

**S-Arylation of thiols with masked *o*-benzoquinones:
Synthesis of alkyl aryl/diaryl sulfides**

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ELECTRONIC SUPPLEMENTARY INFORMATION

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1. General Remarks.

All the reagents were purchased from Aldrich and used without purification. All reactions were monitored by TLC with silica gel-coated plates. All the products were purified by column chromatography using silica gel (100-200 mesh size). ^1H & ^{13}C NMR spectra were recorded on a Bruker 500 & 125 MHz spectrometer using CDCl_3 solvent. NMR Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference (CDCl_3 , δ 7.26 ppm or TMS, δ 0.00 for ^1H and δ 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sext = sextet), coupling constant (Hz) and number of hydrogens. IR spectra were recorded on Thermo Nicolet FTIR Nexus instrument and are reported in reciprocal centimeters. HRMS were recorded on Bruker microTOF Q II using electron spray ionization.

2.1. General procedure for the synthesis of alkyl aryl/diaryl sulfides 3-11 from 2-methoxyphenols derivatives 1a-d:

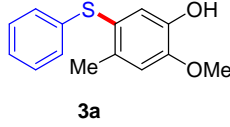
To a solution of a 2-methoxyphenol (**1**, 0.5 mmol, 1 equiv.) in MeOH was added DIB (0.5 mmol, 0.161g, 1 equiv.) and stirred the mixture at room temperature for 5 min. To this mixture then was added 1 equiv. of a thiol and stirred the reaction mixture at same temperature for completion of the reaction (10-120 min). After completion of the reaction which was confirmed by TLC, the crude product (**3-11**) was purified by column chromatography using 5-10% ethyl acetate in hexanes as eluting solvent.

2.2. General procedure for the synthesis of alkyl aryl/diaryl sulfides from naphthalenones 2e,f:

To a solution of an *o*-naphthoquinone monoketal (**2e,f**, 0.5 mmol, 1 equiv.) in MeOH was added 1 equiv. of a thiol and stirred the reaction mixture at room temperature for completion of the reaction (2.5-6 h). After completion of the reaction which was confirmed by TLC, the crude product (**3e,f-11e,f**) was purified by column chromatography using 10-20% ethyl acetate in hexanes as eluting solvent.

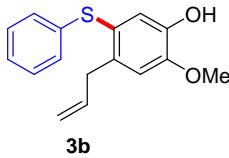
Characterization Data:

2-Methoxy-4-methyl-5-(phenylthio)phenol (3a):


3a

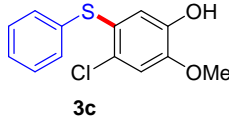
Yield 0.112 g (91%) as reddish brown liquid; IR (KBr) ν_{\max} 3417, 3059, 1587, 1267, 1024, 818, 692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25-7.21 (m, 2H), 7.15-7.10 (m, 3H), 7.07 (s, 1H), 6.79 (s, 1H), 5.53 (s, 1H, OH), 3.90 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.0 (C), 143.9 (C), 137.8 (C), 133.5 (C), 128.9 (CH), 127.6 (CH), 125.4 (CH), 123.3 (C), 120.9 (CH), 112.8 (CH), 55.9 (CH_3), 20.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$: 269.0607, found 269.0607.

4-Allyl-2-methoxy-5-(phenylthio)phenol (3b):


3b

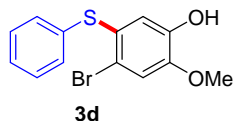
Yield 0.124 g (91%) as yellow viscous liquid; IR (KBr) ν_{\max} 3406, 2935, 1590, 1269, 1051, 824, 693 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.20-7.16 (m, 2H), 7.08 (d, $J = 7.5$ Hz, 3H), 7.05 (d, $J = 1.0$ Hz, 1H), 6.76 (s, 1H), 5.92-5.83 (m, 1H), 5.66 (s, 1H, OH), 5.03-4.97 (m, 2H), 3.83 (s, 3H), 3.49 (d, $J = 6.0$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.2 (C), 144.2 (C), 138.1 (C), 137.0 (CH), 135.2 (C), 128.8 (CH), 127.6 (CH), 125.4 (CH), 123.2 (C), 121.0 (CH), 115.8 (CH_2), 112.0 (CH), 55.8 (CH_3), 37.8 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$: 295.0763, found 295.0755.

4-Chloro-2-methoxy-5-(phenylthio)phenol (3c):


3c

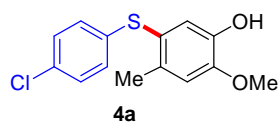
Yield 0.116 g (87%) as brown viscous liquid; IR (KBr) ν_{\max} 3507, 3061, 1576, 1260, 1028, 801, 690 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.22-7.18 (m, 5H), 6.83 (s, 1H), 6.75 (s, 1H), 5.47 (s, 1H, OH), 3.77 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 146.6 (C), 144.7 (C), 134.8 (C), 130.7 (CH), 129.2 (CH), 127.1 (CH), 126.4 (C), 125.8 (C), 118.7 (CH), 112.3 (CH), 56.2 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{ClO}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$: 289.0060, found 289.0065.

4-Bromo-2-methoxy-5-(phenylthio)phenol (3d):



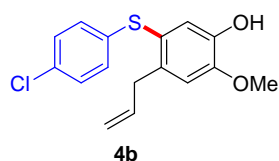
Yield 0.141 g (91%) as brown viscous liquid; IR (KBr) ν_{\max} 3513, 3066, 1499, 1266, 1040, 870, 691 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.29 (m, 5H), 7.08 (s, 1H), 6.81 (s, 1H), 5.52 (s, 1H, OH), 3.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 146.5 (C), 145.3 (C), 134.8 (C), 130.9 (CH), 129.2 (CH), 128.2 (C), 127.2 (CH), 118.4 (CH), 115.3 (CH), 115.3 (C), 56.2 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 332.9555, found 332.9555.

