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Iodine-Mediated Thiolation of Substituted Naphthols/Naphthylamines and Arylsulfonyl Hydrazides via C(sp^2)−H Bond Functionalization

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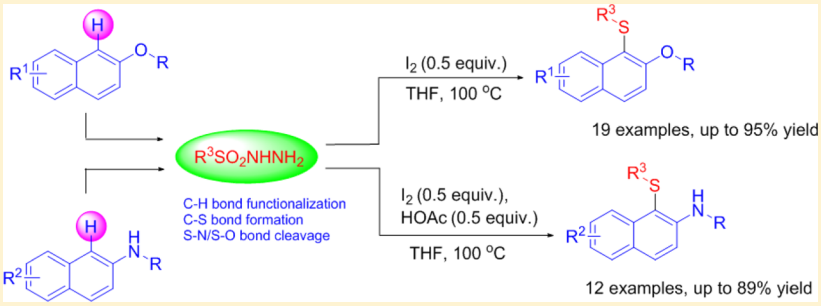
Supporting Information



ABSTRACT: A direct method has been developed for iodine-mediated thiolation of naphthols/naphthylamines and arylsulfonyl hydrazides through the formation of C−S bond and cleavage of S−N/S−O bonds. In this transformation, a range of valuable thioethers are easily achieved in moderate to good yields.

The development of C−S bond formation has emerged as a significant field of research in organic chemistry because organosulfur compounds are widely present in natural products and are applied in total organic synthesis, medical chemistry, and functional materials science.[1] Among them, diaryl sulfides, as valuable building blocks, are found in many pharmacological compounds for HIV and cancer as well as Alzheimer's and Parkinson's diseases.[2] Given the tremendous importance of functionalized diaryl sulfides, numerous catalytic reactions have been improved for C−S bond formation. With the development of green chemistry and increased concern over environmental issues, direct oxidative coupling by selective functionalization of the C−H bond has developed as an efficient methodology for C−S bond formation. Among recent reports, the groups of Yu, Yuan, Fu, Tian, and Jiang et al. have described different approaches for C−S bond formation via C−H bond activation catalyzed by transition metals, such as Pd,[3] Cu,[4] and Fe.[5] In those transformations, different thiolating/sulfenylating reagents, for example, sulfonyl hydrazides, sodium sulfinates, diaryldisulfides, and arylthiols, were employed. Nonetheless, these methods suffer from the use of expensive or toxic metal salts, harsh reaction conditions, and narrow substrate scopes. Certainly, many environmentally friendly methods have also made great progress, which have been reported by the groups of Jiang,[6] Tian,[7] Xiang,[8] and others.[9] However, the development of green, efficient, and practical access to C−S bond formation is still highly desired.

Sulfonyl hydrazides as ideal thiolating agents have been widely used to construct the C−S bond because they are readily accessibile and stable. Inspired by Tian's thiolation reaction of sulfonyl hydrazides and indoles catalyzed by iodine[10] and our experiences in the transformation of C−H bond activation,[11] we envisaged a new method for forming C−S bonds with naphthols/naphthylamines and sulfonyl hydrazides via C(sp^2)−H functionalization. Thus, naphthalen-2-ol (**1a**) and sulfonyl hydrazide (**2b**) were subjected to the reaction conditions reported by Tian to test this approach. As expected, 1-(*p*-tolylthio)naphthalen-2-ol (**3ab**) was successfully obtained in 42% yield in this reaction (Scheme 1, entry 1). Herein, we disclose a practical and convenient procedure to synthesize various thioethers with sulfonyl hydrazides and naphthols/naphthylamines.

Encouraged by this result, we initiated our investigation with the reaction of **1a** and **2b** as a model reaction to identify the optimal reaction conditions. On the basis of the result in Table 1, entry 1, reactions were carried out in the presence of iodine. After screening the temperature of the reaction, we found that the substrate showed the highest activity for this reaction at 100 °C. Moreover, further improvement of the process was achieved when I_2 (0.5 equiv) was used (Table 1, entry 3). Among the different solvents tested, THF gave the best result (Table 1, entry 4). Nevertheless, the yield decreased when

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Scheme 1. I_2-Mediated C(sp^2)−S Bond Formation

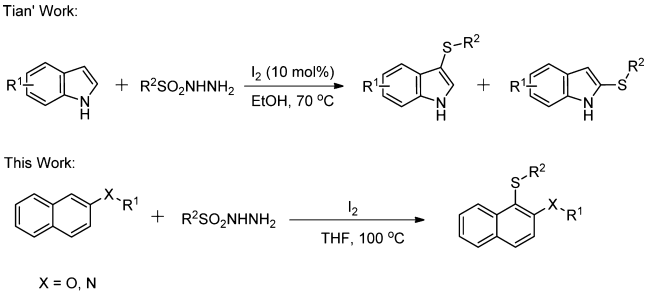
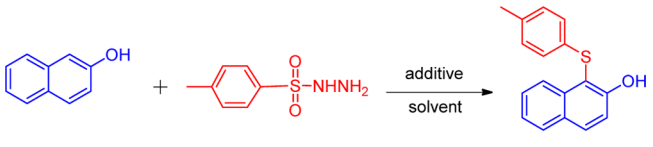


Table 1. Optimization of Reaction Conditions[a]

