Metal-Free O-H/C-H Difunctionalization of Phenols by \(\alpha\)-Hydroxyarylsulfonium Salts in Water

Dengfeng Chen, Qingyuan Feng, Yunqin Yang, Xumin Cai, Fei Wang, and Shenlin Huang*

College of Chemical Engineering, Jiangsu Key Lab of Biomass-Based Green Fuels and Chemicals, Nanjing Forestry University, Nanjing, 210037, P. R. China
Email: shuang@njfu.edu.cn

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I. General Information

Unless otherwise stated, all glassware was oven dried and all reactions were carried out under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise indicated. A 2 wt% TPGS-750-M/H₂O solution was prepared by dissolving TPGS-750-M in water (degassed with argon prior to mixing, HPLC grade), followed by degassing with argon. TPGS-750-M was made as previously described. Sulfoxides were prepared according to the procedures reported in the literature. Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV light as the visualizing agent and High Performance Liquid Chromatography (HPLC) with UV detection at 254 nm. For HPLC yields, UV response factors relative to an internal standard (nitrobenzene). Flash column chromatography was performed using silica gel 60 (230-400 mesh). High resolution mass spectra were acquired by Agilent 6500 QTOFMS (ESI) or Waters GCT Premier TOFMS (EI). All ¹H NMR, ¹³C NMR spectra were recorded on Bruker DRX-600 or AMX-400 instruments. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of CDCl₃, defined at δ = 7.26 (¹H NMR), defined at δ = 77.16 (¹³C NMR). Coupling constants were quoted in Hz (J). ¹H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

II. General Procedure A for the Preparation of Sulfonium Salts

\[
\text{R}^1\text{C(OH)}\text{SO} \quad \text{Tf}_2\text{O} \quad \text{MeCN, 0 °C} \quad \text{R}^1\text{C(OH)}\text{S}^+ \text{OTf}^{-} \quad \text{R}^1\text{C(O)}\text{SO} \quad \text{MeCN, 0 °C} \quad \text{R}^1\text{C(O)}\text{S}^+ \text{OTf}^{-}
\]

An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf₂O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with EtOAc to afford desired sulfonium salts.

(2-Hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3a)

Following the general procedure A, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf₂O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3a (91 mg, 0.19 mmol, 95%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 11.37 (br s, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 9.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.77 – 7.65 (m, 8H), 7.65 – 7.58 (m, 4H), 7.54 – 7.48 (m, 1H).
\[^{13}\text{C NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ 161.4, 139.4, 133.9, 131.1, 130.3, 130.3, 129.9, 129.0, 125.2, 123.9, 120.5, 120.3, 96.5.\]

\textbf{HRMS-ESI (m/z) [M-OTf]+} calculated for C\textsubscript{22}H\textsubscript{17}O3 329.0995, found 329.0985.

\textbf{(7-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3b)}

Following the general procedure A, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf\textsubscript{2}O (40.8 µL, 0.24 mmol) and 7-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3b (102.6 mg, 0.185 mmol, 92%) as a brown oil.

\[^{1}\text{H NMR}\ (400\ \text{MHz, CDCl}_3)\ \delta\ 11.64\ (\text{br s}, 1\text{H}), 8.47\ (\text{s}, 1\text{H}), 8.09\ (\text{d}, J = 9.1\ \text{Hz}, 1\text{H}), 7.78\ (\text{d}, J = 8.7\ \text{Hz}, 1\text{H}), 7.74 – 7.68\ (\text{m}, 7\text{H}), 7.66 – 7.58\ (\text{m}, 5\text{H}).\]

\[^{13}\text{C NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ 162.3, 139.3, 135.2, 134.1, 131.4, 131.2, 130.4, 128.7, 127.4, 125.2, 123.4, 122.9, 120.8, 95.4.\]

\textbf{HRMS-ESI (m/z) [M-OTf]+} calculated for C\textsubscript{22}H\textsubscript{16}BrOS 407.0100, found 407.0083.

\textbf{(6-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3c)}

Following the general procedure A, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf\textsubscript{2}O (40.8 µL, 0.24 mmol) and 6-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3c (100.3 mg, 0.18 mmol, 90%) as a purple oil.

\[^{1}\text{H NMR}\ (400\ \text{MHz, CDCl}_3)\ \delta\ 11.55\ (\text{br s}, 1\text{H}), 8.23\ (\text{d}, J = 9.0\ \text{Hz}, 1\text{H}), 8.05\ (\text{d}, J = 1.8\ \text{Hz}, 1\text{H}), 8.03\ (\text{d}, J = 9.2\ \text{Hz}, 1\text{H}), 7.77\ (\text{dd}, J = 9.0, 1.8\ \text{Hz}, 1\text{H}), 7.73 – 7.68\ (\text{m}, 7\text{H}), 7.65 – 7.59\ (\text{m}, 4\text{H}).\]

\[^{13}\text{C NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ 161.7, 138.2, 134.1, 133.4, 132.6, 131.8, 131.2, 130.3, 130.0, 123.5, 122.3, 121.7, 118.8, 96.8.\]

\textbf{HRMS-ESI (m/z) [M-OTf]+} calculated for C\textsubscript{22}H\textsubscript{16}BrOS 407.0100, found 407.0085.

\textbf{(2-Hydroxy-3-(methoxycarbonyl)naphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3d)}
Following the general procedure A, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf$_2$O (40.8 µL, 0.24 mmol) and methyl-3-hydroxy-2-naphthoate (40.5 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3d (93 mg, 0.174 mmol, 87%) as a brown oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.37 (br s, 1H), 8.99 (s, 1H), 8.77 – 8.59 (m, 1H), 8.06 (d, J = 7.3 Hz, 1H), 8.01 – 7.92 (m, 1H), 7.87 – 7.53 (m, 11H), 4.08 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.5, 160.3, 142.1, 136.6, 134.4, 134.1, 131.8, 131.6, 131.2, 131.1, 130.7, 127.5, 126.9, 123.1, 122.0, 114.7, 100.4, 54.1.

HRMS-ESI (m/z) [M+OTf]$^-$ calculated for C$_{24}$H$_{19}$O$_3$S 387.1049, found 387.1035.

6-Cyano-1-(diphenylsulfonio)naphthalen-2-olate (3e)

Following the general procedure A, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf$_2$O (40.8 µL, 0.24 mmol) and 6-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3e (63.6 mg, 0.18 mmol, 90%) as a brown oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.51 (d, J = 8.7 Hz, 1H), 8.26 (s, 1H), 8.17 (d, J = 9.1 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.77 – 7.70 (m, 7H), 7.63 (t, J = 7.7 Hz, 4H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 163.7, 139.28, 136.06, 135.13, 134.25, 131.30, 131.04, 130.40, 127.89, 123.20, 122.35, 122.19, 121.47, 119.35, 118.19, 108.77, 97.62.

HRMS-ESI (m/z) [M+H]$^+$ calculated for C$_{23}$H$_{16}$NOS 354.0947, found 354.0935.

