SUPPORTING INFORMATION

Sulfination of alcohols with sodium sulfinates promoted by 

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1. General Information
The $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ solution at 500/125 MHz spectrometer at 20-25 °C. $^1$H NMR chemical shifts were reported in ppm using tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. The data of $^1$H NMR was reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $q$ = quartet, $m$ = multiplet), coupling constant ($J$ value) in Hz and integration. $^{13}$C NMR spectra were reported in parts per million using solvent CDCl$_3$ ($\delta = 77.2$ ppm) as an internal standard. All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. Dichloromethane purchased from chemical supplier was firstly dried over 4Å molecular sieve for one week. Column chromatography was performed using silica gel, and analytical thin-layer chromatography (TLC) was used to monitor the reactions, performed on silica gel plates.

2. Preparation for starting materials
$p$-Toluene sulfinic acid$^1$: To a 100 mL round flask that was equipped with a stirring bar, sodium $p$-toluenesulfinate (1.78 g, 10 mmol) was dissolved in H$_2$O (12.5 mL), then added diethyl ether (12.5 mL) and HCl (37%, 0.9 mL). The reaction mixture was stirred during 1 h at room temperature and extracted with diethyl ether (3x 10 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and filtered with diethyl ether. About half of the diethyl ether was removed to get thick residue under reducing pressure and petroleum ether (20 mL) was added. Then the mixture was filtered to afford $p$-toluenesulfinic acid. Yield: 1.50 g, 96%. The white product was kept at -20 °C under nitrogen.

Sodium 4-chlorobenzene sulfinate 2d$^2$: To a 100 mL round flask that was equipped with a stirring bar, 4-chlorobenzenesulfonyl chloride (2.11 g, 10 mmol), sodium sulfite (2.52 g, 20 mmol) and sodium bicarbonate (1.68 g, 20 mmol) were took in water (10.0 mL) at 80 °C. After 4 h, the stirring stoped, reaction mixture cooled to room temperature, water was removed to get thick residue under vacuum and the residue was extracted in ethanol. Then recrystallization from ethanol afforded Sodium 4-chlorobenzene sulfinate 2d (1.39 g, 70%).
The other sodium sulfinates 2c, 2e, 2f and 2g were also prepared their sulfonyl chlorides using the similar methods.

3. Experimental Procedures

Procedure for sulfination of alcohols with sodium sulfinates

To a 50 mL round flask that was equipped with a stirring bar, sodium p-toluenesulfinate (0.65 mmol, 115.8 mg, 1.3 equiv) was dissolved in 1.5 mL of dichloromethane in the atmosphere. Then alcohols (0.5 mmol, 1 equiv) and BF₃·OEt₂ (0.9 mmol, 113.5 μL, 1.8 equiv) were added in the round flask. Then the reaction mixture was heated in oil bath of 50 °C and the stirring was turned on. After 3 h, the stirring stoped, reaction mixture cooled to room temperature, and the dichloromethane was removed to get thick residue under reducing pressure. The resulting residue was purified by thin column chromatography on silica gel column using EtOAc–petroleum ether solution as eluent to afford sulfinates.

Procedure for sulfination of alcohols with benzenesulfinic acid

To a 50 mL round flask that was equipped with a stirring bar, p-toluenesulfonic acid (0.65 mmol, 101.5 mg, 1.3 equiv) was dissolved in 1.5 mL of dichloromethane in the atmosphere. Then benzyl alcohols 1a (0.5 mmol, 52.0 μL, 1 equiv) and BF₃·OEt₂ (0.1 mmol, 12.3 μL, 0.2 equiv) were added in the round flask. Then the reaction mixture was heated in oil bath of 50 °C and the stirring was turned on. After 3 h, the stirring stoped, reaction mixture cooled to room temperature, and the dichloromethane was removed to get thick residue under reducing pressure. The resulting residue was purified by thin column chromatography on silica gel column using EtOAc–petroleum ether solution as eluent to afford sulfinate 3a (99.7 mg, 81%).

