Synthesis A. Rostami et al. Paper

Copper-Catalyzed C–S Bond Formation via the Cleavage of C–O Bonds in the Presence of S_8 as the Sulfur Source

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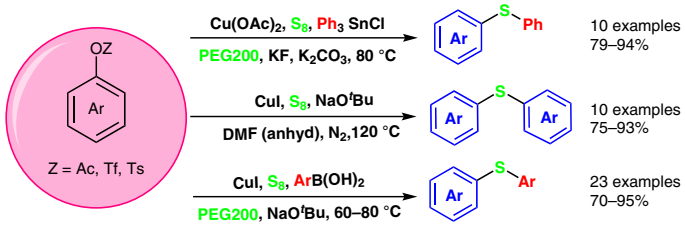

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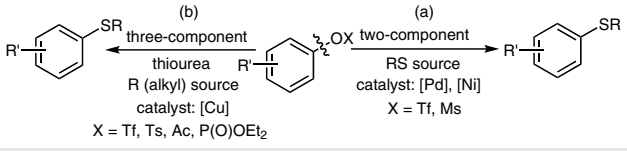
Abstract Useful and applicable methods for one-pot and odorless synthesis of unsymmetrical and symmetrical diaryl sulfides via C–O bond activation are presented. First, a new efficient procedure for the synthesis of unsymmetrical sulfides using the cross-coupling reaction of phenolic esters such as acetates, tosylates, and triflates and with arylboronic acid or triphenyltin chloride as the coupling partners is reported. Depending on the reaction, S_8/KF or S_8/NaO*t*-Bu system is found to be an effective source of sulfur in the presence of copper salts and in poly(ethylene glycol) as a green solvent. Then, the synthesis of symmetrical diaryl sulfides from phenolic compounds by using S_8 as the sulfur source and NaO*t*-Bu in anhydrous DMF at 120 °C under N_2 is described. By these protocols, the synthesis of a variety of unsymmetrical and symmetrical sulfides become easier than the available protocols in which thiols and aryl halides are directly used for the preparation of the sulfides.

Key words phenolic esters, arylboronic acid, triphenyltin chloride, copper salt, catalyst, sulfides

Carbon–oxygen bond activation reactions leading to the functionalized aromatic compounds is one of the most important reactions in organic chemistry.[1] Activation of phenolic C–O bonds have significant synthetic values due to the wide commercial availability of phenol derivatives. Since the hydroxyl group attached to the aromatic ring is almost inert toward displacement reactions, its activation is necessary by conversion into esters, phosphonates, triflates, tosylates, heteroaryl ethers, etc.[2] These phenol derivatives are suitable alternatives to aryl halides as the coupling partner in the cross coupling reactions for the construction of carbon–heteroatom bonds.[3] Among these, carbon–sulfur bond formation reaction is of high importance in organic and medicinal chemistry.[4] Nevertheless, the studies on these kinds of reactions are limited because thiols, which are usually used as starting materials in these reactions are susceptible to oxidation producing disulfides as by-products. In addition, thiols can bind to metals acting as a metal poison.[5]

Two strategies are usually employed for the C–O bond activation followed by C–S bond formation. Activated oxygen can be replaced by an organosulfur nucleophile via two-component or three-component reactions (Scheme 1).[6]



Scheme 1 Two approaches for the construction of C–S bond via C–O bond activation

To date, the most intriguing procedure for thioetherification of aromatic compounds is the in situ generation of thiols or thiolates by the aid of various sulfur sources including thiourea, sodium thiosulfate, sulfur powder, and so on.[7–14] Recently, sulfur powder has been used for S-arylation due to its low cost and its characteristics of being both odorless and environmentally benign. Chen et al. studied the effect of different bases in the synthesis of asymmetrical diaryl disulfides by reacting aryl halides with sulfur power in the presence of a Cu salt.[13f] The reaction of pentafluorobenzene derivatives with S_8 resulted the formation of symmetric diaryl sulfides in the presence of $RhH(PPh_3)_4$ as the catalyst.[14i] A copper-mediated C–S/N–S bond-forming reaction via C–H activation that uses elemental sulfur has been reported.[14j] Very recently, oxidative sulfenylation of electron-rich heteroarenes and annulation/arylthiolation reaction to afford functionalized 3-sulfenylbenzofuran with arylboronic and S_8 in the presence of palladium as catalyst has been developed by Wu and co-workers.[14k,l] The synthe-

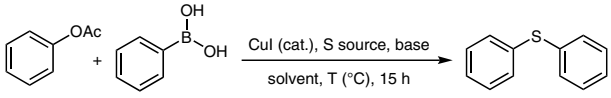
sis of thioarylated imidazoheterocycles from aryl halides and elemental sulfur catalyzed by CuI has also been developed.[14m]

Lately, we have reported an odorless method for the synthesis of unsymmetrical sulfides using the reaction of arylboronic acid/S_8 system as a thiolating agent with aryl/alkyl halides,[15a] and also we have released three protocols for the denitrative thioetherification of different nitroarenes via C–N bond activation.[15b] Very recently, the synthesis of symmetrical and unsymmetrical aryl sulfides by the reaction of triphenyltin chloride and aryl halides with S_8 in poly(ethylene glycol) is described.[15c] The C–S bond formation reactions using arylboronic acids as the coupling partners for the copper-catalyzed synthesis of unsymmetrical sulfides via cleavage of their C–B bonds is available in the literature.[15,16] In order to expand these methods, we became interested in studying the possibility for the C–S bond formation of phenolic esters via thiol-free process by activating the C–O bond. To the best of our knowledge, the utilization of non-thiolic procedures for the synthesis unsymmetrical diaryl sulfides by the reaction of phenolic esters with arylboronic acid or triphenyltin chloride and also the synthesis of symmetrical sulfides by using phenolic esters have not been reported.

In order to optimize the reaction conditions, the reaction of phenyl acetate with phenylboronic acid was selected as the benchmark in the presence of S_8 and CuI in poly(ethylene glycol) (PEG 200) (Table 1). Initially, the reaction was performed in the presence of NaOH at 60 °C (Table 1, entry 1). Under these conditions, the reaction failed to produce the desired products and phenyl acetate just got converted into phenol. Changing the base to K_2CO_3 was not effective for the reaction (entry 2). Only 14% GC yield was observed with Cs_2CO_3 as the base in this reaction (entry 3). No product was obtained by using Et_3N and DABCO as the organic bases (entries 4, 5). The GC yield of the desired product was remarkably improved by switching the base to NaO*t*-Bu (entry 6). By increasing the reaction temperature to 80 °C, the complete conversion of phenyl acetate into the desired product was observed (entry 7). In order to study the effect of the solvents, the reaction was conducted in other solvents; DMF, MeCN, and 1,4-dioxane (entries 8–10). The results showed that the most effective solvent was PEG200 (entry 7). Apart from S_8, other sulfur sources such as $Na_2S_2O_3{\cdot}5H_2O$, thiourea, and Na_2S were also tested.

