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Regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling: expedient construction of 2-(styrylthio)phenols

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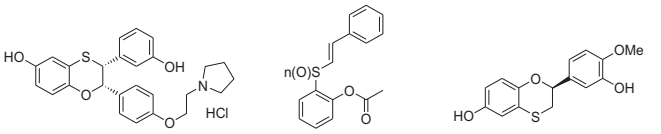
ABSTRACT

Regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling of aryl thiols with vinyl halides was developed. Starting from substituted aryl thiols and vinyl halides, various 2-(styrylthio)phenol derivatives were efficiently prepared. The application of the synthetic methodology to generate the bioactive organic intermediate was also exemplified.

1. Introduction

Organic sulfur compounds are ubiquitous in pharmaceuticals, agrichemicals, and functionalized materials.[1] In addition, as a soft atom, sulfur has more activation pattern and higher coordination ability. However, in comparison to the current state of the art in carbon-,[2] nitrogen-,[3] and oxygen-[4] directed C–H functionalization reactions, sulfur-directed C–H functionalization reaction remains underdeveloped in the past decades.[5,6] The major handicap is that the transition metal catalysts can be easily 'poisoned' by sulfur. It is generally solved by oxidizing sulfur to sulfoxide or sulfone, because sulfoxide and sulfone have a more moderate coordination ability.[7] However, such manipulations will not only increase the reaction steps but also limit the reagent diversity. Consequently, the development of new strategies for sulfur-containing C–H functionalizations is considered as a major challenge in modern organic synthesis.

The 2-(styrylthio)phenol derivatives have been employed as key intermediates in many bioactive compounds synthesis (Scheme 1). However, some drawbacks, including numerous synthesis steps and harsh reaction conditions exist in the previous synthetic methods.[8] Recently, our group reported an efficiently copper(I)-catalyzed direct hydroxylation of arenes directed by an adjacent S atom.[9] Inspired by the results, herein, we reported a regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling of aryl thiols with various vinyl halides for the 2-(styrylthio)phenol derivatives synthesis. We also exemplified this synthetic methodology to generate the bioactive organic intermediate.



Scheme 1. Selected examples of 2-(styrylthio)phenols bioactive compounds.

2. Results and discussion

Initially, the reaction of thiophenol (**1a**) with 1-((*E*)-2-iodovinyl) benzene (**2a**) was chosen as the model reaction. Various structurally similar enaminone ligands **L1**–**L10** were investigated (Scheme 2). The yield was observed increased by changing **L1** to **L5**, as well as **L2** to **L6**. Additionally, other commercial viable ligands such as 1,10-phenanthroline (**L11**) and *N*,*N*-dimethylethane-1,2-diamine (**L12**) were observed ineffective. After analyzing the results, **L5** was found as the best ligand (72% yield).

In order to further confirming the optimal condition, other parameters were optimized such as copper catalyst species, base species, and reactant ratios (Table 1). Experimental results

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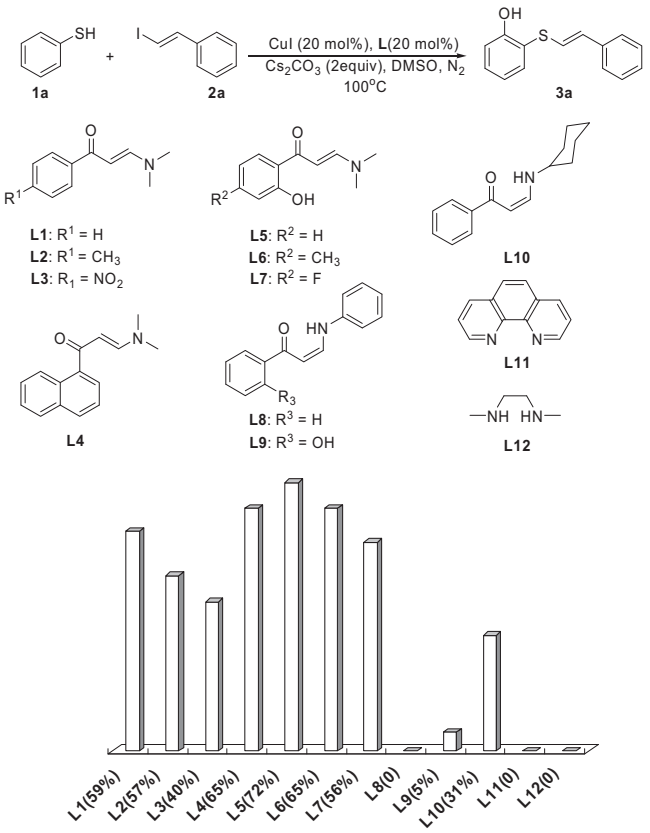
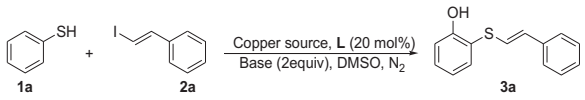


Scheme 2. Ligand performances in copper-catalyzed C–H hydroxylation/C–S coupling reactions.

Table 1
Optimization of the model reaction[a]



Entry	Copper source	Base	**1a**/**2a**	**3a**[b] [%]
1	$Cu(SO_3CF_3)_2$	Cs_2CO_3	1:1	10
2	$Cu(OAc)_2$	Cs_2CO_3	1:1	25
3	$CuBr_2$	Cs_2CO_3	1:1	0
4	CuBr	Cs_2CO_3	1:1	35
5	CuI	Cs_2CO_3	1:1	72
6	CuI	Na_2CO_3	1:1.2	0
7	CuI	K_3PO_4	1:1.2	41
8	CuI	MeONa	1:1.2	50
9	CuI	Cs_2CO_3	1:1.2	58[c]
10	CuI	Cs_2CO_3	1:1.2	75[d]
11	*CuI*	*Cs_2CO_3*	*1:1.2*	*78*(69[e])

[a] Unless otherwise noted, reactions conditions were **1a** (0.5 mmol), copper source (20 mol %), **L5** (20 mol %), Cs_2CO_3 (2 equiv), protected by N_2, in DMSO (3 mL), at 100 °C for 24 h.
[b] Isolated yield.
[c] At 90 °C.
[d] At 110 °C.
[e] In air.

