Article

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Forging C-S Bonds through Nickel-Catalyzed Aryl Anhydrides with Thiophenols : Decarbonylation or Decarbonylation Accompanied by Decarboxylation

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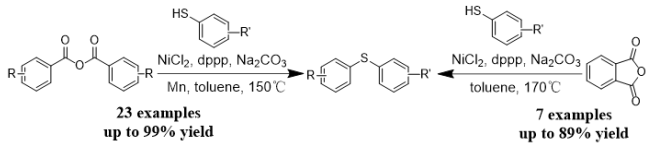


Abstract

A nickel-catalyzed decarbonylation or decarbonylation accompanied by decarboxylation cross-coupling reaction of aryl anhydrides with thiophenols as coupling partners was disclosed. This method is promoted by a commercially-available, moisture-stable and inexpensive nickel(II) precatalyst. The process can tolerate a variety of functional groups, using ubiquitous aryl anhydrides as cross-coupling precursors to produce thioethers in moderate to excellent yields.

Introduction

Aryl sulfides are an important motif, frequently found in biologically and pharmaceutically active compounds (Figure 1).[1] They are also used in advanced materials and industrial chemicals such as organic semiconductors, herbicides, lubricants, and high boiling point solvents.[2] Therefore, the development of effective C-S bonds construction methods is still receiving widespread attention. The cross-coupling reactions of aryl halides with thiols and arylboronic acids with thiols are representative methods for constructing C-S bonds.[3] In recent years, the method of constructing C-S bonds by decarbonylation has attracted people's attention. Many research groups have explored the principle of decarbonylation and used several excellent transition metals such as Pd,[4] Rh,[5] Ir,[6] and Ni[7] to drive the reaction forward. In recent years, there has been an increasing interest in nickel catalysis because of its non-toxic, environmentally friendly and lower price. For example, in 2017, Eric W. Reinheimer and

Jessie Weatherly[8] reported the first systematic study of Ni(0) precursor $Ni(COD)_2$ catalyzed decarbonylation of aromatic aldehydes (**Scheme 1**, a). In the same year, Marc A. Hillmyer and William B. Tolman[9] reported that nickel catalyzed the decarbonylation of carboxylic acids to olefins (**Scheme 1**, b). Recently, Magnus Rueping's group[10] developed a method for decarbonylation using a stable nickel source (II) as a catalyst (**Scheme 1**, c). At the same time, Chengwei Liu and Michal Szostak[11] had the same research discoverys (**Scheme 1**, d). Therefore, nickel-catalyzed cross-coupling reactions have become a rapidly growing field in synthetic chemistry. However, conventional decarbonylation reactions typically use Ni(0) catalysts[12] that are sensitive to air and moisture, which makes the reaction conditions somewhat limited. Both Magnus Rueping and Michal Szostak's research teams used air-stable, easy-to-handle and manipulable $NiCl_2$ and dppp catalytic systems to successfully decarbonylate to give thioethers. Therefore, our laboratory considers the use of aryl anhydrides that are easy to synthesize and widely exist in nature as aryl sources, and utilizes the nucleophilicity of S to obtain thioethers.

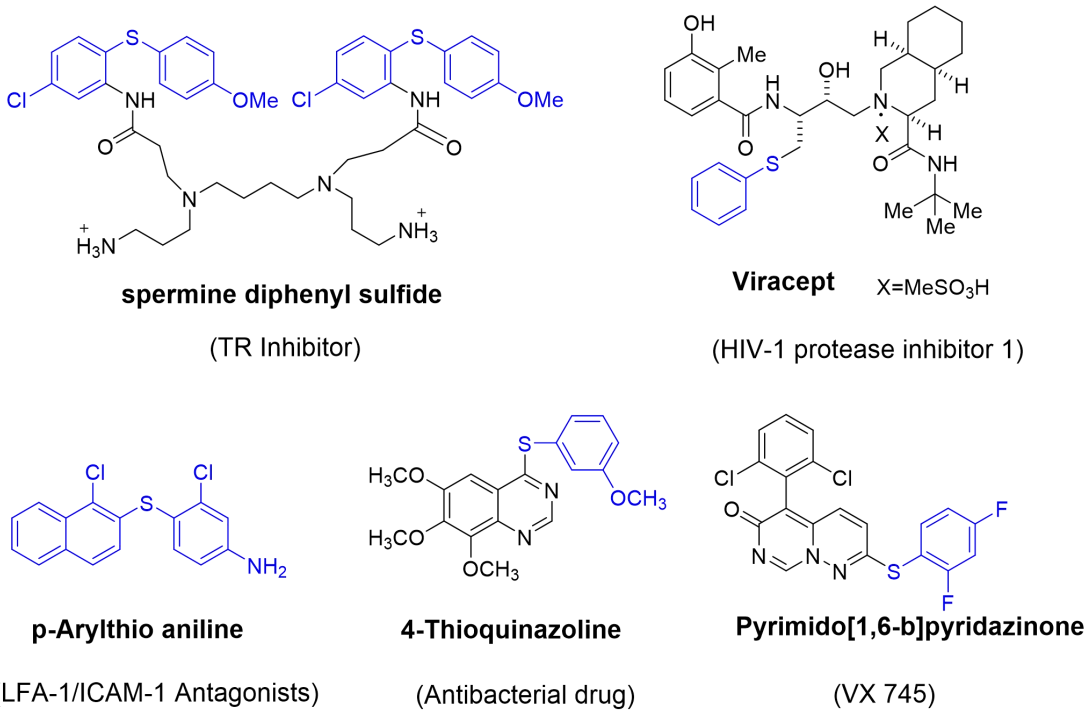
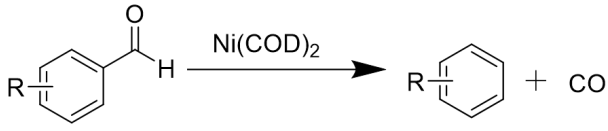


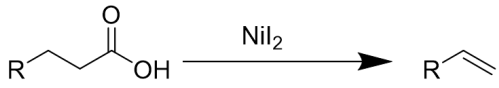
Figure 1. Examples of pharmaceutically-relevant aryl thioethers

Scheme 1. Application of nickel in decarbonylation

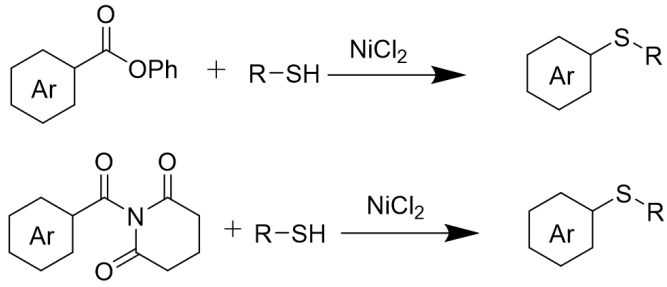
a) Eric W. Reinheimer and Jessie Weatherly's work (2017)



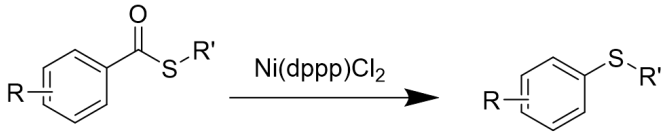
b) Marc A. Hillmyer and William B. Tolman's work(2017)



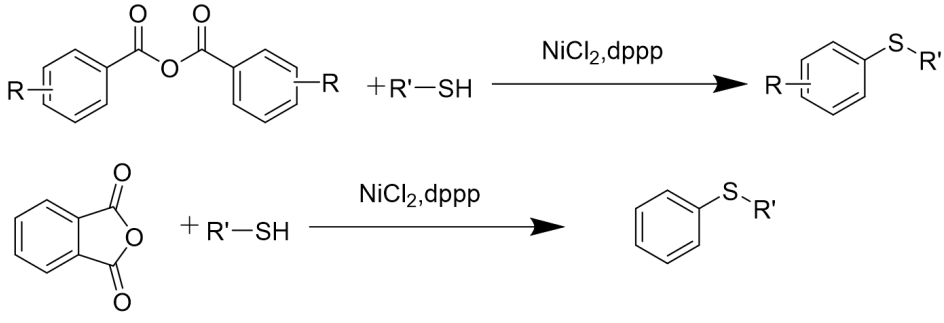
c) Magnus Rueping's work (2018)



d) Chengwei Liu and Michal Szostak's work (2018)



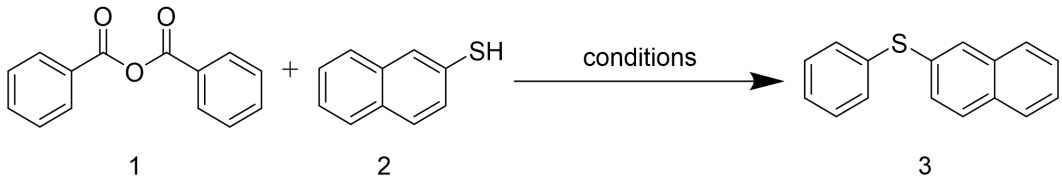
e) This study



Results and Discussion

The reaction was optimized using benzoic anhydride and naphthalene-2-thiol as model substrates. Considering economic factor and stability to air and moisture, we chose nickel (II) as a catalyst. Key optimization experiments are summarized in Table 1.