Among the sulfur sources studied, $Na_2S_2O_3{\cdot}5H_2O$ and thiourea failed to react (Table 1, entries 11, 12), whereas Na_2S gave the desired product in 64% GC yield (entry 13). Utilizing thiophenol instead of phenylboronic acid/S_8 system resulted in only 58% conversion of phenyl acetate (entry 14). The amount of S_8, NaO*t*-Bu and the catalyst were also optimized (entries 15–17). The reaction failed in the absence of the catalyst (entry 18). Under the optimized conditions (entry 7), the coupling reaction of various phenolic esters (ArOAc, ArOTf, ArOTs) with arylboronic acids was studied (Table 2). As shown in Table 2, the expected products were obtained in moderate to high yields irrespective to the position of substituents on phenolic esters (Table 2, entries 2–15). It has been shown that phenolic esters with electron-withdrawing groups reacted faster than the phenolic esters having electron-releasing groups (entries 2–15). Likewise, arylboronic acids containing electron-donating groups showed less reactivity. Among phenolic ester derivatives, the most reactive were found to be aryl triflates. Interestingly, aryl acetates which are relatively unreactive substrates got converted into the corresponding unsymmetrical sulfides in high to excelent yields under the same reaction conditions (Table 2). Another important aspect of this method is the successful reaction of sterically hindered substrates to give the desired products in high yields (Table 2, entries 9, 16, 17). *Ortho*-substituted phenolic esters require longer reaction times giving relatively

Table 1 Optimization of the Reaction Conditions for the Reaction of Phenyl Acetate with Phenylboronic Acid[a]



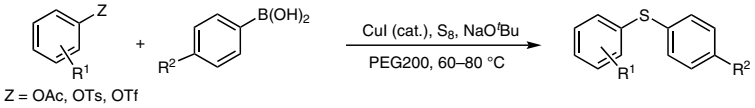
Entry	S source	Base	Solvent	Temp (°C)	GC Yield (%)
1	S_8	NaOH	PEG200	60	–
2	S_8	K_2CO_3	PEG200	60	–
3	S_8	Cs_2CO_3	PEG200	60	14
4	S_8	Et_3N	PEG200	60	–
5	S_8	DABCO	PEG200	60	–
6	S_8	NaO*t*-Bu	PEG200	60	74
7[b]	**S_8**	**NaO*t*-Bu**	**PEG200**	**80**	**100**
8	S_8	NaO*t*-Bu	DMF	80	91
9	S_8	NaO*t*-Bu	MeCN	80	64
10	S_8	NaO*t*-Bu	1,4-dioxane	80	34
11	thiourea	NaO*t*-Bu	PEG200	80	–
12	$Na_2S_2O_3{\cdot}5H_2O$	NaO*t*-Bu	PEG200	80	–
13	Na_2S	NaO*t*-Bu	PEG200	80	64
14	PhSH	NaO*t*-Bu	PEG200	80	58
15[c]	S_8	NaO*t*-Bu	PEG200	80	79
16[d]	S_8	NaO*t*-Bu	PEG200	80	82
17[e]	S_8	NaO*t*-Bu	PEG200	80	74
18	S_8	NaO*t*-Bu	PEG200	80	–

[a] Reaction conditions: phenyl acetate (1 mmol), phenylboronic acid (1.1 mmol), sulfur (1.5 mmol), CuI (15 mol%), base (4 mmol), and solvent (2 mL).
[b] Most effective reaction conditions.
[c] S_8 (1 mmol).
[d] NaO*t*-Bu (3 mmol).
[e] CuI (10 mmol).

lower yields than *para*-substituted phenolic esters (entries 7–9). The reaction of 2-pyridyl esters (acetates, tosylates, and triflates) as a heteroaromatic compound with arylboronic acids gave the products in excellent yields (entries 21, 22).

Based on these observations and also previously reported results,[15] the plausible mechanism for the reaction of arylboronic acids with phenolic esters in the presence of S_8 is presented in Scheme 2. It is hypothesized that S_8 reacts with NaO*t*-Bu to produce sodium disulfide.[13f] Then, stable copper disulfide is formed from the reaction of sodium disulfide with CuI. In the next step, copper disulfide reacts with arylboronic acid via oxidative addition reaction to give intermediate **I**, which gets converted into intermediate **II**, subsequently.[13g] Intermediate **II** reacts with phenolic esters via C–O bond cleavage to provide the key intermediate **III**. The desired product may result from reductive elimination of the key intermediate **III**.

Table 2 C–S Bond Formation of Phenolic Esters with Arylboronic Acids Using S_8 Catalyzed by CuI[a]



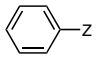
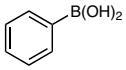
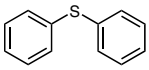
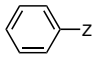
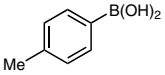
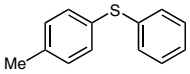
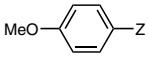
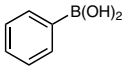
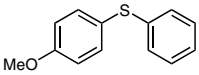
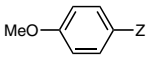
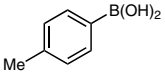
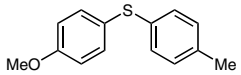
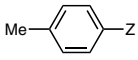
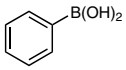
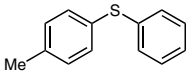
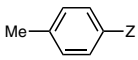
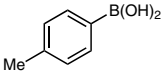
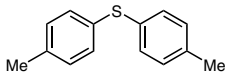
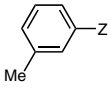
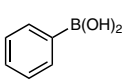
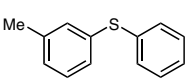
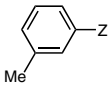
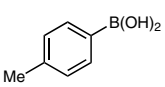
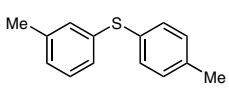
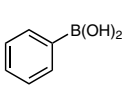
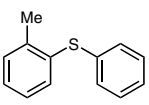
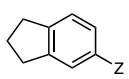
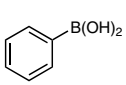
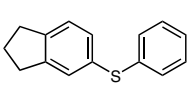
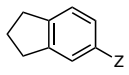
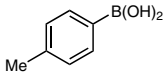
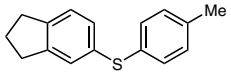
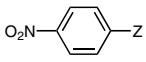
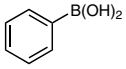
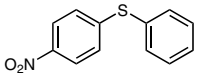
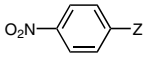
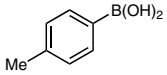
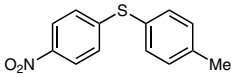
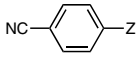
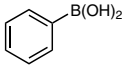
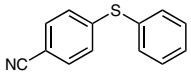
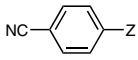
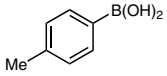
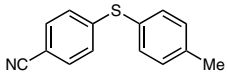
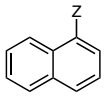
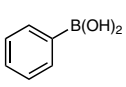
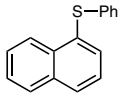
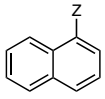
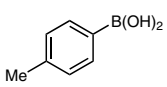
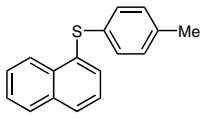
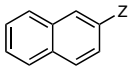
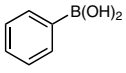
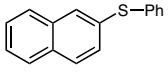
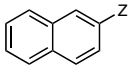
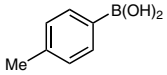
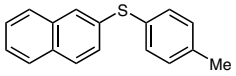
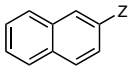
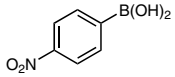
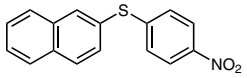
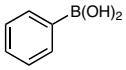
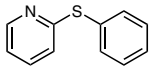
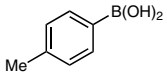
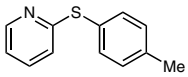
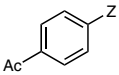
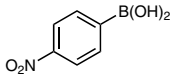
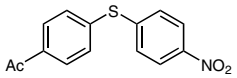
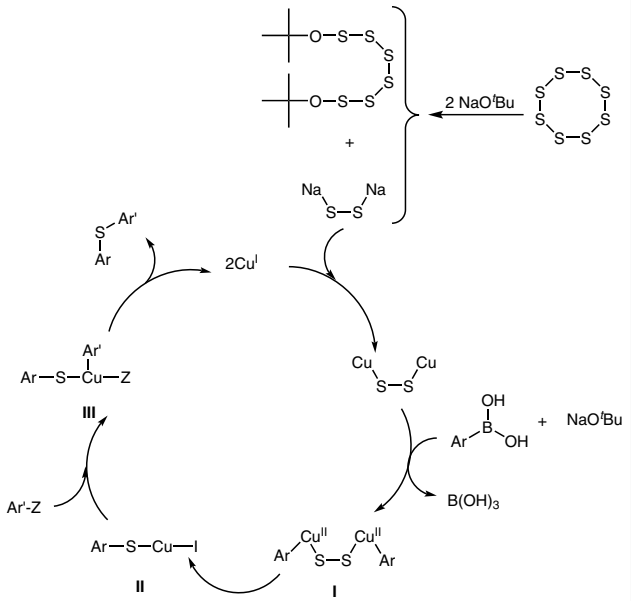
Entry	ArZ	$ArB(OH)_2$	Product	Z = OAc		Z = OTs		Z = OTf	
				Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
1				15	92	9	81	7	84
2				17	93	11	79	9	80
3				24	90	18	80	16	86
4				30	87	21	78	19	82
5				22	92	16	80	13	88
6				25	89	19	77	16	80
7				20	95	15	81	11	89
8				23	91	17	76	14	85
9				26	89	20	74	17	80
10				24	80	20	82	15	79

