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Copper-Catalyzed Three-Component Coupling Reaction of Aryl Iodides, a Disilathiane, and Alkyl Benzoates Leading to a One-Pot Synthesis of Alkyl Aryl Sulfides

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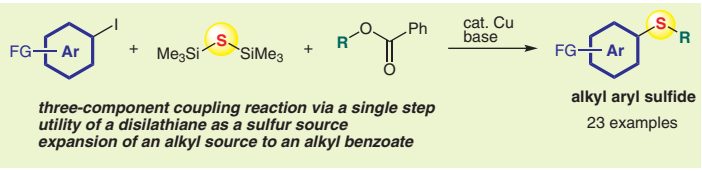

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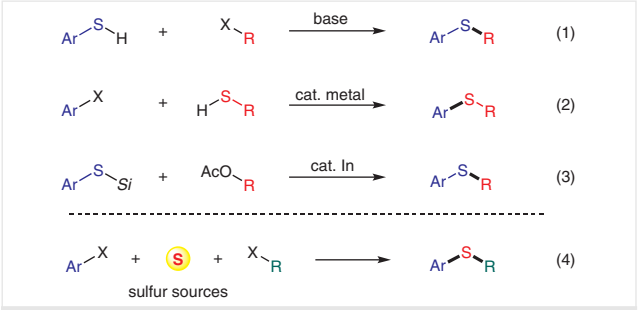
Abstract A copper-catalyzed three-component coupling reaction of aryl iodides, hexamethyldisilathiane and alkyl benzoates leading to alkyl aryl sulfides has been demonstrated. A disilathiane acted as both a sulfur source and a promoter of the sulfidation, and the alkyl moiety of the alkyl benzoate was effectively introduced on one side of the sulfide. Moreover, we found that the protocol can be expanded to the preparation of ethyl phenyl selenide with diphenyl diselenide.

Key words disilathiane, alkyl benzoate, alkyl aryl sulfide, copper, coupling

Alkyl aryl sulfides constitute the basic skeletons of many natural products and biologically active substances, such as pharmaceutical products and agricultural chemicals, and they are a precursor of materials for complex organic molecules.[1] Based on this utility, the development of a facile and effective synthesis of these organosulfur compounds has attracted a significant amount of interest from contemporary organic, pharmaceutical and material chemists.[2] Conventional approaches to alkyl aryl sulfides involve a traditional Williamson type coupling of aryl thiols with alkyl halides/alcohols in the presence of promoters, such as an acid, a base, and a condensation agent (Scheme 1, eq. 1).[3] Cross-coupling reactions between aryl halides and alkyl thiols have also been achieved with a variety of metal catalysts (Scheme 1, eq. 2).[4] Another recent combination involved the indium-catalyzed coupling of a thiosilane with an alkyl acetate leading to alkyl aryl sulfides (Scheme 1, eq. 3).[5] In a further application,[6] a three-component coupling reaction with a combination of aryl halides, alkyl halides and a suitable sulfur source has recently enabled the facile synthesis of alkyl aryl sulfides (Scheme 1, eq. 4). The present protocol enables diverse combinations of reaction substrates leading to the preparation of a variety of alkyl aryl sulfides. For example, when a mixture of iodobenzene and alkyl halide was treated with potassium ethyl xanthate as a sulfur source in the presence of copper particles, the expected sulfides were obtained.[7] Other reports have described the palladium-catalyzed coupling of iodobenzenes, sodium thiosulfate ($Na_2S_2O_3$), and alkyl halides, and also the use of copper-catalyzed nitrobenzenes, sodium thiosulfate ($Na_2S_2O_3$) and alkyl halides, with both approaches leading to the production of alkyl aryl sulfides.[8] Additionally, sulfur sources, such as thiourea,[9] carbon disulfide (CS_2),[10] elemental sulfur (S_8),[11] and Lawesson's reagent,[12] behave as a suitable sulfur source for this type of coupling protocol, leading to alkyl aryl sulfides.

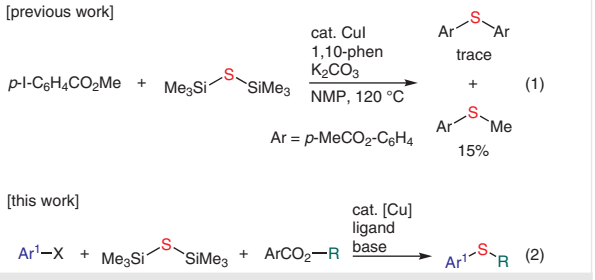


Scheme 1 Diverse approaches to alkyl aryl sulfides

The ongoing search for novel alkyl sources of the sulfidation has included the use of aliphatic alcohols, besides the former alkyl halides and alkyl acetates, in the three-component coupling modes. However, alkyl sources that involve these types of substrates are mostly limited to either those with a relatively long carbon chain or to benzyl halides/alcohols. Moreover, the direct introduction of a short

alkyl group, such as a methyl or an ethyl group, to sulfides has not been studied extensively.[13] Quite recently, to overcome this problem, Jiang et al. reported the single-step introduction of a methyl group onto one side of the sulfide, via a palladium-catalyzed coupling of chlorobenzene, potassium thioacetate as a sulfur source, and dimethyl carbonate as an alkyl source.[14] Therefore, with inexpensive metal catalysts and easily available alkyl sources, the development of a direct and efficient preparation of alkyl aryl sulfides with alkyl groups of various lengths and structures is an extremely promising pursuit.

