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Hypervalent Iodine(III)-Promoted Metal-Free S–H Activation: An Approach for the Construction of S–S, S–N, and S–C Bonds

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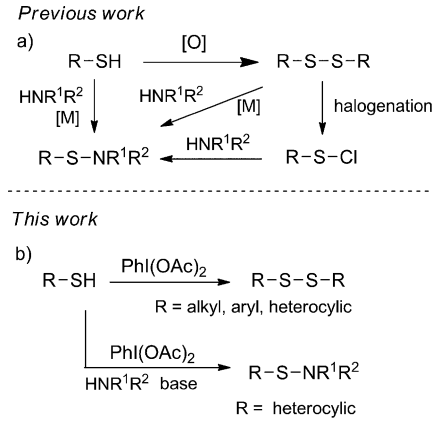
The activation of the sulfur atom of thiols with (diacetoxyiodo)benzene (DIB) has been explored in the preparation of symmetrical disulfides and sulfenamides. Disulfides can be produced in excellent yields (75–95 %) upon treatment of thiols with DIB. The reaction was complete in less than five minutes at room temperature. Aliphatic, aromatic, and heteroaromatic thiols are compatible with this transformation. Moreover, heteroaromatic disulfides obtained from heteroaromatic thiols further reacted with a nucleophilic amine in the presence of a base to provide the corresponding sulfenamides in fair to good yields (43–90 %) in a one-pot fashion. The methodology was successfully extended to indole as a representative electron-rich aromatic compound, which allowed successful construction of a S–C bond in one pot. The key benefits of this reaction include lower toxicity, low cost of DIB reagent, and mild reaction conditions (room temperature, undried solvents and open flask).

Introduction

Organosulfur compounds containing disulfide or sulfur–nitrogen bonds are important building blocks for a broad range of applications in biological, pharmaceutical, and material sciences. Disulfides (S–S) are vital for the stabilization of peptide structures in proteins,[1] chemical protection group,[2] and vulcanization.[3] Organosulfur compounds having an S–N bond, on the other hand, are used as biologically active compounds[4] and as intermediates in organic synthesis[5] and material chemistry.[6] The conventional method for preparing disulfides involves oxidation of thiols by using metal-containing oxidants or catalysts such as Fe, Pb, Ce, Mn, Co, Cr, Cu, or Al.[7] Metal-free oxidation methods using halogen (I_2, Br_2), hydrogen peroxide, azo reagents, graphite, sodium nitrite, or Burgess reagent have also been applied (Scheme 1, a).[8] However, the high toxicity and cost of the reagents, combined with the harsh reaction conditions such as elevated temperature, long reaction time, and risk of over-oxidation represent significant disadvantages. The recent discovery by Beifuss of heterocyclic disulfide formation from the thiol catalyzed by laccase, under air shows an example of a green transformation.[9] To obtain sulfenamides, disulfides have to be converted into sulfenyl chlorides with chlorine or NCS followed by amination.[10] This method not only requires three synthetic steps but it also involves sulfenyl chlorides, which are very unstable and undergo rapid hydrolysis. Recently, a direct synthesis of sulfenamides from either thiols or disulfides was developed by Taniguchi by using a copper-catalyzed amination reaction.[11] Although this reaction is highly efficient and compatible with many functional groups, metal and elevated temperature are still required in the transformation. Therefore, the development of a metal-free method



Scheme 1. (a) Conventional method for the preparation of disulfides and sulfenamides. (b) Utilization of hypervalent iodine reagents for the preparation of disulfides and sulfenamides.

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that can be conducted under mild conditions for the synthesis of dithiols and sulfenamides remains a challenge.

In the past few decades, hypervalent iodine compounds have been developed as selective reagents for oxidative transformation and construction of carbon–heteroatom and carbon–carbon bonds.[12] Importantly, the environmentally friendly character and commercial availability at reasonable cost make these compounds suitable for synthetic organic reactions. Due to the thiophilic nature of hypervalent iodine reagents, such compounds have recently been shown to activate sulfur atoms such as thioethers, thioamides, and thioureas.[13] Recently, Patel demonstrated a synthesis of benzimidazoles by using hypervalent iodine(III) reagents such as (diacetoxyiodo)benzene (DIB) to perform intramolecular C–N bond formation between isothiocyanates and amines.[14] To the best of our knowledge, however, no full investigations on the activation of simple thiols by hypervalent iodine reagents have been reported.[15] Therefore, taking clues from this and other works, we sought to exploit the thiophilic properties of hypervalent iodine(III) compounds for the preparation of disulfides and construction of S–N as well as S–C bonds from the disulfides in a one-pot fashion using thiols as starting materials (Scheme 1, b). This reaction was expected to provide a metal-free approach for the direct synthesis of disulfide, sulfonamides, and aromatic sulfides.

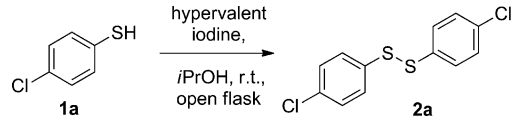
Results and Discussion

Synthesis of Disulfides from Thiols

Initially, various commercially available hypervalent iodine(III) reagents were screened with 4-chlorothiophenol (**1a**) as substrate to establish the most effective oxidant/activator (Table 1). It was our goal to develop a mild and convenient reaction, therefore, all tested reactions were conducted in undried 2-propanol, and in open air conditions at room temperature. The use of [hydroxy(tosyloxy)iodo]-benzene [PhI(OH)OTs], also known as Koser's reagent, gave the corresponding symmetrical disulfide **2a** in 54% yield in 10 min (Table 1, entry 1). Moreover, organic iodine(III) reagents carrying an ester group such as trifluoroacetoxy, *tert*-butoxy, and acetoxy gave better results; converting thiol **1a** into disulfide **2a** in 55, 72, and 87% yield, respectively. Specifically, (diacetoxyiodo)benzene (DIB) not only gave the best yield among the tested hypervalent iodine reagents, but the starting material **1a** was completely consumed within less than one minute under the conditions examined. Considering the high reactivity, combined with benign environmental characteristics, low cost, and wide availability of DIB, this reagent was selected as the oxidizing agent for further investigation.

With the results of the hypervalent iodine reagent screening process in hand, we next studied the effects of solvent and stoichiometry of the oxidation of 4-chlorothiophenol (**1a**) with DIB. Eight solvents (all undried) were tested for the oxidation of **1a** with DIB (1 equiv.) at room temperature (Table 2, entry 1–8). The reactions were monitored by

Table 1. Oxidation of 4-chlorothiophenol with hypervalent iodine(III) reagents.[a]

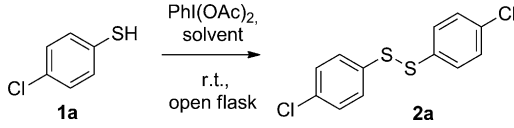


Entry	Hypervalent iodine(III)	Time	Yield [%][b]
1	PhI(OH)(OTs)	10 min	54
2	$PhI(OCOCF_3)_2$	3 h	55
3	$PhI(OCOtBu)_2$	45 min	72
4	$PhI(OCOCH_3)_2$	1 min	87

[a] Reaction conditions: 4-chlorothiophenol (1.0 equiv.), hypervalent iodine (1.0 equiv.), *i*PrOH, r.t., open air. [b] Isolated yield after silica gel chromatography.

HPLC after 5 min and the results show complete conversion into **2a** in every case. These results suggested a broad solvent compatibility and robustness of DIB for thiol oxidation. The effects of the stoichiometry of DIB were investigated as shown in Table 2 (entry 9–11). Only 0.5 equiv. of DIB was found to be sufficient to drive the oxidation completely. At this stage we hypothesized that aerobic oxidation of thiols by the oxygen in air may also be involved. To ensure complete conversion, we decided to use DIB (1 equiv.) in the less toxic solvent, 2-propanol, as the optimized conditions for further studies (entry 4).

