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ARTICLE

Chemoselective Cross-Coupling Reaction of Sodium Sulfinates with Phenols under Aqueous Conditions

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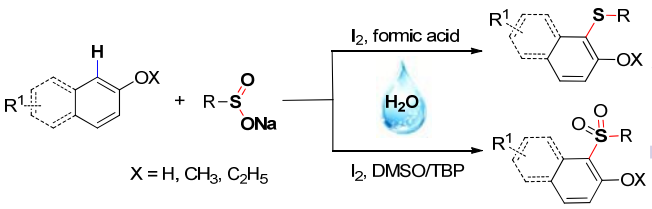
An efficient procedure for the formation of C-S bonds *via* direct C-H functionalization has been developed under aqueous conditions. In this process, stable and readily available sodium sulfinates were used as sulfuration source to provide aryl sulfides and sulfones in good to excellent yields. A broad range of functional groups were well tolerated in this reaction system.

Introduction

In synthetic organic reactions, the sulfur-containing groups serve as an important auxiliary function in synthetic sequences.[1] The sulfur-containing organic compounds also play significant roles in organic synthesis, pharmaceutical drugs and materials science.[2] Among them, aryl sulfides and aryl sulfones have gained intensive attention due to their prominent drug activity, such as anti-HIV-1, antifungal, antibacterial, and antitumoral.[3] Therefore, many researchers have devoted their efforts to developing highly efficient, regioselective, and environmentally friendly C-S bond formation methods.[4] Traditionally, the C-S bond can be constructed by the condensation of halohydrocarbon (or other functional substrates) with sulfuration reagents.[5] However, some of these processes suffer from pre-functionalization of both the coupling partners. In recent years, the direct C-S bond formation *via* C-H functionalization has attracted great interests since this method can potentially lead to more efficient synthesis with a reduced number of synthetic operations.[6]

Direct C-H functionalization for the synthesis of aryl sulfides and sulfones under metal-free conditions is highly desirable especially for pharmaceutical drugs purpose to avoid metal contaimination. Various sulfuration reagents such as disulfides,[7] sulfenyl halides,[8] sulfinic acids,[9] thiols,[10] arylsulfonyl cyanides[11] and *N*-(thio)succinimides[12] have been employed under metal-free conditions. Among the various sulfuration reagents, sodium sulfinates are stable and easy to handle, and they have been widely used as sulfonylating agents.[13] Recently, we and others have developed various approaches for C-H sulfenylation[14] and sulfonylation[15] using sodium sulfinates as the starting materials. However, most of these reactions were carried out in organic solvents. From the perspective of green chemistry, water is an ideal solvent for chemical transformation because of its natural, inexpenstive, nontoxic, and environmentally friendly characteristics.[16] Thus, the development of efficient approach to construct C-S bond under metal-free conditions using water as solvent is highly desirable. As our continuing efforts using sodium sulfinates as the sulfuration agents for the C-S bond formation *via* C-H functionalization. Herein, we disclose a novel, regioselective and chemoselective route for the synthesis of aryl sulfides and sulfones *via* C-H bond functionalization of phenols with sodium sulfinates under aqueous conditions.



Scheme 1 C-S Bonds formation with sodium sulfinates

Results and discussion

To get optimized reaction conditions for the direct sulfenylation 2-naphthol (**1a**) and sodium benzenesulfinate (**2a**) were initially used as the standard substrates under different conditions (Table 1). Several iodide-containing additives were initially investigated, and among them I_2 (100 mol%) showed the best efficiency to give the corresponding product **3a** in 88% yield at 110 °C under an argon atmosphere (Table 1, entry 5). The reaction was less efficient when other acids were used (Table 1, entries 6-9). Decreasing the reaction temperature or the amount of I_2 both slightly dereased the reaction yields (Table 1, entries 10-11). Lower yield was obtained when the reaction was run i air. Formic acid and I_2 both are necessary for the reductive

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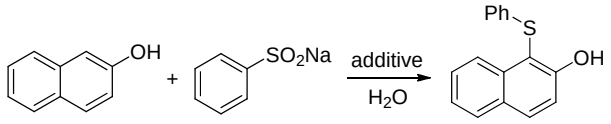
coupling, and much lower yield was obtained when the reaction was carried out in the absence of one of them (Table 1, entries 12-13).

Table 1. Optimization of the direct sulfenylation reaction conditions [a]



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

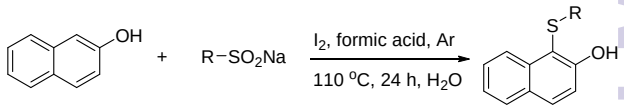
Entry	Additive	Acid	Yield[b](%)
1	KI	formic acid	18
2	NIS	formic acid	55
3	NaI	formic acid	14
4	TBA	formic acid	35
5	I_2	formic acid	88
6	I_2	acetic acid	52
7	I_2	pivalic acid	72
8	I_2	hypophosphite	46
9	I_2	trifluoroacetate	70
10[c]	I_2	formic acid	68
11[d]	I_2	formic acid	79
12[e]	I_2	formic acid	45
13	I_2		35
14		formic acid	8

[a] Conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), H_2O (0.5 mL), Additive (0.2 mmol), Acid (0.1 mL), 24 h, 110 °C, under Ar. [b] GC yield. [c] I_2 (0.1 mmol). [d] 90 °C. [e] Under air.

