Visible-Light-Promoted Direct Amination of Phenols via Oxidative Cross-Dehydrogenative Coupling Reaction

Yating Zhao, Binbin Huang, Chao Yang, and Wujiong Xia*

State Key Lab of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150080, China
E-mail: xiawj@hit.edu.cn

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I. General information

Chemicals were purchased from commercial sources without further purification. Glassware was dried in oven and cooled before use. All reactions were performed with solvents dried by anhydrous MgSO\(_4\). Reactions were monitored by TLC and visualized by UV lamp (254nm) and stained with ethanolic solution of concentrated sulfuric acid or potassium permanganate. Yields generally referred to chromatographically isolated yields, unless otherwise noted.

\(^1\)H NMR (400MHz) and \(^{13}\)C NMR (100 MHz) spectra are recorded on a Bruker AV-400 spectrometer in CDCl\(_3\) or DMSO-d\(_6\). For \(^1\)H NMR (400MHz), CDCl\(_3\) (\(\delta=7.26\) ppm) and DMSO-d\(_6\) (\(\delta=2.5\) ppm) served as internal standard and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (in Hz), and integration. For \(^{13}\)C NMR (100 MHz), CDCl\(_3\) (\(\delta=77.25\) ppm) and DMSO-d\(_6\) (\(\delta=39.46\) ppm) was used as internal standard. GC-MS analysis was performed on 7890A-5975C/Agilent. HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

Starting materials for CDC-amination were generally commercially available. The TMSN\(_4\)-protected phenols were prepared according to previous literature.\(^{[1]}\) 1-(10H-phenothiazin-2-yl)ethanol, used for generation of \(^3\)p in CDC-amination, was prepared by the classical NaBH\(_4\) reduction with commercial 1-(10H-phenothiazin-2-yl)ethanone.

II. General Procedure for CDC-amination of Phenol

A typical procedure is as follows, unless otherwise noted. Phenothiazine (0.4 mmol), phenol (0.8 mmol) or TMS-protected phenol (0.8 mmol) and K\(_2\)S\(_2\)O\(_8\) (1.2 mmol) were combined in dried flask. 8 ml MeCN dried with anhydrous MgSO\(_4\) was added via syringe. The flask was capped with a rubber that pierced through by a needle, and then exposed to 8 W blue LED strips for irradiation in air. After reaction, the mixture was diluted with DCM and filtered through an inch of silica gel. Then the filtrate was concentrated for purification by chromatography on silica gel to afford product.
### Characterizations of Amination Products

#### Compound 3a.
Isolated yield: 32%, white solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 4-methoxyphenol (99 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: EtOAc, 5:1) to provide the title compound with 41 mg. When 4-methoxyphenol was replaced with the TMSN-protected one (156 mg, 0.8 mmol), the title compound was obtained in 30% yield (38 mg).

$^1$H NMR (600 MHz, DMSO): \(\delta\) 9.47 (s, 1H), 7.07 (dd, \(J = 8.9, 2.1\) Hz, 1H), 6.99 (dd, \(J = 4.3, 2.7\) Hz, 3H), 6.93 – 6.88 (m, 2H), 6.82 – 6.78 (m, 3H), 6.09 (d, \(J = 8.2\) Hz, 2H), 3.70 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): \(\delta\) 153.46, 149.23, 142.63, 127.24, 126.39, 126.14, 122.17, 118.20, 117.75, 116.17, 115.33, 115.31, 55.49; IR (neat, cm$^{-1}$): \(v\): 3478, 1500, 1461, 1306, 813, 745; GCNMS (EI): 321.2, 289.1, 273.1, 257.1, 198.1, 167.1; HRMS (m/z): [M]$^+$ calculated for C$_{19}$H$_{15}$NO$_2$S, 321.0823; found 321.0828.

#### Compound 3b.
Isolated yield: 97%, white solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), sesamol (110 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 1.5 h. The crude product was purified by flash column chromatography (petroleum: EtOAc, 5:1) to provide the title compound with 129 mg. When phenol was replaced with the TMS-protected one (168 mg, 0.8 mmol), the title compound was obtained in 95% yield (127 mg).