Table 2. Optimization of oxidation of 4-chlorothiophenol with $PhI(OAc)_2$.[a]

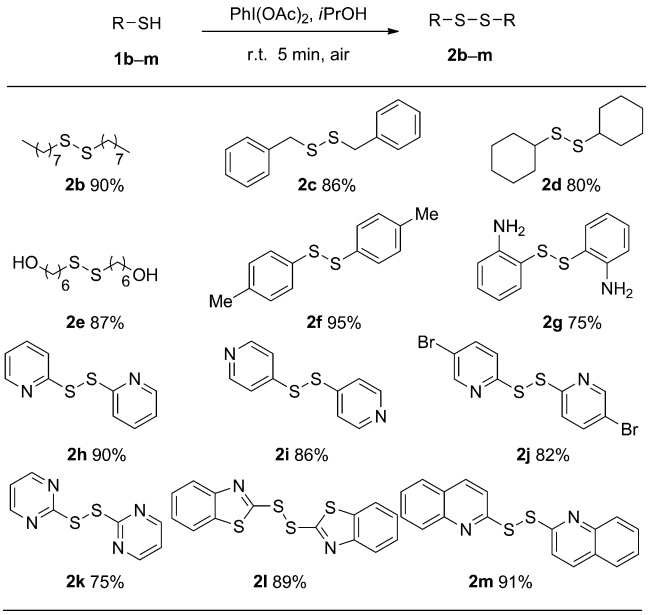


Entry	DIB [equiv.]	Solvent	Conversion [%][b]
1	1.0	EtOAc	100
2	1.0	toluene	100
3	1.0	xylene	100
4	1.0	*i*PrOH	100
5	1.0	*n*BuOH	100
6	1.0	CH_2Cl_2	100
7	1.0	hexane	100
8	1.0	DMSO	100
9	0.3	*i*PrOH	84
10	0.5	*i*PrOH	100
11	0.7	*i*PrOH	100

[a] Reaction conditions: 4-chlorothiophenol (1.0 equiv.), DIB (1.0 equiv.), solvent, r.t., under air, 5 min. [b] Determined by HPLC analysis.

With the optimized conditions in hand, we explored the generality and scope of this reaction by using a variety of thiols including aliphatic, cyclic aromatic, and heterocyclic substrates. Twelve thiols were subjected to the optimized oxidation conditions and the results are presented in Table 3. The oxidation of aliphatic and cyclic thiols proceeded smoothly and the desired disulfides **2b–d** were isolated in 90, 86 and 80% yield, respectively, after column chromatography. Importantly, DIB reacted specifically with only the thiol group, leaving the primary alcohol in **1e** un-

Table 3. Synthesis of symmetrical disulfides from thiols.[a]

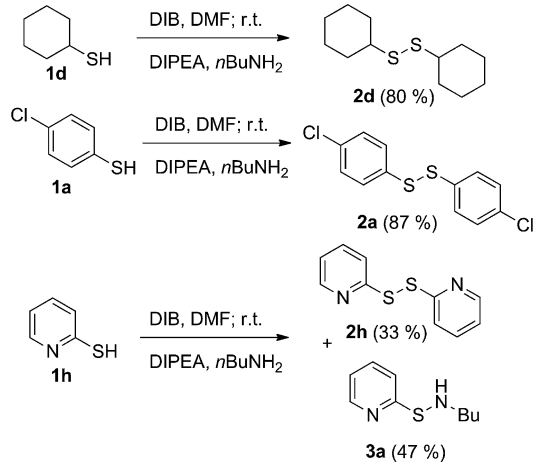


[a] Isolated yield after silica gel chromatography.

touched. Aromatic thiols having electron-donating groups such as amino, and methyl moieties gave the corresponding disulfides **2f** and **2g** in excellent yields. The nitrogen-containing heteroaromatic thiols were also tested with DIB. Monocyclic ring derivatives such as 2- and 4-mercapto-pyridines and pyrimidinethiol **1h–k** smoothly oxidized to provide disulfides **2h–k** in good to excellent yields. Moreover, bicyclic substrates including 2-mercaptobenzothiazole (**1l**) and quinoline-2-thiol (**1m**) were also transformed into disulfides **2l** and **2m** in decent yields. TLC monitoring suggested that, in all cases, the starting thiols were completely consumed within five minutes at room temperature in an open flask setup. These results suggested that this method is highly efficient and convenient, making it applicable for modern organic synthesis.

One-Pot Synthesis of Sulfenamides from Thiols

With successful results from the oxidation of thiols using DIB, we next explored the use of this hypervalent iodine reagent to synthesize various sulfenamides in a one-pot process. Based on recent reports of using hypervalent iodine(III) reagent to activate the sulfur atom,[14b] we hypothesized that the reagent could also be used to further activate the disulfide bond. Subsequent nucleophilic attack by a nucleophile such as an amine should generate a sulfenamide. Therefore, we selected three different classes of substrates including cyclohexane (**1d**), chlorobenzene (**1a**), and pyridine (**1h**) thiols for reaction screening using DIB as the oxidant/activator and used butylamine as a nucleophile in the presence of DIPEA as a base for the neutralization of the acid produced from the reaction (Scheme 2). Disappointingly, only disulfides **2a** and **2d** were isolated as the sole products in 87 and 80% yields, respectively, by conducting the reaction with cyclohexane thiol and 4-methylthiophenol at room temperature overnight. On the other hand, 2-mercaptopyridine (**1h**) generated a mixture of disulfide **2h** and the expected sulfenamide **3a** in 33 and 47% yield, respectively. These encouraging results not only show that the reaction could be used to produce heterocyclic sulfenamides in a one-pot synthesis, but they also provide some clues for the reaction mechanism. The disulfide is most likely an intermediate in this transformation.

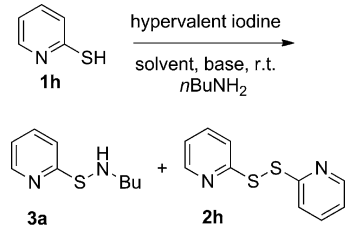


Scheme 2. Amination reaction of thiols with DIB reagent.

Although the reaction is only suitable for the amination of heterocyclic thiols into sulfenamide derivatives, such compounds are valuable building blocks in medicinal chemistry and pharmaceuticals. Sulfenamides containing heterocyclic moieties were reported to show acetylcholine inhibition, insecticidal activities, and antitumor activities among others.[4f,16] We therefore optimized the reaction using 2-

mecaptopyridine (**1h**) with DIB and butylamine (Table 4). Substituting the base DIPEA with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) resulted in the exclusive formation of *N*-butylsulfenamide **3a** in 82% yield after 4 h without remaining disulfide **2h** (entry 1). A short survey of hypervalent iodine(III) reagents showed that DIB is by far the most effective reagent (entries 2–4). Unlike the method used for the preparation of disulfide, this reaction is solvent dependent (entries 5–7). Using MeCN and *N*,*N*-dimethylformamide (DMF) as solvent gave the desired sulfenamide **3a** in 53 and 45%yield, respectively. In addition, disulfide **2h** was also isolated in 26 and 16% yield, respectively. An attempt to drive the reaction to completion by raising the temperature to 125 °C was made, but lower yields of both the sulfenamide and disulfide products were observed (entry 7). In the absence of DBU, the disulfide was isolated as the major product in 56% yield along with the desired sulfenamide **3a** in just 26% yield (entry 8). Changing the base from DBU to DIPEA or K_2CO_3 gave lower yields of the desired sulfenamide **3a** (entries 9 and 10). The amount of DIB reagent was crucial in this reaction (entries 11 and 12). When the reaction was performed without DIB, only a small amount of disulfide **2h** was obtained (25% yield) with no detectable sulfenamide product. When 0.5 equiv. DIB was used, the sulfenamide was produced in only 25% yield along with the disulfide in 51% yield (entry 12). These results suggested that DIB also facilitated the amination reaction after the oxidation step. However, when an excess amount of DIB (2 equiv.) was added to the reaction mixture (entry 13), the reaction efficiency was similar to that obtained when the reaction was conducted with 0.5 equiv. DIB. We suspected that the amine may have lost its nucleophilicity by coordination with the excess DIB reagent. Based on these results, we used DIB (1.1 equiv.) as the oxidant/activator and DBU as the base in 2-propanol at room temperature in an open flask as the optimized conditions for further studies (entry 1).

