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Note

# $O_2$-Mediated Dehydrogenative Phenoxazination of Phenols

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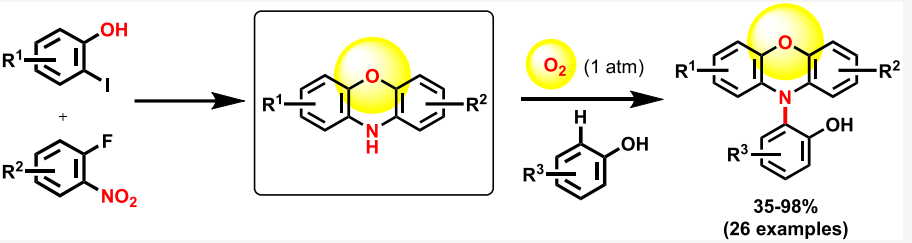
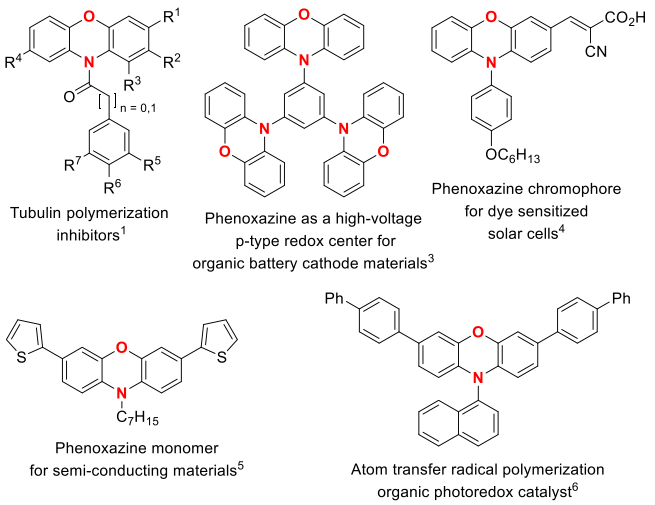



**ABSTRACT:** Phenoxazines, in particular N-arylated phenoxazines, represent an increasingly important scaffold in the material sciences. Moreover, the oxygen-gas-mediated dehydrogenative phenochalcogenazination concept of phenols has been developed and exemplified for X = sulfur and recently for X = selenium and tellurium. The smallest chalcogen, X = oxygen, is herein exemplified with various functional groups under a likewise trivial oxygen atmosphere.

Phenoxazines are promising therapeutic agents and scaffolds in medicinal chemistry.[1] Moreover, due to their photophysical and electronic properties[2] phenoxazines have been applied in organic battery cathode materials,[3] as dyes in dye-sensitized solar cells,[4] and as chemosensors.[5] A number of phenoxazine derivatives have also been developed as visible-light-absorbing organic photoredox catalysts (PCs) with excited-state reduction potentials rivalling those of highly reducing transition metal PCs (Scheme 1).[6] The sulfur- and oxygen-bridged diarylamines phenothiazine (PTZ) and phenoxazine (POZ) are among the most reactive radical transfer agents known.

**Scheme 1. Selected Important Phenoxazines**




Meanwhile, the dehydrogenative phenochalcogenazination of arenes is now a well-understood oxidative click reaction concept.[7] Indeed, phenochalcogenazines are known to possess relatively low oxidation potentials associated with N-centered radical persistency that allow their N−C bonds to be intercepted by certain classes of electron-rich arenes such as phenols, usually under mild oxidative conditions.[8]

The concept is known to operate well with all four chalcogens: sulfur, selenium, tellurium, and oxygen.[9] However, considerably fewer examples are known for phenoxazines (X = O, Scheme 2)[10] compared to phenothiazines (X = S).[11] Impressively, MacMillan and coauthors recently demonstrated that a phenoxazine derivative could be utilized to oxidatively click on tyrosine units within peptides scaffolds in view of their late-stage functionalization (Scheme 2).[10b] In this report, we show that the simple and highly sustainable oxygen gas-mediated[12] dehydrogenative phenochalcogenazination of phenols that we previously developed[8c] can also be applied to variously substituted electron-poor and electron-rich phenoxazines; moreover, it can be applied with a broad range of phenols (Scheme 2). This should facilitate the synthesis of some of the phenoxazine cores utilized in the above-mentioned technologies. Interestingly, relatively few phenoxazines are currently available at commercial suppliers, partly explaining why these have been less investigated