5-(4-Chlorophenylthio)-2-methoxy-4-methylphenol (4a):



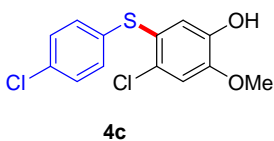
Yield 0.130 g (93%) as white solid: mp 86-87 °C; IR (KBr) ν_{\max} 3447, 2939, 1583, 1208, 1040, 824, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.18 (d, $J = 8.5$ Hz, 2H), 7.05 (s, 1H), 7.00 (d, $J = 8.5$ Hz, 2H), 6.79 (s, 1H), 5.55 (s, 1H, OH), 3.90 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.3 (C), 144.0 (C), 136.6 (C), 133.7 (C), 131.1 (C), 128.9 (CH), 128.6 (CH), 122.7 (C), 121.0 (CH), 112.9 (CH), 55.9 (CH_3), 20.2 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 303.0217, found 303.0216.

4-Allyl-5-(4-chlorophenylthio)-2-methoxyphenol (4b):



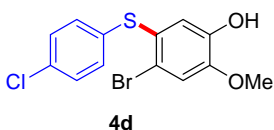
Yield 0.142 g (93%) as yellow viscous liquid; IR (KBr) ν_{\max} 3451, 2939, 1592, 1213, 1112, 812, 702 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.18 (d, $J = 9.0$ Hz, 2H), 7.06 (s, 1H), 7.02 (d, $J = 8.5$ Hz, 2H), 6.80 (s, 1H), 5.94-5.85 (m, 1H), 5.65 (s, 1H, OH), 5.07-5.00 (m, 2H), 3.90 (s, 3H), 3.49 (d, $J = 6.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.4 (C), 144.3 (C), 136.9 (C), 136.9 (CH), 135.5 (C), 131.2 (C), 128.9 (CH), 128.8 (CH), 122.7 (C), 121.1 (CH), 116.0 (CH_2), 112.1 (CH), 55.8 (CH_3), 37.9 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{ClO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 329.0373, found 329.0373.

4-Chloro-5-(4-chlorophenylthio)-2-methoxyphenol (4c):



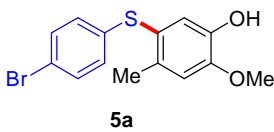
Yield 0.122 g (81%) as brown solid: mp 96-97 °C; IR (KBr) ν_{\max} 3515, 3021, 1564, 1259, 1082, 802, 671 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.18 (d, $J = 4.0$ Hz, 2H), 7.13-7.11 (m, 2H), 6.87 (s, 1H), 6.80 (s, 1H), 5.47 (s, 1H, OH), 3.83 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.0 (C), 144.8 (C), 133.8 (C), 132.9 (C), 131.4 (CH), 129.3 (CH), 127.0 (C), 124.8 (C), 119.2 (CH), 112.4 (CH), 56.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{O}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 322.9671, found 322.9671.

4-Bromo-5-(4-chlorophenylthio)-2-methoxyphenol (4d):



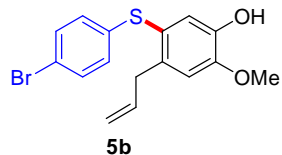
Yield 0.160 g (92%) as brown solid: mp 101-102 °C; IR (KBr) ν_{\max} 3502, 3054, 1478, 1259, 1085, 800, 708 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.21-7.18 (m, 2H), 7.14-7.12 (m, 2H), 7.02 (s, 1H), 6.79 (s, 1H), 5.48 (s, 1H, OH), 3.82 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 146.9 (C), 145.4 (C), 133.9 (C), 133.0 (C), 131.6 (CH), 129.4 (CH), 127.3 (C), 119.0 (CH), 116.1 (C), 115.4 (CH), 56.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{ClBrO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 366.9166, found 366.9168.

5-(4-Bromophenylthio)-2-methoxy-4-methylphenol (5a):



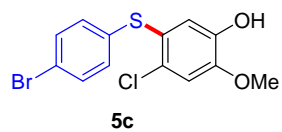
Yield 0.165 g (86%) as white solid: mp 81-82 °C; IR (KBr) ν_{\max} 3423, 2960, 1590, 1395, 1211, 1056, 812, 713 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.31 (d, $J = 8.5$ Hz, 2H), 7.08 (s, 1H), 6.93 (d, $J = 8.5$ Hz, 2H), 6.79 (s, 1H), 5.68 (s, 1H, OH), 3.88 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.3 (C), 143.9 (C), 137.4 (C), 133.8 (C), 131.7 (CH), 128.6 (CH), 122.2 (C), 121.1 (CH), 118.8 (C), 112.8 (CH), 55.8 (CH_3), 20.2 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{BrO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 346.9712, found 346.9712.

4-Allyl-5-(4-bromophenylthio)-2-methoxyphenol (5b):



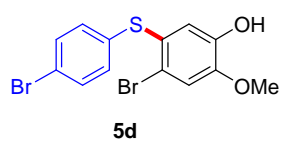
Yield 0.159 g (91%) as yellow viscous liquid; IR (KBr) ν_{\max} 3513, 3066, 1499, 1266, 1084, 870, 691 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.31 (d, $J = 8.5$ Hz, 2H), 7.07 (s, 1H), 6.95 (d, $J = 8.5$ Hz, 2H), 6.80 (s, 1H), 5.93-5.85 (m, 1H), 5.68 (s, 1H, OH), 5.06-5.00 (m, 2H), 3.89 (s, 3H), 3.49 (d, $J = 6.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.5 (C), 144.3 (C), 137.7 (C), 136.8 (CH), 135.6 (C), 131.7 (CH), 128.8 (CH), 122.4 (C), 121.2 (CH), 118.9 (C), 116.0 (CH_2), 112.1 (CH), 55.8 (CH_3), 37.8 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{BrO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 372.9868, found 372.9867.

4-Chloro-5-(4-bromophenylthio)-2-methoxyphenol (5c):



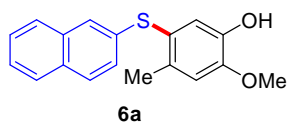
Yield 0.158 g (92%) as brown semi solid; IR (KBr) ν_{\max} 3538, 3063, 1578, 1260, 1040, 816, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.28 (dd, $J = 2.0, 8.5$ Hz, 2H), 7.00 (dd, $J = 2.5, 8.5$ Hz, 2H), 6.83 (d, $J = 2.5$ Hz, 1H), 6.80 (d, $J = 2.5$ Hz, 1H), 5.55 (s, 1H, OH), 3.77 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.1 (C), 144.8 (C), 134.6 (C), 132.2 (CH), 131.4 (CH), 127.3 (C), 124.5 (C), 120.8 (C), 119.4 (CH), 112.4 (CH), 56.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{ClBrO}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 366.9166, found 366.9166.