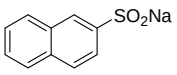
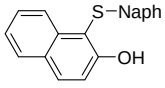
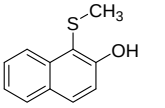
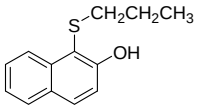
Under the optimized conditions, various sodium sulfinates and 2-naphthol were explored as the substrates, and the results are summarized in Table 2. A series of *para*-substituted sodium sulfinates smoothly reacted with **1a** to give 1-arylsulfenyl-2-naphthols in good to high yields (Table 2, entries 2-5). Functional groups such as halogens, trifluoromethyl, and trifluoromethoxy tolerated well under the optimized reaction conditions (Table 2, entries 6-10). It should be noted that cleavage of the C-halogen bond was not observed as determined by GC-MS analysis. More bulky substrates such as 2-naphthylsulfinic acid sodium salt (**2k**) also reacted with **1a** and gave the product in 75% yield (Table 2, entry 11). To our delight, apart from aromatic sodium sulfinates, less reactive aliphatic sodium sulfinates such as sodium methanesulfinate (**2l**), sodium propane-1-sulfinate (**2m**) also coupled with 2-naphthol to give the desired product **3l** and **3m** in 60%, 80% yields, respectively (Table 2, entries 12 - 13).

To further examine the scope and limitations of the direct sulfenylation reaction, we tested various phenol derivatives for this kind of reaction (Table 3). 2-Naphthol with a bromo group at C-6 and C-7 both smoothly coupled with **2a** and gave the desired products **3n** and **3p** in 92% and 88% yields, respectively. Also, no cleavage of the C-Br bond was observed. Notably, under the optimized reaction conditions, the direct sulfenylation occurred exclusively at the C-1 position of the 2-naphthol moiety. When the C-6 and C-7 position of 2-naphthol was occupied by an active hydroxy group, no C-5 and C-8 sulfenylation products (**3o**, **3q**) were observed. To our delight, 2-methoxynaphthalene and 2-ethoxynaphthalene participated well in this protocol to afford aryl sulfides **3r** and **3s** in good yields. Besides 2-naphthol, this reaction system could also be applied to the direct sulfenylation of phenol derivatives and methoxy-benzenes with sodium benzenesulfinate (**3t**-**3w**). We further tested this method with *N*,*N*-dimethylaniline and the reaction proceeded smoothly to provide the corresponding product **3x** in 48% yield.

Table 2. Reaction of 2-naphthol with sodium sulfinate [a]



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

Entry	Sodium sulfinate		Product		Yield[b] (%)
1	R = H	**2a**		**3a**	80
2	R = CH_3	**2b**		**3b**	89
3	R = *iso*-propyl	**2c**		**3c**	78
4	R = *tert*-butyl	**2d**		**3d**	68
5	R = OCH_3	**2e**		**3e**	85
6	R = F	**2f**		**3f**	70
7	R = Cl	**2g**		**3g**	75
8	R = Br	**2h**		**3h**	75
9	R = CF_3	**2i**		**3i**	71
10	R = OCF_3	**2j**		**3j**	66
11		**2k**		**3k**	75
12	CH_3SO_2Na	**2l**		**3l**	60
13	$CH_3CH_2CH_2SO_2Na$	**2m**		**3m**	80

[a] Conditions: **1a** (0.2 mmol), **2** (0.5 mmol), I_2 (0.2 mmol), formic acid (0.1 mL), H_2O (0.5 mL), 110 °C, Ar, 24 h. [b] Isolated yield.

After screening the direct sulfenylation reaction, we next sought to expand the scope of sulfonylation of 2-naphthols with sodium sulfinates. To get the reaction conditions for sodium sulfinate substrates, we reinvestigated the reaction conditions for this kind of transformation. After systematic investigation, we found that TBP (di-*tert*-butyl peroxide) and DMSO both were necessary (Table S1). When sodium benzenesulfinate (**2a**)