Table 4. Optimization of one-pot synthesis of sulfenamide from 2-mercaptopyridine.[a]

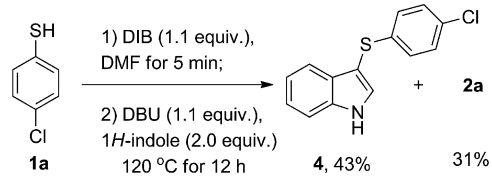


Entry	Oxidant (equiv.)	Base	Solvent	Yield **3a**/**2h** [%][b]
1	$PhI(OCOCH_3)_2$ (1.1)	DBU	*i*PrOH	82:0
2	$PhI(OCOCF_3)_2$ (1.1)	DBU	*i*PrOH	26:67
3	$PhI(OCOtBu)_2$ (1.1)	DBU	*i*PrOH	13:81
4	PhI(OH)(OTs) (1.1)	DBU	*i*PrOH	36:50
5	$PhI(OCOCH_3)_2$ (1.1)	DBU	MeCN	53:19
6	$PhI(OCOCH_3)_2$ (1.1)	DBU	DMF	45:26
7[c]	$PhI(OCOCH_3)_2$ (1.1)	DBU	DMF	5:16
8	$PhI(OCOCH_3)_2$ (1.1)	–	*i*PrOH	25:56
9	$PhI(OCOCH_3)_2$ (1.1)	DIPEA	*i*PrOH	64:25
10	$PhI(OCOCH_3)_2$ (1.1)	K_2CO_3	*i*PrOH	9:79
11	–	DBU	*i*PrOH	0:24
12	$PhI(OCOCH_3$ (0.5))	DBU	*i*PrOH	25:51
13	$PhI(OCOCH_3)$ (2.0)	DBU	*i*PrOH	27:57

[a] Reaction conditions: 2-mercaptopyridine (1.0 equiv.), hypervalent iodine(III) (1.1 equiv.), *i*PrOH, 0 °C, 1 min, then base (2.0 equiv.), *n*-butylamine (2.0 equiv.), 0 °C to r.t., 4 h. [b] Isolated yield after silica gel chromatography. [c] Reaction heated to reflux.

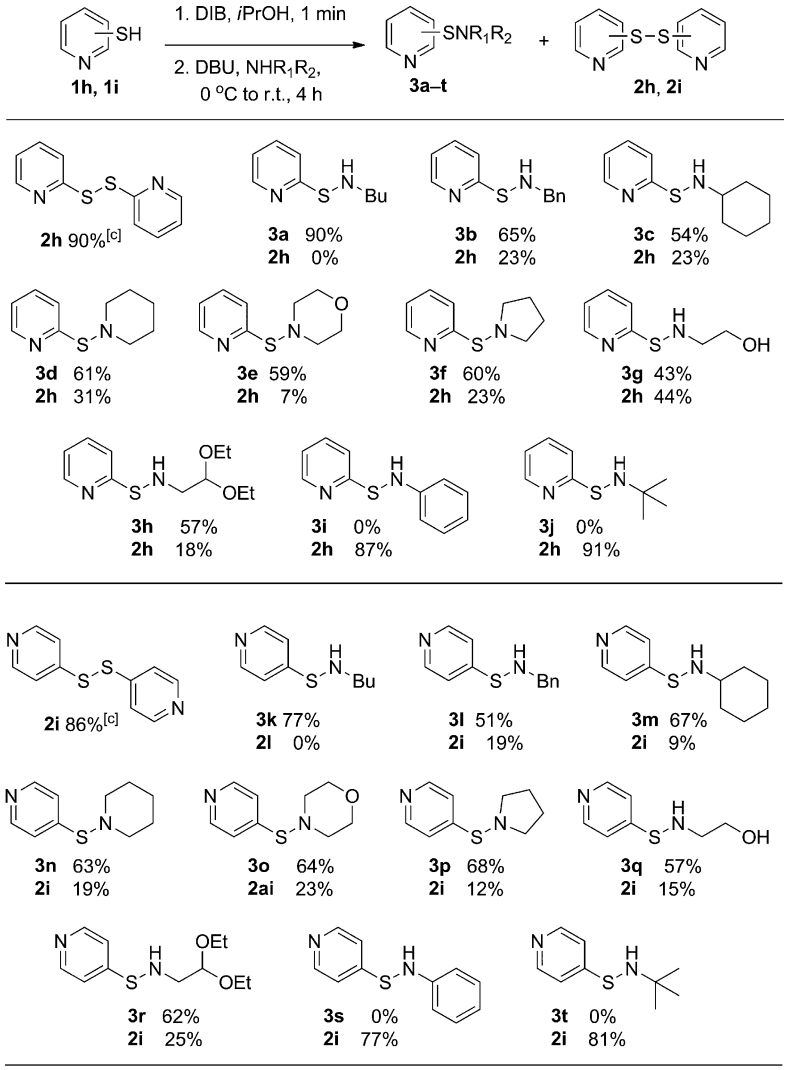
In development of a new methodology, it is important to demonstrate the compatibility of the method with various substrates. Thus, a panel of amine nucleophiles were subjected to the optimized sulfenylation conditions employing two heteroaromatic thiols 2- and 4-mercaptopyridines **1h** and **1i** (Table 5). Without external nucleophile, disulfide **2h** was isolated as the sole product in 90% yield in the case of **1h**. In the presence of simple primary amines such as benzyl and cyclohexylamines, sulfenamides **3b** and **3c** were obtained in 65 and 54% yield, respectively, along with disulfide **2h** in ca. 23% yield. Secondary amines including pyrrolidine, piperidine, and morpholine were acceptable substrates and the corresponding *N*,*N*-dialkyl sulfenamides **3d**–**f** were isolated 58–60% yields along with small amounts of **2h**. Amine nucleophiles carrying other functional groups such as hydroxy or acetal were also compatible with the reaction conditions, generating the corresponding sulfenamides **3g** and **3h**, respectively, in 43 and 57% yields. Attempts to improve the formation of sulfenamide **3** by increasing the temperature, nucleophile amount, or reaction time, resulted in insignificant improvements. Unfortunately, the sterically hindered *tert*-butylamine and the less nucleophilic aniline did not act as a nucleophile and only disulfide **2h** could be isolated. Similarly, 4-mercaptopyridine (**2i**) gave the corresponding sulfenamides **3k**–**r** in slightly better yields compared with 2-mercaptopyridine (**2h**).

Although, this reaction generally gave only moderate yields when compared with traditional multistep synthesis involving oxidation chlorination and amination, this method can provide a complementary way to prepare sulfenamide derivatives under benign and convenient conditions. With these encouraging results in hand, a panel of commercially available heteroaromatic thiols **1j**–**m** was then examined to demonstrate the generality of this DIB-mediated direct amination reaction (Scheme 3); the results are summarized in Table 6. It was shown that this new S–N bond-forming reaction is suitable for generating heteroaromatic sulfenamides ranging from monocyclic to bicyclic with good efficiency. The reaction of benzylamine in the presence of DIB and DBU gave the desired *N*-benzylsulfenamides **3u**–**x** in good yields of 64–73%. We would like to



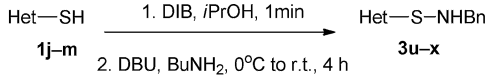
Scheme 3. Synthesis of 3-(4-chlorophenylthio)-1*H*-indole.

