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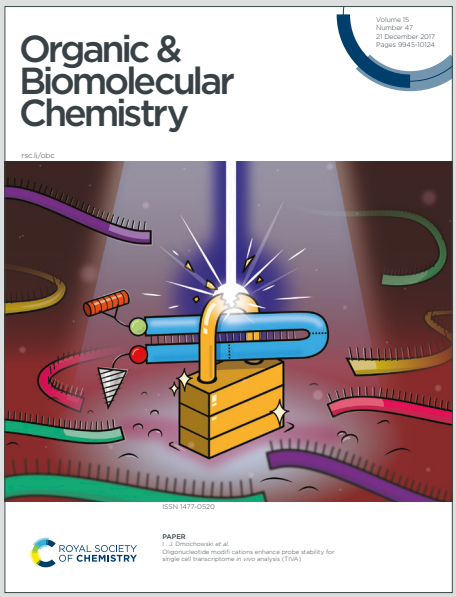

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ARTICLE

Room Temperature Nickel-Catalyzed Cross-Coupling of Aryl-boronic Acids with Thiophenols: Synthesis of Diarylsulfides

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A $NiCl_2$/2,2′-bipyridine-catalyzed cross-coupling of thiophenols with arylboronic acids for the synthesis of symmetric and unsymmetric diarylsulfides has been developed at room temperature and in air conditions. This methodology is reliable and offers a mild and easy operation for the synthesis of arylthioethers, which are essential compounds for pharmaceutical and agricultural applications. The method avoids the use of expensive transition metals like Pd, Ir or Rh, sophisticated ligands and elevated temperatures. It also displays wide substrate scope (55 examples) and provides good to excellent yields (72-93%) of the products.

Introduction

C–S bond construction is one of the noteworthy organic conversion as it is ubiquitous in various biologically active molecules.[1] Sulfides and thioethers are significant moieties in many natural products,[2] in material chemistry,[3] pharmaceuticals,[4] synthetic chemicals,[5] and food and agricultural industries[6] (Figure 1). Diarylsulfides are widely used in medical treatments like cancer, Alzheimer's, Parkinson's, IDS, neoplastic, HCV, diabetic and parasitic diseases.[7] Notably, diarylsufide moiety is found in many marketed drugs like chloropromazine (used to treat psychotic disorders),[7d] Axitinib and Thymitaq (anticancer),[7f] Vortioxetane or Trintellix (for major depressive disorder),[7g] and Esomeprazole (for gastroesophageal reflux disease)[7h] (Figure 1). Moreover, sulfide derivatives like sulfoxides and sulfones are also equally important in many aspects.[4g] Based on various utilities of thioethers, many methods have been developed over the years for their synthesis. A traditional process for C–S bond formation is Stadler–Ziegler reaction wherein an aryldiazonium salt is reacted with thiolates to form diarylsulfides (Scheme 1A).[8] However, this method still faces challenges for the preparation and isolation of diazonium salt and coupling partner sodium thiolate. A recent photochemical Stadler–Ziegler method is efficient for diarylsulfide synthesis, but the use of expensive photocatalyst and the formation of side products like disulfide and explosive diazosulfides make this method undesirable for industrial use.[9] On the other hand, frequent methods for C–S bond formation rely on the transition metal (TM)-catalyzed cross-coupling of an arylhalide and thiol using Pd,[10] Ni,[11] Zn,[12] Cu,[13] Fe,[14] Rh,[15] Ag[16] and Ir,[17] (Scheme 1B). Most of the TM-catalyzed C–S bond formations require high temperatures, highly basic reaction conditions, high catalyst and ligand loading due to strong binding of metals to thiols.[10,18] Many of the TMs are expensive, toxic in nature and the removal of the metal residues are problematic. Several approaches for diarylsulfide formation utilize highly reactive catalysts and ligands, with the drawbacks being air and moisture sensitivity.[10] Ni-catalyzed cross-coupling reactions are preferred nowadays than Pd, Rh and Ir due to its availability, simple operation, facile oxidative addition and economical aspects.[19] Recently, Pd- and Ni-catalyzed decarbonylative C–S bond formation are also reported using expensive ligands and higher temperatures (Scheme 1C).[10h,20]

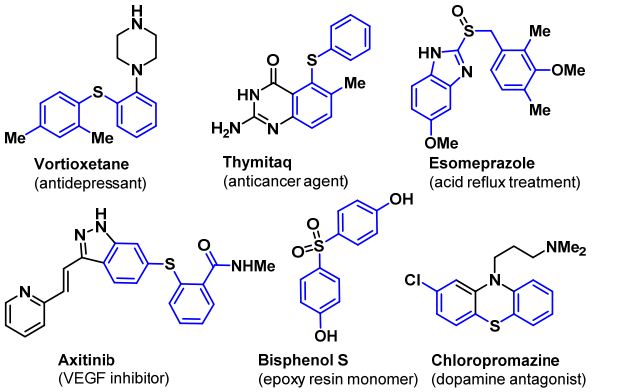

Figure 1 Biologically active drugs and valuable compounds containing diarylsulfide motifs.

The Chan–Lam reaction is also a good substitute for conventional C–S cross-coupling because of the eco-friendly reaction conditions and numerous examples of Cu-catalyzed S-arylation that have been reported.[13] However, there exists only one report on Ni-catalyzed coupling of arylboronic acids with arylsulphonamides.[21] Therefore, the development of a mild, efficient, easily operative and eco-friendly method is highly exigent. Herein, we have developed a simple and easily operational, cheap and environmentally benign method for the

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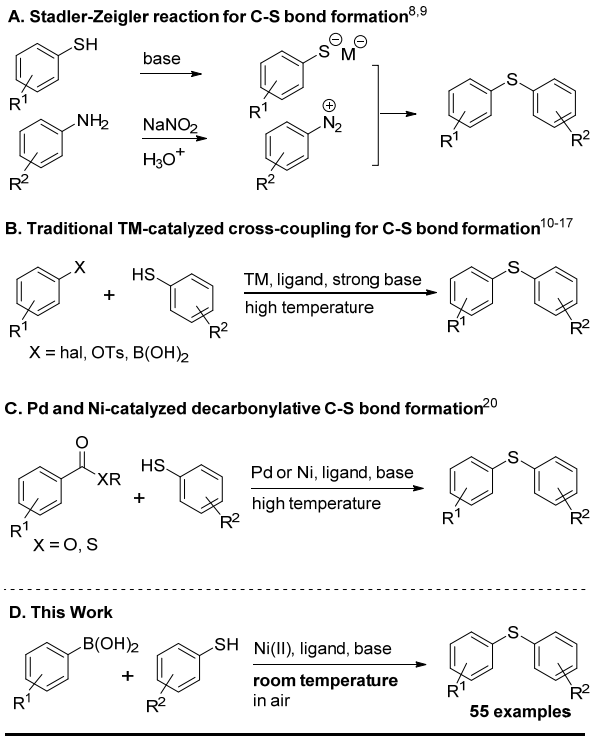
synthesis of diarylsulfides by Ni-catalyzed cross-coupling of different arylboronic acids with thiophenols at room temperature and in air conditions.

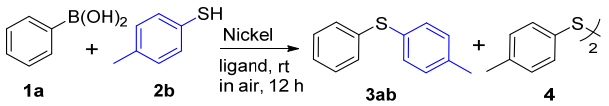


Scheme 1 Overview of diarylsulfide synthesis development.