4-Bromo-5-(4-bromophenylthio)-2-methoxyphenol (5d):



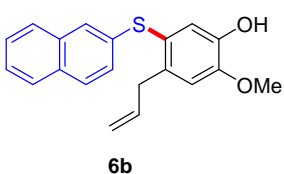
Yield 0.176 g (90%) as yellow solid: mp 105-106 $^{\circ}\text{C}$; IR (KBr) ν_{\max} 3438, 3052, 1581, 1262, 1045, 814, 706 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.41 (d, $J = 8.5$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.10 (s, 1H), 6.88 (s, 1H), 5.55 (s, 1H, OH), 3.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.0 (C), 145.3 (C), 134.6 (C), 132.2 (CH), 131.5 (CH), 126.8 (C), 120.8 (C), 119.2 (CH), 116.4 (C), 115.4 (CH), 56.2 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{O}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 410.8660, found 410.8651.

2-Methoxy-4-methyl-5-(naphthalen-2-ylthio)phenol (6a):



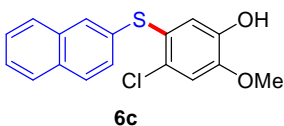
Yield 0.131 g (88%) as white solid: mp 76-77 °C; IR (KBr) ν_{\max} 3418, 2973, 1586, 1262, 1049, 908, 814, 672 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.54 (s, 1H), 7.48-7.40 (m, 2H), 7.28 (d, $J = 8.5$ Hz, 1H), 7.16 (s, 1H), 6.82 (s, 1H), 5.61 (s, 1H, OH), 3.90 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.1 (C), 143.9 (C), 135.2 (C), 133.8 (C), 133.6 (C), 131.5 (C), 128.4 (CH), 127.6 (CH), 127.0 (CH), 126.4 (CH), 126.1 (CH), 125.5 (CH), 125.3 (CH), 123.2 (C), 120.9 (CH), 112.9 (CH), 55.9 (CH_3), 20.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 319.0763, found 319.0764.

4-Allyl-2-methoxy-5-(naphthalen-2-ylthio)phenol (6b):



Yield 0.145 g (90%) as yellow viscous liquid; IR (KBr) ν_{\max} 3521, 2943, 1594, 1210, 811, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.5$ Hz, 1H), 7.75-7.73 (m, 1H), 7.69 (d, $J = 7.5$ Hz, 1H), 7.59 (d, $J = 1.5$ Hz, 1H), 7.45 (dp, $J = 1.5, 7.0$ Hz, 2H), 7.32 (dd, $J = 1.5, 8.5$ Hz, 1H), 7.20 (s, 1H), 6.87 (s, 1H), 6.04-5.95 (m, 1H), 5.75 (s, 1H, OH), 5.12 (s, 1H), 5.09 (dq, $J = 1.5, 8.5$ Hz, 1H), 3.90 (s, 3H), 3.62 (d, $J = 5.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.3 (C), 144.3 (C), 137.0 (CH), 135.5 (C), 135.2 (C), 133.7 (C), 131.5 (C), 130.1 (C), 128.4 (CH), 127.6 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 125.6 (CH), 125.3 (CH), 121.0 (CH), 115.9 (CH_2), 112.1 (CH), 55.8 (CH_3), 37.9 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$: 345.0920, found 345.0916.

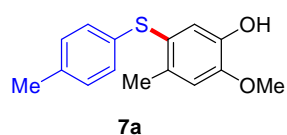
4-Chloro-2-methoxy-5-(naphthalen-2-ylthio)phenol (6c):



Yield 0.116 g (73%) as brown solid: mp 92-93 °C; IR (KBr) ν_{\max} 3479, 3048, 1579, 1261, 1026, 877, 747, 680 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.83-7.72 (m, 4H), 7.49-7.46 (m, 2H), 7.37 (dd, $J = 2.0, 9.0$ Hz, 1H), 6.96 (s, 1H), 6.87 (s, 1H), 5.54 (s, 1H, OH), 3.88 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 146.6 (C), 144.8 (C), 133.8 (C), 132.3 (C), 132.1 (C), 129.6 (CH), 128.9 (CH), 128.3 (CH), 127.7 (CH), 127.4 (CH), 126.6 (CH), 126.3 (C), 126.2 (CH), 125.9 (C), 118.6 (CH), 112.4

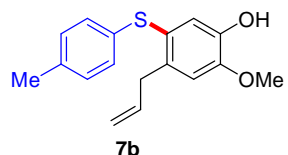
(CH), 56.3 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₇H₁₃ClO₂SNa [M + Na]⁺: 339.0217, found 339.0216.

2-Methoxy-4-methyl-5-(*p*-tolylthio)phenol (7a):



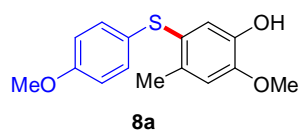
Yield 0.116 g (90%) as white solid; mp 82-84 °C; IR (KBr) ν_{\max} 3502, 2925, 1587, 1394, 1268, 809, 695 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.06-7.00 (m, 4H), 6.95 (s, 1H), 6.72 (s, 1H), 5.53 (s, 1H, OH), 3.82 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.5 (C), 143.8 (C), 135.7 (C), 133.4 (C), 132.4 (C), 129.7 (CH), 128.8 (CH), 124.6 (C), 119.8 (CH), 112.8 (CH), 55.9 (CH₃), 20.9 (CH₃), 20.2 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₅H₁₆O₂SNa [M + Na]⁺: 283.0763, found 283.0763.