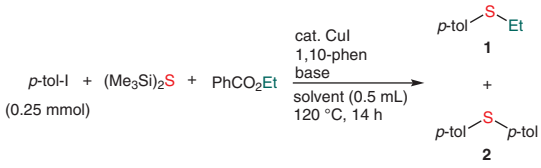
In this context, during extensive efforts to use hexamethyldisilathiane as a sulfur source for the novel synthesis of organosulfur compounds,[15] we found that when the reaction of methyl *p*-iodobenzoate was run with a disilathiane in the presence of a copper(I) catalyst, an unexpected methyl phenyl sulfide derivative was obtained in low yield (Scheme 2, eq. 1). The source of the methyl group of this derivative was an alkyl group on the benzoate, and we noted that an alkyl benzoate could assume the role of a novel alkyl source for this type of sulfidation. Thus, we attempted a one-pot synthesis of alkyl aryl sulfides via a copper(I)-catalyzed three-component coupling reaction of aryl iodides, a disilathiane, and alkyl benzoates (Scheme 2, eq. 2). In this paper, we report details of the scope and limitations of the sulfidation series.



Scheme 2 A new approach to alkyl aryl sulfides using a disilathiane as a sulfur source and an alkyl benzoate as an alkyl source

To obtain unsymmetrical sulfide **1** in our previous study, we sought the optimal conditions for sulfidation (Table 1). Initially, when the coupling reaction of *p*-iodotoluene, hexamethyldisilathiane (1.5 equiv) and ethyl benzoate (1.5 equiv) was performed using 10 mol% CuI and K_2CO_3 (2 equiv) as a base in *N*-methyl-2-pyrrolidinone (NMP) as a solvent, the expected unsymmetrical sulfide **1** and symmetrical sulfide **2** were obtained in 40% and 33% yields (entry 1). When the amount of disilathiane and ethyl benzoate relative to *p*-iodotoluene were increased to 2 equivalents, both the yield and the selectivity of **1** were improved (entry 2). However, a further increase (4 equiv per 4-iodotoluene) resulted in an ineffective product yield (entry 3). The employment of 20 mol% of CuI, however, improved the yield of **1** to 83% (entry 4). After silica gel purification of the crude product, ethyl *p*-tolyl sulfide (**1**) was cleanly isolated in 71% yield from symmetrical sulfide **2**.

Table 1 Optimization of the Reaction Conditions



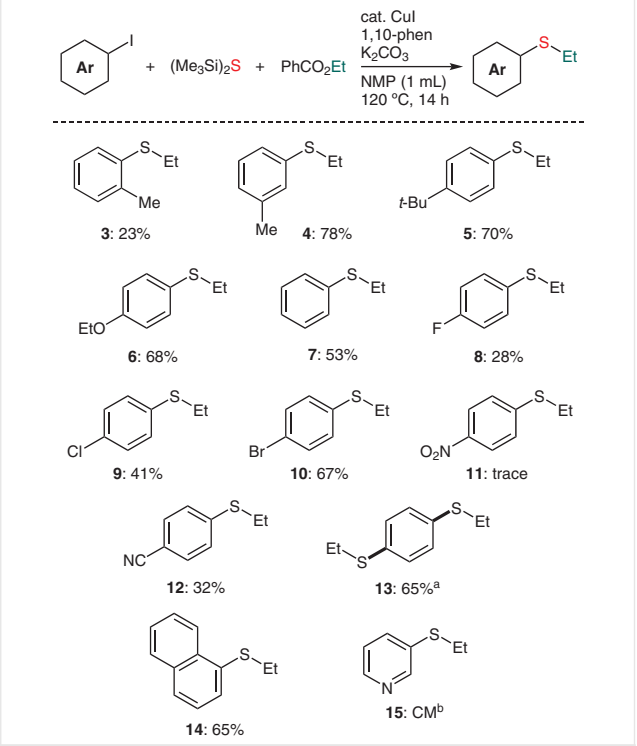
Entry	CuI (mol%)	$(TMS)_2S$ (equiv)	Ethyl benzoate (equiv)	Base	Solvent	GC yield (%) 1	2
1	10	1.5	1.5	K_2CO_3	NMP	40	33
2	10	2	2	K_2CO_3	NMP	72	15
3	10	4	4	K_2CO_3	NMP	70	3
4	20	4	4	K_2CO_3	NMP	83 (71)[a]	4
5	20	4	4	KO^{t}Bu	NMP	56	8
6	20	4	4	KOH	NMP	20	12
7	20	4	4	K_2CO_3	DMF	76	22
8	20	4	4	K_2CO_3	DMSO	21	trace

[a] Isolated yield.

As a base effect, strong bases, such as KO^{t}Bu and KOH, were ineffective for the sulfidation reaction (Table 1, entries 5 and 6). As a solvent, DMF showed the same effect as NMP, but DMSO resulted in a remarkable decrease in the product yield.

