

## Supporting Information for

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

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### General information:

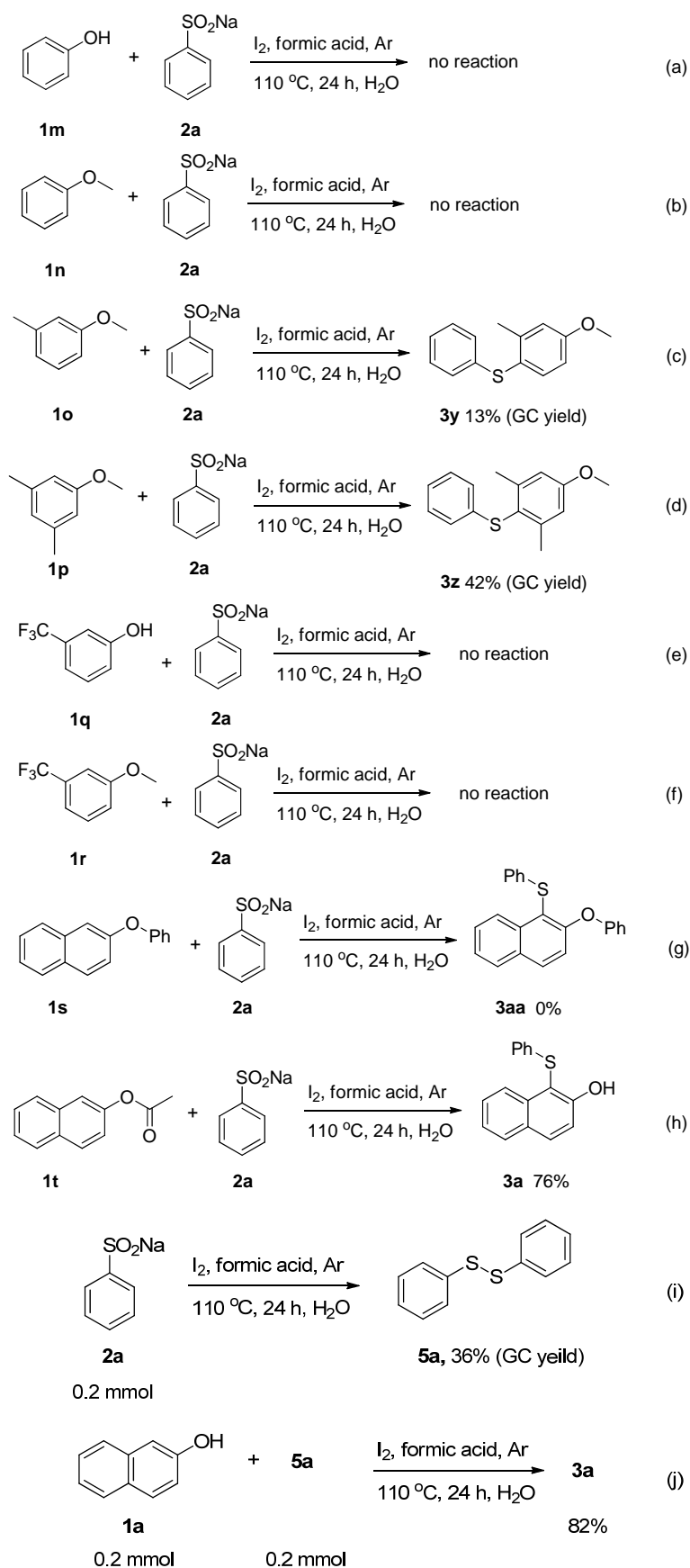
Sulfenylation reaction is conducted under an atmosphere of argon and sulfonylation reaction is carried out in an air atmosphere. Flash column chromatography was performed over silica gel 48-75  $\mu\text{m}$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker-AV (400 and 100 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.