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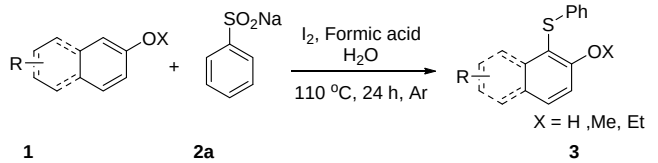
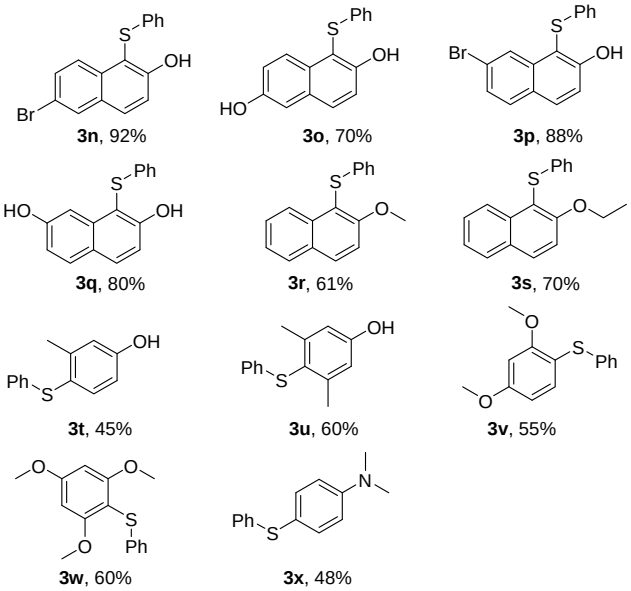
reacted with 2-naphthol at 100 °C under air atmosphere, the desired product **4a** was obtained in 82% isolated yield (Table 5). The reactions with sodium benzenesulfinates bearing electron-donating groups and electron-withdrawing substituents at the *para*-position proceeded smoothly to give the desired products (**4b-4d**, **4i-4j**) in good to excellent yields. Under the optimized conditions, halogen substituents were all well tolerated and afforded the desired products (**4f-4h**) in good yields. When sodium naphthalene-2-sulfinate was subjected to the procedure, the product **4k** was isolated in 71% yield. Notably, the reaction of aliphatic sodium sulfinates, such as sodium methanesulfinate, sodium propane-1-sulfinate, sodium cyclopropanesulfinate, with **1a** afforded the desired products (**4l-4n**) in moderate to good yields. Furthermore, sensitive bromo and active hydroxy group substituents on 2-naphthols were well tolerated, and the desired products (**4o**-**4q**) were obtained in good yields.

Table 3. Substrate scope[a]



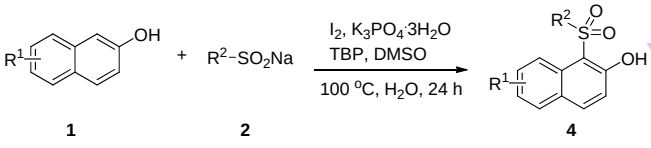
1 2a 3



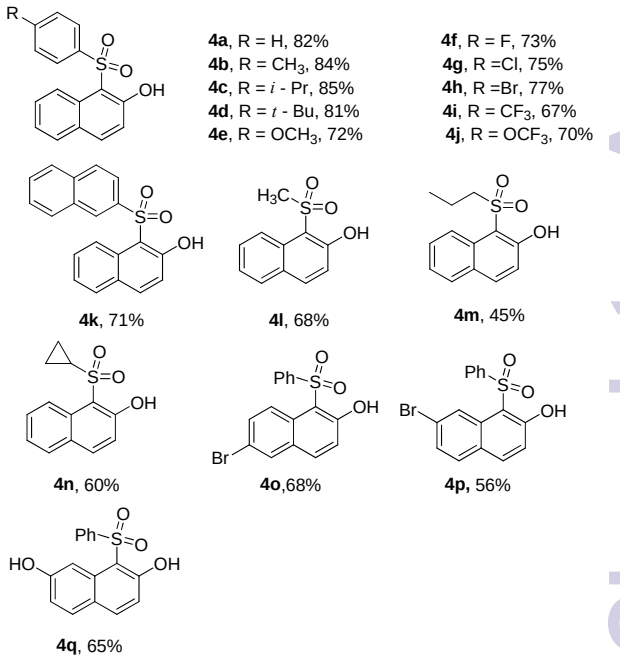
[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.5 mmol), I_2 (0.2 mmol), formic acid (0.1 mL), H_2O (0.5 mL), 110 °C, Ar, 24 h; isolated yield.

To gather more information about the reaction mechanism, a large number of control experiments were set up under various reaction conditions (Scheme S1, S2, S3). The reactions with phenol derivatives (**3t**, **3u**) and methoxy-benzenes (**3v**, **3w**) bearing electron-donating groups substituents proceeded smoothly to give the desired sulfenylation products in good yields. But no desired products were observed when 3-(trifluoromethyl)phenol (**1q**) and 1-methoxy-3-(trifluoromethyl)benzene (**1r**) were used. These results indicate that the reaction may proceed through an electrophilic substitution pathway. Based on these observations, we proposed a plausible mechanism for this transformation on the basis of our previous observations and literature.[17] The reduction of sodium sulfinates with iodine and formic acid generates electrophilic intermediate Ar-SI (**A**). The species Ar-SI liberates the electrophile RS^+, which reacts with 2-naphthol to produce intermediate **B**. This intermediate releases a proton to afford the desired product. On the other hand, the procedure of the direct sulfonylation of 2-naphthol is similar to the direct sulfenylation pathway. Sodium sulfinates react with iodine to give sulfonyl iodide **C** in present of oxidant, which readily mediates iodosulfonylation of the 2-naphthol to give an intermediate **D**. Spontaneous elimination of HI to afford the desired product.

Table 4. Reaction of various sodium sulfinates with 2-naphthols[a]



1 2 4



[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), I_2 (0.2 mmol), $K_3PO_4{\cdot}3H_2O$ (0.2 mmol), TBP (0.2 mmol), DMSO (0.2 mmol), H_2O (0.5 mL), 100 °C, 24 h, air; isolated yield.