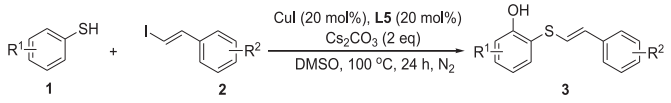
demonstrated that the copper(I) source gave a higher yield than the copper(II) source (entries 1–4). In the presence of **L5** with CuI, the desired product **3a** was formed in 72% yield (entry 5). Besides, results demonstrated that the reaction temperature was as an important parameter, which the desired product was formed in 58% yield at 90 °C (entry 9) and 75% yield at 110 °C (entry 10). Finally, the desired product **3a** was formed in 78% yield when employed the catalyst system **L5** with CuI at 100 °C (entry 11).

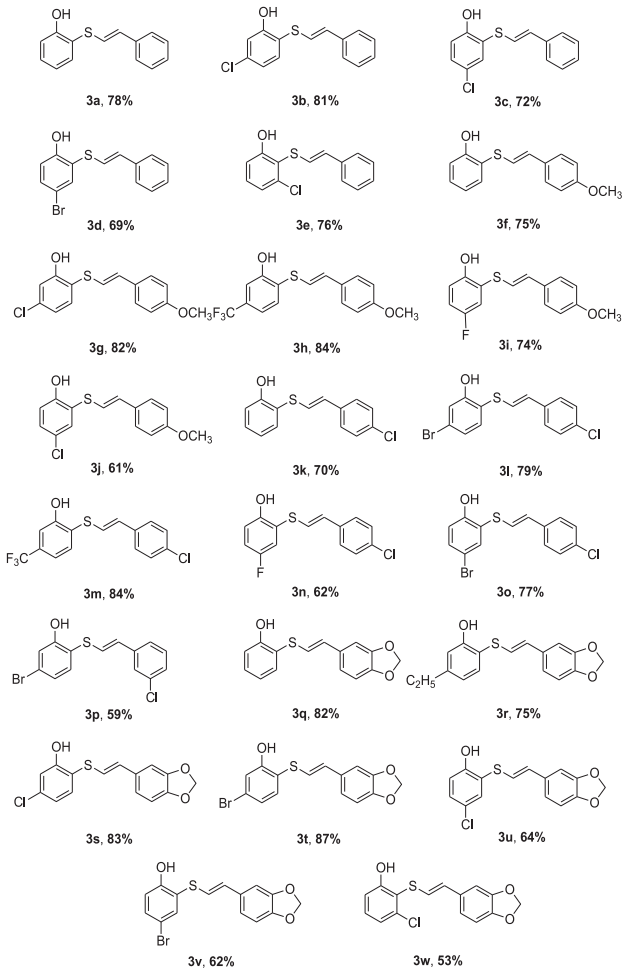
With the optimal condition in hand, we next investigated the reaction scope, which was illustrated by substituted aryl thiols with vinyl iodides in Table 2. Both *meta*- and *para*-substituted aryl thiols were successfully transformed into the corresponding products.

Next, we commenced investigating whether the vinyl bromides were successfully endured in this methodology. To our delight, vinyl bromides were also transformed to the corresponding products in 55–83% yields (Table 3). It is worth noting that the multitude substituent aryl thiols with vinyl bromides also gave the corresponding product in 64–76% yields (entries **5k**–**5n**), which demonstrated that this methodology has a good tolerance of different substrates aryl thiols.

Furthermore, we turned our attention to the hetero-aromatic vinyl halides (Table 4). To our delight, both 2-((*E*)-2-iodovinyl)

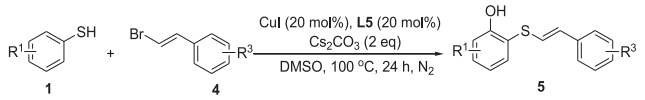
Table 2
Regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling of aryl thiols with vinyl iodides[a]

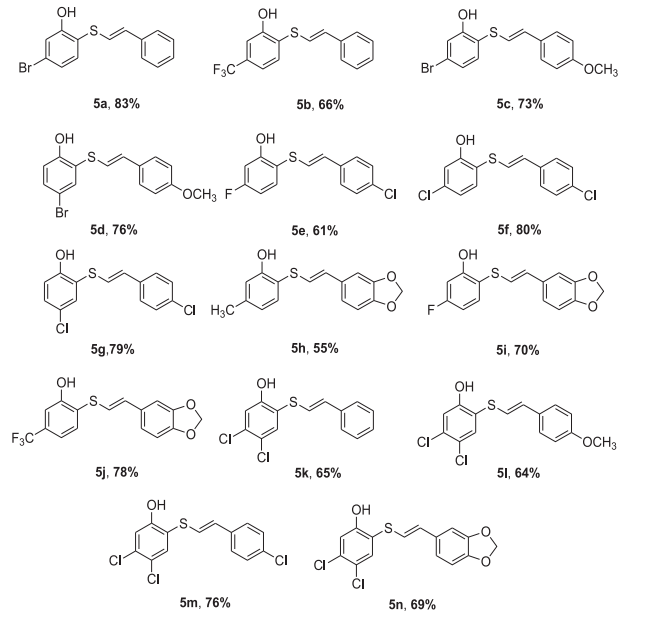




[a] Isolated yields for reactions conditions were **1** (0.5 mmol), **2** (0.6 mmol), CuI (20 mol %), **L5** (20 mol %), Cs_2CO_3 (2 equiv), protected by N_2, in DMSO (3 mL), at 100 °C for 24 h.

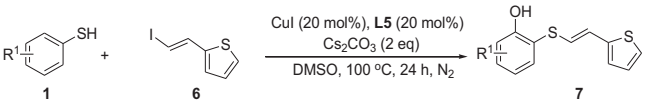
Table 3
Regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling of aryl thiols with vinyl bromides[a]

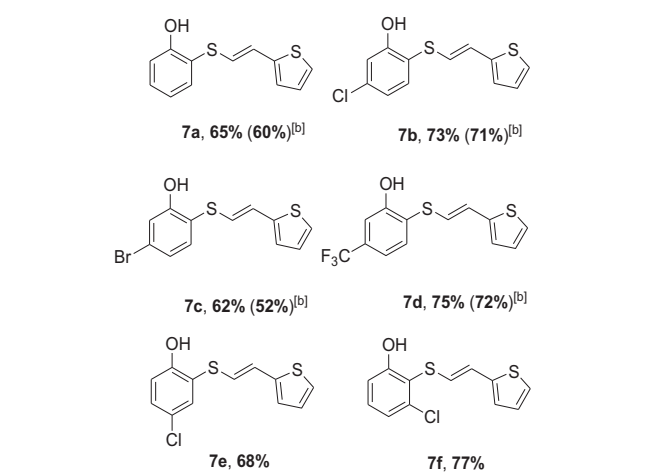




[a] Isolated yields for reactions conditions were **1** (1 mmol), **4** (1.2 mmol), CuI (20 mol %), **L5** (20 mol %), Cs_2CO_3 (2 equiv), protected by N_2, in DMSO (3 mL), at 100 °C for 24 h.