### Optimization of reaction conditions

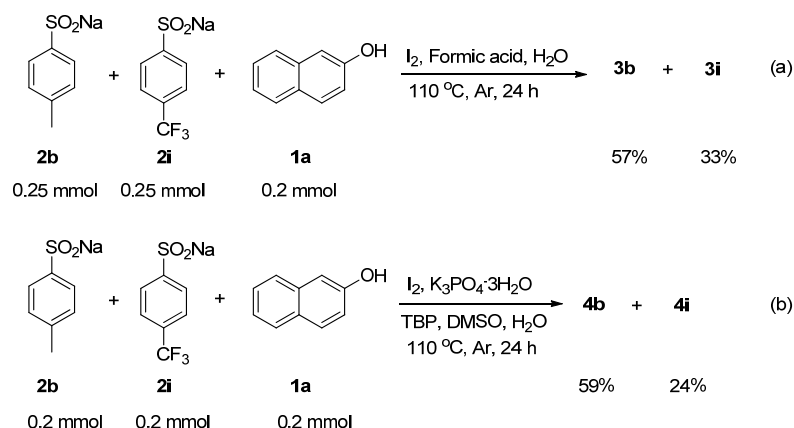
**Table S1.** Optimization of the reaction conditions<sup>a</sup>

<div><div><div></div><div><div><b>1a</b></div><div><b>2a</b></div><div><b>4a</b></div></div></div></div>				
Entry	Additive (equiv.)	Base (equiv.)	Oxidant (equiv.)	Yield <sup>b</sup> (%)
1	I <sub>2</sub> (1)			40
2	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)		48
3	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	O <sub>2</sub>	50
4	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)	60
5	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	TBHP(1)	40
6	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	TBP(1)	61
7	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	20
8	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	Oxone	24
9	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)+TBP(1)	92
10	I <sub>2</sub> (1)	K <sub>2</sub> CO <sub>3</sub> (1)	DMSO(1)+TBP(1)	70
11	I <sub>2</sub> (1)	KHCO <sub>3</sub> (1)	DMSO(1)+TBP(1)	35
12	I <sub>2</sub> (1)	KOH(1)	DMSO(1)+TBP(1)	30
13	I <sub>2</sub> (1)	KTB(1)	DMSO(1)+TBP(1)	27
14	KI(1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)+TBP(1)	3
15	TBAI(1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)+TBP(1)	4
16	NIS(1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)+TBP(1)	50
17 <sup>c</sup>	I <sub>2</sub> (1)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)+TBP(1)	70
18	I <sub>2</sub> (0.5)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O(1)	DMSO(1)+TBP(1)	40

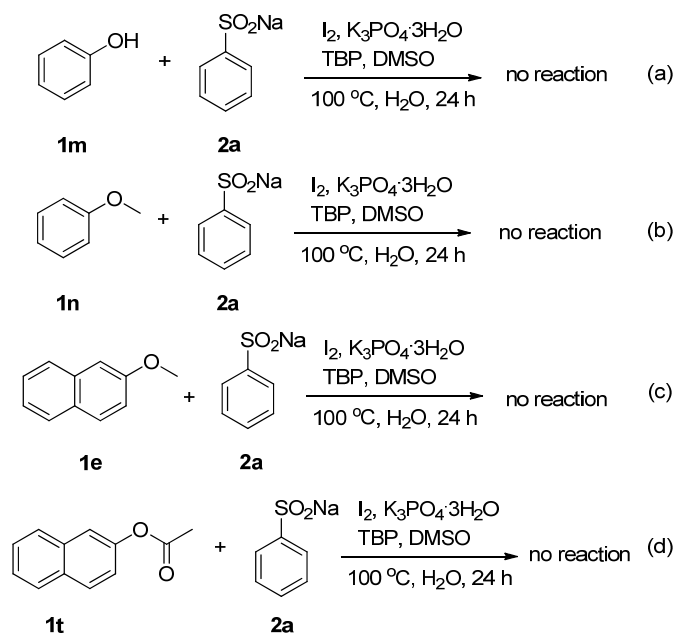
<sup>a</sup> Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), H<sub>2</sub>O (0.5 mL), 24 h, 100 °C under air. <sup>b</sup> GC yield. <sup>c</sup> 80 °C