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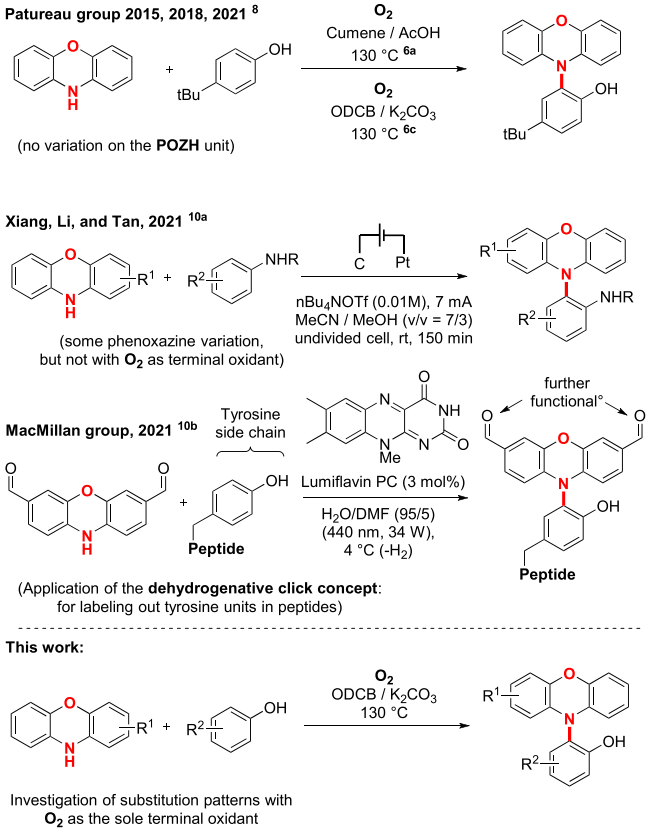
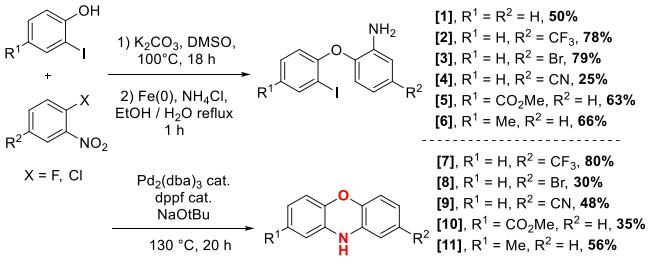
**Scheme 2. Dehydrogenative Phenoxazination**