Table 4
Regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling of aryl thiols with 2-((*E*)-2-iodovinyl)thiophene[a]

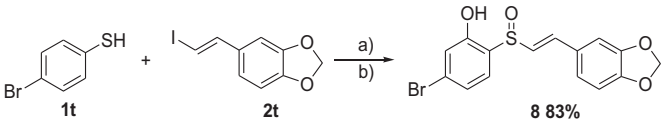




[b] 2-(2-Bromoethenyl)thiophene.
[a] Isolated yields for reactions conditions were **1** (0.5 mmol), **6** (0.6 mmol), CuI (20 mol %), **L5** (20 mol %), Cs_2CO_3 (2 equiv), protected by N_2, in DMSO (3 mL) at 100 °C for 24 h.

thiophenes and 2-((*E*)-2-bromovinyl)thiophenes worked well in this protocol. The corresponding products were isolated in 52–77% yield. The stereochemistry of the 2-((*E*)-2-iodovinyl)thiophene and 2-((*E*)-2-bromovinyl)thiophenes was retained in the corresponding product.

The synthetic application of the regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling reaction was exemplified by the bioactive intermediate (*E*)-styryl-2-hydroxylphenyl sulfoxide synthesis which selective inhibition of COX-2 enzyme (COX denote cyclooxygenases).[8a] The new strategy is very facile and highly efficient (Scheme 3).



[a] Reagents and conditions: (i) **1t** (1 mmol), **2t** (1.2 mmol), CuI (20 mol %), **L5** (20 mol %), Cs_2CO_3 (2 equiv), protected by N_2, in DMSO (3 mL), at 100 °C for 24 h. [b] (ii) 30% H_2O_2 (2 mL), AcOH (1 equiv), 25 °C for 5 h.

Scheme 3. The synthetic application of the regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling in (*E*)-styryl hydroxyphenyl sulfoxide synthesis.

In summary, a regioselective copper(I)-catalyzed C–H hydroxylation/C–S coupling of aryl thiols with vinyl halides for the synthesis of interesting building blocks 2-(styrylthio)phenol derivatives was developed. The process is simple and efficient, using inexpensive catalysts and under mild conditions. The application of the synthetic methodology to generate the bioactive organic intermediate was very facile and highly efficient.

3. Experimental section

3.1. General information

All reagents were obtained from commercial sources and used without further purification. All NMR spectra were recorded on AVANCE DMX-500 spectrometry at 500 MHz and 125 MHz for ^1H and ^{13}C NMR in DMSO-d_6, respectively. The NMR chemical shift was reported in parts per million relative to 2.50 and 40.70 ppm of DMSO as the standards of ^1H and ^{13}C NMR, respectively. Mass spectra were performed on a 3000plus mass spectrometer equipped with ESI interface and ion trap analyzer. The HRMS were tested on 7-tesla FT-ICR MS equipped with an electrospray source.

3.2. General procedure for preparation of L1–L7[10]

Dimethylformamide dimethylacetal (DMFDMA) (1.19 g, 10 mmol) and 1-(2-hydroxyphenyl) ethanone (1.36 g, 10 mmol) were dissolved in *p*-xylene (2 mL). And the mixture was refluxed for 12 h, then a yellow precipitate formation. The precipitate was filtered out and washed with petroleum ether for three times. The solid was dried under vacuum, and 1.79 g (94% yield) **L5** was obtained.

3.3. General procedure for preparation of vinyl halides[11]

β-Unsaturated carboxylic acid (1.48 g, 10 mmol) was added to a solution of LiOAc (0.07 g, 1 mmol) in MeCN/H_2O (97:3 v/v, 30 mL). After the mixture was stirred for 5 min at room temperature, 1-iodopyrrolidine-2,5-dione (2.25 g, 10 mmol) was added. Usual workup by flash column chromatography on silica gel to afford the 1-((*E*)-2-bromovinyl)benzene **2a** (1.36 g, 85%).

3.4. General procedure for synthesis of 2-(styrylthio)phenols derivatives 3a–3w, 5a–5n, 7a–7f

A mixture of thiophenols (0.5 mmol), 1-((*E*)-2-iodovinyl)benzenes (0.6 mmol), CuI (19 mg, 20 mol %), **L5** (19 mg, 20 mol %), and Cs_2CO_3 (326 mg, 2 equiv) in DMSO (3 mL) was stirred in N_2 at 100 °C for 24 h., The mixture was quenched with saturated salt water (10 mL) after the reaction completion. The solution was extracted with ethyl acetate (3×10 mL). The organic layers were combined and dried by sodium sulfate. The product 2-(styrylthio) phenols was obtained by flash column chromatography on silica gel.

*3.4.1. 2-(Styrylthio)phenol (**3a**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.98 (s, 1H), 7.46 (d, J=7.5 Hz, 2H), 7.33–7.27 (m, 4H), 7.24 (d, J=7.5 Hz, 1H), 7.13–7.09 (m, 2H), 6.90 (d, J=8.0 Hz, 1H), 6.86 (t, J=7.5 Hz, 1H), 6.68 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.3, 137.5, 131.6, 131.3, 129.8, 129.3, 128.5, 127.1, 124.1, 121.3, 121.1, 116.5. ESI-HRMS m/z: calcd for $C_{14}H_{11}OS^-$ [M−H]$^-$: 227.0536; found 227.0530.