(2,7-Dihydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3f)

Following the general procedure A, diphenyl sulfoxide (44.5 mmol, 0.22 mmol), Tf$_2$O (40.8 µL, 0.24 mmol) and naphthalene-2,7-diol (32.1 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3f (80.1 mg, 0.162 mmol, 81%) as a red oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (s, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.69 (d, J = 9.1 Hz, 4H), 7.53 (t, J = 7.3 Hz, 3H), 7.45 (t, J = 7.7 Hz, 4H), 7.17 (d, J = 8.8 Hz, 1H), 6.96 (d, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.7, 159.3, 138.7, 136.3, 133.5, 131.3, 130.8, 130.5, 124.5, 123.5, 117.5, 115.8, 104.1, 95.9.

HRMS-ESI (m/z) [M-OTf]$^-$ calculated for C$_{22}$H$_{17}$O$_3$S 345.0944, found 345.0932.
1-(Di-p-tolylsulfonio)naphthalen-2-olate (3g)

Following the general procedure A, 4,4'-sulfinylbis(methylbenzene) (50.7 mg, 0.22 mmol), Tf₂O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3g (64.1 mg, 0.18 mmol, 90%) as a colourless oil.

^1H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 9.1 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.63 – 7.57 (m, 4H), 7.53 – 7.44 (m, 2H), 7.38 (d, J = 8.3 Hz, 4H), 2.44 (s, 6H).

^13C NMR (100 MHz, CDCl₃) δ 145.0, 138.8, 134.1, 131.7, 130.2, 129.9, 129.8, 128.6, 124.7, 122.2, 120.8, 120.4, 119.0, 96.7, 21.7.

HRMS-ESI (m/z) [M+H]^+ calculated for C₂₄H₂₁OS 357.1308, found 357.1298.

(4-Bromophenyl)(2-hydroxynaphthalen-1-yl)(methyl)sulfonium trifluoromethanesulfonate (3h)

Following the general procedure A, 1-bromo-4-(methylsulfinyl)benzene (48.2 mg, 0.22 mmol), Tf₂O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3h (92.1 mg, 0.186 mmol, 93%) as a brown oil.

^1H NMR (400 MHz, CDCl₃) δ 11.13 (br s, 1H), 8.27 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.73 – 7.61 (m, 5H), 7.54 (d, J = 9.1 Hz, 1H), 7.48 (t, J = 7.3 Hz, 1H), 3.79 (s, 3H).

^13C NMR (100 MHz, CDCl₃) δ 161.0, 138.9, 134.1, 133.5, 130.4, 130.3, 129.70, 128.8, 128.7, 125.4, 124.6, 122.1, 121.0, 119.6, 118.9, 97.0, 26.4.

HRMS-ESI (m/z) [M-OTf]^+ calculated for C₁₇H₁₄BrOS 344.9943, found 344.9930.

(5-Acetyl-2-hydroxyphenyl)diphenylsulfonium trifluoromethanesulfonate (3i)

Following the general procedure A, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf₂O (40.8 µL, 0.24 mmol) and 1-(4-hydroxycyclohexa-2,4-dien-1-yl)ethan-1-one (27.6 mg, 0.2 mmol) were
used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3i (24.4 mg, 0.052 mmol, 26%) as a brown oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.75 – 7.68 (m, 4H), 7.64 – 7.55 (m, 6H), 2.50 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.8, 161.6, 137.4, 135.0, 131.9, 130.9, 122.9, 119.1, 110.2, 77.5, 77.2, 76.8, 26.4.

HRMS-ESI (m/z) [M-OTf]$^+$ calculated for C$_{20}$H$_{17}$O$_2$S 321.0944, found 321.0932.

(2-Hydroxynaphthalen-1-yl)(methyl)(naphthalen-2-yl)sulfonium trifluoromethanesulfon-ate (3j)

Following the general procedure A, 2-(methylsulfinyl)naphthalene (41.9 mg, 0.22 mmol), Tf$_2$O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give 3j (88.6 mg, 0.19 mmol, 95%) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.16 (br s, 1H), 8.35 (d, $J = 1.8$ Hz, 1H), 8.32 (d, $J = 8.6$ Hz, 1H), 8.01 (d, $J = 9.1$ Hz, 1H), 7.93 (d, $J = 9.0$ Hz, 1H), 7.90 (d, $J = 8.3$ Hz, 1H), 7.86 – 7.79 (m, 2H), 7.76 – 7.66 (m, 2H), 7.63 – 7.52 (m, 3H), 7.47 (t, $J = 7.5$ Hz, 1H), 3.79 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 138.6, 134.8, 133.5, 133.0, 131.5, 130.6, 130.2, 129.8, 129.7, 123.0, 128.8, 128.5, 128.1, 125.2, 123.0, 122.2, 121.0, 119.8, 97.5, 26.4.

HRMS-ESI (m/z) [M-OTf]$^+$ calculated for C$_{21}$H$_{19}$OS 317.0995, found 317.0993.

III. General Procedure B for rearrangement of sulfonium salts

An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf$_2$O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated in vacuo. K$_3$PO$_4$ (0.88 mmol, 4.4 eq) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H$_2$O (0.27 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After completion, the solution was allowed to cool to room temperature and extracted with EtOAc (1 mL x 3), dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure. The crude
mixture was purified by flash column chromatography (100% petroleum ether to 10% EtOAc/petroleum ether) to afford desired products.

(2-Phenoxynaphthalen-1-yl)(phenyl)sulfane (4aa)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4aa (57 mg, 0.172 mmol, 86%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.57 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.57 (dd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.49 (dd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.23 (d, J = 8.9 Hz, 1H), 7.19 – 7.03 (m, 5H), 6.94 – 6.86 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 157.6, 156.8, 137.8, 136.2, 131.9, 129.8, 128.9, 128.5, 127.9, 127.5, 126.2, 125.5, 125.4, 123.3, 120.1, 119.0, 118.4.

HRMS-ESI (m/z) [M]+ calculated for C₂₂H₁₆O₃ 328.0922, found 328.0910.

(7-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4ba)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 7-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ba (66.9 mg, 0.164 mmol, 82%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, J = 1.8 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.55 (dd, J = 8.6, 1.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.03 (m, 7H), 6.87 (dd, J = 8.6, 0.9 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 157.6, 157.0, 137.7, 137.2, 131.7, 130.1, 129.9, 129.5, 129.0, 128.9, 128.4, 127.8, 125.8, 123.7, 122.8, 112.0, 118.8, 118.1.

HRMS-ESI (m/z) [M]+ calculated for C₂₂H₁₅BrO₃ 406.0027, found 406.0029.

(6-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4ca)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 6-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ca (61.3 mg, 0.15 mmol, 75%) as a white solid.
\[ ^1H\text{ NMR} (400\text{ MHz, CDCl}_3) \delta 8.43 (d, J = 9.1\text{ Hz, 1H}), 8.01 (d, J = 1.8\text{ Hz, 1H}), 7.79 (d, J = 9.0\text{ Hz, 1H}), 7.61 (dd, J = 9.1, 1.9\text{ Hz, 1H}), 7.30 (t, J = 7.9\text{ Hz, 2H}), 7.22 (d, J = 9.0\text{ Hz, 1H}), 7.19 – 7.04 (m, 6H), 6.88 (d, J = 7.8\text{ Hz, 2H}).\]

\[ ^13C\text{ NMR} (100\text{ MHz, CDCl}_3) \delta 157.2, 157.1, 137.4, 134.8, 132.2, 131.1, 130.4, 129.9, 129.0, 128.2, 127.6, 125.7, 123.6, 120.9, 119.5, 119.3, 118.6.\]

HRMS-ESI (m/z) [M]+ calculated for C_{22}H_{15}BrOS 406.0027, found 406.001.