Table 1. Optimization of Reaction Condition[a]



Entry	Ni cat. (mol%)	Ligand (mol%)	Solvent	Base	Additive	Yield
1	$NiCl_2$	dppp	toluene	K_2CO_3	Mn	19%
2	$NiCl_2$	dppp	toluene	Cs_2CO_3	Mn	23%
3	$NiCl_2$	dppp	toluene	Na_2CO_3	Mn	95%
4	$NiCl_2$	dppp	toluene	/	Mn	28%
5	$NiCl_2$	dppp	1,4-dioxane	Na_2CO_3	Mn	55%
6	$NiCl_2$	dppp	DMSO	Na_2CO_3	Mn	30%
7	$NiCl_2$	dppp	DMF	Na_2CO_3	Mn	40%
8	$Ni(OAC)_2{\cdot}H_2O$	dppp	toluene	Na_2CO_3	Mn	80%
9	$Ni(acac)_2$	dppp	toluene	Na_2CO_3	Mn	76%
10	$NiBr_2$	dppp	toluene	Na_2CO_3	Mn	83%
11	$NiCl_2$	dppe	toluene	Na_2CO_3	Mn	76%
12	$NiCl_2$	Pcy_3	toluene	Na_2CO_3	Mn	83%
13	$NiCl_2$	dppf	toluene	Na_2CO_3	Mn	85%
14	$NiCl_2$	dppp	toluene	Na_2CO_3	Mg	64%
15	$NiCl_2$	dppp	toluene	Na_2CO_3	Zn	67%

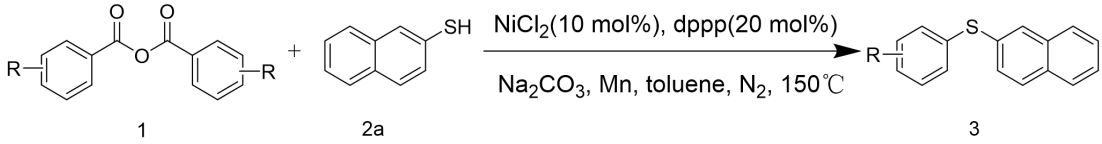
16	$NiCl_2$	dppp	toluene	Na_2CO_3	/	72%

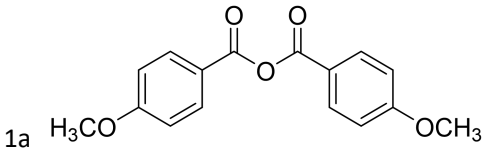
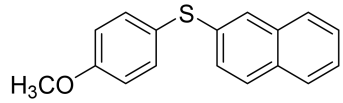
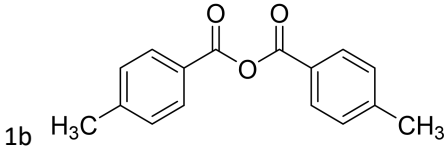
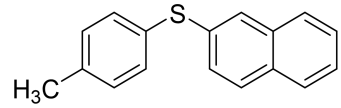
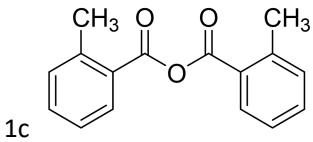
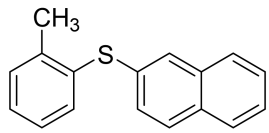
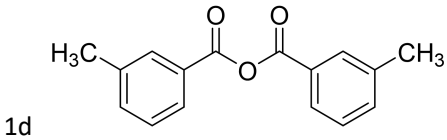
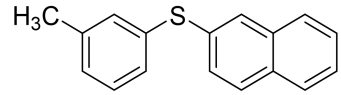
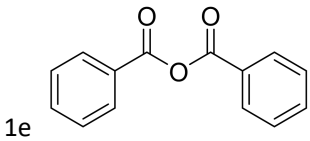
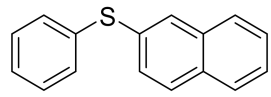
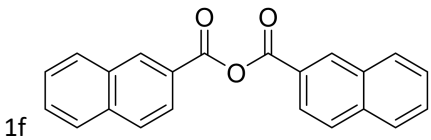
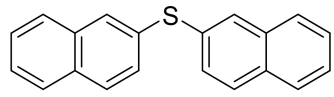
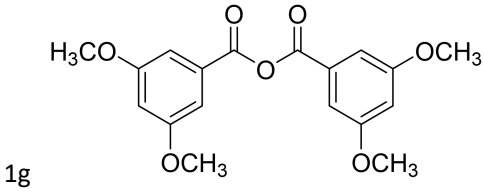
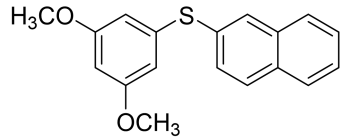
[a]General conditions: the reactions were run on a 0.5 mmol of naphthalene-2-thiol in solvent (1.5 mL), benzoic anhydride (1.2 equiv.), catalyst (10 mol%), ligand (20 mol%), base (0.2 equiv.), additive (1 equiv.) under nitrogen in a sealed tube at 150°C for 24 h. Isolated yield after purification of column chromatography.

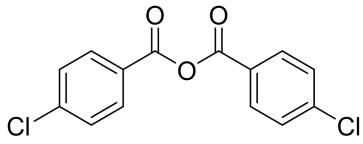
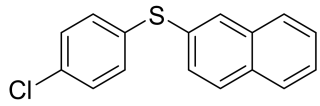
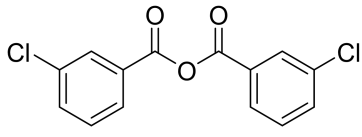
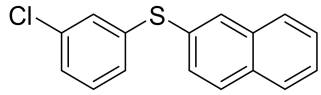
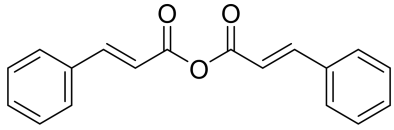
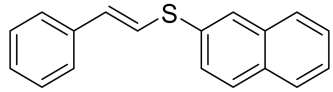
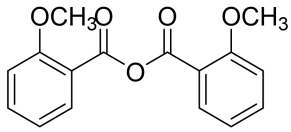
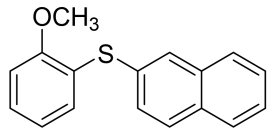
When the reaction was run in the presence of $NiCl_2$ (10 mol%), dppp (20 mol%), K_2CO_3 (0.2 equiv.) and reducing agents Mn in toluene for 24 h under nitrogen, the desired product naphthalen-2-yl(phenyl)sulfane was obtained in 19 % yield (Table 1, entry 1). To our delight, the yield was raised to 95% when inorganic base Na_2CO_3 was used (Table1, entry 3). Compared with other commercially available bases, Na_2CO_3 was optimal for this reaction. In addition, without adding alkali, the reaction does not work well (Table 1, entries 1–4). The results indicated that a suitable inorganic base played an important role in the decarbonylation process. Solvent screening revealed that when the polarity of the solvent increased, the amount of by-products also increased, and the raw materials couldn't be completely reacted. Toluene was clearly superior to other solvents (Table 1, entries 5-7). Compared with other nickle sources, $NiCl_2$ was optimal for this reaction (Table 1, entries 8-10). Switching to other ligands, such as dppe, pcy_3, or dppf, yield was reduced compared to dppp ligand (Table 1, entries 11–13). In order to determine the role of the reducing agent in the reaction, we replaced different reducing agents, such as Mg, Zn. It was found that Mn had the best reactivity in this reaction (Table 1, entries 14–16). Thus, the best conditions for this reaction were thiophenol(1 equiv.), aryl anhydride (1.2 equiv), $NiCl_2$ (10 mol%) and dppp (20 mol%) as the catalyst system, with Na_2CO_3 (0.2 equiv) as the base and toluene as the solvent under nitrogen atmosphere at 150°C.

Having optimized the reaction conditions, the substrate scope of this nickle-catalyzed decarbonylation reaction was investigated. As illustrated in Table 2, a wide variety of reactants bearing either electron-withdrawing or electron-donating substituents on the aryl ring could be transformed into the corresponding compounds 3 in moderate to excellent yields. Halogens, methyl, methoxyl, aryl, aliphatic groups were well-tolerated in this system, and yielded desired products over 80% (Table 2, entries 1−11). The steric hindrance does not have much effect on the yield (Table 2, 3c, 3k).