Conclusions

In conclusion, we have developed a metal-free, green and environmentally friendly method for the synthesis of aryl

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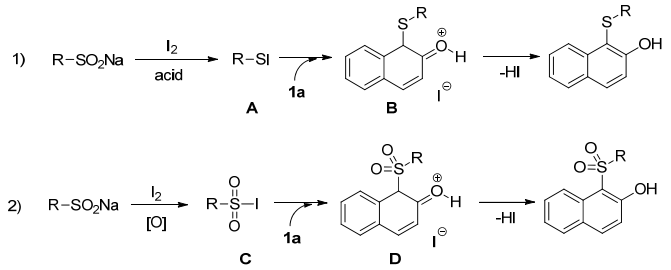
sulfides and sulfones under aqueous conditions. Various sodium sulfinates were used as the sulfur source to smoothly couple with 2-naphthols. Iodine was used as an effective additive in this transformation. Halogen and other functional groups were well tolerated under the optimized reaction conditions. This method affords an efficient alternative approach for the synthesis of biologically important aryl sulfide and aryl sulfones from sodium sulfinates.



Scheme 2 Mechanistic proposal

Experimental

General methods

The sulfenylation reaction is conducted under an atmosphere of argon and the sulfonylation reaction is carried out in an air atmosphere. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or acetone signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at Jiangxi University of Traditional Chinese Medicine. The structures of known compounds were further corroborated by comparing their NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

General procedure: (3a):

A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol), naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol), I_2 (50.8 mg, 0.2 mmol). Formic acid (0.1 mL) and H_2O (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 110 ^{o}C for 24 h. The volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3a** as white solid; yield: 40.3 mg (80%), mp 50-53 ^{o}C.

General procedure: (4a):

A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (**2a**, 65.6 mg, 0.4 mmol), naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol), I_2 (50.8 mg, 0.2 mmol), $K_3PO_4{\cdot}3H_2O$ (53.2 mg, 0.2 mmol). TBP (35 μL, 0.2 mmol), DMSO (15 μL, 0.2 mmol) and H_2O (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 100 ^{o}C for 24 h. The volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4a** as yellow solid; yield: 46.6 mg (82%), mp 129 - 133 ^{o}C.

1-(Phenylsulfonyl)naphthalen-2-ol (3a, CAS: 97992-89-7).[17a] White solid, yield 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.22 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.39-7.33 (m, 2H), 7.12 - 7.01 (m, 4H), 7.03 (d, J = 7.7 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.0, 135.4, 135.3, 132.8, 129.5, 129.1, 128.5, 127.9, 126.3, 125.9, 124.7, 123.8, 116.8, 108.0. MS (EI) *m/z* (%) 252, 191, 146, 115, 77.

1-Tosylnaphthalen-2-ol (3b, CAS: 799764-32-2).[17a] ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.23 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 - 7.32 (m, 2H), 7.21 (s, 1H), 7.00 - 6.91 (m, 4H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.9, 135.8, 135.4, 132.6, 131.7, 129.9, 129.5, 128.5, 127.8, 126.7, 124.7, 123.7, 116.8, 108.7, 20.8. MS (EI) *m/z* (%) 266, 205, 146, 115, 91.

1-((4-*iso*-Propylphenyl)sulfonyl)naphthalen-2-ol (3c). brown semisolid, yield 78%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.25 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.37 - 7.30 (m, 2H), 7.21 (s, 1H), 7.03 - 6.96 (m, 3H), 2.79 (m, 1H), 1.16 (s, 3H), 1.15 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.9, 146.9, 135.5, 132.6, 132.1, 129.5, 128.5, 127.9, 127.4, 126.6, 124.8, 123.8, 116.8, 108.7, 33.6, 23.8. HRMS calcd. for: $C_{19}H_{18}OSNa$ $[M+Na]^+$ 317.09706, found 317.09718.

1-((4-(*tert*-Butyl)phenyl)sulfonyl)naphthalen-2-ol (3d). orange semisolid, yield 68%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.25 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 - 7.32 (m, 2H), 7.21 - 7.15 (m, 3H), 6.99 - 6.94 (m, 2H), 1.23 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.9, 149.1, 135.5, 132.6, 131.8, 129.4, 128.5, 127.8, 126.3, 126.2, 124.8, 123.8, 116.8, 108.6, 34.3, 31.2. HRMS calcd. for: $C_{20}H_{20}OSNa$ $[M+Na]^+$ 331.11271, found 331.11211.

1-((4-Methoxyphenyl)thio)naphthalen-2-ol (3e). yellow solid, yield 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.26 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.38 - 7.27 (m, 3H), 7.04 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.4, 156.7, 135.3, 132.5, 129.5, 128.8, 128.5, 127.8, 125.9, 124.7, 123.7, 116.8, 114.9, 109.7, 55.3. HRMS calcd. for: $C_{17}H_{14}O_2SNa$ $[M+Na]^+$ 305.06067, found 305.06095.

1-((4-Fluorophenyl)thio)naphthalen-2-ol (3f). white solid, yield 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.3 Hz, 1H), 7.40 - 7.30 (m, 2H), 7.17 (s, 1H), 7.04 - 6.96 (m, 2H), 6.88 (t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 161.4 (d, J = 244.4 Hz), 156.9, 135.2, 132.9, 130.3 (d, J = 3.24 Hz), 129.5, 128.6, 128.3 (d, J = 7.87Hz), 128.0, 124.5, 123.9, 116.9, 116.3 (d, J = 22.11Hz), 108.5. HRMS calcd. for: $C_{16}H_{10}FOS$ $[M-H]^-$ 269.04419, found 269.04394.