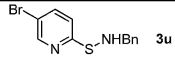
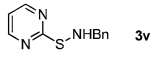
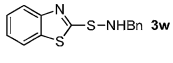
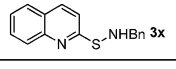
Table 5. The scope of the reaction with respect to amine nucleophiles in the DIB-mediated direct amination of 2- or 4-mercaptopyridine.[a],[b]



[a] Reaction conditions: 2- or 4-mercaptopyridine (1.0 equiv.), DIB (1.1 equiv.), *i*PrOH, 0 °C, 1 min, then DBU (2.0 equiv.), amine (2.0 equiv.), 0 °C to r.t., under air, 4 h. [b] Isolated yield after silica gel chromatography. [c] Amine and DBU were not added.

Table 6. One-pot synthesis of sulfenamide from heterocyclic thiols.[a]



Entry	Starting material	Product	Yield (%)[b]
1	**1j**	 **3u**	67
2	**1k**	 **3v**	72
3[c]	**1l**	 **3w**	73
4	**1m**	 **3x**	64

[a] Reaction conditions: heteroaromatic thiol (1.0 equiv.), DIB (1.1 equiv.), *i*PrOH, 0 °C, 1 min, then DBU (2.0 equiv.), benzylamine (2.0 equiv.), 0 °C to r.t., 4 h. [b] Isolated yield after silica gel chromatography. [c] DMF was used as solvent.

note that, in comparison with pyridinethiols **1h**–**i**, heterocycles **1j**–**m** underwent complete amination reaction without any disulfide remaining in the reaction. The higher reactivity of these heterocyclic thiols in comparison with pyridine is governed by increases in the electrophilicity of the sulfur atom, which facilitates nucleophilic substitution by the amines.

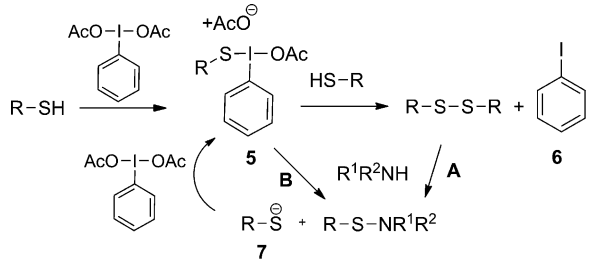
Applications in S–C Bond Formation: Direct Sulfenylation of Indole

In addition to the preparation of sulfenamides, we expanded our discovered methodology to the synthesis of sulfenylindoles. Such compounds represent pharmaceutically and biologically important structures, with their therapeutic value in the treatment of heart disease, allergies, cancer, HIV, and obesity.[17] Traditional approaches for synthesizing this class of compound include sulfenylation of the

indole ring by various sulfenylating agents such as sulfenyl halides, *N*-thioimides, and disulfides.[18] These approaches require multiple-step transformations because the starting sulfenating agents are derived from the thiols. We herein report the applicability of the present DIB-mediated sulfenylation reaction for a direct synthesis of sulfenylindole from thiols (Scheme 3). In a slight modification of the previous conditions for sulfenamide formation, 4-chlorophenylthiol (**1a**) was treated with DIB followed by DBU and 1*H*-indole at 120 °C under open atmosphere for 12 h. To our delight, thioether **4** was obtained in 43% yield along with disulfide **2a** in 31% yield.

Proposed Mechanism for DIB-Mediated Disulfide and Sulfenamide Formation

A plausible mechanism of the DIB-mediated formation of the disulfides and sulfenamides is shown in Scheme 4. Based on previous work on the activation of sulfur by hypervalent iodine reagents,[14b] we hypothesize that the reaction involves ligand exchange between DIB and thiol, leading to the formation of sulfenyl iodide intermediate **5**. A second molecule of thiol then undergoes ligand exchange with **5** to produce the disulfide product. This process is facilitated by the reductive elimination to leave iodobenzene **6**, which is a well-known reaction for hypervalent iodine compounds.[19] From the formation of sulfenamide, there are two possible pathways (A and B). In the presence of a strong nucleophile such as amine, a sulfur atom on the disulfide is attacked and expels a sulfide anion, which undergoes further ligand exchange with DIB reagent to again form the reactive key intermediate **5** (pathway A). This process makes the leaving group sulfide anion form the starting key intermediate **5** and drive the reaction forward. To verify the proposed mechanism, disulfide **2h** was treated with *n*-butylamine in the absence of DIB. Under these conditions, sulfenamide **3a** was isolated in 27% yield, supporting the conclusion that disulfide is an intermediate in this reaction. However, the possibility of direct nucleophilic substitution by the nitrogen amine on the sulfur atom of intermediate **5** could not be ruled out (pathway B).



Scheme 4. A plausible mechanism of disulfide and sulfenamide formation.

Conclusions

We have demonstrated an operationally simple and efficient DIB-mediated one-pot direct methodology for the formation of S–S, S–N and S–C bonds from thiols. The reaction proceeds smoothly under mild conditions without exclusion of air or moisture. The corresponding disulfides and sulfenamides were obtained in fair to good yields. Moreover, the reaction can be used to prepare a representative 3-sulfenylindole directly from indole and thiol. This novel method provides an environment friendly, low cost, and easy to operate alternative synthetic route to disulfides, sulfenamides, and sulfenylindoles directly from thiols.

Experimental Section

General Remarks: All reagents were purchased from Sigma–Aldrich, Fluka (Switzerland) or Merck (Germany) and used without further purification. All reactions were carried out under air atmosphere. All solvents were used without distillation. MS (ESI) and HRMS (ESI) were obtained with a micrOTOF Bruker mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded ($CDCl_3$, CD_3OD, and [D_6]DMSO as solvent) at 400 and 100 MHz, respectively, with a Varian Mercury$^+$ 400 NMR or a Bruker (Avance 400) NMR spectrometer using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm downfield from TMS. Analytical thin-layer chromatography (TLC) was performed on precoated Merck silica gel 60 F_{254} plates (thick layer, 0.25 mm) and visualized by 254 nm ultraviolet lamp and potassium permanganate as the detecting agent. Column chromatography was performed by using Merck silica gel 60 (70–230 mesh).

General Procedure for Synthesis of Thiols 2a–m (Procedure A): To a solution of thiol **2** (1.0 equiv.) in *i*PrOH was added DIB (1.0 equiv.) and the solution was stirred at ambient temperature for 5 min. The solvent was removed by rotary evaporation and the crude product was purified by silica gel chromatography.

1,2-Bis(4-chlorophenyl)disulfane (2a):[20] [CAS: 1142-19-4]: Synthesized according to procedure A using 4-chlorothiophenol (100 mg, 0.691 mmol), DIB (222 mg, 0.691 mmol) in *i*PrOH (4 mL) to afford **1a** (86.6 mg, 0.346 mmol, 87%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40 (d, J = 8.7 Hz, 4 H), 7.27 (d, J = 8.7 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.2, 133.7, 129.4, 129.3 ppm. IR (neat): $\tilde{\nu}$ = 3079, 2925, 1470, 1385 cm^{-1}.

1,2-Dioctyldisulfane (2b):[21] [CAS: 822-27-5]: Synthesized according to procedure A using 1-octanethiol (118 µL, 0.684 mmol), DIB (220 mg, 0.684 mmol) in *i*PrOH (4 mL) to afford **2b** (89.0 mg, 0.342 mmol, 90%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.30 (m, 4 H), 2.70 (m, 4 H), 1.69 (t, J = 7.5 Hz, 4 H), 1.30 (d, J = 2.7 Hz, 16 H), 0.9 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 39.2, 31.8, 29.2, 28.6, 22.6, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3056, 2928, 2859, 1268, 1131 cm^{-1}.

