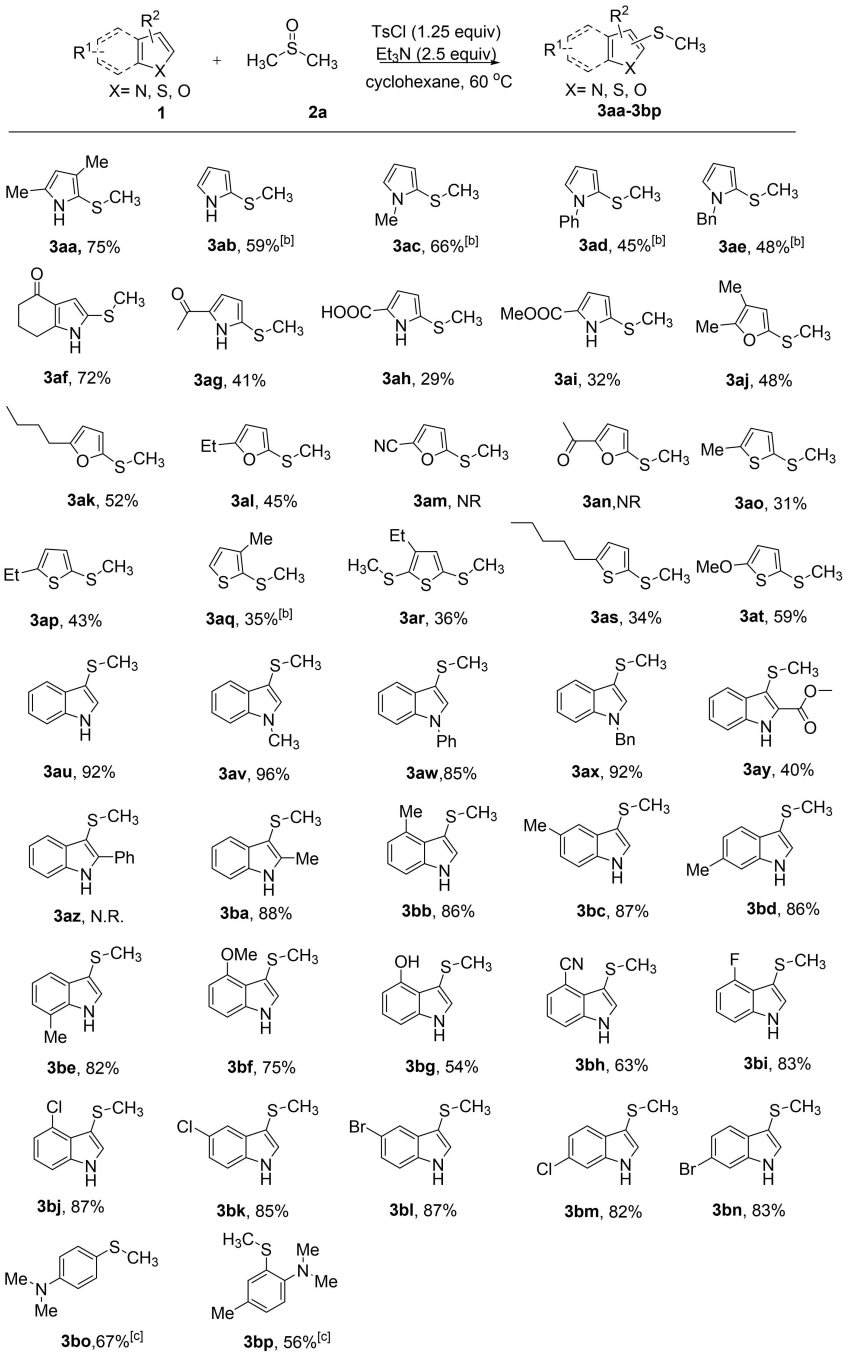
Due to indoles and its derivatives commonly exist in bioactive natural molecules and pharmaceutical agents.[29] We next directed our attention to examine the scope of indoles. Gratifyingly, unprotected indoles and an array of monosubstituted indoles at *N*-position (such as Me, Ph, and Bn) were found to provide the desired products in excellent yields (**3 au**–**3 ax**). When there were different substituted groups (Me and COOMe) at the C2-position of indoles, the yields of the products decreased dramatically. Especially with the strong electron-withdrawing group (**3 ay** *Vs* **3 ba**). Owing to the steric hindrance at the C2-position of indoles, **3 az** was not observed under the standard conditions. When the methyl group was at the different positions of indoles, the products were obtained in good yields (**3 ba**–**3 be**). Furthermore, various electron-withdrawing (CN, F, and Cl) and electron-donating groups (Me, OH, and OMe) at the C4-position of indoles were fully tolerated, giving the desired products in moderate to good yields (**3 bf**–**3 bj**). Different halogen functionalities, in particular, Cl and Br, survived the reaction conditions and provided synthetic handles for further structural elaboration through metal-catalyzed coupling reactions (**3 bk**–**3 bn**). Moreover, the yields of the target products were decreased as the electronegativity of the halogen atom increased. (**3 bk** *Vs* **3 bl**, **3 bm** *Vs* **3 bn**). It was exciting to find that our method was also successfully applied to electron-rich benzene derivatives with moderate yields (**3 bo**–**3 bp**). Unfortunately, the corresponding methylthiolated products of phenyl ethers, phenols, and electron-deficient heteroarenes such as pyridines and pyrimidines were failed to obtain.