Table 2. Reactions of different aryl anhydrides with 2-naphthylthiophenol to synthesize various Aryl sulfides.[a,b]



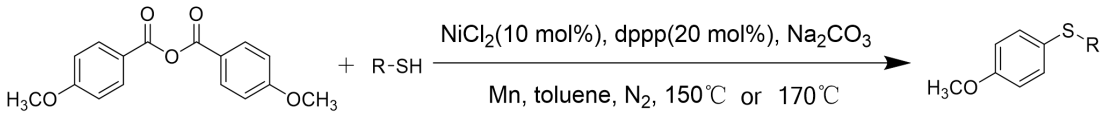
Entry	Substrate	Product	Yield[b]
1	 1a	 3a	92%
2	 1b	 3b	99%
3	 1c	 3c	89%
4	 1d	 3d	94%
5	 1e	 3e	95%
6	 1f	 3f	96%
7	 1g	 3g	99%

8	1h 		3h 	80%
9	1i 		3i 	82%
10	1j 		3j 	98%
11	1k 		3k 	96%

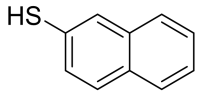
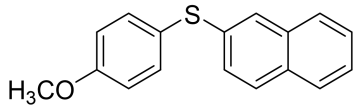
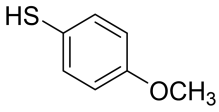
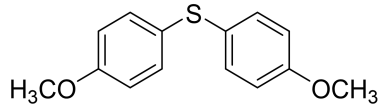
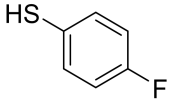
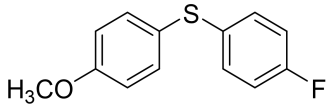
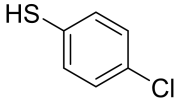
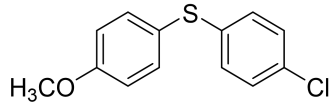
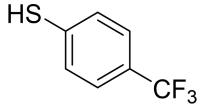
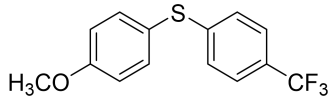
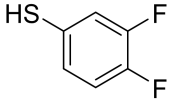
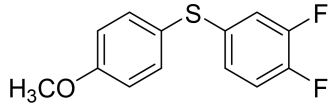
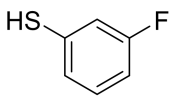
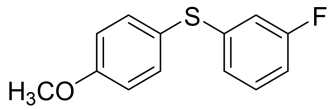
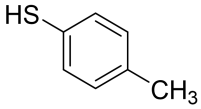
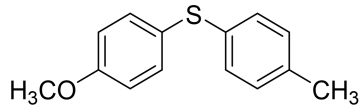
[a]General conditions: the reactions were run on a 0.5 mmol of naphthalene-2-thiol under nitrogen in a sealed tube, using 1 (1.2 equiv.), $NiCl_2$ (10 mol%), dppp (20 mol%), Mn(2 equiv.), Na_2CO_3 (0.2 equiv.) in toluene (1.5 mL) at 150 °C for 24 h. [b] Isolated yields.

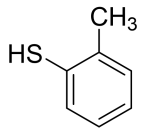
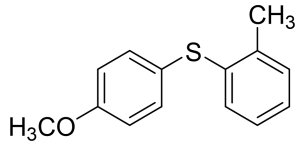
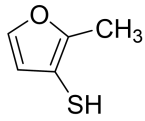
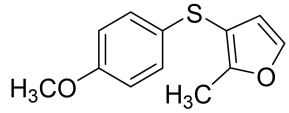
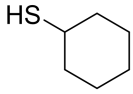
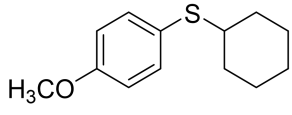
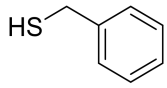
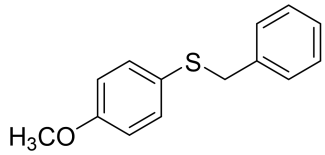
Next, we explored the flexibility of the method for various thiophenols or thiols, using 4-Methoxyphenyl anhydride as a substrate (Table 3). Both electron-rich and electron-poor groups were effectively decarbonylated to get thioethers. And the electron-withdrawing decreases with respect to the yield of electron donating groups (Table 3, 4c-4g). In addition, the steric hindrance effect has little effect on the yield (Table 3, 4i, 4j). Fortunately, aliphatic thiols gave the corresponding products in moderate to high yields (Table 3, 4k, 4l).

Table 3. Reactions of different thiophenols or thiols with 4-methoxybenzoic anhydride to synthesize various aryl sulfides.[a,b]



1a 2 4

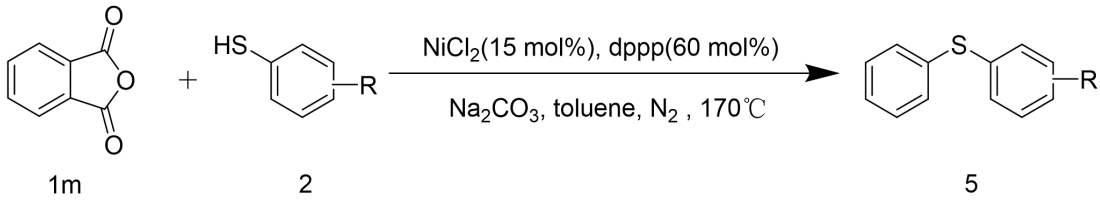
Entry	Substrate	Product	Yield[b]
1	2a 	3a 	92%
2	2b 	4b 	96%[c]
3	2c 	4c 	83%
4	2d 	4d 	75%
5	2e 	4e 	52%
6	2f 	4f 	71%
7	2g 	4g 	74%
8	2h 	4h 	85%

9	 2i		 4i	99%
10	 2j		 4j	83%[c]
11	 2k		 4k	88%[c]
12	 2l		 4l	70%[c]

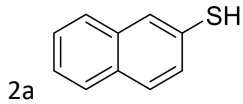
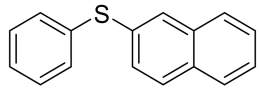
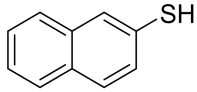
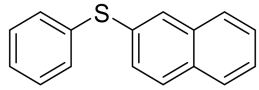
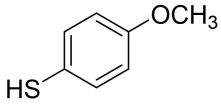
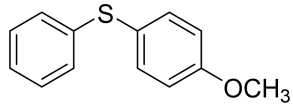
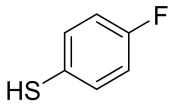
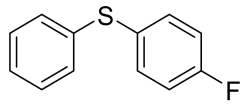
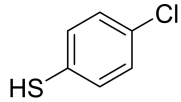
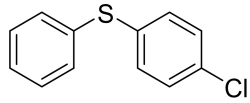
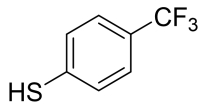
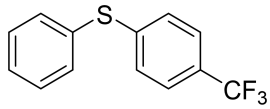
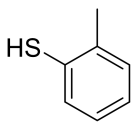
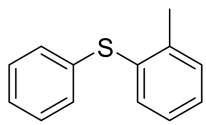
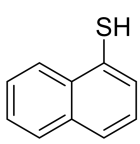
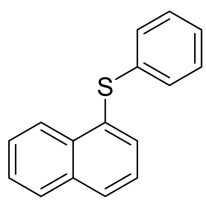
[a]General conditions: the reactions were run on a 0.5 mmol of thiophenols under nitrogen in a sealed tube, using 1a (1.2 equiv.), $NiCl_2$ (10 mol%), dppp (20 mol%), Mn(2 equiv.), Na_2CO_3 (0.2 equiv.) in toluene (1.5 mL) at 150 °C for 24 h. [b] Isolated yields. [c] 170 °C and 48 h

We also apply this method to phthalic anhydride, but only a small amount of target products were produced, most of which were self-coupling products, so we changed the original conditions. Considering that the dppp ligand can also act as a reducing agent in this reaction, first we reacted at 150°C for 48 hours without adding a manganese reducing agent. Found that there were fewer target products and self-couplig products were also observed, but surprisingly there was a large amount of thioester formed (Table 4, 3e'). This result indicates that the reaction is also feasible for the cyclic anhydride, and the principle of the reaction is that the decarbonylation is accompanied by decarboxylation. In order to improve the yield, we further optimized reaction conditions. It was found that after increasing the ratio of the catalyst to the ligand and the amount of the base, the reaction proceeded well, yielding 89% of the desired product. Therefore, we explored the coupling reaction of phthalic anhydride with other thiophenols.

Table 4. Reactions of different thiophenols with phthalic anhydride to synthesize various aryl sulfides.[a,b]