Results and Discussion

We screened various nickel salts and suitable ligands for C–S cross-coupling of phenylboronic acid **1a** with 4-methylthiophenol **2b** as model substrates with variation of solvents and bases (Table 1). The use of 10 mol% of $NiCl_2.6H_2O$ and 20 mol% of 2,2′-bipyridine in presence of *t*-BuOK at room temperature gave phenyl(*p*-tolyl)sulfane **3ab** with 82% yield within 12 h. Further, various other nickel catalysts were screened, however the yields of **3ab** were not superior to $NiCl_2.6H_2O$ (entries 2-7). A few Ni-salts promoted the disulfide **4** formation in 10-19% yields (entries 5-7). Then different ligands were tried, wherein PPh_3 and pyridine failed to deliver the product **3ab** (entries 8-9), while other ligands provided good to moderate yields of **3ab** (entries 10-13) but not better when compared to entry 1, indicating 2,2′-bipyridine to be a superior ligand. We next considered various bases for the cross-coupling reaction (entries 14-19), however most of them yielded the disulfide **4** instead of **3ab,** except *t*-BuONa (entry 14), which gave **3ab** in 69% yield. A further change in solvent did not alter the yields of **3ab** (entries 20-23), although a solvent mixture like CH_3CN/DMF (5:1) was gratifyingly found to be the best for the conversion and gave **3ab** in 93% yield (entry 24 vs 25 and 26). The boronic acid was less soluble in some solvents, lowering the yields (e.g. DMSO). A reaction under oxygen atmosphere retarded the reaction giving **3ab** in only 9% yield (entry 27),

Table 1 Optimization of Reaction Conditions.[a]



Entry	Catalyst (10 mol%)	Ligand (20 mol%)	Base (1.5 eq.)	Solvent	Yield (%) **3ab**	Yield (%) **4**
1	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN	82	–
2	$NiCl_2$.glyme	2,2′-bipy	*t*-BuOK	CH_3CN	54	–
3	$Ni(OAc)_2$	2,2′-bipy	*t*-BuOK	CH_3CN	NR	–
4	$NiBr_2.xH_2O$	2,2′-bipy	*t*-BuOK	CH_3CN	65	–
5	$Ni(SO_4)_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN	NR	16
6	$Ni(CO)_3$. $2Ni(OH)_2.nH_2O$	2,2′-bipy	*t*-BuOK	CH_3CN	NR	19
7	NiO	2,2′-bipy	*t*-BuOK	CH_3CN	NR	10
8	$NiCl_2.6H_2O$	PPh_3	*t*-BuOK	CH_3CN	NR	–
9	$NiCl_2.6H_2O$	pyridine	*t*-BuOK	CH_3CN	NR	–
10	$NiCl_2.6H_2O$	dppp	*t*-BuOK	CH_3CN	61	–
11	$NiCl_2.6H_2O$	dppe	*t*-BuOK	CH_3CN	58	–
12	$NiCl_2.6H_2O$	xantphos	*t*-BuOK	CH_3CN	64	–
13	$NiCl_2.6H_2O$	X-phos	*t*-BuOK	CH_3CN	55	–
14	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuONa	CH_3CN	69	–
15	$NiCl_2.6H_2O$	2,2′-bipy	K_2CO_3	CH_3CN	NR	37
16	$NiCl_2.6H_2O$	2,2′-bipy	Cs_2CO_3	CH_3CN	NR	34
17	$NiCl_2.6H_2O$	2,2′-bipy	DBU	CH_3CN	NR	31
18	$NiCl_2.6H_2O$	2,2′-bipy	K_3PO_4	CH_3CN	NR	29
19	$NiCl_2.6H_2O$	2,2′-bipy	Et_3N	CH_3CN	NR	36
20	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	dioxane	43	–
21	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	THF	30	–
22	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	DMF	77	–
23	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	DMSO	65	–
24	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN/ DMF (5:1)	93	–
25	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN/ DMSO (5:1)	63	–
26	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN/ dioxane (5:1)	59	–
27[b]	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN/ DMF (5:1)	9	–
28[c]	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK	CH_3CN/ DMF (5:1)	47	–
29	–	2,2′-bipy	*t*-BuOK	CH_3CN/ DMF (5:1)	NR	–
30	$NiCl_2.6H_2O$	–	*t*-BuOK	CH_3CN/ DMF (5:1)	–	42
31	$NiCl_2.6H_2O$	2,2′-bipy	–	CH_3CN/ DMF (5:1)	–	36
32	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK (1 equiv)	CH_3CN/ DMF (5:1)	75	–
33	$NiCl_2.6H_2O$	2,2′-bipy	*t*-BuOK (2 equiv)	CH_3CN/ DMF (5:1)	92	–
34[d]	$NiCl_2$	2,2′-bipy	*t*-BuOK	CH_3CN/ DMF (5:1)	12	–

[a]Reaction conditions: **1a** (0.6 mmol), **2b** (0.5 mmol), ligand (20 mol%), base (1.5 equiv). [b]Under O_2 (balloon). [c]Under N_2 (balloon). [d]24 h reaction. NR = No reaction.

which could be due to ligand deactivation. Similarly, under N_2 atmosphere the yield of **3ab** decreased to 47% (entry 28). A reaction without Ni-catalyst gave no reaction, while that without ligand or base provided the diaryldisulfide **4** in 42% and 36% yields (entries 29, 30 and 31, respectively). Change of base

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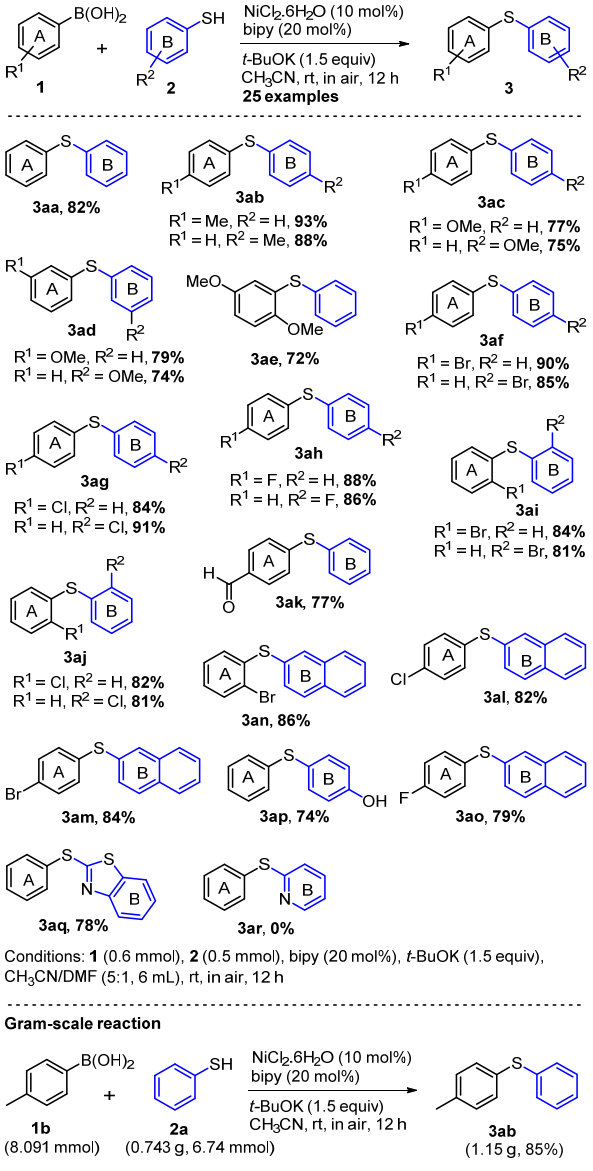
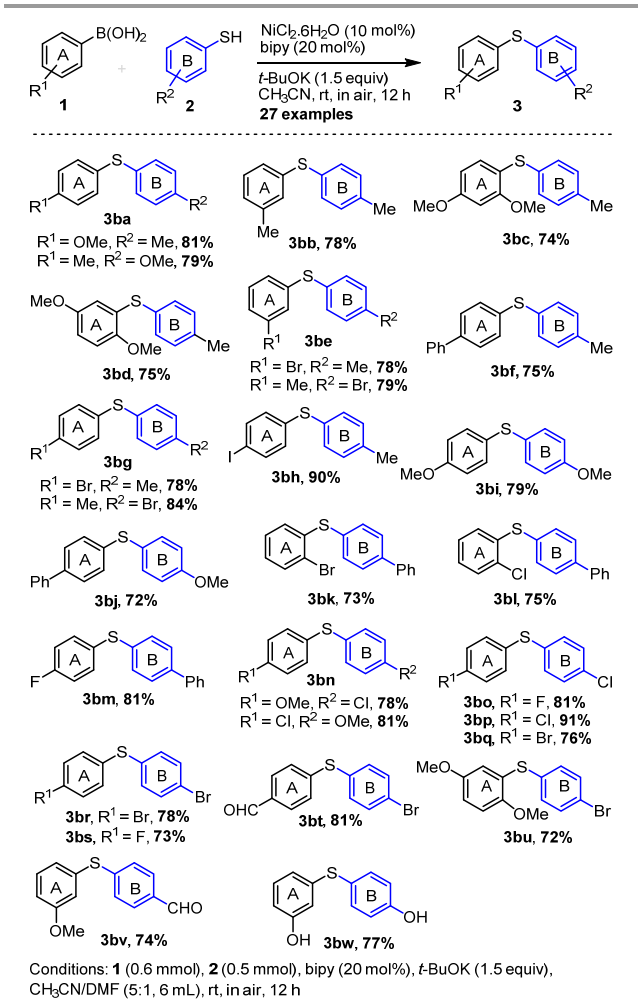
concentration to 1.0 equiv gave **3ab** in decreased yield (75%, entry 32), while that with increased amount of base was not beneficial (entry 33). A reaction with neat $NiCl_2$ gave a sluggish reaction providing **3ab** in 12% yield (entry 34) with the recovery of starting materials. This study revealed that $NiCl_2.6H_2O$ (10 mol%) and 2,2′-bipyridine (20 mol%) in presence of *t*-BuOK at room temperature were optimum requirements for the synthesis of diarylsulfides **3**.