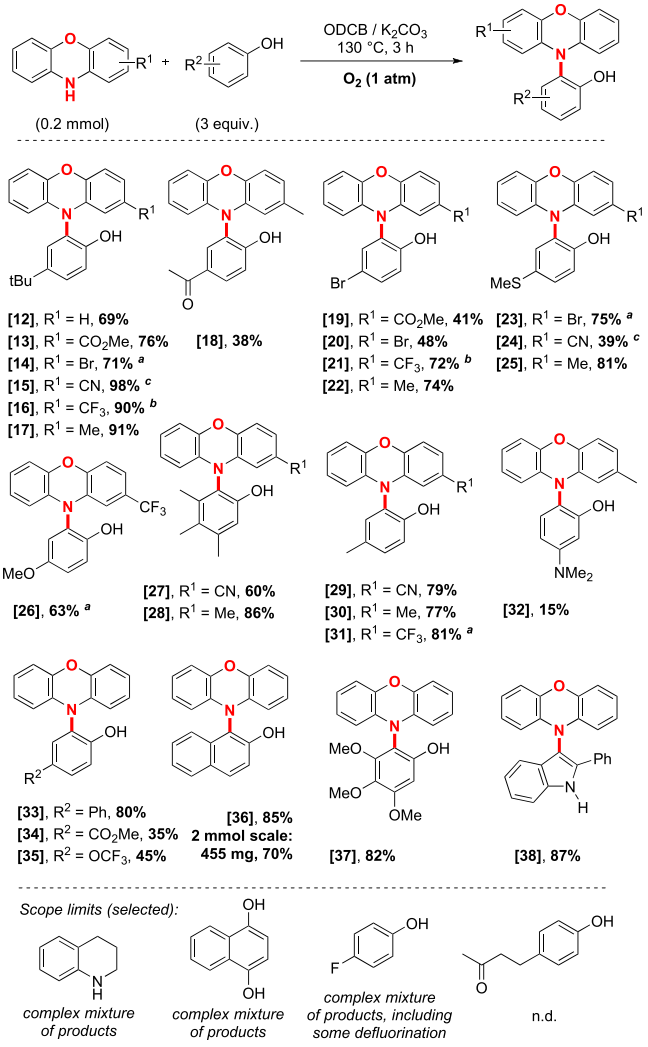

compared to phenothiazines. The method notably developed by Bolm and coauthors was therefore selected,[13] in combination with a Buchwald−Hartwig intramolecular C−N bond formation step,[14] as a robust route to access diversely functionalized phenoxazines (Scheme 3).

**Scheme 3. Access to Functionalized Phenoxazines**




Once we had a representative series of electron-poor and electron-rich phenoxazines in our hands, we proceeded to investigate their performance in the $O_2$-mediated dehydrogenative[15] phenoxazination of some diverse phenols under reactions conditions that were recently reported by us.[8c] The results are depicted in Scheme 4. As hoped for, a good functional group tolerance was observed on the phenoxazines as well as on the phenols. Indeed, electron-withdrawing ($CF_3$, $OCF_3$, Br, CN, and $CO_2Me$) were tolerated as well as electron-donating groups (MeO, MeS, Me, and *t*Bu) on both phenoxazines and phenols. Interestingly, 2-phenylindole also provided the C3−N phenoxazinated product in a high yield. Overall, it can be said that the scope width is similar to that observed for phenothiazines (X = S), likewise under oxygen

**Scheme 4. Substrate Scope and Isolated Yields**




[a]0.25 mmol scale. [b]0.5 mmol scale. [c]$K_2HPO_4$ was utilized instead of $K_2CO_3$. ODCB = *ortho*-dichlorobenzene.

atmosphere.[8] It is even broader than the scope for phenoselenazines (X = Se) and especially phenotellurazines (X = Te). Indeed, the latter tolerate only the most electron-rich phenols.[9] This finding is consistent with earlier initial rate investigations, which showed that phenoxazine (X = O) is the fastest azine substrate of the series compared to the other chalcogen congeners (X = S, Se, and Te).[8c] The proposed reaction mechanism is depicted in Scheme 5[8b] and is based on the EPR characterization of the persistent and neutral N-centered radical, which is produced upon the exposure of phenoxazine to $O_2$.[8c]

In conclusion, although phenoxazines are somewhat less available than phenothiazines, the increasing number and diversity of important applications associated with the former make them scaffolds of interest for organic chemistry and synthesis. We demonstrated herein that phenoxazines have a scope equally as broad as phenothiazines in the $O_2$-mediated dehydrogenative phenochalcogenazination of phenols, which should greatly facilitate the development of new technologies based on these structures.



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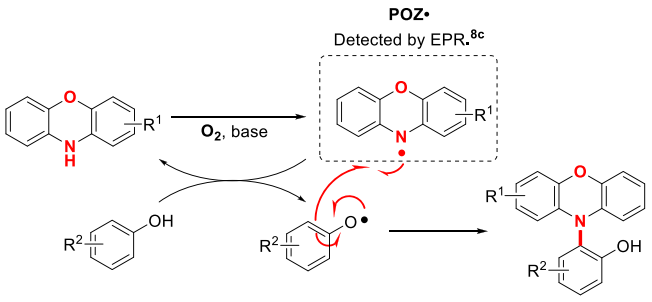
**Scheme 5. Proposed Mechanism**