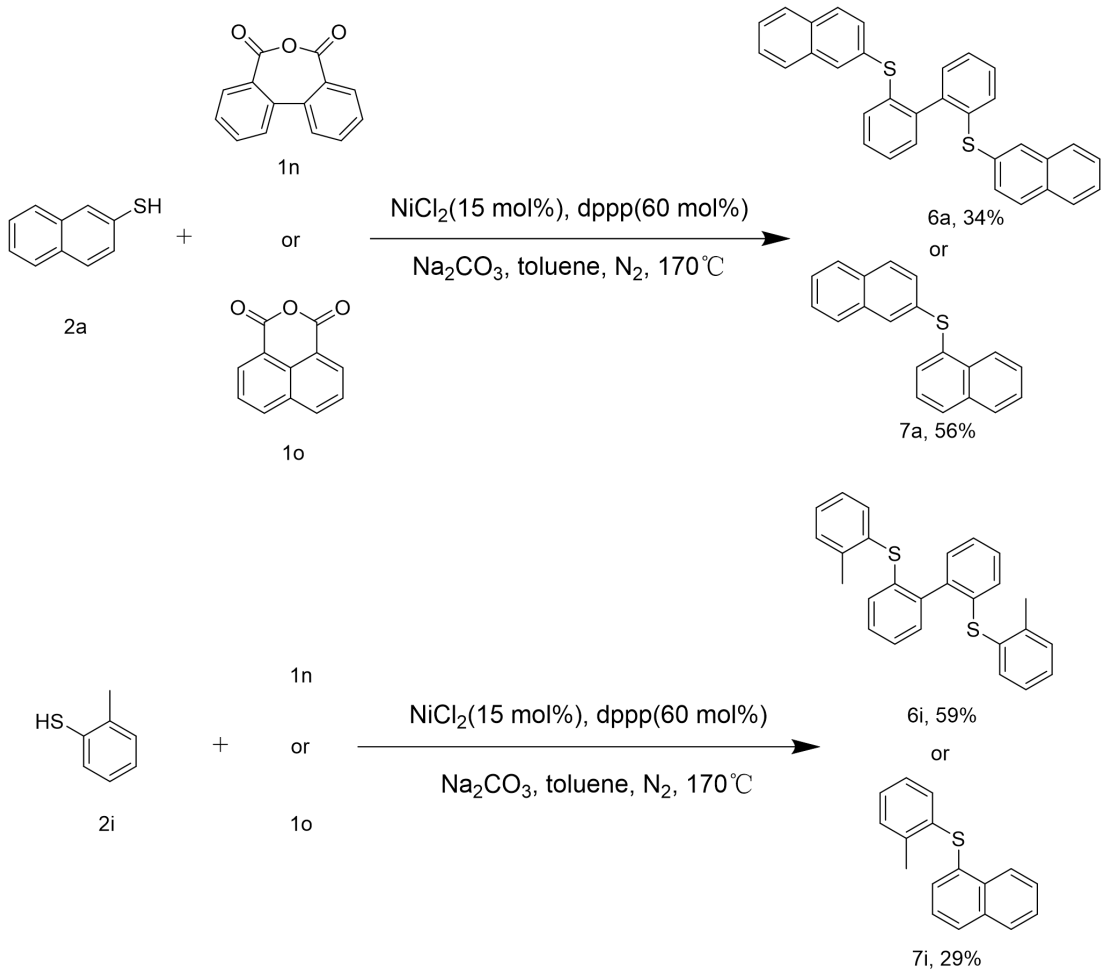
1m 2 5

Entry	Substrate	Product	Yield[b]
1	 2a	 3e	trace[c]
2	 2a	 3e	89%
3	 2b	 5b	52%[d]
4	 2c	 5c	67%
5	 2d	 5d	61%
6	 2e	 5e	66%
7	 2i	 5i	63%
8	 2m	 5m	64%

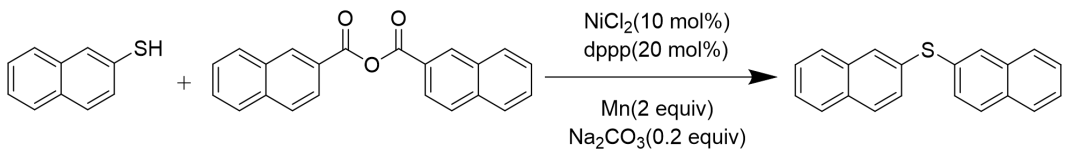
[a]General conditions: the reactions were run on a 0.5 mmol of thiophenols under nitrogen in a sealed tube, using 1m (1.2 equiv.), $NiCl_2$ (15 mol%), dppp (60 mol%), Na_2CO_3 (4.5 equiv.) in toluene (1.5 mL) at 170 °C for 48 h. [b] Isolated yields. [c] Under the conditions of $NiCl_2$ (10 mol%), dppp (20 mol%), Na_2CO_3 (0.2 equiv.) at 150 °C, 74% of the S-(naphthalen-2-yl) benzothioate (3e') was obtained. [d] 72 h

As shown in Table 4, the excellent yield was obtained when the substrate is naphthalene-2-thiol (Table 4, 3e). Moderate yield can be obtained when an electron withdrawing group is present on the benzene ring (Table 4, 5c-5e). Similarly, we also reacted phthalic anhydride with naphthalene-1-thiol and 2-methylbenzenethiol to examine the effect of steric hindrance on the reaction and also to obtain moderate yields (Table 4, 5i, 5m). When the electron donating group is attached to the thiophenol ring, the reaction time is extended to 72 hours, and a moderate yield can be obtained (Table 4, 5b). Therefore, we have also made substrate expansion for other cyclic anhydrides, such as diphenic anhydride and naphthalic anhydride. It was unexpectedly discovered that biphenyl anhydride and naphthalene anhydride could also get thioethers. For biphenyl anhydride, the carboxyl groups on the biphenyl cannot be removed due to the non-coplanarity of the two benzene rings. Thus, the carboxyl group forms a thioester with thiophenol, which is then decarbonylated to generate a disulfide product. (**Scheme 2**, 6a, 6i). Because of the large steric hindrance of the naphthalene-2-thiol, the yield of disulfide produced is lower (**Scheme 2**, 6a). And 2-methylthiophenol has less steric hindrance relative to naphthalene-2-thiol, so the yield is relatively high (**Scheme 2**, 6i). This method is also applicable to naphthalic anhydride. However, due to the large steric hindrance of the naphthalene ring, the carboxyl group can be removed, and finally a monosulfide product is formed. The yield of monosulfide product obtained by the reaction of naphthalene-2-thiol with naphthalic anhydride can reach 56% (**Scheme 2**, 7a). The yield of o-methylthiophenol with higher steric hindrance is lower (**Scheme 2**, 7i).

Scheme 2. Reactions of different thiophenols with cyclic anhydrides to synthesize aryl sulfides.[a,b]



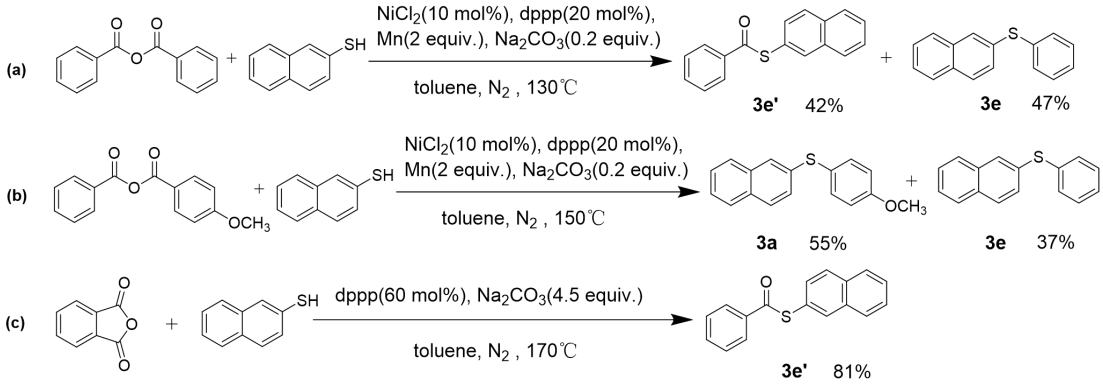
Scheme 3. Gram-Scale Reaction of 3f



2a (1.024 g, 6.4 mmol) **1f** (1.2equiv) **3f** (1.5 g, 82%)

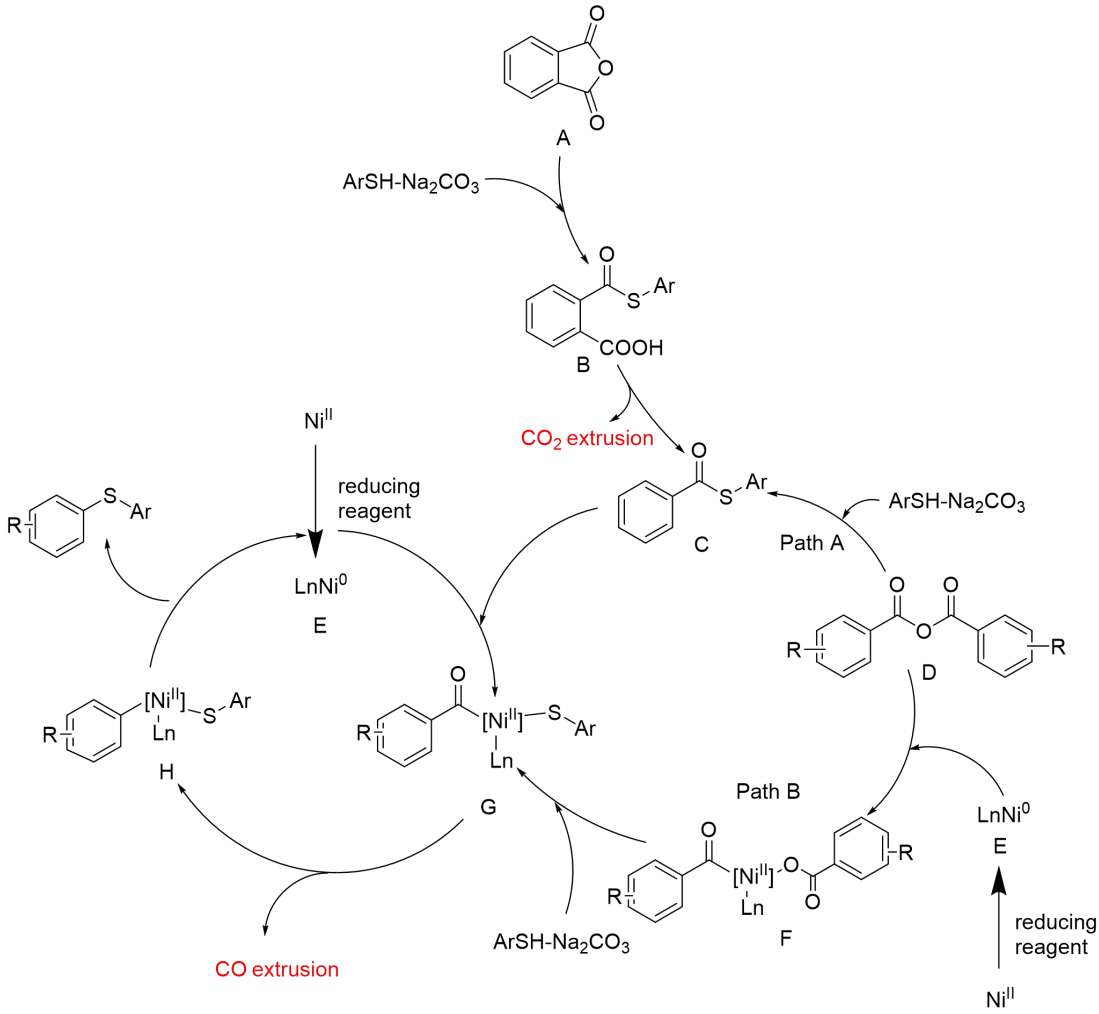
To prove the practicality of this method as a synthetic tool, we also performed scale-up production of 3f. In this case, product 3f was obtained in 82% yield, indicating good scalability of the reaction.

