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Synthesis of Aryl Thioethers through the *N*-Chlorosuccinimide-Promoted Cross-Coupling Reaction of Thiols with Grignard Reagents

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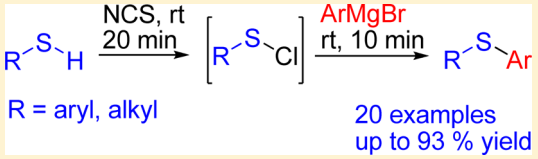
Supporting Information

ABSTRACT: A convenient one-pot approach for the synthesis of aryl sulfides through the coupling of thiols with Grignard reagents in the presence of *N*-chlorosuccinimide is described. The sulfenylchlorides were formed when thiols were treated with *N*-chlorosuccinimide, and the resulting sulfenylchlorides were then directly reacted with Grignard reagents to provide aryl sulfides in good to excellent yields under mild reaction conditions. Functional groups including ester, fluoro, and chloro are tolerated by the reaction conditions employed. It is important to note that this method has a short reaction time (30 min in total) and represents an alternative approach for the synthesis of aryl sulfides over the existing protocols.



INTRODUCTION

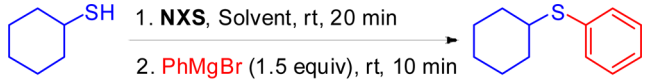
Currently, the synthesis of aryl sulfides through the construction of a C−S bond is an important area of research due to their wide spectrum of biological activity and pharmaceutical applications.[1] The aryl sulfides are present in a variety of biologically active compounds, which are used in the treatment of diabetes, inflammation, Parkinsons, Alzheimers, HIV, and cancer.[2] As a consequence, many protocols have been developed for the synthesis of aryl sulfides. Transition-metal-catalyzed cross-coupling reaction of thiols with aryl halides or pseudo halides is one of the most important methods, and palladiam,[3,4] nickel,[5] copper,[6,7] rhodium,[8] cobalt,[9] iron,[10] and indium[11] have been reported for this purpose. Although many advances have been made by transition metal catalysis, the transition metal contaminant is still a serious issue to the pharmaceutical industry. Indeed, the formation of a carbon−sulfur bond can also be achieved by the coupling of alkyl- and aryllithium or Grignard reagents with diphenyldisulfides, thiosulfonates, or sulfur;[12] however, it requires the preparation of diphenyldisulfides and thiosulfonates. Moreover, from the atom economy point of view, 1 equiv of diphenyldisulfide is required to react with 1 equiv of Grignard reagent; however, another equivalent of phenyl thiolate will be generated as waste. Therefore, the development of inexpensive, straightforward, mild, and convenient protocol is desirable in this area.

The *N*-halosuccinimides such as *N*-iodosuccinimide (NIS), *N*-bromosuccinimide (NBS), and *N*-chlorosuccinimide (NCS) are commonly used as mild sources of electrophilic halogen and have been widely applied to a variety of chemical transformations and the synthesis of biologically important compounds.[13,14] Inexpensive and readily available, NCS has been used for the preparation of sulfenylchlorides under mild reaction conditions.[15] We report here the NCS-promoted cross-coupling reaction of thiols with Grignard reagents, giving the aryl sulfides in a one-pot procedure.

RESULTS AND DISCUSSION

Initially, cyclohexanethiol **1a** and phenylmagnesium bromide **2a** were selected as substrates to determine the appropriate reaction conditions. Only 4% yield of product was obtained when the reaction was carried out in the presence of 1.1 equiv of *N*-iodosuccinimide (Table 1, entry 1). Likely, the intermediate sulfenyliodide is too reactive to react with phenylmagnesium bromide, and the resulting sulfenyliodide reacted with the starting cyclohexanethiol, giving dicyclohexanedisulfide as the side product. When *N*-iodosuccinimide was replaced by *N*-bromosuccinimide, a 62% of isolated yield was achieved (Table 1, entry 2). To our delight, a 92% yield was obtained when the reaction was promoted by *N*-chlorosuccinimide (Table 1, entry

Table 1. Optimization of the Reaction Conditions[a]



1a **3a**

	NXS	solvent	yield (%)
1	NIS	toluene	4
2	NBS	toluene	62
3	NCS	toluene	92
4	NCS	ether	74
5	NCS	THF	22

[a]Reaction conditions: cyclohexanethiol (1.0 mmol), *N*-halosuccinimide (1.1 mmol), phenylmagnesium bromide (1.5 mmol), solvent (1.5 mL).