Table 2 (continued)

Entry	ArZ	$ArB(OH)_2$	Product	Z = OAc		Z = OTs		Z = OTf	
				Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
11				24	80	22	81	17	78
12				9	95	4	84	2	89
13				11	92	5	81	3	84
14				10	90	6	80	4	88
15				13	89	7	79	5	83
16				18	85	12	74	9	80
17				21	93	14	81	11	86
18				17	95	10	85	7	90
19				19	91	13	80	10	86
20				12	91	7	82	5	86
21				12	88	7	70	5	78
22				13	90	8	78	5	80
23				10	89	6	88	3	84

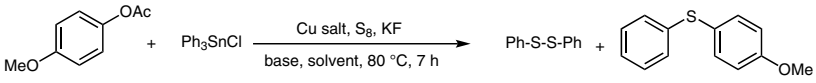
[a] Reaction conditions: phenolic ester (1 mmol), arylboronic acid (1.1 mmol), CuI (15 mol %), sulfur (1.5 mmol), NaO*t*-Bu (4 mmol), PEG200 (2 mL), 60–80 °C.
[b] Isolated yield after column chromatography.



Scheme 2 Proposed mechanism for C–S bond formation using the reaction of arylboronic acid with phenolic esters in the presence of S_8 catalyzed by CuI

In continuation of our studies for the C–S bond formation of phenolic esters by activating the C–O bond, we have investigated the possibility of the synthesis of phenyl aryl sulfides using triphenyltin chloride as phenyl source in the presence of S_8 and a catalytic amount of a copper salt. For this aim, the reaction between *p*-methoxyphenyl acetate and triphenyltin chloride in the presence S_8 was selected as a model reaction. Inspired by the preceding results,[15c] we first conducted the reaction in the presence of $Cu(OAc)_2$, S_8/KF, and K_2CO_3 in PEG200 at 60 °C. Under these conditions, the desired product was obtained in 81% yield (Table 3, entry 1). By increasing the reaction temperature to 80 °C, the complete conversion of *p*-methoxyphenyl acetate into the product was observed (entry 2). As shown in Table 3, the nature of the base was important affecting the yield of the desired product (entries 1–5). Among the organic and inorganic bases, K_2CO_3 was found to be the most effective base for this reaction (entry 2). It was also observed when Et_3N was used as a base in the reaction, diphenyl disulfide was found as the only product (entry 5). In order to study the effect of the solvents, we have conducted the reaction in PEG200, DMF, 1,4-dioxane, and MeCN (entries 2 and 6–8). Among these solvents, the most effective was found to be PEG200 (entry 2). Apart from $Cu(OAc)_2$, CuI and $CuCl_2$ were also active catalysts for the synthesis of desired product in high yields (entries 9 and 10). In the absence of KF, no product was observed (entry 14). Only 55% of diphenyl sulfide was obtained when triphenyltin chloride was replaced with diphenyl disulfide (entry 15). Diphenyl disulfide was produced in the absence of *p*-methoxyphenyl acetate (entry 16). When CuS was used instead of KF/S_8/$Cu(OAc)_2$, longer time is required to complete the reaction (entry 17).

Table 3 Optimization of the Reaction Conditions with Respect to the Effect of Catalysts, Solvent, and Base on the Reaction of *p*-Methoxyphenyl Acetate with Triphenyltin Chloride[a]



Entry	Cu salt	Base	Solvent	GC yield (%) of **a**	GC yield (%) of **b**
1[b]	$Cu(OAc)_2$	K_2CO_3	PEG200	–	81
2[c]	**$Cu(OAc)_2$**	**K_2CO_3**	**PEG200**	**–**	**100**
3	$Cu(OAc)_2$	Cs_2CO_3	PEG200	36	64
4	$Cu(OAc)_2$	NaO*t*-Bu	PEG200	33	67
5	$Cu(OAc)_2$	Et_3N	PEG200	100	–
6	$Cu(OAc)_2$	K_2CO_3	DMF	–	91
7	$Cu(OAc)_2$	K_2CO_3	1,4-dioxane	–	74
8	$Cu(OAc)_2$	K_2CO_3	MeCN	–	63
9	CuI	K_2CO_3	PEG200	–	81
10	$CuCl_2$	K_2CO_3	PEG200	–	94
11[d]	$Cu(OAc)_2$	K_2CO_3	PEG200	–	74
12[e]	$Cu(OAc)_2$	K_2CO_3	PEG200	–	75
13[f]	$Cu(OAc)_2$	K_2CO_3	PEG200	–	88
14[g]	$Cu(OAc)_2$	K_2CO_3	PEG200	–	–

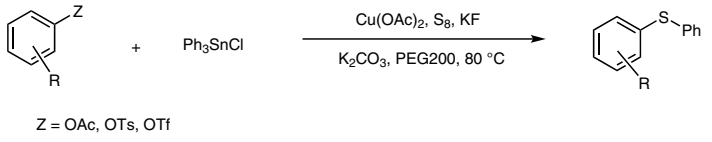
Table 3 (continued)

Entry	Cu salt	Base	Solvent	GC yield (%) of **a**	GC yield (%) of **b**
15[h]	$Cu(OAc)_2$	K_2CO_3	PEG200	45	55
16[i]	$Cu(OAc)_2$	K_2CO_3	PEG200	100	–
17[j]	CuS	K_2CO_3	PEG200	–	100

[a] Reactions conditions: *p*-methoxyphenyl acetate (1 mmol), triphenyltin chloride (0.35 mmol), sulfur (1.5 mmol), Cu salt (15 mol%), KF (3 mmol), base (3 mmol), solvent (1.5 mL), 80 °C.
[b] The reaction was performed at 60 °C.
[c] Most effective reaction conditions.
[d] $Cu(OAc)_2$ (10 mol%) was employed.
[e] KF (2.5 mmol) was used.
[f] Sulfur (1 mmol) was employed.
[g] Without KF.
[h] The reaction was performed using diphenyl disulfide instead of Ph_3SnCl for 48 h.
[i] In the absence of *p*-methoxyphenyl acetate.
[j] The reaction was performed in the absence of KF and S_8 for 13 h.

