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Magnesium-Induced Copper-Catalyzed Synthesis of Unsymmetrical Diaryl Chalcogenide Compounds from Aryl Iodide via Cleavage of the Se−Se or S−S Bond

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The methodology for a copper-catalyzed preparation of diaryl chalcogenide compounds from aryl iodides and diphenyl dichalcogenide molecules is reported. Unsymmetrical diaryl sulfide or diaryl selenide can be synthesized from aryl iodide and PhYYPh (Y = S, Se) with a copper catalyst (CuI or Cu$_2$O) and magnesium metal in one pot. This reaction can be carried out under neutral conditions according to an addition of magnesium metal as the reductive reagent. Furthermore, it is efficiently available for two monophenylchalcogenide groups generated from diphenyl dichalcogenide.

Introduction

The construction of an aryl−heteroatom bond is an important study and a number of reports have been known.[1,2] Similarly, a transition-metal-catalyzed preparation of aryl chalcogenide has been also developed by various methods so far.[3] These compounds are usually synthesized from aryl halide and thiol or selenol by a copper catalyst[4] or other transition metals[5] under basic conditions. However, a catalytic process under neutral conditions has been rarely explored. Actually, to promote the reaction with the present method, it is necessary that a compound with an organochalcogen−metal bond should be employed.[6]

On the other hand, RYH (Y = S, Se) has a property of easy conversion to RYYR by atmosphere oxygen. Herein, the generated compounds are symmetric molecules and have the characters of both stability and ease of handling. Regrettably, the use of these derivatives for organochalcogenation of aryl halide is confined to a synthetic method with one chalcogenide-group by stoichiometric metal reagents.[7,8] Therefore, a catalytic preparation by the availability of two dichalcogenide molecules has been little developed up to now (Figure 1). On the contrary, in a catalytic addition to alkyne,[9] or in a phenylselenation of alkyl halide with diphenyl diselenide,[10] the efficient use of these molecules has been reported.

In the phenylchalcogenation of aryl halide, to exploit two groups in diphenyl dichalogenide, the requirement is an application of a metal catalyst with two abilities as follows. One is a cleavage of the chalcogen−chalcogen bond, and the other is an oxidative addition to aryl halide. To satisfy these qualifications, it seems that the employment of a transition-metal catalyst having a capability to insert into the dichalcogen bond is the most suitable.[11] However, it is possible that production of complexes by the transition metal inserts into dichalcogenide prevents promoting the next step owing to the firmness of the

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(1) For a review on an aryl−chalcogen bond formation, see: *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press, Ltd.: New York, 1991; Vol. 6.

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(7) For an example of phenylthiolation of ArI, see: Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99−103.

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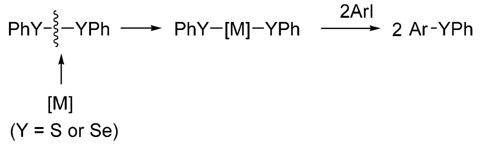
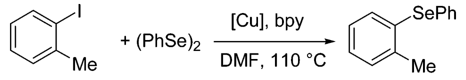


FIGURE 1. Metal-catalyzed phenylchalcogenation of ArI via insertion to dichalcogen bond.

TABLE 1. Reaction between 2-Iodotoluene (1a) and Diphenyl Diselenide (2) with Copper Catalyst[a]



1a **2** **3a**

entry	[Cu]	additive	time (h)	**3a**[c] (%)	**1a**[c] (%)
1	CuI	none	12	0	97
2[b]	none	Mg	12	0	98
3	CuI	Mg	30	87	8
4	Cu_2O	Mg	30	92	4
5	Cu_2O	Zn	30	54	35
6	Cu_2O	Al	30	75	16
7	Cu_2O	Sm	30	80	5
8	Cu_2O	Sn	30	trace	94

[a] The mixture of **1a** (0.3 mmol), **2** (0.15 mmol), and copper catalyst in DMF (0.5 mL) was stirred at 110 °C, and Cu_2O (5 mol %), CuI (10 mol %), and additive metals (0.6 mmol) were used. [b] bpy was not added. [c] Isolated yields after silica gel chromatography.

metal–chalcogen bond. As a solution to this problem, we have found that the addition of magnesium metal could carry out a copper-catalyzed phenylselenation of aryl iodide with diphenyl diselenide under neutral conditions.[12]

In this paper, we wish to report a convenient synthesis of unsymmetrical diaryl chalcogenides with 0.5 equiv of diphenyl diselenide or disulfide by a copper catalyst and magnesium and a study of the detailed reaction mechanism.