**Scheme S1** Control experiments for the direct sulfenylation reaction under various conditions



**Scheme S2** Control experiments



**Scheme S3** Control experiments for the direct sulfonylation reaction under various conditions

**General procedure: (3a):**

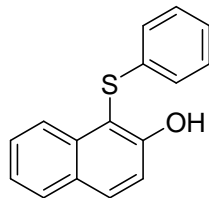
A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol), naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol), I<sub>2</sub> (50.8 mg, 0.2 mmol). Formic acid (0.1 mL) and H<sub>2</sub>O (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 110 °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 °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<sub>2</sub> (50.8 mg, 0.2 mmol), K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O (53.2 mg, 0.2 mmol). TBP (35 μL, 0.2 mmol), DMSO (15 μL, 0.2 mmol) and H<sub>2</sub>O (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 100 °C for 24 h. The

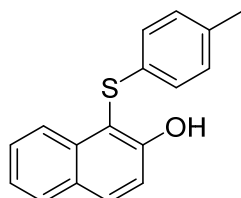
volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4a** as yellow solid; yield: 46.6 mg (82%), mp 129 - 133 °C.

**1-(Phenylsulfonyl)naphthalen-2-ol (3a, CAS: 97992-89-7)<sup>[1]</sup>**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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.

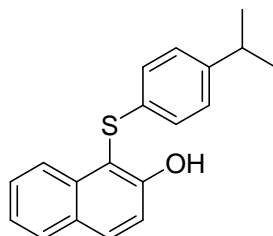
**1-Tosylnaphthalen-2-ol (3b, CAS: 799764-32-2)<sup>[1]</sup>**



The reaction was conducted with sodium 4-methylbenzenesulfinate (**2b**, 89 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3b** as yellow solid; yield: 47.5 mg (89%), mp 81 - 83 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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.

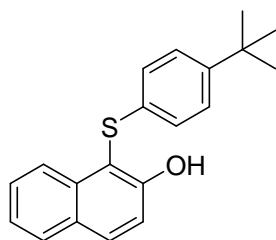
**1-((4-iso-Propylphenyl)sulfonyl)naphthalen-2-ol (3c)**



The reaction was conducted with sodium 4-isopropylbenzenesulfinate (**2c**, 103 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3c** as brown semisolid ; yield: 46 mg (78%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{19}\text{H}_{18}\text{OSNa}$   $[\text{M}+\text{Na}]^+$  317.09706, found 317.09718.

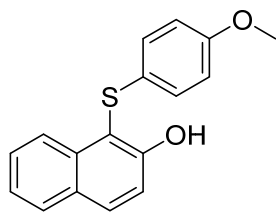
### 1-((4-(*tert*-Butyl)phenyl)sulfonyl)naphthalen-2-ol (**3d**)



The reaction was conducted with sodium 4-(*tert*-butyl)benzenesulfinate (**2d**, 110 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3d** as orange semisolid; yield: 42 mg (68%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{20}\text{H}_{20}\text{OSNa}$   $[\text{M}+\text{Na}]^+$  331.11271, found 331.11211.

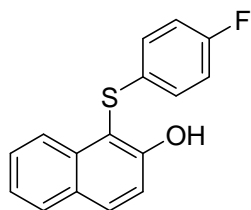
### 1-((4-Methoxyphenyl)thio)naphthalen-2-ol (**3e**)



The reaction was conducted with sodium 4-methoxybenzenesulfinate (**2e**, 97 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3e** as yellow solid; yield: 48 mg (85%), mp 70 - 73 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{SNa}$   $[\text{M}+\text{Na}]^+$  305.06067, found 305.06095.