(3-Bromo-2-phenoxy-1-y1)(phenyl)sulfane (4da)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol), Tf\(_2\)O (40.8 µL, 0.2 mmol) and K\(_3\)PO\(_4\) (188.7 mg, 0.88 mmol) were used to afford 4da (59.5 mg, 0.146 mmol, 73%) as a white solid.

\[ ^1H\text{ NMR} (600\text{ MHz, CDCl}_3) \delta 8.67 (d, J = 8.8\text{ Hz, 1H}), 8.22 (s, 1H), 7.91 (d, J = 9.0\text{ Hz, 1H}), 7.67 (d, J = 8.8\text{ Hz, 1H}), 7.33 (t, J = 7.8\text{ Hz, 2H}), 7.27 (d, J = 8.7\text{ Hz, 1H}), 7.21 – 7.04 (m, 6H), 6.90 (d, J = 7.9\text{ Hz, 2H}).\]

\[ ^13C\text{ NMR} (150\text{ MHz, CDCl}_3) \delta 159.6, 156.4, 156.0, 136.0, 136.9, 134.4, 132.1, 130.1, 129.8, 129.1, 128.4, 127.8, 127.5, 126.0, 124.4, 120.8, 119.3, 119.1, 119.0, 108.8.\]

HRMS-ESI (m/z) [M]+ calculated for C_{23}H_{15}NOS 353.0874, found 353.0880.

Methyl 3-phenoxy-4-(phenylthio)-2-naphthoate (4fa)

\[
\text{S8}
\]
Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), methyl 3-hydroxy-2-naphthoate (40.4 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4fa (38.6 mg, 0.1 mmol, 50%) as a white solid and the hydrolysis product 4fa‘ (25.3 mg, 34%) as a pale yellow solid.

4fa:

1H NMR (400 MHz, CDCl₃) δ 8.60 (s, 1H), 8.54 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 8.4, 7.0, 1.3 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.02 (m, 5H), 6.99 – 6.93 (m, 1H), 6.73 (d, J = 8.7, 0.9 Hz, 2H), 3.72 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ 165.8, 159.2, 152.9, 137.7, 137.0, 135.5, 130.9, 129.8, 129.7 – 129.5, 128.9, 127.9, 126.8, 126.7, 125.7, 125.1, 125.0, 121.8, 115.4, 52.5.

HRMS-ESI (m/z) [M+Na]+ calculated for C₂₄H₁₈O₃S 409.0869, found 409.0851.

4fa’:

1H NMR (600 MHz, CDCl₃) δ 8.80 (s, 1H), 8.52 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.5 Hz, 2H), 7.07 (t, J = 7.2 Hz, 1H), 6.99 (dd, J = 15.3, 7.6 Hz, 3H), 6.73 (d, J = 8.1 Hz, 2H).

13C NMR (151 MHz, CDCl₃) δ 167.6, 158.7, 153.0, 138.4, 137.0, 131.0, 130.4, 130.1, 129.6, 129.0, 127.8, 127.1, 126.7, 125.9, 125.3, 123.3, 122.5, 115.7.

HRMS-ESI (m/z) [M-H]– calculated for C₂₃H₁₅O₃S 371.0747, found 371.0738.

N-(Naphthalen-2-yl)-3-phenoxy-4-(phenylthio)-2-naphthamide (4ga)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3-hydroxy-N-(naphthalen-2-yl)-2-naphthamide (62.7 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ga (15 mg, 0.03 mmol, 15%) as a white solid.

1H NMR (400 MHz, CDCl₃) δ 9.49 (s, 1H), 9.02 (s, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.28 (d, J = 1.7 Hz, 1H), 8.11 (d, J = 7.4 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.65 (dtd, J = 14.6, 6.9, 1.3 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.32 (dd, J = 8.8, 2.1 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.18 – 7.08 (m, 3H), 7.05 – 6.97 (m, 3H), 6.84 (d, J = 7.9 Hz, 2H).

13C NMR (100 MHz, CDCl₃) δ 162.5, 157.9, 151.4, 137.8, 136.9, 136.2, 135.4, 134.0, 131.7, 131.0, 130.20, 130.16, 129.9, 129.1, 128.9, 127.9, 127.7, 127.6, 127.4, 127.2, 126.6, 125.9, 125.3, 124.7, 123.3, 120.3, 117.4, 115.5.

HRMS-EI (m/z) [M]+ calculated for C₃₃H₂₃NO₅S 497.1449, found 497.1455.
(4,5-Dimethyl-2-phenoxyphenyl)(phenyl)sulfane (4ha)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3,4-dimethylphenol (24.5 mmol, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ha (36.8 mg, 60%) as a colourless oil.

1H NMR (600 MHz, CDCl₃) δ 7.34 – 7.25 (m, 6H), 7.20 (t, J = 7.3 Hz, 1H), 7.14 (s, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 2.21 (s, 3H), 2.20 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ 157.8, 153.6, 138.3, 136.0, 134.8, 133.1, 130.5, 129.7, 129.1, 126.7, 123.5, 122.8, 121.5, 117.9, 19.8, 19.2.

HRMS-EI (m/z) [M]+ calculated for C₂₀H₁₈O₃ 306.1078, found 306.1094.

(3-Bromo-2,4-dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ia)

Following the general procedure B, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 4-bromo-3,5-dimethylphenol (40.2 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ia (58.6 mg, 0.12 mmol, 60%) as a colourless oil.

1H NMR (600 MHz, CDCl₃) δ 7.29 – 7.26 (m, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.11 – 7.04 (m, 4H), 6.81 (d, J = 8.2 Hz, 2H), 6.75 (s, 1H), 2.68 (s, 3H), 2.39 (s, 3H).

13C NMR (150 MHz, CDCl₃) δ 157.5, 157.2, 144.6, 141.3, 137.6, 129.8, 129.0, 127.2, 125.5, 123.4, 122.8, 122.6, 119.3, 118.6, 24.7, 23.1.

HRMS-EI (m/z) [M]+ calculated for C₂₀H₁₇BrOS 384.0183, found 384.0185.

(2,4-Dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ja)

Following the general procedure 2, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3,5-dimethylphenol (24.5 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ja (41.7 mg, 0.136 mmol, 68%) as a colourless oil.

1H NMR (600 MHz, CDCl₃) δ 7.27 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.09 – 7.03 (m, 4H), 6.95 (s, 1H), 6.85 (d, J = 8.0 Hz, 2H), 6.65 (s, 1H), 2.44 (s, 3H), 2.29 (s, 3H).

13C NMR (150 MHz, CDCl₃) δ 158.7, 157.6, 145.05, 140.9, 138.1, 129.7, 128.8, 126.93, 126.89, 125.1, 123.1, 120.1, 118.7, 118.1, 21.5, 21.4.
HRMS-EI (m/z) [M]+ calculated for C_{20}H_{18}O_{3} 306.1078, found 306.1069.