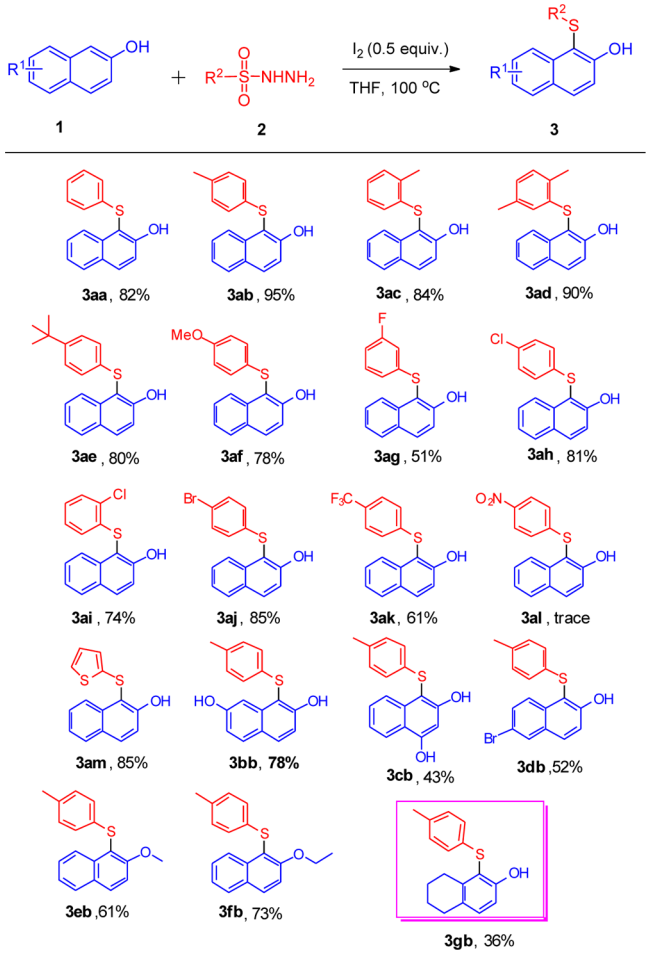


1a 2b 3ab

entry	catalyst/equiv	solvent	temp. (°C)	yield (%)[b]
1	I_2 (0.2)	EtOH	70	42
2	I_2 (0.2)	EtOH	100	61
3	I_2 (0.5)	EtOH	100	70
4	**I_2 (0.5)**	**THF**	**100**	**95**
5	I_2 (1.0)	THF	100	93
6	I_2 (0.5)	THF	25	
7	I_2 (0.5)	CH_3CN	100	73
8	I_2 (0.5)	PhMe	100	72
9	I_2 (0.5)	$ClCH_2CH_2Cl$	100	63
10	I_2 (0.5)	DMF	100	
11	I_2 (0.5)	DMSO	100	
12	NIS (1.2)	THF	100	78
13		THF	100	

[a]Reaction conditions: **1a** (0.3 mmol), **2b** (0.36 mmol), and additive in 2 mL of solvent. [b]Isolated yield.

Table 2. Thiolation of Substituted Naphthols and Sulfonyl Hydrazides[a]



[a]Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), and I_2 (0.15 mmol) in 2 mL of THF at 100 °C for 10 h.

replacing iodine with *N*-iodosuccinimide (NIS) (Table 1, entry 12). In the absence of iodine, no desired product was detected, which indicated that iodine was essential to this reaction (Table 1, entry 13).

With the optimized conditions in hand, the scope of the substrates using naphthols and sulfonyl hydrazides was examined, and the results are illustrated in Table 2. It was gratifying to find that a variety of substituted sulfonyl hydrazides could couple with naphthols in moderate to high yields.

Generally, sulfonyl hydrazides with electron-donating groups gave higher yields than that of substrates with electron-withdrawing groups. Obviously, when 4-nitrobenzenesulfonohydrazide **2l** was employed under the optimized conditions, only a trace amount of **3al** was detected by TLC. Thiophene-2-sulfonohydrazide **2m** was also tolerated in this transformation, generating the target compound **3am** in 85% yield. Further investigation showed that even 2-methoxynaphthalene **1e** and 2-ethoxynaphthalene **1f** can also proceed smoothly in this reaction, and the desired products were isolated in 61 and 73% yields, respectively. Of note, when 5,6,7,8-tetrahydronaphthalen-2-ol **1g** and **2b** were reacted out under standard conditions, 1-(*p*-tolylthio)-5,6,7,8-tetrahydronaphthalen-2-ol **3gb** was obtained in 36% yield.

In order to enlarge the scope of this transformation, further experiments were conducted for the reaction of naphthalen-2-amine **4a** with **2b** under the optimized conditions, and 1-(*p*-tolylthio)naphthalen-2-amine **5ab** was obtained in 62% yield. After screening the paramaters of temperature, acids, and solvents, a higher yield was achieved when the reaction was carried out with I_2 (0.5 equiv) and HOAc (0.5 equiv) in THF at 100 °C. The scope of the substrates using naphthylamines and sulfonyl hydrazides was also examined, and the results are illustrated in Table 3. Generally, the reaction between substituted sulfonyl hydrazides and naphthylamines proceeded smoothly and afforded the corresponding products with high efficiency. It was observed that the nature of the substituent on the aromatic rings of the sulfonyl hydrazides did not significantly affect the yields of this reaction. Sulfonyl hydrazides with electron-withdrawing groups gave slightly higher yields than those with electron-donating groups. When *N*-phenylnaphthalen-2-amine **4b** was subjected to the reaction, only a trace amount of **5bb** was detected.

Remarkably, when naphthalen-1-ol **1h** and naphthalen-1-amine **4c** were subjected to the transformation under standard conditions, the expected products **3hb** and **5cb** were isolated in 72 and 64% yields, respectively (Scheme 2).

