Cu-catalysed direct bis-thiolation of benzoheterocycles with arylsulfonyl hydrazides

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A series of bis-arylsulfenylated indoles (10), benzofurans (3), and benzothiophenes (3) and of monosulfenylated indoles (5), 12 of which are novel, were prepared in good yields *via* a Cu-catalysed direct sulfenylation of benzoheterocycles with arylsulfonyl hydrazides. Sulfonothioates are probably the major thiolated intermediates in this transformation.

Keywords: indoles, benzofurans, benzo[*b*]thiphenes, arylsulfonyl hydrazide, Cu-catalysed disulfenylation

The heterocyclic arylsulfide moiety is a useful building block in medicinal chemistry. It is widely present in biologically active compounds, natural products, pharmaceuticals and organic materials.[1–4] In addition to their potential synthetic value and varying remarkable bioactivities, heterocyclic arylsulfides are useful intermediates in organic syntheses.[5] Several approaches have been reported for the preparation of heterocyclic arylsulfides, such as the direct mono-thiolation of heterocyclic arenes with arylsulfenyl halides,[6] diaryl disulfides,[7,8] sodium sulfinates,[9,10] arylsulfinic acids,[11] aryl thiols,[12,13] aryl-*N*-thioimides,[14–16] and sulfonyl hydrazides[17–20] as sources of the sulfurisation agents. For example, regioselective mono-sulfenylations of indoles with sulfonyl hydrazides in the presence of iodine or a DBU-based ionic liquid as catalyst gave structurally diverse indole thioethers.[17,19] A copper-catalysed regioselective sulfenylation of indoles or pyrrolo[2,3-*b*] pyridines with arylsulfonyl chlorides was also achieved by using PPh_3 as reductant.[21] In addition, aryl benzofuran thioethers were synthesised by the I_2-catalysed cross-coupling of benzofurans with aryl sulfonyl hydrazides.[22]

Although many methods have been successfully used to construct structurally diverse heterocyclic mono-arylsulfides, synthesis of heterocyclic bis-arylsulfides has not been well documented. As early as 1992, the synthesis of 2,3-bis-sulfenyl indoles was achieved by the reaction of indoles and aryl sulfenyl chlorides.[23–25] Subsequently, I_2-mediated mono- and disulfenylation reactions of indoles at the 2- and 3-positions were reported and also various sulfurisation agents such as diaryl disulfides, thiols and sodium sulfinates were used to prepare 2,3-bis-sulfenyl indoles.[13,26,27] Recently, a CuI-catalysed regioselective sulfenylation of indoles with disulfides was developed.[28] Here we describe a novel Cu-catalysed direct bis-sulfenylation of indoles, benzofurans and benzothiophenes with arylsulfonyl hydrazides.

Results and discussion

The initial conditions we tried for the bis-thiolation of 1*H*-indole (**2a**; X = N) by *p*-toluenesulfonyl hydrazide (**1a**; Ar = tosyl) was refluxing at 80 °C in 1,2-dichloroethane (DCE) as solvent in the presence of HOAc using $Cu(OTf)_2$ as a copper source (Scheme 1). Gratifyingly, this led to the formation of 2,3-bis(*p*-tolylthio)-1*H*-indole (**3a**; X = N) in 60% yield as a single product (Table 1, entry 1). We then used this reaction to optimise the reaction conditions and the results are shown in Table 1. Other copper sources such as CuBr, CuI, $Cu(TFA)_2$ and $Cu(OAc)_2$, gave low yields of the desired product **3a** (Table 1, entries 2–5). The reaction did not proceed in the absence of copper (Table 1, entry 6). When we replaced DCE with toluene, a nonpolar solvent, a 57% yield of the desired product

Table 1 Optimisation of the reaction conditions (catalyst, solvent) for the 2,3-disulfenylation of indole (**2**; X = N) using tosylhydrazide (**1a**; Ar = 4-Me-C_6H_4) (Scheme 1)[a]

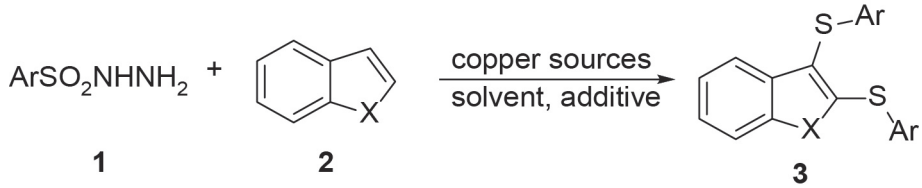
Entry	Catalyst (mmol)	Solvent (mL)	H_2O (mL)	HOAc (mL)	Yield (%)[b]
1	$Cu(OTf)_2$ (0.2)	DCE (2)	–	1	60
2	CuBr (0.2)	DCE (2)	–	1	15
3	CuI (0.2)	DCE (2)	–	1	Trace
4	$Cu(TFA)_2$ (0.2)	DCE (2)	–	1	Trace
5	$Cu(OAc)_2$ (0.2)	DCE (2)	–	1	13
6	–	DCE (2)	–	1	0
7	$Cu(OTf)_2$ (0.2)	Toluene (2)	–	1	57
8	$Cu(OTf)_2$ (0.2)	DMSO (2)	–	1	Trace
9	$Cu(OTf)_2$ (0.2)	Dioxane (2)	–	1	48
10	$Cu(OTf)_2$ (0.2)	MeOH (2)	–	1	34
11	$Cu(OTf)_2$ (0.2)	CH_3CN (2)	–	1	27
12[c]	$Cu(OTf)_2$ (0.2)	DCE (2)	–	1	58
13	$Cu(OTf)_2$ (0.2)	DCE (2)	0.1	1	66
14	$Cu(OTf)_2$ (0.3)	DCE (2)	0.1	2	53
15[d]	$Cu(OTf)_2$ (0.2)	DCE(2)	0.1	2	77
16[d]	$Cu(OTf)_2$ (0.2)	DCE(1)	0.1	2	77
17[d]	$Cu(OTf)_2$ (0.2)	Toluene (1)	0.1	2	82

[a]Reaction conditions: a mixture of tosylhydrazide (**1a**; Ar = 4-Me-C_6H_4) (0.8 mmol), indole (**2**; X = N) (0.3 mmol), a Cu(II) source (0.2 mmol), solvent (1 mL), HOAc (1 or 2 mL) and (sometimes) H_2O (0.1 mL) was stirred under air at 80 °C for 8 h.