To gain insights into the mechanism, several experiments were designed and performed (Scheme 3a). First, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and 2,6-di-*t*-butylphenol (BHT) as two kinds of radical scavengers were added into the reaction of methylthiolation of indole under standard conditions. We found that the yield of **3 au** was not decreased, which excluded the free-radical reaction pathway [Eq. (1), Eq. (2)]. Subsequently, a deuterium-labeling experiment was carried out with DMSO-d^6 to explore the potential role of DMSO in the reaction of methylthiolation [Eq. (3)]. The deuterated product **3 au** was obtained with yield of 91%, (The data of ^{1}H NMR, ^{13}C NMR, and HRMS could be seen in Supporting Information Figure S1–S3), indicating that DMSO-TsCl was generated and reacted in situ. The deuterated experiment not only verified the source of methylthiolation but also provided an efficient synthetic method for introducing deuterated groups into the drug intermediates.

In order to further verify the mechanism, a series of control experiments were also conducted (Scheme 3b). According to the previous reports,[30] sulfur-containing organic compounds such as dimethyldisulfide, methanethiol, and methyl sulfide can be generated by thermal decomposition of DMSO. To confirm whether one of these compounds acted as the intermediate of this newly-developed transformation, we investigated the reaction with dimethyl disulfide, methyl sulfide, and *n*-propylthiol instead of DMSO, no related products were found [Eq. (1), Eq. (2), Eq. (3)]. Fortunately, intermediate **A** was detected by HRMS when only TsCl was added into DMSO under the standard condition, indicating that DMSO-TsCl was generated in situ and acted as the methylthiolation reagent. Also, intermediate **C** was detected by HRMS in the absence of Et_3N at the methylthiolation of indole [Eq. (4), Eq. (5)]. These detected intermediates provided important evidence of the mechanistic pathways.

Based on the experimental results, a plausible mechanism was proposed for the reaction (Scheme 3c). DMSO was originally activated by TsCl to form intermediate **A** (detected by HRMS, Figure S4). Then intermediate **B** was obtained when the sulfonium was attacked by C3-position of indole. Intermediate **B** was converted into a more stable intermediate **C** through deprotonation. (detected by HRMS, Figure S5). Finally, desired product **P** was formed by eliminating a methyl cation under heating.