4. Experimental data

Table S1. Optimization of reaction conditions.⁺
\[
\text{\textbf{5. X-ray structure of 3D (CCDC 1439352)}}
\]

\textbf{Table S2. Crystallographic data}

\begin{tabular}{llllllll}
\hline
\textbf{Empirical formula} & C_{26}H_{34}O_{3}S  \\
\textbf{M} & 426.61  \\
\textbf{Crystal system} & Orthorhombic  \\
\textbf{Space group} & \textbf{P}2_{1}2_{1}2  \\
\textbf{a} (\text{Å}) & 9.7748 (10)  \\
\textbf{b} (\text{Å}) & 36.406 (3)  \\
\textbf{c} (\text{Å}) & 6.5704 (6)  \\
\textbf{\(\alpha\)} (\text{o}) & 90.00  \\
\textbf{\(\beta\)} (\text{o}) & 90.00  \\
\textbf{\(\gamma\)} (\text{o}) & 90.00  \\
\textbf{V/Å}^3 & 2338.2 (4)  \\
\textbf{Z} & 4  \\
\textbf{Dc/g cm}^{-3} & 1.212  \\
\mu/mm^{-1} & 0.162  \\
\hline
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<th>$\theta$ (max) $^\circ$</th>
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<td>12, 47, 8</td>
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<tr>
<td>$F(000)$</td>
<td>920</td>
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<tr>
<td>$R_i,^a wR_f^b [I &gt; 2\sigma(I)]$</td>
<td>0.0566, 0.1695</td>
</tr>
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</table>

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.  
$^b wR = \{\Sigma w[(Fo^2) - (Fc^2)]^2/\Sigma w(Fo^2)^2\}^{1/2}$.

Figure S1. X-ray structure of 3D (CCDC 1439352)

6. Characterizations of Compounds

**Benzyl 4-methylbenzenesulfinate (3a):** Yellow liquid; 87% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.0$ Hz, 2H), 7.35-7.26 (m, 7H), 5.03 (d, $J = 11.0$ Hz, 1H), 4.55 (d, $J = 11.5$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.0, 141.8, 135.7, 129.9, 129.9, 128.7, 128.6, 125.5, 65.8, 21.7.

**4-Methylphenyl $p$-toluenesulfinate (4):** White solid; m.p. 121.3-123.5 $^\circ$C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.7, 142.2, 140.7, 136.7, 130.4, 129.5, 127.8, 124.8, 21.8, 21.7.

**4-Methylbenzyl 4-methylbenzenesulfinate (3b):** Yellow liquid; 83% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 7.15 (q, $J = 8.0$ Hz, 4H), 4.99 (d, $J = 11.5$ Hz, 1H), 4.52 (d, $J = 11$ Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.9, 141.9, 138.5, 132.7, 129.9, 129.4, 128.9, 125.5, 65.9, 21.7, 21.3.
4-Nitrobenzyl 4-methylbenzenesulfinate (3c): Yellow liquid; 73% Yield; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 8.18\) (dt, \(J = 9.0\) Hz, 2.0 Hz, 2H ), 7.64 (d, \(J = 8.5\) Hz, 2H ), 7.44 (d, \(J = 11.0\) Hz, 2H ), 7.37 (d, \(J = 8.0\) Hz, 2H ), 5.09 (d, \(J = 13.0\) Hz, 1H ), 4.61 (d, \(J = 12.5\) Hz, 1H ), 2.45 (s, 3H ); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 147.9, 143.6, 143.3, 141.2, 130.1, 128.8, 125.5, 123.9, 63.5, 21.7\).

4-Cyanobenzyl 4-methylbenzenesulfinate (3d): Yellow liquid; 65% Yield; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.64-7.61\) (m, 4H ), 7.37 (t, \(J = 8.0\) Hz, 4H ), 5.04 (d, \(J = 12.5\) Hz, 1H ), 4.56 (d, \(J = 12.5\) Hz, 1H ), 2.44 (s, 3H ); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 143.5, 141.23, 141.20, 132.4, 130.1, 128.7, 125.4, 118.7, 112.2, 63.9, 21.7\).

4-Hydroxybenzyl 4-methylbenzenesulfinate (3e): White solid; 37% Yield; m.p. 186.9-188.9 °C; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.52\) (d, \(J = 8.0\) Hz, 2H ), 7.26 (d, \(J = 8.5\) Hz, 2H ), 6.95 (dt, \(J = 8.5\), 3 Hz, 2H ), 6.72 (dt, \(J = 8.5\), 3 Hz, 2H ), 5.53 (s, 1H ), 4.22 (s, 2H ), 2.43 (s, 3H ); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 156.4, 144.8, 135.1, 132.4, 129.7, 128.8, 120.2, 115.7, 62.4, 21.8\).