The scope and limitations of this method were further explored on a series of mono substituted arylboronic acids **1** and thiophenols **2** using $NiCl_2.6H_2O$ and 2,2′-bipyridine to give mono arylsubstituted diarylsulfides **3aa**-**3aq** in good to excellent yields (Scheme 2). Various functional groups like Me, OMe, Br, Cl or F group on either the arylboronic acid or thiophenol were well tolerated giving the products **3aa**-**3aj** in 72-93% yields. 4-Formylphenylboronic acid also reacted with benzenethiol and gave exclusively 4-formyl-diarylsulfide **3ak** in 77% yield. Naphthyl-2-thiol also reacted well with various arylboronic acids giving the products **3al**-**3ao** in 79-86% yields. A reaction of 4-hydroxythiophenol and phenylboronic acid also worked well giving 4-(phenylthio)phenol **3ap** exclusively in 74% yield. No biarylether formation was observed in the latter case. Reaction of phenylboronic acid and 2-mercaptobenzothiozole gave the product **3aq** in 78% yield. The reaction of phenylboronic acid with 2-mercaptopyridine did not yield the product **3ar**. It can be noted that *ortho*-substituted arylboronic acid or the thiol did not pose any steric issues in the synthesis of the diarylsulfides, e.g. **3ae**, **3ai**, **3aj** and **3an**. A gram-scale reaction of **1b** with the thiophenol **2a** (6.74 mmol) gave the diarylsulfide **3ab** in 85% yield indicating possible scale-up of the reaction (Scheme 2).

We continued the scope of substrates for synthesis of disubstituted diarylsulfides **3** using both substituted boronic acids and thiophenols as shown in Scheme 3. Various arylboronic acids with substituents like OMe, Me, Ph, Br, Cl, I, F, and CHO worked well with substituted



Scheme 2 Substrate scope to synthesize mono substituted diarylsulfides **3**.



Scheme 3 Substrate scope to synthesize disubstituted diarylsulfides **3**.

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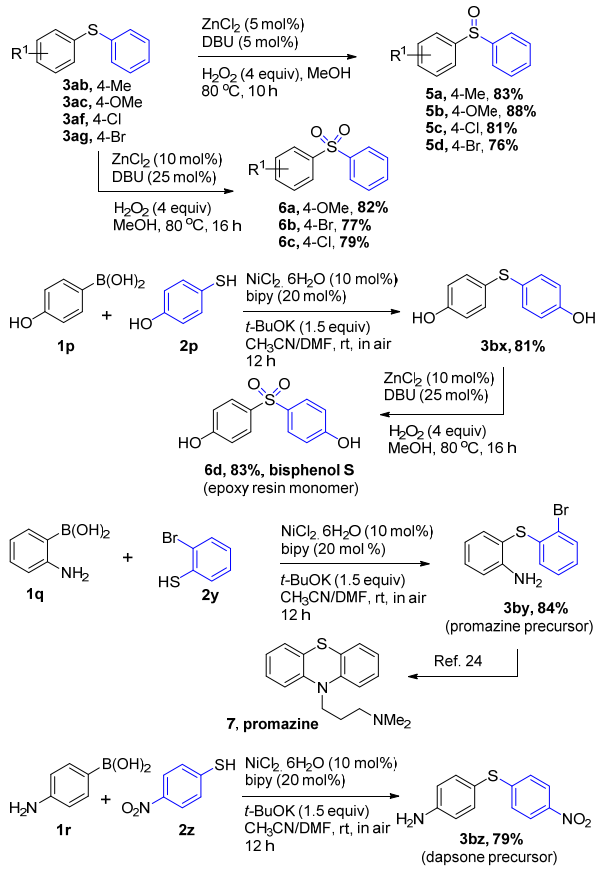
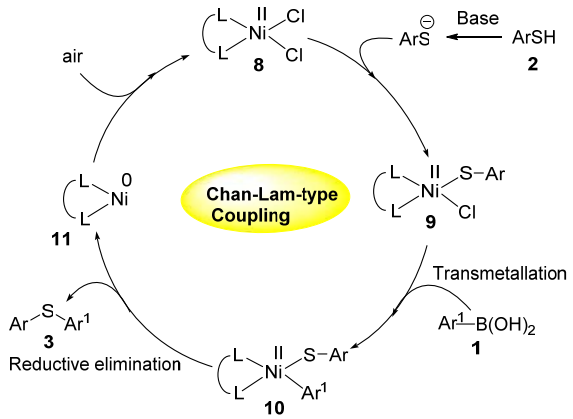
arylthiols having similar groups to provide the disubstituted diarylsulfides **3ba**-**3bw** in good yields (72-91%, Scheme 3). Notably, the presence of *ortho*-substituents or disubstituted arylboronic acids worked well to provide diarylsulfides like **3bc**, **3bd**, **3bk**, **3bl**, and **3bu** in good yields. Also formyl substituent on arylboronic acid or the thiophenol provided the products **3bt** and **3bv** efficiently. A reaction of 4-hydroxythiophenol and 3-hydroxy-phenylboronic acid also worked well giving **3bw** with 77% yield.

We considered exploring the synthetic utility of this method toward useful scaffolds as shown in Scheme 4. The diarylsulfides **3ab**, **3ac**, **3af** and **3ag** were oxidized to the sulfoxides **5a**-**d**, respectively in good yields (76-88%).[22] Similarly, the oxidation of **3ac**, **3af** and **3ag** to the sulfones **6a-c** in 77-82% yields was also achieved. Bisphenol S **6d** is an epoxy resin monomer used as a constituent of plastic substitute for production of babybottles.[23] Toward its synthesis, the coupling of boronic acid **1p** with the 4-hydroxythiophenol **2p** gave the diarylsulfide **3bx** (81%) that on further oxidation provided bisphenol S **6d** in 81% yield. The coupling of 2-aminoboronic acid **1q** with 2-bromothiophenol **2y** occurred chemoselectively through the present protocol giving the diarylsulfide **3by** in 84% yield. This is a precursor to the drug molecule promazine that is used as antipsychotic drug belonging to the phenothiazine family.[24] We also synthesized the dapsone precursor **3bz** in 79% yield by coupling of 4-amino- phenylboronic acid **1r** with 4-nitrothiophenol **2z**. Dapsone is used as a drug for skin diseases.[25]



Scheme 4 Product modification and application towards the synthesis of sulfoxides, sulfones, promazine and dapsone precursors.