## EXPERIMENTAL SECTION

All reactions were carried out in 20 mL reaction vials with sealed aluminous headspace caps under an atmosphere of $O_2$ unless otherwise specified. Aluminum blocks equipped with slots that accommodated the glass vial reactors, which were utilized for all experiments described herein that required heating. NMR spectra were recorded on a VNMRS 300, VNMRS 400, VNMRS 600, or Bruker Avance 400 or 600 system at 298 K. Chemical shifts are given in parts per million (ppm), and coupling constants ($J$) are given in hertz (Hz). Flash chromatography was performed on silica gel (60 M, 0.04−0.063 mm) using the standard technique. All the chemicals used for the synthesis were purchased from Sigma-Aldrich-Merck, ABCR, Alfa Aesar, TCI, Fisher Scientific, or chemPUR and were used directly. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer. IR spectra were recorded on a PerkinElmer 100 FT-IR spectrometer with an UATR Diamond KRS-5 unit.

**Important Safety Note.** The sustainable synthetic method reported herein operates under an atmosphere of $O_2$. Standard laboratory protection should therefore be utilized. We recommend not exceeding a 2 mmol scale in a single batch.

**Synthesis of 2-(2-Iodophenoxy)anilines.** *General Procedure GP1 by Bolm*[13] *and Satoh.*[16] 4-Substituted 2-iodophenol (1 equiv), 2-substituted 2-halo-nitrobenzene (1 equiv), and potassium carbonate (2 equiv) were weighed in a 20 mL vial and dissolved in 1.5 mL/mmol DMSO. The mixture was stirred for 18 h at 100 °C. After full consumption, the reaction was quenched with water. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were extracted three times with water and one time using a saturated sodium chloride solution and dried over magnesium sulfate. The solvent was removed under reduced pressure to obtain the resultant crude product. Iron powder (4 equiv) and ammonium chloride (0.5 equiv) were added to the crude product, and the mixture was dissolved in a 10 mL/mmol 1:3 water/ethanol mixture. The mixture was refluxed for 1 h. After full consumption, the solution was filtrated, and the filtrate was concentrated. To the mixture was added a saturated sodium bicarbonate solution, and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were extracted three times with water and one time with saturated sodium chloride solution and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with a mixture of *n*-hexane and ethyl acetate as the eluent to afford the corresponding product.

**Synthesis of 2-Substituted Phenoxazines.** *General procedure GP2 by Patureau.*[9] 2-(2-Iodophenoxy)aniline (1 equiv), NaO*t*Bu (1.4 equiv), $Pd_2(dba)_3$ (5 mol %), and DPPF (10 mol %) were weighed in a 20 mL vial and dissolved in toluene (2 mL/mmol). The reaction mixture was heated at 130 °C and stirred for 20 h. After cooling at RT, the mixture was filtrated over silica and washed with DCM and ethyl acetate. The crude product was concentrated on silica under reduced pressure, and the residue was purified by flash chromatography on silica gel with a mixture of *n*-hexane and ethyl acetate as the eluent to afford the corresponding product.

**$O_2$-Mediated Dehydrogenative Phenoxazination of Phenols.** *General procedure GP3.* Unless otherwise stated, phenoxazine (0.2 mmol), phenol (0.6 mmol, 3 equiv), and $K_2CO_3$ (28 mg, 0.2 mmol, 1 equiv) were dissolved in ODCB (0.6 mL) in a closed 20 mL vial, and $O_2$ was bubbled through the solution for about 2 min. The reaction mixture was stirred for 3 h (unless otherwise stated) at 130 °C. The crude product was purified directly by flash column chromatography to yield the title compound.

*2-(2-Iodophenoxy)aniline (**1**).* The title compound was synthesized according to the general procedure GP1 using 2-iodophenol (220.0 mg, 1.00 mmol) and 1-fluoro-2-nitrobenzene (141,1 mg, 1.00 mmol), providing 155.7 mg (0.50 mmol, 50% yield) of the product as a brown oil after purification by flash chromatography (ethyl acetate/*n*-hexane 3:7). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.85 (s, 1H), 7.26 (s, 1H), 7.00, (s, 2H), 6.83 (m, 4H), 6.74 (s,1H), 3.84 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 156.5, 143.0, 139.9, 138.6, 129.8, 125.4, 124.8, 120.0, 118.9, 117.0, 116.7, 87.3. Characterization data are in accordance with those from the literature.[17]