2-Chlorobenzyl 4-methylbenzenesulfinate (3f): Yellow liquid; 82% Yield; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.66\) (d, \(J = 8.0\) Hz, 2H ), 7.39-7.34 (m, 4H ), 7.26-7.24 (m, 2H ), 5.14 (d, \(J = 12\) Hz, 1H ), 4.72 (d, \(J = 12.5\) Hz, 1H ), 2.43 (s, 3H ); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 143.2, 141.6, 133.9, 133.7, 130.1, 129.95, 129.90, 129.7, 127.1, 125.5, 63.3, 21.7\).

4-Chlorobenzyl 4-methylbenzenesulfinate (3g): Yellow liquid; 95% Yield; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.62\) (d, \(J = 7.5\) Hz, 2H ), 7.34 (d, \(J = 7\) Hz, 2H ), 7.29 (d, \(J = 7.5\) Hz, 2H ), 7.19 (d, \(J = 7.5\) Hz, 2H ), 4.97 (d, \(J = 11.5\) Hz, 1H ), 4.51 (d, \(J = 11.5\) Hz, 1H ),
2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.2, 141.7, 134.5, 134.3, 130.04, 129.99, 128.9, 125.5, 64.7, 21.7.

2-Fluorobenzyl 4-methylbenzenesulfinate (3h): Yellow liquid; 78% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, $J = 8.0$ Hz, 2H), 7.35-7.28 (m, 4H), 7.11 (t, $J = 7.0$ Hz, 1H), 7.03 (t, $J = 8.5$ Hz, 1H), 7.03 (d, $J = 8.5$ Hz, 1H), 5.08 (d, $J = 11.5$ Hz, 1H), 4.67 (d, $J = 11.5$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.1 (d, $J_{C-F} = 247.3$ Hz, 1C), 143.1, 141.6, 131.1 (d, $J_{C-F} = 3.6$ Hz, 1C), 130.6 (d, $J_{C-F} = 8.1$ Hz, 1C), 129.9, 125.5, 124.4 (d, $J_{C-F} = 3.6$ Hz, 1C), 123.1 (d, $J_{C-F} = 14.3$ Hz, 1C), 115.6 (d, $J_{C-F} = 21.0$ Hz, 1C), 59.7 (d, $J_{C-F} = 4.1$ Hz, 1C), 21.7.

4-Fluorobenzyl 4-methylbenzenesulfinate (3i): Yellow liquid; 90% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 7.5$ Hz, 2H), 7.25-7.23 (m, 2H), 7.01 (t, $J = 8.5$ Hz, 2H), 4.98 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 11.5$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.9 (d, $J_{C-F} = 245.9$ Hz, 1C), 143.1, 141.6, 131.55 (d, $J_{C-F} = 3.1$ Hz, 1C), 130.66 (d, $J_{C-F} = 8.3$ Hz, 1C), 129.9, 125.5, 115.7 (d, $J_{C-F} = 21.5$ Hz, 1C), 64.9, 21.7.

3,4-Difluorobenzyl 4-methylbenzenesulfinate (3j): Yellow liquid; 49% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.13-7.06 (m, 2H), 7.02-6.95 (m, 1H), 4.94 (d, $J = 12$ Hz, 1H), 4.48 (d, $J = 12$ Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.5 (dd, $J_{C-F} = 12.4$ Hz, 5.8 Hz, 1C), 149.5 (dd, $J_{C-F} = 12.4$ Hz, 7.4 Hz, 1C), 143.4, 141.5, 132.9 (dd, $J_{C-F} = 5.6$ Hz, 3.9 Hz, 1C), 123.0, 125.5, 124.7 (dd, $J_{C-F} = 6.5$ Hz, 3.6 Hz, 1C), 117.6 (dd, $J_{C-F} = 21.8$ Hz, 17.6 Hz, 2C), 64.1, 21.7.

4-(Trifluoromethyl)benzyl 4-methylbenzenesulfinate (3k): Yellow liquid; 52% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 5.05 (d, $J = 12.0$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H).
= 12.0 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.4, 141.5, 139.9, 130.8, 130.5, 130.0, 128.6, 125.7 (q, $J_{C,F} = 3.8$ Hz 1C), 125.5, 64.3, 21.7.

Naphthalen-1-ylmethyl 4-methylbenzenesulfinate (3l): Yellow liquid; 22% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.5$ Hz, 1H), 7.87-7.83 (m, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.55-7.49 (m, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 5.51 (d, $J = 11.5$ Hz, 1H), 4.97 (d, $J = 11.5$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.1, 141.6, 133.9, 131.8, 131.2, 129.93, 129.87, 128.8, 128.2, 126.8, 126.2, 125.5, 125.4, 123.8, 63.9, 21.7.