In order to gain further insight into the mechanism, some control experiments were investigated. First, when coupling **1a**

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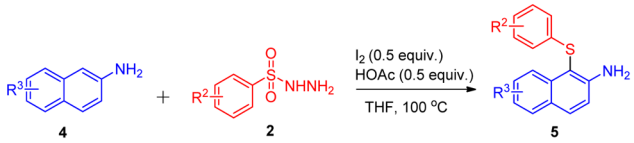
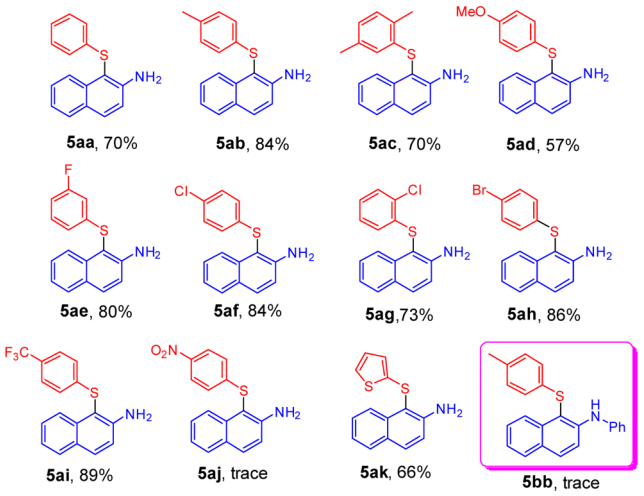
Table 3. Thiolation of Substituted Naphthylamines and Sulfonyl Hydrazides[a]

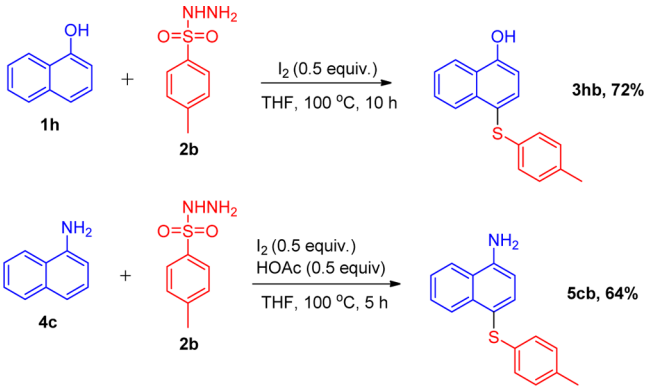


4 2 5



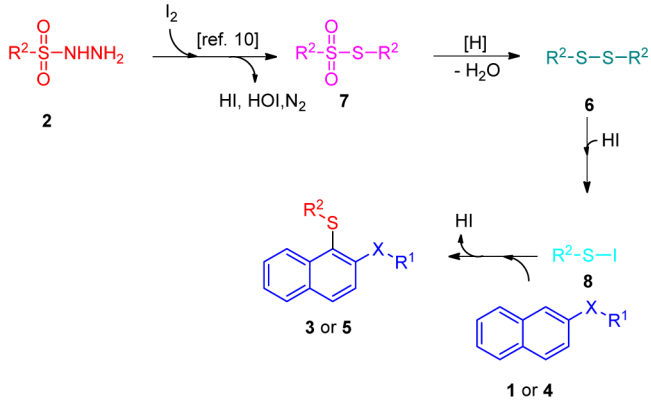
[a]Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), I_2 (0.15 mmol), and HOAc (0.15 mmol) in 2 mL of THF at 100 °C for 5 h.

Scheme 2. Reaction of 1h and 4c with Sulfonyl Hydrazide



and **2b** were carried out at 70 °C with 0.5 equiv of I_2 in THF after 5 h, byproducts **6** and **7** were observed in the reaction mixture. In this transformation, the molar ratio of isolated **3ab**/**6**/**7** was approximately 8:8:15. Then, when compound **6** was subjected to the reaction with **1a** under the optimized conditions, desired product **2b** was also isolated in 82% yield (Scheme 3). Thus, we speculate that compound **6** is the intermediate of this reaction. On the basis of these results, a proposed mechnism for C(sp^2)−S bond formation is illustrated in Scheme 4. Initially, substrate **2** is converted to intermediate **7**

Scheme 4. Proposed Mechanism



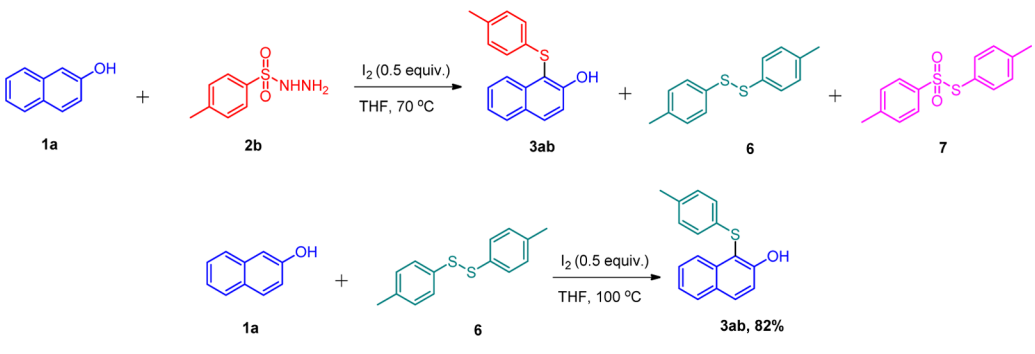
with the aid of iodine. Meanwhile, N_2, HOI, and HI are released in this transformation. Subsequently, intermediate **6** is produced by reduction of **7**.[10] Then, **6** reacts with HI to give sulfenyl iodide **8**, which attacks sustrates **1** or **4** to produce desired compounds **3** or **5** via an electrophilic reaction (Scheme 4).