4-Allyl-2-methoxy-5-(*p*-tolylthio)phenol (7b):



Yield 0.136 g (95%) as yellow viscous liquid; IR (KBr) ν_{\max} 3389, 2939, 1591, 1397, 1221, 839, 702 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.14-7.12 (m, 2H), 7.10-7.08 (m, 2H), 7.05 (s, 1H), 6.81 (s, 1H), 6.02-5.93 (m, 1H), 5.67 (s, 1H, OH), 5.13-5.07 (m, 2H), 3.90 (s, 3H), 3.57 (dd, J = 1.0, 6.5 Hz, 2H), 2.34 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.8 (C), 144.2 (C), 137.0 (CH), 135.7 (C), 134.3 (C), 133.8 (C), 129.6 (CH), 128.8 (CH), 124.6 (C), 120.1 (CH), 115.8 (CH₂), 111.9 (CH), 55.8 (CH₃), 37.8 (CH₂), 20.8 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₇H₁₈O₂SNa [M + Na]⁺: 309.0920, found 309.0918.

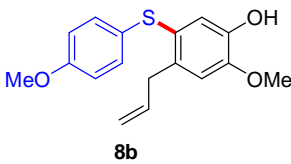
2-Methoxy-5-(4-methoxyphenylthio)-4-methylphenol (8a):



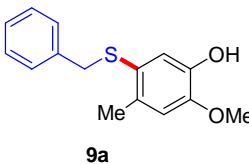
Yield 0.126 g (91%) as brown viscous liquid; IR (KBr) ν_{\max} 3376, 2934, 1592, 1214, 806, 706 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.20 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 1.5 Hz, 2H), 6.81 (s, 1H), 6.71 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.32 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 158.6 (C), 145.9 (C), 143.8 (C), 132.1 (CH), 130.7 (C), 126.5 (C), 126.4 (C), 118.1 (CH), 114.6 (CH), 112.8

(CH), 55.8 (CH₃), 55.1 (CH₃), 19.9 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₅H₁₆O₃SNa [M + Na]⁺: 299.0712, found 299.0709.

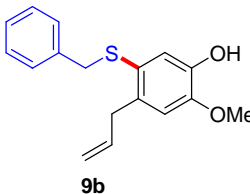
4-Allyl-2-methoxy-5-(4-methoxyphenylthio)phenol (8b):


Yield 0.142 g (94%) as yellow viscous liquid; IR (KBr) ν_{\max} 3434, 2939, 1589, 1398, 1210, 822, 703 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, J = 9.0 Hz, 2H), 6.86 (s, 1H), 6.84 (d, J = 8.5 Hz, 2H), 6.74 (s, 1H), 5.99-5.91 (m, 1H), 5.60 (s, 1H, OH), 5.10-5.04 (m, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.53 (d, J = 6.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 158.7 (C), 146.2 (C), 144.2 (C), 136.9 (CH), 132.7 (C), 132.4 (CH), 126.8 (C), 126.6 (C), 118.4 (CH), 115.8 (CH₂), 114.7 (CH), 111.9 (CH), 55.9 (CH₃), 55.2 (CH₃), 37.7 (CH₂) ppm; HRMS (ESI+) m/z calcd for C₁₇H₁₈O₃SNa [M + Na]⁺: 325.0869, found 325.0864.

5-(Benzylthio)-2-methoxy-4-methylphenol (9a):

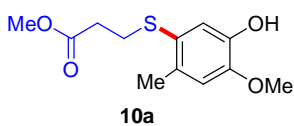

Yield 0.107 g (84%) as yellow viscous liquid; IR (KBr) ν_{\max} 3376, 2934, 1592, 1397, 1214, 806, 706 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.15-7.09 (m, 5H), 6.86 (s, 1H), 6.54 (s, 1H), 5.42 (s, 1H, OH), 3.85 (s, 2H), 3.71 (s, 3H), 2.12 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.7 (C), 143.6 (C), 137.7 (C), 131.5 (C), 128.8 (CH), 128.3 (CH), 126.9 (CH), 126.0 (C), 118.0 (CH), 112.4 (CH), 55.8 (CH₃), 39.9 (CH₂), 20.0 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₅H₁₆O₂SNa [M + Na]⁺: 283.0763, found 283.0761.

4-Allyl-5-(benzylthio)-2-methoxyphenol (9b):


Yield 0.132 g (95%) as yellow viscous liquid; IR (KBr) ν_{\max} 3409, 2930, 1586, 1401, 1209, 823, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.14 (m, 5H), 7.00 (s, 1H), 6.62 (s, 1H), 5.85-5.77 (m, 1H), 5.65 (s, 1H, OH), 5.02-4.94 (m, 2H), 3.92 (s, 2H), 3.78 (s, 3H), 3.37 (d, J = 6.0 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.1 (C), 143.9 (C), 137.6 (C), 137.3 (CH), 133.8 (C), 128.7 (CH), 128.2 (CH), 126.8 (CH), 125.7 (C), 118.8 (CH), 115.5 (CH₂), 111.6 (CH), 55.7

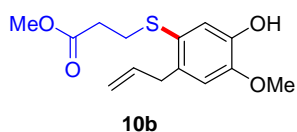
(CH₃), 40.6 (CH₂), 37.6 (CH₂) ppm; HRMS (ESI+) *m/z* calcd for C₁₇H₁₈O₂SNa [M + Na]⁺: 309.0920, found 309.0919.

Methyl 3-(5-hydroxy-4-methoxy-2-methylphenylthio)propanoate (10a):



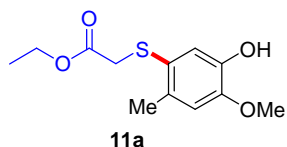
Yield 0.108 g (85%) as brown semi solid; IR (KBr) ν_{\max} 3392, 2944, 1725, 1582, 1359, 1270, 828, 659 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.97 (s, 1H), 6.68 (s, 1H), 3.84 (s, 3H), 3.65 (s, 3H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 172.3 (C), 146.0 (C), 143.7 (C), 131.8 (C), 124.8 (C), 118.3 (CH), 112.7 (CH), 55.9 (CH₃), 51.6 (CH₃), 34.2 (CH₂), 29.7 (CH₂), 20.1 (CH₃) ppm; HRMS (ESI+) *m/z* calcd for C₁₂H₁₆O₄SNa [M + Na]⁺: 279.0662, found 279.0664.