[b]Isolated yield.

[c]**1a**:**2a** = 0.6 mmol:0.3 mmol.

[d]At 110 ºC.



Scheme 1

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was obtained (Table 1, entry 7). Polar solvents such as DMSO, 1,4-dioxane, methanol and acetonitrile resulted in lower yields of the product (Table 1, entries 8–11). Next, these studies were carried out at temperatures ranging from 80 °C to 110 °C using different amounts of $Cu(OTf)_2$, DCE, or toluene/H_2O, and HOAc (Table 1, entries 12–17). On the basis of these results, the optimum conditions were: stirring a mixture of $Cu(OTf)_2$ (0.2 mmol), toluene (1 mL), H_2O (0.1 mL) and HOAc (2 mL) at 110 °C for 8 h.

With the optimal reaction conditions in hand, we next examined the scope and limitations of the reaction. As shown in Table 2, benzenesulfonohydrazide (**1b**; Ar = Ph) underwent the thioether reaction to give a 59% yield of bis-thioether product (**3b**; Ar = Ph). Benzenesulfonohydrazides bearing electron-withdrawing functional groups at the *para* and *meta* positions (**1c**–**g**; Ar = various) also afforded bis-thioether products (**3c**–**g**; Ar = various) in 47–61% yields, as did the substrates with electron-donating groups such as 4-(*t*-butyl)benzenesulfonohydrazide (**1h**; Ar = 4-Bu^t-C_6H_4) and 4-methoxybenzenesulfonohydrazide (**1i**; Ar = 4-MeO-C_6H_4), which gave the corresponding bis-thioether products **3h** (Ar = 4-Bu^t-C_6H_4) and **3i** (Ar = 4-MeO-C_6H_4) in 58% and the surprisingly low 14% yield, respectively.

Table 2 Yields of a series of 2,3-bis(arylthio)-1H-indoles (**3b–i**; X = N; Ar = various) prepared from the reaction of an arylhydrazide (**1**; Ar = various) with indole (**2**; X = N) in the presence of Cu(II) triflate (Scheme 1)[a]

Entry	Product **3**	Ar/**1**	Yield (%)[b]
1	**3b**	C_6H_5–/**1b**	59
2	**3c**	4-Cl-C_6H_4–/**1c**	61
3	**3d**	4-F-C_6H_4–/**1d**	50
4	**3e**	3-F-C_6H_4–/**1e**	56
5	**3f**	4-CF_3O-C_6H_4–/**1f**	55
6	**3g**	4-CF_3-C_6H_4–/**1g**	47
7	**3h**	4-^{t}Bu-C_6H_4–/**1h**	58
8	**3i**	4-MeO-C_6H_4–/**1i**	14

[a]Reaction conditions: a mixture of an arylhydrazide (**1**; Ar = various) (0.8 mmol), indole (**2**; X = N) (0.3 mmol), $Cu(OTf)_2$ (0.2 mmol), toluene (1 mL), HOAc (2 mL) and H_2O (0.1 mL) was stirred at 110 °C for 8 h.
[b]Isolated yield.

Table 3 Yields of a series of 2- or 3-(tolylthio)-1*H*-indoles (**5a–f**; R, R′ = various) prepared from the reaction of tosylhydrazide (**1a**) with variously substituted indoles (**4**; R, R′ = various) in the presence of Cu(II) triflate (Scheme 2)[a]

Entry	Product **5**	R	R′	*n*	Yield (%)[b]
1	**5a**	H	Me	2	70
2	**5b**	2-Me	H	1	39
3	**5c**	3-Me	H	1	24
4	**5d**	7-NO_2	H	1	82
5	**5e**	5-NO_2	H	1	59
6	**5f**	7-CN	H	1	41

[a]Reaction conditions: a mixture of tosylhydrazide (**1a**) (0.8 mmol), variously substituted indoles (**4**; R, R′ = various) (0.3 mmol), $Cu(OTf)_2$ (0.2 mmol), toluene (1 mL), HOAc (2 mL) and H_2O (0.1 mL) was stirred at 110 °C for 8 h.
[b]Isolated yields.

Variously substituted indole derivatives were investigated as coupling partners for this transformation (Scheme 2 and Table 3). The position and electronic properties of the substituent groups have a very significant effect on the result of the reaction under the standard conditions. For example, 1-methyl-1*H*-indole (**4**; R = H, R′ = Me) afforded a bis-thioether product (**5a**; R = H, R′ = Me, *n* = 2) in 70% yield. However, when 2-methyl-1*H*-indole (**4**; R = 2-Me, R′ = H) was reacted, sulfenylation took place at the C3 position of the indole ring to give the product (**5b**; R = 2-Me, R′ = H; *n* = 1) in 39% yield and 3-methyl-1*H*-indole (**4**; R = 3-Me, R′ = H) gave the 2-thiolated product (**5c**; R = 2-Me, R′ = H; *n* = 1) in 24% yield. For three 1*H*-indoles with strong electron-withdrawing substituents, such as $–NO_2$, and –CN in the aromatic ring (**4**; R = 7-NO_2, 5-NO_2, 4-CN, R′ = H), only mono-thioether products at the C3 position of the indole ring were obtained (**5d–f**; R = 7-NO_2, 5-NO_2, 4-CN , R′ = H; *n* = 1), and bis-thioether products were not detected.