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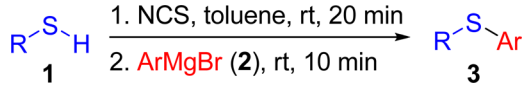
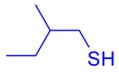
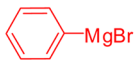
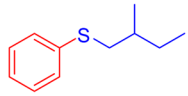
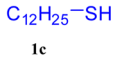
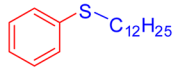
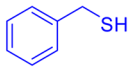
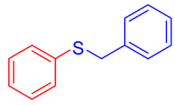
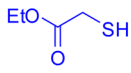
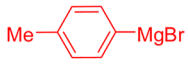
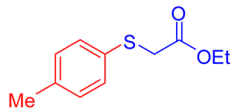
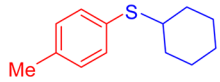
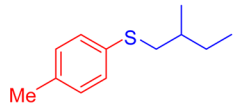
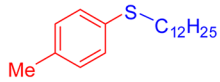
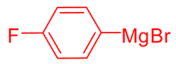
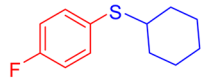
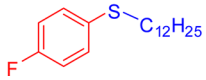
Table 2. NCS-Promoted Coupling of Alkyl Thiols with Grignard Reagent[a]



Entry	1	2	product		Yield (%)
1	 1b	 2a		3b	74
2	 1c	2a		3c	80
3	 1d	2a		3d	79
4	 1e	 2b		3e	46
5	1a	2b		3f	65
6	1b	2b		3g	76
7	1c	2b		3h	83
8	1a	 2c		3i	86
9	1c	2c		3j	81

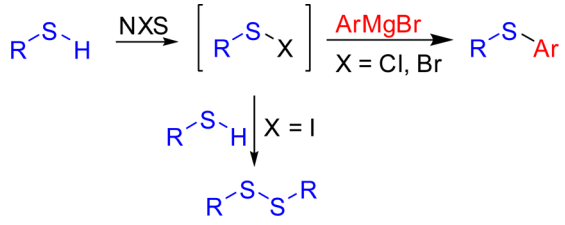
[a]Reaction conditions: alkylthiol (1.0 mmol), *N*-chlorosuccinimide (1.1 mmol), Grignard reagent (1.5 mmol), toluene (1.5 mL).

3). Other solvents such as ether and THF could not provide satisfied results (Table 1, entries 4 and 5, respectively).

As illustrated in Table 2, a variety of alkyl thiols including 2-methylbutane-1-thiol (**1b**), dodecane-1-thiol (**1c**), and benzylthiol (**1d**) were coupled with Grignard reagents, giving the corresponding aryl sulfides in moderate to excellent yields within a short period of time. Functional groups including ester (Table 2, entry 4) and fluoro (Table 2, entries 8 and 9) are tolerated by the reaction conditions employed.

To further explore the generality and scope of this methodology, a wide array of aryl thiols and Grignard reagents were examined, and the results are summarized in Table 3. The aryl thiols were reacted smoothly with various Grignard reagents under the optimized reaction conditions and afforded the corresponding aryl sulfides in good to excellent yields. Thiophenol (**1f**), 4-methoxythiophenol (**1g**), 4-*tert*-butylthiophenol (**1h**), 4-chlorothiophenol (**1i**), benzo[*d*]thiazole-2-thiol (**1j**), and 2-naphthalenethiol (**1k**) were reacted with Grignard reagents to provide the desired aryl sulfides in good yields. Functional groups such as chloro (Table 3, entry 4), heteroatom-containing aryl (Table 3, entry 5), and fluoro (Table 3, entries 9 and 10) are tolerated by the reaction conditions.