Scheme 5 Plausible mechanism.

The reaction may take a similar course as the Chan–Lam-type coupling.[13,21] The co-ordination of bipy ligand with $NiCl_2$ will give **8** (Scheme 5). The deprotonated thiol displaces a chloride from **8** giving the species **9**. Transmetallation with arylboronic acid **1** give the species **10** that undergoes reductive elimination giving the product **3**.[11e,21] The Ni(0) complex **11** is oxidized to Ni(II) **8** in air to continue the catalytic cycle. Since the $NiCl_2.6H_2O$ (10 mol%) used is a hexahydrate, the actual content of Ni catalyzing the reaction is well around 5.5 mol% if water molecules are excluded.

Conclusion

In summary, in this paper, we have developed an efficient and mild method for C–S coupling using $NiCl_2.6H_2O$ as the catalyst and 2,2′-bipy as ligand at room temperature. Various arylboronic acids are cross-coupled with thiols giving diarylsulfides in 72-93% yield (55 examples). Our protocol showed good functional group tolerance, chemoselective reaction of arylboronic acid with thiophenol and requires ambient temperature. The method was applied to synthesize various sulfoxides and sulfones and also drug intermediates.

Experimental Section

General information. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. ^{1}H-NMR and ^{13}C-NMR were recorded with a spectrometer operating at 400 or 500 and 100 or 125 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on the $CDCl_3$ peak at δ = 7.26 ppm for proton NMR and the $CDCl_3$ peak at δ = 77.00 ppm (t) for carbon NMR. IR spectra were obtained on an FT-IR spectrometer by evaporating compounds dissolved in $CHCl_3$ on CsCl pellete. HRMS (ESI-TOF) spectra were recorded using positive electrospray ionization by the TOF method.

General procedure for synthesis of diarylsulfides (3). To a stirred solution of thiol **2** (0.5 mmol) in acetonitrile/DMF (5:1, 6 mL) was added $NiCl_2.6H_2O$ (11.9 mg, 0.05 mmol, 10 mol%) and 2,2′-bipyridine

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(15.6 mg, 0.1 mmol, 20 mol%) at room temperature. After 5 min, boronic acid (0.6 mmol) was added followed by *t*-BuOK (84.2 mg, 0.75 mmol, 1.5 equiv) addition portionwise. The reaction mixture was stirred at room temperature in air for 12 h. It was then quenched with saturated aq. NH_4Cl solution and the mixture was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (99:1) as eluent to afford diarylsulfides **3**.

Diphenylsulfane (**3aa**).[11g] Colorless oil (76.4 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.35 (m, 4H), 7.33–7.27 (m, 4H), 7.25–7.24 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 135.8, 131.0, 129.2, 127.0 ppm. IR ($CHCl_3$): ν_{max} = 3071, 3054, 3020, 2922, 1578, 1474, 1440, 1302, 1219, 1178, 1158, 1081, 1022, 997, 912, 770, 737, 688, 632 cm^{-1}.

Phenyl(*p*-tolyl)sulfane (**3ab**).[11g] Colorless oil (93.1 mg, 93% and 88.1 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.2 Hz, 2H), 7.29–7.25 (m, 3H), 7.23–7.18 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 137.5, 137.1, 132.2, 131.2, 130.0, 129.7, 129.0, 126.4, 21.1 ppm. IR ($CHCl_3$): ν_{max} = 3071, 3054, 3021, 2921, 2864, 1582, 1491, 1477, 1439, 1396, 1302, 1180, 1083, 1024, 1015, 905, 809, 739, 690 cm^{-1}.

(4-Methoxyphenyl)(phenyl)sulfane (**3ac**).[11g] Yellow oil (83.3 mg, 77% and 81.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.9 Hz, 2H), 7.24–7.18 (m, 2H), 7.16–7.12 (m, 3H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.8, 138.6, 135.4, 128.9, 128.1, 125.7, 124.2, 115.0, 55.3 ppm. IR ($CHCl_3$): ν_{max} = 3057, 3006, 2962, 2939, 2837, 1592, 1493, 1478, 1459, 1440, 1288, 1247, 1172, 1100, 1083, 1032, 909, 828, 797, 740, 690 cm^{-1}.

(3-Methoxyphenyl)(phenyl)sulfane (**3ad**).[11g] Yellow oil (85.4 mg, 79% and 80 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 6.8 Hz, 2H), 7.34–7.30 (m, 2H), 7.28–7.27 (m, 1H), 7.22–7.20 (m, 1H), 6.92 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.88 (t, *J* = 2.2 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.76 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.0, 137.2, 135.2, 131.4, 129.9, 129.2, 127.2, 122.9, 115.8, 112.7, 55.2 ppm. IR ($CHCl_3$): ν_{max} = 3064, 3003, 2952, 2935, 2837, 1590, 1477, 1439, 1425, 1307, 1283, 1247, 1230, 1180, 1071, 1044, 1024, 993, 910, 860, 846, 773, 738, 689, 649, 612 cm^{-1}.

(2,5-Dimethoxyphenyl)(phenyl)sulfane (**3ae**). Colorless oil (88.7 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.34 (m, 2H), 7.32 (dt, *J* = 8.9, 1.7 Hz, 2H), 7.29–7.27 (m, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.73 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 3.83 (s, 3H), 3.66 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 154.0, 151.4, 133.8, 132.2, 129.3, 127.5, 125.8, 116.8, 112.4, 111.8, 56.6, 55.7 ppm. IR ($CHCl_3$): ν_{max} = 3003, 2959, 2939, 2835, 1595, 1576, 1490, 1463, 1436, 1411, 1304, 1282, 1253, 1162, 1087, 1075, 1032, 937, 918, 836, 804, 636 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{14}H_{14}O_2SK$ 285.0346; Found 285.0339.

(4-Bromophenyl)(phenyl)sulfane (**3af**).[13g] Yellow oil (119.3 mg, 90% and 112.7 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.6 Hz, 2H), 7.38–7.36 (m, 2H), 7.35–7.31 (m, 2H), 7.30–7.27 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 135.4, 134.8, 132.2, 132.0, 131.5, 129.3, 127.5, 120.8 ppm. IR ($CHCl_3$): ν_{max} = 3071, 3059, 3016, 2928, 2850, 2803, 1581, 1473, 1439, 1385, 1300, 1175, 1158, 1093, 1082, 1068, 1024, 1008, 812, 742, 704, 690 cm^{-1}.

(4-Chlorophenyl)(phenyl)sulfane (**3ag**).[13g] Colorless oil (92.7 mg, 84% and 100.4 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.34 (m, 4H), 7.32–7.28 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 135.1, 134.6, 132.9, 132.0, 131.3 129.3, 129.26, 127.4 ppm. IR ($CHCl_3$): ν_{max} = 3074, 3058, 3016, 1583, 1475, 1440, 1390, 1095, 1087, 1022, 1012, 912, 818, 740, 704, 690, 549 cm^{-1}.

(4-Fluorophenyl)(phenyl)sulfane (**3ah**).[11g] Colorless oil (89.9 mg, 88% and 87.8 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.34–7.28 (m, 4H), 7.25–7.22 (m, 1H), 7.05 (t, *J* = 8.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 163.4 and 161.4 ($J_{C\text{-}F}$ = 247.7 Hz), 136.6, 134.1 and 134.03 ($J_{C\text{-}F}$ = 8.1 Hz), 130.2 and 130.15 ($J_{C\text{-}F}$ = 2.9 Hz), 129.9, 129.15, 126.7, 116.5 and 116.3 ($J_{C\text{-}F}$ = 21.8 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –114.0 ppm. IR ($CHCl_3$): ν_{max} = 3074, 3060, 1589, 1489, 1478, 1439, 1397, 1291, 1228, 1156, 1082, 1070, 1024, 1013, 831, 740, 706, 690, 667, 628 cm^{-1}.