$^1$H NMR (400 MHz, DMSO): \(\delta\) 9.61 (s, 1H), 6.95 (dd, \(J = 7.5, 1.4\) Hz, 2H), 6.93 – 6.86 (m, 2H), 6.81 (s, 1H), 6.78 (td, \(J = 7.4, 1.1\) Hz, 2H), 6.71 (s, 1H), 6.17 – 6.10 (m, 2H), 6.04 (s, 2H); $^{13}$C NMR (151 MHz, DMSO): \(\delta\) 150.33, 147.86, 142.80, 140.87, 127.19, 126.07, 122.08, 118.17, 117.84, 115.29, 110.18, 101.50, 98.58; IR (neat, cm$^{-1}$): \(v\): 3413, 1460, 1305, 1217, 1034, 745; GC-MS (EI): 335.1, 301.1, 276.1, 244.1, 198.1, 167.2; HRMS (m/z): [M]$^+$ calculated for C$_{19}$H$_{13}$NO$_3$S, 335.0616; found 335.0613.
**Compound 3c.** Isolated yield: 95%, dark foamy solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 1.5 h. The crude product was purified by flash column chromatography (petroleum: EtOAc, 5:1) to provide the title compound with 133 mg. $^1$H NMR (600 MHz, DMSO): δ 9.48 (s, 1H), 6.97 (dd, $J = 7.5, 1.3$ Hz, 2H), 6.93 – 6.86 (m, 2H), 6.78 (dd, $J = 10.7, 4.1$ Hz, 2H), 6.76 (s, 1H), 6.74 (s, 1H), 6.16 – 6.09 (m, 2H), 3.81 (s, 3H), 3.67 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): δ 149.69, 149.36, 143.02, 142.90, 127.20, 126.06, 122.03, 118.25, 116.94, 115.43, 113.87, 113.47, 56.06, 55.44; IR (neat, cm$^{-1}$): v: 3395, 1507, 1461, 1234, 914, 744; GC-MS (EI): 351.2, 335.1, 319.1, 276.1, 198.1, 167.1; HRMS (m/z): [M+H]$^+$ calculated for C$_{20}$H$_{18}$NO$_3$S, 352.1007; found 352.1009.

**Compound 3d.** Isolated yield: 61%, white sticky solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 3,4-dimethylphenol (97 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: DCM, 2:1) to provide the title compound with 77 mg. $^1$H NMR (400 MHz, DMSO): δ 9.55 (s, 1H), 7.00 – 6.93 (m, 3H), 6.91 (s, 1H), 6.90 – 6.84 (m, 2H), 6.77 (t, $J = 7.0$ Hz, 2H), 6.08 (d, $J = 8.2$ Hz, 2H), 2.23 (s, 3H), 2.15 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): δ 153.12, 142.96, 138.23, 131.39, 128.67, 127.16, 126.07, 123.62, 122.00, 118.27, 118.20, 115.44, 19.38, 18.26; IR (neat, cm$^{-1}$): v: 3410, 2994, 1495, 1460, 1306, 744; GC-MS (EI): 319.2, 303.1, 286.1, 271.1, 198.1, 167.1; HRMS (m/z): [M]$^+$ calculated for C$_{20}$H$_{17}$NOS, 319.1031; found 319.1028.

**Compound 3e.** Isolated yield: 41%, white solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 4-ethoxyphenol (110 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product
was purified by flash column chromatography (petrol: EtOAc, 5:1) to provide the title compound with 54 mg. $^1$H NMR (400 MHz, DMSO): $\delta$ 9.43 (s, 1H), 7.05 (d, $J = 8.9$ Hz, 1H), 7.00 – 6.94 (m, 3H), 6.83 – 6.74 (m, 3H), 3.95 (q, $J = 6.9$ Hz, 2H), 1.27 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 152.68, 149.10, 142.62, 127.22, 126.32, 126.12, 122.14, 118.14, 117.77, 116.72, 115.96, 115.29, 63.48, 14.70; IR (neat, cm$^{-1}$): v: 3386, 2913, 1500, 1460, 1231, 743; GCNMS (EI): 335.2, 306.1, 289.1, 273.1, 198.1, 167.1; HRMS (m/z): [M]$^+$ calculated for C$_{20}$H$_{17}$NO$_2$S, 335.0980; found 335.0987.

