Supporting Information for

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

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General information:
Sulfonylation 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 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.

Optimization of reaction conditions

Table S1. Optimization of the reaction conditions$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive (equiv.)</th>
<th>Base (equiv.)</th>
<th>Oxidant (equiv.)</th>
<th>Yield$^b$(%)</th>
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<tbody>
<tr>
<td>1</td>
<td>I$_2$(1)</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<tr>
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<td>DMSO(1)+TBP(1)</td>
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<td>DMSO(1)+TBP(1)</td>
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$^a$Conditions: 1a (0.2 mmol), 2a (0.4 mmol), H$_2$O (0.5 mL), 24 h, 100 °C under air. $^b$GC yield. $^c$80 °C
Scheme S1 Control experiments for the direct sulfenylation reaction under various conditions

(a) \( \text{Ph} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O no reaction

(b) \( \text{Ph} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O no reaction

(c) \( \text{Ph} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O \( 3y \) 13% (GC yield)

(d) \( \text{Ph} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O \( 3z \) 42% (GC yield)

(e) \( \text{F}_3\text{C} \) \( \text{OH} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{F}_3\text{C} \text{OH} \) 110°C, 24 h, H₂O no reaction

(f) \( \text{F}_3\text{C} \) \( \text{O} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{F}_3\text{C} \text{O} \) 110°C, 24 h, H₂O no reaction

(g) \( \text{Ph} \) \( \text{O} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O \( 3\text{aa} \) 0%

(h) \( \text{Ph} \) \( \text{CO} \) \( + \) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O \( 3\text{a} \) 76%

(i) \( \text{SO}_2\text{Na} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O \( 5\text{a} \) 35% (GC yield)

(j) \( \text{Ph} \) \( \text{OH} \) \( + \) \( 5\text{a} \) \( \xrightarrow{\text{I}_2, \text{formic acid, Ar}} \) \( \text{PhS} \) 110°C, 24 h, H₂O \( 3\text{a} \) 82%
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), I₂ (50.8 mg, 0.2 mmol). Formic acid (0.1 mL) and H₂O (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), I₂ (50.8 mg, 0.2 mmol), K₃PO₄·3H₂O (53.2 mg, 0.2 mmol). TBP (35 μL, 0.2 mmol), DMSO (15 μL, 0.2 mmol) and H₂O (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 100 °C for 24 h. The
Volatiless 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)[1]

\[
\begin{align*}
\text{OH} \\
\text{S} \\
\text{phenyl}
\end{align*}
\]

\[^{1}H\text{ NMR (CDCl}_{3}, 400 MHz, ppm): \delta 8.22 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 - 7.33 (m, 2H), 7.12 - 7.01 (m, 4H), 7.03 (d, J = 7.7 Hz, 2H).\]

\[^{13}C\text{ NMR (CDCl}_{3}, 100 MHz, ppm): \delta 157.0, 135.4, 135.3, 132.8, 129.5, 129.1, 128.5, 127.9, 126.3, 125.9, 124.7, 123.8, 116.8, 108.0. MS (EI) m/z (%) 252, 191, 146, 115, 77.\]

1-Tosylnaphthalen-2-ol (3b, CAS: 799764-32-2)[1]

\[
\begin{align*}
\text{OH} \\
\text{S} \\
\text{4-methylbenzenesulfinate}
\end{align*}
\]

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.

\[^{1}H\text{ NMR (CDCl}_{3}, 400 MHz, ppm): \delta 8.23 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 - 7.32 (m, 2H), 7.21 (s, 1H), 7.00 - 6.91 (m, 4H), 2.24 (s, 3H). \]

\[^{13}C\text{ NMR (CDCl}_{3}, 100 MHz, ppm): \delta 156.9, 135.8, 135.4, 132.6, 131.7, 129.9, 129.5, 128.5, 127.8, 126.7, 124.7, 123.7, 116.8, 108.7, 20.8. MS (EI) m/z (%) 266, 205, 146, 115, 91.\]