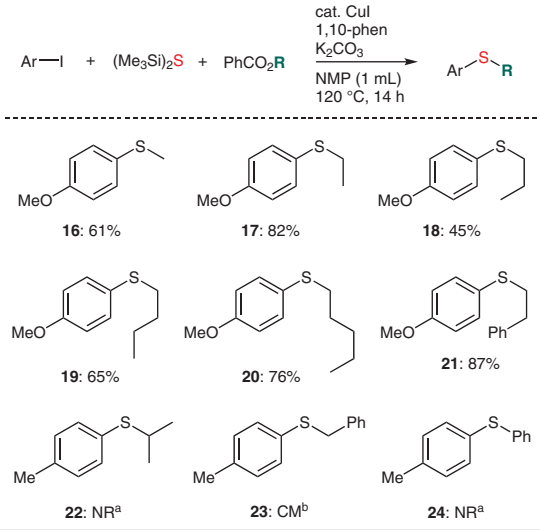
With the optimal conditions in hand, the three-component coupling with a variety of aryl iodides, a disilathiane, and ethyl benzoate was then examined; the results are outlined in Scheme 3. Initially, when the coupling reaction was carried out using *o*-tolyl iodide, the corresponding unsymmetrical sulfide **3** was obtained in low yield, probably because of steric repulsion. On the other hand, the case of *m*-substituted aryl iodide produced the expected sulfide **4** in relatively good yield. In the cases of aryl iodide with a typically electron-rich group, both an aryl group of aryl iodides and an ethyl group derived from ethyl benzoate were skillfully introduced to both sides of disilathiane, and afforded the expected sulfides **5** and **6** in good yields. For iodobenzene without a substituent, ethyl phenyl sulfide (**7**) was also obtained in 53% yield. With the exception of a *p*-fluoro substituent, when aryl iodides with an electron-withdrawing group, such as a *p*-chloro or a *p*-bromo substituent, were treated under the optimal conditions, the corresponding sulfides **9** and **10** were obtained in moderate to good yields.[16] In contrast, typically strong electron-withdrawing groups, such as a nitro and a cyano group, led to a remarkable decrease in the yield of sulfides **11** and **12**.[17] When 1,4-diiodobenzene was treated with a double dose of the catalyst, double sulfidation effectively proceeded, affording sulfide **13** in 65% yield. Additionally, unsymmetrical sulfida-

tion of 1-iodonaphthalene proceeded cleanly, giving sulfide **14** in 65% yield. For a heterocycle such as 3-iodopyridine, unfortunately, the expected sulfidation did not occur. Instead, the reaction system led to a complex mixture. In all cases, the formation (less than 5%) of symmetrical sulfides as a by-product was detected by gas chromatographic analysis, but the desired unsymmetrical sulfides were successfully separated after common silica gel column purification.



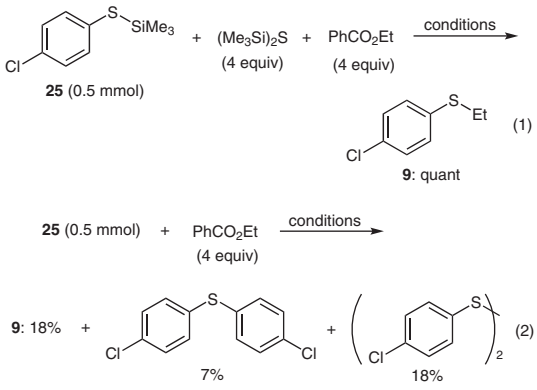
Scheme 3 Substrate scope of aryl iodides. *Reagents and conditions*: aryl iodide (0.5 mmol), disilathiane (2 mmol), ethyl benzoate (2 mmol), CuI (20 mol%), 1,10-phen (20 mol%), and K_2CO_3 (2 equiv). Isolated yield after silica gel column chromatography. [a] Double dose of the catalyst. [b] A complex mixture.

The scope and limitations of the reaction with several alkyl benzoates were then examined in the presence of 4-iodoanisole and a disilathiane (Scheme 4). Irrespective of the length of the alkyl group, a linear carbon chain on alkyl benzoates functioned effectively as an alkyl group source to afford the corresponding *p*-anisyl alkyl sulfides **16**–**20** in relatively good yields. A phenethyl group on phenethyl benzoate was also introduced onto a disilathiane and yielded unsymmetrical sulfide **21** in 87% yield. In contrast, an alkyl benzoate with an isopropyl, a benzyl and a phenyl group did not work as an alkyl source.[18] For example, when isopropyl benzoate was used, the formation of only the symmetrical sulfide and disulfide was observed, which was probably due to steric hindrance. In the cases of a benzyl group and a phenyl group, the former led to a complex mixture and the latter did not achieve the expected sulfidation. In particular, a low reactivity of phenyl benzoate in the substitution step would be expected to lead to the recovery of the starting benzoate. Thus, to improve the leaving ability of a benzoate anion, an electron-withdrawing group, such as a chloro or a nitro group, was introduced onto the *p*-position of ethyl benzoate, and the subsequent reaction with a disilathiane and *p*-tolyl iodide was attempted. However, the expected positive effect was not observed, and the yield of **1** decreased.[19]