Results and Discussion

Synthesis of Diaryl Selenide from ArI and $(PhSe)_2$. To obtain a diaryl selenide from aryl iodide and diphenyl diselenide, we searched for a reaction condition with a copper catalyst. First, when 2-iodotoluene (**1a**) and diphenyl diselenide (**2**) were treated with CuI (10 mol %) in DMF at 110 °C for 12 h, the expected product was not obtained at all and **1a** was recovered in 97% yield (entry 1 in Table 1). Fortunately, the addition of magnesium (0.6 mmol) to the reaction mixture, in the reaction between **1a** (0.3 mmol) and **2** (0.15 mmol), could afford the corresponding phenyl 2-tolyl selenide (**3a**) in 87% yield after 30 h (entry 3). The use of Cu_2O (5 mol %) also gave **3a** in 92% yield (entry 4). However, other copper salts (CuOTf, CuBr, CuCl, $CuBr_2$, $CuCl_2$, and $Cu(OAc)_2$) were not effective for this reaction. Remarkably, magnesium alone could not promote this reaction in the absence of the copper catalyst and **1a** was recovered 98% yield (entry 2).[13]

In addition, the employment of other metals (Zn, Al, Sm, and Sn) instead of magnesium was investigated. Whereas zinc, aluminum, or samarium gave yields of 54%, 75%, and 80%, respectively, for the formation of **2a** (entries 5, 6, and 7), the use of tin was ineffective (entry 8). Thus, it was obvious that in the phenylselenation of aryl iodide with diphenyl diselenide, a combination of both the copper catalyst (CuI or Cu_2O) and magnesium gave an excellent result.

Application to the Copper-Catalyzed Preparation of Diaryl Selenides and Diaryl Sulfides. We next directed our attention to the preparation of diaryl selenides using this method. The results of the synthesis of diaryl selenides with the Cu_2O catalyst and magnesium are presented in Table 2. Various unsymmetrical diaryl selenides **3** were obtained in 53–95% yields by substituted aryl iodides **1** and diphenyl diselenide (**2**) treated with Cu_2O (5 mol %), bpy (10 mol %), and magnesium in DMF at 110 °C for 18–36 h (entries 1–16).

Similarly, the above method can be applied to the synthesis of unsymmetrical diaryl sulfides **5** with diaryl disulfide (**4a** and **4b**). In this reaction, the CuI catalyst has been employed because the Cu_2O catalyst lowered the yield of diaryl sulfide **5**.[14] The CuI-catalyzed reaction between aryl iodide **1** and diaryl disulfide **4** afforded the corresponding sulfides in good yields (Table 3). Also, this condition was accessible to synthesize *n*-butyl aryl sulfides from aryl iodides and di-*n*-butyl disulfide (**4c**) (entries 4 and 14). Moreover, in the reaction of 1-bromo-4-iodobenzene, two halogen groups could be converted to a phenylthio-substituent in 75% yield by the use of 1.0 equiv of **4a** (entry 11).[15] Unfortunately, in the case of 4-nitro-1-iodobenzene, a significant decrease in the obtained yield was observed, and the starting material **1** was recovered in 70% yield (entry 15). However, on the whole, unsymmetrical diaryl sulfides or diaryl selenides could be synthesized from aryl iodide and 0.5 equiv of $(PhY)_2$ by the combination of the copper catalyst and magnesium.

Proposed Reaction Mechanism of the Copper-Catalyzed Phenylselenation of Aryl Iodide. To investigate the present reaction mechanism, we examined the phenylselenation of aryl iodide, and subsequent experiments were carried out in detail. As shown in Table 4, some interesting results were obtained.

In the phenylselenation of 2-iodotoluene (**1a**), when Cu_2O was employed, the reaction was not promoted, and both **1a** and diphenyl diselenide (**2**) were recovered unconsumed (entries 1 and 2).

Furthermore, the case with Cu(powder) was researched. Stoichiometric Cu (100 mol %) gave **3a** in 80% yield (entry 3), and the use of Cu (50 mol %) also yielded

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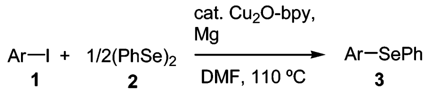
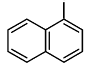
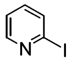
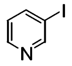
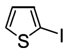
(14) In the reaction between 2-iodotoluene (**1a**) and diphenyl disulfide (**2**) with Cu_2O (5 mol %) and Mg (0.6 mmol) at 110 °C for 48 h, the yield of phenyl 2-tolyl sulfide was 25% yield.