1,2-Dibenzyldisulfane (2c):[8g] [CAS: 150-60-7]: Synthesized according to procedure A using benzyl mercaptan (94.0 µL, 0.804 mmol), DIB (277 mg, 0.804 mmol) in *i*PrOH (4 mL) to afford **2c** (85.7 mg, 0.402 mmol, 86%) as pink crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37–7.29 (m, 10 H), 3.65 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.4, 129.4, 128.5, 127.4, 43.4 ppm. IR (neat): $\tilde{\nu}$ = 3052, 3029, 2914, 2857, 1497, 1456, 1405 cm^{-1}.

1,2-Dicyclohexyldisulfane (2d):[8g] [CAS: 2550-40-5]: Synthesized according to procedure A using cyclohexanethiol (101 µL, 0.860 mmol), DIB (277 mg, 0.860 mmol) in *i*PrOH (4 mL) to afford **2d** (79.7 mg, 0.430 mmol, 80%) as white crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.65 (m, 2 H), 2.01 (s, 4 H), 1.77 (s, 4 H), 1.60 (t, J = 6 Hz, 2 H), 1.25 (m, 10 H) ppm. ^{13}C NMR ($CHCl_3$, 100 MHz):

δ = 50.0, 32.9, 26.1, 25.7 ppm. IR (neat): $\tilde{\nu}$ = 2931, 2853, 1450, 1340, 1262 cm^{-1}.

6,6′-Disulfanediyldihexan-1-ol (2e):[22] [CAS: 80901-86-6]: Synthesized according to procedure A using 6-mercapto-1-hexanol (101 µL, 0.745 mmol), DIB (240 mg, 0.745 mmol) in *i*PrOH (4 mL) to afford **2e** (87.0 mg, 0.373 mmol, 87%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.66 (t, J = 6.6 Hz, 4 H), 2.77–2.62 (m, 4 H), 1.71 (m, 4 H), 1.59 (m, 4 H), 1.51–1.34 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 62.8, 39.1, 32.6, 29.1, 28.2, 25.4 ppm. IR (neat): $\tilde{\nu}$ = 3346, 2934, 2859, 1465, 1053 cm^{-1}.

1,2-Di-*p*-tolyldisulfane (2f):[8g] [CAS: 103-19-5]: Synthesized according to procedure A using 4-methyl thiophenol (100 mg, 0.804 mmol), DIB (259 mg, 0.804 mmol) in *i*PrOH (4 mL) to afford **2f** (94.4, 0.402 mmol, 95%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.30 (d, J = 8.4 Hz, 4 H), 7.03 (d, J = 8.4 Hz, 4 H), 2.24 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.5, 133.9, 129.8, 128.6, 21.0 ppm. IR (neat): $\tilde{\nu}$ = 3020, 2914, 2852, 1488, 1397 cm^{-1}.

2,2′-Disulfanediyldianiline (2g):[8c] [CAS: 1141-88-4]: Synthesized according to procedure A using 2-aminothiophenol (85.0 µL, 0.799 mmol), DIB (257 mg, 0.799 mmol) in *i*PrOH (4 mL) to afford **2g** (74.6 mg, 0.399 mmol, 75%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.18 (t, J = 11.0 Hz, 4 H), 6.74 (m, 2 H), 6.62 (m, 2 H), 4.19 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.6, 136.8, 131.6, 118.8, 115.3 ppm. IR (neat): $\tilde{\nu}$ = 3377, 3294, 3067, 2925, 2852, 1606, 1580, 1470, 1441 cm^{-1}.

1,2-Di(pyridine-2-yl)disulfane (2h):[8g] [CAS: 2127-03-9]: Synthesized according to procedure A using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol) in *i*PrOH (4 mL) to afford **2h** (44.4 mg, 0.202 mmol, 90%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.40 (d, J = 8.1 Hz, 2 H), 7.60–7.49 (m, 4 H), 7.04 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.0, 149.6, 137.4, 121.1, 119.7 ppm. IR (neat): $\tilde{\nu}$ = 3168, 3098, 1604, 1570, 1487, 1438 cm^{-1}. IR (neat): $\tilde{\nu}$ = 3046, 2987, 1574, 1556, 1444, 1414 cm^{-1}.

1,2-Di(pyridin-4-yl)disulfane (2i):[23] [CAS: 2645-22-9]: Synthesized according to procedure A using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB [159 mg, 0.495 mmol in *i*PrOH (4 mL)] to afford **2i** (42.6 mg, 0.194 mmol, 86%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.42 (d, J = 5.5 Hz, 4 H), 7.29 (d, J = 5.5 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9, 145.3, 119.0 ppm. IR (neat): $\tilde{\nu}$ = 3032, 3002, 2922, 1568, 1544, 1479, 1405 cm^{-1}.

1,2-Bis(5-bromopyridin-2-yl)disulfane (2j):[24] [CAS: 872273-36-4]: Synthesized according to procedure A using 5-bromopyridine-2-thiol (100 mg, 0.526 mmol), DIB (169 mg, 0.526 mmol) in *i*PrOH (4 mL) to afford **2j** (81.5 mg, 0.263 mmol, 82%) as yellow crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.45 (d, J = 2.4 Hz, 2 H), 7.66 (dd, J = 8.5, 2.4 Hz, 2 H), 7.43 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.2, 150.6, 139.9, 121.1, 118.3 ppm. IR (neat): $\tilde{\nu}$ = 3099, 3058, 2922, 1550, 1438, 1343 cm^{-1}.

1,2-Di(pyrimidin-2-yl)disulfane (2k):[25] [CAS: 15718-46-4]: Synthesized according to procedure A using 2-mercaptopyrimidine (100.00 mg, 0.89 mmol), DIB (287.31 mg, 0.89 mmol) in *i*PrOH (4.0 mL) to afford **2k** (74.00 mg, 0.45 mmol, 75%) as yellow crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.52 (d, J = 4.8 Hz, 4 H), 7.02 (t, J = 4.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.8, 157.9, 118.1, 29.7 ppm. IR (neat): $\tilde{\nu}$ = 3114, 3067, 2919, 2846, 1550, 1426, 1364, 1264 cm^{-1}.

1,2-Bis(benzo[*d*]thiazol-2-yl)disulfane (2l):[8g] [CAS: 120-78-5]: Synthesized according to procedure A using 2-mercaptobenzothiazole (100 mg, 0.599 mmol), DIB (192 mg, 0.599 mmol) in *i*PrOH (4 mL) to afford **2l** (85.9 mg, 0.299 mmol, 89%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (d, J = 8.1 Hz, 2 H), 7.70 (d, J = 8.1 Hz, 2 H), 7.40 (t, J = 7.2 Hz, 2 H), 7.29 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.8, 154.5, 136.2, 126.6, 125.3, 122.7, 121.3 ppm. IR (neat): $\tilde{\nu}$ = 3058, 2978, 2928, 2869, 1464, 1423, 1317, 1237 cm^{-1}.

1,2-Di(quinolin-2-yl)disulfane (2m):[26] [CAS: 2889-13-6]: Synthesized according to procedure A using quinoline-2-thiol (100 mg, 0.620 mmol), DIB (199 mg, 0.620 mmol) in *i*PrOH (4 mL) to afford **2m** (90.4 mg, 0.310 mmol, 91%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (m, 4 H), 7.74 (d, J = 8.0 Hz, 2 H), 7.65 (m, 4 H), 7.42 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.3, 146.9, 136.5, 129.4, 127.3, 126.7, 125.4, 124.4, 116.3 ppm. IR (neat): $\tilde{\nu}$ = 3058, 2922, 2849, 1612, 1585, 1556, 1491, 1447, 1423 cm^{-1}.