In order to generalize the scope of the reaction, a series of structurally diverse phenolic ester was subjected to reaction with triphenyltin chloride under the optimized reaction conditions in PEG200 as the solvent. The reactions proceeded well to produce the corresponding phenyl aryl sulfides in moderate to excellent yields ranging from 79 to 94% (Table 4). It was observed that phenolic esters with electron-withdrawing groups show greater activity than those having electron-donating groups (Table 4, entries 2–7). Another important aspect of this method is the successful reaction of sterically demanding substrates to give the desired products in good yields (entry 5). We have also applied this method to the reaction of 2-pyridyl esters (acetates, triflates, and tosylates) with triphenyltin chloride as heteroaromatic compounds (entry 10).

Table 4 C–S Bond Formation of Phenolic Esters with Ph_3SnCl Using S_8 Catalyzed by $Cu(OAc)_2$[a]



Z = OAc, OTs, OTf

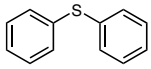
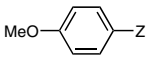
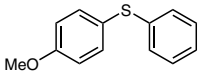
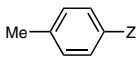
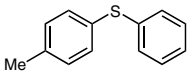
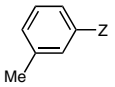
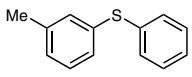
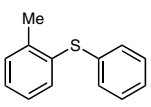
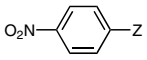
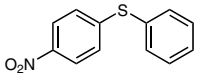
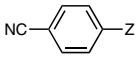
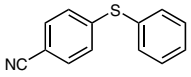
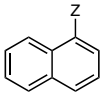
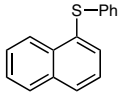
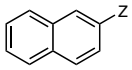
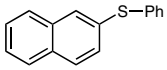
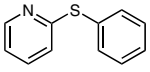
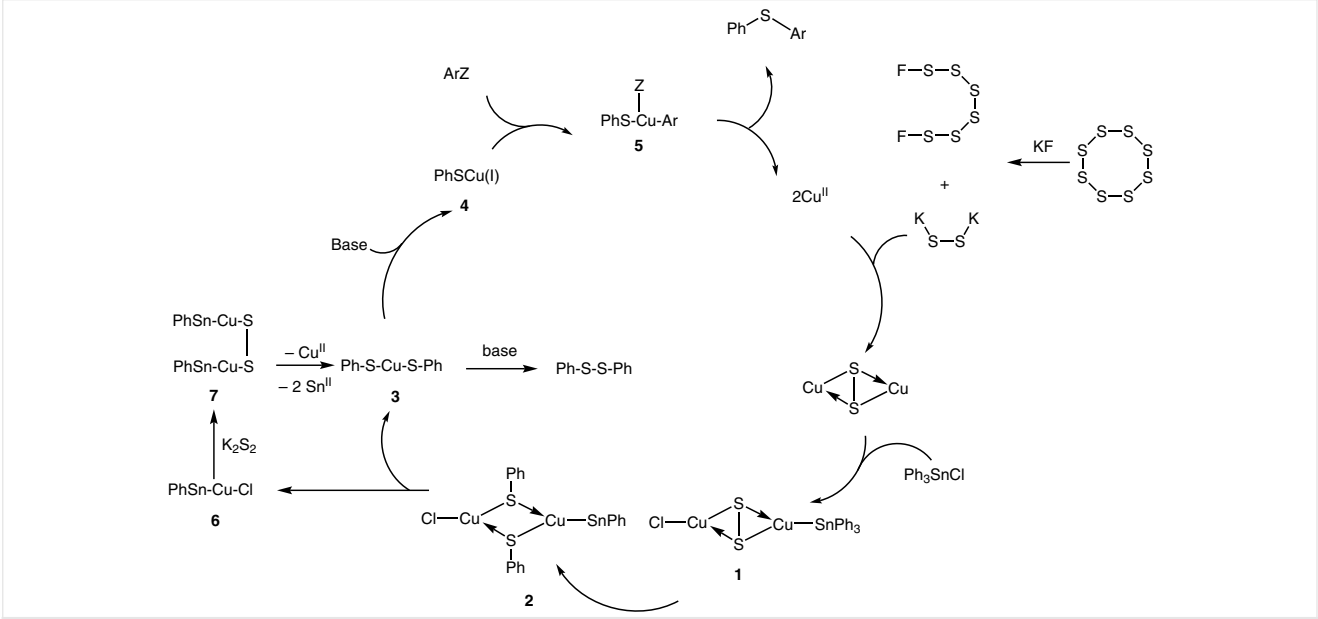
Entry	ArZ	Product	Z = OAc		Z = OTs		Z = OTf	
			Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
1			7	93	3	88	2	86
2			15	90	10	83	8	89
3			12	89	7	81	5	80
4			11	94	8	80	6	86
5			15	87	9	79	7	80

Table 4 (continued)

Entry	ArZ	Product	Z = OAc		Z = OTs		Z = OTf	
			Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
6			2	92	0.5	88	0.1	94
7			3.5	92	1	86	0.5	88
8			11	90	6	83	4	81
9			8	90	7	80	5	81
10			5	91	2	80	1	80

[a] Reaction conditions: phenolic ester (1 mmol), triphenyltin chloride (0.35 mmol), sulfur (1.5 mmol), $Cu(OAc)_2$ (15 mol%), KF (3 mmol), K_2CO_3 (3 mmol), PEG200 (1.5 mL).
[b] Isolated yield after column chromatographic separation.

Based on our observations (Table 3, entries 5 and 14–17) and the previously reported mechanism for C–S bond formation reactions in the presence of S_8 as a sulfur source[13f,g] and Ph_3SnCl as a phenyl source,[15] the proposed mechanism for the reaction of triphenyltin chloride with phenolic esters in the presence of S_8 is depicted in Scheme 3. Potassium disulfide, produced from the reaction of S_8 with KF, reacts with $Cu(OAc)_2$ to generate Cu_2S_2. Triphenyltin chloride reacts with copper sulfide by oxidative addition and subsequent phenyl group immigration to form in-



Scheme 3 Proposed pathway for the synthesis of phenyl aryl sulfides via C–S bond formation reaction of phenolic ester with triphenyltin chloride using S_8 in the presence of $Cu(OAc)_2$ as a catalyst

termediate **2**. Dissociation of the intermediate **2** generates two intermediates **3** and **6**. The employed base might play an effective role upon intermediate **3**. In the presence of K_2CO_3, intermediate **3** converts into intermediate **4** and then reacts with phenolic esters by oxidative addition to form **5**. Reductive elimination affords the diaryl sulfide to complete the catalytic cycle. The intermediate **3** can also produce diphenyl disulfide when Et_3N was used instead of K_2CO_3. We observed that in the absence of phenolic esters, triphenyltin chloride produces diphenyl disulfide in quantitative yield under similar reaction conditions within 24 hours.