(2-(4-Chlorophenoxy)-5-fluorophenyl)(4-chlorophenyl)sulfane (4kb)

Following the general procedure B, 4,4′-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 4-fluorophenol (22.5 mg, 0.2 mmol), T\textsubscript{f}\textsubscript{2}O (40.8 µL, 0.2 mmol) and K\textsubscript{3}PO\textsubscript{4} (188.7 mg, 0.88 mmol) were used to afford 4kb (25.6 mg, 0.07 mmol, 35%) as a colourless oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.39 – 7.32 (m, 4H), 7.30 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 6.93 – 6.86 (m, 2H), 6.85 – 6.83 (m, 1H), 6.83 – 6.81 (m, 1H), 6.71 (dd, J = 8.6, 2.7 Hz, 1H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 159.6 (d, J = 245.7 Hz), 156.2, 149.2 (d, J = 2.8 Hz), 135.1, 135.0, 131.9 (d, J = 8.1 Hz), 130.6, 130.0, 129.9, 128.3, 121.5 (d, J = 8.7 Hz), 118.7, 116.9 (d, J = 25.8 Hz), 114.6 (d, J = 23.5 Hz).

HRMS-EI (m/z) [M]+ calculated for C\textsubscript{18}H\textsubscript{11}Cl\textsubscript{2}OS 363.9892, found 363.9884.

(4-Chlorophenyl)(2,4-dichloro-6-(4-chlorophenoxy)phenyl)sulfane (4lb)

Following the general procedure B, 4,4′-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 3,5-dichlorophenol (32.6 mg, 0.2 mmol), T\textsubscript{f}\textsubscript{2}O (40.8 µL, 0.2 mmol) and K\textsubscript{3}PO\textsubscript{4} (188.7 mg, 0.88 mmol) were used to afford 4lb (25 mg, 0.06 mmol, 30%) as a colourless oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.33 – 7.26 (m, 3H), 7.22 – 7.16 (m, 2H), 7.14 – 7.09 (m, 2H), 6.79 – 6.71 (m, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 159.7, 154.3, 141.7, 136.6, 134.2, 132.6, 130.3, 130.1, 130.0, 129.2, 125.4, 122.8, 120.5, 117.7.

HRMS-EI (m/z) [M]+ calculated for C\textsubscript{18}H\textsubscript{16}Cl\textsubscript{4}OS 415.9177, found 415.9165.

(5-Bromo-2-(4-chlorophenoxy)phenyl)(4-chlorophenyl)sulfane (4mb)
Following the general procedure B, 4,4’-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 4-bromophenol (34.6 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4mb (28.1 mg, 33%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.26 (m, 3H), 7.20 (d, J = 2.4 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.77 (d, J = 8.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 155.3, 153.2, 134.8, 134.4, 133.4, 131.2, 131.1, 131.0, 130.0, 129.9, 128.9, 121.1, 119.5, 117.4.

HRMS-EI (m/z) [M]⁺ calculated for C₁₈H₁₁BrCl₂OS 423.9091, found 423.9083.

(3-Bromo-6-(4-chlorophenoxy)-2,4-dimethylphenyl)(4-chlorophenyl)sulfane (4ib)

Following the general procedure B, 4,4’-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 4-bromo-3,5-dimethylphenol (40.2 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ib (70 mg, 0.154 mmol, 77%) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.00 – 6.93 (m, 2H), 6.76 (s, 1H), 6.75 – 6.70 (m, 2H), 2.67 (s, 3H), 2.40 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 156.9, 153.2, 134.8, 134.4, 133.4, 131.2, 131.1, 131.0, 130.0, 129.9, 128.5, 123.4, 122.5, 119.7, 119.5, 100.1, 24.7, 23.05.

HRMS-EI (m/z) [M]⁺ calculated for C₂₀H₁₅BrCl₂OS 451.9404, found 451.9415.

(2-(4-Chlorophenoxy)naphthalen-1-yl)(4-chlorophenyl)sulfane (4ab)

Following the general procedure B, 4,4’-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ab (58 mg, 0.146 mmol, 73%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.59 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.51 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.13 – 7.07 (m, 2H), 7.05 – 6.97 (m, 2H), 6.85 – 6.74 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 156.3, 156.2, 136.1, 136.0, 132.4, 131.50, 131.47, 129.8, 129.0, 128.9, 128.7, 128.4, 128.2, 126.0, 125.9, 120.1, 119.3, 119.2.

HRMS-EI (m/z) [M]⁺ calculated for C₂₂H₁₄Cl₂OS 396.0142, found 396.0156.
p-Tolyl(2-(p-tolyloxy)naphthalen-1-yl)sulfane (4ac)

Following the general procedure B, 4,4′-sulfinylbis(methylbenzene) (50.7 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ac (48.5 mg, 0.136 mmol, 68%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, J = 8.5 Hz, 1H), 7.86 (t, J = 8.0 Hz, 2H), 7.56 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.47 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.19 (d, J = 9.0 Hz, 1H), 7.13 – 7.03 (m, 4H), 6.96 (d, J = 8.1 Hz, 2H), 6.85 – 6.76 (m, 2H), 2.32 (s, 3H), 2.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 157.1, 155.3, 136.2, 135.3, 134.3, 132.8, 131.6, 131.1, 130.3, 129.7, 128.5, 127.9, 127.8, 126.2, 125.3, 119.8, 119.1, 118.5, 21.0, 20.8.

HRMS-El (m/z) [M]+ calculated for C₂₄H₂₀O₃S 356.123, found 356.1236.

(2-Phenoxy-naphthalen-1-yl)(p-tolyl)sulfane (4ad)

Following the general procedure B, 1-methyl-4-(phenylsulfinyl)benzene (47.6 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ad (49.5 mg, 0.144 mmol, 72%) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.59 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 8.9 Hz, 1H), 7.09 – 7.03 (m, 3H), 6.96 (d, J = 7.8 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 2.24 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 157.7, 156.6, 136.2, 135.4, 134.1, 131.7, 131.3, 129.8, 129.7, 128.5, 128.0, 127.8, 126.3, 125.5, 123.2, 120.2, 119.9, 118.3, 21.0.

HRMS-El (m/z) [M]+ calculated for C₂₃H₁₈O₃S 342.1078, found 342.1071.

(2-(4-Nitrophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ae)

Following the general procedure B, 1-methyl-4-((4-nitrophenyl)sulfinyl)benzene (57.5 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ae (50.4 mg, 0.144 mmol, 65%) as a pale yellow oil.

¹H NMR (600 MHz, CDCl₃) δ 8.61 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.29
(d, J = 9.0 Hz, 1H), 6.95 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 2.22 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 163.3, 154.1, 142.6, 136.13, 136.10, 133.1, 132.24, 132.23, 129.8, 128.7, 128.5, 128.2, 126.6, 126.5, 125.9, 122.8, 121.2, 116.6, 21.1.

HRMS-ESI (m/z) [M]$^+$ calculated for C$_{23}$H$_{17}$NO$_3$S 387.0929, found 387.0920.

p-Tolyl(2-(4-(trifluoromethyl)phenoxy)naphthalen-1-yl)sulfane (4af)

Following the general procedure B, 1-methyl-4-((4-(trifluoromethyl)phenyl)sulfinyl)benzene (62.6 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf$_2$O (40.8 µL, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4af (67.3 mg, 0.164 mmol, 82%) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.61 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.60 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.53 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.8 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.94 – 6.89 (m, 2H), 6.85 (d, J = 8.5 Hz, 2H), 2.22 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.7, 156.0, 136.2, 135.9, 133.5, 132.0, 131.9, 129.7, 128.6, 128.5, 128.0, 127.05 (q, J = 3.7 Hz), 126.5, 126.1, 124.7 (q, J = 32.7 Hz), 124.4 (q, J = 27.1 Hz), 122.1, 121.0, 117.1, 21.0.