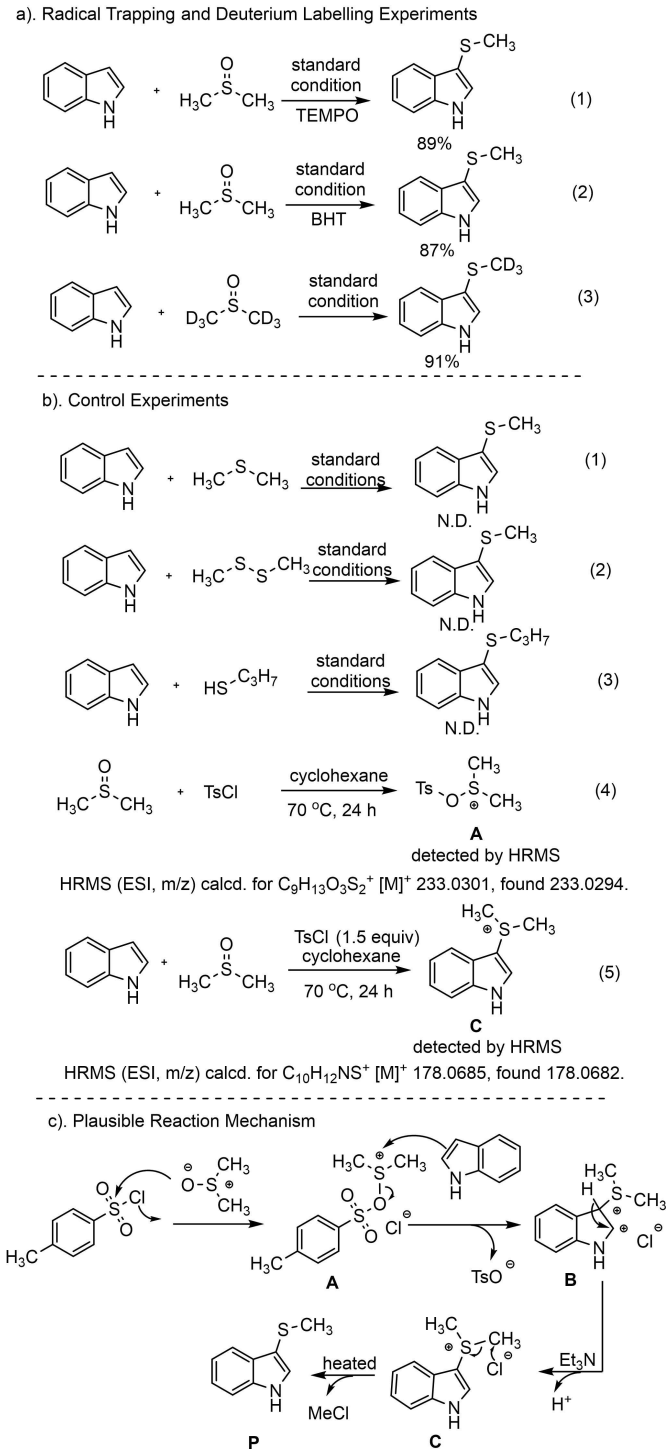
To demonstrate further applications of the methylthiolation of heteroarenes, a gram scale reaction was carried out to form **3 au** under open-air conditions. To our delight, the desired product was obtained in a yield of 88% (Scheme 4a). Because sulfoxides and sulfones are important precursors of numerous chemically and biologically active molecules.[31] We converted **3 au** to **4 a** and **5 a** in the yield of 72% and 65% respectively under the different conditions with H_2O_2 (30% in water). Moreover, methylthiolation of C2 position of indole (**6 a**) and cross-coupling product (**7 a**) were also obtained with the yield of 42% and 47% respectively (Scheme 4b).



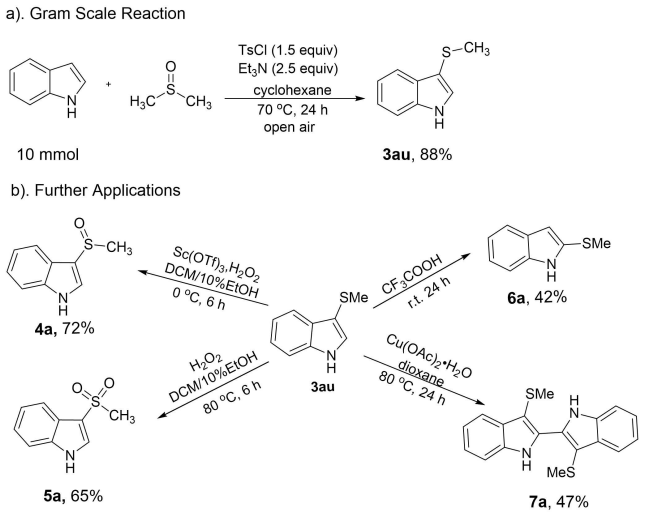
Scheme 2. Substrates Scope for the Methylthiolation of Heteroarenes with DMSO-TsCl.[a] [a] Reaction conditions: for five-membered heteroarenes, **1** (1.0 mmol 1.0 equiv), TsCl (1.25 equiv), Et_3N (2.5 equiv), DMSO (**2a**, 1.5 mL) and cyclohexane (1.5 mL) in sealed tube under 60 °C for 24 h; for indoles, **1** (1.0 mmol 1.0 equiv), TsCl (1.5 equiv), Et_3N (2.5 equiv), DMSO (**2a**, 1.5 mL) and cyclohexane (1.5 mL) in sealed tube under 70 °C for 24 h, unless otherwise noted. [b] TsCl (1.0 equiv). [c] under 120 °C.