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

\[
\begin{align*}
\text{OH} \\
\text{S} \\
\text{iso-propyl}
\end{align*}
\]

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%).
\[ \delta 8.25 \ (d, \ J = 8.3 \ Hz, 1H), 7.88 \ (d, \ J = 8.8 \ Hz, 1H), 7.80 \ (d, \ J = 7.9 \ Hz, 1H), 7.48 \ (t, \ J = 7.6 \ Hz, 1H), 7.37 - 7.30 \ (m, 2H), 7.21 \ (s, 1H), 7.03 - 6.96 \ (m, 3H), 2.79 \ (m, 1H), 1.16 \ (s, 3H), 1.15 \ (s, 3H). \]

\[ \delta 156.9, 146.9, 135.5, 132.6, 132.1, 129.5, 128.5, 127.9, 127.4, 126.6, 124.8, 123.8, 116.8, 108.7, 33.6, 23.8. \]

HRMS calcd. for: C_{19}H_{18}O_{5}Na [M+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%).

\[ \delta 8.25 \ (d, \ J = 8.2 \ Hz, 1H), 7.89 \ (d, \ J = 8.8 \ Hz, 1H), 7.80 \ (d, \ J = 7.8 \ Hz, 1H), 7.49 \ (t, \ J = 7.5 \ Hz, 1H), 7.38 - 7.32 \ (m, 2H), 7.21 - 7.15 \ (m, 3H), 6.99 - 6.94 \ (m, 2H), 1.23 \ (s, 9H). \]

\[ \delta 156.9, 149.1, 135.5, 132.6, 131.8, 129.4, 128.5, 127.8, 126.3, 126.2, 124.8, 123.8, 116.8, 108.6, 34.3, 31.2. \]

HRMS calcd. for: C_{20}H_{20}O_{5}Na [M+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.

\[ \delta 8.26 \ (d, \ J = 8.4 \ Hz, 1H), 7.87 \ (d, \ J = 8.9 \ Hz, 1H), 7.79 \ (d, \ J = 8.0 \ Hz, 1H), 7.50 \ (t, \ J = 7.5 \ Hz, 1H), 7.38 - 7.27 \ (m, 3H), 7.04 \ (d, \ J = 8.7 \ Hz, 2H), 6.73 \ (d, \ J = 8.7 \ Hz, 2H), 3.71 \ (s, 3H). \]

\[ \delta 158.4, 156.7, 135.3, 132.5, 129.5, 128.8, 128.5, 127.8, 125.9, 124.7, 123.7, 116.8, 114.9, 109.7, 55.3. \]

HRMS calcd. for: C_{17}H_{14}O_{3}SNa [M+Na]^+ 305.06067, found 305.06095.
1-((4-Fluorophenyl)thio)naphthalen-2-ol (3f)

The reaction was conducted with sodium 4-fluorobenzenesulfinic acid (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.

$^1$H NMR (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). $^{13}$C NMR (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: C$_{16}$H$_{10}$FOS [M-H] - 269.04419, found 269.04394.

1-((4-Chlorophenyl)thio)naphthalen-2-ol (3g)

The reaction was conducted with sodium 4-chlorobenzenesulfinic acid (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.

$^1$H NMR (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). $^{13}$C NMR (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)

The reaction was conducted with sodium 4-bromobenzenesulfinic acid (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.

\[
1^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 8.15 (d, J = 8.4 \text{ Hz, 1H}), 7.92 (d, J = 8.9 \text{ Hz, 1H}), 7.82 (d, J = 8.0 \text{ Hz, 1H}), 7.50 (t, J = 7.6 \text{ Hz, 1H}), 7.43 - 7.32 (m, 3H), 7.28 (d, J = 8.2 \text{ Hz, 1H}), 7.08 (s, 1H), 6.88 (d, J = 8.2 \text{ Hz, 2H}).
\]

\[
1^3C \text{ NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta 157.0, 135.1, 134.6, 133.1, 132.2, 129.5, 128.6, 128.1, 127.9, 124.4, 124.0, 119.6, 116.9, 107.4. \text{ MS (EI) m/z } (\%) 331, 218, 189, 146, 115.
\]