HRMS-ESI (m/z) [M]$^+$ calculated for C$_{24}$H$_{17}$F$_3$OS 410.0952, found 410.0943.

(2-(4-Chlorophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ag)

Following the general procedure B, 1-chloro-4-(p-tolylsulfinyl)benzene (55.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf$_2$O (40.8 µL, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4ag (45.2 mg, 0.12 mmol, 60%) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.60 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.53 – 7.47 (m, 1H), 7.23 – 7.17 (m, 2H), 7.04 – 6.99 (m, 2H), 6.94 (d, J = 8.1 Hz, 2H), 6.81 – 6.74 (m, 2H), 2.24 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.5, 156.0, 136.2, 135.6, 133.9, 131.8, 131.6, 129.71, 129.67, 128.5, 128.2, 128.0, 127.9, 126.4, 125.7, 120.7, 120.3, 119.2, 21.0.

HRMS-ESI (m/z) [M]$^+$ calculated for C$_{23}$H$_{17}$ClOS 376.0689, found 376.0665.
(2-(2-Bromophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ah)

Following the general procedure B, 1-bromo-2-(p-tolylsulfinyl)benzene (65.0 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ah (67.4 mg, 0.16 mmol, 80%) as a colorless oil.

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 8.61 \ (d, J = 8.2 \text{ Hz, 1H}), \ 7.87 \ (t, J = 9.2 \text{ Hz, 2H}), \ 7.61 \ (dd, J = 8.0, 1.6 \text{ Hz, 1H}), \ 7.57 \ (ddd, J = 8.4, 6.9, 1.3 \text{ Hz, 1H}), \ 7.48 \ (ddd, J = 8.0, 6.9, 1.2 \text{ Hz, 1H}), \ 7.18 - 7.08 \ (m, 4H), \ 7.00 - 6.92 \ (m, 3H), \ 6.68 \ (dd, J = 8.2, 1.4 \text{ Hz, 1H}), \ 2.23 \ (s, 3H). \]

\[ ^{13}C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 156.2, \ 154.1, \ 136.3, \ 135.5, \ 133.9, \ 133.8, \ 131.4, \ 129.7, \ 128.61, \ 128.54, \ 128.51, \ 127.9, \ 126.4, \ 125.5, \ 124.7, \ 119.6, \ 119.5, \ 119.1, \ 114.3, \ 21.1. \]

HRMS-EI (m/z) [M]+ calculated for C₂₃H₁₇BrO₄S 420.0183, found 420.0195.

(2-Methoxynaphthalen-1-yl)(phenyl)sulfane (4ai)

Following the general procedure B, (methyIsulfanyl)benzene (30.8 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ai (48 mg, 0.18 mmol, 90%) as a colorless oil.

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 8.46 \ (d, J = 8.6 \text{ Hz, 1H}), \ 7.98 \ (d, J = 9.1 \text{ Hz, 1H}), \ 7.83 \ (d, J = 8.1 \text{ Hz, 1H}), \ 7.50 \ (ddd, J = 8.4, 6.9, 1.2 \text{ Hz, 1H}), \ 7.42 - 7.34 \ (m, 2H), \ 7.17 - 7.10 \ (m, 2H), \ 7.07 - 6.99 \ (m, 3H), \ 3.97 \ (s, 3H). \]

HRMS-EI (m/z) [M]+ calculated for C₁₇H₁₄OS 266.0765, found 266.0775.

Spectroscopic data matches that reported in the literature.⁴

(2-Ethoxynaphthalen-1-yl)(phenyl)sulfane (4aj)

Following the general procedure B, (ethylsulfanyl)benzene (34.0 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4aj (47.6 mg, 0.17 mmol, 85%) as a colorless oil.

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 8.52 \ (d, J = 8.6 \text{ Hz, 1H}), \ 7.93 \ (d, J = 9.0 \text{ Hz, 1H}), \ 7.83 \ (d, J = 8.1 \text{ Hz, 1H}), \ 7.51 \ (ddd, J = 8.4, 6.8, 1.2 \text{ Hz, 1H}), \ 7.43 - 7.37 \ (m, 1H), \ 7.33 \ (d, J = 9.0 \text{ Hz, 1H}), \ 7.19 - 7.11 \ (m, 2H), \ 7.11 - 7.02 \ (m, 3H), \ 4.19 \ (q, J = 7.0 \text{ Hz, 2H}), \ 1.31 \ (t, J = 7.0 \text{ Hz, 3H}). \]

HRMS-EI (m/z) [M]+ calculated for C₁₉H₁₆OS 280.0922, found 280.0933.
Spectroscopic data matches that reported in the literature.

(2-(Hexyloxy)naphthalen-1-yl)(p-tolyl)sulfane (4ak)

Following the general procedure B, 1-(hexylsulfinyl)-4-methylbenzene (49.4 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ak (53.3 mg, 0.152 mmol, 76%) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 9.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 4.10 (t, J = 6.4 Hz, 2H), 2.23 (s, 3H), 1.74 – 1.65 (m, 2H), 1.37 – 1.29 (m, 2H), 1.29 – 1.21 (m, 4H), 0.86 (t, J = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 158.8, 136.6, 135.1, 134.7, 131.6, 129.6, 129.5, 128.3, 127.6, 127.1, 125.7, 124.1, 115.0, 114.8, 70.0, 31.7, 29.5, 25.6, 22.7, 21.0, 14.2.

HRMS-EI (m/z) [M]+ calculated for C₂₃H₂₆O₃S 350.1704, found 350.1694.

(2-(Benzyloxy)naphthalen-1-yl)(phenyl)sulfane (4al)

Following the general procedure B, (benzylsulfinyl)benzene (47.6 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4al (49.5 mg, 0.144 mmol, 72%) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.29 – 7.20 (m, 5H), 7.13 (t, J = 7.6 Hz, 2H), 7.08 – 7.03 (m, 3H), 5.23 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 158.3, 138.5, 136.9, 136.6, 131.8, 129.9, 128.8, 128.6, 128.4, 127.9, 127.8, 127.2, 126.8, 125.7, 125.0, 124.4, 115.3, 114.7, 71.5.

HRMS-EI (m/z) [M]+ calculated for C₂₃H₁₈O₃S 342.1078, found 342.1094.

Spectroscopic data matches that reported in the literature.

(2-Methoxynaphthalen-1-yl)(naphthalen-2-yl)sulfane (4am)
Following the general procedure B, 2-(methylsulfinyl)naphthalene (41.9 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4am (55.7 mg, 0.176 mmol, 88%) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.52 (dd, J = 8.4, 3.4 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.21 (dd, J = 8.6, 1.6 Hz, 1H), 3.96 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 136.5, 135.9, 133.9, 132.3, 131.4, 129.8, 128.5, 128.4, 128.0, 127.8, 127.0, 126.4, 125.6, 125.3, 125.1, 124.3, 124.0, 113.6, 113.0, 57.1.

HRMS-EI (m/z) [M]+ calculated for C₂₁H₁₆OS 316.0935.