Methyl 3-(2-allyl-5-hydroxy-4-methoxyphenylthio)propanoate (10b):



Yield 0.115 g (82%) as colorless semi solid; IR (KBr) ν_{\max} 3395, 2992, 1721, 1578, 1367, 1205, 838, 694 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.01 (s, 1H), 6.68 (s, 1H), 5.96-5.87 (m, 1H), 5.71 (s, 1H, OH), 5.05-4.97 (m, 2H), 3.84 (s, 3H), 3.65 (s, 3H), 3.50 (d, *J* = 5.0 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 172.2 (C), 146.3 (C), 144.1 (C), 137.2 (CH), 133.9 (C), 124.8 (C), 118.6 (CH), 115.6 (CH₂), 112.0 (CH), 55.8 (CH₃), 51.6 (CH₃), 37.7 (CH₂), 34.1 (CH₂), 30.4 (CH₂) ppm; HRMS (ESI+) *m/z* calcd for C₁₄H₁₈O₄SNa [M + Na]⁺: 305.0818, found 305.0819.

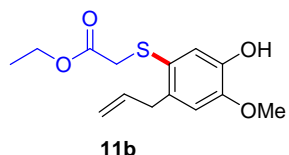
Ethyl 2-(5-hydroxy-4-methoxy-2-methylphenylthio)acetate (11a):



Yield 0.109 g (86%) as yellow viscous liquid; IR (KBr) ν_{\max} 3443, 2978, 1730, 1584, 1405, 1205, 822, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.98 (s, 1H), 6.65 (s, 1H), 5.90 (s, 1H, OH), 4.08 (q, *J* = 7.5 Hz, 2H), 3.78 (s, 3H), 3.44 (s, 2H), 2.34 (s, 3H), 1.17 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 169.9 (C), 146.4 (C), 143.6 (C), 131.8 (C), 124.0 (C), 118.8 (CH), 112.5 (CH),

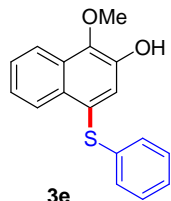
61.2 (CH₂), 55.7 (CH₃), 37.2 (CH₂), 19.9 (CH₃), 13.8 (CH₃) ppm; HRMS (ESI+) *m/z* calcd for C₁₂H₁₆O₄SNa [M + Na]⁺: 279.0662, found 279.0669.

Ethyl 2-(2-allyl-5-hydroxy-4-methoxyphenylthio)acetate (11b):



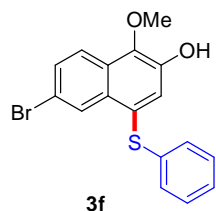
Yield 0.125 g (89%) as yellow viscous liquid; IR (KBr) ν_{\max} 3444, 2980, 1730, 1581, 1412, 1209, 827, 686 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.04 (s, 1H), 6.66 (s, 1H), 5.95-5.87 (m, 1H), 5.05-4.87 (m, 2H), 4.09 (q, *J* = 7.5 Hz, 2H), 3.81 (s, 3H), 3.52 (d, *J* = 6.5 Hz, 2H), 3.44 (s, 2H), 1.18 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 169.8 (C), 146.8 (C), 144.0 (C), 137.2 (CH), 134.0 (C), 124.2 (C), 119.3 (CH), 115.6 (CH₂), 111.8 (CH), 61.2 (CH₂), 55.7 (CH₃), 38.0 (CH₂), 37.6 (CH₂), 13.8 (CH₃) ppm; HRMS (ESI+) *m/z* calcd for C₁₄H₁₈O₄SNa [M + Na]⁺: 305.0818, found 305.0819.

1-Methoxy-4-(phenylthio)naphthalen-2-ol (3e):



Yield 0.125 g (89%) as reddish brown viscous liquid; IR (KBr) ν_{\max} 3417, 3062, 1598, 1201, 822, 692 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 3.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.20-7.17 (m, 4H), 7.12 (sext, *J* = 4.0 Hz, 1H), 6.10 (s, 1H, OH), 3.93 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 144.9 (C), 140.4 (C), 136.4 (C), 129.5 (C), 129.1 (CH), 129.0 (C), 128.7 (C), 128.2 (CH), 126.8 (CH), 126.3 (CH), 126.1 (CH), 124.5 (CH), 123.9 (CH), 120.8 (CH), 61.7 (CH₃) ppm; HRMS (ESI+) *m/z* calcd for C₁₆H₁₀O₂SNa [M - CH₄ + Na]⁺: 289.0294, found 289.0299.

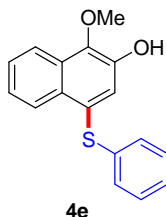
6-Bromo-1-methoxy-4-(phenylthio)naphthalen-2-ol (3f):



Yield 0.164 g (91%) as reddish brown viscous liquid; IR (KBr) ν_{\max} 3425, 2925, 1587, 1267, 1102, 817, 690 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.48 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.56 (dd, *J* = 2.0, 9.0 Hz, 1H), 7.39 (s, 1H), 7.25-7.16 (m, 5H), 5.96 (s, 1H, OH), 3.93 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.3 (C), 140.4 (C), 135.7 (C), 130.7 (C), 130.2 (CH), 129.6 (CH),

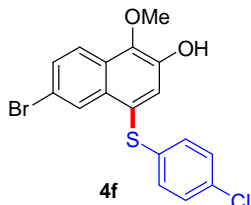
129.2 (CH), 128.3 (CH), 127.9 (C), 127.2 (C), 126.7 (CH), 124.7 (CH), 122.7 (CH), 118.8 (C), 61.9 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₆H₉BrO₂SNa [M – CH₄ + Na]⁺: 366.9399, found 366.9403.

4-(4-Chlorophenylthio)-1-methoxynaphthalen-2-ol (4e):



Yield 0.135 g (85%) as reddish brown solid: mp 87-88 °C; IR (KBr) ν_{\max} 3390, 2934, 1591, 1209, 1073, 811, 704 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.57-7.52 (m, 1H), 7.48 (s, 1H), 7.42-7.37 (m, 1H), 7.21-7.17 (m, 2H), 7.13-7.09 (m, 2H), 5.97 (s, 1H, OH), 4.00 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.0 (C), 140.8 (C), 135.3 (C), 132.1 (C), 130.0 (CH), 129.6 (C), 129.2 (CH), 128.7 (C), 127.3 (C), 126.9 (CH), 126.1 (CH), 124.7 (CH), 124.4 (CH), 120.9 (CH), 61.8 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₆H₉ClO₂SNa [M – CH₄ + Na]⁺: 322.9904, found 322.9907.