Scheme 4. Mechanistic Experiments



To deeper explore the reaction mechanism, we tested the mechanism of the reaction between monoanhydride and thiophenol. When the reaction was carried out at 130 °C for 12 hours, we observed the formation of the target product thioether and intermediate thioester. (**Scheme 4**, a). Therefore, we believe that the reaction mechanism of monoanhydride may proceed in two paths. At the same time, We used benzoic 4-methoxybenzoic anhydride as a raw material for the reaction, and found that a mixture of the two products was obtained (**Scheme 4**, b). In addition, we investigated whether nickel participates in the decarboxylation process of phthalic anhydride (**Scheme 4**, c). We have found that in the reaction without nickel, a large amount of thioester is obtained. This result indicates that nickel may not participate in the decarboxylation process in this reaction.

Scheme 5. Plausible Mechanism for the Synthesis of thioethers



According to previous literature reports[10, 13-17] and control experiments, a plausible mechanism for the Ni(II)-catalyzed anhydrides reacting with thiophenols is shown in **Scheme 5**. Initially, carbon dioxide is removed from anhydride A to form thioester C with thiophenol in the presence of base. At the same time, Ni^{II} is reduced to be $LnNi^0$ E by the reducing reagent. The C-S bond of thioester C is oxidatively added with $LnNi^0$ complex E to give acyl nickel (II) intermediate G. Anhydride D forms acyl nickel (II) intermediate G through two paths. The anhydride D can be converted into a thioester intermediate C by the action of thiophenol and a base, followed by oxidative addition to obtain an acyl nickel compound G, or first oxidative addition with $LnNi^0$ E to obtain a compound F through the path B, then attack by the phenyl sulfide anion to give compound G. Acyl nickel (II) intermediate G is decarbonylated to obtain intermediate H. Finally, the C-S bond formation by reductive elimination provides the thioether and the active catalyst (Ni^0).

Conclusion

In summary, we have developed a novel and convenient nickel-catalyzed decarbonylation or decarbonylation as well as decarboxylation protocol which allows the transfer of a series of readily available aromatic anhydrides to the corresponding thioether. This provides a new way to effectively build C-S bonds. More interestingly, we found that dibasic anhydride could also be used as an aryl source, through decarbonylation accompanied by decarboxylation, finally give the thioether. Various thiophenols and a wide range of aromatic anhydrides bearing various substituents are tolerated in this process, which afforded products in moderate to excellent yields.

EXPERIMENTAL SECTION

General Information. In addition to benzoic anhydride, other monoanhydrides were prepared according to previously reported methods.[18] Reactants and reagents were purchased from commercial suppliers and used without further purification. All anhydrous solvents used in the reactions were dried and freshly distilled. TLC was performed on silica HSGF254 plates. Melting points were determined with a digital melting-point apparatus. ^{1}H (400 MHz) and ^{13}C(101 or 151 MHz) NMR spectra were obtained from solutions in $CDCl_3$ or with tetramethylsilane as an internal standard using 400 or 600 MHz spectrometers. High-resolution mass spectra (HRMS) analyses were carried out on a chemical ionization (CI) apparatus using time-of-flight (TOF) mass spectrometry.

General Procedure for the Synthesis of Aryl Sulfide[3a-3l, 4a-4k]: Thiophenol (0.5mol), Anhydride (0.6 mmol), $NiCl_2$ (7 mg, 0.05 mmol), Dppp (41 mg, 0.1 mmol), Mn (55 mg, 1 mmol), and Na_2CO_3 (11 mg, 0.1 mmol) were successively added into a 15 mL sealed tube, using anhydrous toluene (1.5 mL) as solvent. The mixture was stirred in a 150 °C oil bath under nitrogen for 24 h. Upon completion of the reaction as indicated by TLC, the mixture was diluted with EtOAc, and then filtered through a pad of Celite. The solvent was removed under vacuum. The residue was purified on a silica gel column (petroleum ether) to give the pure target product.

General Procedure for the Synthesis of Aryl Sulfide[5a-5m, 6a, 6i, 7a, 7i]: Thiophenol (0.5 mol), Anhydride (0.6 mmol), $NiCl_2$ (12 mg, 0.09 mmol), Dppp (148 mg, 0.36 mmol), and Na_2CO_3 (286 mg, 2.7 mmol) were successively added into a 15 mL sealed tube, using anhydrous toluene (1.5 mL) as solvent. The mixture was stirred in a 170 °C oil bath under nitrogen for 48 h. Upon completion of the reaction as indicated by TLC, the mixture was diluted with EtOAc, and then filtered through a pad of Celite. The solvent was removed under vacuum. The residue was purified on a silica gel column (petroleum ether) to give the pure target product.

4-Methoxybenzoic anhydride(1a)[18a] White solid (8578 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 4H), 6.98 (d, J = 8.8 Hz, 4H), 3.90 (s, 6H).

4-Methylbenzoic anhydride(1b)[18b] White solid (458 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.6 Hz, 4H), 7.32 (d, J = 7.6 Hz, 4H), 2.46 (s, 6H).

2-Methylbenzoic anhydride(1c)[18b] White solid (416 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.37 – 7.30 (m, 4H), 2.70 (s, 6H).

3-Methylbenzoic anhydride(1d)[18b] Yellow solid (442 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 6H).

2-Naphthoic anhydride(1f)[18b] White solid (568 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 2H), 8.20 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 3H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H).

3,5-Dimethoxybenzoic anhydride(1g)[18b] Yellow oil (610 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.75 (s, 2H), 3.85 (s, 12H).

4-Chlorobenzoic anhydride(1h)[18b] White solid (566 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 4H).

3-Chlorobenzoic anhydride(1i)[18b] White solid (506 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H).

Cinnamic anhydride(1j)[18b] White solid (456 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 16.0 Hz, 2H), 7.59 (m, 4H), 7.50 – 7.37 (m, 6H), 6.54 (d, *J* = 16.0 Hz, 2H).

2-Methoxybenzoic anhydride(1k)[18b] Yellow oil (539 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.58 – 7.51 (m, 2H), 7.02 (m, 4H).

(4-Methoxyphenyl)(naphthalen-2-yl)sulfane (**3a**)[19] White solid (122 mg, 92%); mp 69.3-71.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 1H), 7.69 (m, 2H), 7.59 (s, 1H), 7.49 – 7.38 (m, 4H), 7.29 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.0 (s),136.0 (s), 135.4 (s), 133.9 (s), 131.9 (s), 128.7 (s), 127.8 (s), 127.3 (s), 126.9 (s), 126.7 (s), 126.6 (s), 125.8 (s), 124.6 (s), 115.2 (s), 55.5 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}OS$ 267.0844; Found 267.0843.

Naphthalen-2-yl(p-tolyl)sulfane (**3b**)[10] White solid (124 mg, 99%); mp 68.7-71.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.66 (m, 3H), 7.50 – 7.40 (m, 2H), 7.34 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 2H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 137.8 (s), 134.5 (s), 134. 0(s), 132.3 (s), 132.2 (s), 131.5 (s), 130.2 (s), 128.8 (s), 128.5 (s), 128.1 (s), 127.9 (s), 127.4 (s), 126.7 (s), 126.1 (s), 21.3 (s)

Naphthalen-2-yl(o-tolyl)sulfane (**3c**)[20] Light yellow oil (111mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 6.7 Hz, 1H), 7.65 (s, 1H), 7.45 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 3H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.1 (s), 134.0 (s), 134.0 (d, *J* = 15.3 Hz), 133.9 (s), 133.7 (s), 133.1 (s), 132.1 (s), 130.8 (s), 128.9(s), 128.2 (s), 128.2 (d, *J* = 20.4 Hz), 128.2 (d, *J* = 20.4 Hz), 127.9 (s), 127.9 (d, *J* = 4.8 Hz), 127.8 (s), 127.4 (s), 126.9 (s), 126.7 (s), 126.0 (s), 20.8 (s).

Naphthalen-2-yl(m-tolyl)sulfane (**3d**)[3d] White solid (118 mg, 94%); mp 61.4-66.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 4H), 7.51 – 7.42 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.07 (d, *J* = 6.4 Hz, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 139.3 (s), 135.5 (s), 133.9 (s), 133.5 (s), 132.4 (s), 131.9 (s), 129.7 (s), 129.2 (s), 128.9 (s), 128.8 (s), 128.4 (s), 128.2(s), 127.9 (s), 127.5 (s), 126.7 (s), 126.3 (s), 21.5 (s).