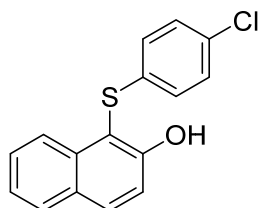
### 1-((4-Fluorophenyl)thio)naphthalen-2-ol (**3f**)



The reaction was conducted with sodium 4-fluorobenzenesulfinate (**2f**, 97 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3f** as white solid; yield: 38 mg (70%), mp 116 - 119 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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,  $J$  = 7.87 Hz), 128.0, 124.5, 123.9, 116.9, 116.3 (d,  $J$  = 22.11 Hz), 108.5. HRMS calcd. for:  $\text{C}_{16}\text{H}_{10}\text{FOS}$  [ $\text{M}-\text{H}$ ] $^-$  269.04419, found 269.04394.

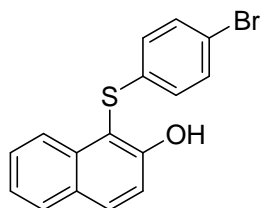
### 1-((4-Chlorophenyl)thio)naphthalen-2-ol (**3g**)<sup>[1]</sup>



The reaction was conducted with sodium 4-chlorobenzenesulfinate (**2g**, 99 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3g** as brown solid; yield: 43 mg (75%), mp 81 - 84 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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**)<sup>[1]</sup>

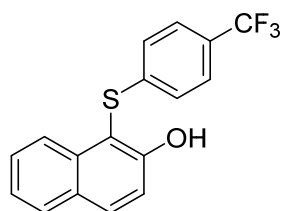


The reaction was conducted with sodium 4-bromobenzenesulfinate (**2h**, 121 mg, 0.5 mmol) and

naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3h** as yellow solid; yield: 50 mg (75%), mp 118 - 123 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  157.0, 135.1, 134.6, 133.1, 132.2, 129.5, 128.6, 128.1, 127.9, 124.4, 124.0, 119.6, 116.9, 107.4. MS (EI)  $m/z$  (%) 331, 218, 189, 146, 115.

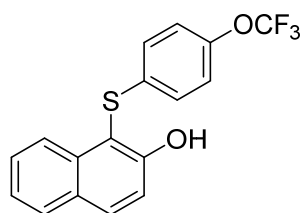
### 1-((4-(Trifluoromethyl)phenyl)thio)naphthalen-2-ol (**3i**)



The reaction was conducted with sodium 4-(trifluoromethyl)benzenesulfinate (**2i**, 121 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3i** as white solid; yield: 39 mg (60%), mp 102 - 106 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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<sub>17</sub>H<sub>12</sub>F<sub>3</sub>OS [M+H]<sup>+</sup> 321.05555, found 321.05563.

### 1-((4-(Trifluoromethoxy)phenyl)thio)naphthalen-2-ol (**3j**)

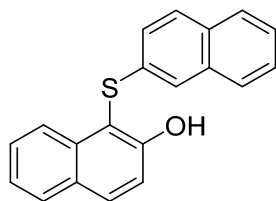


The reaction was conducted with sodium 4-(trifluoromethoxy)benzenesulfinate (**2j**, 124 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3j** as white solid; yield: 44.5 mg (66%), mp 65 - 69 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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<sub>17</sub>H<sub>12</sub>F<sub>3</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 337.05046, found 337.05051.



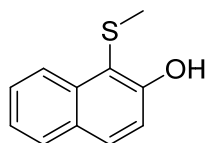
### 1-(Naphthalen-2-ylthio)naphthalen-2-ol (**3k**, CAS: 5432-97-3)<sup>[1]</sup>



The reaction was conducted with sodium 4-(trifluoromethoxy)benzenesulfinate (**2k**, 107 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3k** as white solid; yield: 45 mg (75%), mp 91 - 94 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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.

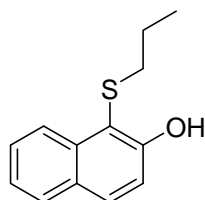
### 1-(Methylthio)naphthalen-2-ol (**3l**, CAS: 7439-28-3)<sup>[2]</sup>



The reaction was conducted with sodium methanesulfinate (**2l**, 51 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3l** as brown liquid; yield: 23 mg (60%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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.