In conclusion, we have developed a significant method to afford synthetically valuable thioethers easily with readily accessible substrates: substituted naphthols/naphthylamines and sulfonyl hydrazides. The thiolation of naphthols/naphthylamines and sulfonyl hydrazides undergoes C−H bond functionalization, C−S bond formation, and S−N/S−O bonds cleavage. In this procedure, various substituents, such as alkyl, methoxyl, chloro, bromo, and fluoro groups, are achieved smoothly by the thiolation in moderate to good yields.

EXPERIMENTAL SECTION

General Remarks. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz in $CDCl_3$. All chemical shifts are given as δ values (ppm) with reference to tetramethylsilane (TMS) as an internal standard. HRMS was performed on an FT-ICRMS mass instrument and measured with electrospray ionization (ESI). Copies of the ^{1}H and ^{13}C NMR spectra are provided in the Supporting Information. Products were purified by flash chromatography on 200−300 mesh

Scheme 3. Control Experiments



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silica gel. All melting points were determined without correction. Commercially available reagents and solvents were used without further purification except where noted.

General Procedure for the Synthesis of the Desired Thioethers 3. An oven-dried pressure tube was charged with 0.3 mmol of naphthols **1**, 0.36 mmol of arylsulfonyl hydrazides **2**, I_2 (0.15 mmol), and 2 mL of THF. Then, the reaction was stirred at 100 °C for 10 h. After cooling to room temperature, the solvent was evaporated in vacuo, and the residues were purified by column chromatography, eluting with petroleum ether/EtOAc to afford the disired thioethers **3**.

General Procedure for the Synthesis of the Desired Thioethers 5. An oven-dried pressure tube was charged with 0.3 mmol of naphthylamine **4**, 0.36 mmol of arylsulfonyl hydrazides **2**, I_2 (0.15 mmol), HOAc (0.15 mmol), and 2 mL of THF. Then, the reaction was stirred at 100 °C for 5 h. After cooling to room temperature, the solvent was evaporated in vacuo, and the residues were purified by column chromatography, eluting with petroleum ether/EtOAc to afford the disired thioethers **5**.

1-(Phenylthio)naphthalen-2-ol (3aa). Yellow solid (62.0 mg, 82% yield); mp 65−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22−8.20 (d, J = 8.0 Hz, 1H), 7.90−7.88 (d, J = 8.0 Hz, 1H), 7.81−7.79 (d, J = 8.0 Hz, 1H), 7.50−7.46 (m, 1H), 7.38−7.32 (m, 2H), 7.23 (s, 3H), 7.17−7.14 (m, 1H), 7.10−7.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 135.4, 135.3, 132.8, 129.5, 129.2, 128.6, 127.9, 126.4, 125.9, 124. 7, 123.8, 116.9, 108.1. HRMS (ESI): m/z calcd for $C_{16}H_{13}OS$ $[M + H]^+$, 253.0682; found, 253.0685.

1-(*p*-Tolylthio)naphthalen-2-ol (3ab). Yellow solid (75.8 mg, 95% yield); mp 77−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23−8.21 (d, J = 8.0 Hz, 1H), 7.83−7.81 (d, J = 8.0 Hz, 1H), 7.75−7.73 (d, J = 8.0 Hz, 1H), 7.46−7.23 (m, 1H), 7.32−7.28 (m, 2H), 7.22 (s, 1H), 6.92 (s, 4H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 135.8, 135.4, 132.6, 131.7, 129.9, 129.4, 128.5, 127.8, 126.6, 124.7, 123.7, 116.8, 108.7, 20.8. HRMS (ESI): m/z calcd for $C_{17}H_{15}OS$ $[M + H]^+$, 267.0838; found, 267.0839.

1-(*o*-Tolylthio)naphthalen-2-ol (3ac). Yellow solid (67.0 mg, 84% yield); mp 65−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.11 (d, J = 8.0 Hz, 1H), 7.90−7.87 (d, J = 12.0 Hz, 1H), 7.80−7.78 (d, J = 8.0 Hz, 1H), 7.47−7.43 (m, 1H), 7.36−7.32 (m, 2H), 7.16−7.14 (d, J = 8.0 Hz, 1H), 7.07 (s, 1H), 7.00−6.94 (m, 1H), 6.84−6.80 (m, 1H), 6.38−6.36 (d, J = 8.0 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 135.5, 135.1, 134.3, 132.7, 130.3, 129.5, 128.6, 127.9, 126.7, 125.4, 124.7, 124.6, 123.8, 116.9, 107.3, 20.0. HRMS (ESI): m/z calcd for $C_{17}H_{15}OS$ $[M + H]^+$, 267.0838; found, 267.0839.

1-((2,5-Dimethylphenyl)thio)naphthalen-2-ol (3ad). Yellow solid (75.6 mg, 90% yield); mp 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.12 (d, J = 12.0 Hz, 1H), 7.91−7.89 (d, J = 8.0 Hz, 1H), 7.81−7.79 (d, J = 8.0 Hz, 1H), 7.48−7.44 (m, 1H), 7.37−7.33 (m, 2H), 7.08−7.04 (m, 2H), 6.81−6.79 (d, J = 8 Hz, 1H), 6.21(s, 1H), 2.53 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 136.4, 135.6, 133.9, 132.7, 132.2, 130.2, 129.5, 128.5, 127.8, 126.4, 125.3, 124.7, 123.8, 116.9, 107.6, 21.0, 19.6. HRMS (ESI): m/z calcd for $C_{18}H_{17}OS$ $[M + H]^+$, 281.0995; found,281.0998.