*3.4.2. 5-Chloro-2-(styrylthio)phenol (**3b**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.58 (s, 1H), 7.48 (d, J=7.5 Hz, 2H), 7.33–7.23 (m, 4H), 7.11 (d, J=15.5 Hz, 1H), 6.92–6.89 (m, 2H), 6.72 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.1, 137.4, 133.1, 132.6, 132.2, 129.8, 128.7, 127.3, 123.2, 121.1, 121.0, 116.1. ESI-HRMS m/z: calcd for $C_{14}H_{10}ClOS^-$ [M−H]$^-$: 261.0146; found 261.0138.

*3.4.3. 4-Chloro-2-(styrylthio)phenol (**3c**).* Yellow liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.34 (s, 1H), 7.54 (d, J=8.0 Hz, 2H), 7.35–7.32 (m, 2H), 7.27 (d, J=7.3 Hz, 1H), 7.24 (d, J=2.0 Hz, 1H), 7.21 (d, J=15.5 Hz, 1H), 7.14 (d, J=8.0 Hz, 1H), 6.89 (d, J=8.5 Hz, 1H), 6.83 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.6, 137.3, 134.1, 131.8, 129.8, 128.9, 128.7, 128.3, 127.5, 124.7, 124.4, 122.1, 117.5. ESI-HRMS m/z: calcd for $C_{14}H_{10}ClOS^-$ [M−H]$^-$: 261.0146; found 261.0139.

*3.4.4. 4-Bromo-2-(styrylthio)phenol (**3d**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.37 (s, 1H), 7.54 (d, J=8.0 Hz, 2H), 7.42–7.33 (m, 3H), 7.29–7.24 (m, 2H), 7.21 (d, J=15.5 Hz, 1H), 6.83 (m, 1H), 7.21 (d, J=10.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.1, 137.3, 134.1, 131.5, 131.2, 129.8, 129.0, 127.5, 125.1, 122.1, 118.0, 111.9. ESI-HRMS m/z: calcd for $C_{14}H_{10}BrOS^-$ [M−H]$^-$: 304.9715; found 304.9714.

*3.4.5. 3-Chloro-2-(styrylthio)phenol (**3e**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.46 (s, 1H), 7.31 (d, J=2.0 Hz, 2H), 7.28–7.24 (m, 3H), 7.17 (d, J=7.6 Hz, 1H), 7.08 (d, J=8.0 Hz, 1H), 6.97–6.94 (m, 2H), 6.20 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.1, 139.8, 137.6, 132.5, 129.8, 128.0, 126.8, 126.7, 125.7, 121.7, 117.2, 116.1. ESI-HRMS m/z: calcd for $C_{14}H_{10}ClOS^-$ [M−H]$^-$: 261.0146; found 261.0139.

*3.4.6. 2-(4-Methoxystyrylthio)phenol (**3f**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.96 (s, 1H), 7.43 (d, J=8.5 Hz, 2H), 7.23 (d, J=8.0 Hz, 1H), 7.11 (d, J=7.5 Hz, 1H), 6.93–6.81 (m, 5H), 6.70 (d, J=15.5 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.9, 155.7, 134.0, 132.7, 130.2, 129.3, 128.6, 128.5, 127.8, 122.2, 120.9, 120.2, 116.1, 115.1, 56.2. ESI-HRMS m/z: calcd for $C_{15}H_{13}O_2S^-$ [M−H]$^-$: 257.0639; found 257.0635.

*3.4.7. 2-(4-Methoxystyrylthio)-5-chlorophenol (**3g**).* Pale yellow liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.55 (s, 1H), 7.45 (d, J=7.5 Hz, 2H), 7.23 (d, J=8.0 Hz, 2H), 6.92–6.89 (m, 5H), 6.75 (d, J=15.5 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.2, 156.6, 134.0, 132.5, 131.2, 130.1, 128.8, 122.2, 121.0, 11.3, 115.9, 115.3, 56.4. ESI-HRMS m/z: calcd for $C_{15}H_{12}ClO_2S^-$ [M−H]$^-$: 291.0252; found 291.0246.

*3.4.8. 2-(4-Methoxystyrylthio)-5-(trifluoromethyl)phenol (**3h**).* Yellow liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.77 (s, 1H), 7.53 (d, J=8.5 Hz, 2H), 7.39 (d, J=8.0 Hz, 1H), 7.17 (d, J=8.5 Hz, 1H), 7.04–7.00 (m, 2H), 6.94–6.92 (m, 3H), 3.77(s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.5, 155.0, 136.6, 134.2, 129.9, 129.5, 129.2, 128.7, 117.5, 117.4, 116.1, 115.3, 111.7, 56.4. ESI-HRMS m/z: calcd for $C_{16}H_{12}F_3O_2S^-$ [M−H]$^-$: 325.0516; found 325.0508.

*3.4.9. 2-(4-Methoxystyrylthio)-4-fluorophenol (**3i**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.98 (s, 1H), 7.51 (d, J=8.5 Hz, 2H), 7.04–6.98 (m, 2H), 6.92–6.90 (m, 2H), 6.90 (d, J=8.0 Hz, 1H), 6.83 (d, J=8.5 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.3, 157.9, 156.1, 151.5, 135.2, 130.0, 129.0, 125.1, 118.4, 116.6, 116.5, 115.3, 115.2, 115.0, 114.1, 114.0, 56.4. ESI-HRMS m/z: calcd for $C_{15}H_{12}FO_2S^-$ [M−H]$^-$: 275.0548; found 275.0540.

*3.4.10. 2-(4-Methoxystyrylthio)-4-chlorophenol (**3j**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.32 (s, 1H), 7.51 (d, J=8.5 Hz, 2H), 7.16 (s, 1H), 7.11 (d, J=8.3 Hz, 1H), 7.01 (d, J=15.5 Hz, 1H), 6.92 (d, J=8.5 Hz, 2H), 6.86–6.82 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.4, 154.2, 135.5, 130.0, 129.1, 127.9, 127.7, 125.7, 124.5, 118.3, 117.3, 115.3, 56.4. ESI-HRMS m/z: calcd for $C_{15}H_{12}ClO_2S^-$ [M−H]$^-$: 291.0252; found 291.0246.