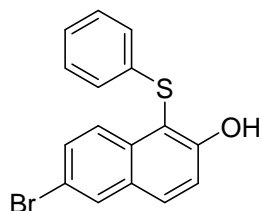
### 1-(Propylthio)naphthalen-2-ol (**3m**)



The reaction was conducted with sodium propane-1-sulfinate (**2m**, 65 mg, 0.5 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3m** a blue liquid; yield: 35 mg (80%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{13}\text{H}_{15}\text{OS}$   $[\text{M}+\text{H}]^+$  219.08381, found 219.08379.

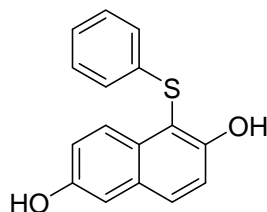
### 6-Bromo-1-(phenylthio)naphthalen-2-ol (**3n**)<sup>[3]</sup>



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 6-bromonaphthalen-2-ol (**1b**, 44.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3n** as white solid; yield: 61 mg (92%), mp 99 - 103 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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.

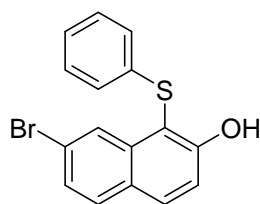
### 1-(Phenylthio)naphthalene-2,6-diol (**3o**)



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and naphthalene-2,6-diol (**1c**, 32 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3o** as yellow solid; yield: 37.3 mg (70%), mp 188 - 191 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{16}\text{H}_{11}\text{O}_2\text{S}$   $[\text{M}-\text{H}]^-$  267.04853, found 267.05017.

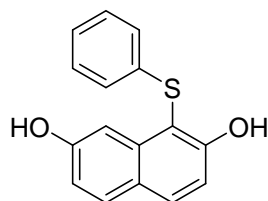
### 7-Bromo-1-(phenylthio)naphthalen-2-ol (**3p**)



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 7-bromonaphthalen-2-ol (**1d**, 44.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3p** as white solid; yield: 58.5 mg (88%), mp 85 - 88 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>16</sub>H<sub>10</sub>BrOS [M-H]<sup>-</sup> 328.96412, found 328.96377.

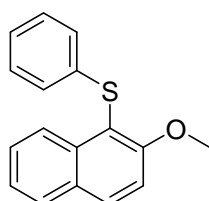
#### 1-(Phenylthio)naphthalene-2,7-diol (**3q**)



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and naphthalene-2,7-diol (**1e**, 32 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3q** as white solid; yield: 43 mg (80%), mp 172 - 175 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>16</sub>H<sub>13</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 269.06308, found 269.06284.

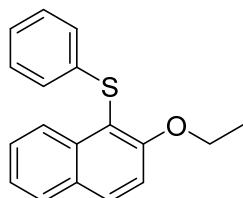
#### (2-Methoxynaphthalen-1-yl)(phenyl)sulfane (**3r**, CAS: 108979-03-9)<sup>[4]</sup>



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 2-methoxynaphthalene (**1f**, 31.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3r** as white solid; yield: 32.5 mg (61%), mp 79 - 81 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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.

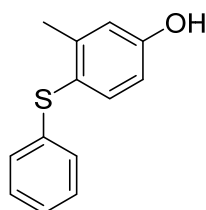
**(2-Ethoxynaphthalen-1-yl)(phenyl)sulfane (3s)**



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 2-ethoxynaphthalene (**1g**, 34.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3s** as brown solid; yield: 39.4 mg (70%), mp 56 - 59 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{18}\text{H}_{17}\text{OS}$   $[\text{M}+\text{H}]^+$  281.09946, found 281.09972.

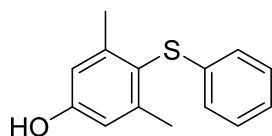
**3-Methyl-2-(phenylthio)phenol (3t, CAS: 1350814-76-4)<sup>[5]</sup>**



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and m-cresol (**1h**, 20.8 uL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3t** as brown liquid; yield: 19.5 mg (45%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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.