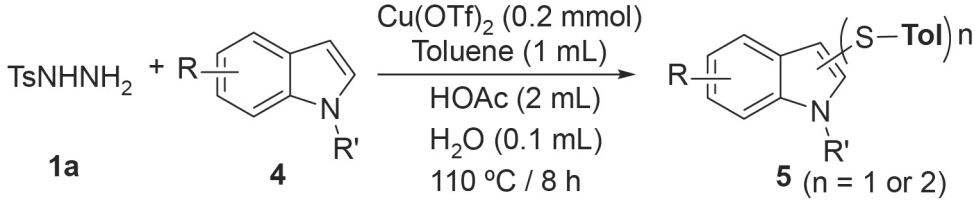
Benzofuran (**2**; X = O) and benzothiophene (**2**; X = S) also suffered bis-thiolation with 4-substituted arylsulfonyl hydrazides (**1**; Ar = 4-Me-C_6H_4, 4-MeO-C_6H_4, 4-Bu^t-C_6H_4, 4-F-C_6H_4), proceeding with 35–87% yields to furnish the corresponding heterocycles (**3j–p**; X = O or S; Ar = 4-Me-C_6H_4, 4-MeO-C_6H_4, 4-Bu^t-C_6H_4, 4-F-C_6H_4) (Table 4). The electronic effects of the substituents had no noticeable effect on the yields of the reactions.

To gain further insight into the mechanism, a series of control experiments were performed (Scheme 3). When one equivalent of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger was added to the reaction mixture of $TsNHNH_2$ and 1*H*-indole, the yield was decreased to 40%. Hydroquinone replacement of TEMPO completely inhibited the formation of thioether **3a** (Scheme 3, [1]). These results suggested that possibly both sulfur radicals (Tol-S•) and sulfonyl radicals (Tol-SO_2•) were generated through decomposition of $TsNHNH_2$ during the sulfenylation reaction. When only $TsNHNH_2$ as

Table 4 Yields of a series of 2,3-(diarylthio)-benzofurans (**3j–l**; X = O; Ar = various) and 2,3-(diarylthio)-benzo[b]thiophenes (**3m–p**; X = S; Ar = various) prepared from the reaction of an arylhydrazide (1; Ar = various) with benzofuran (**2**; X = O) or benzo[*b*]thiophene (**2**; X = S) in the presence of Cu(II) triflate (Scheme 1)[a]

Entry	Product **3**	X	Ar	Yield (%)[b]
1	**3j**	O	4-Me-C_6H_4–	60 (trace)[c]
2	**3k**	O	4-MeO-C_6H_4–	55
3	**3l**	O	4-^{t}Bu-C_6H_4–	35
4	**3m**	S	4-Me-C_6H_4–	54
5	**3n**	S	4-MeO-C_6H_4–	39
6	**3o**	S	4-^{t}Bu-C_6H_4–	87
7	**3p**	S	4-F-C_6H_4–	52

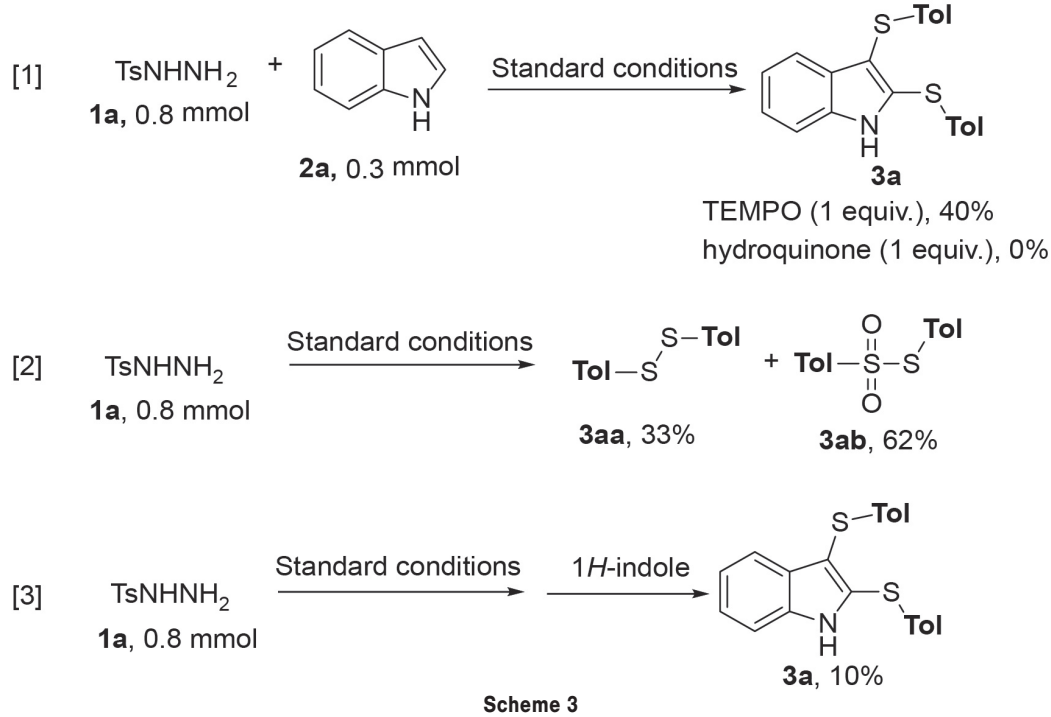
[a]Reaction conditions: a mixture of an arylhydrazide (**1**; Ar = various) (0.8 mmol), benzofuran (**2**; X = O) or benzo[*b*]thiophene (**2**; X = S) (0.3 mmol), $Cu(OTf)_2$ (0.2 mmol), DCE (2 mL), HOAc (2 mL) and H_2O (0.1 mL) was stirred at 110 °C for 8 h.
[b]Isolated yields.
[c]Toluene (2 mL) as solvent. Only a trace of product with DCE.