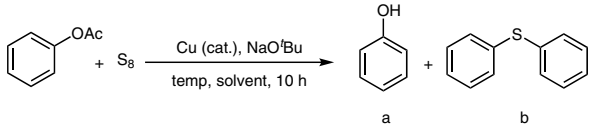
It is very likely that in the absence of phenolic esters, intermediate **4** reverses back to intermediate **3** resulting in diphenyl disulfide. The intermediate **6** reacts with potassium sulfide to give intermediate **7**, which is capable of transferring to intermediate **3**. When Et_3N is used instead of K_2CO_3, intermediate **3** yields diphenyl disulfide exclusively (Table 3, entry 5).

In another effort, we studied the homocoupling reaction of phenolic esters in the presence of S_8 to produce symmetrical diaryl sulfides. To optimize the reaction conditions, phenyl acetate was employed as the starting material (Table 5). Encouraged by the above results, we have performed the reaction in the presence of CuI, S_8, and NaO*t*-Bu in PEG200 at 80 °C. Under these conditions, the reaction failed to give the required product (Table 5, entry 1). By increasing the reaction temperature to 100 °C, the complete conversion of phenyl acetate into the phenol was observed (entry 2). Using DMF as a solvent led to 11% conversion into the desired product along with phenol (89%) (entry 3). The GC yield was increased to 46% by increasing the temperature to 120 °C (entry 4). The complete conversion of phenyl acetate into the desired product was achieved using anhydrous DMF as the solvent under an inert atmosphere within 10 hours (entries 5, 6). In order to expand our studies to show the effect of the different solvents, the reaction was conducted in toluene, MeCN, and also under solvent-free conditions (entries 7–9). The results showed that, again, complete conversion into the desired product was achieved under solvent-free conditions in the presence of Bu_4NBr within 13 hours (entry 9). Using $Cu(OAc)_2$ and $CuCl_2$ instead of CuI lower yields were obtained (entries 10, 11).

With the optimal conditions in hand, DMF as the solvent, CuI as the catalyst at 120 °C (Table 5, entry 6), the generality and the applicability of this method was further examined for the synthesis of symmetrical sulfides from the reaction of phenolic esters with S_8.

As shown in Table 6, the expected products were obtained in high to excellent yields. Generally, phenolic esters with electron-withdrawing groups showed much more reactivity than those having electron-donating groups (Table 6, entries 2–7). Interestingly, *o*-methylphenolic ester as the

Table 5 Optimization of the Reaction Conditions for the Conversion of Phenyl Acetate into Diphenyl Sulfide Using S_8[a]



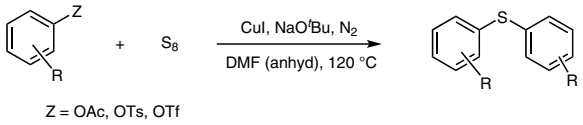
Entry	Cu salt	Solvent	Temp (°C)	GC yield (%) of **a**	GC yield (%) of **b**
1	CuI	PEG200	80	–	–
2	CuI	PEG200	100	100	–
3	CuI	DMF	100	89	11
4	CuI	DMF	120	56	46
5	CuI	DMF (anhyd)	120	13	**87**
6[b,c]	**CuI**	**DMF (anhyd)**	**120**	**–**	**100**
7[b]	CuI	MeCN (anhyd)	120	–	64
8[b]	CuI	toluene (anhyd)	120	–	43
9[b,d]	**CuI**	**Solvent-free**	**120**	**–**	**100**
10[b]	$Cu(OAc)_2$	DMF (anhyd)	120	–	93
11[b]	$CuCl_2$	DMF (anhyd)	120	–	88
12[b,e]	CuI	DMF (anhyd)	120	–	100
13[b,f]	CuI	DMF (anhyd)	120	–	79
14[b,g]	CuI	DMF (anhyd)	120	–	82

[a] Reaction conditions: phenyl acetate (1 mmol), sulfur (0.5 mmol), CuI (5 mol%), base (4 mmol), and solvent (2 mL).
[b] The reaction was performed under an inert atmosphere.
[c] Most effective reaction conditions.
[d] The reaction was carried out in the presence of Bu_4NBr (1 mmol) for 13 h.
[e] S_8 (1 mmol).
[f] NaO*t*-Bu (3 mmol).
[g] CuI (2.5 mmol%).

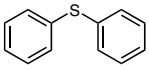
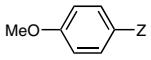
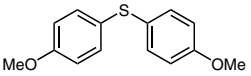
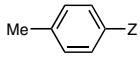
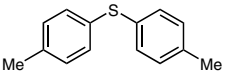
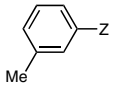
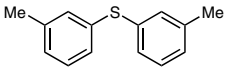
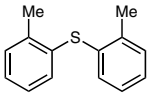
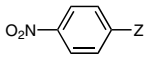
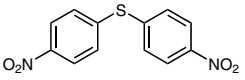
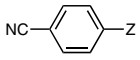
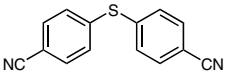
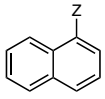
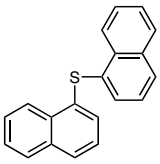
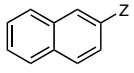
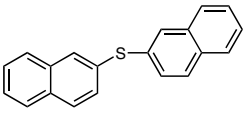
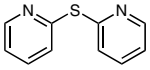
model for the hindered phenolic esters was also converted into the desired products in high yields (entry 5). We have also applied this method to the reaction of 2-pyridyl acetate, tosylate, and triflate with S_8 giving 92, 76, and 87% yield, respectively (entry 10).

A mechanism for this reaction is proposed on the basis of our observations (Table 5, entries 6–9) and previously reported mechanism.[13f] We believe that the synthesis of symmetrical diaryl sulfides proceeds through a mechanism similar to that suggested for the synthesis unsymmetrical sulfides. As shown in Scheme 4, S_8 reacts with NaO*t*-Bu to produce sodium disulfide.[13f,15b] Then, the produced copper disulfide from the reaction of sodium disulfide and CuI, reacts with phenolic ester via C–O bond cleavage followed by oxidative addition to give intermediate **A**, which may convert into intermediate **B** through aryl group migration. Intermediate **B** can be converted into intermediate **C** with NaO*t*-Bu and DMF.[15] Then, with the addition of other phenolic compound the desired product is released after reductive elimination completing the catalytic cycle.