Conclusion

In summary, we have developed a general and efficient methylthiolation methodology. The DMSO-TsCl reagent exhibits excellent activity for methylthiolation of heteroarenes and arenes under facile conditions. Various heteroarenes including pyrroles, furans, thiophenes, indoles, and arenes are smoothly converted to the corresponding products in moderate to excellent yields with excellent functional group tolerance. Several further applications of methylthiolated products were also conducted, providing a powerful methodology for the synthesis of thioethers compounds. The DMSO-TsCl reagent provides a practical methodology for the synthesis of useful heteroaromatic sulfides and aryl sulfides. Further studies and synthetic applications are currently ongoing in our laboratory.



Scheme 3. Mechanism Studies.



Scheme 4. Gram Scale Reaction and Further Applications.

Experimental Section

General Procedure of Heteroaromatic Sulfides.

In a sealed tube with magnetic stir bar was charged with heteroarenes (1.0 mmol, 1.0 equiv), TsCl (1.25 mmol, 1.25 equiv), DMSO (1.5 mL), cyclohexane (1.5 mL) and Et_3N (2.5 mmol, 2.5 equiv). Then the tube was sealed with Teflon cape and heated at 60 °C for 24 h. After completion of the reaction, the mixture was quenched with 10 mL water, then extracted with ethyl acetate (15 mL) 3 times. The combined organic phase was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum ether and ethyl acetate as eluent to provide the desired products.

General Procedure of 4 a

$Sc(OTf)_3$ (49 mg, 0.1 mmol, 20 mol%) was suspended in CH_2Cl_2/10% EtOH (2.0 mL) and 30% H_2O_2 (227 mg, 4 equiv) was added under stirring. **3 au** (0.5 mmol, 1.0 equiv) dissolved in CH_2Cl_2/10%EtOH (1.5 mL) was added (17.8 mg, 0.1 mmol, 1 equiv) as follow. The vial in which **3 au** was weighed was further washed with CH_2Cl_2/10% EtOH (1.5 mL) and added to the reaction mixture. Then the mixture was stirring at room temperature for 3 h. After completion of the reaction, the mixture was quenched with 15 mL water, then extracted with ethyl acetate (10 mL) 3 times. The combined organic phase was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel (200–300 mesh) using dichloromethane and methanol as eluent to provide **4 a** with the yield of 72%.

General Procedure of 5 a

In a sealed tube with magnetic stir bar was charged with **3 au** (0.5 mmol, 1.0 equiv), CH_2Cl_2/10%EtOH (2.5 mL), and 30% H_2O_2 (340 mg, 6 equiv). Then the tube was sealed with Tefloncape and heated at 70 °C for 10 h. After completion of the reaction, the mixture was quenched with 15 mL water, then extracted with ethyl acetate (10 mL) 3 times. The combined organic phase was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum ether and ethyl acetate as eluent to provide **5 a** with a yield of 65%.

General Procedure of 6 a

3 au (0.5 mmol, 1.0 eqviv) dissolved in CF_3COOH (2.5 mL), the mixture was stirring at room temperature for 3 h. After completion of the reaction, the mixture was quenched with 15 mL water, then extracted with ethyl acetate (10 mL) 3 times. The combined organic

phase was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel (200–300 mesh) using dichloromethane and methanol as eluent to provide the desired product **6 a** with a yield of 42 %.

General Procedure of 7 a

In a sealed tube with magnetic stir bar was charged with $Cu(OAc)_2 \cdot H_2O$ (0.25 mmol, 0.5 equiv.), **3 au** (0.5 mmol, 1.0 eqviv) and dioxane (2.5 mL). Then the tube was sealed with Teflon cape and heated at 80 °C for 10 h. After completion of the reaction, the mixture was quenched with 15 mL water, then extracted with ethyl acetate (10 mL) 3 times. The combined organic phase was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum ether and ethyl acetate as eluent to provide the desired product **7 a** with a yield of 47 %.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–S bond coupling · Methylthiolation · Heterocycles · Synthetic methods

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