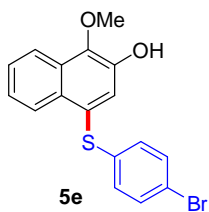
6-Bromo-4-(4-chlorophenylthio)-1-methoxynaphthalen-2-ol (4f):



Yield 0.182 g (92%) as brown solid: mp 96-97 °C; IR (KBr) ν_{\max} 3432, 2943, 1445, 1034, 769, 718 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.45 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.59 (dd, J = 2.0, 9.0 Hz, 1H), 7.43 (s, 1H), 7.22-7.19 (m, 2H), 7.12-7.10 (m, 2H), 5.99 (s, 1H, OH), 3.96 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.3 (C), 140.8 (C), 134.6 (C), 132.6 (C), 130.8 (C), 130.4 (CH), 130.3 (CH), 129.3 (CH), 128.2 (CH), 127.3 (C), 127.0 (C), 125.3 (CH), 122.8 (CH), 119.0 (C), 62.0 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₆H₈BrClO₂SNa [M – CH₄ + Na]⁺: 400.9009, found 400.9009.

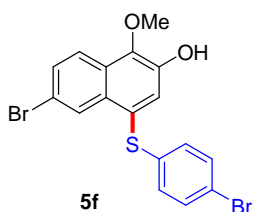
4-(4-Bromophenylthio)-1-methoxynaphthalen-2-ol (5e):

Yield 0.164 g (94%) as reddish brown semi solid; IR (KBr) ν_{\max} 3372, 2939, 1594, 1207, 1070, 812, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.56-7.52 (m, 1H), 7.51 (s, 1H), 7.41-7.36 (m, 1H), 7.32-7.29 (m, 2H), 7.04-7.00 (m, 2H), 6.26 (s, 1H, OH), 3.99 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.0 (C), 140.9 (C), 136.2 (C),



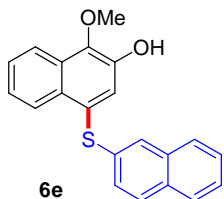
132.0 (CH), 130.0 (CH), 129.6 (C), 128.8 (C), 126.9 (C), 126.8 (CH), 126.0 (CH), 124.9 (CH), 124.7 (CH), 120.9 (CH), 119.8 (C), 61.7 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₆H₉BrO₂SNa [M – CH₄ + Na]⁺: 366.9398, found 366.9384.

6-Bromo-4-(4-bromophenylthio)-1-methoxynaphthalen-2-ol (5f):



Yield 0.196 g (89%) as brown solid: mp 118-119 °C; IR (KBr) ν_{\max} 3357, 2926, 1584, 1202, 1084, 810, 715 cm⁻¹; ¹H NMR (125 MHz, CDCl₃) δ 8.44 (d, J = 2.0 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.59 (dd, J = 2.0, 9.0 Hz, 1H), 7.45 (s, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 5.94 (s, 1H, OH), 3.96 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.3 (C), 140.9 (C), 135.4 (C), 132.2 (CH), 130.8 (C), 130.4 (CH), 130.3 (CH), 128.2 (CH), 127.3 (C), 126.7 (C), 125.5 (CH), 122.8 (CH), 120.4 (C), 119.1 (C), 62.0 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₆H₈Br₂O₂SNa [M – CH₄ + Na]⁺: 444.8503, found 444.8506.

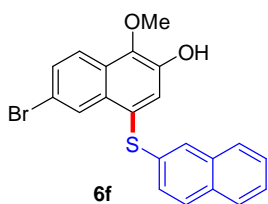
1-Methoxy-4-(naphthalen-2-ylthio)naphthalen-2-ol (6e):



Yield 0.145 g (87%) as reddish brown viscous liquid; IR (KBr) ν_{\max} 3434, 2924, 1630, 1270, 1019, 893, 673 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.79-7.75 (m, 1H), 7.74-7.70 (m, 2H), 7.68-7.65 (m, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.50 (s, 1H), 7.47-7.41 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 6.00 (s, 1H, OH), 4.00 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.0 (C), 140.4 (C), 133.8 (C), 133.7 (C), 131.9 (C), 129.5 (CH), 128.8 (C), 128.7 (C), 128.3 (C), 127.8 (CH), 127.7 (CH), 127.2 (CH), 126.9 (CH), 126.5 (CH), 126.1 (CH), 125.8 (CH), 124.5 (CH), 123.8 (CH), 120.9 (CH), 61.8 (CH₃) ppm; HRMS (ESI+) m/z calcd for C₁₇H₁₂O₂SNa [M – CH₄ + Na]⁺: 339.0450, found 339.0450.

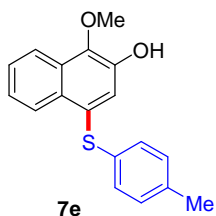
6-Bromo-1-methoxy-4-(naphthalen-2-ylthio)naphthalen-2-ol (6f):

Yield 0.182 g (88%) as yellow solid: mp 100-101 °C; IR (KBr) ν_{\max} 3442, 2931, 1579, 1202, 1098, 810, 691 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.56 (d, J = 1.5 Hz, 1H), 7.86 (d, J = 9.0 Hz,



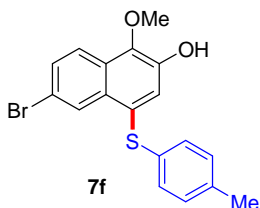
1H), 7.79-7.76 (m, 1H), 7.73 (d, $J = 9.0$ Hz, 1H), 7.71 (d, $J = 1.5$ Hz, 1H), 7.70-7.67 (m, 1H), 7.59 (dd, $J = 1.5, 8.5$ Hz, 1H), 7.48-7.43 (m, 2H), 7.42 (s, 1H), 7.32 (dd, $J = 2.0, 8.5$ Hz, 1H), 5.88 (s, 1H, OH), 3.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 145.4 (C), 140.5 (C), 133.8 (C), 133.0 (C), 132.1 (C), 130.7 (C), 130.3 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.0 (C), 127.7 (CH), 127.5 (CH), 127.3 (CH), 126.6 (CH), 126.1 (CH), 124.5 (CH), 122.7 (CH), 118.9 (C), 61.9 (CH₃) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{20}\text{H}_{11}\text{BrO}_2\text{SNa}$ [$\text{M} - \text{CH}_4 + \text{Na}$]⁺: 416.9555, found 416.9555.