1-Phenylethyl 4-methylbenzenesulfinate (3m): White solid; m.p. 127.1-129.2 °C; 39% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J = 7.5$ Hz, 2H), 7.31-7.24 (m, 3H), 7.19 (d, $J = 8.0$ Hz, 2H), 4.22 (q, $J = 7.0$ Hz, 1H), 2.40 (s, 3H), 1.76 (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.6, 134.1, 129.6, 129.43, 129.40, 128.9, 128.5, 66.2, 21.8, 14.3.

Benzhydryl 4-methylbenzenesulfinate (3n): White solid; m.p. 186.2-191.4 °C; 92% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 3.5$ Hz, 4H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.32-7.31 (m, 6H), 7.15 (d, $J = 7.5$ Hz, 2H), 5.26 (s, 1H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.6, 135.5, 133.3, 130.1, 129.4, 129.84, 128.76, 76.7, 21.8.

(4-Fluorophenyl)(phenyl)methyl 4-methylbenzenesulfinate (3o): White solid; m.p. 155.7-158.0 °C; 80% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.53-7.48 (m, 6H), 7.32-7.31 (m, 3H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.01 (t, $J = 8.5$ Hz, 2H), 5.25 (s, 1H), 2.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 163.0 (d, $J_{C,F} = 242.1$ Hz, 1C), 162.0, 144.8, 135.3, 133.1, 131.9 (d, $J_{C,F} = 8.3$ Hz, 1C), 130.0, 129.5, 129.19, 129.16 (d, $J_{C,F} = 2.9$ Hz, 1C), 128.94, 128.89, 115.9 (d, $J_{C,F} = 21.5$ Hz, 1C), 75.8, 21.8.
Allyl 4-methylbenzenesulfinic acid (3p): White liquid; 83% Yield; 
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.61 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 5.90-5.82 (m, 1H), 5.30 (dq, $J = 17.0$, 1.5 Hz, 1H), 5.23 (dq, $J = 10.5$, 1.5 Hz, 1H), 4.50 (qt, $J = 6.0$, 1.5 Hz, 1H), 4.12 (qt, $J = 6.0$, 1.5 Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.0, 141.9, 132.6, 129.9, 125.4, 119.4, 65.2, 21.7.

Cinnamyl 4-methylbenzenesulfinic acid (3q): Yellow liquid; 22% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.34-7.30 (m, 7H), 6.39 (d, $J = 15.5$ Hz, 2H), 6.11 (d, $J = 16.0$, 7.5 Hz, 2H), 3.94 (d, $J = 7.0$ Hz, 2H), 2.44 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.0, 139.2, 136.0, 135.7, 129.9, 128.8, 128.71, 128.69, 126.8, 115.5, 60.7, 21.8.

(E)-2-methyl-3-phenylallyl 4-methylbenzenesulfinic acid (3r): Yellow liquid; 33% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.5$ Hz, 2H), 7.34-7.30 (m, 4H), 7.23 (t, $J = 7.0$ Hz, 1H), 7.08 (d, $J = 7.5$ Hz, 2H), 6.08 (s, 1H), 3.88 (s, 2H), 2.44 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.9, 136.8, 135.5, 134.9, 129.8, 128.9, 128.8, 128.3, 127.3, 126.4, 67.3, 21.8, 18.8.

Octyl 4-methylbenzenesulfinic acid (3s): White liquid; 92% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, $J = 7.5$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.03-3.99 (m, 1H), 3.62-3.57 (m, 1H), 2.43 (s, 3H), 1.61 (dt, $J = 13.5$, 6.5 Hz, 2H), 1.30-1.24 (m, 10H), 0.87 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 142.6, 141.8, 129.7, 125.2, 64.6, 31.7, 29.7, 29.10, 29.06, 25.7, 22.6, 21.5, 14.1.