Naphthalen-2-yl(phenyl)sulfane (**3e**)[19] White solid (112 mg, 95%); mp 54.2-56.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.83 – 7.79 (m, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.35 (m, 3H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.0 (s), 133.9 (s), 133.1 (s), 132.4 (s), 131.1 (s), 130.0 (s), 129.4 (s),129.0 (s), 128.9 (s), 127.9 (s), 127.6 (s), 127.2 (s), 126.7 (s), 126.3 (s).

S-(naphthalen-2-yl) benzothioate (**3e'**)[11] White solid (98 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.0 Hz, 3H), 7.96 – 7.82 (m, 3H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.47 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.5 (s), 136.8 (s), 135.1 (s), 133.9 (s), 133.8 (s), 133.6 (s), 131.6 (s), 129.0 (s), 128.9 (s), 128.2 (s), 128.0 (s), 127.7 (s), 127.3 (s), 126.7 (s), 124.8 (s).

Di(naphthalen-2-yl)sulfane (**3f**)[21] White solid (137 mg, 96%); mp 154.7-155.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.85 – 7.80 (m, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.53 – 7.45 (m, 4H), 7.44 (d, *J* = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 134. 0(s), 133.2 (s), 132.5 (s), 129.9 (s), 129.0 (s), 128.8 (s), 127.9 (s), 127.6 (s), 126.8 (s), 126.4 (s).

(3,5-Dimethoxyphenyl)(naphthalen-2-yl)sulfane (**3g**) Light yellow oil (147 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.84 – 7.80 (m, 1H), 7.80 – 7.73 (m, 2H), 7.53 – 7.46 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 1.6 Hz, 2H), 6.34 (s, 1H), 3.73 (s, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.2 (s), 138.2 (s), 133.9 (s), 132.6 (s), 132.2 (s), 130.8 (s), 129.3 (s), 129.0 (s), 127.9 (s), 127.7 (s), 126.7 (s), 126.5 (s), 108.4 (s), 99.6 (s), 55.6 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}O_2S$ 297.0949; Found 297.0947.

(4-Chlorophenyl)(naphthalen-2-yl)sulfane (**3h**)[3c] White solid (108 mg, 80%); mp 108.5-110.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.78 (m, 3H), 7.53 – 7.45 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 1H),

7.27 (s, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 134.8 (s), 133.9 (s), 133.2 (s), 132.6 (s), 132.4 (s), 132.1 (s), 130.5 (s), 129.5 (s), 129.2 (s), 128.9 (s), 127.9 (s), 127.6 (s), 126.9 (s), 126.6 (s).

(3-Chlorophenyl)(naphthalen-2-yl)sulfane (**3i**)[22] White solid (111 mg, 82%); mp 64.3-68.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.88 – 7.74 (m, 3H), 7.55 – 7.47 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.28 (s, 1H), 7.19 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 139.0 (s), 135.1 (s), 133.9 (s), 132.8 (s), 131.7 (s), 131.2 (s), 130.3 (s), 129.6 (s), 129.4 (s), 128.0 (d, *J* = 11.4 Hz), 127.7 (s), 126.9 (s), 126.9 (s), 126.8 (s).

Naphthalen-2-yl(styryl)sulfane (**3j**)[23] White solid (128 mg, 98%); mp 79.4-81.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.84 – 7.74 (m, 3H), 7.53 – 7.43 (m, 3H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 8 Hz, 2H), 6.98 (d, *J* = 15.2 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 136.7 (s), 134.0 (s), 132.8 (s), 132.4 (s), 132.34 (s), 128.9 (s), 128.9 (s), 128.4 (s), 127.9 (s), 127.8 (s), 127.8 (s), 127.5 (s), 126.9 (s), 126.3 (s), 123.3 (s).

(2-Methoxyphenyl)(naphthalen-2-yl)sulfane (**3k**) Light yellow oil (80 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82 – 7.70 (m, 3H), 7.51 – 7.44 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.25 (t, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 3.88 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 157.5 (s), 134.0 (s), 132.5 (s), 132.0 (s), 131.8 (s), 130.4 (s), 129.2 (s), 128.9 (s), 128.5 (s), 127.9 (s), 127.6 (s), 126.6 (s), 126.3 (s), 124.2 (s), 121.4 (s), 111.1 (s), 56.1 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}OS$ 267.0844; Found 267.0836.

Bis(4-methoxyphenyl)sulfane (**4b**)[24] Yellow solid (118 mg, 96%); mp 49.5-50.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 4H), 3.79 (s, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.2 (s), 132.9 (s), 127.6 (s), 114.9 (s), 55.5 (s).

(4-Fluorophenyl)(4-methoxyphenyl)sulfane (**4c**)[25] Colorless oil (97 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.15 (m, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.8 (d , $J_{C\text{-}F}$ = 247.0 Hz) , 159.9 (s), 134.6 (s), 133.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 131.3 (d, $J_{C\text{-}F}$= 8.0 Hz), 125.5 (s), 116.2 (d , $J_{C\text{-}F}$ = 22.0 Hz) , 115.2 (s), 55.5 (s).

(4-Chlorophenyl)(4-methoxyphenyl)sulfane(**4d**)[26] Yellow solid (94 mg, 75%); mp 63.9-64.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2 (s), 137.5 (s), 135.6 (s), 131.8 (s), 129.5 (s), 129.2 (s), 124.0 (s), 115.3 (s), 55.5 (s).

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)sulfane (**4e**)[27] Light yellow oil (74 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 13.2, 8.4 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H),

3.85 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 160.8 (s), 145.0 (s), 136.8 (s), 127.4 (q, J_{C-F} = 32.6 Hz), 126.6 (s), 125.8 (q, J_{C-F} = 3.4 Hz), 124.3 (q, J_{C-F} = 272.1 Hz), 121.8 (s), 115.5 (s), 55.6 (s).

(3,4-Difluorophenyl)(4-methoxyphenyl)sulfane (**4f**) Light yellow oil (89 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.03 (m, 1H), 6.92 (d, *J* = 8.5 Hz, 4H), 3.83 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.4 (s), 150.6 (dd, J_{C-F} = 251.7 Hz, J_{C-F} = 13.4 Hz), 149.0 (dd, J_{C-F} = 248.6 Hz, J_{C-F} = 12.9 Hz), 135.8 (s), 135.4 (q, *J* = 3.5 Hz), 124.2 (q, J_{C-F} = 3.5 Hz), 123.7 (s), 117.8 (d, J_{C-F} = 17.5 Hz), 117.3 (d, J_{C-F} = 19.0 Hz), 115.4 (s), 77.16 (s), 55.6 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}F_2OS$ 253.0499; Found 253.0500.

(3-fluorophenyl)(4-methoxyphenyl)sulfane (**4g**)[28] Colorless oil (87 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.13 (m, 1H), 6.96 – 6.87 (m, 3H), 6.84 – 6.72 (m, 2H), 3.84 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} =248.6 Hz), 160.5 (s), 141.9 (d, J_{C-F} = 7.6 Hz), 136.4 (s), 130.2 (d, J_{C-F} = 8.6 Hz), 122.9 (d, J_{C-F} = 3.0 Hz), 122.8 (s), 115.4 (s), 114.2 (d, J_{C-F} = 23.7 Hz), 112.4 (d, J_{C-F} = 21.4 Hz), 55.5 (s).

(4-Methoxyphenyl)(p-tolyl)sulfane (**4h**)[26] Yellow solid (98 mg, 85%); mp 46.1-47.1°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 2.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, cdcl$_3$) δ 159.6 (s), 136.3 (s), 134.5 (s), 134.5 (s), 129.9 (s), 129.5 (s), 125.8 (s), 115.0 (s), 55.5 (s), 21.1 (s).

(4-Methoxyphenyl)(o-tolyl)sulfane (**4i**)[26] Light yellow oil (114 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 3H), 2.38 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.7 (s), 137.3 (s), 137.2 (s), 134.7 (s), 130.4 (s), 129.3 (s), 126.6 (s), 126.3 (s), 124.7 (s), 115.2(s), 55.5 (s), 20.4 (s).

3-((4-Methoxyphenyl)thio)-2-methylfuran (**4j**) Yellow oil (91 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.33 (s,1H), 3.77 (s, 3H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.4 (s), 155.8 (s), 141.2 (s), 129.5 (s), 128.4(s), 115.3 (s), 114.8 (s), 109.9 (s), 55.5 (s), 12.0 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}O_2S$ 221.0636; Found 221.0637.

Cyclohexyl(4-methoxyphenyl)sulfane (**4k**)[29] Light yellow oil (98 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 2.89 (m, 1H), 1.93 (m, 2H), 1.75 (m, 2H), 1.60 (m, 1H), 1.33 – 1.21 (m, 6H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 159.4 (s), 135.7 (s), 125.1 (s), 114.4 (s), 55.5 (s), 48.1 (s), 33.5 (s), 26.3 (s), 25.9 (s).

Benzyl(4-methoxyphenyl)sulfane (**4l**)[30] White solid (81 mg, 70%); mp 48.3-48.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 7H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 2H), 3.78 (s, 3H); $^{13}C\{^{1}H\}$

NMR (151 MHz, $CDCl_3$) δ 159.4 (s), 138.3 (s), 134.2 (s), 129.0 (s), 128.5 (s), 127.1 (s), 126.2 (s), 114.6 (s), 55.5 (s), 41.4 (s).