*3.4.11. 2-(4-Chlorostyrylthio)phenol (**3k**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.02 (s, 1H), 7.54–7.48 (m, 2H), 7.37 (d, J=8.5 Hz, 2H), 7.30–7.28 (m, 1H), 7.19–7.13 (m, 2H), 6.90 (d, J=8.0 Hz, 1H), 6.86–6.83 (m, 1H), 6.63 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.8, 135.8, 132.1, 130.8, 129.1, 129.1, 128.9, 128.1, 126.7, 124.9, 120.4, 120.2, 115.8. ESI-HRMS m/z: calcd for $C_{14}H_{10}ClOS^-$ [M−H]$^-$: 261.0146; found 261.0140.

*3.4.12. 2-(4-Chlorostyrylthio)-5-bromophenol (**3l**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.59 (s, 1H), 7.520 (d, J=8.5 Hz, 2H), 7.38 (d, J=8.5 Hz, 2H), 7.24 (d, J=8.0 Hz, 1H), 7.18 (d, J=15.5Hz, 1H), 7.05–7.01 (m, 2H), 6.71 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.0, 136.2, 132.8, 132.4, 130.6, 129.6, 128.8, 124.2, 123.7, 121.2, 121.1, 118.8. ESI-HRMS m/z: calcd for $C_{14}H_9BrClOS^-$ [M−H]$^-$: 338.9245; found 338.9240.

*3.4.13. 2-(4-Chlorostyrylthio)-5-(trifluoromethyl)phenol (**3m**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.84 (s, 1H), 7.59 (d, J=8.5 Hz, 2H), 7.47 (d, J=8.0 Hz, 1H), 7.41 (d, J=8.0 Hz, 2H), 7.30 (d, J=15.5 Hz, 1H), 7.18 (d, J=8.0 Hz, 1H), 7.10 (s, 1H), 6.93 (d, J=15.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.4, 136.2, 133.5, 129.9, 129.7, 129.3, 128.7, 128.6, 122.6, 117.5, 111.9. ESI-HRMS m/z: calcd for $C_{15}H_{10}ClF_3OS^-$ [M−H]$^-$: 330.0016; found 330.0012.

*3.4.14. 2-(4-Chlorostyrylthio)-4-fluorophenol (**3n**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.04 (s, 1H), 7.57 (d, J=8.0 Hz, 2H), 7.40 (d, J=8.0 Hz, 2H), 7.27 (d, J=15.5 Hz, 1H), 7.14–7.12 (m, 1H), 6.93–6.91 (m, 1H), 6.85 (d, J=8.5 Hz, 1H), 6.81 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.7, 155.8, 151.8, 136.1, 133.0, 131.6, 129.6, 129.0, 123.5, 116.6, 116.5, 115.9, 115.7, 114.7, 114.6. ESI-HRMS m/z: calcd for $C_{14}H_9ClFOS^-$ [M−H]$^-$: 279.0052; found 279.0047.

*3.4.15. 2-(4-Chlorostyrylthio)-4-bromophenol (**3o**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.42 (s, 1H), 7.57 (d, J=7.5 Hz, 2H), 7.39–7.35 (m, 2H), 7.27–7.24 (m, 2H), 6.84 (d, J=9.0 Hz, 1H), 6.79 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.0, 136.1, 133.1,

131.9, 131.5, 131.2, 129.7, 129.0, 124.5, 123.4, 117.9, 111.7. ESI-HRMS *m*/*z*: calcd for $C_{14}H_{10}BrClOS$ $[M-H]^-$: 338.9330; found 338.9324.

*3.4.16. 2-(3-Chlorostyrylthio)-5-bromophenol (**3p**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.61 (s, 1H), 7.62 (s, 1H), 7.45 (d, *J*=8.0 Hz, 1H), 7.35 (d, *J*=8.5 Hz, 1H), 7.29–7.25 (m, 3H), 7.07–7.02 (m, 2H), 6.68 (d, *J*=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.3, 139.6, 134.7, 132.8, 131.6, 130.2, 128.2, 126.7, 126.0, 125.7, 123.8, 121.5, 121.0, 119.0. ESI-HRMS *m*/*z*: calcd for $C_{14}H_9BrClOS^-$ $[M-H]^-$: 338.9330; found 338.9324.

*3.4.17. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)phenol (**3q**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 9.96 (s, 1H), 7.25 (d, *J*=7.7 Hz, 2H), 7.11–7.08 (m, 1H), 6.98 (d, *J*=15.5 Hz, 1H), 6.89–6.8 (m, 4H), 6.67 (d, *J*=15.5 Hz, 1H), 6.01 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.9, 149.0, 148.0, 134.2, 132.7 132.1, 130.5, 130.2, 128.8, 128.7, 122.2 122.1, 121.2, 121.1, 116.3, 109.5, 106.6, 102.2. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{11}O_3S$ $[M-H]^-$: 271.0434; found 271.0426.

*3.4.18. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-5-ethylphenol (**3r**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 9.83 (s, 1H), 7.18–7.16 (m, 2H), 6.93 (d, *J*=15.0 Hz, 1H), 6.84 (s, 2H), 6.73 (s, 2H), 6.70 (d, *J*=8.0 Hz, 1H), 6.68 (d, *J*=15.5 Hz, 1H), 6.00 (s, 2H), 2.54–2.49 (m, 2H), 1.16–1.13 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.4, 149.0, 147.9, 145.4, 132.2, 131.5, 131.3, 122.3, 122.0, 120.7, 118.3, 115.9, 109.5, 106.5, 102.2, 19.0, 16.7. ESI-HRMS *m*/*z*: calcd for $C_{17}H_{15}O_3S^-$ $[M-H]^-$: 299.0747; found 299.0740.

*3.4.19. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-5-chlorophenol (**3s**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.51 (s, 1H), 7.25 (d, *J*=8.0 Hz, 2H), 6.97 (d, *J*=15.5 Hz, 1H), 6.90–6.88 (m, 3H), 6.86 (d, *J*=8.0 Hz, 1H), 6.71 (d, *J*=15.5 Hz, 1H), 6.01 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.4, 148.8, 147.9, 133.5, 132.3, 131.7, 131.1, 122.2, 121.7, 120.7, 120.0, 115.7, 109.2, 106.4, 102.1. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{10}ClO_3S^-$ $[M-H]^-$: 305.0045; found 305.0037.