(2-Bromophenyl)(phenyl)sulfane (**3ai**).[13g] Colorless oil (111.4 mg, 84% and 107.4 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47–7.44 (m, 2H), 7.42–7.36 (m, 3H), 7.15 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.03 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.5 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.7, 133.5, 133.0, 132.8, 129.7, 129.6, 128.4, 127.8, 127.2, 123.0 ppm. IR ($CHCl_3$): ν_{max} = 3059, 2915, 1658, 1578, 1475, 1446, 1427, 1310, 1251, 1158, 1120, 1105, 1020, 914, 705, 690, 649 cm^{-1}.

(2-Chlorophenyl)(phenyl)sulfane (**3aj**).[13g] Colorless oil (90.5 mg, 82% and 89.4 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.9 Hz, 2H), 7.41–7.37 (m, 4H), 7.13–7.11 (m, 2H), 7.00–6.97 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 136.5, 133.2, 133.1, 132.6, 130.0, 129.7, 129.5, 128.3, 127.2, 127.16 ppm. IR ($CHCl_3$): ν_{max} = 3060, 3027, 2922, 1575, 1562, 1476, 1450, 1439, 1430, 1274, 1252, 1159, 1118, 1090, 1066, 1032, 1022, 1000, 912, 746, 705, 690, 660 cm^{-1}.

4-(Phenylthio)benzaldehyde (**3ak**). Colorless oil (82.5 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.53–7.50 (m, 2H), 7.43–7.40 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 191.1, 147.1, 134.3, 133.6, 131.2, 130.0, 129.7, 129.1, 127.1 ppm. IR ($CHCl_3$): ν_{max} = 3064, 3007, 2961, 2937, 2834, 2735, 1698, 1670, 1589, 1562, 1480, 1442, 1424, 1414, 1387, 1355, 1303, 1283, 1248, 1232, 1168, 1087, 1074, 1040, 1012, 992, 861, 836, 816, 777, 690 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{13}H_{10}OSK$ 253.0084; Found 253.0086.

(4-Chlorophenyl)(naphthalen-2-yl)sulfane (**3al**). White semi-solid (111.0 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.82–7.80 (m, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.76–7.74 (m, 1H), 7.49–7.48 (m, 2H), 7.39 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.27 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 134.7, 133.7, 133.0, 132.4, 132.3, 131.9, 130.3, 129.3, 129.1, 128.7, 127.7, 127.4, 126.7, 126.4 ppm. IR ($CHCl_3$): ν_{max} = 2925, 2861, 1659, 1645, 1474, 1393, 1352, 1114, 1092, 964, 907,

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868, 820, 816, 771, 748 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ calcd for $C_{16}H_{11}ClSK$ 308.9902; Found 308.9900.

(4-Bromophenyl)(naphthalen-2-yl)sulfane (**3am**). White solid (132.4 mg, 84%), M.p. = 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 1.8 Hz, 1H), 7.83–7.80 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.76–7.74 (m, 1H), 7.52–7.47 (m, 2H), 7.43–7.38 (m, 3H), 7.22–7.18 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 135.5, 133.7, 132.5, 132.2, 132.0, 130.6, 129.1, 128.9, 127.8, 127.5, 126.7, 126.5, 120.9 ppm. IR ($CHCl_3$): ν_{max} = 2923, 2864, 1664, 1471, 1386, 1356, 1114, 1085, 905, 866, 822, 812, 648 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ calcd for $C_{16}H_{11}BrSK$ 352.9396; Found 354.9395.

(2-Bromophenyl)(naphthalen-2-yl)sulfane (**3an**). Colorless oil (135.5 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.82–7.79 (m, 1H), 7.59 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54–7.52 (m, 2H), 7.48 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.12 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.04 (dt, *J* = 7.8, 1.7 Hz, 1H), 6.95 (dd, *J* = 7.8, 1.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.8, 133.9, 133.0, 133.97, 132.9, 130.3, 130.0, 129.8, 129.3, 127.8, 127.77, 127.7, 127.2, 126.8, 126.7, 122.9 ppm. IR ($CHCl_3$): ν_{max} = 3057, 2922, 2850, 1666, 1571, 1445, 1425, 1264, 1230, 1198, 1037, 1020, 961, 944, 909, 890, 858, 814, 770, 744, 626, 604 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ calcd for $C_{16}H_{11}BrSK$ 352.9396; Found 354.9395.

(4-Fluorophenyl)(naphthalen-2-yl)sulfane (**3ao**). White semi-solid (100.4 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.53–7.49 (m, 1H), 7.40–7.36 (m, 1H), 7.34 (d, *J* = 9.1 Hz, 1H), 7.18 (s, 1H), 7.03–7.00 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 162.6 and 160.2 ($J_{C\text{-}F}$ = 245.6 Hz), 156.9, 135.2, 132.9, 130.3, 129.5, 128.6 and 128.4 ($J_{C\text{-}F}$ = 25.5 Hz), 128.3 and 128.0 ($J_{C\text{-}F}$ = 27.9 Hz), 124.5, 123.9, 116.9, 116.4 and 116.2 ($J_{C\text{-}F}$ = 22.2 Hz), 108.5 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −116.30 ppm. IR ($CHCl_3$): ν_{max} = 2925, 2847, 1635, 1589, 1488, 1397, 1291, 1230, 1155, 1093, 1076, 1013, 826, 771, 622 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ calcd for $C_{16}H_{11}FSK$ 293.0197; Found 293.0198.

4-(Phenylthio)phenol (**3ap**).[13g] Yellow oil (74.8 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.18–7.11 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.25 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 155.9, 138.5, 135.5, 128.9, 128.2, 125.8, 124.5, 116.5 ppm. IR ($CHCl_3$): ν_{max} = 3384, 3071, 3054, 2924, 2854, 1639, 1599, 1583, 1494, 1478, 1439, 1361, 1264, 1217, 1169, 1098, 1081, 1022, 830, 740, 690, 530 cm^{-1}.

2-(Phenylthio)benzo[*d*]thiazole (3aq). Colorless oil (95 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.2 Hz, 1H), 7.75–7.72 (m, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.54–7.45 (m, 3H), 7.40 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.26 (dt, *J* = 7.5, 1.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.7, 153.8, 135.4, 135.3, 130.4, 129.9, 129.8, 126.1, 124.3, 121.9, 120.7 ppm. IR ($CHCl_3$): ν_{max} = 3006, 2962, 2942, 2837, 1632, 1600, 1556, 1498, 1478, 1451, 1434, 1388, 1344, 1285, 1256, 1195, 1178, 1161, 1100, 1059, 1042, 1031, 929, 902, 890, 861, 810, 744, 653 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_9NS_2Na$ 266.0069; Found 266.0077.

(4-Methoxyphenyl)(*p*-tolyl)sulfane (**3ba**).[10c] Colorless oil (93.3 mg, 81% and 91 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 6.8 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 3.82 (s, 3H), 2.32 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.4, 136.0, 134.3, 129.7, 129.3, 125.5, 114.8, 55.3, 20.9 ppm. IR ($CHCl_3$): ν_{max} = 2965, 2942, 2908, 2841, 1593, 1571, 1497, 1464, 1403, 1289, 1250, 1185, 1120, 1107, 1098, 1032, 1005, 838, 815, 798, 648, 634 cm^{-1}.

m-Tolyl(*p*-tolyl)sulfane (**3bb**).[10c] Colorless oil (87.9 mg, 82%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.3 Hz, 2H), 7.18–7.07 (m, 5H), 7.02 (d, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 138.9, 137.4, 136.6, 132.0, 131.6, 130.6, 130.0, 128.9, 127.4, 127.1, 21.3, 21.1 ppm. IR ($CHCl_3$): ν_{max} = 3074, 3054, 3016, 2922, 2864, 1593, 1573, 1492, 1474, 1403, 1302, 1181, 1163, 1117, 1105, 1081, 1046, 1017, 873, 854, 809, 688 cm^{-1}.