(4-Methoxyphenyl)(phenyl)sulfane (**5b**)[3b] Yellow oil (19 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.22 (m, 2H), 7.20 – 7.10 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.0 (s), 138.7 (s), 135.5 (s), 129.1 (s), 128.4 (s), 125.9 (s), 124.6 (s), 115.2 (s), 55.5 (s).

(4-Fluorophenyl)(phenyl)sulfane (**5c**)[11] Colorless oil (68 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.1, 5.5 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.17 (m, 3H), 7.02 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4 (s), 161.7 (s), 136.8 (s), 134.2 (d, *J* = 8.2 Hz), 131.2 (s), 130.1 (s), 129.3 (s), 126.9 (s), 116.6 (s), 116.5 (s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$= 248.5Hz), 136.8 (s), 134.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 130.3 (d, $J_{C\text{-}F}$= 3.4 Hz), 130.1 (s), 129.3 (s), 126.9 (s), 116.6 (s), 116.4 (s).

(4-Chlorophenyl)(phenyl)sulfane (**5d**)[11] White solid (67 mg, 61%); mp 49.7-52.6 °C. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.3 (s), 134.8 (s), 133.2 (s), 132.2 (s), 131.5 (s), 129.5 (d, *J* = 1.8 Hz), 127.6 (s).

Phenyl(4-(trifluoromethyl)phenyl)sulfane (**5e**)[11] Colorless oil (84 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 5H), 7.39 (d, *J* = 5.3 Hz, 3H), 7.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ143.0 (s),133.7 (s), 132.70 (s), 129.8 (s), 128.8 (s), 128.5 (s), 128.1 (s), 126.0 (q, $J_{C\text{-}F}$= 3.8 Hz), 122.9(s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.98 (d, $J_{C\text{-}F}$ = 1.2 Hz), 133.7 (s), 132.7 (s), 131.2 (s), 129.8 (s), 128.8 (s), 128.5 (s), 1260. (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.6 (s), 122.9 (s).

phenyl(o-tolyl)sulfane (**5i**)[11] Colorless oil (63 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.09 (m, 9H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1 (s), 136.3 (s), 133.9 (s), 133.2 (s), 130.7 (s), 129.8 (s), 129.3 (s), 128.04 (s), 126.8 (s), 126.5 (s), 20.7 (s).

naphthalen-1-yl(phenyl)sulfane(**5m**)[3b] Colorless oil (75 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.34 (m, 1H), 7.86 (m, 2H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.52 (m, 2H), 7.43 (t, *J* = 8 Hz, 1H), 7.27 – 7.16 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.0 (s), 134.4 (s), 133.7 (s), 132.7 (s), 131.3 (s), 129.3 (s), 129.2 (s), 129.1 (s), 128.7 (s), 127.08 (s), 126.6 (s), 126.3 (s), 126.0 (s), 125.8 (s).

2,2'-Bis(naphthalen-2-ylthio)-1,1'-biphenyl (**6a**)[31] Yellow solid (80 mg, 34%); mp 175.9-176.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 4H), 7.68 (d, *J* = 8.0 Hz, 4H), 7.44 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25 (m, 8H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 141.3 (s), 136.4 (s), 133.9 (s), 132.8 (s), 132.5

(s), 131.2 (s), 131.1 (d, J = 21.2 Hz), 131.1 (s), 130.8 (s), 129.7 (s), 128.9 (s), 128.8 (d, J = 19.4 Hz), 128.7 (s), 127.8 (s), 127.6 (s), 126.6 (s), 126.6 (d, J = 14.4 Hz), 126.5 (s), 126.3 (s).

2,2'-Bis(o-tolylthio)-1,1'-biphenyl (**6i**)[31] White solid (117 mg, 59%); mp 148.7-152.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.21 (m, 10H), 7.14 (s, 2H), 6.96 – 6.88 (m, 2H), 2.31 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.3 (s), 140.1 (s), 137.2 (s), 134.7 (s), 133.5 (s), 130.7 (s), 130.5 (s), 128.6 (s), 128.6 (s), 128.4 (s), 126.8 (s), 125.7 (s), 20.8 (s).

Naphthalen-1-yl(naphthalen-2-yl)sulfane (**7a**)[32] White solid (80 mg, 56%); mp 48.3-48.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.85 - 7.67 (m, 7H), 7.55 - 7.36 (m, 7H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 134.0 (s), 133.3 (s), 132.5 (s), 130.0 (s), 129.1 (s), 128.8 (s), 127.9 (s), 127.6 (s), 126.8 (s), 126.4 (s).

Naphthalen-1-yl(o-tolyl)sulfane (**7i**)[33] Light yellow oil (36 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (m, 1H), 7.88 (m, 1H), 7.84 – 7.77 (m, 1H), 7.53 (m, 2H), 7.43 – 7.35 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.4 (s), 135.0 (s), 134.3 (s), 133.2 (s), 132.1 (s), 130.9 (s), 130.6 (s), 130.4 (s), 128.7 (s), 128.4 (s), 127.0 (s), 126.9 (s), 126.8 (s), 126.5 (s), 126.0 (s), 125.4 (s), 20.6 (s).

ASSOCIATED CONTENT

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NOTES

The author declare no competing financial interest

Supporting Information

Supporting Information Figures giving ^{1}H, ^{13}C NMR spectra.

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REFERENCES

(1) (a) Liu, G.; Huth, J. R.; Olejniczak, E. T.; Mendoza, R.; DeVries, P.; Leitza, S.; Reilly, E. B; Okasinski, G. F; Fesik, S. W; von Geldern, T. W. Novel p-arylthio cinnamides as antagonists of leukocyte function-associated antigen-1/intracellular adhesion molecule-1 interaction. 2. Mechanism of inhibition and structure-based improvement of pharmaceutical properties. *J. Med. Chem.* **2001**,44, 1202-1210. (b) Kaldor, S. W.; Kalish, V. J.; Davies, J. F.; Shetty, B. V.; Fritz, J. E.; Appelt, K.; Burgess, J. A.; Campanale, K. M.; Chirgadze, N. Y.; Clawson, D. K.; Dressman, B. A.; Hatch, S. D.; Khalil, D. A.; Kosa, M. B.; Lubbehusen, P. P.; Muesing, M. A.; Patick, A. K.; Reich, S. H.; Su, K. S.; Tatlock, J.H. Viracept (nelfinavir mesylate, AG1343): a potent, orally bioavailable inhibitor of HIV-1 protease. *J. Med. Chem.* **1997**,40, 3979-3985. (c) Parveen, S.; Khan, M. O.; Austin, S. E.; Croft, S. L.; Yardley, V.; Rock, P.; Douglas, K. T. Antitrypanosomal, antileishmanial, and antimalarial activities of quaternary arylalkylammonium 2-amino-4-chlorophenyl phenyl sulfides, a new class of trypanothione reductase inhibitor, and of N-acyl derivatives of 2-amino-4-chlorophenyl phenyl sulfide. *J. Med. Chem.* **2005**, 48, 8087-8097. (d) Yang, S.; Li, Z.; Jin, L.-H.; Song, B.; Liu, G.; Chen, J.; Zhou,C.; Hu,D; Xue,W.; Xu, R.-Q. Synthesis and bioactivity of 4-alkyl(aryl) thioquinazoline derivatives. *Bioorg. Med. Chem. Lett.***2007**, 17, 2193-2196. (e) Liu, G.; Ma, W.-Q.; Chen, H.-G.; Liu, C.-P.; Xu, S.-G.; Liu, X.-G.; Ji, C.-N.; Liu, X.-Y. Synthesis of 4-Thioquinazoline Compounds in Aqueous Media Catalyzed by Indium. *Asian J. Chem.* **2013**, 25.

(2) (a) Murphy, A. R.; Frechet, J. M. Organic semiconducting oligomers for use in thin film transistors. *Chem. Rev.* **2007**, 107, 1066-1096. (b) Beletskaya, I. P.; Ananikov, V. P. Transition-metal-catalyzed C−S, C−Se, and C−Te bond formation via cross-coupling and atom-economic addition reactions. *Chem. Rev.* **2011**, 111, 1596-1636.

(3) (a) Rostami, A.; Rostami, A.; Ghaderi, A. Copper-Catalyzed Thioetherification Reactions of Alkyl Halides, Triphenyltin Chloride, and Arylboronic Acids with Nitroarenes in the Presence of Sulfur Sources. *J. Org. Chem.* **2015**, 80, 8694-8704. (b) Jones, K. D.; Power, D. J.; Bierer, D.; Gericke, K. M.; Stewart, S. G. Nickel phosphite/phosphine-catalyzed C–S cross-coupling of aryl chlorides and thiols. *Org. Lett*. **2017**, 20, 208-211. (c) Wu, W.-Y.; Wang, J.-C.; Tsai, F. Y. A reusable $FeCl_3 \cdot 6H_2O$/cationic 2, 2′-bipyridyl catalytic system for the coupling of aryl iodides with thiols in water under aerobic conditions. *Green Chem.* **2009**, 11, 326-329. (d) Xu, H.-J.; Zhao, Y.-Q.; Feng, T.; Feng, Y.-S. Chan–Lam-type S-Arylation of thiols with boronic acids at room temperature. *J. Org. Chem.* **2012**, 77, 2878-2884.