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1-((4-Chlorophenyl)thio)naphthalen-2-ol (3g).[17a] brown solid, yield 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.15 (d, J = 8.2 Hz, 1H), 7.91 - 7.89 (m, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.1 Hz, 1H), 7.38 - 7.30 (m, 2H), 7.12 - 7.10 (m, 2H), 6.93 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.9, 135.1, 133.9, 133.0, 131.8, 129.5, 129.2, 128.6, 128.0, 127.6, 124.4, 123.9, 116.9, 107.6. MS (EI) *m/z* (%) 286, 225, 218, 146, 115.

1-((4-Bromophenyl)thio)naphthalen-2-ol (3h).[17a] yellow solid, yield 75%. 1H NMR (CDCl3, 400 MHz, ppm): δ 8.15 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.43 - 7.32 (m, 3H), 7.28 (d, J = 8.2 Hz, 1H), 7.08 (s, 1H), 6.88 (d, J = 8.2 Hz, 2H). MS (EI) m/z (%) 331, 218, 189, 146, 115.

1-((4-(Trifluoromethyl)phenyl)thio)naphthalen-2-ol (3i). white solid, yield 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.42 - 7.33 (m, 4H), 7.07 (d, J = 7.7 Hz, 2H), 7.00 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 7. 152, 140.6, 135.2, 133.4, 129.6, 128.7, 128.2, 128.1, 127.8, 126.0, 125.97, 125.93, 125.90, 124.1 (q, J = 90.1 Hz), 117.0. HRMS calcd. for: $C_{17}H_{12}F_3OS$ $[M+H]^+$ 321.05555, found 321.05563.

1-((4-(Trifluoromethoxy)phenyl)thio)naphthalen-2-ol (3j). white solid, yield 66%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.40 - 7.32 (m, 2H), 7.09 (s, 1H), 7.02 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.1, 147.4, 135.2, 134.1, 133.2, 129.5, 128.7, 128.1, 127.5, 124.4, 124.0, 121.9, 121.6, 116.9, 107.5. HRMS calcd. for: $C_{17}H_{12}F_3O_2S$ $[M+H]^+$ 337.05046, found 337.05051.

1-(Naphthalen-2-ylthio)naphthalen-2-ol (3k, CAS: 5432-97-3).[17a] white solid, yield 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.25 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.56 (d, J = 6.3 Hz, 1H), 7.50 - 7.36 (m, 6H), 7.23 - 7.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.1, 135.4, 133.7, 132.9, 132.7, 131.7, 129.5, 128.9, 128.5, 127.9, 127.6, 127.0, 126.6, 125.6, 124.64, 124.61, 124.5, 123.8, 116.9, 108.1. MS (EI) *m/z* (%) 302, 269, 128, 115.

1-(Methylthio)naphthalen-2-ol (3l, CAS: 7439-28-3).[18] brown liquid, yield 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.33 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.56 (t, J = 7.1 Hz, 1H), 7.37 - 7.34 (m, 2H), 7.25 - 7.23 (m, 1H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.8, 134.8, 131.5, 129. 4, 128.7, 127.5, 124.3, 123.5, 116.4, 112.5, 18.6. MS (EI) *m/z* (%) 190, 175, 147, 115, 102.

1-(Propylthio)naphthalen-2-ol (3m). blue liquid, yield 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.34 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.40 (s, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.26 - 7.23 (m, 1H), 2.67 (t, J = 7.4 Hz, 2H), 1.58 - 1.52 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.4, 135.4, 131.4, 129.4, 128.6, 127.4, 124.6, 123.4, 116.3, 111.2, 37.8, 23.3, 13.4. MS (EI) *m/z* (%) 218, 176, 147, 115, 103. HRMS calcd. for: $C_{13}H_{15}OS$ $[M+H]^+$ 219.08381, found 219.08379.

6-Bromo-1-(phenylthio)naphthalen-2-ol (3n).[19] white solid, yield 92%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (d, J = 8.9 Hz, 1H), 7.96 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.18 - 7.12 (m, 4H), 7.00 (d, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.1, 134.9, 134.0, 131.7, 131.1, 130.5, 130.4, 129.2, 126.6, 126.4, 126.1, 118.0, 117.7, 108.5. MS (EI) *m/z* (%)332, 251, 225, 146, 116.

1-(Phenylthio)naphthalene-2,6-diol (3o). yellow solid, yield 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.88 (s, 1H), 8.26 (d, J = 8.9 Hz, 1H), 7.94 (d, J = 7.7 Hz, 2H), 7.78 (d, J = 9.0 Hz, 1H), 7.56 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.16 (d, J = 9.1 Hz, 1H), 7.07 - 7.05 (m, 3H). ^{13}C NMR (CD_3COCD_3, 100 MHz, ppm): δ 156.6, 154.2, 142.3, 136.4, 133.8, 130.7, 129.5, 126.5, 124.5, 123.2, 120.3, 120.2, 112.2, 111.4. HRMS calcd. for: $C_{16}H_{11}O_2S$ $[M-H]^-$ 267.04853, found 267.05017.