1-((4-(*tert*-Butyl)phenyl)thio)naphthalen-2-ol (3ae). Yellow solid (73.9 mg, 80% yield); mp 71−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.81−7.79 (d, J = 8.0 Hz, 1H), 7.72−7.70 (d, J = 8.0 Hz, 1H), 7.43−7.38 (m, 1H), 7.29−7.23 (m, 2H), 7.15−7.09 (m, 3H), 6.91−6.87 (m, 2H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.1, 135.6, 132.6, 131.8, 129.5, 128.5, 127.9, 126.3, 126.2, 124.8, 123.8, 116.8, 108.6, 34.4, 31.2. HRMS(ESI) m/z calcd for $C_{20}H_{21}OS$ $[M + H]^+$, 309.1308; found, 309.1310.

1-((4-Methoxyphenyl)thio)naphthalen-2-ol (3af). Yellow solid (66.0 mg, 78% yield); mp 68−70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27−8.25 (d, J = 8.0 Hz, 1H), 7.86−7.84 (d, J = 8.0 Hz, 1H), 7.79−7.77 (d, J = 8.0 Hz, 1H), 7.51−7.46 (m, 1H), 7.36−7.29 (m, 3H), 7.04−7.02 (d, J = 8 Hz, 2H), 6.72−6.70 (d, J = 8 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 156.7, 135.3, 132.5, 129.5, 128.7, 128.5, 127.8, 125.9, 124.7, 123.7, 116.8, 114.9, 109.7, 55.3. HRMS (ESI): m/z calcd for $C_{17}H_{15}O_2S$ $[M + H]^+$, 283.0788; found, 283.0789.

1-((3-Fluorophenyl)thio)naphthalen-2-ol (3ag). Yellow solid (41.3 mg, 51% yield); mp 79−81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.08 (d, J = 8.0 Hz, 1H), 7.85−7.83 (d, J = 8.0 Hz, 1H), 7.75−7.73 (d, J = 8.0 Hz, 1H), 7.44−7.42 (m, 1H), 7.40−7.25 (m, 2H), 7.08−7.02 (m, 1H), 6.99 (s, 1H), 6.76−6.68 (m, 2H), 6.60−6.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4−161.9 (d, J = 247.2 Hz), 157.1, 137.9−137.8 (d, J = 7.6 Hz), 135.3, 133.2, 130.5−130.4 (d, J = 8.3 Hz), 129.5, 128.7, 128.1, 124.4, 124.0, 121.9−121.8 (d, J = 2.9 Hz), 116.9, 113.4−113.1 (d, J = 24.1 Hz), 113.0−112.8 (d, J = 21.5 Hz), 107.2. HRMS (ESI): m/z calcd for $C_{16}H_{12}FOS$ $[M + H]^+$, 271.0588; found, 271.0591.

1-((4-Chlorophenyl)thio)naphthalen-2-ol (3ah). Yellow solid (69.5 mg, 81% yield); mp 85−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16−8.14 (d, J = 8.0 Hz, 1H), 7.91−7.89 (d, J = 8.0 Hz, 1H), 7.81−7.79 (d, J = 8.0 Hz, 1H), 7.51−7.47 (m, 1H), 7.39−7.31 (m, 2H), 7.13−7.10 (m, 3H), 7.94−6.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 135.2, 133.9, 133.1, 131.9, 129.5, 129.3, 128.6, 128.1, 127.6, 124.4, 124.0, 116.9, 107.6. HRMS (ESI): m/z calcd for $C_{16}H_{12}ClOS$ $[M + H]^+$287.0292, found 287.0294.

1-((2-Chlorophenyl)thio)naphthalen-2-ol (3ai). Yellow solid (63.5 mg, 74% yield); mp 59−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (d, J = 8.0 Hz, 1H), 7.87−7.85 (d, J = 8.0 Hz, 1H), 7.76−7.74 (d, J = 8.0 Hz, 1H), 7.44−7.40 (m, 1H), 7.33−7.26 (m, 3H), 6.97−6.94 (m, 2H), 6.84−6.80 (m, 1H), 6.30−6.28 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 135.4, 134.5, 133.3, 131.6, 129.7, 129.6, 128.6, 128.2, 127.4, 126.6, 126.4, 124.5, 124.1, 117.0, 106.6. HRMS (ESI)m/z calcd for $C_{16}H_{12}ClOS$ $[M + H]^+$, 287.0292, found 287.0295.

1-((4-Bromophenyl)thio)naphthalen-2-ol (3aj). Yellow solid (83.9 mg, 85% yield); mp 103−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.13 (d, J = 8.0 Hz, 1H), 7.89−7.87 (d, J = 8.0 Hz, 1H), 7.80−7.78 (d, J = 8.0 Hz, 1H), 7.49−7.45 (m, 1H), 7.37−7.30 (m, 2H), 7.25−7.23 (m, 2H), 7.08 (s, 1H), 6.86−6.84 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 135.1, 134.6, 133.1, 132.1, 129.5, 128.6, 128.1, 127.9, 124.4, 124.0, 119.6, 116.9, 107.4. HRMS (ESI): m/z calcd for $C_{16}H_{12}BrOS$ $[M + H]^+$, 330.9787; found, 330.9788.