(4) (a) Ogiwara, Y.; Sakurai, Y.; Hattori, H.; Sakai, N. Palladium-catalyzed reductive conversion of acyl fluorides via ligand-controlled decarbonylation. *Org. Lett.* **2018**, 20, 4204-4208. (b) Murahashi, S.; Naota, T.; Nakajima, N. Palladium-catalyzed decarbonylation of acyl cyanides. *J. Org. Chem.* **1986**, 51, 898-901.

(5) (a) Monrad, R. N.; Madsen, R. Rhodium-catalyzed decarbonylation of aldoses. *J. Org. Chem.*. **2007**, 72, 9782-9785. (b) Malcho, P.; Garcia-Suarez, E. J.; Mentzel, U. V.; Engelbrekt, C.; Riisager, A.

Supported Rh-phosphine complex catalysts for continuous gas-phase decarbonylation of aldehydes. *Dalton Trans.* **2014**, 43, 17230-17235.

(6) (a) Iwai, T.; Fujihara, T.; Tsuji, Y. The iridium-catalyzed decarbonylation of aldehydes under mild conditions. *Chem. Commun.* **2008**, 6215-6217. (b) Olsen, E. P.; Singh, T.; Harris, P.; Andersson, P. G.; Madsen, R. Experimental and Theoretical Mechanistic Investigation of the Iridium-Catalyzed Dehydrogenative Decarbonylation of Primary Alcohols. *J. Am. Chem. Soc.* **2015**, 137, 834-842.

(7) (a) Guo, L.; Rueping, M. Decarbonylative cross-couplings: nickel catalyzed functional group interconversion strategies for the construction of complex organic molecules. *Acc. Chem. Res*. **2018**, 51, 1185-1195. (b) Ichiishi, N.; Malapit, C. A.; Woźniak, Ł.; Sanford, M. S. Palladium-and nickel-catalyzed decarbonylative C–S coupling to convert thioesters to thioethers. *Org. Lett.* **2017**, 20, 44-47.

(8) Ding, K.-Y.; Xu, S.; Alotaibi, R.; Paudel, K.; Reinheimer, E. W.; Weatherly, J. Nickel-Catalyzed Decarbonylation of Aromatic Aldehydes. *J. Org. Chem.* **2017**, 82, 4924-4929.

(9) John, A.; Hillmyer, M. A.; Tolman, W. B. Anhydride-additive-free nickel-catalyzed deoxygenation of carboxylic acids to olefins. *Organometallics.* **2017**, 36, 506-509.

(10) Lee, S. C.; Liao, H. H.; Chatupheeraphat, A.; Rueping, M. Nickel-Catalyzed C−S Bond Formation via Decarbonylative Thioetherification of Esters, Amides and Intramolecular Recombination Fragment Coupling of Thioesters. *Chem. - Eur. J.* **2018**, 24, 3608-3612.

(11) Liu, C.; Szostak, M. Decarbonylative thioetherification by nickel catalysis using air-and moisture-stable nickel precatalysts. *Chem. Commun.* **2018**, 54, 2130-2133.

(12) (a) Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. Decarbonylative C–H coupling of azoles and aryl esters: unprecedented nickel catalysis and application to the synthesis of muscoride A. *J. Am. Chem. Soc.* **2012**, 134, 13573-13576. (b) Pu, X.-H.; Hu, J.-F.; Zhao, Y.; Shi, Z.-Z. Nickel-catalyzed decarbonylative borylation and silylation of esters. *ACS Catal.* **2016**, 6, 6692-6698.

(13) Kajita, Y.; Matsubara, S.; Kurahashi, T. Nickel-catalyzed decarbonylative addition of phthalimides to alkynes. *J. Am. Chem. Soc.* **2008**, 130, 6058-6059.

(14) Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. Decarbonylative C–H coupling of azoles and aryl esters: unprecedented nickel catalysis and application to the synthesis of muscoride A. *J. Am. Chem. Soc.* **2012**, 134, 13573-13576.

(15) Havlik, S. E.; Simmons, J. M.; Winton, V. J.; Johnson, J. B. Nickel-mediated decarbonylative cross-coupling of phthalimides with in situ generated diorganozinc reagents. *J. Org. Chem.* **2011**, 76, 3588-3593.

(16) Guo, L.; Rueping, M. Functional group interconversion: Decarbonylative borylation of esters for the synthesis of organoboronates. *Chem. - Eur. J.* **2016**, 22, 16787-16790.

(17) Yue, H.-F.; Guo, L.; Liao, H.-H.; Cai, Y.-F.; Zhu, C.; Rueping, M. Catalytic Ester and Amide to Amine Interconversion: Nickel-Catalyzed Decarbonylative Amination of Esters and Amides by C− O and C− C Bond Activation. *Angew. Chem., Int. Ed.* **2017**, 56, 4282-4285.

(18) (a) Spránitz, P.; Sőregi, P.; Botlik, B. B.; Berta, M.; Soós, T. Organocatalytic Desymmetrisation of Fittig's Lactones: Deuterium as a Reporter Tag for Hidden Racemisation. *Synthesis*, **2019**, 51, 1263-1272. (b) Phakhodee, W.; Duangkamol, C.; Wangngae, S.; Pattarawarapan, M. Acid anhydrides and the unexpected N, N-diethylamides derived from the reaction of carboxylic acids with Ph3P/I2/Et3N. *Tetrahedron Lett.* **2016**, 57, 325-328.

(19) Eichman, C. C.; Stambuli, J. P. Zinc-Mediated Palladium-Catalyzed Formation of Carbon− Sulfur Bonds. *J. Org. Chem.* **2009**, 74, 4005-4008.

(20) Prasad, D. J. C.; Sekar, G. An efficient, mild and intermolecular ullmann-type synthesis of thioethers catalyzed by a diol-copper (I) complex. *Synthesis*, **2010**, 2010, 79-84.

(21) Kuhn, M.; Falk, F. C.; Paradies, J. Palladium-catalyzed C–S coupling: access to thioethers, benzo [b] thiophenes, and thieno [3, 2-b] thiophenes. *Org. Lett.* **2011**, 13, 4100-4103.

(22)Correa, A.; Carril, M.; Bolm, C. Iron-catalyzed S-Arylation of thiols with aryl iodides. *Angew. Chem., Int. Ed*. **2008**, 47, 2880-2883.

(23) Reddy, V. P.; Swapna, K.; Kumar, A. V.; Rao, K. R. Recyclable nano copper oxide catalyzed stereoselective synthesis of vinyl sulfides under ligand-free conditions. *Synlett.* **2009**, 2009, 2783-2788.

(24) Jang, Y.-J.; Kim, K. T.; Jeon, H. B. Deoxygenation of sulfoxides to sulfides with thionyl chloride and triphenylphosphine: Competition with the Pummerer reaction. *J. Org. Chem.* **2013**, 78, 6328-6331.

(25) Cheng, J.-H.; Ramesh, C.; Kao, H.-L.; Wang, Y.-J.; Chan, C. C.; Lee, C. F. Synthesis of aryl thioethers through the N-chlorosuccinimide-promoted cross-coupling reaction of thiols with Grignard reagents. *J. Org. Chem.* **2012**, 77, 10369-10374.

(26) Wang, C.-L.; Zhang, Z.-M.; Tu, Y.-L.; Li, Y.; Wu, J.-L; Zhao, J.-F. Palladium-Catalyzed Oxidative Cross-Coupling of Arylhydrazines and Arenethiols with Molecular Oxygen as the Sole Oxidant. *J. Org. Chem.* **2018**, 83, 2389-2394.

(27) Qiao, Z.-J.; Jiang, X.-F. Ligand-controlled divergent cross-coupling involving organosilicon compounds for thioether and thioester synthesis. *Org. Lett.* **2016**, 18, 1550-1553.

(28) Kibriya, G.; Mondal, S.; Hajra, A. Visible-Light-Mediated Synthesis of Unsymmetrical Diaryl Sulfides via Oxidative Coupling of Arylhydrazine with Thiol. *Org. Lett.* **2018**, 20, 7740-7743.

(29) Xu, X.-B.; Liu, J.; Zhang, J.-J.; Wang, Y.-W.; Peng, Y. Nickel-mediated inter-and intramolecular C–S coupling of thiols and thioacetates with aryl iodides at room temperature. *Org. Lett.* **2013**, 15, 550-553.

(30) Li, Y.-M.; Pu, J.-H.; Jiang, X.-F. A highly efficient Cu-Catalyzed S-transfer reaction: from amine to sulfide. *Org. Lett.* **2014**, 16, 2692-2695.

(31) Sibbel, F.; Daniliuc, C. G.; Studer, A. 2, 2′-Bis-substituted Biphenyls by the Addition of Nucleophiles to Benzyne Followed by In Situ Oxidative Homocoupling. *Eur. J. Org. Chem.* **2015**, 2015, 4635-4644.

(32) Bandna.; Guha, N. R.; Shil, A. K.; Sharma, D.; Das, P. Ligand-free solid supported palladium (0) nano/microparticles promoted C–O, C–S, and C–N cross coupling reaction. *Tetrahedron Lett.* **2012**, 53, 5318-5322.

(33) Nakazawa, T.; Hirose, N.; Itabashi, K. An Efficient Synthesis of Naphthyl Alkyl and Aryl Sulfides by the Reaction of Naphthols with Alkane-and Arenethiols. *Synthesis.* **1989**, 1989, 955-957.