(15) The reaction between bromobenzene (0.3 mmol) and $(PhS)_2$ (0.15 mmol) with CuI (10 mol %) and Mg (0.6 mmol) at 110 °C for 48 h afforded diphenyl sulfide in 34% yield.

TABLE 2. Preparation of ArSePh from 1 and 2 with Cu_2O Catalyst



entry	ArI **1**	time (h)	**3** (%)[a]	entry	ArI **1**	time (h)	**3** (%)[a]
1	C_6H_5I	30	94	9[b]	4-$MeOC_6H_4I$	36	78
2	2-MeC_6H_4I	30	92	10	4-BrC_6H_4I	36	70
3	2-$MeOC_6H_4I$	18	83	11	4-$F_3CC_6H_4I$	18	90
4	2-$AcHNC_6H_4I$	36	82	12	4-$O_2NC_6H_4I$	18	53
5	2-$MeOCH_2C_6H_4I$	18	92	13		18	83
6	2-$O_2NC_6H_4I$	18	61	14		18	95
7	2-$F_3CC_6H_4I$	18	89	15		18	93
8	4-MeC_6H_4I	36	85	16		18	88

[a] Isolated yields after silica gel chromatography. [b] Cu_2O (10 mol %) was used .

it in 44% (entry 4).[16] Thus, it appears that when more than 50 mol % Cu(0) is used, the redox of Cu(0) and Cu(II) occurs. Although a catalytic amount Cu (10−30 mol %) was not effective for this reaction, **2** was consumed by the catalytic amount (entries 5, 6, and 7). These facts show that in the use of 10 mol % of Cu(0), the redox of Cu(0) and Cu(II) is little promoted. On the other hand, the addition of magnesium in the presence of Cu (10 mol %) could afford **3a** in 87% yield (entry 8). In the case of a stoichiometric amount of CuI (100 mol %), **2** was used up completely, **3a** was not obtained, and **1a** was recovered in 98% yield (entry 9).[17] The catalytic amount did not provide **3a** (entry 10). When magnesium was added in the absence of the copper catalyst, **1a** and **2** were recovered in yields of 98% and 98% without formation of any other products (entry 11). Moreover, when **1a** and magnesium in DMF were treated at 110 °C for 24 h, no Grignard reaction was observed, and ArI and magnesium metal were recovered (Scheme 1).[13] It was proved that magnesium itself had no ability to cleave the Se−Se bond and to produce ArMgI in DMF.

From these experimental results, in the phenylselenation with the Cu_2O catalyst, it can be seen that magnesium works as the reductive reagent. In the catalytic cycle, the first step is the generation of Cu(0) from Cu_2O by the reduction of magnesium, $Cu(II)(SePh)_2$ is produced by the insertion of Cu(0) into the diselenide bond, and subsequently the reduction of $Cu(SePh)_2$ by magnesium converts into Cu(I)SePh.

Similarly, in the use of the CuI catalyst, the role of magnesium suggests the reduction of a copper complex. However, as compared with the case of the Cu_2O catalyst, two pathways are considered in order to form CuSePh, because CuI itself has the capability to insert into the Se−Se bond (Figure 2). One process is that Cu(0) is produced from CuI by the reduction of magnesium as well as the Cu_2O catalyst. The other is that Cu(I)SePh is produced after a generated complex $Cu(III)I(SePh)_2$ via the oxidative addition of CuI to $(PhSe)_2$,is reduced by magnesium.[17] In practice, although the CuI catalyst alone could not carry out the reaction, the addition of magnesium after the mixture of **1a**, CuI (10 mol %), and **2** was stirred at 110 °C for 24 h afforded **3a** in 80% yield after 48 h (Scheme 2). In addition, in the course of these steps, it is also considered that $(PhSe)_2Cu(II)$ was produced by the redox of Cu(I) and Cu(III). Therefore, it is presumed that the CuI catalyst can pass through these processes to produce Cu(I)SePh.

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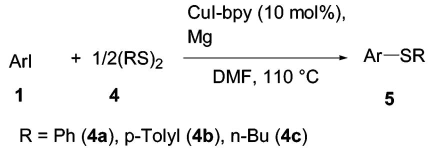
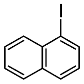
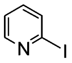
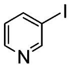
(16) Yamamoto, Y.; Sekine, Y. *Can. J. Chem.* **1984**, *62*, 1544−1547.