General Procedure for Synthesis of 3a–x (Procedure B): A solution of N-heterocyclic thiol (1.0 equiv.) in *i*PrOH and DIB (1.1 equiv.) was stirred at 0 °C for 1 min, then DBU (2.0 equiv.) and amine (2.0 equiv.) were added and the mixture was stirred at 0 °C to room temperature for 4 h. The crude product was purified by silica gel column chromatography.

***N*-Butyl-2-pyridinesulfenamide (3a):** Synthesized according to procedure B using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 µL, 0.900 mmol), *n*-butylamine (88.9 µL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3a** (73.7 mg, 0.405 mmol, 90%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.36 (d, J = 4.0 Hz, 1 H), 7.51 (td, J = 8.0, 4.0 Hz, 1 H), 7.26 (d, J = 8.0 Hz, 1 H), 6.89 (dd, J = 8.0, 4.0 Hz, 1 H), 3.07 (br. s, 1 H), 2.92 (m, 2 H), 1.50 (m, 2 H), 1.30 (m, 2 H), 0.85 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.9, 148.1, 135.2, 118.1, 116.8, 52.5, 32.6, 20.0, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3366, 3017, 2957, 2927, 2396, 1708, 1649, 1627, 1578, 1557, 1439, 1422, 1359, 1326 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_9H_{14}N_2S + H]^+$ 183.0956; found 183.0950.

***N*-Benzyl-2-pyridinesulfenamide (3b):** Synthesized according to procedure B using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 µL, 0.900 mmol), benzylamine (98.3 µL, 0.90 mmol) in *i*PrOH (4 mL) to afford **3b** (63.2 mg, 0.293 mmol, 65%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.48 (d, J = 4.8 Hz, 1 H), 7.57 (td, J = 8.0, 4.8 Hz, 1 H), 7.44–7.27 (m, 6 H), 6.89 (dd, J = 8.0, 4.8 Hz, 1 H), 4.15 (d, J = 8.0 Hz, 2 H), 3.55 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.0, 149.5, 139.3, 136.3, 128.5, 128.4, 127.6, 119.6, 118.3, 56.7 ppm. IR (neat): $\tilde{\nu}$ = 3323, 3059, 3028, 2987, 1599, 1577, 1556, 1500, 1495, 1456, 1416, 1280, 1220 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_{12}H_{12}N_2S\text{-}H]^-$ 215.0643; found 215.0637.

***N*-Cyclohexyl-2-pyridinesulfenamide (3c):** [CAS: 178735-21-2]: Synthesized according to procedure B using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 µL, 0.900 mmol), cyclohexylamine (103 µL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3c** (50.5 mg, 0.243 mmol, 54%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.33 (d, J = 4.0 Hz, 1 H), 7.50 (m, 1 H), 7.36 (d, J = 8.0 Hz, 1 H), 6.88 (m, 1 H), 2.98 (br. s, 1 H), 2.67 (m, 1 H), 1.95 (m, 2 H), 1.66 (m, 2 H), 1.52 (m, 1 H), 1.25–0.99 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.9, 148.1, 135.2, 118.1, 116.8, 58.5, 32.6, 24.8, 23.8 ppm. IR (neat): $\tilde{\nu}$ = 3342, 3040, 3013, 2937, 2847, 1572, 1552, 1449, 1413, 1367, 1343, 1272, 1258 cm^{-1}. MS (ESI): *m*/*z* calcd. for $[C_{11}H_{16}N_2S + H]^+$ 209.11; found 209.11.

***N*-Piperidinyl-2-pyridinesulfenamide (3d):** [CAS: 178735-24-5]: Synthesized according to procedure B using 2-mercaptopyridine

(35.0 mg, 0.450 mmol), DIB (111 mg, 0.346 mmol), DBU (94 μL, 0.630 mmol), piperidine (62 μL, 0.630 mmol) *i*PrOH (3 mL) to afford **3d** (37.3 mg, 0.192 mmol, 61%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.40 (d, J = 4.3 Hz, 1 H), 7.58 (td, J = 8.1, 1.7 Hz, 1 H), 7.48 (d, J = 8.1 Hz, 1 H), 6.93 (dd, J = 6.8, 5.4 Hz, 1 H), 3.21–3.10 (m, 4 H), 1.68 (dt, J = 11.2, 5.8 Hz, 4 H), 1.50 (dd, J = 11.6, 6.0 Hz, 2 H), 1.66 (m, 2 H), 1.52 (m, 1 H), 1.25–0.99 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.8, 149.3, 136.4, 119.1, 118.0, 57.6, 27.4, 23.3 ppm. IR (neat): $\tilde{\nu}$ = 3016, 2937, 2857, 2827, 1575, 1555, 1442, 1419, 1363, 1213 cm^{-1}. MS (ESI): *m*/*z* calcd. for $[C_{10}H_{14}N_2S + H]^+$ 195.10; found 195.10.

***N*-Morpholinyl-2-pyridinesulfenamide (3e):** [CAS: 2244-48-6]: Synthesized according to procedure B using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), morpholine (77.9 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3e** (52.1 mg, 0.266 mmol, 59%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.36 (d, J = 4.4 Hz, 1 H), 7.53 (td, J = 8.0, 0.8 Hz, 1 H), 7.39 (d, J = 8.0 Hz, 1 H), 6.91 (m, 1 H), 3.71 (m, 4 H), 3.17 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.2, 149.4, 136.5, 119.6, 118.1, 67.9, 56.2 ppm. IR (neat): $\tilde{\nu}$ = 3040, 2953, 2914, 2844, 1569, 1555, 1452, 1412, 1280, 1246 cm^{-1}. MS (ESI): *m*/*z* calcd. for $[C_9H_{12}N_2OS + H]^+$ 197.07; found 197.07.

***N*-Pyrrolidinyl-2-pyridinesulfenamide (3f):** Synthesized according to procedure B using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), pyrrolidine (73.9 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3f** (48.6 mg, 0.270 mmol, 60%) as a colorless oil. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.21 (d, J = 4.4 Hz, 1 H), 7.61 (td, J = 8.0, 2.0 Hz, 1 H), 7.30 (d, J = 8.0 Hz, 1 H), 6.96 (m, 1 H), 3.14 (t, J = 6.6 Hz, 4 H), 1.86 (m, 4 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 167.2, 149.9, 138.4, 120.6, 119.1, 56.5, 27.2 ppm. IR (neat): $\tilde{\nu}$ = 3016, 2967, 2860, 1572, 1555, 1452, 1412, 1210 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_9H_{12}N_2S + H]^+$ 181.0799; found 181.0786.

***N*-(2-Hydroxyethyl)-2-pyridinesulfenamide (3g):** Synthesized according to procedure B using 2-mercaptopyridine (35.0 mg, 0.315 mmol), DIB (111 mg, 0.346 mmol), DBU (94.0 μL, 0.630 mmol), ethanolamine (38.0 μL, 0.630 mmol) in *i*PrOH (3 mL) to afford **3g** (23.0 mg, 0.135 mmol, 43%) as a yellow oil. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.35 (d, J = 4.6 Hz, 1 H), 7.74 (td, J = 8.1, 1.7 Hz, 1 H), 7.57 (d, J = 8.1 Hz, 1 H), 7.10 (dd, J = 6.8, 5.4 Hz, 1 H), 3.68 (t, J = 5.6 Hz, 2 H), 3.11 (t, J = 5.6 Hz, 1 H), 3.10 ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 167.5, 149.8, 138.4, 120.8, 119.2, 62.2, 55.4 ppm. IR (neat): $\tilde{\nu}$ = 3336, 3020, 2947, 2923, 2864, 1575, 1552, 1442, 1412, 1280, 1213 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_7H_{10}N_2OS + H]^+$ 171.0595; found 171.0592.