Scheme 1. The Mechanism for NCS-Promoted Synthesis of Aryl Sulfides



A plausible mechanism toward the synthesis of aryl sulfides is presented in Scheme 1. The first step involves the formation of a sulfenylhalide.[15] Our results suggested that the corresponding sulfenyliodide is too reactive to react with a Grignard reagent, and the resulting sulfenyliodide then reacted with the starting thiol, giving disulfide as a side product. When *N*-iodosuccinimide was replaced by *N*-bromosuccinimide and *N*-chlorosuccinimide, the corresponding aryl sulfide was obtained in 62% and 92% yield, respectively, in one pot.

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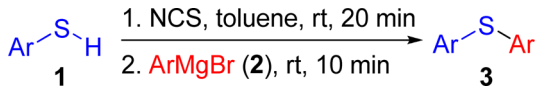
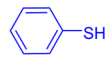
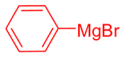
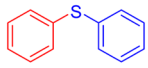
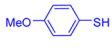
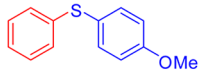
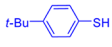
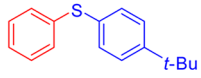
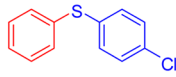
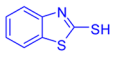
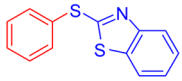
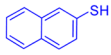
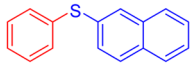
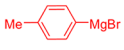
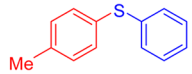
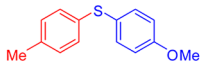
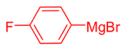
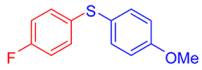
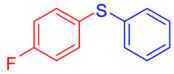
Table 3. NCS-Promoted Coupling of Aryl Thiols with Grignard Reagent[a]



Entry	1	2	Product		Yield (%)
1	 1f	 2a		3k	85
2	 1g	2a		3l	81
3	 1h	2a		3m	89
4	 1i	2a		3n	67
5	 1j	2a		3o	66
6	 1k	2a		3p	79
7	1f	 2b		3q	68
8	1g	2b		3r	72
9	1g	 2c		3s	80
10	1f	2c		3t	93

[a]Reaction conditions: aryl thiol (1.0 mmol), *N*-chlorosuccinimide (1.1 mmol), Grignard reagent (1.5 mmol), toluene (1.5 mL).

CONCLUSION

We have developed a convenient one-pot protocol for the synthesis of aryl sulfides through the coupling of thiols with Grignard reagents in the presence of NCS under the mild reaction conditions. A number of alkyl and aryl thiols underwent coupling with various Grignard reagents, giving the aryl sulfides in good to excellent yields with a short reaction time. This system is compatible with functional groups including ester, fluoro, and chloro. Application of NCS-promoted strategy for other cross-coupling reactions is in progress in our laboratory.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from commercial suppliers and used without further purification. Grignard reagents were purchased from commercial sources and used as received. Toluene, ether, and THF were dried over CaH_2 and stored in the presence of activated molecular sieves. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on silica gel 60 (230−400 mesh).

Analysis. NMR spectra were recorded using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad. Melting points (mp) were determined using an apparatus and are reported uncorrected. High-resolution mass spectra (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer.

General Procedure for Table 1. A 10 mL flask, sealed and equipped with a magnetic stirrer bar, was charged with cyclohexanethiol (**1a**, 0.12 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol), and toluene (1.5 mL). After the mixture was stirred for 20 min, toluene (1.0 mL) and phenylmagnesium bromide (**2a**, 3.0 M ether solution, 0.5 mL, 1.5 mmol) were added by syringe under a nitrogen atmosphere. After being stirred for another 10 min, the reaction mixture was quenched with saturated aqueous K_2CO_3 solution (2.0 mL) and diluted with ethyl acetate (10 mL). The resulting solution was filtered through a pad of silica gel, then washed with ethyl acetate (10 mL), and the organic layers were concentrated to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to give **3a**.

*Representative Example of Table 1. Cyclohexylphenylsulfide **3a** (Entry 3).*[6a] Following the general procedure for Table 1, cyclohexanethiol (0.12 mL, 1.0 mmol, 1.0 equiv), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3a** as a colorless oil (0.17 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21−1.38 (m, 5H), 1.58−1.62 (m, 1H), 1.74−1.78 (m, 2H), 1.96−2.00 (m, 2H), 3.06−3.12 (m, 1H), 7.17−7.28 (m, 3H), 7.37−7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 26.0, 33.2, 46.4, 126.5, 128.6, 131.7, 135.1.