**Compound 3f**. Isolated yield: 45%, white solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 4-(benzyloxy)phenol (160 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 3 h. The crude product was purified by flash column chromatography (petroleum: EtOAc, 5:1) to provide the title compound with 71 mg. When phenol was replaced with the TMSN-protected one (217 mg, 0.8 mmol), the title compound was obtained in 34% yield (53 mg). $^1$H NMR (400 MHz, DMSO): $\delta$ 9.48 (s, 1H), 7.42 (d, $J = 7.0$ Hz, 2H), 7.36 (t, $J = 7.3$ Hz, 2H), 7.32 (d, $J = 7.0$ Hz, 1H), 7.06 (s, 2H), 6.98 (dd, $J = 7.5$, 1.4 Hz, 2H), 6.92 – 6.85 (m, 3H), 6.79 (t, $J = 7.0$ Hz, 2H), 6.07 (d, $J = 7.6$ Hz, 2H), 5.03 (s, 2H); $^{13}$C NMR (151 MHz, DMSO) $\delta$ 152.41, 149.40, 142.62, 137.09, 128.32, 127.78, 127.73, 127.21, 126.30, 126.13, 122.16, 118.22, 117.81, 117.35, 116.61, 115.32, 69.86; IR (neat, cm$^{-1}$): v: 3408, 3062, 1500, 1462, 815, 746; GCNMS (EI): 397.2, 306.1, 289.1, 273.1, 199.1, 91.2; HRMS (m/z): [M+K]$^+$ calculated for C$_{25}$H$_{19}$KNO$_2$S, 436.0774; found 436.0772.

**Compound 3g**. Isolated yield: 67%, white foamy to sticky solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 2-chloro-4-methoxyphenol (126 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: DCM, 3:1) to provide the title compound with 95 mg. When phenol was replaced with the TMS-protected one (184 mg, 0.8 mmol), the title compound was obtained in 51% yield (72 mg). $^1$H NMR (400 MHz, DMSO): $\delta$ 9.48 (s, 1H), 7.21 (d, $J = 3.0$ Hz, 1H), 6.99 (s, 1H), 6.97 (d, $J = 1.3$ Hz, 1H), 6.91 (dd, $J = 10.9$, 4.5 Hz, 2H), 6.85 (d, $J = 3.0$ Hz, 1H), 6.80 (t, $J = 7.4$ Hz, 2H), 6.03 (d, $J = 8.1$ Hz, 2H), 3.73 (s, 3H); $^{13}$C NMR (151 MHz, DMSO) $\delta$ 153.33, 145.59, 142.10, 128.94, 127.73, 127.21, 126.13, 122.16, 118.22, 117.35, 116.61, 115.32, 69.86; IR (neat, cm$^{-1}$): v: 3484, 1581, 1461, 1229, 1041, 758; GCNMS (EI): 355.2, 323.1, 287.1, 198.1, 167.1, 152.4; HRMS (m/z):
[M+H]$^+$ calculated for C$_{19}$H$_{15}$ClNO$_2$S, 356.0512; found 356.0519.

**Compound 3h.** Isolated yield: 69%, white foamy solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 2-methoxyphenol (99 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 88 mg. $^1$H NMR (400 MHz, DMSO): $\delta$ 9.43 (s, 1H), 7.05 – 6.98 (m, 3H), 6.94 – 6.87 (m, 3H), 6.81 (t, $J$ = 7.1 Hz, 3H), 6.22 (d, $J$ = 8.2 Hz, 2H), 3.77 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 149.37, 146.60, 144.04, 130.93, 127.22, 126.34, 122.92, 118.37, 116.67, 115.53, 113.97, 55.78; IR (neat, cm$^{-1}$): $\nu$: 3404, 1585, 1507, 1460, 1305, 746; GCNMS (EI): 321.2, 306.1, 278.1, 260.1, 198.1, 130.4; HRMS ($m/z$): [M+Na]$^+$ calculated for C$_{19}$H$_{15}$NaNO$_2$S, 344.0721; found 344.0725.

![Chemical structure of Compound 3h](image)

**Compound 3i.** Isolated yield: 52%, white foamy solid. Prepared following the general procedure using phenothiazine (40 mg, 0.2 mmol), 2-methoxy-4-methylphenol (55 mg, 0.4 mmol) and K$_2$S$_2$O$_8$ (162 mg, 0.6 mmol) in MeCN (4.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: DCM, 2:1) to provide the title compound with 34 mg. $^1$H NMR (400 MHz, DMSO): $\delta$ 8.93 (s, 1H), 7.00 – 6.94 (m, 3H), 6.91 – 6.84 (m, 2H), 6.77 (td, $J$ = 7.4, 1.0 Hz, 2H), 6.63 (s, 1H), 6.07 (dd, $J$ = 8.2, 0.8 Hz, 2H), 3.87 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 148.85, 142.62, 142.39, 129.49, 127.19, 126.18, 126.09, 122.18, 122.07, 118.20, 115.36, 113.07, 55.91, 20.51; IR (neat, cm$^{-1}$): $\nu$: 3403, 1584, 1500, 1460, 1234, 742; GC-MS (EI): 335.1, 319.1, 303.1, 287.1, 198.0, 167.1; HRMS ($m/z$): [M+H]$^+$ calculated for C$_{20}$H$_{18}$NO$_2$S, 336.1058; found 336.1056.