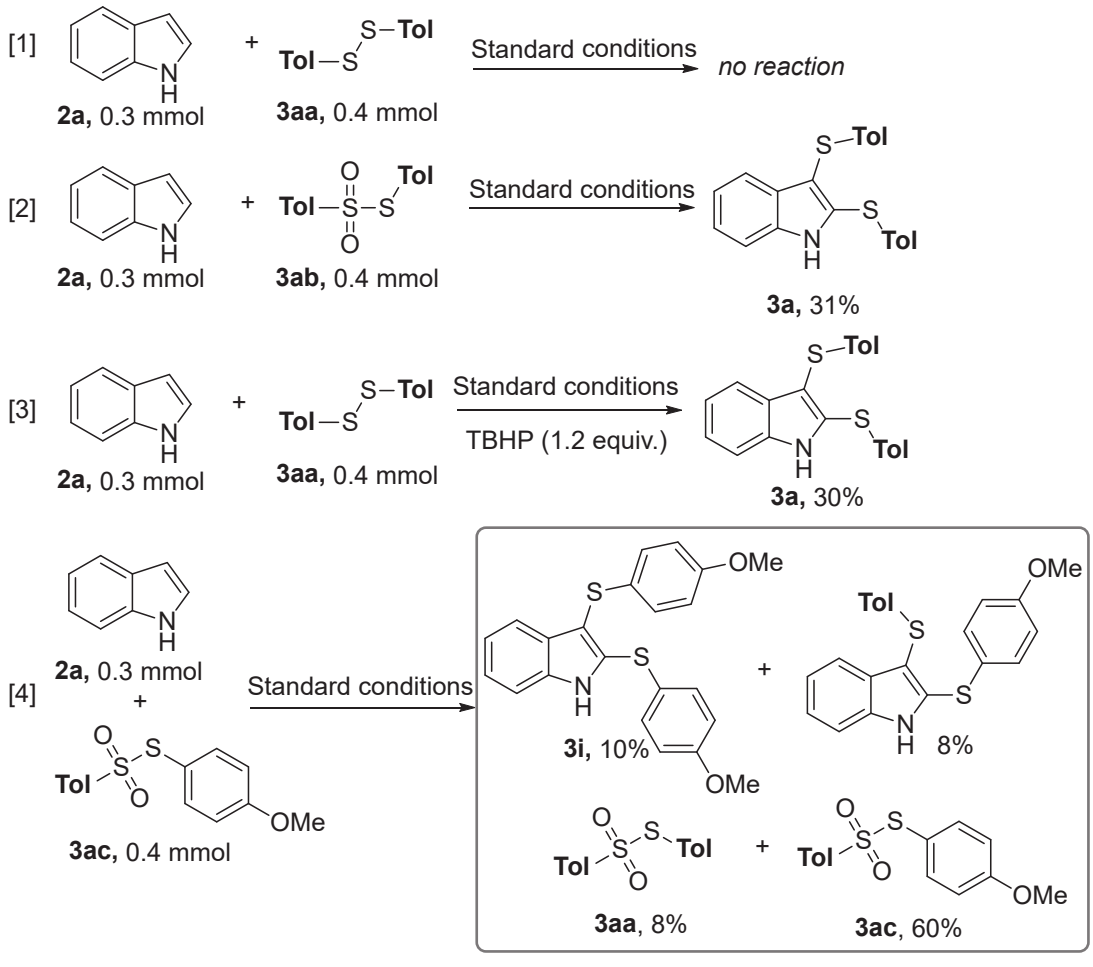
Scheme 2

substrate was used, *S*-*p*-tolyl-4-methylbenzenesulfonothioate (**3ab**) and 1,2-di-*p*-tolyldisulfane (**3aa**) were obtained in a ratio of 2:1 under the standard conditions (Scheme 3, [2]). If 1*H*-indole was added to the above reaction mixture, bis-thioether product **3a** was formed in 10% yield (Scheme 3, [3]). Therefore, we can speculate that intermediates **3aa** or **3ab**, or both, play an important role in the thioetherification.