(4-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4an)

Following the general procedure B, 1-bromo-4-(methylsulfinyl)benzene (48.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4an (47.7 mg, 0.138 mmol, 69%) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.41 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 3.97 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.4, 137.7, 136.2, 132.5, 131.8, 129.7, 128.5, 128.1, 128.0, 125.3, 124.4, 118.5, 113.5, 112.6, 57.1.

HRMS-EI (m/z) [M]+ calculated for C₁₇H₁₃BrOS 343.9870, found 343.9874.

(3-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ao)

Following the general procedure B, 1-bromo-3-(methylsulfinyl)benzene (48.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4ao (58 mg, 84%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 9.1 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.52 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.19 – 7.13 (m, 2H), 7.01 – 6.95 (m, 1H), 6.93 – 6.88 (m, 1H), 3.98 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 140.8, 136.3, 132.7, 130.1, 129.7, 128.9, 128.5, 128.1, 128.0, 125.3, 124.9, 124.4, 122.9, 113.5, 112.1, 57.1.

HRMS-EI (m/z) [M]+ calculated for C₁₇H₁₃BrOS 343.9870, found 343.9865.
(2-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ap)

Following the general procedure B, 1-methyl-4-(phenylsulfinyl)benzene (48.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf$_2$O (40.8 µL, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4ap (42.8 mg, 0.124 mmol, 62%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.36 (d, $J$ = 8.5 Hz, 1H), 8.02 (d, $J$ = 9.1 Hz, 1H), 7.85 (d, $J$ = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.44 – 7.36 (m, 2H), 6.95 – 6.85 (m, 2H), 6.36 – 6.29 (m, 1H), 3.97 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8, 139.4, 136.3, 132.8, 129.8, 128.5, 128.1, 127.6, 126.4, 125.7, 125.4, 124.4, 120.7, 113.6, 112.2, 57.1.

HRMS-EL (m/z) [M]$^+$ calculated for C$_{17}$H$_{13}$BrOS 343.9870, found 343.9878.

(4-Chlorophenyl)(2-methoxynaphthalen-1-yl)sulfane (4aq)

Following the general procedure B, 1-chloro-4-(methylsulfinyl)benzene (38.5 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf$_2$O (40.8 µL, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4aq (46.4 mg, 0.154 mmol, 77%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, $J$ = 8.6 Hz, 1H), 7.99 (d, $J$ = 9.1 Hz, 1H), 7.83 (d, $J$ = 8.1 Hz, 1H), 7.51 (ddd, $J$ = 8.4, 6.8, 1.3 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.37 (d, $J$ = 9.0 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.97 – 6.91 (m, 2H), 3.97 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.4, 139.4, 136.3, 132.5, 130.7, 129.8, 128.9, 128.5, 128.1, 127.8, 125.4, 124.4, 113.6, 112.8, 57.1.

HRMS-EL (m/z) [M]$^+$ calculated for C$_{17}$H$_{13}$ClOS 300.0376, found 300.0381.

4-((1-(Methylthio)naphthalen-2-yl)oxy)benzonitrile (4ar)

Following the general procedure B, 4-(methylsulfinyl)benzonitrile (36.4 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf$_2$O (40.8 µL, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4ar (40.8 mg, 0.14 mmol, 70%) as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.65 (d, $J$ = 8.5 Hz, 1H), 7.89 (d, $J$ = 8.6 Hz, 2H), 7.65 (t, $J$ = 7.6 Hz, 1H), 7.60 (d, $J$ = 8.7 Hz, 2H), 7.55 (t, $J$ = 7.5 Hz, 1H), 7.22 (d, $J$ = 8.8 Hz, 1H), 6.97 (d, $J$ = 8.7 Hz, 2H), 2.37 (s, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 161.8, 153.6, 135.6, 134.3, 132.1, 131.2, 128.7, 127.8, 126.3, 126.2, 125.6, 121.0, 119.0, 117.3, 105.9, 19.1.

HRMS-EI (m/z) [M]$^+$ calculated for C$_{18}$H$_{13}$NOS 291.0718, found 291.0733.

(8R,9S,13S,14S)-3-Methoxy-13-methyl-2-(phenylthio)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4ni)

Following the general procedure B, (methylsulfinyl)benzene (30.9 mg, 0.22 mmol), estrone (54.1 mg, 0.22 mmol), Tf$_2$O (40.8 $\mu$L, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4ni (53.4 mg, 0.136 mmol, 68%) as a white oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 – 7.20 (m, 5H), 7.19 – 7.15 (m, 1H), 6.66 (s, 1H), 3.80 (s, 3H), 2.96 – 2.88 (m, 2H), 2.49 (dd, $J$ = 18.7, 8.6 Hz, 1H), 2.23-2.18 (m, 2H), 2.16 – 2.10 (m, 1H), 2.10 – 2.05 (m, 1H), 2.03 – 1.98 (m, 1H), 1.92 – 1.86 (m, 1H), 1.67-1.56 (m, 2H), 1.55 – 1.49 (m, 1H), 1.46 – 1.38 (m, 3H), 0.89 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 220.8, 156.7, 138.4, 136.5, 132.9, 131.5, 129.4, 129.0, 126.2, 119.4, 111.8, 56.1, 50.5, 48.1, 44.0, 38.4, 36.0, 31.6, 29.8, 26.6, 25.9, 21.7, 14.0.

HRMS-ESI (m/z) [M+Na]$^+$ calculated for C$_{25}$H$_{33}$NaO$_3$S 415.1702, found 415.1720.

(8R,9S,13S,14S)-3-(4-Chlorophenoxy)-2-((4-chlorophenyl)thio)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4nb)

Following the general procedure B, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), estrone (54.1 mg, 0.22 mmol), Tf$_2$O (40.8 $\mu$L, 0.2 mmol) and K$_3$PO$_4$ (188.7 mg, 0.88 mmol) were used to afford 4nb (71.2 mg, 68%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (s, 1H), 7.24 – 7.18 (m, 4H), 7.18 – 7.13 (m, 2H), 6.78 – 6.73 (m, 2H), 6.68 (s, 1H), 2.84 (dd, $J$ = 8.6, 3.9 Hz, 2H), 2.51 (dd, $J$ = 18.9, 8.6 Hz, 1H), 2.28 (dt, $J$ = 16.8, 8.9 Hz, 2H), 2.16 (dd, $J$ = 18.5, 9.4 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.95 (dd, $J$ = 9.1, 2.0 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.54 – 1.48 (m, 2H), 1.47 – 1.37 (m, 2H), 0.92 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 220.5, 156.0, 153.8, 139.4, 136.9, 134.8, 132.5, 132.1, 131.1, 129.7, 129.2, 128.1, 122.8, 120.4, 119.2, 50.5, 48.0, 44.2, 38.1, 35.9, 31.6, 29.4, 26.4, 25.9, 21.7, 14.0.

HRMS-ESI (m/z) [M+Na]$^+$ calculated for C$_{30}$H$_{28}$Cl$_3$NaO$_3$S 545.1079, found 545.1062.
7-Methoxy-8-(phenylthio)-2-naphthonitrile (4oi)

Following the general procedure B, (methylsulfinyl)benzene (30.9 mg, 0.22 mmol), 7-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol) and K₃PO₄ (188.7 mg, 0.88 mmol) were used to afford 4oi (51 mg, 88%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.94 – 8.89 (m, 1H), 8.01 (d, J = 9.1 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.19 – 7.13 (m, 2H), 7.11 – 7.06 (m, 1H), 7.04 – 6.99 (m, 2H), 3.99 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 160.5, 137.2, 135.8, 132.1, 130.8, 129.1, 126.9, 125.6, 124.8, 119.5, 116.4, 114.7, 111.4, 57.1.