(2,4-Dimethoxyphenyl)(*p*-tolyl)sulfane (**3bc**). Colorless oil (96.3 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.30 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 161.3, 159.7, 135.7, 135.4, 133.3, 129.6, 128.9, 113.6, 105.2, 99.1, 55.9, 55.4, 20.9 ppm. IR ($CHCl_3$): ν_{max} = 3071, 3002, 2959, 2939, 2836, 1596, 1575, 1490, 1463, 1436, 1412, 1303, 1282, 1254, 1162, 1087, 1075, 1031, 936, 919, 834, 804, 636 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{16}O_2SNa$ 283.0763; Found 283.0758.

(2,5-Dimethoxyphenyl)(*p*-tolyl)sulfane (**3bd**). White solid (97.6 mg, 75%), M.p. = 110–112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.67 (dd, *J* = 9.3, 2.8 Hz, 1H), 6.47 (s, 1H), 3.84 (s, 3H), 3.64 (s, 3H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 153.9, 150.6, 138.1, 133.4, 130.2, 129.0, 127.4, 115.5, 111.4, 111.1, 56.4, 55.6, 21.1 ppm. IR ($CHCl_3$): ν_{max} = 3003, 2938, 2833, 1598, 1584, 1508, 1485, 1459, 1440, 1432, 1407, 1324, 1298, 1274, 1232, 1216, 1188, 1176, 1149, 1141, 1105, 1059, 1045, 1019, 807, 790, 737, 709 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{16}O_2SNa$ 283.0763; Found 283.0761.

(3-Bromophenyl)(*p*-tolyl)sulfane (**3be**). Colorless oil (108.9 mg, 78% and 110.3 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.33 (m, 3H), 7.29–7.27 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14–7.08 (m, 2H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.3, 138.5, 133.3, 131.1, 130.3, 130.2, 129.5, 129.0, 127.2, 122.9, 21.2 ppm. IR ($CHCl_3$): ν_{max} = 3054, 3023, 2918, 2861, 1574, 1556, 1492, 1458, 1402, 1300, 1286, 1254, 1247, 1180, 1147, 1117, 1081, 1068, 1017, 993, 866, 810, 773, 715, 705, 677, 653 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ calcd for $C_{13}H_{11}BrSK$ 316.9396; Found 316.9404.

Biphenyl-4-yl(*p*-tolyl)sulfane (**3bf**). White solid (103.6 mg, 75%), M.p. 104–106 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.36–7.32 (m, 5H), 7.17 (d, *J* = 8.1 Hz, 2H), 2.17 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 140.4, 139.3, 137.7, 136.3, 132.4, 131.1, 130.1, 130.0, 128.8, 127.7, 127.3, 126.9, 21.1 ppm. IR ($CHCl_3$): ν_{max} = 3063, 2919,

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1592, 1578, 1507, 1489, 1476, 1446, 1394, 1374, 1178, 1161, 1125, 1105, 1085, 1046, 1019, 903, 825, 811, 688 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{19}H_{16}SK$ 315.0604; Found 315.0603.

(4-Bromophenyl)(*p*-tolyl)sulfane (**3bg**).[13g] White solid (114.5 mg, 82% and 117.2 mg, 84%), M.p. = 81–84 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38 (dd, *J* = 6.7, 2.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 6.7, 2.0 Hz, 2H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 138.1, 136.7, 132.6, 132.0, 130.8, 130.3, 130.2, 120.0, 21.1 ppm. IR ($CHCl_3$): ν_{max} = 3077, 3054, 2959, 2861, 1491, 1472, 1388, 1363, 1307, 1110, 1095, 1082, 1006, 829, 811, 729, 705 cm^{-1}.

(4-Iodophenyl)(*p*-tolyl)sulfane (**3bh**)**.** Yellow solid (146.8 mg, 90%), M.p. = 98–100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 8.3 Hz, 2H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.2, 137.9, 137.8, 132.9, 130.8, 130.2, 130.0, 91.0, 21.2 ppm. IR ($CHCl_3$): ν_{max} = 2913, 1652, 1493, 1470, 1383, 1303, 1220, 1112, 1083, 1039, 873, 807, 770, 517 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{13}H_{11}ISK$ 364.9258; Found 364.9253.

Bis(4-methoxyphenyl)sulfane (**3bi**).[10c] Colorless oil (97.3 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.79 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.9, 132.6, 127.3, 114.7, 55.2 ppm. IR ($CHCl_3$): ν_{max} = 3084, 3013, 2965, 2945, 2911, 2842, 1592, 1571, 1495, 1468, 1440, 1403, 1342, 1286, 1249, 1237, 1185, 1176, 1154, 1119, 1107, 1098, 1032, 1007, 837, 814, 798 cm^{-1}.

Biphenyl-4-yl(4-methoxyphenyl)sulfane (**3bj**). White solid (105.3 mg, 72%), M.p. = 90–93 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.0 Hz, 2H), 7.54–7.40 (m, 6H), 7.35–7.31 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.9, 140.4, 138.7, 137.7, 135.4, 128.8, 128.5, 127.6, 127.2, 126.8, 124.2, 115.0, 55.4 ppm. IR ($CHCl_3$): ν_{max} = 2962, 2938, 2840, 1590, 1493, 1479, 1479, 1397, 1289, 1247, 1219, 1183, 1173, 1129, 1100, 1032, 910, 838, 828, 766, 688 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{19}H_{16}OSK$ 331.0553; Found 331.0554.

Biphenyl-4-yl(2-bromophenyl)sulfane (**3bk**). Colorless oil (124.6 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.60 (m, 5H), 7.55–7.53 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.42–7.38 (m, 1H), 7.21–7.17 (m, 1H), 7.09–7.04 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.0, 138.7, 133.7, 133.0, 131.7, 129.8, 128.8, 128.2, 127.8, 127.7, 127.3, 127.0, 123.0 ppm. IR ($CHCl_3$): ν_{max} = 3064, 3054, 3027, 1592, 1576, 1554, 1477, 1445, 1428, 1396, 1360, 1334, 1274, 1251, 1176, 1106, 1095, 1038, 1016, 1006, 911, 839, 746, 718, 690, 662 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{18}H_{13}BrSK$ 378.9553; Found 378.9555.

Biphenyl-4-yl(2-chlorophenyl)sulfane (**3bl**). Colorless oil (111.3 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.49–7.44 (m, 4H), 7.40–7.36 (m, 3H), 7.08 (t, *J* = 8.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.6, 161.1, 140.2, 139.7, 135.7, 134.1, 134.06, 130.2, 128.8, 127.8, 127.4, 126.9, 116.5, 116.3 ppm. IR ($CHCl_3$): ν_{max} = 3061, 3044, 3033, 1592, 1574, 1559, 1477, 1445, 1429, 1395, 1357, 1339, 1273, 1252, 1178, 1159, 1106, 1093, 1018, 910, 839, 746, 690 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + Na]^+$ calcd for $C_{18}H_{13}ClSNa$ 319.0319; Found 319.0315.

Biphenyl-4-yl(4-fluorophenyl)sulfane (3bm). White semi-solid (113.5 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.46–7.41 (m, 4H), 7.37–7.32 (m, 3H), 7.05 (t, *J* = 8.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.2 and 139.7 ($J_{C\text{-}F}$ = 50.4 Hz), 135.7, 134.18 and 134.1 ($J_{C\text{-}F}$ = 7.9 Hz), 130.2, 128.8, 127.8, 127.5, 126.9, 116.6 and 116.3 ($J_{C\text{-}F}$ = 22.1 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –113.8 ppm. IR ($CHCl_3$): ν_{max} = 3061, 3030, 2952, 2922, 2894, 2854, 1588, 1508, 1491, 1478, 1397, 1224, 1154, 1090, 1049, 909, 826, 690, 670, 624 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + H]^+$ calcd for $C_{18}H_{14}SF$ 281.0795; Found 281.0788.