To further identify the active intermediates of the reaction, different sulfur sources were investigated (Scheme 4). When **3aa** was used as thioether reagent under the standard conditions,



Scheme 3

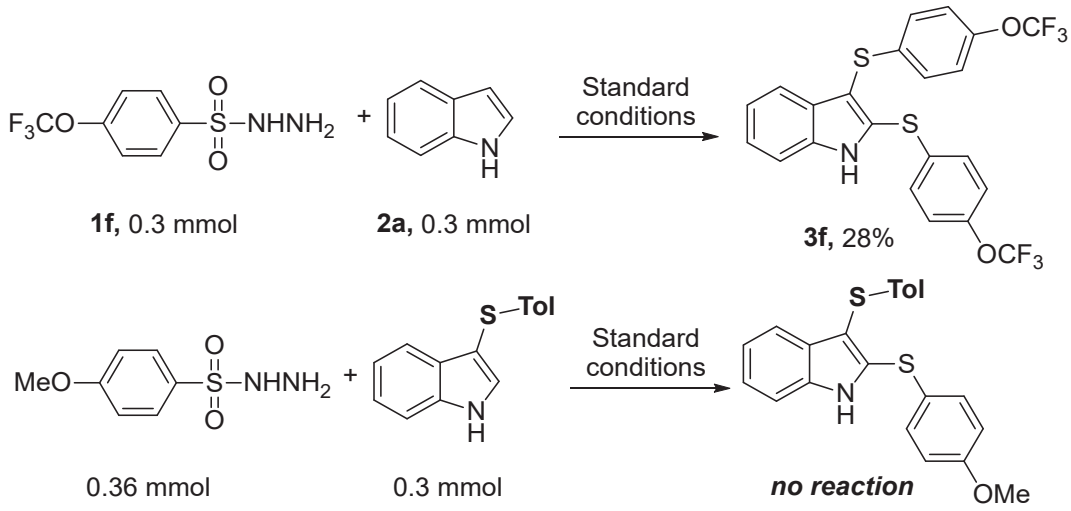


Scheme 4

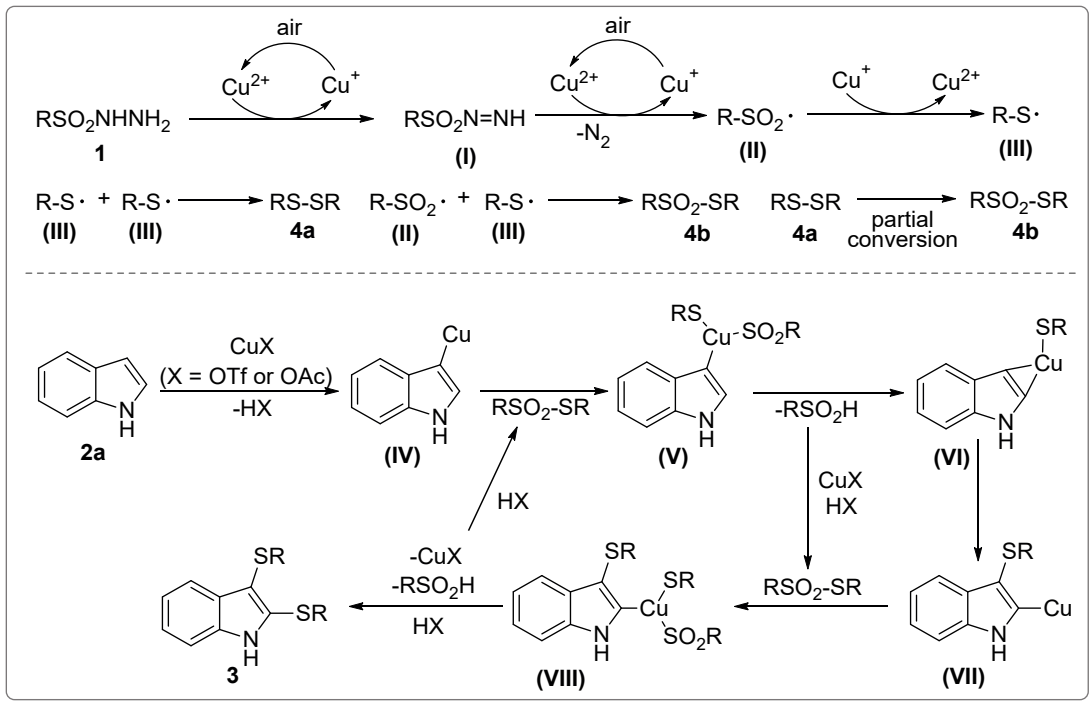
the bis-thioether product **3a** was not detected (Scheme 4, [1]). In contrast, the reaction of **2a** with **3ab** as a sulfur source proceeded smoothly to give a 31% yield of **3a** (Scheme 4, [2]). Moreover, the reaction with **2a** and **3aa** in the presence of tetrabutyl hydroperoxide (TBHP) also afforded the desired product **3a** in 30% yield (Scheme 4, [3]). As THBP converts **3aa** into **3ab**, we speculated that intermediate **3ab** plays an important role in the thioetherification. The reaction of (4-methoxyphenyl) 4-methylbenzenesulfonothioate **3ac** as a sulfur source with indole (**2a**) was tested under the standard conditions, and the bis-thioether products 2,3-bis((4-methoxyphenyl)thio)-1*H*-indole (**3i**, 10%) and 2-((4-methoxyphenyl)thio)-3-(*p*-tolylthio)-1*H*-indole (8%) were obtained, accompanied by an 8% yield of the product **3ab** and recovery of unchanged **3ac** (60%) (Scheme 4, [4]).

In previous reports[13–16], it was mentioned that mono- or di-sulfenylated products can be selectively obtained by changing the amount of sulfonylhydrazine. However, when the ratio of 4-(trifluoromethoxy)benzenesulfonohydrazide and indole (**2a**) was 1:1, we still obtained the bis-sulfenylated product (**3f**), and the mono-sulfide was not detected. In addition, we found that the reaction of 3-(*p*-tolylthio)-1*H*-indole as substrate and 4-methoxybenzenesulfonohydrazide did not give product 2-((4-methoxyphenyl)thio)-3-(*p*-tolylthio)-1*H*-indole (Scheme 5).