Decyl 4-methylbenzenesulfinic acid (3t): White liquid; 91% Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 4.04-3.99 (m, 1H), 3.62-3.57 (m, 1H), 2.43 (s, 3H), 1.61 (dt, $J = 14.0$, 7.0 Hz, 2H), 1.30-1.24 (m, 14H), 0.88 (t, $J = 6.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 142.7, 142.0, 129.8, 125.4, 64.7, 32.0, 29.8, 29.7, 29.6, 29.4, 29.3, 25.9, 22.8, 21.7, 14.3.
Dodecyl 4-methylbenzenesulfinate (3u): White liquid; 84% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.0\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 4.01 (dt, \(J = 9.5\), 7.0 Hz, 1H), 3.60 (dt, \(J = 10.0\), 6.0 Hz, 1H), 2.43 (s, 3H), 1.64-1.59 (m, 2H), 1.31-1.24 (m, 18H), 0.88 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.8, 142.0, 129.8, 125.4, 64.8, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 25.9, 22.9, 21.7, 14.3.

Hexadecyl 4-methylbenzenesulfinate (3v): White liquid; 80% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.0\) Hz, 2H), 7.33 (d, \(J = 7.5\) Hz, 2H), 4.01 (dt, \(J = 10.0\), 6.5 Hz, 1H), 3.60 (dt, \(J = 9.5\), 6.5 Hz, 1H), 2.43 (s, 3H), 1.64-1.58 (m, 2H), 1.31-1.23 (m, 26H), 0.88 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.8, 142.1, 129.8, 125.4, 64.8, 32.1, 29.88, 29.87, 29.84, 29.81, 29.7, 29.6, 29.5, 29.3, 25.9, 22.9, 21.7, 14.3.

Phenethyl 4-methylbenzenesulfinate (3w): White liquid; 76% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 8.0\) Hz, 2H), 7.29-7.26 (m, 4H), 7.23-7.20 (m, 1H), 7.14 (d, \(J = 7.0\) Hz, 2H), 4.23 (dt, \(J = 10.0\), 7.0 Hz, 1H), 3.80 (dt, \(J = 10.0\), 7.0 Hz, 1H), 2.94-2.91 (m, 2H), 2.41 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.8, 141.7, 137.5, 129.8, 129.1, 128.6, 126.8, 125.4, 64.9, 36.4, 21.6.

3-Phenylpropyl 4-methylbenzenesulfinate (3x): White liquid; 83% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.5\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 7.26 (t, \(J = 7.5\) Hz, 2H), 7.18 (t, \(J = 7.5\) Hz, 1H), 7.13 (d, \(J = 7.0\) Hz, 2H), 4.04 (dt, \(J = 10.0\), 6.5 Hz, 1H), 3.63 (dt, \(J = 10.0\), 6.5 Hz, 1H), 2.66 (td, \(J = 7.5\), 2.0 Hz, 2H), 2.43 (s, 3H), 1.96-1.91 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.9, 141.9, 141.2, 129.9, 128.59, 128.58, 126.2, 125.4, 63.8, 32.1, 31.5, 21.7.

2-Ethylhexyl 4-methylbenzenesulfinate (3y): Four isomers; White liquid; 94% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.0\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 3.93 (td, \(J = 9.5\), 5.5 Hz, 1H), 3.46 (ddd, \(J = 12.5\), 5.5 Hz, 1H), 2.43 (s, 3H), 1.51 (dt, \(J = 12.0\), 6.0 Hz, 1H), 1.40-1.12 (m, 8H), 0.86 (t, \(J = 6.5\) Hz, 1H), 0.82 (td, \(J = 7.5\), 4.5 Hz, 1H).
3.0 Hz, 1H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.7, 141.89, 141.87, 129.8, 125.4, 66.3, 66.2, 39.70, 39.66, 30.3, 30.2, 29.0, 28.9, 23.6, 23.1, 23.0, 21.6, 14.2, 11.03, 10.98.

**Isopropyl 4-methylbenzenesulfinate (3z):** White liquid; 91% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 7.0$ Hz, 2H), 4.61-4.59 (m, 1H), 2.42 (s, 3H), 1.38 (d, $J = 5.5$ Hz, 3H), 1.25 (d, $J = 6.0$ Hz, 3H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.0, 142.6, 129.7, 125.2, 72.8, 23.6, 23.1, 23.0, 21.6, 14.2, 11.03, 10.98.

**Cyclohexyl 4-methylbenzenesulfinate (3A):** White liquid; 63% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 7.5$ Hz, 2H), 4.35-4.30 (m, 1H), 2.42 (s, 3H), 2.01 (dd, $J = 12.5$, 3.5 Hz, 1H), 1.81-1.70 (m, 3H), 1.62-1.44 (m, 3H), 1.38-1.19 (m, 3H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.0, 142.5, 129.7, 125.2, 77.9, 33.85, 33.76, 25.3, 24.00, 23.97, 21.6.