7-Bromo-1-(phenylthio)naphthalen-2-ol (3p). white solid, yield 88%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.32 (s, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.37 - 7.34 (m, 1H), 7.24 (s, 1H), 7.12 - 7.09 (m, 3H), 7.05 - 7.02 (m, 1H), 6.93 (d, J = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.7, 136.8, 134.7, 132.6, 130.1, 129.3, 127.9, 127.3, 126.9, 126.4, 126.1, 122.8, 117.3, 107.6. HRMS calcd. for: $C_{16}H_{10}BrOS$ $[M-H]^-$ 328.96412, found 328.96377.

1-(Phenylthio)naphthalene-2,7-diol (3q). white solid, yield 80%).^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.81 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.51 (s, 1H), 7.14 (m, 6H), 7.03 - 6.94 (m 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.7, 155.6, 137.3, 135.2, 132.7, 130.8, 129.2, 126.2, 125.9, 124.7, 115.3, 114.3, 107.2, 106.4. HRMS calcd. for: $C_{16}H_{13}O_2S$ $[M+H]^+$ 269.06308, found 269.06284.

(2-Methoxynaphthalen-1-yl)(phenyl)sulfane (3r, CAS: 108979-03-9).[20] white solid; yield: 32.5 mg (61%), mp 79 - 81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.46 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H) 7.39 - 7.34(m, 2H), 7.12 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 6.9 Hz, 3H), 3.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.2, 138.1, 136.2, 132.0, 129.5, 128.7, 128.2, 127.71, 127.69, 126.2, 125.4, 124.7, 124.1, 113.4, 56.9. MS (EI) *m/z* (%) 266, 251, 223, 178, 115.

(2-Ethoxynaphthalen-1-yl)(phenyl)sulfane (3s). brown solid, yield 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.49 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.14 - 7.10 (m, 2H), 7.06 - 7.01 (m, 3H), 4.17 (q, J = 6.9 Hz, 2H), 1.28 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.5, 138.5, 136.3, 131.6, 129.6, 128.6, 128.2, 127.5, 126.8, 125.5, 124.8, 124.1, 114.9, 114.4, 65.5, 14.8. HRMS calcd. for: $C_{18}H_{17}OS$ $[M+H]^+$ 281.09946, found 281.09972.

3-Methyl-2-(phenylthio)phenol (3t, CAS: 1350814-76-4).[21] brown liquid, yield 45%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.38 (d, J = 8.3 Hz, 1H), 7.20 (t, J = 7.5 Hz, 2H), 7.11 - 7.03 (m, 4H), 6.79 (s, 1H), 6.68 (d, J = 8.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.4, 144.1, 138.4, 137.5, 128.9, 126.9, 125.2, 122.8, 117.8, 113.9, 20.9. MS (EI) *m/z* (%) 216, 183, 138, 107, 77.

3,5-Dimethyl-2-(phenylthio)phenol (3u, CAS: 52145-51-4). brown solid, yield 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.17 (t, J = 7.5 Hz, 2H), 7.04 (t, J = 7.1 Hz, 1H), 6.90 (d, J = 7.6 Hz, 2H), 6.68 (s, 2H), 2.37 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.1, 145.9, 138.6, 128.8, 125.2, 124.4, 121.5, 115.4, 21.9. MS (EI) *m/z* (%) 230, 182, 152, 91, 77.

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(2,6-Dimethoxyphenyl)(phenyl)sulfane (3v, CAS: 146643-79-0).[22] yellow liquid, yield 55%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.34 (d, J = 8.3 Hz, 1H), 7.23 - 7.19 (m, 2H), 7.13 - 7.09 (m, 3H), 6.53 - 6.47 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 161.8, 160.3, 137.7, 136.7, 128.7, 127.7, 125.4, 112.2, 105.4, 99.3, 55.9, 55.4. MS (EI) *m/z* (%) 246, 231, 198, 171, 77.

Phenyl(2,4,6-trimethoxyphenyl)sulfane (3w, CAS: 41280-62-0).[17a] white solid, yield 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.15 (t, J = 7.7 Hz, 2H), 7.03 (t, J = 6.0 Hz, 3H), 6.22 (s, 2H), 3.87 (s, 3H), 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 162.8, 162.4, 138.6, 128.3, 125.5, 124.2, 98.6, 91.1, 56.1, 55.3. MS (EI) *m/z* (%) 276, 228, 207, 141, 69.

N,N-Dimethyl-4-(phenylthio)aniline (3x, CAS: 42881-80-1).[17a] brown solid, yield 48%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.39 (d, J = 8.5 Hz, 2H), 7.20 (t, J = 7.3 Hz, 2H), 7.12 - 7.07 (m, 3H), 6.73 (d, J = 5.2 Hz, 2H), 2.99 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 150.5, 140.2, 136.1, 128.6, 126.7, 124.9, 117.3, 112.9, 40.2. MS (EI) *m/z* (%) 229, 197, 184, 152, 77. MS (EI) *m/z* (%) 229, 197, 184, 152, 77.

1-(Phenylsulfonyl)naphthalen-2-ol (4a).[22] yellow solid, yield 82%. ^{1}H NMR (CDCl3, 400 MHz, ppm): δ 11.11 (s, 1H), 8.33 (d, J = 8.5 Hz, 1H), 7.96 - 7.93 (m, 3H), 7.72 (d, J = 7.8 Hz, 1H), 7.55 - 7.44 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 7.19 (d, J = 9.0 Hz, 1H). ^{13}C NMR (CDCl3, 100 MHz, ppm): δ 158.9, 142.0, 137.5, 133.5, 129.4, 129.2, 129.1, 128.7, 128.7, 126.5, 124.3, 122.9, 120.1, 111.7. MS (EI) m/z (%) 284, 219, 203, 115, 77. HRMS calcd. for: $C_{16}H_{12}O_3SNa$ $[M+Na]^+$ 307.03994, found 307.03987.