***N*-(2,2-Diethoxyethyl)-2-pyridinesulfenamide (3h):** Synthesized according to procedure B using 2-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), aminoacetaldehyde diethylacetal (131 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3h** (62.1 mg, 0.257 mmol, 57%) as a yellow oil. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.22 (d, J = 4.4 Hz, 1 H), 7.64 (td, J = 8.0, 1.6 Hz, 1 H), 7.49 (d, J = 8.0 Hz, 1 H), 6.97 (m, 1 H), 4.52 (t, J = 5.3 Hz, 1 H), 3.62 (m, 2 H), 3.46 (m, 2 H), 2.97 (d, J = 5.4 Hz, 2 H), 1.10 (t, J = 5.4 Hz, 6 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 167.6, 149.8, 138.4, 120.8, 119.2, 103.5, 63.7, 56.0, 15.7 ppm. IR (neat): $\tilde{\nu}$ = 3345, 3040, 2970, 2920, 1569, 1552, 1449, 1416, 1373, 1296, 1276, 1236, 1213 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_{11}H_{18}N_2O_2S + Na]^+$ 265.1009; found 265.0987.

***N*-Butyl-4-pyridinesulfenamide (3k):** Synthesized according to procedure B using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), *n*-butylamine (88.9 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3k** (63.1 mg, 0.47 mmol, 77%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.33 (d, J = 6.1 Hz, 2 H), 7.10 (d, J = 6.1 Hz, 2 H), 2.92 (m, 1 H), 2.66 (br. s, 1 H), 1.49 (m, 2 H),1.31 (m, 2 H), 0.86 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.0, 148.1, 115.6, 51.1, 31.6, 19.0, 12.8 ppm. IR (neat): $\tilde{\nu}$ = 3209, 3063, 3026, 3000, 2953, 2920, 2870, 2867, 2442, 2392, 1665, 1575, 1542, 1476, 1436, 1406, 1376, 1366, 1313, 1296, 1213 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_9H_{14}N_2S + H]^+$ 183.0956; found 183.0950.

***N*-Benzyl-4-pyridinesulfenamide (3l):** Synthesized according to procedure B using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), benzylamine (98.3 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3l** (49.6 mg, 0.230 mmol, 51%) as a pale-yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (d, J = 5.9 Hz, 2 H), 7.32–7.23 (m, 5 H), 7.13 (d, J = 5.9 Hz, 2 H), 4.06 (d, J = 5.7 Hz, 2 H), 3.00 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3, 149.2, 138.8, 128.7, 128.2, 127.9, 116.7, 56.4 ppm. IR (neat): $\tilde{\nu}$ = 3335, 3086, 3063, 3033, 2960, 2445, 2395, 1668, 1572, 1545, 1495, 1479, 1452, 1409, 1353, 1316, 1216 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_{12}H_{12}N_2S + H]^+$ 217.0799; found 217.0793.

***N*-Cyclohexyl-4-pyridinesulfenamide (3m):** [CAS: 178735-22-3]: Synthesized according to procedure B using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), cyclohexylamine (103 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3m** (62.7 mg, 0.302 mmol, 67%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.31 (d, J = 6.1 Hz, 2 H), 7.14 (d, J = 6.1 Hz, 2 H), 2.64 (br. m, 2 H), 1.93 (d, J = 11.4 Hz, 2 H), 1.67 (d, J = 12.4 Hz, 2 H), 1.53 (d, J = 11.5 Hz, 1 H), 1.26–1.00 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.7, 149.0, 116.7, 59.6, 33.7, 25.7, 24.8 ppm. IR (neat): $\tilde{\nu}$ = 3345, 3066, 3013, 2930, 2860, 2449, 2395, 1715, 1668, 1582, 1542, 1469, 1442, 1409, 1366, 1349, 1316, 1250, 1210 cm^{-1}. MS (ESI): *m*/*z* calcd. for $[C_{11}H_{16}N_2S + H]^+$ 209.11; found 209.11.

***N*-Piperidinyl-4-pyridinesulfenamide (3n):** Synthesized according to procedure B using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), piperidine (88.9 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3n** (55.0 mg, 0.284 mmol, 63%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.33 (m, 2 H), 7.13 (d, J = 6.0 Hz, 2 H), 2.99 (t, J = 6.0 Hz, 4 H), 1.63 (m, 4 H), 1.44 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.5, 148.2, 116.0, 56.6, 26.2, 22.2 ppm. IR (neat): $\tilde{\nu}$ = 3070, 3013, 2940, 2850, 2824, 2442, 2389, 1569, 1535, 1476, 1452, 1439, 1402, 1366, 1353, 1309, 1216 cm^{-1}. MS (ESI): *m*/*z* calcd. for $[C_{10}H_{14}N_2S + H]^+$ 195.0956; found 195.0950.

***N*-Morpholinyl-4-pyridinylsufenamide (3o):** Synthesized according to procedure B using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159.0 mg, 0.495 mmol), DBU (134 μL, 0.900 mmol), morpholine (77.9 μL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3o** (56.5 mg, 0.288 mmol, 64%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.36 (d, J = 6.1 Hz, 2 H), 7.15 (d, J = 6.1 Hz, 2 H), 3.72 (t, J = 4.0 Hz, 4 H), 3.02 (t, J = 4.0 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.1, 148.4, 116.1, 66.7, 55.2 ppm. IR (neat): $\tilde{\nu}$ = 3070, 3020, 2970, 2890, 2429, 2392, 1569, 1542, 1519, 1476, 1449, 1406, 1363, 1313, 1256, 1223 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $[C_9H_{12}N_2OS + H]^+$ 197.0749; found 197.0742.

***N*-Pyrrolidinyl-4-pyridinesulfenamide (3p):** Synthesized according to procedure B using 4-mercaptopyridine (100 mg, 0.900 mmol), DIB (318.0 mg, 0.990 mmol), DBU (269 μL, 1.80 mmol), pyrrolidine (148 μL, 1.80 mmol) in *i*PrOH (5 mL) to afford **3p** (111 mg, 0.612 mmol, 68%) as a colorless oil. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.31 (d, J = 6.3 Hz, 2 H), 7.24 (d, J = 6.3 Hz, 2 H),

3.20 (t, J = 6.5 Hz, 4 H), 1.97 (m, 4 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 158.1, 149.4, 118.1, 56.5, 27.2 ppm. IR (neat): $\tilde{\nu}$ = 3063, 2967, 2857, 2445, 2395, 1665, 1575, 1539, 1482, 1456, 1452, 1406, 1339, 1319, 1286, 1216 cm^{-1}. HRMS (ESI): m/z calcd. for [$C_9H_{12}N_2S$ + H]$^+$ 181.0799; found 181.0800.

***N*-(2-Hydroxyethyl)-4-pyridinesulfenamide (3q):** Synthesized according to procedure B using 4-mercaptopyridine (50.0 mg, 0.450 mmol), DIB (159.0 mg, 0.495 mmol), DBU (134 µL, 0.900 mmol), ethanolamine (54.3 µL, 0.900 mmol) in *i*PrOH (4 mL) to afford **3q** (43.7 mg, 0.257 mmol, 57%) as a yellow oil. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.19 (d, J = 6.4 Hz, 2 H), 7.25 (d, J = 6.4 Hz, 2 H), 3.55 (t, J = 5.6 Hz, 2 H), 2.96 (t, J = 5.6 Hz, 2 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 158.8, 149.2, 118.3, 67.3, 55.0 ppm. IR (neat): $\tilde{\nu}$ = 3458, 3405, 3020, 2970, 2927, 2442, 2399, 1751, 1711, 1618, 1575, 1539, 1519, 1479, 1412, 1363, 1220 cm^{-1}. HRMS (ESI): m/z calcd. for [$C_7H_{10}N_2OS$ + H]$^+$ 171.0622; found 171.0592.