(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-methylbenzenesulfinate (3B): Two isomers; White solid; m.p. 158.5-163.3 °C; 82% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.59-7.57 (m, 2H), 7.32 (d, $J = 7.5$ Hz, 2H), 5.72 (s, 1H), 4.10 (dt, $J = 40.5$ Hz, 8 Hz, 1H), 2.42-2.14 (m, 8H), 2.05-1.95 (m, 2H), 1.81-1.26 (m, 9H), 1.17 (d, $J = 7.0$ Hz, 3H), 1.02-0.87 (m, 3H), 0.83 (d, $J = 2.5$ Hz, 3H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.6, 171.04, 171.00, 142.93, 142.87, 142.66, 142.63, 129.75, 129.71, 125.4, 125.3, 124.09, 124.05, 87.3, 85.4, 53.9, 53.8, 50.12, 50.07, 43.2, 43.1, 38.7, 36.5, 36.0, 35.85, 35.83, 35.59, 35.55, 34.1, 32.8, 31.6, 31.5, 29.4, 28.7, 23.7, 23.6, 21.7, 20.6, 20.5, 17.53, 17.50, 12.1, 12.0.

(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl benzenesulfinate (3C): Two isomers; White solid; m.p. 144.5-149.0 °C; 82% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.72-7.69 (m, 2H), 7.57-7.51 (m, 3H), 5.72 (s, 1H), 4.12 (dt, $J = 42.0$, 8.5 Hz, 1H), 2.46-2.16 (m, 4H), 2.06-1.95 (m, 1H), 1.85-1.49.
(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-methylbenzenesulfinate (3D): Two isomers; White solid; m.p. 153.2-155.7 °C; 81% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 8.5\) Hz, 2H), 7.33 (q, \(J = 4\) Hz, 2H), 5.38 (dd, \(J = 60.5, 5\) Hz, 1H), 4.24-4.16 (m, 1H), 2.51-2.45 (m, 2H), 2.42 (d, \(J = 3.0\) Hz, 3H), 2.14-2.02 (m, 2H), 1.98-1.56 (m, 9H), 1.55-1.42 (m, 2H), 1.30-1.24 (m, 2H), 1.17-1.05 (m, 1H), 1.02 (d, \(J = 1.0\) Hz, 3H), 1.00-0.97 (m, 1H), 0.88 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 143.0, 142.9, 142.7, 140.06, 140.04, 129.8, 125.2, 125.1, 122.3, 122.2, 79.1, 78.7, 51.9, 50.2, 47.7, 40.5, 40.3, 37.3, 37.2, 36.8, 36.0, 31.6, 31.5, 30.94, 30.91, 30.1, 29.9, 22.0, 21.7, 20.49, 20.47, 19.4, 13.7.

(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl benzenesulfinate (3E): Two isomers; White solid; m.p. 166.4-172.1 °C; 80% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.74-7.71 (m, 2H), 7.56-7.52 (m, 2H), 5.38 (dd, \(J = 68.0\) Hz, 5Hz, 1H), 4.25-4.18 (m, 1H), 2.54-2.43 (m, 2H), 2.14-2.04 (m, 2H), 1.98-1.62 (m, 8H), 1.59 (s, 3H), 1.56-1.42 (m, 2H), 1.31-1.24 (m, 2H), 1.18-1.06 (m, 1H), 1.02 (s, 3H), 1.01-0.97 (m, 1H), 0.88 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 145.9, 145.8, 140.03, 140.00, 132.2, 129.2, 125.24, 125.21, 122.4, 122.3, 79.3, 79.0, 51.9, 50.3, 47.7, 40.5, 40.3, 37.31, 37.27, 36.83, 36.81, 36.0, 31.62, 31.57, 30.97, 30.93, 30.1, 30.0, 22.0, 20.5, 19.5, 13.7.

1-Ethynylcyclohexyl 4-methylbenzenesulfinate (3F): Yellow liquid; 48% Yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, \(J = 8.0\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H), 2.83 (s, 1H), 2.42 (s, 3H), 2.25-
2.23 (m, 1H), 2.05-1.96 (m, 2H), 1.83-1.76 (m, 2H), 1.74-1.69 (m, 1H), 1.66-1.61 (m, 2H), 1.59-1.54 (m, 1H), 1.33-1.26 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.6, 142.5, 129.8, 125.2, 84.1, 79.3, 39.3, 39.2, 24.9, 23.0, 22.9, 21.7.