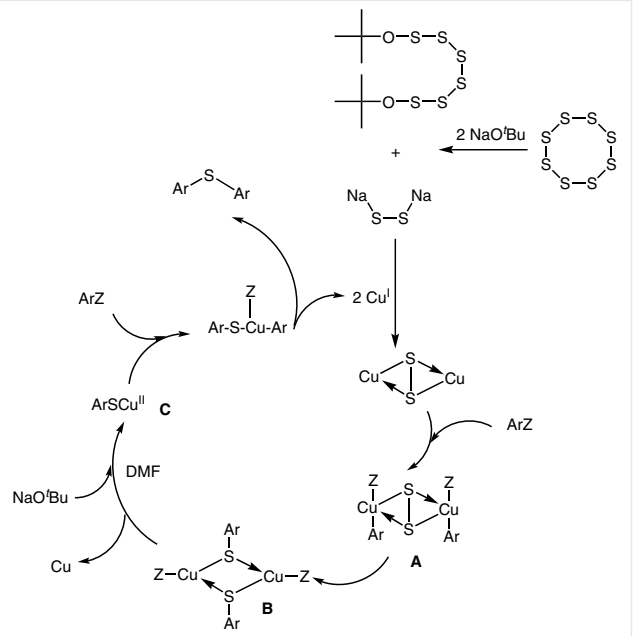
Table 6 Reaction of Various Phenolic Esters with S_8 for the Synthesis of Symmetrical Diaryl Sulfides[a]



Z = OAc, OTs, OTf

Entry	ArZ	Product	Z = OAc		Z = OTs		Z = OTf	
			Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
1			10	90	5	84	3	87
2			18	89	11	80	9	86
3			15	88	8	79	6	83
4			14	93	7	79	5	85
5			18	86	12	76	9	83
6			5	90	1	83	0.3	90
7			6.5	91	2	81	1	88
8			13	90	8	80	6	86
9			11	92	9	83	8	89
10			7	92	3	75	2	87

[a] Reaction conditions: phenolic ester (1 mmol), NaO^{t}Bu (4 mmol), sulfur (0.5 mmol), CuI (5 mol%), anhyd DMF (2 mL), 120 °C.
[b] Isolated yield after column chromatographic separation.



Scheme 4 Proposed mechanism for the synthesis of symmetrical diaryl sulfides using phenolic esters in the presence of S_8 and CuI catalyst

In summary, we have developed new and efficient methodologies for the synthesis of unsymmetrical diaryl sulfides by the reaction of arylboronic acid and triphenyltin chloride as thiolating agents with phenolic ester compounds as the effective and available starting materials in the presence of S_8 and copper salts as the catalyst via C–O bond activation. Also, the synthesis of symmetrical diaryl sulfides was performed through homocoupling reaction of phenolic ester compounds in the presence of S_8 as a sulfur surrogate and CuI as a catalyst. Important features of these procedures are as follows: (1) avoidance of unclean-smelling thiols and aryl halides, which makes the methods more easy and practical; (2) use of commercially accessible, cheap, easy-to-handle and chemically stable starting materials, sulfur source, and catalyst; and (3) the ability to prepare structurally diverse unsymmetrical and symmetrical diaryl sulfides.

^{1}H NMR spectra were recorded at 400 MHz and ^{13}CNMR were recorded at 100 MHz in $CDCl_3$ using TMS as internal standard. The reaction monitoring was carried out by silica gel analytical sheets or by GC analysis using a 3 m length column packed with DC-200 stationary phase. Tosylates, triflates, and aryl acetates as phenolic compounds were prepared in our laboratory as described in the following sections.

Phenyl Acetate; Typical Procedure

Ac_2O (0.6 mL, 6 mmol) was added to a mixture of phenol (0.47 g, 5 mmol), and K_2CO_3 (1.35 g, 10 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred for 24 h at r.t. The resulting mixture was washed several times with H_2O. The organic phase was dried (anhyd Na_2SO_4) and then evaporated under reduced pressure. Pure phenyl acetate was obtained in 95% yield (120 mg) after column chromatography.

1-Naphthyl 4-Methylbenzenesulfonate; Typical Procedure

4-Toluenesulfonyl chloride (2.85 g, 15 mmol) was added to a mixture of 1-naphthol (1.4 g, 10 mmol) and Et_3N (2.8 mL, 20 mmol) in CH_2Cl_2 (50 mL) and the resulting mixture was stirred at r.t. for 24 h. To the resulting mixture was added H_2O (30 mL) and the CH_2Cl_2 layer was separated and dried (anhyd Na_2SO_4). Evaporation of the solvent gave the desired crude product. Purification of the product was performed by crystallization from EtOH to give the pure 1-naphthyl tosylate in 85% yield (253 mg).

Phenyl Trifluoromethanesulfonate; Typical Procedure

A mixture of phenol (0.45 g, 5 mmol), trifluoromethanesulfonyl chloride (0.8 mL, 7.5 mmol) and Et_3N (1.4 mL, 10 mmol) in THF (30 mL) was stirred at 0 °C for 24 h. The solvent was evaporated and to the resulting residue were added H_2O (20 mL) and EtOAc (20 mL). The organic phase was decanted and dried (anhyd Na_2SO_4). Evaporation of the solvent and purification by column chromatography on silica gel (hexane/EtOAc, 4:1) gave the pure triflate in 85% yield (191 mg).

Unsymmetrical Diaryl Sulfides from Arylboronic Acid and Phenolic Esters; General Procedure

A one-necked flask was charged with CuI (30 mg, 0.15 mmol), NaO*t*-Bu (376 mg, 4.0 mmol), S_8 (47 mg, 1.5 mmol), phenolic ester (1 mmol), arylboronic acid (1.1 mmol), and PEG200 (2 mL). The mixture was magnetically stirred and heated at 60–80 °C for the appropriate reaction time (Table 2). After completion of the reaction, the reaction mixture was cooled to r.t. H_2O (4 mL) was added and the product was extracted with EtOAc (3 × 4 mL) and dried (anhyd Na_2SO_4). Evaporation of the solvent and purification by column chromatography on silica gel (*n*-hexane/EtOAc) gave the desired unsymmetrical diaryl sulfides in 74–95% yields.

The yields given below for the products from Table 2 are based on the corresponding aryl acetates.

Diphenyl Sulfide[8] (Table 2, entry 1)

Colorless liquid; yield: 171 mg (92%, 0.92 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26–7.43 (10 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.8, 131.1, 129.3, 127.2.

p-Methoxyphenyl *p*-Tolyl Sulfide[14h] (Table 2, entry 4)

Yellow oil; yield: 200 mg (87%, 0.87 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (2 H, d, *J* = 7.6 Hz), 7.16 (2 H, d, *J* = 8.4 Hz), 7.13 (2 H, d, *J* = 7.6 Hz), 6.96 (2 H, d, *J* = 8.4 Hz), 3.7 (3 H, s), 2.4 (3 H, s),

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.5, 136.1, 134.4, 129.8, 129.4, 125.6, 114.9, 55.3, 21.0.

Phenyl *p*-Tolyl Sulfide[8] (Table 2, entry 5)

Colorless oil; yield: 184 mg (92%, 0.92 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.0–7.3 (9 H, m), 2.5 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.0, 133.6, 131.0, 129.4, 129.1, 127.7, 127.0, 126.1, 21.2.

Phenyl *m*-Tolyl Sulfide[6g] (Table 2, entry 7)

Colorless oil; 190 mg (95%, 0.95 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.28–7.35 (4 H, m), 7.10–7.26 (4 H, m), 7.03–7.05 (1 H, d, *J* = 7 Hz), 2.26 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.4, 136.7, 135.8, 135.0, 131.5, 130.6, 128.9, 128.7, 127.8, 126.8, 21.5.