1-Tosylnaphthalen-2-ol (4b, CAS: 108980-64-9).[22] yellow solid, yield 84%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.13 (s, 1H), 8.34 (d, J = 8.6 Hz, 1H), 7.93 - 7.83 (m, 3H), 7.71 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.35 - 7.27 (m, 3H), 7.18 (d, J = 9.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.6, 144.6, 139.1, 137.3, 129.8, 129.4, 129.1, 128.7, 128.6, 126.5, 124.3, 122.9, 120.1, 112.1, 21.5. MS (EI) *m/z* (%) 298, 233, 219, 114, 91.

1-((4-*iso*-Propylphenyl)sulfonyl)naphthalen-2-ol (4c). yellow solid, yield 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.14 (s, 1H), 8.38 (d, J = 8.6 Hz, 1H), 7.93 - 7.86 (m, 3H), 7.72 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.36 - 7.31 (m, 3H), 7.18 (d, J = 9.0 Hz, 1H), 2.91 (m, 1H), 1.20 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.7, 155.2, 139.3, 137.3, 129.5, 129.2, 128.7, 128.7, 127.3, 126.7, 124.3, 123.1, 120.1, 112.2, 34.1, 23.5. MS (EI) m/z (%) 326, 219, 201, 115, 77. HRMS calcd. for: $C_{19}H_{18}O_3SNa$ $[M+Na]^+$ 349.08689, found 349.08715.

1-((4-(*tert*-Butyl)phenyl)sulfonyl)naphthalen-2-ol (4d). yellow solid, yield 81%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.14 (s, 1H), 8.40 (d, J = 8.7 Hz, 1H), 7.94 - 7.86 (m, 3H), 7.72 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.4 Hz, 3H), 7.34 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 9.0 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.7, 157.5, 139.0, 137.3, 129.5, 129.0, 128.7, 128.7, 126.4, 126.2, 124.3, 123.1, 120.1, 112.2, 35.2, 30.9. MS (EI) *m/z* (%) 340, 261, 219, 135, 115. HRMS calcd. for: $C_{20}H_{20}O_3SNa$ $[M+Na]^+$ 341.12059, found 341.12081.

1-((4-Methoxyphenyl)sulfonyl)naphthalen-2-ol (4e). white solid, yield 72%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.15 (s, 1H), 8.36 (d, J = 8.7 Hz, 1H), 7.92-7.88 (m, 3H), 7.71 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 7.3 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 163.5, 158.4, 137.2, 133.6, 129.4, 129.1, 128.8, 128.7, 128.6, 124.2, 122.9, 120.1, 114.4, 112.5, 55.6. MS (EI) *m/z* (%) 314, 249, 219, 207, 108. HRMS calcd. for: $C_{17}H_{15}O_4S$ $[M+H]^+$ 315.06856, found 315.06846.

1-((4-Fluorophenyl)sulfonyl)naphthalen-2-ol (4f). white solid, yield 73%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.04 (s, 1H), 8.31 (d, J = 8.6 Hz, 1H), 7.99 - 7.93 (m, 3H), 7.73 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.3 Hz, 1H), 7.20 - 7.13 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.7, 164.2, 158.8, 137.7, 129.4(d, J = 9.6 Hz), 129.3, 129.03(d, J = 32 Hz), 128.7, 124.5, 122.7, 120.1, 116.7, 116.4, 111.6. MS (EI) *m/z* (%) 302, 237, 221, 131, 114. HRMS calcd. for: $C_{16}H_{11}FO_3SNa$ $[M+Na]^+$ 325.03052, found 325.03076.

1-((4-Chlorophenyl)sulfonyl)naphthalen-2-ol (4g). white solid, yield 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.02 (s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 7.96 - 7.87 (m, 3H), 7.73 (d, J = 7.9 Hz, 1H), 7.50 - 7.43 (m, 3H), 7.36 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.0, 140.5, 140.1, 137.8, 129.5, 129.3, 129.2, 128.9, 128.7, 128.0, 124.5, 122.7, 120.1, 111.2. HRMS calcd. for: $C_{16}H_{11}ClO_3SNa$ $[M+Na]^+$ 341.00097, found 341.00081.

1-((4-Bromophenyl)sulfonyl)naphthalen-2-ol (4h). white solid yield 77%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.01 (s, 1H), 8.29 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.82 - 7.72 (m, 3H), 7.61 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.0, 141.0, 137.8, 132.5, 129.3, 129.2, 128.9, 128.7, 128.7, 127.9, 124.5, 122.7, 120.1, 111.2. MS (EI) *m/z* (%) 364, 219, 201, 115, 75. HRMS calcd. for: $C_{16}H_{11}BrO_3SNa$ $[M+Na]^+$ 384.95045, found 384.95013.