Adamantan-1-yl 4-methylbenzenesulfinate (3G): Yellow solid; m.p. 104.5-108.6 °C; 52% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 3H), 2.26 (m, 3H), 2.14-2.07 (m, 6H), 1.69 (m, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.9, 142.2, 129.8, 125.1, 82.1, 44.0, 36.0, 31.3, 21.6.

(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl butane-1-sulfinate (3H):  Two isomers; White solid; m.p. 75.4-78.0 °C; 42% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.73 (s, 1H), 4.14-4.07 (m, 1H), 2.81-2.67 (m, 2H), 2.44-2.26 (m, 4H), 2.17-2.11 (m, 1H), 2.07-1.99 (m, 2H), 1.89-1.77 (m, 2H), 1.89-1.77 (m, 2H), 1.74-1.55 (m, 8H), 1.50-1.35 (m, 4H), 1.19 (s, 1H), 1.04-1.01 (m, 1H), 0.97-0.92 (m, 4H), 0.84 (d, $J = 2.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 188.2, 171.1, 171.0, 124.2, 124.1, 89.0, 88.4, 57.6, 57.5, 54.0, 53.90, 53.85, 50.5, 50.2, 43.5, 43.1, 38.80, 38.77, 36.8, 36.3, 35.92, 35.89, 35.87, 35.7, 35.6, 34.1, 32.9, 31.6, 31.5, 29.0, 28.6, 23.8, 23.7, 23.5, 22.20, 22.15, 20.64, 20.59, 17.6, 13.9, 12.00, 11.98.

(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-chlorobenzenesulfinate (3I): Two isomers; White solid; m.p. 167.1-171.9 °C; 72% Yield; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.66-7.62 (m, 2H), 7.52-7.50 (m, 2H), 5.72 (s, 1H), 4.11 (dt, $J = 38.0$ Hz, 8 Hz, 1H), 2.45-2.25 (m, 4H), 2.06-2.00 (m, 1H), 1.85-1.77 (m, 2H), 1.71-1.52 (m, 6H), 1.44-1.29 (m, 2H), 1.18 (d, $J = 6.5$ Hz, 3H), 1.02-0.85 (m, 4H), 0.83 (d, $J = 4.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.60, 199.58, 170.93, 170.89, 144.42, 144.38, 138.53, 138.52,
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-bromobenzenesulfinate (3J): Two isomers; White solid; m.p. 176.0-177.2 °C; 69% Yield; 1H NMR (500 MHz, CDCl3) δ 7.68-7.66 (m, 2H), 7.59-7.55 (m, 2H), 5.72 (s, 1H), 4.10 (dt, J = 37.0 Hz, 8.5 Hz, 1H), 2.46-2.25 (m, 4H), 2.06-2.00 (m, 1H), 1.85-1.78 (m, 2H), 1.75-1.52 (m, 6H), 1.44-1.29 (m, 2H), 1.18 (d, J = 6.5 Hz, 3H), 1.04-0.86 (m, 4H), 0.83 (d, J = 4.0 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 199.61, 199.59, 170.93, 170.91, 144.94, 144.89, 132.4, 132.3, 127.11, 127.06, 126.95, 126.92, 124.2, 124.1, 88.0, 86.0, 53.9, 53.8, 50.1, 50.0, 43.2, 43.1, 38.7, 36.5, 36.1, 35.88, 35.86, 35.60, 35.57, 34.1, 32.8, 31.55, 31.51, 29.3, 28.7, 23.7, 23.6, 20.6, 20.5, 17.56, 17.55, 12.1, 12.0.

(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-nitrobenzenesulfinate (3K): Two isomers; Yellow solid; m.p. 175.6-178.0 °C; 45% Yield; 1H NMR (500 MHz, CDCl3) δ 8.41-8.38 (m, 2H), 7.92-7.88 (m, 2H), 5.72 (s, 1H), 4.16 (dt, J = 34.0 Hz, 8.0 Hz, 1H), 2.43-2.25 (m, 4H), 2.06-2.00 (m, 1H), 1.86-1.79 (m, 2H), 1.71-1.54 (m, 6H), 1.43-1.40 (m, 1H), 1.26 (s, 1H), 1.18 (d, J = 7.5 Hz, 3H), 1.02-0.86 (m, 4H), 0.84 (d, J = 4.5 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 199.5, 199.5, 170.8, 170.7, 152.2, 150.24, 150.21, 126.83, 126.78, 124.39, 124.35, 124.21, 124.19, 89.1, 87.0, 53.84, 53.76, 50.1, 50.0, 43.4, 43.2, 38.75, 38.73, 36.6, 36.1, 35.89, 35.87, 35.58, 35.57, 34.08, 34.07, 32.8, 31.52, 31.49, 29.3, 28.8, 23.7, 23.6, 20.6, 20.5, 17.6, 12.2, 12.1.