1-Methoxy-4-(*p*-tolylthio)naphthalen-2-ol (7e):



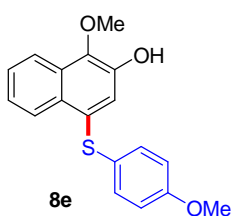
Yield 0.136 g (92%) as brown semi solid; IR (KBr) ν_{max} 3388, 2928, 1581, 1448, 1271, 808, 709 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.33 (d, $J = 8.5$ Hz, 1H), 8.00 (d, $J = 8.5$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.33-7.31 (m, 1H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.08 (s, 1H, OH), 3.97 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 145.0 (C), 139.8 (C), 136.9 (C), 131.8 (C), 130.6 (CH), 130.0 (CH), 129.8 (C), 129.0 (C), 128.5 (C), 126.8 (CH), 125.9 (CH), 124.3 (CH), 122.1 (CH), 120.8 (CH), 61.7 (CH₃), 21.0 (CH₃) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{SNa}$ [$\text{M} - \text{CH}_4 + \text{Na}$]⁺: 303.0450, found 303.0446.

6-Bromo-1-methoxy-4-(*p*-tolylthio)naphthalen-2-ol (7f):



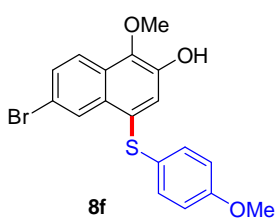
Yield 0.168 g (90%) as brown solid: mp 92-93 °C; IR (KBr) ν_{max} 3407, 2934, 1593, 1405, 1206, 1072, 809, 690 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.51 (s, 1H), 7.84 (d, $J = 9.0$ Hz, 1H), 7.58 (dd, $J = 2.0, 9.0$ Hz, 1H), 7.27 (s, 1H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.03 (s, 1H, OH), 3.94 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 145.3 (C), 139.8 (C), 137.3 (C), 131.2 (C), 130.9 (CH), 130.1 (CH), 130.1 (CH), 129.4 (C), 128.0 (CH), 127.1 (C), 123.1 (CH), 122.6 (CH), 118.6 (C), 61.8 (CH₃), 21.0 (CH₃) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{11}\text{BrO}_2\text{SNa}$ [$\text{M} - \text{CH}_4 + \text{Na}$]⁺: 380.9555, found 380.9556.

1-Methoxy-4-(4-methoxyphenylthio)naphthalen-2-ol (8e):



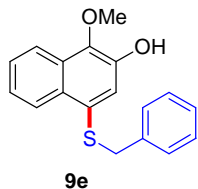
Yield 0.141 g (93%) as reddish brown solid: mp 101-102 °C; IR (KBr) ν_{\max} 3431, 2928, 1589, 1450, 1246, 1021, 823, 719 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.32 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.5$ Hz, 1H), 7.55-7.51 (m, 1H), 7.43-7.39 (m, 1H), 7.37 (d, $J = 9.0$ Hz, 2H), 7.10 (s, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 6.09 (s, 1H, OH), 3.94 (s, 3H), 3.79 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 159.5 (C), 145.0 (C), 139.0 (C), 134.1 (CH), 131.8 (C), 128.4 (C), 128.0 (C), 126.7 (CH), 125.3 (CH), 124.6 (C), 124.0 (CH), 120.8 (CH), 119.8 (CH), 115.0 (CH), 61.6 (CH_3), 55.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{O}_3\text{SNa}$ [$\text{M} - \text{CH}_4 + \text{Na}$] $^+$: 319.0399, found 319.0407.

6-Bromo-1-methoxy-4-(4-methoxyphenylthio)naphthalen-2-ol (8f):



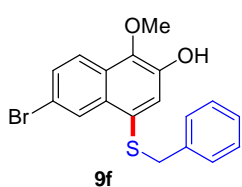
Yield 0.178 g (91%) as brown solid: mp 95-96 °C; IR (KBr) ν_{\max} 3309, 2940, 1582, 1408, 1248, 1012, 818, 711 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.49 (d, $J = 1.5$ Hz, 1H), 7.81 (d, $J = 9.0$ Hz, 1H), 7.57 (dd, $J = 1.5, 9.0$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.06 (s, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 5.98 (s, 1H, OH), 3.90 (s, 3H), 3.80 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 159.7 (C), 145.4 (C), 139.1 (C), 134.4 (CH), 131.4 (C), 130.0 (CH), 129.2 (C), 127.6 (CH), 127.0 (C), 123.9 (C), 122.6 (CH), 120.7 (CH), 118.3 (C), 115.2 (CH), 61.8 (CH_3), 55.3 (CH_3) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{11}\text{BrO}_3\text{SNa}$ [$\text{M} - \text{CH}_4 + \text{Na}$] $^+$: 396.9504, found 396.9505.

4-(Benzylthio)-1-methoxynaphthalen-2-ol (9e):



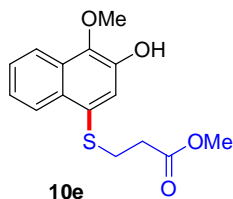
Yield 0.112 g (76%) as brown semi solid; IR (KBr) ν_{\max} 3435, 2921, 1632, 1445, 1024, 763, 707 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.34 (d, $J = 8.5$ Hz, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 1H), 7.43-7.39 (m, 1H), 7.29 (s, 1H), 7.25-7.21 (m, 5H), 5.76 (s, 1H, OH), 4.13 (s, 2H), 3.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 144.8 (C), 139.3 (C), 137.1 (C), 130.4 (C), 129.1 (C), 128.9 (CH), 128.5 (CH), 128.4 (C), 127.2 (CH), 126.7 (CH), 125.8 (CH), 124.0 (CH), 120.8 (CH), 120.8 (CH), 61.8 (CH_3), 39.7 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{SNa}$ [$\text{M} - \text{CH}_4 + \text{Na}$] $^+$: 303.0450, found 303.0457.