(17) A green participate was produced by the reaction between CuI and $(PhSe)_2$.

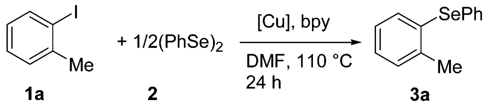
TABLE 3. Preparation of Aryl Sulfide from 1 and 4 by CuI Catalyst



entry	ArI **1**	**4**	time (h)	**5** (%)[c]	entry	ArI **1**	**4**	time (h)	**5** (%)[c]
1	C_6H_5I	**4a**	18	90	10	4-MeC_6H_4I	**4a**	72	73
2	2-MeC_6H_4I	**4a**	30	87	11[c]	4-BrC_6H_4I	**4a**	72	75[d]
3		**4b**	18	95	12	4-$F_3CC_6H_4I$	**4a**	48	67
4		**4c**	40	71	13		**4b**	40	78
5	2-$MeOC_6H_4I$	**4a**	48	74	14		**4c**	40	81
6	2-$AcHNC_6H_4I$	**4b**	48	80	15	4-$O_2NC_6H_4I$	**4a**	48	10
7	2-$F_3CC_6H_4I$	**4a**	72	80	16		**4a**	40	72
8	4-$MeOC_6H_4I$	**4a**	72	70	17		**4a**	40	78
9		**4b**	48	84	18		**4a**	40	75

[a] Isolated yields after silica gel chromatography. [b] CuI (15 mol %) was used. [c] $(PhS)_2$ (1.0 equiv) was used. [d] Yield of 1,4-bis(phenylthio)benzene.

TABLE 4. Phenylselenation of 1a with Copper Catalyst in the Absence of Magnesium[a]



entry	[Cu] (mol %)	ArSePh **3a**[b] (%)	ArI **1a**[b] (%)	recovery of **2**[b] (%)
1	Cu_2O (100)	0	98	97
2	(10)	0	97	97
3[c]	Cu (100)	80	10	2
4[c]	(50)	44	53	11
5[c]	(30)	3	94	40
6[c]	(20)	1	96	81
7[c]	(10)	0	98	88
8[c,d]	(10) + Mg	87	7	0
9	CuI (100)	0	98	1
10	(10)	0	97	89
11[c,d]	None + Mg	0	98	98

[a] **1a** and **2** were used (0.3 and 0.15 mmol, respectively). [b] Isolated yields after silica gel chromatography. [c] Cu (75 μm powder) was used. [d] Mg (0.6 mmol) was added.

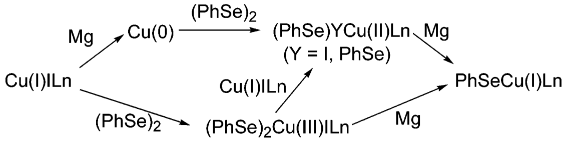
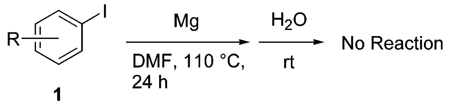


FIGURE 2. Plausible process to produce CuSePh from CuI.

SCHEME 1



1

R	Recovered Yield of **1** (%)
o-Me	98
p-MeO	98

The above-described Cu(I)SePh (100 mol %) can provide ArSePh **3** in good yields without the addition of magnesium in the presence of bpy (Table 5).[18] The same result is also observed from the reaction between aryl iodide and Cu(I)SPh.[19] Accordingly, Cu(I)SePh works as an activating species in the catalytic phenylselenation of aryl iodide.

Our proposed mechanism for this reaction is outlined in Figure 3. When Cu_2O was employed as the catalyst, the reaction process was considered as follows. After the Cu_2O was reduced to Cu(0), the insertion of Cu(0) to $(PhSe)_2$ produced $Cu(II)(SePh)_2$ **8**. On account of the fact

SCHEME 2

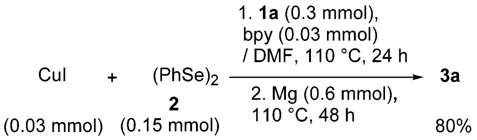
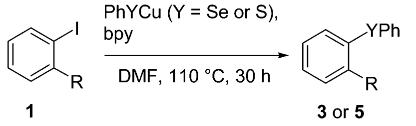


TABLE 5. Reaction between ArI 1 and PhYCu(I) (Y = Se or S)[a]



entry	R	PhYCu	ArYPh[b] (%)
1[c]	H	Se	trace
2	H	Se	81
3	Me	Se	82
4	Me	S	80

[a] The mixture of **1** (0.3 mmol), bpy (0.3 mmol), and PhYCu (0.3 mmol) in DMF (1.0 mL) was stirred at 110 °C. [b] Isolated yields after silica gel chromatography. [c] bpy was not added.