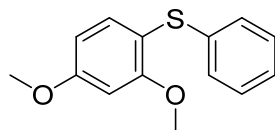
**3,5-Dimethyl-2-(phenylthio)phenol (3u, CAS: 52145-51-4)**



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 3,5-dimethylphenol (**1i**, 25.3 uL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3u** as brown solid; yield: 27.7 mg (60%), mp 105 - 108 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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.

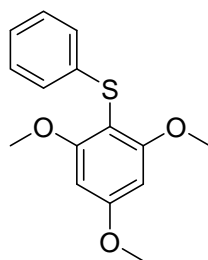
**(2,6-Dimethoxyphenyl)(phenyl)sulfane (3v, CAS: 146643-79-0)**<sup>[6]</sup>



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 1,3-dimethoxybenzene (**1j**, 26.2 uL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3v** as yellow liquid, yield: 27 mg (55%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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.

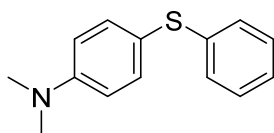
**Phenyl(2,4,6-trimethoxyphenyl)sulfane (3w, CAS: 41280-62-0)**<sup>[1]</sup>



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and 1,3,5-trimethoxybenzene (**1k**, 33.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3w** as white solid; yield: 33 mg (60%), mp 94 - 97 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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.

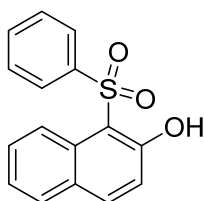
**N,N-Dimethyl-4-(phenylthio)aniline (3x, CAS: 42881-80-1)**<sup>[1]</sup>



The reaction was conducted with sodium benzenesulfinate (**2a**, 82 mg, 0.5 mmol) and N,N-dimethylaniline (**1l**, 26.3  $\mu$ L, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3x** as brown solid; yield: 22 mg (48%), mp 64 - 68 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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.

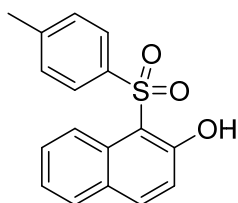
**1-(Phenylsulfonyl)naphthalen-2-ol (4a)**<sup>[4]</sup>



The reaction was conducted with sodium benzenesulfinate (**2a**, 65.6 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). 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 128 - 134 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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<sub>16</sub>H<sub>12</sub>O<sub>3</sub>SNa [M+Na]<sup>+</sup> 307.03994, found 307.03987.

**1-Tosylnaphthalen-2-ol (4b, CAS: 108980-64-9)**<sup>[4]</sup>

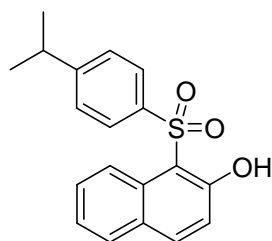


The reaction was conducted with sodium 4-methylbenzenesulfinate (**2b**, 71.3 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4b** as yellow solid; yield: 50 mg (84%), mp 134 - 137 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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.

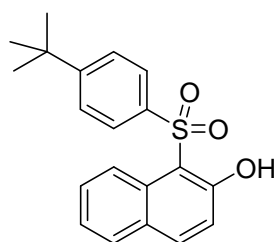
#### 1-((4-*iso*-Propylphenyl)sulfonyl)naphthalen-2-ol (**4c**)



The reaction was conducted with sodium 4-isopropylbenzenesulfinate (**2c**, 82.4 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4c** as yellow solid; yield: 55.6 mg (85%), mp 140-143 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$  349.08689, found 349.08715.