*2-(2-Iodophenoxy)-5-(trifluoromethyl)aniline (**2**).* The title compound was synthesized according to the general procedure GP1 using using 2-iodophenol (1.30 g, 6.22 mmol) and 1-fluoro-2-nitro-4-(trifluoromethyl)benzene (1.36 g, 6.5 mmol), providing 1.83 g (4.82 mmol, 78% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 3:7). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.88, (m, 1H), 7.32 (m, 1H), 7.06 (d, $J$ = 2.1 Hz, 1H), 6.92 (m, 3H), 6.72 (d, $J$ = 8.4 Hz, 1H), 4.08 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 155.2 (s, $C_{quat}$) 145.4 (s, $C_{quat}$), 140.0 (s, $C_{quat}$), 139.7 (s, CH), 130.2 (s, CH), 126.2 (s, CH), 124.6 (q, $^2J_{CF}$ = 30.7 Hz, $C_{quat}$), 124.5 (q, $^1J_{CF}$ = 271.4 Hz, $C_{quat}$), 119.6 (s, CH), 117.1 (s, CH), 112.6 (q, $^3J_{CF}$ = 4.3 Hz, CH), 111.3 (q, $^3J_{CF}$ = 3.9 Hz, CH), 89.6 (s, $C_{quat}$). HRMS (ESI, $m/z$) calculated for $C_{13}H_{10}ONF_3I$ [(M + H)$^+$]: 379.9754. Found: 379.9750. IR (neat, cm$^{-1}$) 3408, 3316, 3200, 3067, 2930, 2668, 2163, 2038, 1861, 1737, 1624, 1578, 1512, 1442, 1334, 1262, 1221, 1162, 1104, 1019, 924, 867, 810, 737. Characterization data are in accordance with those from the literature.[17]

*5-Bromo-2-(2-iodophenoxy)aniline (**3**).* The title compound was synthesized according to the general procedure GP1 using 2-iodophenol (1.30 g, 5.91 mmol) and 4-bromo-1-fluoro-2-nitrobenzene (1.30 g, 5.91 mmol), providing 1.82 g (4.67 mmol, 79% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 7:3). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.84 (dd, $J$ = 7.9, 1.6 Hz, 1H), 7.26 (td, $J$ = 7.5, 7.0, 1.6 Hz, 1H), 6.96 (d, $J$ = 2.3 Hz, 1H), 6.82 (m, 3H), 6.63 (d, $J$ = 8.5 Hz, 1H), 3.91 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 156.0 (s, $C_{quat}$), 142.3 (s, $C_{quat}$), 140.0 (s, CH), 139.80 (s, $C_{quat}$), 129.9 (s, CH), 125.3 (s, CH), 121.3 (s, CH), 120.8 (s, CH), 119.0 (s, CH), 117.70 (s, $C_{quat}$), 117.4 (s, CH), 87.6 (s, $C_{quat}$). HRMS (ESI, $m/z$) calculated for $C_{12}H_{10}ONBrI$ [(M + H)$^+$]: 389.8950. Found: 389.8984. IR (neat, cm$^{-1}$) 3371, 2279, 3197, 3060, 2983, 2664, 2323, 2101, 1995, 1907, 1726, 1613, 1491, 1462, 1436, 1277, 1220, 1185, 1136, 1084, 1018, 935, 898, 843, 805, 747.