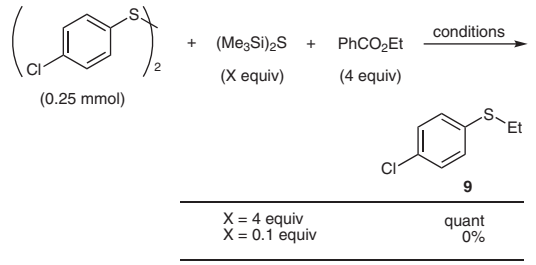
Scheme 4 Scope and limitations of alkyl benzoates for sulfidation. *Reagents and conditions*: *p*-anisyl iodide (0.5 mmol), disilathiane (2 mmol), alkyl benzoate (2 mmol), CuI (20 mol%), 1,10-phen (20 mol%), and K_2CO_3 (2 equiv). Isolated yield after silica gel column chromatography. [a] No reaction. [b] A complex mixture.

Our previous study, and related work,[5] showed that the formation of diaryl sulfide would proceed through a thiosilane intermediate. Therefore, we again anticipated that a thiosilane would be a key intermediate in the present sulfidation. Thus, when thiosilane **25**, which was prepared from a thiol and trimethylchlorosilane, was subjected to the optimal conditions with a disilathiane and ethyl benzoate, the expected unsymmetrical sulfide **9** was selectively obtained in almost quantitative yield (Scheme 5, eq. 1). Without a disilathiane, in contrast, the yield of **9** was decreased drastically to 18% with the formation of a symmetrical sulfide (7%) and a corresponding disulfide (18%) as by-products (Scheme 5, eq. 2). Consequently, Scheme 5 shows that a thiosilane is the primary key intermediate in the sulfidation series, and strongly implies that a disilathiane could drive the desired unsymmetrical sulfidation forward.



Scheme 5 Control experiment with thiosilane **25**. *Reagents and conditions*: CuI (20 mol%), 1,10-phen (20 mol%), K_2CO_3 (2 equiv), NMP (1 mL), 120 °C, 14 h. GC yield.

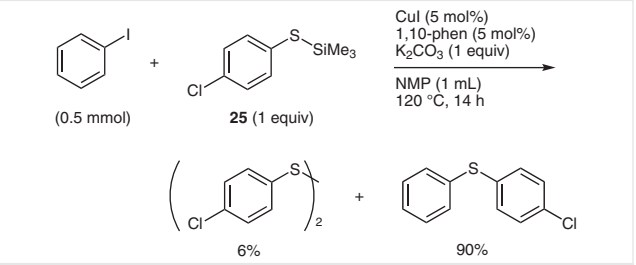
Based on the results shown in Scheme 5, the formation (18% GC yield) of the corresponding symmetrical disulfide was observed. Thus, to seek possible reaction intermediates, a control experiment using a diaryl disulfide was further examined (Scheme 6). Initially, when *p*-chlorophenyl disulfide as a model disulfide was treated with 4 equiv of a disilathiane and ethyl benzoate under the optimal conditions, the desired unsymmetrical sulfide **9** was provided in almost quantitative yield. When the amount of disilathiane was reduced to 0.1 equiv, however, a contrasting change was observed, and sulfide **9** was not obtained. Consequently, the results shown in Scheme 6 suggest the existence of an alternative route via a disulfide intermediate, and this strongly supports the function of a disilathiane as a promoter, as shown in Scheme 5.



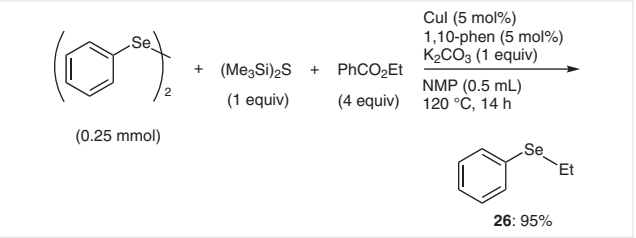
Scheme 6 Control experiment with a disulfide. *Reagents and conditions*: CuI (20 mol%), 1,10-phen (20 mol%), K_2CO_3 (2 equiv), NMP (1 mL), 120 °C, 14 h. GC yield.

In the next attempt, we investigated how a disulfide is formed from a starting thiosilane. When the reaction of iodobenzene and thiosilane **25** was conducted under the optimal conditions, the expected disulfide was obtained in only 6% yield, but unsymmetrical diaryl sulfide was selectively obtained in a 90% yield (Scheme 7).

To further account for the role of the disilathiane that remains in the reaction system, a coupling with diphenyl diselenide, instead of a diaryl disulfide, was finally conducted using a disilathiane (1 equiv for Se atom) and ethyl benzoate (4 equiv for Se atom) (Scheme 8). As expected, unsymmetrical ethyl phenyl selenide **26** was selectively produced in 95% yield.[20] Consequently, the sulfur moiety of a final alkyl aryl sulfide was derived from the sulfur atom of an in-situ generated thiosilane or from that of a disulfide intermediate. Furthermore, from both the results shown in Scheme 6, where the sulfidation did not proceed without the disilathiane, and the results shown in Scheme 8, the disilathiane assumes a dual role both as a sulfur source of sulfidation and as a promoter to activate a disulfide (diselenide) or an alkyl benzoate.