*3.4.20. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-5-bromophenol (**3t**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.49 (s, 1H), 7.24 (m, 1H), 7.24 (d, *J*=17.0 Hz, 1H), 7.02–7.00 (m, 2H), 6.96 (d, *J*=15.5 Hz, 1H), 6.91 (d, *J*=8.0 Hz, 1H), 6.87 (d, *J*=8.0 Hz, 1H), 6.72 (d, *J*=15.5 Hz, 1H), 6.01 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.4, 148.8, 148.0, 133.7, 131.7, 131.3, 123.6, 122.4, 122.2, 120.4, 119.8, 118.5, 109.3, 106.5, 102.1. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{10}BrO_3S^-$ $[M-H]^-$: 348.9612; found 348.9608.

*3.4.21. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-4-chlorophenol (**3u**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.32 (s, 1H), 7.32 (s, 1H), 7.18 (d, *J*=2.0 Hz, 1H), 7.10 (d, *J*=8.5 Hz, 1H), 7.06 (d, *J*=15.5 Hz, 1H), 6.95–6.93 (m, 1H), 6.88–6.83 (m, 2H), 6.80 (d, *J*=15.5 Hz, 1H), 6.02 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.2, 149.0, 148.4, 135.2, 131.8, 127.4, 127.0, 125.5, 124., 122.8, 119.1, 117.3, 109.5, 106.8, 102.3. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{10}ClO_3S^-$ $[M-H]^-$: 305.0045; found 305.0037.

*3.4.22. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-4-bromophenol (**3v**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.34 (s, 1H), 7.31 (d, *J*=1.5 Hz, 1H), 7.28 (d, *J*=2.0 Hz, 1H), 7.22 (d, *J*=8.5 Hz, 1H), 7.05 (d, *J*=15.5 Hz, 1H), 6.97–6.93 (m, 1H), 6.87 (d, *J*=8.0 Hz, 1H), 6.81 (d, *J*=15.5 Hz, 1H), 6.02 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.7, 149.0, 148.4, 135.2, 131.8, 130.7, 126.0, 124.2, 122.8, 119.1, 117.9, 111.9, 109.5, 106.8, 102.3. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{10}BrO_3S^-$ $[M-H]^-$: 348.9504; found 348.9532.

*3.4.23. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-3-chlorophenol (**3w**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.41 (s, 1H), 7.28–7.24 (m, 1H), 7.06 (d, *J*=6.0 Hz, 2H), 6.95 (d, *J*=8.0 Hz, 1H), 6.80–6.77 (m, 2H), 6.72 (d, *J*=8.0 Hz, 1H), 6.17 (d, *J*=15.5 Hz, 1H), 5.98 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.1, 149.0, 147.5, 139.7, 132.3, 132.2, 127.3, 123.4, 121.7, 121.5, 117.6, 116.1, 109.4, 106.1, 102.1. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{10}ClO_3S^-$ $[M-H]^-$: 305.0045; found 305.0050.

*3.4.24. 5-Bromo-2-(styrylthio)phenol (**5a**).* Pale yellow liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.57 (s, 1H), 7.49 (d, *J*=7.5 Hz, 2H), 7.34–7.31 (m, 2H), 7.25 (d, *J*=7.5 Hz, 2H), 7.12 (d, *J*=15.5 Hz, 1H), 7.05–7.02 (m, 2H), 6.74 (d, *J*=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.1, 137.4, 132.9, 132.3, 129.8, 128.8, 127.3, 123.8, 122.9, 121.8, 121.2, 118.9. ESI-HRMS *m*/*z*: calcd for $C_{14}H_{10}BrOS^-$ $[M-H]^-$: 304.9715; found 304.9710.

*3.4.25. 5-(Trifluoromethyl)-2-(styrylthio)phenol (**5b**).* Pale yellow liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.79 (s, 1H), 7.56 (d, *J*=7.5 Hz, 2H), 7.45 (d, *J*=8.0 Hz, 1H), 7.37 (d, *J*=7.5 Hz, 2H), 7.29 (d, *J*=7.5 Hz, 1H), 7.23 (d, *J*=15.5 Hz, 1H), 7.18 (d, *J*=8.0 Hz, 1H), 7.11 (s, 1H), 6.96 (d, *J*=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.8, 136.6, 134.9, 129.3, 128.8, 128.6, 128.5, 128.0, 127.7, 127.0, 125.8, 123.7, 120.6, 116.9, 111.2. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{10}F_3OS^-$ $[M-H]^-$: 295.0486; found 295.0480.

*3.4.26. 2-(4-Methoxystyrylthio)-5-bromophenol (**5c**).* Pale yellow liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.52 (s, 1H), 7.46 (d, *J*=8.5 Hz, 2H), 7.17 (d, *J*=8.5 Hz, 1H), 7.02 (d, *J*=5.5 Hz, 2H), 6.92–6.89 (m, 3H), 6.77 (d, *J*=15.0 Hz, 1H), 3.77(s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.2, 156.6, 134.2, 131.4, 130.1, 128.9, 123.8, 122.8, 120.5, 119.1, 118.7, 115.3. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{12}BrO_2S^-$ $[M-H]^-$: 334.9747; found 334.9739.

*3.4.27. 2-(4-Methoxystyrylthio)-4-bromophenol (**5d**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.35 (s, 1H), 7.50 (d, *J*=8.5 Hz, 2H), 7.26 (s, 1H), 7.23–7.21 (m, 1H), 7.00 (d, *J*=15.5 Hz, 1H), 6.92 (d, *J*=8.5 Hz, 2H), 6.84–6.80 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.4, 154.7, 135.6, 130.7, 130.0, 129.1, 126.2, 118.3, 117.9, 115.3, 111.9, 56.4. ESI-HRMS *m*/*z*: calcd for $C_{15}H_{12}BrO_2S^-$ $[M-H]^-$: 334.9747; found 334.9741.

*3.4.28. 2-(4-Chlorostyrylthio)-5-fluorophenol (**5e**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.57 (s, 1H), 7.46 (d, *J*=8.5 Hz, 2H), 7.36–7.33 (m, 3H), 7.13 (d, *J*=15.5 Hz, 1H), 6.73–6.69 (m, 2H), 6.51 (d, *J*=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.7, 162.7, 158.6, 158.5, 136.5, 134.4, 134.3, 132.6, 129.7, 128.7, 128.6, 126.1, 116.0, 108.0, 107.9, 104.1, 103.9. ESI-HRMS *m*/*z*: calcd for $C_{14}H_9ClFOS^-$ $[M-H]^-$: 279.0125; found 279.0120.