According to the above results of control experiments, a plausible mechanism catalysed by $Cu(OTf)_2$ is proposed in Scheme 6. First, $TsNHNH_2$ (**1**) is oxidised to intermediate (**I**) in the presence of $Cu(OTf)_2$, and then intermediate (**I**) is oxidised to generate sulfonyl radicals (**II**). Some of the sulfonyl radicals are subsequently reduced to arylthio radicals (**III**) by monovalent copper ions. Then, the aryl sulfonyl radical (**II**) interacts with the arylthio radical (**III**) to yield two important thioether intermediates **4a** and **4b**, respectively. The following catalytic cycle is proposed: 1*H*-indole (**2a**) reacts with monovalent copper to produce a 1*H*-indole(C3) monovalent-copper intermediate (**IV**), which reacts with **4b** to form the intermediate (**V**). After eliminating arylsulfurous acid to give



Scheme 5



Scheme 6

the intermediate (**VI**), followed by its reductive elimination to give a mono-sulfenylated 1*H*-indole(C3) copper(I) intermediate (**VII**). Subsequently, intermediate (**VII**) undergoes an oxidative addition reaction with **4b** to give intermediate (**VIII**), which suffers reductive elimination to give a bis-sulfenylated 1*H*-indole (**3**), while the monovalent-Cu catalyst is released and ready for use in the next catalytic cycle.

Conclusions

In summary, we have proposed an efficient Cu-catalysed bis-thiolation of indoles, benzofurans and benzo[*b*]thiophenes with arylsulfonyl hydrazides. This system features environmental friendliness, wide substrate scope and good functional group tolerance. Experimental analysis suggests that both free-radical formation and a Cu-catalysed cycle may be involved in the reaction pathway, and the sulfonothioates are the main thiolation intermediates in this transformation.

Experimental

NMR spectra were obtained on a Bruker DPX-400 spectrometer (^{1}H NMR at 400 Hz, ^{13}C NMR at 100 Hz) in $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) are given in Hz. EI mass spectra were measured on a LC/Q–TOF MS (Micromass, England). All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (PE) (60–90 °C); unless otherwise noted 1*H*-indoles and its derivatives, arylsulfonyl hydrazides, $Cu(OTf)_2$ and solvents of analytical grade were purchased from Adamas-beta Pharmaceuticals, Inc.

Direct thiolation of benzoheterocycles with arylsulfonyl hydrazides; general procedure

First, a solution of a benzoheterocycle (an indole, a benzofuran or a benzo[*b*]thiophene) (0.3 mmol), an arylsulfonyl hydrazide (0.8 mmol), $Cu(OTf)_2$ (0.2 mmol), HOAc (2 mL) and H_2O (0.1 mL) in toluene (1 mL) was stirred at 110 °C for 8 h under air. Second, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined EtOAc extracts were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE/EtOAc as the eluent.

2,3-Bis(p-*tolylthio)-1*H-*indole* (**3a**)[13]: Light yellow oil; yield 89 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.25–7.19 (m, 3H), 7.15–7.11 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.9, 136.9, 135.0, 134.8, 134.6, 130.9, 130.4, 130.3, 130.2, 129.6, 127.1, 123.6, 121.2, 119.8, 111.1, 108.4, 21.2, 21.1.

*2,3-Bis(phenylthio)-1*H-*indole* (**3b**)[29]: White solid; yield 59 mg (59%); m.p. 87.8–88.8 °C (lit.[29] m.p. 96–98 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 2.4, 1.2 Hz, 3H), 7.25–7.19 (m, 3H), 7.16 (dd, *J* = 0.8, 1.6 Hz, 2H), 7.13–7.09 (m, 3H), 7.08–7.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.2, 137.0, 134.4, 133.7, 130.1, 129.8, 129.5, 128.8, 127.4, 126.7, 125.2, 124.0, 121.3, 120.0, 111.3, 109.3.

*2,3-Bis((4-chlorophenyl)thio)-1*H-*indole* (**3c**)[30]: Light yellow oil; yield 74 mg (61%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.19 (s, 1H), 7.17 (s, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.0, 136.6, 133.6, 132.99, 132.95, 131.2, 130.8, 129.9, 129.6, 129.0, 128.0, 124.4, 121.7, 120.0, 111.5, 109.7.

*2,3-Bis((4-fluorophenyl)thio)-1*H-*indole* (**3d**)[13]: Light yellow oil; yield 55 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.29–7.24 (m, 3H), 7.19–7.14 (m, 1H), 7.11–7.06 (m, 2H), 6.94 (t, *J* = 8.8 Hz, 2H), 6.85 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (d, *J* = 249.4 Hz), 161.3 (d, *J* = 245.5 Hz), 137.0, 133.9, 133.0 (d, *J* = 3.4 Hz), 132.5 (d, *J* = 8.5 Hz), 130.0, 129.2 (d, *J* = 3.5 Hz), 128.9 (d, *J* = 8.0 Hz), 124.2, 121.5, 119.9, 116.7 (d, *J* = 22.3 Hz), 115.9 (d, *J* = 22.2 Hz), 111.3, 109.6.

*2,3-Bis((3-fluorophenyl)thio)-1*H-*indole* (**3e**): Light yellow solid; yield 62 mg (56%); m.p. 97.7–101.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.34–7.29 (m, 1H), 7.24–7.20 (m, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.10 (td, *J* = 4.0, 4.0 Hz, 1H), 6.98 (dt, *J* = 1.2, 1.2 Hz, 1H), 6.88 (dd, *J* = 1.2, 1.2 Hz, 3H), 6.80–6.72 (m, 1H), 6.72–6.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.12 (d, *J* = 247.7 Hz), 163.08 (d, *J* = 249.6 Hz), 140.6 (d, *J* = 7.5 Hz), 137.1 (d, *J* = 7.6 Hz), 132.3, 130.7 (d, *J* = 8.4 Hz), 130.1 (d, *J* = 8.5 Hz), 129.9, 124.6, 124.5 (d, *J* = 3.1 Hz), 122.1 (d, *J* = 2.9 Hz), 121.8, 120.1, 115.9 (d, *J* = 23.7 Hz), 114.2 (d, *J* = 21.3 Hz), 113.4 (d, *J* = 24.0 Hz), 112.2 (d, *J* = 21.5 Hz), 111.6, 110.0. HRMS (EI) *m*/*z* calcd for $C_{20}H_{13}F_2NS_2$ [M]: 369.0457; found: 369.0444.