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.

\[
1^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 8.13 (d, J = 8.3 \text{ Hz, 1H}), 7.94 (d, J = 8.7 \text{ Hz, 1H}), 7.83 (d, J = 8.0 \text{ Hz, 1H}), 7.50 (t, J = 7.6 \text{ Hz, 1H}), 7.42 - 7.33 (m, 4H), 7.07 (d, J = 7.7 \text{ Hz, 2H}), 7.00 (s, 1H).
\]

\[
1^3C \text{ NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta 7. 152, 140.6, 135.2, 133.4, 129.6, 128.7, 128.2, 128.1, 127.8, 126.0, 125.97, 125.93, 125.90, 124.1 (q, J = 90.1 \text{ Hz}), 117.0. \text{ HRMS calcd. for: C}_{17}H_{12}F_3OS [M+H]^+ 321.05555, found 321.05563.
\]

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

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.

\[
1^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 8.18 (d, J = 8.4 \text{ Hz, 1H}), 7.92 (d, J = 8.9 \text{ Hz, 1H}), 7.82 (d, J = 8.0 \text{ Hz, 1H}), 7.51 (t, J = 7.6 \text{ Hz, 1H}), 7.40 - 7.32 (m, 2H), 7.09 (s, 1H), 7.02 (s, 4H). \text{ HRMS calcd. for: C}_{17}H_{12}F_3O_2S [M+H]^+ 337.05046, found 337.05051.
\]
1-(Naphthalen-2-ylthio)naphthalen-2-ol (3k, CAS: 5432-97-3) \[1\]

![Chemical Structure]

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.

$^1$H NMR (CDCl$_3$, 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). $^{13}$C NMR (CDCl$_3$, 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) \[2\]

![Chemical Structure]

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%).

$^1$H NMR (CDCl$_3$, 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). $^{13}$C NMR (CDCl$_3$, 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)

![Chemical Structure]

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%).
1H NMR (CDCl₃, 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). 13C NMR (CDCl₃, 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: C₁₃H₁₅OS [M+H]+ 219.08381, found 219.08379.

6-Bromo-1-(phenylthio)naphthalen-2-ol (3n)

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.

1H NMR (CDCl₃, 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). 13C NMR (CDCl₃, 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)

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.

1H NMR (CDCl₃, 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). 13C NMR (CD2COCD3, 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: C₁₆H₁₁O₂S [M-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.

\[ ^1\text{H NMR (CDCl}_3, 400 MHz, ppm): \delta 8.32 \text{ (s, 1H), 7.76 (d, } J = 8.9 \text{ Hz, 1H), 7.57 (d, } J = 8.6 \text{ Hz, 1H), 7.37 - 7.34 \text{ (m, 1H), 7.24 (s, 1H), 7.12 - 7.09 \text{ (m, 3H), 7.05 - 7.02 \text{ (m, 1H), 6.93 (d, } J = 7.4 \text{ Hz, 2H).} \]

\[ ^{13}\text{C NMR (CDCl}_3, 100 MHz, ppm): \delta 157.7, 136.8, 134.7, 132.6, 130.1, 129.3, 127.9, 127.3, 126.9, 126.4, 126.1, 122.8, 117.3, 107.6. \]

HRMS calcd. for: C\text{\text{}}_{16}\text{H}_{10}\text{BrOS }[\text{M-H}]^{-} 328.96412, \text{ 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.

\[ ^1\text{H NMR (CDCl}_3, 400 MHz, ppm): \delta 7.81 \text{ (d, } J = 8.9 \text{ Hz, 1H), 7.71 (d, } J = 8.7 \text{ Hz, 1H), 7.51 (s, 1H), 7.14 \text{ (m, 6H), 7.03 - 6.94 \text{ (m, 3H).} \]

\[ ^{13}\text{C NMR (CDCl}_3, 100 MHz, ppm): \delta 157.7, 155.6, 137.3, 135.2, 132.7, 130.8, 129.2, 126.2, 125.9, 124.7, 115.3, 114.3, 107.2, 106.4. \]

HRMS calcd. for: C\text{\text{}}_{16}\text{H}_{13}\text{O}_{2}\text{S }[\text{M+H}^+] 269.06308, \text{ found 269.06284.}

(2-Methoxynaphthalen-1-yl)(phenyl)sulfane (3r, CAS: 108979-03-9)\[^4\]

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.
1H NMR (CDCl₃, 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). 13C NMR (CDCl₃, 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)

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.