4-(Benzylthio)-6-bromo-1-methoxynaphthalen-2-ol (9f):



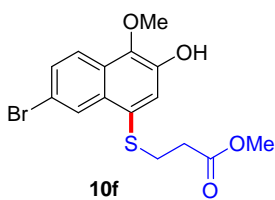
Yield 0.165 g (86%) as yellow solid: mp 89-90 °C; IR (KBr) ν_{\max} 3398, 2928, 1591, 1493, 1197, 1083, 813, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.45 (d, $J = 2.0$ Hz, 1H), 7.79 (d, $J = 9.0$ Hz, 1H), 7.54 (dd, $J = 2.0, 9.0$ Hz, 1H), 7.27 (s, 1H), 7.24-7.17 (m, 5H), 5.95 (s, 1H, OH), 4.07 (s, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 145.0 (C), 139.5 (C), 136.8 (C), 130.5 (C), 129.9 (CH), 129.4 (C), 128.8 (CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 127.0 (C), 122.6 (CH), 122.5 (CH), 118.4 (C), 61.8 (CH_3), 39.9 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{11}\text{BrO}_2\text{SNa} [\text{M} - \text{CH}_4 + \text{Na}]^+$: 380.9555, found 380.9557.

Methyl 3-(3-hydroxy-4-methoxynaphthalen-1-ylthio)propanoate (10e):



Yield 0.115 g (72%) as brown solid: mp 92-93 °C; IR (KBr) ν_{\max} ; 3387, 2983, 1717, 1587, 1379, 1215, 808, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.34 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.5$ Hz, 1H), 7.55-7.50 (m, 1H), 7.45-7.40 (m, 2H), 5.95 (s, 1H, OH), 3.96 (s, 3H), 3.67 (s, 3H), 3.18 (t, $J = 7.5$ Hz, 1H), 2.62 (t, $J = 7.5$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 172.2 (C), 144.8 (C), 139.7 (C), 129.5 (C), 129.0 (C), 128.6 (C), 126.7 (CH), 125.8 (CH), 124.2 (CH), 121.8 (CH), 120.9 (CH), 61.7 (CH_3), 51.8 (CH_3), 34.2 (CH_2), 29.8 (CH_2) ppm; HRMS (ESI+) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4\text{SNa} [\text{M} + \text{Na}]^+$: 315.0662, found 315.0666.

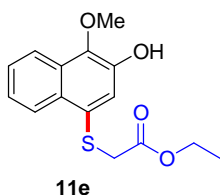
Methyl 3-(7-bromo-3-hydroxy-4-methoxynaphthalen-1-ylthio)propanoate (10f):



Yield 0.131 g (71%) as brown solid: mp 120-121 °C; IR (KBr) ν_{\max} 3355, 2937, 1716, 1596, 1369, 1201, 803, 685 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.51 (d, $J = 1.5$ Hz, 1H), 7.82 (d, $J = 9.0$ Hz, 1H), 7.58 (dd, $J = 1.5, 9.0$ Hz, 1H), 7.44 (s, 1H), 5.98 (s, 1H, OH), 3.94 (s, 3H), 3.69 (s, 3H), 3.16 (t, $J = 7.5$ Hz, 2H), 2.61 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 172.1 (C), 145.1 (C), 140.0 (C), 130.9 (C), 130.1 (CH), 128.2 (C), 128.2 (CH), 123.2 (CH),

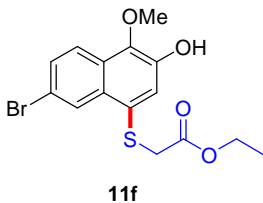
122.8 (CH), 118.6 (C), 61.8 (CH₃), 51.9 (CH₃), 34.2 (CH₂), 30.2 (CH₂) ppm; HRMS (ESI+) *m/z* calcd for C₁₅H₁₅BrO₄SNa [M + Na]⁺: 392.9767, found 392.9777.

Ethyl 2-(3-hydroxy-4-methoxynaphthalen-1-ylthio)acetate (11e):



Yield 0.115 g (72%) as brown semi solid; IR (KBr) ν_{\max} 3395, 2987, 1724, 1602, 1367, 1195, 759, 703 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.45-7.40 (m, 1H), 6.15 (s, 1H, OH), 4.10 (q, *J* = 7.5 Hz, 2H), 3.94 (s, 3H), 3.62 (s, 2H), 1.15 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 169.7 (C), 144.8 (C), 140.1 (C), 129.4 (C), 128.6 (C), 128.4 (C), 126.7 (CH), 125.6 (CH), 124.3 (CH), 122.8 (CH), 120.9 (CH), 61.6 (CH₃), 61.5 (CH₂), 37.5 (CH₂), 13.9 (CH₃) ppm; HRMS (ESI+) *m/z* calcd for C₁₅H₁₆O₄SNa [M + Na]⁺: 315.0662, found 315.0663.

Ethyl 2-(7-bromo-3-hydroxy-4-methoxynaphthalen-1-ylthio)acetate (11f):



Yield 0.138 g (74%) as brown viscous liquid; IR (KBr) ν_{\max} 3417, 2981, 1727, 1589, 1290, 820, 712 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.57 (dd, *J* = 2.0, 9.0 Hz, 1H), 7.53 (s, 1H), 6.04 (s, 1H, OH), 4.12 (q, *J* = 7.0 Hz, 2H), 3.93 (s, 3H), 3.59 (s, 2H), 1.18 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 169.5 (C), 145.2 (C), 140.5 (C), 130.9 (C), 130.1 (CH), 128.1 (CH), 127.6 (C), 127.2 (C), 124.4 (CH), 122.8 (CH), 118.8 (C), 61.8 (CH₃), 61.6 (CH₂), 37.8 (CH₂), 14.0 (CH₃) ppm; HRMS (ESI+) *m/z* calcd for C₁₅H₁₅BrO₄SNa [M + Na]⁺: 392.9767, found 392.9757.