***m*-Tolyl *p*-Tolyl Sulfide[6g] (Table 2, entry 8)**

Colorless liquid; yield: 195 mg (91%, 0.91 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.25–7.28 (2 H, m), 7.07–7.17 (5 H, m), 6.99 (1 H, d, *J* = 7.5 Hz), 2.38 (3 H, s), 2.32 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.4, 135.4, 135.3, 134.3, 132.9, 129.5, 129.2, 128.9, 128.6, 126.4, 125.0, 21.1, 21.0.

Phenyl *o*-Tolyl Sulfide[8] (Table 2, entry 9)

Colorless oil; yield: 178 mg (89%, 0.89 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.17–7.38 (9 H, m), 2.43 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.0, 137.0, 131.1, 133.0, 131.0, 130.6, 129.1, 128.7, 127.0, 126.3, 20.6.

(2,3-Dihydroinden-5-yl)phenyl Sulfide (Table 2, entry 10)

Yellow oil; yield: 180 mg (80%, 0.80 mmol).

IR (film): 3055, 2949, 2843, 1610, 1490, 1439, 1103, 713, 472 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73–7.78 (2 H, m), 7.47–7.57 (5 H, m), 7.08–7.10 (1 H, m), 2.84–2.90 (4 H, m), 2.08–2.11 (2 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.0, 136.2, 133.3, 132.2, 131.6, 128.6, 128.5, 124.9, 33.0, 31.9, 25.8.

Anal. Calcd for $C_{15}H_{14}S$ (226.34): C, 79.60; H, 6.23; S, 14.16. Found: C, 80.50; H, 6.73; S, 12.77.

(2,3-Dihydroinden-5-yl) *p*-Tolyl Sulfide (Table 2, entry 11)

Yellow oil; 192 mg (80%, 0.80 mmol).

IR (film): 3016, 2950, 2844, 1607, 1490, 1436, 912, 744, 516 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73–7.79 (2 H, m), 7.48–7.51 (2 H, m), 7.29 (2 H, d, *J* = 7.5 Hz), 7.11 (2 H, d, *J* = 7.5 Hz), 2.86–2.91 (4 H, m), 2.49 (3 H, s), 2.08–2.12 (2 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.0, 141.2, 136.2, 134.9, 132.3, 132.2, 131.6, 128.5, 124.9, 33.0, 31.9, 25.8, 21.7.

Anal. Calcd for $C_{16}H_{16}S$ (240.36): C, 79.95; H, 6.71; S, 13.34. Found: C, 80.70; H, 7.50; S, 11.80.

***p*-Nitrophenyl *p*-Tolyl Sulfide[14h] (Table 2, entry 13)**

Yellow solid; yield: 225 mg (92%, 0.92 mmol); mp 81 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (2 H, d, *J* = 8 Hz), 7.42 (2 H, d, *J* = 8 Hz), 7.25 (2 H, d, *J* = 7.6 Hz), 7.13 (2 H, d, *J* =7.6 Hz), 2.3 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.5, 139.9, 140.2, 135.1, 130.9, 126.4, 126.1, 124.0, 21.3.

***p*-Cyanophenyl *p*-Tolyl Sulfide[14h] (Table 2, entry 15)**

White solid; yield: 200 mg (89%, 0.89 mmol); mp 95–97 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.63–7.60 (4 H, m), 7.27 (2 H, d, *J* = 8.4 Hz), 7.13 (2 H, d, *J* = 8.4 Hz), 2.43 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.6, 140.0, 134.9, 133.9, 132.7, 130.7, 126.8, 118.8, 111.2, 108.3, 21.3.

1-Naphthyl Phenyl Sulfide[6d] (Table 2, entry 16)

Colorless oil; yield: 200 mg (85%, 0.85 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.36–8.39 (3 H, m), 7.92 (1 H, dd, *J* = 7.2, 8 Hz), 7.58–7.63 (2 H, m), 7.56 (1 H, dd, *J* = 7.2, 1.2 Hz), 7.02–7.38 (5 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 123.7, 124.6, 126.1, 126.3, 127.0, 127.6, 128.7, 128.6, 129.7, 130.0, 131.8, 134.3, 135.4, 136.0. 136.5.

1-Naphthyl *p*-Tolyl Sulfide[14h] (Table 2, entry 17)

Colorless oil; yield: 232 mg (93%, 0.93 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87–7.95 (2 H, m), 7.53–7.57 (3 H, m), 7.29–7.44 (2 H, m), 6.99–7.05 (4 H, m), 2.29 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.9, 135.4, 132.7, 131.8, 130.0, 129.5, 128.6, 127.9, 126.7, 124.8, 123.8, 20.9.

2-Naphthyl Phenyl Sulfide[6d] (Table 2, entry 18)

White solid; yield: 224 mg (95%, 0.95 mmol); mp 48–49 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.27–7.29 (1 H, m), 7.86–7.97 (2 H, m), 7.57–7.67 (1 H, m), 7.45–7.56 (2 H, m), 7.39–7.44 (1 H, m), 7.10–7.29 (5 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.3, 135.4, 134.4, 132.9, 129.5, 129.2, 128.6, 128.0, 126.4, 125.9, 124.7, 123.9.

2-Naphthyl *p*-Tolyl Sulfide[14h] (Table 2, entry 19)

White solid; yield: 227 mg (91%, 0.91 mmol); mp 67–69 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.60–7.99 (3 H, m), 7.21–7.40 (1 H, m), 7.11–7.20 (3 H, m), 7.07–7.10 (4 H, m), 2.28 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.1, 124.7, 125.9, 126.4, 127.1, 127.9, 128.6, 128.9, 129.0, 129.2, 129.3, 132.8, 135.5, 136.4, 138.3.

2-Naphthyl *p*-Nitrophenyl Sulfide (Table 2, entry 20)

Yellow solid; yield: 251 mg (91%, 0.91 mmol); mp 156–157 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83–7.87 (2 H, d, *J* = 6.5 Hz), 7.63–7.77 (3 H, m), 7.52–7.55 (2 H, d, *J* = 6.5 Hz), 7.45–7.49 (4 H, m),

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.4, 133.3, 132.4, 132.3, 132.2, 131.3, 131.2, 128.6, 128.4, 126.5, 124.4, 116.2.

Anal. Calcd for $C_{16}H_{11}NO_2S$ (281.33): C, 68.31; H, 3.94; N, 4.98; S, 11.40. Found: C, 68.11; H, 4.10; N, 5.12; S, 11.19.

Phenyl 2-Pyridyl Sulfide[14h] (Table 2, entry 21)

Colorless oil; yield: 165 mg (88%, 0.88 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.50 (1 H, d, *J* = 4.8 Hz), 7.52–7.58 (2 H, m), 7.38–7.40 (4 H, m), 6.92–6.95 (1 H, m), 6.80 (1 H, d, *J* = 4.8 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.8, 149.4, 138.0 136.0, 129.0, 128.5, 127.1, 121.1, 119.6.

2-Pyridyl *p*-Tolyl Sulfide[14h] (Table 2, entry 22)

Colorless oil; yield: 180 mg (90%, 0.90 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.39 (1 H, d, *J* = 4.8 Hz), 7.51–7.55 (1 H, m), 7.42–7.44 (1 H, m), 7.39–7.51 (1 H, m), 7.21–7.30 (2 H, m), 6.94–6.99 (1 H, m), 6.85 (1 H, d, *J* = 4.8 Hz), 2.29 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.4, 149.5, 140.1, 136.8, 135.9, 130.1, 127.6, 120.9, 119.9, 21.1.