1-((4-(Trifluoromethyl)phenyl)sulfonyl)naphthalen-2-ol (4i). white solid, yield 67%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.98 (s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 8.1 Hz, 3H), 7.49 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 9.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.3, 145.4, 138.2, 135.3, 134.9, 129.31, 129.29, 129.1, 128.8, 127.0, 126.4 (q, J = 3.7 Hz), 124.6, 122.6, 120.2, 110.7. HRMS calcd. for: $C_{17}H_{11}F_3O_3SNa$ $[M+Na]^+$ 375.02732, found 375.02738.

1-((4-(Trifluoromethoxy)phenyl)sulfonyl)naphthalen-2-ol (4j). white solid, yield 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.01 (s, 1H), 8.32 (d, J = 8.5 Hz, 1H), 8.02 – 7.95 (m, 3H), 7.75 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.20 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.0, 152.7, 140.2, 137.9, 129.3, 129.2, 129.0, 128.8, 124.5, 122.7, 121.4, 120.9, 120.2, 118.8, 111.2. HRMS calcd. for: $C_{17}H_{11}F_3O_4SNa$ $[M+Na]$ 391.02224, found 391.02189.

1-(Naphthalen-2-ylsulfonyl)naphthalen-2-ol (4k, CAS:51739-34-5). white solid, yield 71%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.20 (s, 1H), 8.62 (s, 1H), 8.42 (d, J = 8.6 Hz, 1H), 8.00 - 7.79 (m, 5H), 7.71-7.61 (m, 3H), 7.43 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.9, 138.8, 137.6, 135.1, 131.9, 129.7, 129.5, 129.4, 129.3, 129.1, 128.8, 128.7, 127.9, 127.9, 127.7, 124.3, 122.9, 121.4 , 120.1, 111.7. MS (EI) *m/z* (%) 334, 269, 128, 115, 77.

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1-(Methylsulfonyl)naphthalen-2-ol (4l, CAS: 19365-95-8). yellow solid; yield: 30.2 mg (68%), mp 100-104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.78 (s, 1H), 8.51 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 9.0 Hz, 1H), 3.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.1, 137.4, 129.7, 129.4, 129.2, 128.7, 124.5, 122.4, 120.2, 112.0, 44.8. MS (EI) *m/z* (%) 222, 159, 143, 131, 115. MS (EI) *m/z* (%) 222, 159, 143, 131, 115.

1-(Propylsulfonyl)naphthalen-2-ol (4m). brown liquid, yield 45%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.85 (s, 1H), 8.52 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.62 (t, J = 3.7 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H), 3.34 (t, J = 4.0 Hz, 2H), 1.79 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.0, 137.3, 129.9, 129.4, 129.1, 128.8, 124.4, 122.6, 120.1, 110.3, 58.1, 16.2, 12.7. HRMS calcd. for: $C_{13}H_{15}O_3S$ $[M+H]^+$ 251.07364, found 251.07386.

1-(Cyclopropylsulfonyl)naphthalen-2-ol (4n). yellow solid, yield 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.60 (s, 1H), 8.65 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 2.94 - 2.87 (m, 1H), 1.45 - 1.44 (m, 2H), 1.04 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.7, 136.9, 130.0, 129.3, 128.9, 124.4, 123.2, 120.1, 112.7, 112.6, 34.2, 5.8. HRMS calcd. for: $C_{13}H_{13}O_3S$ $[M+H]^+$ 249.05799, found 249.05776.

6-Bromo-1-(phenylsulfonyl)naphthalen-2-ol (4o). yellow solid, yield 68%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.09 (s, 1H), 8.23 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 7.7 Hz, 2H), 7.87 - 7.83 (m, 2H), 7.59 - 7.48 (m, 4H), 7.22 - 7.20 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.9, 141.7, 136.4, 133.8, 131.8, 130.9, 129.9, 129.3, 128.0, 126.4, 124.6, 121.4, 118.2, 112.1. HRMS calcd. for: $C_{16}H_{11}BrO_3SNa$ $[M+Na]^+$ 384.95045, found 384.94951.

7-Bromo-1-(phenylsulfonyl)naphthalen-2-ol (4p). white solid, yield 56%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.13 (s, 1H), 8.56 (s, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.88 (d, J = 9.0 Hz, 1H), 7.6 - 7.55 (m, 4H), 7.43 (d, J = 7.4 Hz, 1H), 7.19 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.3, 141.6, 137.2, 133.8, 130.6, 130.4, 129.3, 127.8, 127.1, 126.6, 125.5, 123.7, 120.6, 110.4. MS (EI) *m/z* (%) 364, 219, 201, 189, 77.

1-(Phenylsulfonyl)naphthalene-2,7-diol (4q). white solid, yield 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.03 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 8.9 Hz, 1H), 7.73 (s, 1H), 7.62 (d, J = 8.7 Hz, 1H), 7.58 - 7.47 (m, 4H), 7.03 (d, J = 9.0 Hz, 1H), 6.94 - 6.92 (m, 1H); ^{13}C NMR (CD_3COCD_3, 100 MHz, ppm): δ 159.3, 158.0, 142.0, 137.7, 133.8, 131.5, 131.2, 129.4, 126.5, 123.4, 116.3, 116.0, 110.5, 106.1. HRMS calcd. for: $C_{16}H_{12}O_4SNa$ $[M+Na]^+$ 323.03485, found 323.03513.

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