![Chemical structure of Compound 3i](image)

**Compound 3j.** Isolated yield: 93%, white solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 2-naphthol (115 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol)
in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 126 mg. When phenol was replaced with the TMS-protected one (172 mg, 0.8 mmol), the title compound was obtained in 86% yield (117 mg). 

\[ \text{H NMR (400 MHz, DMSO)} \delta 10.34 (s, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.97 - 7.91 (m, 2H), 7.45 (t, J = 8.6 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.2 Hz, 2H), 6.86 - 6.74 (m, 4H), 6.01 (d, J = 7.8 Hz, 2H); \]

\[ \text{13C NMR (151 MHz, DMSO): } \delta 153.84, 142.13, 131.60, 130.30, 129.15, 128.44, 127.60, 127.36, 126.26, 123.52, 122.36, 120.92, 118.91, 117.84, 115.30; \]

\[ \text{IR (neat, cm}^{-1}) : \nu: 3415, 1598, 1461, 1307, 817, 743; \]

\[ \text{GC-MS (EI): } 341.2, 280.1, 198.1, 144.2, 115.1; \]

\[ \text{HRMS (m/z): } [M]^+ \text{ calculated for } C_{22}H_{15}NO_S, 341.0874; \text{ found 341.0877.} \]

**Compound 3k.** Isolated yield: 89%, white fluffy solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 2,6-dihydroxynaphthalene (128 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 126 mg. 

\[ \text{H NMR (400 MHz, DMSO)} \delta 10.11 (s, 1H), 9.75 (s, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 6.99 (dd, J = 7.2, 1.9 Hz, 2H), 6.88 (dd, J = 8.7, 2.4 Hz, 1H), 6.78 (pd, J = 7.3, 1.7 Hz, 4H), 5.97 (dd, J = 7.8, 1.6 Hz, 2H); \]

\[ \text{13C NMR (151 MHz, DMSO): } \delta 156.84, 153.91, 141.89, 133.49, 130.23, 129.97, 127.32, 126.12, 123.74, 122.17, 118.50, 116.26, 115.90, 115.21, 115.08, 102.75; \]

\[ \text{IR (neat, cm}^{-1}) : \nu: 3425, 3241, 1683, 1460, 828, 745; \]

\[ \text{GC-MS (EI): } 357.1, 331.0, 315.1, 253.0, 199.0, 167.1; \]

\[ \text{HRMS (m/z): } [M]^+ \text{ calculated for } C_{22}H_{13}NO_2S, 357.0823; \text{ found 357.0828.} \]

**Compound 3l.** Isolated yield: 70%, white fluffy solid. Prepared following the general procedure using phenothiazine (40 mg, 0.2 mmol), 6-bromo-N$_2$N-naphthol (89 mg, 0.4 mmol) and K$_2$S$_2$O$_8$ (162 mg, 0.6 mmol) in MeCN (4.0 ml). The reaction mixture was stirred open to air for 2 h. The crude product was purified by flash column chromatography (petroleum: DCM, 2:1) to provide the title compound with 58 mg. 

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.07 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 9.0 Hz, 1H), 7.11 (d, J = 7.4 Hz, 2H), 6.88 (t, J = 7.4 Hz, 2H), 6.80 (t, J = 7.7 Hz, 2H), 6.38 (s, 1H), 6.10 (d, J = 8.1 Hz, 2H); \]

\[ \text{13C NMR (151 MHz, CDCl}_3\text{)} \delta 152.16, 142.35, 130.93, 130.91, 130.73, 129.82, 127.50, 127.00, 124.82,
Compound 3m. Isolated yield: 52%, brown foamy solid. Prepared following the general procedure using phenothiazine (80 mg, 0.4 mmol), 1-naphthol (115 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 12 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 70 mg. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.31 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.05 – 6.93 (m, 3H), 6.73 (dd, J = 17.0, 7.4, 1.3 Hz, 4H), 6.05 (dd, J = 7.9, 1.0 Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 152.10, 127.78, 126.93, 126.48, 126.02, 123.72, 122.75, 122.32, 115.81, 108.93, 77.28, 77.07, 76.86; IR (neat, cm$^{-1}$): $\nu$: 3398, 3061, 1589, 1461, 1305, 744; GCNMS (EI): 341.1, 308.1, 280.1, 199.1, 167.1, 115.1; HRMS (m/z): [M]$^+$ calculated for C$_{22}$H$_{15}$NOS, 341.0874; found 341.0873.