HRMS-EI (m/z) [M⁺] calculated for C₁₈H₁₃NOS 291.0718, found 291.0732.

IV. Procedure C for one-pot oxidation to sulfoxide in water

An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf₂O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated in vacuo. K₃PO₄ (0.88 mmol, 4.4 eq) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H₂O (0.27 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After completion, the solution was allowed to cool to room temperature. mCPBA (0.2 mmol, 1.0 eq) was slowly added to the resulting mixture at 0 °C. After stirred for 8 h at 0 °C, the aqueous phase was exacted with EtOAc (1 mL x 3), dried over anhydrous Na₂SO₄, concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (10% ethyl acetate in petroleum ether) to afford desired products.

2-Phenoxy-1-(phenylsulfinyl)naphthalene (5aa)

Following the general procedure C, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol), K₃PO₄ (188.7 mg, 0.88 mmol) and mCPBA (40.6 mg, 0.2 mmol) were used to afford 5aa (55.1 mg, 0.16 mmol, 80%) as a colourless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.87 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.42 (dt, J = 23.3, 7.5 Hz, 3H),
7.38 – 7.32 (m, 3H), 7.15 (t, \( J = 7.4 \) Hz, 1H), 7.09 (d, \( J = 9.0 \) Hz, 1H), 7.01 (d, \( J = 7.9 \) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 156.6, 154.4, 144.9, 134.6, 131.7, 131.2, 130.0, 129.9, 129.0, 128.9, 128.2, 127.8, 125.8, 124.6, 124.1, 123.8, 118.9, 118.8.

HRMS-ESI (m/z) [M+H]\(^+\) calculated for C\(_{22}\)H\(_{17}\)O\(_2\)S 345.0944, found 345.0929; [M+Na]\(^+\) calculated for C\(_{22}\)H\(_{16}\)NaO\(_2\)S 367.0763, found 367.0749.

V. Procedure D for one-pot oxidation to sulfone in water

An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf\(_2\)O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated \textit{in vacuo}. K\(_3\)PO\(_4\) (0.88 mmol, 4.4 eq) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H\(_2\)O (0.27 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After completion, the solution was cooled to room temperature, followed by mCPBA (0.48 mmol, 2.4 eq). After stirred for 8 h at room temperature, the aqueous phase was extracted with EtOAc (1 mL x 3), dried over anhydrous Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (10% ethyl acetate in petroleum ether) to afford desired products.

2-Phenoxy-1-(phenylsulfonyl)naphthalene (6aa)

Following the general procedure D, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf\(_2\)O (40.8 \( \mu \)L, 0.2 mmol), K\(_3\)PO\(_4\) (188.7 mg, 0.88 mmol) and mCPBA (40.6 mg, 0.2 mmol) were used to afford 6aa (59.9 mg, 0.166 mmol, 83%) as a white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.63 (d, \( J = 8.9 \) Hz, 1H), 8.04 – 7.97 (m, 2H), 7.93 (d, \( J = 9.0 \) Hz, 1H), 7.83 (d, \( J = 8.1 \) Hz, 1H), 7.73 (ddd, \( J = 8.7, 6.9, 1.4 \) Hz, 1H), 7.57 – 7.51 (m, 1H), 7.49 – 7.43 (m, 1H), 7.37 (t, \( J = 7.6 \) Hz, 2H), 7.29 – 7.21 (m, 2H), 7.15 – 7.06 (m, 1H), 6.95 (d, \( J = 9.0 \) Hz, 1H), 6.70 (d, \( J = 7.7 \) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 155.8, 155.3, 155.3, 143.8, 136.4, 132.8, 131.4, 130.7, 129.9, 129.2, 128.9, 128.6, 127.7, 125.8, 125.7, 124.6, 124.4, 119.2, 118.8.

HRMS-ESI (m/z) [M+Na]\(^+\) calculated for C\(_{22}\)H\(_{16}\)NaO\(_2\)S 383.0712, found 383.0707.

6-(4-Chlorophenoxy)-5-tosyl-2-naphthonitrile (6eg)
Following the general procedure, 1-chloro-4-(p-tolylsulfinyl)benzene (55.2 mg, 0.22 mmol), 6-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol), Tf₂O (40.8 µL, 0.2 mmol), K₃PO₄ (188.7 mg, 0.88 mmol) and mCPBA (97.5 mg, 0.48 mmol) were used to afford 6eg (67.7 mg, 0.156 mmol, 78%) as a white solid.

**¹H NMR** (600 MHz, CDCl₃) δ 9.76 (d, J = 9.2 Hz, 1H), 8.20 (d, J = 1.4 Hz, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.85 (dd, J = 8.8, 2.1 Hz, 3H), 7.27 – 7.24 (m, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 9.0 Hz, 1H), 6.70 – 6.65 (m, 2H), 2.37 (s, 3H).

**¹³C NMR** (150 MHz, CDCl₃) δ 157.1, 153.8, 144.4, 140.1, 136.6, 134.4, 133.1, 130.4, 130.2, 129.6, 129.4, 127.9, 126.7, 126.2, 120.7, 120.3, 118.5, 109.7, 21.7.

**HRMS-ESI** (m/z) [M+H]⁺ calculated for C₂₄H₁₇ClNO₃S 434.0612, found 434.0618.

### VI. Crossover experiment

An oven-dried vial was charged with 2b 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 2c 4,4'-sulfinylbis(methylbenzene) (50.7 mg, 0.22 mmol) and anhydrous MeCN (4 mL, 0.1 M) under argon. Tf₂O (81.6 µL, 0.48 mmol) was then added to the resulting mixture at 0 °C, followed by addition of 1a naphthalen-2-ol (57.8 mg, 0.4 mmol). The reaction mixture was stirred for 3 h at 0 °C and then concentrated in vacuo. K₃PO₄ (377.4 mg, 1.76 mmol) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H₂O (0.53 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After cooled to room temperature, the mixture was extracted with EtOAc (3 x 1 mL) and the combined organic layers was dried over anhydrous MgSO₄, concentrated in vacuo. The crude product was purified by flash column chromatography (1% to 5% ethyl acetate in petroleum ether) to afford afford 4ab (68 mg, 78%) as a white solid and 4ac (31 mg, 39%) as a colorless oil.
VII. Recycle Study and E Factor Calculation

Initial reaction:

\[
\begin{align*}
\text{3a} \quad \text{K}_3\text{PO}_4 \quad 2\% \text{TPGS-750-MH}_2\text{O}, 70^\circ \text{C} \\
\text{4aa}
\end{align*}
\]

To a 2 mL vial, sulfonium salt 3a (179.5 mg, 0.375 mmol) was added followed by K\textsubscript{3}PO\textsubscript{4} (241.2 mg, 1.125 mmol), and 2 wt% TPGS-750-M/H\textsubscript{2}O (0.5 mL, 0.75 M). The solution was heated at 70 °C for 24 h and then allowed to cool to room temperature. The mixture was extracted two times with EtOAc (0.2 mL + 0.2 mL), placed in a round bottom flask and concentrated in \textit{vacuo}. The crude product was purified by flash column chromatography (2% ethyl acetate in petroleum ether) to afford the desired product 4aa (111 mg, 0.18 mmol, 90%).