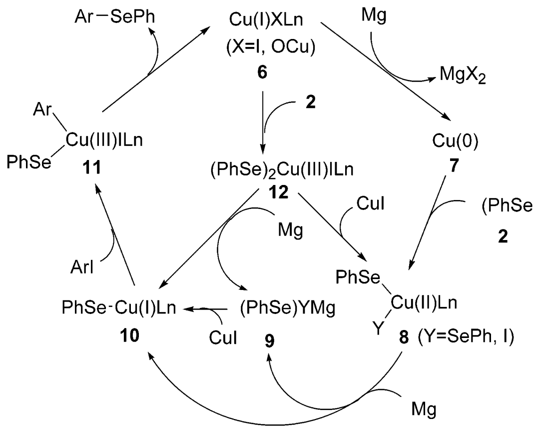


FIGURE 3. Plausible reaction mechanism.

that complex **8** is impossible to perform this reaction, it is reduced by magnesium to readily produce Cu(I)SePh **10** which is the activating species. Finally, the complex **10** is converted into ArSePh by the reaction of ArI, and in this step, the generated CuI provides **10** again through two ways.

On the other hand, MgY(SePh) **9** is formed by the reductive reaction of a copper−phenylselenide complex (**8** or **12**) by magnesium, and it is reused as the phenylselenium source in the presence of Cu(I)I in the catalytic system.[4a] Similarly, it is anticipated that the same mechanism is applicable to the copper-catalyzed synthesis of diaryl sulfide with disulfide compounds. Thus, the present method is feasible to synthesize ArYPh (Y = S or Se) from ArI in good yields by only using 0.5 equiv of $(PhY)_2$.

In conclusion, we have developed a magnesium-induced copper-catalyzed synthesis of the unsymmetrical diaryl selenide or diaryl sulfide from aryl iodide and diphenyl diselenide or diphenyl disulfide. In this method, the copper catalyst was reduced by magnesium at each step, and these processes were the important steps for the preparation of the aryl−chalcogen bond via cleavage of the dichalcogenide bond. Thus, in the copper-catalyzed phenylchalcogenation, the addition of magnesium enabled the efficient use of two PhY (Y = S or Se) groups generated from diphenyl dichalcogenide under neutral conditions.

Experimental Section

General Procedure. All reactions were carried out under a nitrogen atmosphere. NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ^1H, 67.5 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR. IR spectra were measured by Perkin-Elmer Spectrum One FT-IR spectrometer.

Copper-Catalyzed Synthesis of Diaryl Selenide from Aryl Iodide and Diselenide (Table 2). Entry 4: ^1H NMR ($CDCl_3$) δ 2.01 (s, 3H), 7.07 (t, J = 7.2 Hz, 1H), 7.18−7.25 (m, 5H), 7.41 (t, J = 7.2 Hz, 1H), 7.69 (d, J = 7.2 Hz, 1H), 8.12 (br, 1H), 8.38 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.5, 120.9, 124.6, 127.1, 129.3, 129.5, 129.9, 130.0, 130.7, 131.1, 137.4, 168.2; IR (neat) 3289, 3059, 1668, 1581, 1515, 1428 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NOSe$: C, 57.94; H, 4.51; N, 4.83. Found: C, 57.85; H, 4.53; N, 4.80.

Entry 5: ^1H NMR ($CDCl_3$) δ 3.39 (s, 3H), 4.56 (s, 2H), 7.14 (t, J = 8.4 Hz, 1H), 7.24−7.29 (m, 4H), 7.34 (d, J = 8.4 Hz, 1H), 7.41−7.45 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 58.1, 74.4, 127.3, 127.4, 128.4, 128.6, 129.3, 130.9, 131.7, 133.1, 133.8, 139.3; IR (neat) 3057, 1577, 1476 cm^{-1}. Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.77; H, 5.12.