*2,3-Bis((4-(trifluoromethoxy)phenyl)thio)-1*H-*indole* (**3f**): Light yellow oil; yield 83 mg (55%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.32–7.27 (m, 1H), 7.24–7.17 (m, 3H), 7.06 (td, *J* = 4.4, 4.2 Hz, 4H), 6.98 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.5 (d, *J* = 2.0 Hz), 147.1 (d, *J* = 2.0 Hz), 137.0, 136.8, 133.3, 132.8, 130.8, 129.9, 127.9, 124.6, 121.97, 121.96, 121.8, 121.6, 120.1, 111.6, 110.1. HRMS (EI) *m*/*z* calcd for $C_{22}H_{13}F_6NO_2S_2$ [M]: 501.0292; found: 501.0279.

*2,3-Bis((4-(trifluoromethyl)phenyl)thio)-1*H-*indole* (**3g**): Light yellow oil; yield 66 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 3.6, 3.2 Hz, 3H), 7.37–7.33 (m, 3H), 7.24–7.17 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.1 (d, *J* = 1.5 Hz), 140.2 (d, *J* = 1.6 Hz), 137.2, 131.4, 129.8, 128.1, 126.3, 126.24, 126.2, 126.0, 125.7, 125.7, 125.65, 125.0, 122.0, 120.2, 111.8, 110.2. HRMS (EI) *m*/*z* calcd for $C_{22}H_{13}F_6NS_2$ [M]: 469.0394; found: 469.0374.

2,3-Bis((4-(t-*butyl)phenyl)thio)-1*H-*indole* (**3h**): Light yellow solid; yield 78 mg (58%); m.p. 131.5–133.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.29 (d, *J* = 2.0 Hz, 2H), 7.26 (s, 1H), 7.25–7.20 (m, 2H), 7.20–7.16 (m, 2H), 7.16–7.12 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 1.29 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 148.3, 136.9, 134.8, 130.5, 130.4, 130.3, 126.7, 126.67, 125.9, 123.6, 121.2, 120.0, 111.1, 108.6, 34.7, 34.5, 31.5, 31.4. HRMS (EI) *m*/*z* calcd for $C_{28}H_{31}NS_2$ [M]: 445.1898; found: 445.1884.

*2,3-Bis((4-methoxyphenyl)thio)-1*H-*indole* (**3i**)[31]: Light yellow solid; yield 17 mg (14%); m.p. 142.3–143.7 °C (lit.[31] m.p. 134–137 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.24 (s, 1H), 7.19 (dd, *J* = 1.2, 1.2 Hz, 1H), 7.16–7.10 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 158.1, 138.5, 136.7, 135.8, 133.9, 130.4, 130.1, 129.4, 123.3, 121.1, 119.6, 115.3, 114.6, 110.9, 55.6, 29.9.

2,3-Bis(p-*tolylthio)benzofuran* (**3j**)[32]: Colourless oil; yield 65 mg (60%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.29–7.22 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.1, 153.2, 138.1, 136.3, 131.8, 131.3, 130.2, 129.9, 129.4, 129.2, 128.6, 125.7, 123.5, 120.6, 116.5, 111.7, 21.3, 21.1.

2,3-Bis((4-methoxyphenyl)thio)benzofuran (**3k**): Light yellow oil; yield 65 mg (55%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 1.6, 1.2 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 15.2 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 158.8, 155.9, 153.4, 133.9, 131.2, 129.4, 125.8, 125.5, 123.5, 122.9, 120.4, 116.5, 115.0, 114.8, 111.6, 55.5, 55.4. HRMS (EI) *m*/*z* calcd for $C_{22}H_{18}O_3S_2$ [M]: 394.0694; found: 394.0678.

2,3-Bis((4-(t-*butyl)phenyl)thio)benzofuran* (**3l**): Light yellow oil; yield 47 mg (35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.33–7.25 (m, 4H), 7.23 (d, *J* = 4.8 Hz,

1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 1.28 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.1, 153.4, 151.2, 149.5, 132.0, 130.9, 129.5, 129.4, 128.2, 126.5, 126.2, 125.7, 123.6, 120.7, 116.7, 111.7, 34.7, 34.6, 31.4, 31.37. HRMS (EI) *m/z* calcd for $C_{28}H_{30}OS_2$ [M]: 446.1738; found: 446.1722.

*2,3-Bis(*p-*tolylthio)benzo[*b*]thiophene* (**3m**): White solid; yield 61 mg (54%); m.p. 75.3–78.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.29 (m, 1H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1, 140.6, 139.5, 139.3, 135.7, 133.3, 132.8, 130.3, 130.0, 129.9, 127.7, 125.1, 124.8, 123.03, 123.0, 122.0, 21.4, 21.1. HRMS (EI) *m/z* calcd for $C_{22}H_{18}S_3$ [M]: 378.0571; found: 378.0554.