General Procedure for Table 2. A 10 mL flask, sealed and equipped with a magnetic stirrer bar, was charged with thiol (**1**, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL). After the mixture was stirred for 20 min, toluene (1.0 mL) and Grignard reagent (**2**, 1.5 mmol, 1.5 equiv) were added by syringe under a nitrogen atmosphere. After being stirred for another 10 min, the reaction mixture was quenched with saturated aqueous K_2CO_3 solution (2.0 mL) and diluted with ethyl acetate (10 mL). The resulting solution was filtered through a pad of silica gel, then washed with ethyl acetate (10 mL), and the organic layers were concentrated to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to give **3**.

*2-Methylbutylphenyl Sulfide **3b** (Table 2, Entry 1).*[16a] Following the general procedure for Table 2, 2-methyl-1-butanethiol (0.12 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3b** as a colorless oil (0.13 g, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.4 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H), 1.25 (m, 1H), 1.54 (m, 1H), 1.66 (m, 1H), 2.74 (dd, J = 7.2, 7.6 Hz, 1H), 2.94 (dd, J = 6.0, 6.0 Hz, 1H), 7.12−7.16 (m, 1H), 7.23−7.27 (m, 2H), 7.30−7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 18.9, 28.7, 34.4, 40.6, 125.4, 128.7, 128.7, 137.5.

*Dodecyl Phenyl Sulfide **3c** (Table 2, Entry 2).*[16b] Following the general procedure for Table 2, 1-dodecanethiol (0.24 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3c** as a colorless oil (0.22 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.25−1.66 (m, 20H), 2.91 (t, J = 7.4 Hz, 2H), 7.26−7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.8, 29.1, 29.2, 29.3, 29.5, 29.6, 29.6, 31.9, 33.5 125.5, 127.1, 128.8, 137.1.

*Benzyl Phenyl Sulfide **3d** (Table 2, Entry 3).*[17a] Following the general procedure for Table 2, α-toluenethiol (0.11 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5

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mmol, 1.5 equiv) provided **3d** as a pink solid (0.15 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10 (s, 2H), 7.16−7.31 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 39.0, 126.3, 127.1, 128.4, 128.8, 128.8, 129.7, 136.3, 137.4.

Ethyl 2-(p-Tolylthio)acetate ***3e*** *(Table 2, Entry 4).*[17b] Following the general procedure for Table 2, ethyl 2-mercaptoacetate (0.11 mL, 1.0 mmol, 1.0 equiv), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 0.5 M solution of *p*-tolylmagnesium bromide solution in ether (3.0 mL, 1.5 mmol, 1.5 equiv) provided **3e** as a colorless oil (0.09 g, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, J = 7.2 Hz, 3H), 2.31 (s, 3H), 3.57 (s, 2H), 4.14 (q, J = 7.2 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H). ^{13}C NMR($CDCl_3$, 75 MHz): δ = 14.0, 20.1, 37.3, 61.3, 129.7, 130.8, 137.2, 169.7.

Cyclohexyl 4-Methylphenylsulfide ***3f*** *(Table 2, Entry 5).*[9] Following the general procedure for Table 2, cyclohexanethiol (0.12 mL, 1.0 mmol, 1.0 equiv), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 0.5 M solution of *p*-tolylmagnesium bromide solution in ether (3.0 mL, 1.5 mmol, 1.5 equiv) provided **3f** as a colorless oil (0.13 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21−1.38 (m, 5H), 1.56−1.59 (m, 1H), 1.74−1.77 (m, 2H), 1.94−1.97 (m, 2H), 2.32 (s, 3H), 2.99−3.04 (m, 1H), 7.09 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.0, 25.7, 26.0, 33.3, 47.0, 129.4, 131.1, 132.7, 136.7.