Compound 3n. Isolated yield: 96%, white solid. Prepared following the general procedure using phenoxazine (73 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 12 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 128 mg. $^1$H NMR (600 MHz, DMSO): $\delta$ 9.36 (s, 1H), 6.77 (s, 1H), 6.70 (s, 1H), 6.63 (ddd, J = 18.7, 11.7, 7.5 Hz, 6H), 5.88 (d, J = 7.6 Hz, 2H), 3.78 (s, 3H), 3.66 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 149.76, 149.16, 143.39, 142.87, 133.70, 123.55, 120.77, 114.81, 114.04, 112.82, 101.86, 56.13, 55.41; IR (neat, cm$^{-1}$): $\nu$: 3425, 1588, 1487, 1270, 1202, 744; GC-MS (EI): 335.2, 319.2, 291.1, 248.1, 220.1, 182.1; HRMS (m/z): [M]$^+$ calculated for C$_{20}$H$_{17}$NO$_4$, 335.1158; found 335.1159.
**Compound 3o.** Isolated yield: 82%, dark brown viscous oil. Prepared following the general procedure using 2-(ethylthio)-10H-phenothiazine (103 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 1.5 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 134 mg.

$^1$H NMR (400 MHz, DMSO): δ 9.53 (s, 1H), 7.01 – 6.86 (m, 3H), 6.82 – 6.70 (m, 4H), 6.12 (dd, $J = 8.2$, 0.9 Hz, 1H), 6.05 (d, $J = 1.8$ Hz, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 2.74 (q, $J = 7.3$ Hz, 2H), 1.11 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (151 MHz, DMSO): δ 149.81, 149.30, 143.35, 142.93, 142.73, 134.75, 127.25, 126.49, 126.11, 122.24, 121.65, 118.29, 116.61, 115.84, 115.63, 113.69, 101.35, 56.07, 55.46, 26.45, 14.15; IR (neat, cm$^{-1}$): v: 3391, 1508, 1461, 1385, 1233, 749; GC-MS (EI): 411.2, 367.1, 335.1, 317.1, 259.1, 230.0, 198.1; HRMS (m/z): [M]$^+$ calculated for C$_{22}$H$_{21}$NO$_3$S$_2$, 411.0963; found 411.0963.

**Compound 3p.** Isolated yield: 88%, dark red viscous oil. Prepared following the general procedure using 1-(10H-phenothiazin-2-yl)ethanol (97 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 1.5 h. The crude product was purified by flash column chromatography (petroleum: EA, 2:1) to provide the title compound with 139 mg.

$^1$H NMR (400 MHz, DMSO): δ 9.46 (s, 1H), 6.96 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.89 (ddd, $J = 9.6$, 6.8, 2.4 Hz, 2H), 6.80 – 6.73 (m, 4H), 6.24 (s, 1H), 6.10 (d, $J = 8.2$ Hz, 1H), 4.98 (d, $J = 4.0$ Hz, 1H), 4.49 – 4.35 (m, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 1.14 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (151 MHz, DMSO): δ 149.59, 149.48, 146.68, 143.25, 142.91, 142.72, 127.10 126.03, 125.66, 121.93, 119.15, 118.55, 117.06, 116.07, 115.48, 114.01, 112.81, 101.31, 74.78, 56.06, 55.38, 25.75; IR (neat, cm$^{-1}$): v: 3415, 3370, 1508, 1463, 1236, 748; GC-MS (EI): 395.2, 377.2, 335.1, 318.1, 240.1, 198.1; HRMS (m/z): [M+H]$^+$ calculated for C$_{22}$H$_{22}$NO$_4$S, 396.1270; found 396.1270.
**Compound 3q.** Isolated yield: 90%, white foamy to sticky solid. Prepared following the general procedure using 2-chloro-10H-phenothiazine (93 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 48 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 138 mg. $^1$H NMR (600 MHz, DMSO): δ 9.63 (s, 1H), 7.02 – 6.95 (m, 2H), 6.91 (dd, $J = 11.4, 4.1$ Hz, 1H), 6.80 (ddd, $J = 22.4, 10.1, 1.7$ Hz, 4H), 6.15 – 6.10 (m, 1H), 6.06 (d, $J = 2.2$ Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): δ 149.96, 149.12, 144.40, 143.02, 142.28, 131.67, 127.45, 127.30, 126.19, 122.67, 121.53, 118.01, 117.51, 116.26, 115.78, 114.76, 113.40, 101.45, 56.02, 55.42; IR (neat, cm$^{-1}$): ν: 3382, 1506, 1460, 1384, 1238, 746; GC-MS (EI): 385.2, 353.1, 335.1, 317.1, 232.1, 198.1; HRMS ($m/z$): [M]$^+$ calculated for C$_{20}$H$_{16}$ClNO$_3$S, 385.0539; found 385.0537.