1-((4-(Trifluoromethyl)phenyl)thio)naphthalen-2-ol (3ak). Yellow solid (58.6 mg, 61% yield); mp 82−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18−8.16 (d, J = 8.0 Hz, 1H), 7.98−7.95 (d, J = 12.0 Hz, 1H), 7.87−7.85 (d, J = 8.0 Hz, 1H), 7.55−7.51 (m, 1H), 7.44−7.37 (m, 4H), 7.11−7.05 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 140.5, 135.2, 133.4, 129.6, 128.3, 128.2, 128.5−127.5 (q, J = 32.5 Hz), 126.03−125.93 (m), 126.0, 124.3, 124.1, 128.0−120.0 (q, J = 270.1 Hz), 117.0, 106.5. HRMS (ESI): m/z calcd for $C_{17}H_{12}F_3OS$ $[M + H]^+$, 321.0556; found, 321.0559.

1-(Thiophen-2-ylthio)naphthalen-2-ol (3am). Yellow solid (65.8 mg, 85% yield); mp 54−56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46−8.44 (d, J = 8.0 Hz, 1H), 7.83−7.80 (d, J = 1.20 Hz, 1H), 7.77−7.75 (d, J = 8.0 Hz, 1H), 7.58−7.54 (m, 1H), 7.38−7.34 (m, 1H), 7.28−7.23 (m, 2H), 7.15−7.13 (m, 1H), 7.10−7.09 (m, 1H), 6.86−6.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 134.8, 133.8, 132.7, 130.6, 129.5, 128.6, 127.8, 127.7, 127.4, 124.5, 123.8, 116.9, 111.6. HRMS (ESI): m/z calcd for $C_{14}H_{11}OS_2$ $[M + H]^+$, 259.0246; found, 259.0249.

1-(*p*-Tolylthio)naphthalene-2,7-diol (3bb). Yellow solid (66.0 mg, 78% yield); mp 71−73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.77 (d, J = 8.0 Hz, 1H), 7.69−7.67 (d, J = 8.0 Hz, 1H), 7.52−7.51 (d, J = 4.0 Hz, 1H), 7.19−7.14 (m, 2H), 6.98−6.90 (m, 5H), 5.37 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 155.5, 137.3, 135.8, 132.5, 131. 6, 130.7, 123.0, 126.4, 124.7, 115.2, 114.2, 107.3, 107.0, 20.8. HRMS (ESI): m/z calcd for $C_{17}H_{15}O_2S$ $[M + H]^+$, 283.0788; found, 287.0790.

4-(*p*-Tolylthio)naphthalene-1,3-diol (3cb). Yellow solid (36.4 mg, 43% yield); mp 75−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.06 (m, 2H), 7.43−7.39 (m, 1H), 7.29−7.25 (m, 1H), 7.17−7.15 (d, J = 8.0 Hz, 1H), 6.91−6.83 (m, 4H), 6.62 (s, 1H), 5.90 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 155.3, 136.4, 135.6, 132.5, 129.9, 128.6, 126.2, 124.6, 123.2, 122.3, 121.2, 100.3, 99.7, 20.8. HRMS (ESI): m/z calcd for $C_{17}H_{15}O_2S$ $[M + H]^+$, 283.0788; found, 283.0791.

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6-Bromo-1-(*p*-tolylthio)naphthalen-2-ol (3db). Yellow solid (53.7 mg, 52% yield); mp 112−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (d, J = 8 Hz, 1H), 7.85−7.84 (d, J = 4.0 Hz, 1H), 7.69−7.67 (d, J = 8.0 Hz, 1H), 7.45−7.42 (m, 1H), 7.26−7.23 (d, J = 12.0 Hz, 1H), 7.12 (s, 1H), 6.90−6.88 (d, J = 8.0 Hz, 2H), 6.84−6.82 (d, J = 8.0 Hz, 2H), 2.15(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 136.2, 134.0, 131.5, 131.3, 131.0, 130.5, 130.4, 130.0, 126.8, 126.7, 118.0, 117.6, 109.2, 20.9. HRMS (ESI): m/z calcd for $C_{17}H_{14}BrOS$ $[M + H]^+$, 344.9943; found, 344.9945.

(2-Methoxynaphthalen-1-yl)(*p*-tolyl)sulfane (3eb). Yellow solid (51.2 mg, 61% yield); mp 57−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41−8.38 (d, J = 8.0 Hz, 1H), 7.84−7.82 (d, J = 8.0 Hz, 1H), 7.71−7.69 (d, J = 8.0 Hz, 1H), 7.40−7.37 (m, 1H), 7.28−7.22 (m, 2H), 6.87−6.82(m, 4H), 3.84 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 136.3, 134.5, 131.8, 129.5, 129.4, 128.2, 127.6, 126.7, 125.5, 124.0, 113.7, 113.5, 56.9, 20.8. HRMS (ESI): m/z calcd for $C_{18}H_{17}OS$ $[M + H]^+$, 281.0995; found, 281.0998.

(2-Ethoxynaphthalen-1-yl)(*p*-tolyl)sulfane (3fb). Yellow solid (64.4 mg, 73% yield); mp 63−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45−8.43 (d, J = 8.0 Hz, 1H), 7.83−7.81 (d, J = 8.0 Hz, 1H), 7.73−7.71(d, J = 8.0 Hz, 1H), 7.43−7.39 (m, 1H), 7.31−7.27 (m, 1H), 7.24−7.17 (m, 1H), 6.92−6.85 (m,4H), 4.12−4.07 (m, 2H), 2.15 (s, 3H), 1.25−1.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 136.3, 134.8, 134.6, 131.4, 129.6, 129.4, 128.2, 127.4, 127.2, 125.6, 124.0, 115.1, 65.5, 20.9, 14.9. HRMS (ESI): m/z calcd for $C_{19}H_{19}OS$ $[M + H]^+$, 295.1151; found, 295.1154.