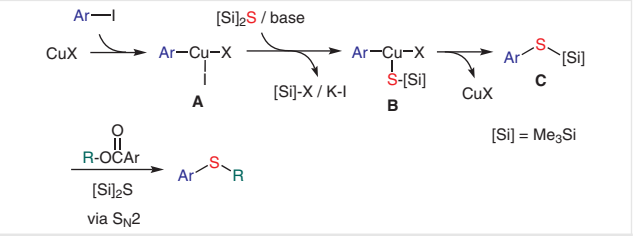


Scheme 7 Control experiment with iodobenzene and a thiosilane. GC yield.



Scheme 8 Control experiment with diphenyl diselenide

On the basis of the results shown above, a plausible reaction mechanism for the preparation of an unsymmetrical sulfide is shown in Scheme 9. Initially, copper(I) iodide oxidatively inserts into an aryl iodide, thereby producing the corresponding copper(III) complex **A**. Then, the reaction of complex **A** with a disilathiane in the presence of a base proceeds with a ligand exchange, forming Ar-Cu-S-[Si] complex **B**. Through reductive elimination of the copper catalyst from species **B**, the corresponding aryl thiosilane intermediate **C** is generated, followed by an S_N2 mode with an alkyl benzoate, and finally, alkyl aryl sulfide is generated. During the final step, it is assumed that a disilathiane will remain, and although its actual role is unclear at this stage, some activation would be undertaken toward S_N2-type substitution of an alkyl moiety of a benzoate ester with intermediate **C** (see Scheme 5 and Scheme 6).[21,22] As to the possible reaction route via a disulfide, at this stage, we have no positive evidence to support the formation of a disulfide from a starting aryl iodide and a disilathiane in the presence of a copper catalyst (see Scheme 7).



Scheme 9 Plausible reaction mechanism for the unsymmetrical sulfidation

We have demonstrated, as a novel utility for a disilathiane, a copper-catalyzed three-component coupling reaction of aryl iodides, a disilathiane and alkyl benzoates, leading to the facile preparation of unsymmetrical alkyl aryl sulfides with a variety of substituents. The primary finding of the present study shows that a disilathiane acts as both sulfur source and as a promoter of the coupling, and that, unlike conventional alkylation reagents, an alkyl moiety of alkyl benzoates is easily and efficiently introduced to one side of the desired sulfides. Furthermore, during the investigation of the reaction mechanism, we found that the protocol could apply to the use of a diselenide, and that this would lead to the direct preparation of an alkyl aryl selenide.

All reactions were performed under ambient atmosphere, unless otherwise noted. Reactions were monitored by GC analysis of reaction aliquots. GC yields were determined using decane as an internal standard. 1-Methyl-2-pyrrolidone was purchased and purified over CaH_2 by distillation under reduced pressure. Iodobenzenes were purchased and purified by bulb-to-bulb distillation prior to use. Hexamethyldisilathiane, potassium carbonate, 1,10-phenanthroline, iodobenzenes and alkyl benzoates were purchased and used without further purification. Column chromatography was performed using silica gel 60. Thin-layer chromatography (TLC) was performed on silica gel F_{254}, and components were located by UV light observation. ^{1}H NMR spectra were measured at 500 (300) MHz with tetramethylsilane as an internal standard (δ = 0.00 ppm). ^{13}C NMR spectra were measured at 125 (75) MHz using the center peak of chloroform (δ = 77.0 ppm). Spectroscopic data of symmetrical sulfide **2** were in agreement with our previously reported data.[15b] All alkyl aryl sulfides, alkyl aryl selenide **26**, and thiosilane **25** are known compounds, and the spectroscopic data were in agreement with cited data.

Synthesis of Alkyl Aryl Sulfides; General Procedure

To a screw-capped test tube, 1,10-phenanthroline (18 mg, 0.10 mmol), iodobenzene (0.5 mmol), potassium carbonate (138.2 mg, 1.000 mmol), CuI (19 mg, 0.10 mmol), 1-methyl-2-pyrrolidone (1 mL), alkyl benzoate (2 mmol), and hexamethyldisilathiane (356.8 mg, 2.000 mmol) were successively added under an ambient atmosphere. After the tube was sealed with a cap, the mixture was heated at 120 °C for 14 h. After the reaction, H_2O (3 mL) was added to the mixture, and the organic layer was then extracted with EtOAc (3 × 3 mL). The combined organic phases were dried over Na_2SO_4 and were evaporated under reduced pressure. The crude material was purified by silica gel column chromatography to give the corresponding alkyl aryl sulfide.

Ethyl 4-Tolyl Sulfide (1)[23]

The general procedure was followed with 4-methyl-1-iodobenzene (110.4 mg, 0.5063 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **1**.