**Compound 3r.** Isolated yield: 91%, red sticky solid. Prepared following the general procedure using 2-bromo-10H-phenothiazine (55 mg, 0.2 mmol), 3,4-dimethoxyphenol (62 mg, 0.4 mmol) and K$_2$S$_2$O$_8$ (162 mg, 0.6 mmol) in MeCN (4.0 ml). The reaction mixture was stirred open to air for 24 h. The crude product was purified by flash column chromatography (petroleum: EA, 3:1) to provide the title compound with 78 mg. $^1$H NMR (400 MHz, DMSO): δ 9.52 (s, 1H), 7.17 (d, $J = 2.3$ Hz, 1H), 7.06 (dd, $J = 8.8, 2.3$ Hz, 1H), 6.99 – 6.95 (m, 1H), 6.94 – 6.88 (m, 1H), 6.80 (dd, $J = 7.5, 1.0$ Hz, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 6.11 (dd, $J = 8.2, 0.8$ Hz, 1H), 6.02 (d, $J = 8.8$ Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): δ 149.84, 149.15, 142.98, 142.52, 129.71, 127.76, 127.49, 126.15, 122.37, 120.87, 117.52, 116.95, 116.46, 115.56, 113.59, 113.04, 101.49, 56.05, 55.43; IR (neat, cm$^{-1}$): ν: 3414, 1506, 1458, 1237, 747, 668; GC-MS (EI): 431.2, 350.2, 335.1, 278.1, 198.1, 153.1; HRMS ($m/z$): [M]$^+$ calculated for C$_{20}$H$_{16}$BrNO$_3$S, 429.0034; found 429.0028.
**Compound 3s.** Isolated yield: 94%, yellow foamy solid. Prepared following the general procedure using 1-(10H-phenothiazin-2-yl)ethanone (96 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 48 h. The crude product was purified by flash column chromatography (petroleum: DCM: EA, 8:10:1) to provide the title compound with 147 mg. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (dd, $J$ = 8.0, 1.7 Hz, 1H), 7.11 (d, $J$ = 7.9 Hz, 1H), 7.04 (dd, $J$ = 7.4, 1.7 Hz, 1H), 6.98 – 6.86 (m, 3H), 6.82 (s, 1H), 6.77 (s, 1H), 6.37 (dd, $J$ = 8.1, 1.3 Hz, 1H), 5.51 (s, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 196.88, 150.74, 147.65, 144.08, 143.61, 142.90, 127.85, 126.90, 126.70, 123.66, 123.53, 116.06, 114.54, 113.04, 100.97, 56.73, 56.11, 26.44; IR (neat, cm$^{-1}$): $\nu$: 3413, 1678, 1509, 1465, 1236, 748; GC-MS (EI): 393.2, 377.1, 335.1, 318.1, 240.1, 198.1; HRMS (m/z): [M+H]$^+$ calculated for C$_{22}$H$_{20}$NO$_4$S, 394.1113; found 394.1117.