2-Methylbutyl 4-Methylphenylsulfide ***3g*** *(Table 2, Entry 6).*[6b] Following the general procedure for Table 2, 2-methyl-1-butanethiol (0.12 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 0.5 M solution of *p*-tolylmagnesium bromide solution in ether (3.0 mL, 1.5 mmol, 1.5 equiv) provided **3g** as a colorless oil (0.14 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.6 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 1.21−1.28 (m, 1H), 1.49−1.65 (m, 2H), 2.31 (s, 3H), 2.70 (dd, J = 7.2, 12.6 Hz, 1H), 2.90 (dd, J = 7.2, 12.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 18.8, 20.9, 28.7, 34.5, 41.4, 129.5, 129.5, 133.6, 135.6.

Dodecyl 4-Methylphenylsulfide ***3h*** *(Table 2, Entry 7).*[17b] Following the general procedure for Table 2, 1-dodecanethiol (0.2 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 0.5 M solution of *p*-tolylmagnesium bromide solution in ether (3.0 mL, 1.5 mmol, 1.5 equiv) provided **3h** as a colorless oil (0.24 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.25−1.41 (m, 18H), 1.55−1.63 (m, 2H), 2.31 (s, 3H), 2.87 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 21.0, 22.7, 28.8, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 34.4, 129.6, 129.7, 133.1, 135.8.

Cyclohexyl 4-Fluorophenylsulfide ***3i*** *(Table 2, Entry 8).* Following the general procedure for Table 2, cyclohexanethiol (0.12 mL, 1.0 mmol, 1.0 equiv), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 1.0 M solution of 4-fluorophenylmagnesium bromide solution in THF (1.5 mL, 1.5 mmol, 1.5 equiv) provided **3i** as a colorless oil (0.18 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20−1.37 (m, 5H), 1.58−1.62 (m, 1H), 1.74−1.76 (m, 2H), 1.92−1.95 (m, 2H), 2.95−3.00 (m, 1H), 6.96−7.00 (m, 2H), 7.38−7.41 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.7, 26.0, 33.2, 47.5, 115.6, 115.8, 129.7, 134.9, 135.0, 160.9, 163.4. HRMS (EI) (m/z) calcd for $C_{12}H_{15}FS$ 210.0878, found 210.0870.

Dodecyl 4-Fluorophenylsulfide ***3j*** *(Table 2, Entry 9).* Following the general procedure for Table 2, 1-dodecanethiol (0.2 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 1.0 M solution of 4-fluorophenylmagnesium bromide solution in THF (1.5 mL, 1.5 mmol, 1.5 equiv) provided **3j** as a colorless oil (0.24 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.25−1.40 (m, 18H), 1.55−1.61 (m, 2H), 2.83 (t, J = 7.2 Hz, 2H), 6.95 (t, J = 7.4 Hz, 2H), 7.30 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.7, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 35.0, 115.8, 116.0, 131.7, 131.9, 131.9, 160.4, 162.8. HRMS (EI) (m/z) calcd for $C_{18}H_{29}FS$ 296.1974, found 296.1967.

General Procedure for Table 3. A 10 mL flask, sealed and equipped with a magnetic stirrer bar, was charged with aryl thiol (**1**, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL). After the mixture was stirred for 20 min, toluene (1.0 mL) and Grignard reagent (**2**, 1.5 mmol, 1.5 equiv) were added by syringe under a nitrogen atmosphere. After being stirred for another 10 min, the reaction mixture was quenched with saturated aqueous K_2CO_3 solution (2.0 mL) and diluted with ethyl acetate (10 mL). The resulting solution was filtered through a pad of silica gel, then washed with ethyl acetate (10 mL), and the organic layers were concentrated to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to give **3**.

Diphenyl Sulfide ***3k*** *(Table 3, Entry 1).*[10c] Following the general procedure for Table 3, thiophenol (0.10 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3k** as a colorless oil (0.16 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23−7.35 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.9, 129.1, 130.9, 135.7.

4-Methoxyphenyl Phenyl Sulfide ***3l*** *(Table 3, Entry 2).*[9] Following the general procedure for Table 3, 4-methoxythiophenol (0.12 mL, 1.00 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3l** as a colorless oil (0.17 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3H), 6.87 (d, J = 6.8 Hz, 2H), 7.10−7.22 (m, 5H), 7.40 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 115.0, 124.3, 125.7, 128.2, 128.9, 135.3, 138.6, 159.8.