1H NMR (CDCl₃, 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). 13C NMR (CDCl₃, 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: C₁₈H₁₇OS [M+H]⁺ 281.09946, found 281.09972.

3-Methyl-2-(phenylthio)phenol (3t, CAS: 1350814-76-4)[5]

The reaction was conducted with sodium benzenesulfinate (2a, 82 mg, 0.5 mmol) and m-cresol (1h, 20.8 μL, 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%).

1H NMR (CDCl₃, 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). 13C NMR (CDCl₃, 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)
The reaction was conducted with sodium benzenesulfinate (\(2a\), 82 mg, 0.5 mmol) and 3,5-dimethylphenol (\(1i\), 25.3 \(\mu\)L, 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.

\[\text{\(\delta 7.17 (t, J = 7.5 \text{ Hz}, 2\text{H}), 7.04 (t, J = 7.1 \text{ Hz}, 1\text{H}), 6.90 (d, J = 7.6 \text{ Hz}, 2\text{H}), 6.68 (s, 2\text{H}), 2.37 (s, 6\text{H}).\)}\]

\[\text{\(13C \text{ NMR (CDCl}\(_3\), 100 MHz, ppm): \delta 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)[6]

The reaction was conducted with sodium benzenesulfinate (\(2a\), 82 mg, 0.5 mmol) and 1,3-dimethoxybenzene (\(1j\), 26.2 \(\mu\)L, 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%).

\[\text{\(\delta 7.34 (d, J = 8.3 \text{ Hz}, 1\text{H}), 7.23 - 7.19 (m, 2\text{H}), 7.13 - 7.09 (m, 3\text{H}), 6.53 - 6.47 (m, 2\text{H}), 3.83 (s, 3\text{H}), 3.80 (s, 3\text{H}).\)}\]

\[\text{\(13C \text{ NMR (CDCl}\(_3\), 100 MHz, ppm): \delta 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)[1]

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.

\[\text{\(\delta 7.15 (t, J = 7.7 \text{ Hz}, 2\text{H}), 7.03 (t, J = 6.0 \text{ Hz}, 3\text{H}), 6.22 (s, 2\text{H}), 3.87 (s, 3\text{H}), 3.80 (s, 6\text{H}).\)}\]

\[\text{\(13C \text{ NMR (CDCl}\(_3\), 100 MHz, ppm): \delta 162.8, 162.4, 138.6, 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)[1]

\[ \text{S} \]
\[ \text{S} \]

The reaction was conducted with sodium benzenesulfinate (2a, 82 mg, 0.5 mmol) and N,N-dimethylaniline (1l, 26.3 μL, 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.

\(^1\)H NMR (CDCl₃, 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 (CDCl₃, 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.

1-(Phenylsulfonyl)naphthalen-2-ol (4a)[4]

\[ \text{S} \]
\[ \text{S} \]

The reaction was conducted with sodium benzenesulfinate (2a, 66.5 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.

\(^1\)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: C₁₆H₁₂O₃SNa [M+Na]+ 307.03994, found 307.03987.

1-Tosylnaphthalen-2-ol (4b, CAS: 108980-64-9)[4]

\[ \text{S} \]
\[ \text{S} \]

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.

\(^1\)H NMR (CDCl₃, 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)

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.

$^1$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$_3$SNa [M+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.

$^1$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, 139.3, 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$_3$SNa [M+Na]$^+$ 341.12059, found 341.12081.