1-(*p*-Tolylthio)-5,6,7,8-tetrahydronaphthalen-2-ol (3gb). White solid (29.4 mg, 36% yield); mp 53−55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.14 (d, J = 16.0 Hz, 1H), 6.98−6.92 (m, 4H), 6.68 (s, 1H), 6.18 (s, 1H), 2.68−2.60 (m, 4H), 2.20 (s, 3H), 1.71−1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 141.8, 136.8, 135.9, 132.8, 130.1, 129.9, 127.2, 115.1, 113.8, 29.5, 28.4, 23.2, 22.9, 20.9. HRMS (ESI): m/z calcd for $C_{17}H_{19}OS$ $[M + H]^+$, 271.1151; found, 271.1154.

4-(*p*-Tolylthio)naphthalen-1-ol (3hb). Yellow solid (57.5 mg, 72% yield); mp 73−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27−8.25 (m, 1H), 8.16−8.13 (m, 1H), 7.57−7.55 (d, J = 8.0 Hz, 1H), 7.45−7.39 (m, 2H), 6.92−6.87 (m, 4H), 6.70−6.68 (d, J = 8.0 Hz, 1H), 5.54 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 135.4, 135.2, 134.9, 134.8, 129.7, 127.6, 127.5, 126.1, 125.7, 125.3, 122.2, 121.6, 108.8, 20.9. HRMS (ESI): m/z calcd for $C_{17}H_{15}OS$ $[M + H]^+$, 267.0838; found, 267.0839..

1-(Phenylthio)naphthalen-2-amine (5aa). Red solid (52.7 mg, 70% yield); mp 99−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.17 (d, J = 8.0 Hz, 1H), 7.65−7.60 (m, 2H), 7.35−7.31 (m, 1H), 7.18−7.12 (m, 1H), 7.06−7.03 (m, 2H), 6.97−6.91 (m, 4H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 136.8, 136.6, 131.8, 128.9, 128.4, 128.3, 127.7, 125.8, 125.0, 124.2, 122.5, 117.6, 104.6. HRMS (ESI): m/z calcd for $C_{16}H_{14}NS$ $[M + H]^+$, 252.0842; found, 252.0845.

1-(*p*-Tolylthio)naphthalen-2-amine (5ab). Red solid (66.8 mg, 84% yield); mp 113−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20−8.18 (d, J = 8.0 Hz, 1H), 7.62−7.58 (m, 2H), 7.34−7.29 (m, 1H), 7.16−7.12 (m, 1H), 6.90−6.81 (m, 5H), 4.56 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 136.6, 134.8, 133.2, 131.6, 129.7, 128.3, 128.2, 127.7, 126.0, 124.2, 122.5, 117.6, 105.2, 20.8. HRMS (ESI): m/z calcd for $C_{17}H_{16}NS$ $[M + H]^+$, 266.0998; found, 266.0999.

1-((2,5-Dimethylphenyl)thio)naphthalen-2-amine (5ac). Red solid (58.6 mg, 70% yield); mp 60−62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.13 (d, J = 8.0 Hz, 1H), 7.70−7.64 (m, 2H), 7.36−7.32(m, 1H), 7.21−7.17 (m, 1H), 7.00−6.96 (m, 2H), 6.72−6.70 (d, J = 8.0 Hz, 1H), 6.19 (s, 1H), 2.43 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 136.8, 136.1, 135.1, 131.9, 131.6, 130.0, 128.5, 128.3, 127.7, 125.6, 124.7, 124.3, 122.5, 117.6, 104.3, 21.1, 19.6. HRMS (ESI): m/z calcd for $C_{18}H_{18}NS$ $[M + H]^+$, 280.1155; found, 280.1158.

1-((4-Methoxyphenyl)thio)naphthalen-2-amine (5ad). Red solid (48.1 mg, 57% yield); mp 101−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25−8.23 (d, J = 8.0 Hz, 1H), 7.65−7.61 (m, 2H), 7.38−7.34 (m, 1H), 7.19−7.15 (m, 1H), 6.95−6.92 (m, 3H), 6.65−6.62 (m, 2H), 4.65 (s, 2H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.2, 136.6, 131.5, 128.4, 128.3, 127.9, 127.7, 127.5, 124.3, 122.5, 117.6, 114.8, 106.2, 55.3. HRMS (ESI): m/z calcd for $C_{17}H_{16}NOS$ $[M + H]^+$, 282.0947; found, 282.0950.

1-((3-Fluorophenyl)thio)naphthalen-2-amine (5ae). Red solid (64.6 mg, 80% yield); mp 113−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.11 (d, J = 8.0 Hz, 1H), 7.67−7.61 (m, 2H), 7.36−7.32 (m, 1H), 7.19−7.12 (m, 1H), 7.03−6.98 (m, 1H), 6.93−6.91 (d, J = 8.0 Hz, 1H), 6.74−6.72 (m, 1H), 6.66−6.64 (m, 1H), 6.62−6.55 (m, 1H), 4.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4−162.0 (d, J = 246.1 Hz), 148.6, 139.5−139.4 (d, J = 7.5 Hz), 136.4, 132.2, 130.2−130.1 (d, J = 8.5 Hz), 128.4, 128.3, 127.9, 123.9, 122.7, 121.4−121.4 (d, J = 2.8 Hz), 117.6, 112.8−112.5 (d, J = 24.0 Hz), 112.1−111.9 (d, J = 21.3 Hz), 103.6. HRMS (ESI): m/z calcd for $C_{16}H_{13}FNS$ $[M + H]^+$, 270.0747; found, 270.0751.