*3.4.29. 2-(4-Chlorostyrylthio)-5-chlorophenol (**5f**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.59 (s, 1H), 7.51 (d, *J*=8.5 Hz, 2H), 7.37 (d, *J*=8.5 Hz, 2H), 7.31 (d, *J*=8.0 Hz, 1H), 6.18 (d, *J*=15.5 Hz, 1H), 6.91–6.89 (m, 2H), 6.68 (d, *J*=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.2, 136.4, 133.3, 133.0, 132.5, 130.6, 129.8, 128.9, 124.6, 121.0, 120.6, 116.2. ESI-HRMS *m*/*z*: calcd for $C_{14}H_9Cl_2OS^-$ $[M-H]^-$: 294.9829; found 294.9822.

*3.4.30. 2-(4-Chlorostyrylthio)-4-chlorophenol (**5g**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 10.38 (s, 1H), 7.57 (d, *J*=8.5 Hz, 2H), 7.39–7.38 (m, 2H), 7.28–7.25 (m, 2H), 7.15–7.13 (m, 1H), 6.89–6.86 (m, 1H), 6.80 (d, *J*=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.7, 136.3, 133.2, 132.1, 131.5, 129.8, 129.7, 129.2, 128.9, 128.5, 124.4, 124.2, 123.6, 117.5. ESI-HRMS *m*/*z*: calcd for $C_{14}H_9Cl_2OS^-$ $[M-H]^-$: 294.9829; found 294.9822.

*3.4.31. 2-(4-Bromophenylthio)-5-methylphenol (**5h**).* Colorless liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 9.90 (s, 1H), 7.45 (d, *J*=8.3 Hz, 2H), 7.19 (d, *J*=7.8 Hz, 1H), 6.99 (d, *J*=8.3 Hz, 2H), 6.78 (s, 1H), 6.68

(d, J=7.8 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.87, 142.18, 138.29, 136.68, 132.93, 130.08, 122.17, 119.31, 117.93, 114.57, 22.15. ESI-HRMS m/z: calcd for $C_{16}H_{13}O_3S^-$ $[M-H]^-$: 285.0590; found 285.0583.

*3.4.32. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-5-fluorophenol (**5i**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.49 (s, 1H), 7.30 (d, J=8.0 Hz, 2H), 7.18 (s, 1H), 6.92 (d, J=15.5 Hz, 1H), 6.84 (s, 2H), 6.71–6.67 (m, 2H), 6.56 (d, J=15.0 Hz, 1H), 6.00 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.1, 162.1, 157.8, 157.7, 148.8, 147.7, 132.9, 132.9, 131.8, 131.5, 121.8, 121.6, 117.1, 109.2, 107.7, 107.5, 106.3, 103.7, 103.5, 102.0. ESI-HRMS m/z: calcd for $C_{15}H_{10}FO_3S^-$ $[M-H]^-$: 289.0340; found 289.0333.

*3.4.33. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-5-(trifluoromethyl)phenol (**5j**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.76 (s, 1H), 7.41 (d, J=8.0 Hz, 1H), 7.32 (d, J=2.0 Hz, 1H), 7.16 (d, J=8.0 Hz, 1H), 7.09–7.04 (m, H), 6.98–6.96 (m, 1H), 6.90–6.87 (m, 2H), 6.03 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.0, 149.1, 148.5, 136.3, 131.7, 129.7, 128.8, 128.6, 128.2, 127.9, 126.5, 124.3, 122.9, 118.3, 117.5, 111.7, 109.5, 106.9, 102.4. ESI-HRMS m/z: calcd for $C_{16}H_{10}F_3O_3S^-$ $[M-H]^-$: 339.0308; found 339.0299.

*3.4.34. 4,5-Dichloro-2-(styrylthio)phenol (**5k**).* Pale yellow liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.85 (s, 1H), 7.55 (d, J=7.5 Hz, 2H), 7.41 (s, 1H), 7.36–7.33 (m, 2H), 7.28–7.25 (m, 1H), 7.23 (d, J=15.5 Hz, 1H), 7.04 (s, 1H), 6.86 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.0, 137.0, 134.5, 129.9, 129.7, 128.9, 127.5, 124.2, 122.4, 121.3, 117.1. ESI-HRMS m/z: calcd for $C_{14}H_9Cl_2OS^-$ $[M-H]^-$: 294.9829; found 294.9822.

*3.4.35. 2-(4-Methoxystyrylthio)-4,5-dichlorophenol (**5l**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.80 (s, 1H), 7.50 (d, J=8.5 Hz, 2H), 7.32 (s, 1H), 7.02–6.98 (m, 2H), 6.92 (d, J=8.5 Hz, 1H), 6.86 (d, J=15.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.5, 154.8, 136.0, 131.3, 129.9, 129.6, 129.3, 129.2, 125.4, 122.6, 117.7, 117.1, 115.3, 115.1, 56.4. ESI-HRMS m/z: calcd for $C_{15}H_{11}Cl_2O_2S^-$ $[M-H]^-$: 324.9862; found 324.9853.

*3.4.36. 2-(4-Chlorostyrylthio)-4,5-dichlorophenol (**5m**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.86 (s, 1H), 7.57 (d, J=8.5 Hz, 2H), 7.44 (s, 1H), 7.39 (d, J=8.0 Hz, 2H), 7.28 (d, J=15.5 Hz, 1H), 7.04 (s, 1H), 6.82 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.3, 136.2, 133.3, 132.5, 131.5, 130.5, 129.8, 129.7, 129.3, 125.6, 123.8, 123.0, 122.6, 117.3. ESI-HRMS m/z: calcd for $C_{14}H_8Cl_3OS^-$ $[M-H]^-$: 328.9367; found 328.9376.

*3.4.37. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylthio)-4,5-dichlorophenol (**5n**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.81 (s, 1H), 7.36 (d, J=15.5 Hz, 2H), 7.07–7.01 (m, 2H), 6.96 (d, J=8.0 Hz, 1H), 6.89 (d, J=8.0 Hz, 1H), 6.83 (d, J=15.0 Hz, 1H), 6.03 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.7, 149.0, 148.5, 135.7, 131.7, 129.6, 129.3, 125.2, 123.0, 122.6, 118.5, 117.1, 109.5, 106.9, 102.4. ESI-HRMS m/z: calcd for $C_{15}H_9Cl_2O_3S^-$ $[M-H]^-$: 338.9728; found 338.9721.