*2,3-Bis((4-methoxyphenyl)thio)benzo[*b*]thiophene* (**3n**): White solid; yield 48 mg (39%); m.p. 127.2–127.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* =8.0 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 (m, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.8, 158.5, 148.4, 140.8, 139.1, 136.0, 130.2, 126.8, 125.1, 124.4, 123.5, 122.6, 122.2, 121.9, 115.2, 114.8, 55.5, 55.4. HRMS (EI) *m/z* calcd for $C_{22}H_{18}O_2S_3$ [M]: 410.0469; found: 410.0446.

*2,3-Bis((4-(*t*-butyl)phenyl)thio)benzo[*b*]thiophene* (**3o**): White solid; yield 116 mg (87%); m.p. 104.6–107.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 (m, 1H), 7.26 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 1.31 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 148.9, 146.9, 140.6, 139.6, 132.9, 132.8, 130.2, 127.3, 126.6, 126.2, 125.1, 124.8, 123.4, 123.1, 122.0, 34.8, 34.5, 31.41, 31.4. HRMS (EI) *m/z* calcd for $C_{28}H_{30}S_3$ [M]: 462.1510; found: 462.1515.

*2,3-Bis((4-fluorophenyl)thio)benzo[*b*]thiophene* (**3p**): White solid; yield 60 mg (52%); m.p. 75.8–78.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.70 (m, 1H), 7.66 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.50 (dd, *J* = 5.2, 5.2 Hz, 2H), 7.35–7.27 (m, 2H), 7.12 (dd, *J* = 5.2, 5.2 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.89 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 162.8, 162.1, 160.3, 146.3, 140.3, 139.5, 135.33, 135.3, 131.22, 131.2, 129.7, 129.6, 128.7, 128.6, 125.4, 125.2, 123.7, 123.0, 122.2, 116.9, 116.7, 116.4, 116.2. HRMS (EI) *m/z* calcd for $C_{20}H_{12}F_2S_3$ [M]: 386.0069; found: 386.0054.

*1,2-Di-*p-*tolyldisulfane* (**3aa**)[33]: White solid; yield 24 mg (33%); m.p. 39–40 °C (lit.[33] m.p. 39–40 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 2.32 (s, 6H).

S-*(*p-*tolyl)-4-methylbenzenesulfonothioate* (**3ab**)[34]: White solid; yield 52 mg (62%); m.p. 76.0–76.8 °C (lit.[34] m.p. 76.7–77.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).

S-*(4-methoxyphenyl)-4-methylbenzenesulfonothioate* (**3ac**)[34]: White solid; yield 53 mg (60%); m.p. 126.5–127.2 °C (lit.[34] m.p. 127.2–128.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H).

*1-Methyl-2,3-bis(*p-*tolylthio)-1*H-*indole* (**5a**): White solid; yield 79 mg (70%); m.p. 97.3–99.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.22–7.18 (m, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.66 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.5, 136.3, 135.0, 134.9, 134.8, 132.3, 130.0, 129.5, 129.3, 128.0, 127.1, 123.9, 121.0, 120.5, 111.5, 110.2, 31.2, 21.1, 21.0. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}NS_2^+$ [M + H]$^+$: 376.11882; found: 376.11850.

*2-Methyl-3-(*p-*tolylthio)-1*H-*indole* (**5b**)[31]: White solid; yield 30 mg (39%); m.p. 98.7–96.9 °C (lit.[31] m.p. 94–96 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 (td, *J* = 8.0, 7.6, 1.2 Hz, 1H), 7.13–7.08 (m, 1H), 6.95 (s, 4H), 2.49 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.0, 135.8, 135.5, 134.4, 130.5, 129.6, 125.9, 122.2, 120.8, 119.1, 110.7, 100.0, 21.0, 12.3.

*3-Methyl-2-(*p-*tolylthio)-1H-indole* (**5c**)[35]: White solid; yield 18 mg (24%); m.p. 100.1–100.6 °C (lit.[35] m.p. 93–95 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.29–7.21 (m, 2H), 7.15–7.11 (m, 1H), 7.05–6.97 (m, 4H), 2.40 (d, *J* = 6.8 Hz, 3H), 2.27 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 135.9, 133.4, 130.0, 128.6, 127.2, 123.5, 122.4, 119.7, 119.5, 119.4, 110.9, 21.0, 9.6.

*7-Nitro-3-(*p-*tolylthio)-1H-indole* (**5d**): Yellow solid; yield 70 mg (82%); m.p. 177.2–179.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.6, 134.3, 133.6, 132.7, 132.5, 130.1, 129.8, 128.0, 127.0, 120.4, 120.3, 106.6, 21.0. HRMS (EI) *m/z* calcd for $C_{15}H_{12}N_2O_2S$ [M]: 284.0619; found: 284.0609.

*5-Nitro-3-(*p-*tolylthio)-1*H-*indole* (**5e**)[31]: Yellow solid; yield 50 mg (59%); m.p. 169.6–171.2 °C (lit.[31] m.p. 204–207 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.57 (d, *J* = 2.0 Hz, 1H), 8.16 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 135.4, 134.0, 129.8, 128.3, 127.2, 122.7, 118.2, 116.7, 104.5, 103.2, 21.1.

*3-(*p-*Tolylthio)-1*H-*indole-7-carbonitrile* (**5f**): White solid; yield 33 mg (41%); m.p. 175.5–178.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 7.68–7.62 (m, 2H), 7.52 (dd, *J* = 0.8, 0.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 135.4, 135.4, 133.9, 129.8, 128.6, 128.3, 127.3, 122.7, 118.1, 116.6, 104.7, 103.3, 21.1. HRMS (EI) *m/z* calcd for $C_{16}H_{12}N_2S$ [M]: 264.0721; found: 264.0710.

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