1-((4-Chlorophenyl)thio)naphthalen-2-amine (5af). Red solid (71.8 mg, 84% yield); mp 123−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.10 (d, J = 8.0 Hz, 1H), 7.65−7.60 (m, 2H), 7.35−7.31 (m, 1H), 7.18−7.12 (m, 1H), 7.01−6.99 (m, 2H), 6.92−6.90 (d, J = 8.0 Hz, 1H), 6.84−6.81 (m, 2H), 4.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 136.4, 135.4, 132.0, 130.8, 129.0, 128.4, 128.3, 127.9, 127.1, 123.9, 122.7, 117.6, 104.0. HRMS (ESI): m/z calcd for $C_{16}H_{13}ClNS$ $[M + H]^+$, 286.0452; found, 286.0454.

1-((2-Chlorophenyl)thio)naphthalen-2-amine (5ag). Red solid (62.4 mg, 73% yield); mp 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.09 (d, J = 8.0 Hz, 1H), 7.69−7.62 (m, 2H), 7.36−7.27 (m, 1H), 7.26−7.25 (d, J = 4.0 Hz, 1H), 7.19−7.14(m, 1H), 6.96−6.87 (m, 2H), 6.81−6.77 (m, 1H), 6.34−6.32 (m, 1H), 4.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 136.5, 135.6, 132.2, 131.3, 129.5, 128.4, 128.0, 127.1, 125.9, 125.7, 124.0, 122.7, 117.6, 102.9. HRMS (ESI): m/z calcd for $C_{16}H_{13}ClNS$ $[M + H]^+$, 286.0452; found, 286.0453.

1-((4-Bromophenyl)thio)naphthalen-2-amine (5ah). Red solid (84.9 mg, 86% yield); mp 119−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.08 (d, J = 8.0 Hz, 1H), 7.62−7.57 (m, 2H), 7.33−7.29 (m, 1H), 7.16−7.10 (m, 3H), 6.88−6.85(d, J = 8.0 Hz, 1H), 6.75−6.73 (d, J = 8.0 Hz, 2H), 4.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 136.3, 136.1, 132.0, 131.9, 128.4, 128.3, 127.9, 127.4, 123.9, 122.6, 118.5, 117.5, 103.8. HRMS (ESI): m/z calcd for $C_{16}H_{13}BrNS$ $[M + H]^+$, 329.9947; found, 329.9949.

1-((4-(Trifluoromethyl)phenyl)thio)naphthalen-2-amine (5ai). Red solid (85.2 mg, 89% yield); mp 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.07 (d, J = 8.0 Hz, 1H), 7.69−7.62 (m, 2H), 7.36−7.32 (m, 1H), 7.29−7.27 (d, J = 8.0 Hz, 2H), 7.20−7.12 (m, 1H), 6.98−6.92 (m, 3H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 142.1, 136.4, 132.4, 128.5, 128.4, 128.1, 127.1 (q, J = 32.5 Hz), 125.7 (q, J = 3.9 Hz), 125.5, 123.8, 122.8, 117.6, 102.8. HRMS (ESI): m/z calcd for $C_{17}H_{13}F_3NS$ $[M + H]^+$, 320.0716; found, 320.0718.

1-(Thiophen-2-ylthio)naphthalen-2-amine (5ak). Red solid (50.1 mg, 66% yield); mp 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42−8.40 (d, J = 8.0 Hz, 1H), 7.62−7.60 (d, J = 8.0 Hz, 2H), 7.45−7.41 (m, 1H), 7.21−7.17 (m, 1H), 7.04−7.03 (m, 1H), 6.97−6.96 (m, 1H), 6.92−6.90 (d, J = 8.0 Hz, 1H), 6.79−6.77 (m, 1H), 4.75 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 136.0, 135.9, 131.7, 129.0, 128.4, 128.3, 127.7, 127.2, 126.6, 124.1, 122.5, 117.7, 108.2. HRMS (ESI): m/z calcd for $C_{14}H_{12}NS_2$ $[M + H]^+$, 258.0406; found, 258.0410.

4-(*p*-Tolylthio)naphthalen-1-amine (5cb). Red solid (50.9 mg, 64% yield); mp 75−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.70 (m, 2H), 7.44−7.37 (m, 3H), 7.18−7.16 (d, J = 8.0 Hz, 1H), 6.93 (s, 4H), 4.90 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 135.3, 134.9, 133.5, 133.4, 129.8, 128.6, 126.9, 126.8, 125.3, 123.2, 121.5, 118.5, 109.0, 20.9. HRMS (ESI): m/z calcd for $C_{17}H_{16}NS$ $[M + H]^+$, 266.0998; found, 266.0995.

1,2-Di-*p*-tolyldisulfane (6). Yellow solid; mp 47−49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.39 (d, J = 8.0 Hz, 4H), 7.13−7.11 (d, J = 8.0 Hz, 4H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.9, 129.8, 128.6, 21.0. HRMS (ESI): m/z calcd for $C_{14}H_{15}S_2$ $[M + H]^+$, 247.0610; found, 247.0611.

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***S*-(*p*-Tolyl)4-methylbenzenesulfonothioate (7).** White solid; mp 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.45 (d, J = 8.0 Hz, 2H), 7.26−7.20 (m, 4H), 7.15−7.13 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.0, 140.5, 136.5, 130.2, 129.3, 127.6, 124.6, 21.6, 21.4. HRMS (ESI): m/z calcd for $C_{14}H_{15}O_2S_2$ $[M + H]^+$, 279.0508; found, 279.0511.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all 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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