1-((4-Methoxyphenyl)sulfonyl)naphthalen-2-ol (4e)
The reaction was conducted with sodium 4-methoxybenzenesulfinic acid (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.

\[ ^1H \text{NMR (CDCl}_3, 400 MHz, ppm): \delta 11.15 \text{ (s, 1H), 8.36 (d, } J = 8.7 \text{ Hz, 1H), 7.92-7.88 (m, 3H), 7.71 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.48 (d, } J = 7.7 \text{ Hz, 1H), 7.33 (d, } J = 7.3 \text{ Hz, 1H), 7.17 (d, } J = 9.0 \text{ Hz, 1H), 6.93 (d, } J = 8.8 \text{ Hz, 2H), 3.81 (s, 3H).} \]

\[ ^13C \text{NMR (CDCl}_3, 100 MHz, ppm): \delta 163.5, 158.4, 137.2, 133.6, 129.4, 129.1, 128.8, 128.7, 128.6, 124.2, 122.9, 120.1, 114.4, 112.5, 55.6. \]

MS (EI) \[ m/z \text{ (%): 314, 249, 219, 207, 108. HRMS calcd. for: C}_{17}H_{15}O_4S [M+H]^+ 315.06856, found 315.06846.} \]

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

The reaction was conducted with sodium 4-fluorobenzenesulfinic acid (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.

\[ ^1H \text{NMR (CDCl}_3, 400 MHz, ppm): \delta 11.04 \text{ (s, 1H), 8.31 (d, } J = 8.6 \text{ Hz, 1H), 7.99 - 7.93 (m, 3H), 7.73 \text{ (d, } J = 7.9 \text{ Hz, 1H), 7.48 (t, } J = 7.7 \text{ Hz, 1H), 7.36 (t, } J = 7.3 \text{ Hz, 1H), 7.20 - 7.13 (m, 3H).} \]

\[ ^13C \text{NMR (CDCl}_3, 100 MHz, ppm): \delta 166.7, 164.2, 158.8, 137.7, 129.4(\text{d, } J = 9.6 \text{ Hz), 129.3, 129.03(\text{d, } J = 32 \text{ Hz), 128.7, 124.5, 122.7, 120.1, 116.7, 116.4, 111.6. MS (EI) } m/z \text{ (%): 302, 237, 221, 131, 114. HRMS calcd. for: C}_{16}H_{11}FO_3SNa [M+Na]^+ 325.03052, found 325.03076.} \]

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

The reaction was conducted with sodium 4-chlorobenzenesulfinic acid (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.

1H NMR (CDCl3, 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).

13C NMR (CDCl3, 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: C16H11ClO3SNa [M+Na]+ 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.

1H NMR (CDCl3, 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).

13C NMR (CDCl3, 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: C16H11BrO3SNa [M+Na]+ 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.

1H NMR (CDCl3, 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).

13C NMR (CDCl3, 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, $J = 3.7 \text{ Hz}$), 124.6, 122.6, 120.2, 110.7. HRMS calcd. for: \( \text{C}_{17}\text{H}_{11}\text{F}_{3}\text{O}_{3}\text{SNa} \) [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.

\(^1\)H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 11.01 (s, 1H), 8.32 (d, $J = 8.5 \text{ Hz}$, 1H), 8.02 - 7.95 (m, 3H), 7.75 (d, $J = 7.7 \text{ Hz}$, 1H), 7.50 (t, $J = 7.5 \text{ Hz}$, 1H), 7.40 - 7.28 (m, 3H), 7.20 (d, $J = 9.0 \text{ Hz}$, 1H).

\(^1\)C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 159.0, 152.7, 140.2, 137.9, 129.3, 129.2, 129.0, 128.5, 124.5, 122.7, 121.4, 120.9, 120.2, 118.8, 111.2. HRMS calcd. for: \( \text{C}_{17}\text{H}_{11}\text{F}_{3}\text{O}_{4}\text{SNa} \) [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.