*3.4.38. 2-((E)-2-(Thiophen-2-yl)vinylthio)phenol (**7a**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.04 (s, 1H), 7.47–7.41 (m, 2H), 7.41 (d, J=2.5 Hz, 1H), 7.31 (d, J=3.5 Hz, 1H), 6.89 (d, J=8.0 Hz, 1H), 7.02 (d, J=8.5 Hz, 1H), 6.90–6.83 (m, 2H), 6.80 (d, J=6.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.5, 142.1, 131.6, 130.7, 130.1, 129.7, 129.0, 126.6, 126.2, 125.3, 122.9, 121.2, 120.9, 116.6. ESI-HRMS m/z: calcd for $C_{12}H_9OS_2^-$ $[M-H]^-$: 233.0173; found 233.0166.

*3.4.39. 2-((E)-2-(Thiophen-2-yl)vinylthio)-5-chlorophenol (**7b**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.60 (s, 1H), 7.48–7.42 (m, 2H), 7.25 (d, J=8.5 Hz, 1H), 7.12 (d, J=2.0 Hz, 1H), 7.03–7.00 (m, 1H), 6.92–6.88 (m, 2H), 6.88 (d, J=12.5 Hz, 1H), 6.78 (d, J=15.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.2, 141.9, 133.3, 132.4, 131.5, 130.6, 129.0, 127.0, 126.5, 126.4, 121.7, 121.0, 120.7, 116.2. ESI-HRMS m/z: calcd for $C_{12}H_8ClOS_2^-$ $[M-H]^-$: 266.9783; found 266.9776.

*3.4.40. 2-((E)-2-(Thiophen-2-yl)vinylthio)-5-bromophenol (**7c**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.60 (s, 1H), 7.44 (d, J=5.0 Hz, 1H), 7.18 (d, J=9.0 Hz, 1H), 7.13 (d, J=3.0 Hz, 1H), 7.06–7.01 (m, 3H), 6.90–6.87 (d, J=10.5 Hz, 1H), 6.78 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.2, 141.9, 132.5, 129.0, 127.1, 126.6, 123.9, 121.5, 121.4, 119.0. ESI-HRMS m/z: calcd for $C_{12}H_8BrOS_2^-$ $[M-H]^-$: 310.9278; found 310.9271.

*3.4.41. 2-((E)-2-(Thiophen-2-yl)vinylthio)-5-(trifluoromethyl)phenol (**7d**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.83 (s, 1H), 7.49 (d, J=5.0 Hz, 1H), 7.39 (d, J=8.5 Hz, 1H), 7.22 (d, J=3.0 Hz, 1H), 7.18 (d, J=8.0 Hz, 1H), 7.13–7.19 (m, 2H), 7.06 (d, J=8.0 Hz, 1H), 6.89 (d, J=15.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.3, 141.6, 130.6, 129.4, 129.1, 128.9, 128.7, 128.4, 128.3, 127.8, 127.2, 126.4, 124.2, 119.5, 117.6, 111.9. ESI-HRMS m/z: calcd for $C_{13}H_8F_3OS_2^-$ $[M-H]^-$: 301.0047; found 301.0040.

*3.4.42. 2-((E)-2-(Thiophen-2-yl)vinylthio)-4-chlorophenol (**7e**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.38 (s, 1H), 7.46 (d, J=5.0 Hz, 1H), 7.18–7.15 (m, 3H), 7.14 (d, J=2.0 Hz, 1H), 7.04 (d, J=8.5 Hz, 1H), 6.99 (d, J=15.5 Hz, 1H), 6.88 (d, J=13.5 Hz, 1H), 6.86 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 154.8, 141.7, 129.1, 129.0, 128.6, 127.9, 127.4, 126.9, 124.4, 120.7, 117.6. ESI-HRMS m/z: calcd for $C_{12}H_8ClOS_2^-$ $[M-H]^-$: 266.9783; found 266.9776.

*3.4.43. 2-((E)-2-(Thiophen-2-yl)vinylthio)-3-chlorophenol (**7f**).* Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.51 (s, 1H), 7.34 (d, J=3.0 Hz, 1H), 7.30–7.26 (m, 1H), 7.07 (d, J=8.0 Hz, 1H), 6.96 (d, J=8.5 Hz, 3H), 6.68 (d, J=15.0 Hz, 1H), 6.37–6.34 (d, J=15.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.1, 142.3, 139.7, 132.6, 128.9, 125.8, 125.5, 124.4, 121.8, 120.9, 116.9, 116.2. ESI-HRMS m/z: calcd for $C_{12}H_8ClOS_2^-$ $[M-H]^-$: 266.9783; found 266.9776.

*3.4.44. 2-((E)-2-(Benzo[d][1,3]dioxol-5-yl)vinylsulfinyl)-5-bromophenol (**8**).* A mixture of 2-((*E*)-2-(benzo[*d*][1,3]dioxol-5-yl) vinylthio)-5-bromophenol **3t** (175 mg, 0.5 mmol), AcOH (44 mg, 0.5 mmol), and 30% H_2O_2 (2 mL) was stirred in air at 25 °C for 5 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL) and the solution was extracted with ethyl acetate (3×10 mL). The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel to afford **8** (174 mg, 95% yield). The spectroscopic data of all the products are presented below. Colorless liquid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.11 (s, 1H), 7.68 (s, 1H), 7.47 (d, J=8.5 Hz, 1H), 7.30 (d, J=12.0 Hz, 1H), 7.25 (d, J=6.0 Hz, 2H), 7.22 (d, J=1.5 Hz, 2H), 6.92 (d, J=9.0 Hz, 1H), 6.07 (d, J=18.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.0, 149.7, 149.2, 136.0, 130.8, 129.4, 127.1, 125.7, 125.0, 124.1, 119.6, 109.6, 108.0, 102.6. ESI-HRMS m/z: calcd for $C_{15}H_{10}BrO_4S^-$ $[M-H]^-$: 364.9561; found 364.9554.

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Supplementary data

These data include ^{1}H and ^{13}C NMR spectra of the most important compounds described in this article. Supplementary data

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