**Compound 3t.** Isolated yield: 94%, yellow foamy solid. Prepared following the general procedure using 10H-phenothiazine-2-carbonitrile (89 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 72 h. The crude product was purified by flash column chromatography (petroleum: DCM, 5:1) to provide the title compound with 120 mg, with 87% recovery of 10H-phenothiazine-2-carbonitrile (12 mg). $^1$H NMR (400 MHz, DMSO): $\delta$ 9.62 (s, 1H), 7.19 (dt, $J$ = 17.2, 4.7 Hz, 2H), 6.99 (dd, $J$ = 7.5, 1.4 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.83 (td, $J$ = 7.5, 1.0 Hz, 1H), 6.80 (s, 1H), 6.76 (s, 1H), 6.21 (d, $J$ = 1.4 Hz, 1H), 6.09 (d, $J$ = 7.5 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 150.07, 148.98, 143.51, 143.15, 141.88, 127.90, 127.07, 126.28, 126.04, 125.60, 122.95, 118.78, 117.02, 116.80, 115.85, 115.72, 113.21, 109.45, 101.59, 56.02, 55.42; IR (neat, cm$^{-1}$): $\nu$: 3426, 2224, 1507, 1463, 1235, 745; GC-MS (EI): 376.2, 361.1, 344.1, 301.1, 223.1, 192.1; HRMS (m/z): [M]$^+$ calculated for C$_{21}$H$_{16}$N$_2$O$_3$S, 376.0882; found 376.0882.
**Compound 3u.** Isolated yield: 86%, dark viscous oil. Prepared following the general procedure using 2-(trifluoromethyl)-10H-phenothiazine (106 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 72 h. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide the title compound with 122 mg, with 85% recovery of 2-(trifluoromethyl)-10H-phenothiazine (16 mg). $^1$H NMR (400 MHz, DMSO): $\delta$ 9.66 (s, 1H), 7.19 (d, $J = 7.9$ Hz, 1H), 7.10 (dd, $J = 8.0$, 1.1 Hz, 1H), 7.00 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.84 (dd, $J = 7.5$, 1.2 Hz, 1H), 6.81 (d, $J = 2.9$ Hz, 1H), 6.78 (s, 1H), 6.31 (d, $J = 1.4$ Hz, 1H), 6.11 (dd, $J = 8.2$, 1.0 Hz, 1H), 3.83 (s, 3H), 3.67 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 150.05, 149.23, 143.61, 143.07, 142.26, 127.92, 127.72, 126.85, 126.25, 124.84, 124.19 (d, $J = 1.5$ Hz), 123.04, 122.85, 118.87-118.00 (m), 117.41, 116.00, 115.85, 113.36, 110.85 (q, $J = 4.1$ Hz), 101.33, 56.03, 55.41, 54.86; $^{19}$F NMR (376 MHz, DMSO): $\delta$ -61.60; IR (neat, cm$^{-1}$): $\nu$: 3408, 1509, 1468, 1120, 955, 748; GC-MS (EI): 419.2, 266.2, 235.1, 209.6, 95.0, 69.0; HRMS (m/z): [M]$^+$ calculated for C$_{21}$H$_{16}$F$_3$NO$_3$S, 419.0803; found 419.0803.

**Compound 3v.** Isolated yield: 79%, dark viscous oil. Prepared following the general procedure using 2-methoxy-10H-phenothiazine (91 mg, 0.4 mmol), 3,4-dimethoxyphenol (123 mg, 0.8 mmol) and K$_2$S$_2$O$_8$ (324 mg, 1.2 mmol) in MeCN (8.0 ml). The reaction mixture was stirred open to air for 1 h. The crude product was purified by flash column chromatography (petroleum: EA, 4:1) to provide the title compound with 48 mg, with 66% recovery of 2-methoxy-10H-phenothiazine (31 mg). $^1$H NMR (400 MHz, DMSO): $\delta$ 8.94 (s, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.99 – 6.87 (m, 5H), 6.83 – 6.77 (m, 2H), 6.75 (d, $J = 7.9$ Hz, 1H), 6.67 (s, 1H), 6.45 (d, $J = 8.4$ Hz, 1H), 6.12 (d, $J = 8.2$ Hz, 1H), 5.66 (s, 1H), 3.70 (s, 3H), 3.57 (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta$ 158.98, 156.64, 144.11, 144.07, 142.54, 141.40, 128.37, 127.60, 127.15, 126.73, 126.28, 126.14, 122.28, 122.26, 121.29, 118.93, 116.55, 115.34, 114.69, 109.36, 108.12, 106.26, 102.97, 99.66, 55.51, 55.03; IR (neat, cm$^{-1}$): $\nu$: 3439, 2925, 1463, 1258, 1207, 745; HRMS (m/z): [M+Na]$^+$ calculated for C$_{26}$H$_{20}$N$_2$NaO$_2$S$_2$, 479.0864; found 479.0860.
### Gram scale reaction

Phenothiazine **1a** (0.50 g, 2.5 mmol), TMS-protected sesamol (1.05 g, 5.0 mmol) and K$_2$S$_2$O$_8$ (2.02 g, 7.5 mmol) were combined in dried flask. 30 ml MeCN was added via syringe. The flask was capped with a rubber that pierced through by a needle, and then exposed to 8 W blue LED strips for irradiation in air. After reaction for 5 h, the mixture was diluted with DCM and filtered through an inch of silica gel. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide **3b** as white solid in 93% yield (0.77 g).

### Control Experiments

Phenothiazine **1a** (40 mg, 0.2 mmol), phenol **2a** (50 mg, 0.4 mmol), prop-1-en-2-ylbenzene **9** (70 mg, 0.6 mmol) and K$_2$S$_2$O$_8$ (162 mg, 0.6 mmol) were combined in dried flask. 4 ml MeCN was added via syringe. The flask was capped with a rubber that pierced through by a needle, and then exposed to 8 W blue LED strips for irradiation in air. After reaction for 72 h, the mixture was diluted with DCM and filtered through an inch of silica gel. Then the filtrate was used for GC-MS analysis.