Entry 7: ^1H NMR ($CDCl_3$) δ 7.22−7.38 (m, 6H), 7.57−7.66 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 126.3, 126.6, 126.7, 127.7, 128.6, 129.1, 129.6, 131.5, 132.0, 133.3, 135.5; IR (neat) 1570, 1476, 1313 cm^{-1}. Anal. Calcd for $C_{13}H_9F_3Se$: C, 51.84; H, 3.01. Found: C, 51.54; H, 3.16.

Entry 11: ^1H NMR ($CDCl_3$) δ 7.24−7.37 (m, 3H), 7.40−7.47 (m, 4H), 7.55−7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 125.8, 125.8, 125.9, 126.0, 128.5, 128.7, 129.7, 131.0, 134.8; IR (neat) 1601, 1325 cm^{-1}. Anal. Calcd for $C_{13}H_9F_3Se$: C, 51.84; H, 3.01. Found: C, 51.69; H, 3.14.

Entry 15: ^1H NMR ($CDCl_3$) δ 7.16−7.20 (m, 1H), 7.26−7.32 (m, 3H), 7.47−7.51 (m, 2H), 7.72 (d, J = 7.9 Hz, 1H), 8.47−8.49 (m, 1H), 8.66 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 124.2, 127.9, 128.8, 129.5, 129.6, 133.4, 140.0, 148.2, 152.7; IR (neat) 1576, 1476, 1463, 1438, 1403 cm^{-1}. Anal. Calcd for $C_{11}H_9NSe$: C, 56.42; H, 3.87; N, 5.98. Found: C, 56.43; H, 3.97; N, 6.00.

Copper-Catalyzed Synthesis of Diaryl Sulfide from Aryl Iodide and Disulfide (Table 3). Entry 3: ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.37 (s, 3H), 7.08−7.23 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 20.4, 21.0, 126.5, 127.0, 128.5, 129.9, 130.0, 131.0, 131.3, 135.1, 136.8, 138.7; IR (neat) 1491, 1467 cm^{-1}. Anal. Calcd for $C_{14}H_{14}S$: C, 78.45; H, 6.58. Found: C, 78.40; H, 6.61.

Entry 6: ^1H NMR ($CDCl_3$) δ 2.05 (s, 3H), 2.29 (s, 3H), 7.00−7.11 (m, 5H), 7.43 (t, J = 8.2 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 8.18 (br, 1H), 8.43 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.9, 24.7, 120.8, 120.9, 124.3, 127.8, 127.9, 130.0, 130.5, 135.9, 136.5, 139.5, 168.2; IR (neat) 3360, 1693, 1511 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44. Found: C, 69.94; H, 5.98; N, 5.47.

Entry 7: ^1H NMR ($CDCl_3$) δ 7.19 (d, J = 7.9 Hz, 1H), 7.20−7.43 (m, 7H), 7.68 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 126.2, 126.5, 126.6, 126.7, 128.1, 129.5, 132.0, 132.3, 133.0, 133.8, 136.7; IR (neat) 1594, 1473, 1440, 1312 cm^{-1}. Anal. Calcd for $C_{13}H_9F_3S$: C, 61.41; H, 3.57. Found: C, 61.71; H, 3.90.

Entry 9: mp 46−47 °C; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 3.79 (s, 3H), 6.85 (d, J = 6.5 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H),

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7.12 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 6.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 55.3, 114.8, 125.6, 129.3, 129.7, 134.3, 136.1, 138.0, 159.4; IR ($CHCl_3$) 1591, 1492 cm^{-1}. Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 72.92; H, 6.22.

Entry 13: mp 95−96 °C; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 7.18−7.22 (m, 4H), 7.37−7.46 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.2, 125.6, 125.7, 125.8, 127.4, 128.5, 129.7, 130.5, 134.2, 139.2; IR ($CHCl_3$) 1606, 1326, 1215 cm^{-1}. Anal. Calcd for $C_{14}H_9F_3S$ C, 62.67; H, 4.13. Found: C, 62.65; H, 4.15.

Entry 14: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, $J = 7.2$ Hz, 3H), 1.43−1.54 (m, 2H), 1.61−1.70 (m, 2H), 2.97 (t, $J = 7.4$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 21.9, 30.8, 32.1, 125.4, 125.5, 125.6, 127.1, 142.8; IR (neat) 2961, 1607 cm^{-1}. Anal. Calcd for $C_{11}H_{13}F_3S$: C, 56.39; H, 5.59. Found: C, 56.66; H, 5.68.

Supporting Information Available: Analytical data (^{1}H and ^{13}C NMR spectra) and literature citations for known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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