***N*-(2,2-Diethoxyethyl)-4-pyridinesulfenamide (3r):** Synthesized according to procedure B using 4-mercaptopyridine (100 mg, 0.900 mmol), DIB (318.0 mg, 0.990 mmol), DBU (269 µL, 1.80 mmol), aminoacetaldehyde diethylacetal (262 µL, 1.80 mmol) in *i*PrOH (5 mL) to afford **3r** (136 mg, 0.558 mmol, 62%) as a colorless oil. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.32 (d, J = 6.4 Hz, 2 H), 7.35 (d, J = 6.4 Hz, 2 H), 4.61 (t, J = 5.3 Hz, 1 H), 3.72 (m, 2 H), 3.57 (m, 2 H), 3.07 (d, J = 5.3 Hz, 2 H), 1.22 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 158.8, 149.2, 118.2, 103.5, 63.8, 55.7, 15.7 ppm. IR (neat): $\tilde{\nu}$ = 3355, 3013, 2973, 2923, 2485, 2452, 2402, 1661, 1572, 1542, 1479, 1439, 1409, 1376, 1346, 1316, 1300, 1210 cm^{-1}. HRMS (ESI): m/z calcd. for [$C_{11}H_{18}N_2O_2S$ + H]$^+$ 243.1167; found 243.1167.

***N*-Benzyl-5-bromo-2-pyridinesulfenamide (3u):** Synthesized according to procedure B using 5-bromopyridine-2-thiol (50.0 mg, 0.262 mmol), DIB (92.8 mg, 0.288 mmol), DBU (78.4 µL, 0.524 mmol), benzylamine (57.2 µL, 0.524 mmol) in *i*PrOH (3 mL) to afford **3u** (51.6 mg, 0.176 mmol, 67%) as a white solid. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 8.32 (s, 1 H), 7.72 (dd, J = 4.0, 8.0 Hz, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 7.23–7.12 (m, 5 H), 4.00 (s, 2 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 166.2, 150.8, 140.9, 140.5, 129.5, 129.4, 128.4, 120.9, 116.6, 57.1 ppm. IR (neat): $\tilde{\nu}$ = 3261, 3066, 3023, 2918, 1700, 1601, 1555, 1533, 1499, 1444, 1342 cm^{-1}. HRMS (ESI): m/z calcd. for [$C_{12}H_{11}BrN_2S$ + H]$^+$ 294.9921; found 294.9905.

***N*-Benzyl-2-pyrimidinesulfenamide (3v):** Synthesized according to procedure B using 2-pyrimidinethiol (50.0 mg, 0.446 mmol), DIB (158 mg, 0.490 mmol), DBU (133 µL, 0.892 mmol), benzylamine (97.4 µL, 0.892 mmol) in *i*PrOH (4 mL) to afford **3v** (69.7 mg, 0.321 mmol, 72%) as a yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.52 (d, J = 4.8 Hz, 2 H), 7.37–7.17 (m, 5 H), 6.92 (t, J = 4.6 Hz, 1 H), 4.14 (s, 2 H), 3.56 (br. s, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 175.9, 157.4, 139.2, 128.5, 128.4, 127.5, 116.8, 56.3 ppm. IR (neat): $\tilde{\nu}$ = 3325, 3056, 3020, 2927, 2402, 1612, 1588, 1562, 1545, 1489, 1449, 1416, 1376, 1290, 1223, 1193 cm^{-1}. HRMS (ESI): m/z calcd. for [$C_{11}H_{11}N_3S$ + H]$^+$ 218.0745; found 218.0752.

***N*-Benzyl-2-benzothiazolsulfenamide (3w):**[15] [CAS: 26773-69-3]: Synthesized according to procedure B using 2-Mercaptobenzothiazole (50.0 mg, 0.299 mmol), DIB (106.0 mg, 0.329 mmol), DBU (89.4 µL, 0.598 mmol), benzylamine (65.3 µL, 0.598 mmol) in DMF (3 mL) to afford **3w** (59.4 mg, 0.218 mmol, 73%) as a white-yellow solid. ^{1}H NMR ([D$_4$]MeOH, 400 MHz): δ = 7.73–7.73 (m, 2 H), 7.35–7.17 (m, 7 H), 4.19 (d, J = 8.0 Hz, 2 H), 3.49 (t, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR ([D$_4$]MeOH, 100 MHz): δ = 177.2, 154.8, 138.5, 135.1, 128.7, 128.4, 128.0, 126.0, 123.8, 121.7, 121.1, 57.1 ppm. IR (neat): $\tilde{\nu}$ = 3345, 3176, 3063, 3016, 2973, 2392, 1492, 1456, 1429, 1353, 1309, 1273, 1220 cm^{-1}. MS (ESI): m/z calcd. for [$C_{14}H_{12}N_2S$ + H]$^+$ 273.00; found 273.05.

***N*-Benzyl-2-quinolinesulfenamide (3x):** Synthesized according to procedure B using 2-quinolinethiol (60.0 mg, 0.372 mmol), DIB (132.0 mg, 0.409 mmol) in *i*PrOH (4 mL) to afford **3x** (63.4 mg, 0.238 mmol, 64%) as a yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.91 (d, J = 8.6 Hz, 2 H), 7.67 (d, J = 8.6 Hz, 1 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.41–7.16 (m, 7 H), 4.15 (d, J = 5.2 Hz, 2 H), 3.68 (br. s, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 163.9, 148.3, 136.0, 129.9, 128.6, 128.5, 128.1, 127.8, 127.6, 125.4, 117.0, 56.8 ppm. IR (neat): $\tilde{\nu}$ = 3276, 3060, 3023, 2920, 1612, 1588, 1555, 1489, 1456, 1419, 1293 cm^{-1}. HRMS (ESI): m/z calcd. for [$C_{16}H_{14}N_2S$ + H]$^+$ 267.0956; found 267.0954.

3-(4-Chlorophenylthio)-1*H*-indole (4): A solution of 4-chlorothiophenol (50.0 mg, 0.346 mmol, 1.00 equiv.) and DIB (123 mg, 0.381 mmol, 1.10 equiv.) in DMF (3.50 mL) was stirred at ambient temperature for 5 min. DBU (103 µL, 0.692 mmol, 2.00 equiv.) and 1*H*-indole (81.3 mg, 0.692 mmol, 2.00 equiv.) were added and the mixture was stirred at 120 °C for 12 h. The crude product was purified by silica gel chromatography to afford **4** (33.5 mg, 0.149 mmol, 43%) as a colorless oil and **2a** (8.41 mg, 0.0294 mmol, 17%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 11.74 (s, 1 H), 7.79 (d, J = 2.7 Hz, 1 H), 7.50 (d, J = 8.1 Hz, 1 H), 7.38 (d, J = 7.8 Hz, 1 H), 7.30–7.23 (m, 2 H), 7.20 (t, J = 7.1 Hz, 1 H), 7.08 (t, J = 7.5 Hz, 1 H), 7.04–6.97 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 138.4, 136.7, 132.6, 129.3, 128.7, 128.4, 126.8, 122.2, 120.2, 118.1, 112.4, 98.6 ppm. HRMS (ESI): m/z calcd. for $C_{14}H_{10}ClNS$ 259.0222; found 259.0228.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra for all products.

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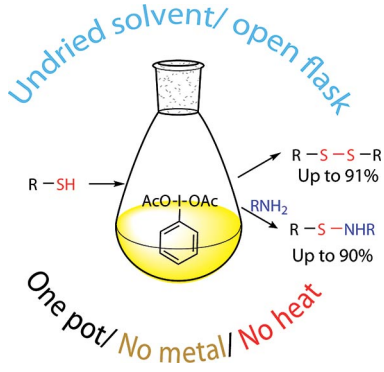
Disulfides and sulfenamides can be easily prepared from the corresponding thiols by using (diacetoxyiodo)benzene as activator at room temperature under open-flask conditions.



Keywords: Hypervalent compounds / Oxidation / Iodine / Sulfur / Heterocycles / Disulfides