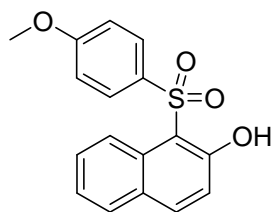
#### 1-((4-*tert*-Butyl)phenyl)sulfonyl)naphthalen-2-ol (**4d**)



The reaction was conducted with sodium 4-(*tert*-butyl)benzenesulfinate (**2d**, 88 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4d** as yellow solid; yield: 55 mg (81%), mp 190 - 193 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{20}\text{H}_{20}\text{O}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$  341.12059, found 341.12081.

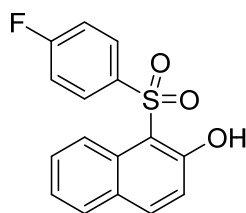
#### 1-((4-Methoxyphenyl)sulfonyl)naphthalen-2-ol (**4e**)



The reaction was conducted with sodium 4-methoxybenzenesulfinate (**2e**, 77.6 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4e** as white solid; yield: 45 mg (72%), mp 109 - 113 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>17</sub>H<sub>15</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 315.06856, found 315.06846.

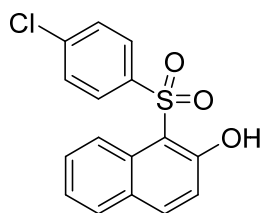
#### 1-((4-Fluorophenyl)sulfonyl)naphthalen-2-ol (**4f**)



The reaction was conducted with sodium 4-fluorobenzenesulfinate (**2f**, 72.8 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4f** as white solid; yield: 44 mg (73%), mp 125 - 128 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>16</sub>H<sub>11</sub>FO<sub>3</sub>SNa [M+Na]<sup>+</sup> 325.03052, found 325.03076.

#### 1-((4-Chlorophenyl)sulfonyl)naphthalen-2-ol (**4g**)



The reaction was conducted with sodium 4-chlorobenzenesulfinate (**2g**, 79.2 mg, 0.4 mmol) and

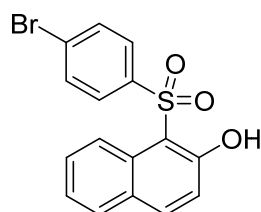


naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4g** as white solid; yield: 47.4 mg (75%), mp 141 - 144 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>16</sub>H<sub>11</sub>ClO<sub>3</sub>SNa [M+Na]<sup>+</sup> 341.00097, found 341.00081.

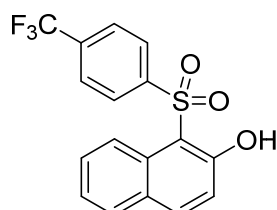
#### 1-((4-Bromophenyl)sulfonyl)naphthalen-2-ol (**4h**)



The reaction was conducted with sodium 4-bromobenzenesulfinate (**2h**, 96.4 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4h** as white solid; yield: 56 mg (77%), mp 165 - 171 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>16</sub>H<sub>11</sub>BrO<sub>3</sub>SNa [M+Na]<sup>+</sup> 384.95045, found 384.95013.

#### 1-((4-(Trifluoromethyl)phenyl)sulfonyl)naphthalen-2-ol (**4i**)

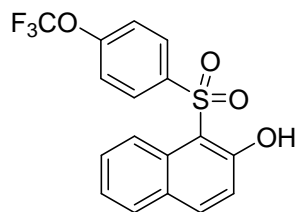


The reaction was conducted with sodium 4-(trifluoromethyl)benzenesulfinate (**2i**, 92.8 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4i** as white solid; yield: 47 mg (67%), mp 146 - 150 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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.

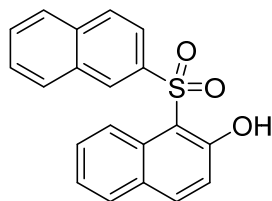
**1-((4-(Trifluoromethoxy)phenyl)sulfonyl)naphthalen-2-ol (4j)**



The reaction was conducted with sodium 4-(trifluoromethoxy)benzenesulfinate (**2j**, 99.2 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4j** as white solid; yield: 49.3 mg (70%), mp 104 - 109 °C.

$^1H$  NMR ( $CDCl_3$ , 400 MHz, ppm):  $\delta$  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):  $\delta$  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.