Yield: 54.8 mg (71%); yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.25 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.10 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 2.90 (q, *J* = 7.5 Hz, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 1.28 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.9, 132.7, 129.9, 129.6, 28.3, 21.0, 14.5.

MS (EI): *m*/*z* (%) = 153 (12) [M$^+$+1], 152 (100), 137 (58), 135 (14), 124 (32), 123 (20), 91 (76), 79 (13), 77 (19), 66 (11).

Ethyl 2-Tolyl Sulfide (3)[24]

The general procedure was followed with 2-methyl-1-iodobenzene (109 mg, 0.499 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **3**.

Yield: 17.6 mg (23%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.25 (d, *J* = 8.0 Hz, 1 H, Ar*H*), 7.15 (t, *J* = 8.0 Hz, 2 H, Ar*H*), 7.08 (d, *J* = 8.0 Hz, 1 H, Ar*H*), 2.92 (q, *J* = 7.0 Hz, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 1.33 (t, *J* = 7.0 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.2, 136.0, 130.0, 127.3, 126.3, 125.3, 26.7, 20.3, 14.1.

MS (EI): *m*/*z* (%) = 154 (85) [M$^+$+2], 139 (100), 111 (11), 95 (10), 77 (10).

Ethyl 3-Tolyl Sulfide (4)[25]

The general procedure was followed with 3-methyl-1-iodobenzene (110.4 mg, 0.5063 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **4**.

Yield: 60.4 mg (78%); yellow oil.

IR (neat): 3051, 2924, 779 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.18–7.12 (m, 3 H, Ar*H*), 6.98 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 2.93 (q, *J* = 7.5 Hz, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 1.31 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 138.6, 136.3, 129.6, 128.6, 126.6, 125.9, 27.6, 21.3, 14.4.

HRMS (FAB): *m*/*z* [M$^+$] calcd. for $C_9H_{12}S$: 152.0660; found: 152.0660.

4-*t*-Butylphenyl Ethyl Sulfide (5)[26]

The general procedure was followed with 4-*tert*-butyl-1-iodobenzene (130 mg, 0.500 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **5**.

Yield: 67.8 mg (70%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32–7.25 (m, 4 H, Ar*H*), 2.92 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.30 (m, 12 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 149.1, 132.9, 129.4, 125.9, 34.4, 28.1, 14.6.

MS (EI): *m*/*z* (%) = 194 (36) [M$^+$], 180 (14), 179 (100), 117 (11).

4-Ethoxyphenyl Ethyl Sulfide (6)[27]

The general procedure was followed with 4-ethoxy-1-iodobenzene (124.9 mg, 0.5035 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **6**.

Yield: 62.6 mg (68%); yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 6.83 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 4.01 (q, *J* = 7.0 Hz, 2 H, CH_2), 2.83 (q, *J* = 7.0 Hz, 2 H, CH_2), 1.41 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.24 (t, *J* = 7.0 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.2, 133.2, 126.2, 115.0, 63.5, 29.8, 14.8, 14.6.

MS (EI): *m*/*z* (%) = 183 (11) [M$^+$+1], 182 (100), 154 (58), 153 (32), 139 (39), 126 (49), 125 (76), 97 (27), 53 (11).

Ethyl Phenyl Sulfide (7)[28]

The general procedure was followed with iodobenzene (105.8 mg, 0.5186 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **7**.

Yield: 37.9 mg (53%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.28 (t, *J* = 7.5 Hz, 2 H, Ar*H*), 7.17 (t, *J* = 7.5 Hz, 1 H, Ar*H*), 2.95 (q, *J* = 7.0 Hz, 2 H, CH_2), 1.31 (t, *J* = 7.0 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 136.6, 129.0, 128.8, 125.7, 27.6, 14.4.

MS (EI): *m*/*z* (%) = 138 (100) [M$^+$], 123 (65), 110 (62), 109 (17), 77 (12), 66 (23), 65 (20), 51 (17).

Ethyl 4-Fluorophenyl Sulfide (8)[29]

The general procedure was followed with 4-fluoro-1-iodobenzene (119.7 mg, 0.5490 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **8**.

Yield: 23.4 mg (27%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35–7.32 (m, 2 H, Ar*H*), 7.01–6.97 (m, 2 H, Ar*H*), 2.88 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.27 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 161.7 (d, J_{C-F} = 245.3 Hz), 132.2 (d, J_{C-F} = 7.5 Hz), 131.2 (d, J_{C-F} = 3.8 Hz), 115.9 (d, J_{C-F} = 22.6 Hz), 29.0, 14.4.

MS (EI): *m*/*z* (%) = 156 (100) [M$^+$], 141 (64), 128 (85), 127 (21), 108 (33), 84 (16), 83 (35), 57 (14).

4-Chlorophenyl Ethyl Sulfide (9)[28]

The general procedure was followed with 4-chloro-1-iodobenzene (119.9 mg, 0.5028 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) and subsequent gel permeation chromatography (chloroform) afforded **9**.

Yield: 36 mg (41%); yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.25 (s, 4 H, Ar*H*), 2.92 (q, *J* = 7.5 Hz, 2.0 H, CH_2), 1.30 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.1, 131.7, 130.3, 128.9, 27.9, 14.2.