GC-MS (**10**) calculated for, 240.1150; found 240.2 as Fig. S1 showed.$^{[1]}$

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$^{[1]}$
Phenothiazine \(1a\) (40 mg, 0.2 mmol), phenol \(2a\) (50 mg, 0.4 mmol), TEMPO (62 mg, 0.4 mmol) and \(K_2S_2O_8\) (162 mg, 0.6 mmol) were combined in dried flask. 4 ml MeCN was added via syringe. The flask was capped with a rubber that pierced through by a needle, and then exposed to 8 W blue LED strips for irradiation in air. After reaction for 1h, the mixture was diluted with DCM and filtered through an inch of silica gel. The crude product was purified by flash column chromatography (petroleum: EA, 5:1) to provide \(3a\) as white solid in 62% yield (39 mg).

**Fig S1.** Detected GC-MS data for \(10\).
Phenothiazine 1v (46 mg, 0.2 mmol), phenol 2g (61 mg, 0.4 mmol), TEMPO (62 mg, 0.4 mmol) and K₂S₂O₈ (162 mg, 0.6 mmol) were combined in dried flask. 4 ml MeCN was added via syringe. The flask was capped with a rubber that pierced through by a needle, and then exposed to 8 W blue LED strips for irradiation in air. After reaction for 1h, the mixture was diluted with DCM and filtered through an inch of silica gel. The crude product was purified by flash column chromatography (petroleum: EA, 4:1) to provide 3v′ in 58% yield (44 mg).

**Compound 3v′**, dark viscous liquid. 

1H NMR (400 MHz, CDCl₃): δ 7.08 (d, J = 8.9 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.97 – 6.85 (m, 2H), 6.83 (s, 1H), 6.75 (s, 1H), 6.48 (d, J = 44.1 Hz, 2H), 6.04 (d, J = 2.2 Hz, 1H), 5.61 (s, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 3.63 (s, 3H);

13C NMR (151 MHz, DMSO): δ 158.99, 149.70, 149.22, 144.20, 142.86, 142.64, 127.02, 126.54, 126.02, 122.04, 118.78, 116.91, 115.52, 113.75, 109.29, 105.93, 103.40, 101.43, 56.06, 55.44, 55.00; IR (neat, cm⁻¹): ν: 3394, 1573, 1462, 1261, 1206, 745; GCNMS (EI): 381.2, 349.1, 333.1, 317.1, 228.1, 185.1; HRMS (m/z): [M]⁺ calculated for C₂₁H₁₉NO₄S, 381.1035; found 381.1039.

![Chemical Structure of 3v′](image)

Phenothiazine 1a (40 mg, 0.2 mmol), 2-phenyl-1H-indole 11 (77 mg, 0.4 mmol) and K₂S₂O₈ (162 mg, 0.6 mmol) were combined in dried flask. 4 ml MeCN was added via syringe. The flask was capped with a rubber that pierced through by a needle, and then exposed to 8 W blue LED strips for irradiation in air. After reaction for 4h, the mixture was diluted with DCM and filtered through an inch of silica gel. The crude product was purified by flash column chromatography (petroleum: DCM, 4:1) to provide 3w in 69% yield (53 mg).

**Compound 3w**, yellow solid. 

1H NMR (400 MHz, DMSO): δ 11.93 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 8.1 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.25 (t, J = 7.7 Hz, 2H), 7.07 (dd, J = 14.5, 7.6 Hz, 3H), 6.89 – 6.78 (m, 4H), 6.29 (d, J = 8.2 Hz, 2H);

13C NMR (151 MHz, DMSO): δ 143.43, 135.10, 132.98, 130.49, 128.88, 128.15, 127.47, 126.60, 126.17, 125.71, 122.78, 122.72, 120.26, 119.61, 117.99, 115.69, 112.62, 112.44; IR (neat, cm⁻¹): ν: 3440, 1586, 1459, 1297, 1250, 743; GC-MS (EI): 390.2, 358.2, 286.1, 254.1, 193.1, 178.2; HRMS (m/z): [M]⁺ calculated for C₂₆H₁₈NO₃S, 390.1191; found 390.1189.

Apart from the TMSNprotected sesamol, AcN and BzN protected sesamols were also examined in standard conditions, but failed to give corresponding CDC-amination products. Therefore we conducted Cyclic Voltammetry (CV) tests[3] for evaluation of their redox potentials. Cyclic Voltammograms were showed as Fig. S2.
Fig S2. Cyclic Voltammograms for sesamol and Ac-/Bz-protected sesamol.

**VI. Reference**


VII. NMR Spectra