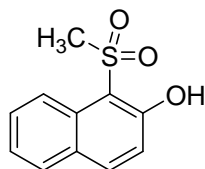
**1-(Naphthalen-2-ylsulfonyl)naphthalen-2-ol (4k, CAS:51739-34-5)**



The reaction was conducted with sodium naphthalene-2-sulfinate (**2k**, 85.6 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4k** as white solid; yield: 47.3 mg (71%), mp 160 - 164 °C.

$^1H$  NMR ( $CDCl_3$ , 400 MHz, ppm):  $\delta$  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):  $\delta$  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.

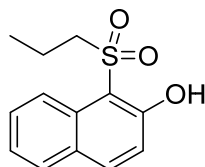
**1-(Methylsulfonyl)naphthalen-2-ol (4l, CAS: 19365-95-8)**



The reaction was conducted with sodium methanesulfinate (**2l**, 40.8 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4l** as yellow solid; yield: 30.2 mg (68%), mp 100 - 104 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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.

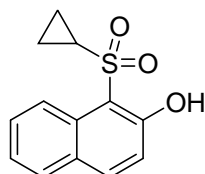
#### 1-(Propylsulfonyl)naphthalen-2-ol (**4m**)



The reaction was conducted with sodium propane-1-sulfinate (**2m**, 52 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4m** as brown liquid; yield: 22.5 mg (45%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sub>13</sub>H<sub>15</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 251.07364, found 251.07386.

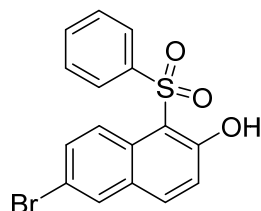
#### 1-(Cyclopropylsulfonyl)naphthalen-2-ol (**4n**)



The reaction was conducted with sodium cyclopropanesulfinate (**2n**, 51.2 mg, 0.4 mmol) and naphthalen-2-ol (**1a**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4n** as yellow solid; yield: 30 mg (60%), mp 84 - 87 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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<sub>13</sub>H<sub>13</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 249.05799, found 249.05776.

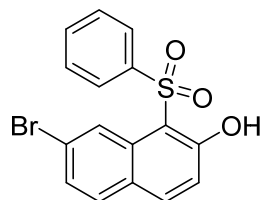
#### 6-Bromo-1-(phenylsulfonyl)naphthalen-2-ol (**4o**)



The reaction was conducted with sodium benzenesulfinate (**2a**, 65.6 mg, 0.4 mmol) and 6-bromonaphthalen-2-ol (**1b**, 44.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4o** as yellow solid; yield: 49.2 mg (68%), mp 152 - 157 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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<sub>16</sub>H<sub>11</sub>BrO<sub>3</sub>SNa [M+Na]<sup>+</sup> 384.95045, found 384.94951.

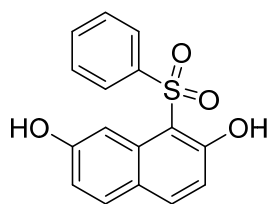
#### 7-Bromo-1-(phenylsulfonyl)naphthalen-2-ol (**4p**)



The reaction was conducted with sodium benzenesulfinate (**2a**, 65.6 mg, 0.4 mmol) and 7-bromonaphthalen-2-ol (**1d**, 44.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4p** as white solid; yield: 40 mg (56%), mp 184 - 189 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  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**)



The reaction was conducted with sodium benzenesulfinate (**2a**, 65.6 mg, 0.4 mmol) and naphthalene-2,7-diol (**1e**, 32 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **4q** as white solid; yield: 39 mg (65%), mp 231 - 234 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 100 MHz, ppm):  $\delta$  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:  $\text{C}_{16}\text{H}_{12}\text{O}_4\text{SNa}$   $[\text{M}+\text{Na}]^+$  323.03485, found 323.03513.

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# <sup>1</sup>H and <sup>13</sup>C NMR spectra of products