MS (EI): *m*/*z* (%) = 174 (35) [M$^+$+2], 173 (11), 172 (100), 159 (18), 157 (49), 146 (23), 144 (63), 143 (12), 109 (25), 108 (27).

4-Bromophenyl Ethyl Sulfide (10)[30]

The general procedure was followed with 4-bromo-1-iodobenzene (141 mg, 0.498 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **10**.

Yield: 72.5 mg (67%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39 (d, *J* = 8.5 Hz, 4 H, Ar*H*), 7.18 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 2.92 (d, *J* = 7.0 Hz, 2 H, CH_2), 1.30 (t, *J* = 7.0 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.9, 131.8, 130.5, 119.5, 27.7, 14.2.

MS (EI): *m*/*z* (%) = 218 (79) [M$^+$+1], 216 (74), 203 (23), 201 (22), 190 (23), 188 (24), 122 (61), 110 (10), 109 (100), 108 (46), 82 (11), 69 (15), 65 (11), 63 (14), 50 (11).

Ethyl 4-Cyanophenyl Sulfide (12)[4c]

The general procedure was followed with 4-cyano-1-iodobenzene (114.5 mg, 0.5000 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **12**.

Yield: 26 mg (32%); orange oil.

IR (neat): 2972, 2931, 2230, 822 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.29 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 3.01 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 145.0, 132.2, 126.7, 118.9, 107.9, 26.0, 13.7.

HRMS (FAB): *m*/*z* [M]$^+$ calcd for C_9H_9NS: 163.0456; found: 163.0459.

1,4-Bis(ethylthio)benzene (13)[28]

The general procedure was followed with 1,4-diiodobenzene (167.8 mg, 0.5086 mmol) and ethyl benzoate (600.6 mg, 4.000 mmol) for 14 h. Column chromatography (hexane) afforded **13**.

Yield: 66 mg (65%); colorless solid; mp 45–46 °C.

IR (neat): 2924, 2972, 819 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.24 (s, 4 H, Ar*H*), 2.91 (q, *J* = 7.5 Hz, 4 H, CH_2), 1.29 (t, *J* = 7.5 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 134.0, 129.7, 27.9, 14.3.

HRMS (FAB): *m*/*z* [M]$^+$ calcd for $C_{10}H_{14}S_2$: 198.0537; found: 198.0538.

Ethyl 1-Naphthyl Sulfide (14)[31]

The general procedure was followed with 1-iodonaphthalene (130 mg, 0.512 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **14**.

Yield: 63.1 mg (65%); colorless oil.

IR (neat): 3051, 2963, 787, 770 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.40 (d, *J* = 8.5 Hz, 1 H, Ar*H*), 7.84 (d, *J* = 8.5 Hz, 1 H, Ar*H*), 7.72 (d, *J* = 8.5 Hz, 1 H, Ar*H*), 7.56–7.49 (m, 4 H, Ar*H*), 7.41 (t, *J* = 8.5 Hz, 1 H, Ar*H*), 3.00 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.33 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 133.9, 133.7, 132.9, 128.5, 127.6, 126.9, 126.2, 126.1, 125.5, 125.0, 28.1, 14.4.

HRMS (FAB): *m*/*z* [M]$^+$ calcd for $C_{12}H_{12}S$: 188.0660; found: 188.0663.

4-Methoxyphenyl Methyl Sulfide (16)[32]

The general procedure was followed with 4-methoxy-1-iodobenzene (117.3 mg, 0.5012 mmol) and methyl benzoate (272.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **16**.

Yield: 46.8 mg (61%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.27 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 6.85 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 3.79 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.2, 130.2, 128.7, 114.6, 55.4, 18.1.

MS (EI): *m*/*z* (%) = 154 (85) [M$^+$], 139 (100), 111 (11), 95 (10), 77 (10).

Ethyl 4-Methoxyphenyl Sulfide (17)[7]

The general procedure was followed with 4-methoxy-1-iodobenzene (118.4 mg, 0.5059 mmol) and ethyl benzoate (300.3 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **17**.

Yield: 69.6 mg (82%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.25 (t, *J* = 7.0 Hz, 3 H, CH_3), 2.84 (q, *J* = 7.0 Hz, 2 H, CH_2), 3.80 (s, 3 H, CH_3), 6.85 (d, *J* = 9.0 Hz, 2 H, ArH), 7.35 (d, *J* = 9.0 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.6, 29.8, 55.3, 114.4, 126.4, 133.1, 158.8.

MS (EI): *m*/*z* (%) = 169 (10) [M$^+$+1], 168 (100), 153 (30), 140 (19), 139 (47), 125 (20).

4-Methoxyphenyl Propyl Sulfide (18)[33]

The general procedure was followed with 4-methoxy-1-iodobenzene (118 mg, 0.504 mmol) and propyl benzoate (328.4 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **18**.

Yield: 41.5 mg (45%); yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.34 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 6.84 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 3.80 (s, 3 H, CH_3), 2.79 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.60 (sext, *J* = 7.0 Hz, 2 H, CH_2), 0.99 (t, *J* = 7.0 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.7, 133.0, 126.8, 114.5, 55.3, 37.8, 22.7, 13.3.