(4-Chlorophenyl)(4-methoxyphenyl)sulfane (**3bn**).[29] White semi-solid (102.8 mg, 82% and 101.5 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.0, 137.3, 135.5, 131.6, 129.3, 129.0, 123.7, 115.1, 55.4 ppm. IR ($CHCl_3$): ν_{max} = 3084, 2967, 2938, 2839, 1589, 1568, 1495, 1475, 1408, 1390, 1287, 1250, 1180, 1173, 1114, 1103, 1090, 1026, 1009, 837, 819, 741 cm^{-1}.

(4-Chlorophenyl)(4-fluorophenyl)sulfane (**3bo**). Colorless oil (96.7 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38 (dd, *J* = 8.9, 2.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H) ppm.$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 163.5 and 161.6 ($J_{C\text{-}F}$ = 248.7 Hz), 135.4, 134.4 and 134.3 ($J_{C\text{-}F}$ = 8.2 Hz), 132.7, 131.0, 129.6, 129.3, 116.7 and 116.5 ($J_{C\text{-}F}$ = 21.9 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –113.29 ppm. IR ($CHCl_3$): ν_{max} = 3074, 3027, 2939, 1589, 1505, 1489, 1475, 1391, 1290, 1230, 1156, 1089, 1012, 832, 817, 746, 639, 625 cm^{-1}. HRMS (ESI-TOF) *m/*z: $[M + K]^+$ calcd for $C_{12}H_8ClFSK$ 276.9651; Found 276.9652.

Bis(4-chlorophenyl)sulfane (**3bp**).[26] White solid (116 mg, 91%), M.p. = 95–97 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.8 Hz, 4H), 7.25 (d, *J* = 8.8 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 134.0, 133.5, 132.3, 129.5 ppm. IR ($CHCl_3$): ν_{max} = 3081, 2925, 2844, 1523, 1474, 1425, 1394, 1295, 1249, 1094, 1078, 1011, 824, 814, 742 cm^{-1}.

(4-Bromophenyl)(4-chlorophenyl)sulfane (**3bq**).[13d] White solid (113.8 mg, 76%), M.p. = 96–99 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.17 (d, *J* = 8.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 134.7, 133.6, 133.5, 132.5, 132.3, 132.28, 129.5, 121.3 ppm. IR ($CHCl_3$): ν_{max} = 3088, 3069, 3054, 2942, 2850, 1493, 1473, 1391, 1093, 1085, 1069, 1008, 954, 820, 811, 743, 726 cm^{-1}.

Bis(4-bromophenyl)sulfane (**3br**).[26] White solid (134.2 mg, 78%), M.p. = 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.7 Hz, 4H), 7.18 (d, *J* = 8.5 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 134.4, 132.5, 132.4, 121.4 ppm. IR ($CHCl_3$): ν_{max} = 3062, 3040, 1503, 1486, 1472, 1391, 1090, 1081, 1066, 1007, 956, 815, 810, 724 cm^{-1}.

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(4-Bromophenyl)(4-fluorophenyl)sulfane (**3bs**). Yellow oil (103.3 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 4H), 7.11–6.99 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ= 163.8 and 161.3 ($J_{C\text{-}F}$ = 249 Hz), 136.2, 134.54 and 134.46 ($J_{C\text{-}F}$ = 7.8 Hz), 132.2, 131.0, 129.27 and 129.24 ($J_{C\text{-}F}$ = 3.2 Hz), 120.5, 116.7 and 116.5 ($J_{C\text{-}F}$ = 21.4 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –113.0 ppm. IR ($CHCl_3$): ν_{max} = 3067, 2922, 1473, 1391, 1092, 1082, 1068, 1007, 953, 819, 809, 727 cm^{-1}. HRMS (ESI-TOF) *m/*z: [M + K]$^+$ calcd for $C_{12}H_8BrFSK$ 320.9146; Found 320.9145.

4-(4-Bromophenylthio)benzaldehyde (**3bt**). White Solid (118.7 mg, 81%), M.p. = 62–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ= 191.0, 146.0, 135.4, 133.9, 132.9, 130.7, 130.2, 127.6, 123.4 ppm. IR ($CHCl_3$): ν_{max} = 2925, 2845, 2740, 1699, 1673, 1590, 1563, 1472, 1409, 1387, 1302, 1283, 1168, 1089, 1078, 1008, 836, 820, 809, 771, 728, 693, 666 cm^{-1}. HRMS (ESI-TOF) *m/*z: [M + K]$^+$ calcd for $C_{13}H_9BrOSK$ 330.9189; Found 330.9189.

(4-Bromophenyl)(2,5-dimethoxyphenyl)sulfan*e* (3bu). Colorless oil (117.0 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.78 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ= 153.9, 151.8, 133.8, 132.6, 132.2, 124.1, 121.0, 117.7, 113.3, 112.0, 56.5, 55.7 ppm. IR ($CHCl_3$): ν_{max} = 2999, 2959, 2937, 2834, 1596, 1584, 1566, 1486, 1472, 1456, 1442, 1408, 1385, 1325, 1277, 1221, 1189, 1141, 1059, 1045, 1019, 1010, 862, 816, 801, 792, 739, 731, 688 cm^{-1}. HRMS (ESI-TOF) *m/*z: [M + K]$^+$ calcd for $C_{14}H_{13}BrSO_2K$ 362.9451; Found 362.9448.

4-(3-Methoxyphenylthio)benzaldehyde (**3bv**). Colorless oil (90.4 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.88 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 2.2 Hz, 1H), 6.93 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.78 (s, 3H) ppm.$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 191.1, 160.3, 146.8, 133.6, 132.3, 130.5, 130.0, 127.3, 126.2, 119.1, 115.0, 55.3 ppm. IR ($CHCl_3$): ν_{max} = 3061, 3006, 2961, 2936, 2834, 2734, 1697, 1672, 1590, 1563, 1480, 1442, 1425, 1415, 1387, 1303, 1283, 1247, 1232, 1168, 1087, 1073, 1041, 1013, 993, 861, 836, 816, 778, 690, 629 cm^{-1}. HRMS (ESI-TOF) *m/*z: [M + K]$^+$ calcd for $C_{14}H_{12}O_2SK$ 283.0190; Found 283.0185.

3-(4-Hydroxyphenylthio)phenol (**3bw**). Colorless oil (84.0 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.66 (d, *J* = 5.9 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.82 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.35–7.32 (m, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 157.1, 155.3, 148.8, 137.7, 133.0, 127.5, 124.2, 121.9, 116.2 ppm. IR ($CHCl_3$): ν_{max} = 3383, 3077, 3054, 2929, 2861, 1658, 1595, 1581, 1561, 1492, 1458, 1424, 1362, 1267, 1241, 1167, 1093, 1041, 1003, 907, 828, 815, 809, 624, 600 cm^{-1}. HRMS (ESI-TOF) *m/*z: [M + H]$^+$ calcd for $C_{12}H_{11}O_2S$ 219.0475; Found 219.0469.

General procedure for synthesis of diarylsulfoxides (5a-d). To a stirred solution of **3ab**, **3ac**, **3af** or **3ag** (0.5 mmol) in MeOH (2 mL) were added $ZnCl_2$ (3.4 mg, 0.025 mmol, 5 mol%) and DBU (3.8 mg, 0.025 mmol, 5 mol%). Then H_2O_2 (2 mmol, 4 equiv) was added at room temperature and the mixture stirred for 10 h at 80 °C. After completion of the reaction, MeOH was evaporated and the mixture extracted with EtOAc (2 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to give **5a**-**d**.

1-Methyl-4-(phenylsulfinyl)benzene (**5a**).[26] White solid (89.8 mg, 83%), M. p. = 64–65 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.62 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.46–7.42 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 145.7, 142.4, 141.7, 130.9, 130.0, 129.2, 125.0 124.7, 21.4 ppm. IR ($CHCl_3$): ν_{max} = 2924, 2853, 1654, 1591, 1493, 1443, 1400, 1384, 1307, 1087, 1046, 1015, 955, 914, 814, 750, 705, 687, 621 cm^{-1}.