\(^1\)H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 11.20 (s, 1H), 8.62 (s, 1H), 8.42 (d, $J = 8.6 \text{ Hz}$, 1H), 8.00 - 7.79 (m, 5H), 7.71 - 7.61 (m, 3H), 7.43 (t, $J = 7.7 \text{ Hz}$, 1H), 7.29 (d, $J = 7.2 \text{ Hz}$, 1H), 7.22 (d, $J = 9.0 \text{ Hz}$, 1H).

\(^1\)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, 127.7, 127.4, 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.

^1^H NMR (CDCl₃, 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 (CDCl₃, 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%).

^1^H NMR (CDCl₃, 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 (CDCl₃, 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: C₁₃H₁₅O₃S [M+H]^+ 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.
$^1$H NMR (CDCl$_3$, 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). $^{13}$C NMR (CDCl$_3$, 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$_{13}$H$_{13}$O$_3$S [M+H]$^+$ 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.

$^1$H NMR (CDCl$_3$, 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). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 158.9, 141.7, 136.4, 133.8, 131.8, 130.9, 129.9, 129.3, 128.0, 126.4, 121.4, 118.2, 112.1. HRMS calcd. for: C$_{16}$H$_{11}$BrO$_3$SNa [M+Na]$^+$ 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.

$^1$H NMR (CDCl$_3$, 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). $^{13}$C NMR (CDCl$_3$, 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.

$^1$H NMR (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). $^{13}$C NMR (CD$_3$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: C$_{18}$H$_{12}$O$_4$Na [M+Na]$^+$ 323.03485, found 323.03513.

References
$^1$H and $^{13}$C NMR spectra of products

3a

\[ \text{3a} \]

\[ \text{11.0} \quad 10.5 \quad 10.0 \quad 9.5 \quad 9.0 \quad 8.5 \quad 8.0 \quad 7.5 \quad 7.0 \quad 6.5 \quad 6.0 \quad 5.5 \quad 5.0 \quad 4.5 \quad 4.0 \quad 3.5 \quad 3.0 \quad 2.5 \quad 2.0 \quad 1.5 \quad 1.0 \quad 0.5 \quad 0.0 \]

\[ \text{180} \quad 170 \quad 160 \quad 150 \quad 140 \quad 130 \quad 120 \quad 110 \quad 100 \quad 90 \quad 80 \quad 70 \quad 60 \quad 50 \quad 40 \quad 30 \quad 20 \quad 10 \quad 0 \]

\[ \text{0} \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \quad 11 \quad 12 \quad 13 \quad 14 \quad 15 \quad 16 \quad 17 \quad 18 \quad 19 \quad 20 \quad 21 \quad 22 \quad 23 \quad 24 \quad 25 \quad 26 \quad 27 \quad 28 \quad 29 \quad 30 \quad 31 \quad 32 \quad 33 \quad 34 \quad 35 \quad 36 \quad 37 \quad 38 \quad 39 \quad 40 \quad 41 \quad 42 \quad 43 \quad 44 \quad 45 \quad 46 \quad 47 \quad 48 \quad 49 \quad 50 \quad 51 \quad 52 \quad 53 \quad 54 \quad 55 \quad 56 \quad 57 \quad 58 \quad 59 \quad 60 \quad 61 \quad 62 \quad 63 \quad 64 \quad 65 \quad 66 \quad 67 \quad 68 \quad 69 \quad 70 \quad 71 \quad 72 \quad 73 \quad 74 \quad 75 \quad 76 \quad 77 \quad 78 \quad 79 \quad 80 \quad 81 \quad 82 \quad 83 \quad 84 \quad 85 \quad 86 \quad 87 \quad 88 \quad 89 \quad 90 \quad 91 \quad 92 \quad 93 \quad 94 \quad 95 \quad 96 \quad 97 \quad 98 \quad 99 \quad 100 \]

\[ \text{156.9637} \quad 115.2986 \quad 129.5531 \quad 128.5967 \quad 129.0541 \quad 125.3340 \quad 124.9330 \]

\[ \text{77.1379} \quad 77.7404 \quad 76.0623 \]
3m

3n
3x

4a