MS (EI): *m*/*z* (%) = 183 (12) [M$^+$+1], 182 (100), 153 (29), 140 (72), 139 (22), 125 (36), 109 (11).

Butyl 4-Methoxyphenyl Sulfide (19)[34]

The general procedure was followed with 4-methoxy-1-iodobenzene (118 mg, 0.504 mmol) and butyl benzoate (356.5 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **19**.

Yield: 64.2 mg (65%); orange oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 6.84 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 3.79 (s, 3 H, CH_3), 2.82 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.59–1.53 (m, 2 H, CH_2), 1.45–1.38 (m, 2 H, CH_2), 0.90 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.7, 132.9, 126.9, 114.4, 55.3, 35.5, 31.4, 21.8, 13.6.

MS (EI): *m*/*z* (%) = 196 (61) [M$^+$], 153 (16), 140 (100), 139 (16), 125 (38).

4-Methoxyphenyl Pentyl Sulfide (20)[35]

The general procedure was followed with 4-methoxy-1-iodobenzene (117.3 mg, 0.5012 mmol) and pentyl benzoate (384.5 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **20**.

Yield: 80.1 mg (76%); orange oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 6.84 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 3.79 (s, 3 H, CH_3), 2.81 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.61–1.55 (m, 2 H, CH_2), 1.40–1.26 (m, 4 H, CH_2), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.7, 132.9, 126.9, 114.4, 55.3, 35.8, 30.9, 29.0, 22.2, 14.0.

MS (EI): *m*/*z* (%) = 210 (52) [M$^+$], 153 (11), 140 (100), 139 (15), 125 (26).

4-Methoxyphenyl Phenethyl Sulfide (21)[36]

The general procedure was followed with 4-methoxy-1-iodobenzene (118 mg, 0.504 mmol) and phenethyl benzoate (452.5 mg, 2.000 mmol) for 14 h. Column chromatography (hexane) afforded **21**.

Yield: 106.9 mg (87%); brown oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 7.30–7.16 (m, 5 H, Ar*H*), 6.86 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 3.80 (s, 3 H, CH_3), 3.07 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.87 (t, *J* = 7.5 Hz, 2 H, CH_2).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.9, 140.3, 133.2, 130.1, 129.5, 129.0, 128.5, 128.4, 126.3, 114.6, 55.3, 37.2, 35.9.

MS (EI): *m*/*z* (%) = 244 (41) [M$^+$], 154 (11), 153 (100), 151 (20), 140 (13), 139 (13), 138 (20), 109 (34), 107 (17), 105 (83), 104 (30), 103 (19), 92 (28), 79 (27), 78 (15), 77 (52), 66 (16), 64 (10).

4-Chloro-1-[(trimethylsilyl)thio]benzene (25)[5]

To a solution of 4-chlorobenzenethiol (2.92 g, 20.0 mmol) in diethyl ether (20 mL) was slowly added *n*-butyl lithium (1.6 M in hexane, 22 mmol, 14 mL) at –78 °C. Chlorotrimethylsilane (2.4 g, 22 mmol) was then added dropwise to the reaction mixture at the same temperature. In addition, the resultant mixture was stirred at r.t. for 4 h, and hexane (13 mL) was added. The mixture was directly evaporated, and the precipitated solid was filtered off. The organic layer was evaporated, and the residue was purified by distillation under reduced pressure to afford the desired thiosilane.

Yield: 2.29 g (52%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.22 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 0.27 (s, 9 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 136.3, 133.1, 130.0, 128.9, 0.8.

HRMS (FAB): *m*/*z* [M]$^+$ calcd. for $C_9H_{13}ClSSi$: 216.0196; found: 216.0197.

Ethyl Phenyl Selenide (26)[37]

The general procedure was followed with diphenyl diselenide (78 mg, 0.25 mmol) and ethyl benzoate (75 mg, 0.50 mmol) for 14 h. Column chromatography (hexane) afforded **26**.

Yield: 87.9 mg (95%); colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.50–7.48 (m, 2 H, Ar*H*), 7.27–7.22 (m, 3 H, Ar*H*), 2.92 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.43 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.5, 130.2, 129.0, 126.7, 21.3, 15.5.

MS (EI): *m*/*z* (%) = 188 (17) [M$^+$+3], 186 (90), 184 (46), 183 (16), 182 (17), 160 (13), 158 (67), 157 (23), 156 (35), 155 (21), 154 (18), 91 (15), 78 (100), 77 (40).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610869.

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(18) When the typical sulfidation was conducted with an aliphatic ester, ethyl acetate, the yield of **1** decreased greatly to 31% GC yield with the formation of symmetrical sulfide **2** (41% GC yield).
(19) One reviewer pointed out that introduction of an election-withdrawing group, such as a chloro or nitro group, onto the *p*-position of ethyl benzoate did not show a significantly positive result. The authors anticipate that an increase in electrophilicity of a carbonyl moiety of ethyl benzoate by introduction of an electron-withdrawing group would lead a side reaction of a thiosilane intermediate with an alkyl benzoate. There has been no reasonable explanation for the result at this stage.
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