\textit{Re-use of surfactant solution (1\textsuperscript{st} recycle)}:

\[
\begin{align*}
\text{3j} \quad \text{K}_3\text{PO}_4 \quad 2\% \text{TPGS-750-MH}_2\text{O}, 70^\circ \text{C} \\
\text{4am}
\end{align*}
\]

The septum was removed quickly and the vial was charged with sulfonium salt 3j (175.0 mg, 0.375 mmol) and capped, followed by K\textsubscript{3}PO\textsubscript{4} (241.2 mg, 1.125 mmol). The solution was heated at 70 °C for 24 h and then allowed to cool to room temperature. The mixture was extracted two times with EtOAc (0.2 mL + 0.2 mL), placed in a round bottom flask and concentrated in \textit{vacuo}. The crude product was purified by flash column chromatography (3% ethyl acetate in petroleum ether) to afford the desired product 4am (108 mg, 0.182 mmol, 91%).

\textit{Re-use of surfactant solution (2\textsuperscript{nd} recycle)}:

\[
\begin{align*}
\text{3b} \quad \text{K}_3\text{PO}_4 \quad 2\% \text{TPGS-750-MH}_2\text{O}, 70^\circ \text{C} \\
\text{4ba}
\end{align*}
\]

The septum was removed quickly and the vial was charged with sulfonium salt 3b (209.0 mg, 0.375 mmol) and capped, followed by K\textsubscript{3}PO\textsubscript{4} (241.2 mg, 1.125 mmol). The solution was heated at 70 °C for 24 h and then allowed to cool to room temperature. The mixture was extracted two times with EtOAc (0.2 mL + 0.2 mL), placed in a round bottom flask and concentrated in \textit{vacuo}. The crude product was purified by flash column chromatography (3% ethyl acetate in petroleum ether) to afford the desired product 4ba (134 mg, 0.176 mmol, 88%).
E Factor calculation

Note: Density of each liquid at 25 °C; ethyl acetate = 0.897 g/mL; water = 1.00 g/mL.

Initial Reaction:

Water Not included as waste

Solvents: $0.5 \text{ mL EtOAc (449 mg)}$

\[
\frac{449 \text{ mg waste}}{111 \text{ mg product}} = 4.0 \text{ E Factor}
\]

Waster included as waste

Solvents: $0.5 \text{ mL EtOAc (449 mg)}$
$0.5 \text{ mL H}_2\text{O (500 mg)}$

\[
\frac{949 \text{ mg waste}}{111 \text{ mg product}} = 8.6 \text{ E Factor}
\]

1st recycle

Solvents: $0.5 \text{ mL EtOAc (449 mg)}$

\[
\frac{449 \text{ mg waste}}{108 \text{ mg product}} = 4.2 \text{ E Factor}
\]

2nd recycle

Solvents: $0.5 \text{ mL EtOAc (449 mg)}$

\[
\frac{449 \text{ mg waste}}{134 \text{ mg product}} = 3.4 \text{ E Factor}
\]

VIII. Reference:


IX. $^1$H and $^{13}$C NMR Spectral data:

(2-Hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3a)
(7-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3b)
(6-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3c)
(2-Hydroxy-3-(methoxycarbonyl)naphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3d)
6-Cyano-1-(diphenylsulfonyl)naphthalen-2-olate (3e)
(2,7-Dihydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3f)
1-(Di-p-tolylsulfonio)naphthalen-2-olate (3g)
(4-Bromophenyl)(2-hydroxnaphthalen-1-yl)(methyl)sulfonium trifluoromethanesulfonate (3h)
(5-Acetyl-2-hydroxyphenyl)diphenylsulfonium trifluoromethanesulfonate (3i)
(2-Hydroxynaphthalen-1-yl)(methyl)(naphthalen-2-yl)sulfonium trifluoromethanesulfonate (3j)
(2-Phenoxy napthalen-1-yl)(phenyl)sulfane (4aa)
(7-Bromo-2-phenoxy-naphthalen-1-yl)(phenyl)sulfane (4ba)
(6-Bromo-2-phenoxy-naphthalen-1-yl)(phenyl)sulfane (4ca)
(3-Bromo-2-phenoxy-naphthalen-1-yl)(phenyl)sulfane (4da)
6-Phenoxy-5-(phenylthio)-2-naphthonitrile (4ea)
Methyl 3-phenoxy-4-(phenylthio)-2-naphthoate (4fa)
3-Phenoxy-4-(phenylthio)-2-naphthoic acid (4fa')
N-(Naphthalen-2-yl)-3-phenoxy-4-(phenylthio)-2-naphthamide (4ga)
(4,5-Dimethyl-2-phenoxypyphenyl)(phenyl)sulfane (4ha)
(3-Bromo-2,4-dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ia)
(2,4-Dimethyl-6-phenoxypyphenyl)(phenyl)sulfane (4ja)
(2-(4-Chlorophenoxy)-5-fluorophenyl)(4-chlorophenyl)sulfane (4kb)
(4-Chlorophenyl)(2,4-dichloro-6-(4-chlorophenoxy)phenyl)sulfane (4lb)
(5-Bromo-2-(4-chlorophenoxy)phenyl)(4-chlorophenyl)sulfane (4mb)
(3-Bromo-6-(4-chlorophenoxy)-2,4-dimethylphenyl)(4-chlorophenyl)sulfane (4ib)
(2-(4-Chlorophenoxy)naphthalen-1-yl)(4-chlorophenyl)sulfane (4ab)
p-Tolyl(2-(p-tolyloxy)naphthalen-1-yl)sulfane (4ac)
(2-Phenoxy-1-yl)(p-tolyl)sulfane (4ad)
(2-(4-Nitrophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ae)
p-Tolyl(2-(4-(trifluoromethyl)phenoxy)naphthalen-1-yl)sulfane (4af)
(2-(4-Chlorophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ag)
(2-(2-Bromophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ah)
(2-Methoxynaphthalen-1-yl)(phenyl)sulfane (4ai)

(2-Ethoxynaphthalen-1-yl)(phenyl)sulfane (4aj)
(2-(Benzyloxy)naphthalen-1-yl)(phenyl)sulfane (4al)
(2-Methoxynaphthalen-1-yl)(naphthalen-2-yl)sulfane (4am)
(4-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4an)
(3-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ao)
(2-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ap)
(4-Chlorophenyl)(2-methoxynaphthalen-1-yl)sulfane (4aq)
4-((1-(Methylthio)naphthalen-2-yl)oxy)benzonitrile (4ar)
(8R,9S,13S,14S)-3-Methoxy-13-methyl-2-(phenylthio)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4ni)
(8R,9S,13S,14S)-3-(4-Chlorophenoxy)-2-((4-chlorophenyl)thio)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[ajphenanthren-17-one (4nb)
7-Methoxy-8-(phenylthio)-2-naphthonitrile (4oi)
2-Phenoxy-1-(phenylsulfinyl)naphthalene (5aa)
2-Phenoxy-1-(phenylsulfonyl)naphthalene (6aa)
6-(4-Chlorophenoxy)-5-tosyl-2-naphthonitrile (6eg)