(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl thiophene-2-sulfinate (3L): Two isomers; White solid; m.p. 124.6-127.8 °C; 87%
Yield; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64-7.62 (m, 1H), 7.47 (dt, $J$ = 4.0 Hz, 1.0 Hz, 1H), 7.15 (dd, $J$ = 5.0 Hz, 4.0 Hz, 1H), 5.72 (s, 1H), 4.25 (dt, $J$ = 52.0 Hz, 8.0 Hz, 1H), 2.43-2.25 (m, 4H), 2.06-1.99 (m, 1H), 1.86-1.78 (m, 2H), 1.72-1.54 (m, 6H), 1.45-1.33 (m, 2H), 1.18 (d, $J$ = 6.0 Hz, 3H), 1.04-0.88 (m, 4H), 0.87 (d, $J$ = 3.0 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 199.6, 170.99, 170.95, 131.5, 131.4, 129.8, 129.7, 127.8, 124.2, 124.1, 87.2, 85.9, 53.9, 53.8, 50.13, 50.12, 43.3, 43.2, 38.79, 38.78, 36.5, 36.0, 35.90, 35.88, 35.7, 35.6, 34.1, 32.9, 31.59, 31.56, 29.4, 28.8, 23.8, 23.7, 20.63, 20.57, 17.58, 17.56, 12.2, 12.1.

7. References


8. Copies of $^1$H- and $^{13}$C-NMR
Benzy 4-methylbenzenesulfinate (3a)

![NMR spectrum image]
4-Methylphenyl $p$-toluenesulfinate (4)
4-Methylbenzyl 4-methylbenzenesulfinic acid (3b)
4-Nitrobenzyl 4-methylbenzenesulfinate (3c)
4-Cyanobenzyl 4-methylbenzenesulfinate (3d)
4-Hydroxybenzyl 4-methylbenzenesulfinate (3e)
2-Chlorobenzyl 4-methylbenzenesulfinate (3f)
4-Chlorobenzyl 4-methylbenzenesulfinate (3g)
2-Fluorobenzyl 4-methylbenzenesulfinate (3h)
4-Fluorobenzyl 4-methylbenzenesulfinate (3i)
3,4-Difluorobenzyl 4-methylbenzenesulfinate (3j)
4-(Trifluoromethyl)benzyl 4-methylbenzenesulfinate (3k)
Naphthalen-1-ylmethyl 4-methylbenzenesulfinate (3l)
1-Phenylethyl 4-methylbenzenesulfinic acid (3m)
Benzhydryl 4-methylbenzenesulfinate (3n)
(4-Fluorophenyl)(phenyl)methyl 4-methylbenzenesulfinate (3o)
Allyl 4-methylbenzenesulfinate (3p)
Cinnamyl 4-methylbenzenesulfinate (3q)
(E)-2-methyl-3-phenylallyl 4-methylbenzenesulinate (3r)
Octyl 4-methylbenzenesulfinate (3s)
Decyl 4-methylbenzenesulfinate (3t)
Dodecyl 4-methylbenzenesulfinate (3u)
Hexadecyl 4-methylbenzenesulfinate (3v)
Phenethyl 4-methylbenzenesulfinate (3w)
3-Phenylpropyl 4-methylbenzenesulfinate (3x)
2-Ethylhexyl 4-methylbenzenesulfinate (3y)
Isopropyl 4-methylbenzenesulfinic acid (3z)
Cyclohexyl 4-methylbenzenesulfinate (3A)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-methylbenzenesulfinate (3B)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl benzenesulfinate (3C)
(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-methylbenzenesulfinate (3D)
(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl benzenesulfinate (3E)
1-Ethynylcyclohexyl 4-methylbenzenesulfinate (3F)
Adamantan-1-yl 4-methylbenzenesulfinate (3G)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl butane-1-sulfinate (3H)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-chlorobenzenesulfinate (3I)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-bromobenzenesulfinate (3J)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-nitrobenzenesulfinate (3K)
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl thiophene-2-sulfinate (3L)