4-Acetylphenyl *p*-Nitrophenyl Sulfide (Table 2, entry 23)

Yellow solid; yield: 242 mg (89%, 0.89 mmol); mp 47–48 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73–7.78 (2 H, d, *J* = 6.8 Hz), 7.50–7.57 (2 H, d, *J* = 6.8 Hz), 7.46–7.48 (4 H, m),

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 197.0, 171.2, 135.8, 132.3, 131.9, 129.8, 129.1, 128.4, 123.5, 26.25.

Anal. Calcd for $C_{14}H_{11}NO_3S$ (273.31): C, 61.53; H, 4.06; N, 5.13; S, 11.73. Found: C, 61.26; H, 4.29; N, 5.75; S, 11.19.

C–S Bond Formation by the Reaction of Triphenyltin Chloride with Phenolic Esters; General Procedure

A one-necked flask was charged with $Cu(OAc)_2$ (30 mg, 0.15 mmol), K_2CO_3 (414 mg, 3.0 mmol), S_8 (48 mg, 1.5 mmol), KF (180 mg, 3 mmol), phenolic ester (1 mmol), triphenyltin chloride (0.35 mmol), and PEG200 (1.5 mL). The mixture was magnetically stirred and heated at 80 °C for the appropriate reaction time (Table 4). After completion of the reaction, the reaction mixture was cooled to r.t. H_2O (4 mL) was added and the product was extracted with EtOAc (3 × 4 mL) and dried (anhyd Na_2SO_4). Evaporation of the solvent and purification by column chromatography on silica gel (*n*-hexane/EtOAc) gave the desired phenyl aryl sulfides in 79–94% yields.

Diphenyl Sulfide[8] (Table 4, entry 1)

Colorless liquid; yield: 173 mg (93%, 0.93 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26–7.40 (10 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 127.1, 129.3, 131.1, 135.9.

Phenyl *p*-Tolyl Sulfide[8] (Table 4, entry 3)

Colorless oil; yield: 178 mg (89%, 0.89 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.1–7.4 (9 H, m), 2.3 (3 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.1. 133.7, 131.1, 129.5, 129.1, 127.7, 127.1, 126.1, 21.3.

2-Naphthyl Phenyl Sulfide[6d] (Table 4, entry 9)

White solid; yield: 212 mg (90%, 0.9 mmol); mp 47–49 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.25–8.27 (1 H, m), 7.83–7.95 (2 H, m), 7.53–7.64 (1 H, m), 7.43–7.55 (2 H, m), 7.36–7.40 (1 H, m), 7.10–7.30 (5 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 136.8, 135.3, 134.5, 132.8, 129.7, 129.3, 128.8, 128.1, 126.3, 125.8.

Phenyl 2-Pyridyl Sulfide[14h] (Table 4, entry 10)

Colorless oil; yield: 170 mg (91%, 0.91 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.40 (1 H, d, *J* = 4.8 Hz), 7.54–7.58 (2 H, m), 7.38–7.40 (4 H, m), 6.94–6.97 (1 H, m), 6.86 (1 H, d, *J* = 4.8 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.5, 149.5, 136.8, 134.9, 131.0, 129.7, 129.1, 121.4, 119.9.

Symmetrical Diaryl Sulfides via Homocoupling Reaction Phenolic Esters; General Procedure

A one-necked flask was charged with CuI (10 mg, 0.05 mmol), NaO*t*-Bu (376 mg, 4.0 mmol), S_8 (16 mg, 0.5 mmol), phenolic ester (1 mmol), anhyd DMF (2 mL) under an inert atmosphere. The mixture was magnetically stirred and heated at 120 °C for the appropriate reaction time (Table 6). After completion of the reaction, the mixture was cooled to r.t. H_2O (4 mL) was added and the product was extracted with EtOAc (3 × 4 mL) and dried (anhyd Na_2SO_4). Evaporation of the solvent and purification by column chromatography on silica gel (*n*-hexane/EtOAc) gave the desired symmetrical diaryl sulfides in 75–93% yields.

The yields given below for the products from Table 6 are based on the corresponding aryl acetates.

4,4′-Dimethoxy Diphenyl Sulfide[5] (Table 6, entry 2)

Colorless oil; yield: 219 mg (89%, 0.89 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.30 (4 H, d, *J* = 6.8 Hz), 6.73 (4 H, d, *J* = 6.8 Hz), 3.7 (6 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.7, 132.6, 128.3, 114.7, 55.4.

Di-*p*-tolyl Sulfide[12d] (Table 6, entry 3)

White solid; yield: 189 mg (88%, 0.88 mmol); mp 55–56 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.32 (4 H, d, *J* = 8 Hz), 7.08 (4 H, d, *J* = 8 Hz), 2.25 (6 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.4, 131.1, 129.8, 128.5, 21.0.

Di-*m*-tolyl Sulfide[12d] (Table 6, entry 4)

Yellow liquid; yield: 199 mg (93%, 0.93 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34–7.38 (1 H, m), 7.01–7.11 (4 H, m), 6.80–6.82 (2 H, m), 2.23 (6 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.1, 135.7, 131.7, 129.1, 128.2, 128.0, 21.4.

Di-*o*-tolyl Sulfide[12d] (Table 6, entry 5)

White solid; yield: 184 mg (86%, 0.86 mmol); mp 58–59 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.31–7.46 (2 H, m), 7.19–7.29 (2 H, m), 7.02–7.04 (4 H, m), 2.32 (6 H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.0, 134.6, 131.2, 129.6, 127.9, 126.8, 20.7.

4,4′-Dinitrodiphenyl Sulfide[10] (Table 6, entry 6)

Yellow solid; yield: 248 mg (90%, 0.90 mmol); mp 154–155 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.11–8.16 (4 H, m), 7.38–7.47 (4 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.9, 141.6, 130.1, 123.6.

4,4′-Dicyanodiphenyl Sulfide[7b] (Table 6, entry 7)

White solid; yield: 214 mg (91%, 0.91 mmol); mp 135–136 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47–7.56 (4 H, m), 7.33–7.36 (4 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.6, 133.0, 131.1, 118.2, 111.4.

Di-1-naphthyl Sulfide[7b] (Table 6, entry 8)

White solid; yield: 257 mg (90%, 0.90 mmol); mp 109–110 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85–8.40 (2 H, m), 7.60–7.84 (2 H, m), 7.41–7.58 (2 H, m), 7.39–7.40 (4 H, m), 7.38 (4 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.9, 135.4, 132.7, 131.8, 130.0, 129.5, 128.6, 127.9, 126.7, 124.8.

Di-2-naphthyl Sulfide[7b] (Table 6, entry 9)

White solid; yield: 263 mg (92%, 0.92 mmol); mp 150–152 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.27–8.30 (2 H, m), 7.80–7.83 (2 H, m), 7.54–7.57 (5 H, m), 7.38–7.53 (4 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 133.0, 132.6, 127.5, 127.2, 125.6, 124.9, 124.4, 123.0.

Di-2-pyridyl Sulfide[12d] **(Table 6, entry 10)**

Red solid; yield: 172 mg (92%, 0.92 mmol); mp 218–220 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.46–8.47 (2 H, m), 7.65–7.69 (2 H, m), 7.49–7.51 (2 H, m), 7.22–7.29 (2 H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.7, 150.1, 137.2, 126.0, 121.9.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588508.

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