1-Methoxy-4-(phenylsulfinyl)benzene (**5b**).[26] White solid (102.2 mg, 88%), M.p. = 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.45–7.39 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 161.9, 145.6, 136.6, 130.6, 129.1, 127.1, 124.5, 114.7, 55.4 ppm. IR ($CHCl_3$): ν_{max} = 3071, 3002, 2959, 2939, 2836, 1596, 1575, 1490, 1463, 1436, 1412, 1303, 1282, 1254, 1210, 1162, 1087, 1075, 1031, 936, 919, 834, 804, 636 cm^{-1}.

1-Chloro-4-(phenylsulfinyl)benzene (**5c**).[27] Colorless oil (95.9 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.63–7.62 (m, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.47–7.42 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 145.4, 144.3, 137.3, 131.4, 129.7, 129.5, 126.1, 124.8 ppm. IR ($CHCl_3$): ν_{max} = 3081, 3057, 2928, 2854, 1655, 1644, 1571, 1474, 1444, 1390, 1171, 1086, 1048, 1011, 914, 823, 751, 740, 703, 688 cm^{-1}.

1-Bromo-4-(phenylsulfinyl)benzene (**5d**).[27] Colorless oil (106.8 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.63–7.61 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.47–7.45 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ= 145.2, 144.8, 132.6, 131.4, 129.5, 126.3, 125.6, 124.8 ppm. IR ($CHCl_3$): ν_{max} = 2928, 1653, 1573, 1444, 1387, 1324, 1308, 1274, 1157, 1105, 1069, 1009, 812, 744, 687, 604 cm^{-1}.

General procedure for synthesis of diarylsulfones (6a-c). To a stirred solution of **3ac**, **3af** or **3ag** (0.5 mmol) in MeOH (2 mL) were added $ZnCl_2$ (6.8 mg, 0.05 mmol,10 mol%) and DBU (19 mg, 0.125 mmol, 25 mol%). Then H_2O_2 (2 mmol, 4 equiv) was added at room temperature and the mixture stirred for 16 h at 80 °C. After completion of the reaction, MeOH was evaporated and the mixture extracted with EtOAc (2 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to give **6a**-**c**.

1-Methoxy-4-(phenylsulfonyl)benzene (**6a**).[28] White solid (101.8 mg, 82%). M.p. = 91–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.90 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.53–7.50 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 163.3, 142.2, 133.0, 132.8, 129.8, 129.1, 127.2,

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114.4, 55.6 ppm. IR ($CHCl_3$): ν_{max} = 2942, 1594, 1574, 1496, 1466, 1446, 1315, 1297, 1261, 1183, 1147, 1107, 1072, 1017, 909, 836, 804, 729, 693, 653, 626, 577, 556 cm^{-1}.

1-Bromo-4-(phenylsulfonyl)benzene (**6b**).[28] Yellow solid (114.4 mg, 77%). M.p. = 101–104 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.91 (m, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.59–7.56 (m, 1H), 7.52–7.49 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 141.1, 140.6, 133.4, 132.6, 129.4, 129.2, 128.4, 127.6 ppm. IR ($CHCl_3$): ν_{max} = 3092, 3067, 2918, 1578, 1474, 1447, 1391, 1319, 1310, 1281, 1175, 1155, 1108, 1088, 1068, 834, 824, 768, 721, 687, 612, 568 cm^{-1}.

1-Chloro-4-(phenylsulfonyl)benzene (**6c**).[28] White solid (99.8 mg, 79%), M.p. = 94–95 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.59–7.45 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.1, 140.1, 139.8, 133.4, 129.6, 129.4, 129.1, 127.6 ppm. IR ($CHCl_3$): ν_{max} = 3094, 2928, 1654, 1582, 1475, 1445, 1393, 1322, 1309, 1281, 1173, 1158, 1107, 1088, 1071, 1009, 828, 752, 720, 688, 616, 567 cm^{-1}.

4,4'-Thiodiphenol (**3bx**).[29] The titled compound was prepared from **1p** (82.8 mg, 0.6 mmol) and **2p** (63.1 mg, 0.5 mmol) by following similar procedure as described for **3ab** to give **3bx** (88.4 mg, 81%) as white solid, M.p. = 155–157 °C. ^1H NMR (400 MHz, DMSO-d_6): δ = 9.62 (s, 2H), 7.13 (d, *J* = 8.6 Hz, 4H), 6.73 (d, *J* = 8.7 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ = 157.0, 132.8, 124.6, 116.3 ppm. IR ($CHCl_3$): ν_{max} = 3317, 2925, 1629, 1600, 1584, 1492, 1440, 1376, 1235, 1168, 1047, 936, 822, 770, 575 cm^{-1}.

4,4'-Sulfonyldiphenol (**6d**).[26] The titled compound was prepared from **3bx** (109.1 mg, 0.5 mmol) by following a similar procedure as described for **6a** to give **6d** (103.9 mg, 83%) as white solid, M.p. = 238–241 °C. ^1H NMR (400 MHz, CD_3OD): δ = 7.90 (d, *J* = 8.9 Hz, 4H), 7.05 (d, *J* = 8.9 Hz, 4H), 5.05 (s, 2H), ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ = 164.6, 135.1, 132.0, 118.2 ppm. IR ($CHCl_3$): ν_{max} = 3416, 2922, 1643, 1378, 1300, 1219, 1149, 1107, 1049, 820, 771, 719, 558 cm^{-1}.

2-(2-Bromophenylthio)aniline (3by).[30] The titled compound was prepared from **1q** (82.1 mg, 0.6 mmol) and **2y** (94.5 mg, 0.5 mmol) by following similar procedure as described for **3ab** to give **3by** (117.7 mg, 84%) as yellow solid, M.p. = 58–60 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (dt, *J* = 7.5, 1.4 Hz, 1H), 6.84–6.78 (m, 2H), 6.63 (dd, *J* = 8.0 Hz, 1.3 Hz, 1H), 4.06 (br s, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.9, 137.9, 137.8, 132.7, 131.7, 127.7, 126.23, 126.2, 120.7, 119.1, 115.5, 113.2 ppm. IR ($CHCl_3$): ν_{max} = 3467, 3368, 3062, 1607, 1478, 1445, 1427, 1309, 1271, 1250, 1159, 1134, 1102, 1036, 1018, 940, 848, 836, 750, 650 cm^{-1}.

4-(4-Nitrophenylthio)aniline (**3bz**).[31] The titled compound was prepared from **1r** (82.1 mg, 0.6 mmol) and **2z** (77.6 mg, 0.5 mmol) by following similar procedure as described for **3ab** to give **3bz** (97.3 mg, 79%) as yellow solid, M.p. = 142–145 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 151.0, 148.3, 144.8, 125.2, 123.9, 116.4, 116.1 ppm. IR ($CHCl_3$): ν_{max} = 3474, 3380, 2938, 1621, 1576, 1492, 1331, 1295, 1183, 1079, 1049, 910, 851, 841, 826, 743 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{11}N_2O_2S$ 247.0536; Found 247.0532.

Conflicts of interest

There are no conflicts to declare.

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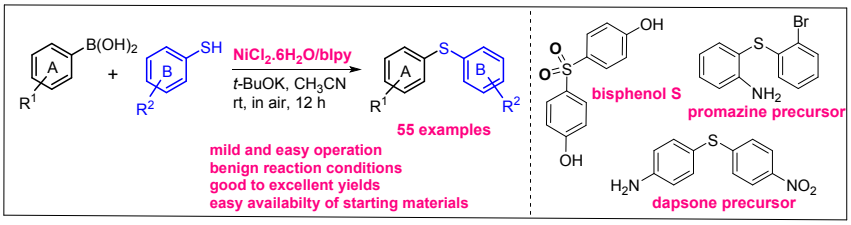
Abstract



A mild and easily operated $NiCl_2$/2,2′-bipyridine-catalyzed cross-coupling of thiophenols with arylboronic acids for the synthesis of symmetric and unsymmetric diarylsulfides has been developed at room temperature and in air conditions.