4-tert-Butylphenyl Phenyl Sulfide ***3m*** *(Table 3, Entry 3).*[10b] Following the general procedure for Table 3, 4-*tert*-butylbenzenethiol (0.17 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3m** as a colorless oil (0.21 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 9H), 7.30−7.37 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.2, 34.5, 126.3, 126.6, 129.0, 130.2, 131.4, 131.6, 136.6, 150.5.

4-Chlorophenyl Phenyl Sulfide ***3n*** *(Table 3, Entry 4).*[17a] Following the general procedure for Table 3, 4-chlorobenzenethiol (0.14 g, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3n** as a colorless oil (0.15 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24−7.34 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 127.4, 129.3, 129.3, 130.5, 131.3, 132.0, 133.0, 134.7, 135.1, 138.7.

2-Phenylsulfanyl-benzothiazole ***3o*** *(Table 3, Entry 5).*[10c] Following the general procedure for Table 3, 2-mercaptobenzothiazole (0.17 g, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3o** as a colorless oil (0.16 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.04 (s, 2H), 7.09−7.23 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 120.6, 121.7, 124.1, 126.0, 129.7, 129.7, 130.3, 135.1, 135.3, 153.7, 170.4.

2-Naphthylphenyl Sulfide ***3p*** *(Table 3, Entry 6).*[10c] Following the general procedure for Table 3, 2-naphthalenethiol (0.16 g, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 3.0 M solution of phenylmagnesium bromide in ether (0.5 mL, 1.5 mmol, 1.5 equiv) provided **3p** as a colorless oil (0.18 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16−7.26 (m, 3H), 7.33−7.41 (m, 5H), 7.64−7.73 (m, 3H), 7.80 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 126.1, 126.5, 127.0, 127.3, 127.6, 128.6, 128.8, 129.1, 129.8, 130.8, 132.2, 132.9, 133.7, 135.8.

4-Methylphenyl Phenyl Sulfide ***3q*** *(Table 3, Entry 7).*[10c] Following the general procedure for Table 3, thiophenol (0.10 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 0.5 M solution of *p*-tolylmagnesium bromide solution in ether (3.0 mL, 1.5 mmol, 1.5 equiv) provided **3q** as a colorless oil (0.13 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 7.10−7.30 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.1, 126.3, 129.0, 129.7, 130.0, 131.2, 132.2, 137.1, 137.5.

4-Methoxyphenyl 4-Methylphenyl Sulfide ***3r*** *(Table 3, Entry 8).*[9] Following the general procedure for Table 3, 4-methoxythiophenol (0.12 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 0.5 M solution of *p*-tolylmagnesium bromide solution in ether (3.0 mL, 1.5 mmol, 1.5 equiv) provided **3r** as a

colorless oil (0.16 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 3.77 (s, 3H), 6.85 (dt, J = 8.8 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.35 (dt, J = 8.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.9, 55.2, 114.8, 125.5, 129.3, 129.7, 134.3, 136.0, 159.4.

4-Fluorophenyl 4-Methoxyphenyl Sulfide ***3s*** *(Table 3, Entry 9).*[18] Following the general procedure for Table 3, 4-methoxythiophenol (0.12 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 1.0 M solution of 4-fluorophenylmagnesium bromide solution in THF (1.5 mL, 1.5 mmol, 1.5 equiv) provided **3s** as a colorless oil (0.18 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 6H), 6.87 (d, J = 8.4 Hz, 2H), 6.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 114.9, 115.8, 116.1, 125.1, 130.9, 130.9, 133.1, 134.4, 159.6, 160.2, 162.7.

4-Fluorophenyl Phenyl Sulfide ***3t*** *(Table 3, Entry 10).*[9] Following the general procedure for Table 3, thiophenol (0.10 mL, 1.0 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.1 equiv), and toluene (1.5 mL) and a 1.0 M solution of 4-fluorophenylmagnesium bromide solution in THF (1.5 mL, 1.5 mmol, 1.5 equiv) provided **3t** as a colorless oil (0.19 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (ddt, J = 8.8 Hz, 2H), 7.20−7.22 (m, 1H), 7.24−7.27 (m, 4H), 7.37 (ddt, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.3, 116.5, 126.7, 129.1, 129.9, 130.2, 134.0, 134.1, 136.6, 161.1, 163.6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR copies of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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