*3-Amino-4-(2-iodophenoxy)benzonitrile (**4**).* The title compound was synthesized according to the general procedure GP1 using 2-iodophenol (1.57 g, 7.14 mmol) and 4-chloro-3-nitrobenzonitrile (1.30 g, 7.12 mmol), providing 604 mg (1.79 mmol, 25% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 1:1). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.89 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.36 (m, 1H), 7.06 (d, $J$ = 1.9 Hz, 1H), 6.96 (m, 3H), 6.60 (d, $J$ = 8.3 Hz, 1H), 4.15 (d, $J$ = 8.2 Hz, 2H). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 7.93 (dd, $J$ = 7.6, 1.7, 0.8 Hz, 1H), 7.43 (t, 1H), 7.10 (d, $J$ = 2.0 Hz, 1H), 7.02 (m, 2H), 6.89 (dd, $J$ = 8.2, 2.1 Hz, 1H), 6.50 (d, $J$ = 8.3 Hz, 1H), 5.55 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 154.7 (s, $C_{quat}$), 147.4 (s, $C_{quat}$), 140.4 (s, CH), 138.3 (s, $C_{quat}$), 130.2 (s, CH), 126.8 (s, CH), 123.0 (s, CH), 120.3 (s, CH), 119.2 (s, $C_{quat}$), 118.7 (s, CH), 116.9 (s, CH), 107.4 (s, $C_{quat}$), 89.2 (s, $C_{quat}$). $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 154.7 (s, $C_{quat}$), 146.6 (s, $C_{quat}$), 140.1 (s, $C_{quat}$), 139.8 (s, CH), 130.3 (s, CH), 126.7 (s, CH), 120.4 (s, CH), 120.2 (s, CH), 119.3 (s, $C_{quat}$), 117.2 (s, CH), 116.7 (s, CH), 105.9 (s, $C_{quat}$), 90.0 (s, $C_{quat}$). HRMS (ESI, $m/z$) calculated for $C_{13}H_9O\,N_2INa$ [(M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+ Na)$^+$]: 358.9652. Found: 385. 9645. IR (neat, cm$^{-1}$) 3453, 3360, 3204, 3062, 2922, 2655, 2321, 2221, 2167, 2109, 2035, 1987, 1918, 1856, 1728, 1614, 1574, 1541, 1505, 1460, 1432, 1357, 1300, 1257, 1222, 1150, 1086, 1019, 953, 861, 810, 776, 750, 697. Characterization data are in accordance with those from the literature.[17]

*Methyl 4-(2-Aminophenoxy)-3-iodobenzoate (**5**).* The title compound was synthesized according to the general procedure GP1 using methyl 3-hydroxy-4-iodobenzoate (1.95 g, 7.0 mmol) and 1-fluoro-2-nitrobenzene (1.00 g, 7.1 mmol), providing 1.63 g (4.41 mmol, 63% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 2:8). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.37 (d, $J$ = 2.1 Hz, 1H), 7.88 (dd, $J$ = 8.6, 2.1 Hz, 1H), 7.00 (td, $J$ = 8.2, 7.3, 1.4 Hz, 1H), 6.85 (td, $J$ = 7.9, 1.5 Hz, 2H), 6.61 (m, 2H), 4.94 (s, 2H), 3.82 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 164.6 (s, $C_{quat}$), 160.6 (s, $C_{quat}$), 140.4 (s, $C_{quat}$), 140.2 (s, CH), 131.2 (s, CH), 126.3 (s, CH), 125.1 (s, $C_{quat}$), 121.0 (s, CH), 116.6 (s, CH), 116.3 (s, CH), 114.7 (s, CH), 86.8 (s, $C_{quat}$), 52.2 (s, $CH_3$). HRMS (ESI, $m/z$) calculated for $C_{14}H_{13}O_3NI$ [(M + H)$^+$]: 369.9935. Found: 369.9948. IR (neat, cm$^{-1}$) 3456, 3367, 3209, 3065, 2950, 2841, 2476, 2221, 2066, 1921, 1713, 1620, 1584, 1499, 1476, 1433, 1387, 1280,1238, 1183, 1111, 1033, 968, 888, 839, 745, 668. Characterization data are in accordance with those from the literature.[17]

*2-(2-Iodo-4-methylphenoxy)aniline (**6**).* The title compound was synthesized according to the general procedure GP1 using 2-iodo-4-methylphenol (1.47 g, 6.28 mmol) and 1-fluoro-2-nitrobenzene (886 mg, 6.28 mmol), providing 1.35 g (4.15 mmol, 66% yield) of the product as a brown oil. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 7.69 (m, 1H), 7.11 (dd, $J$ = 8.5, 2.4 Hz, 1H), 6.85 (m, 2H), 6.57 (m, 3H), 4.85 (d, $J$ = 2.5 Hz, 2H), 2.24 (d, $J$ = 2.6 Hz, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 154.1 (s, $C_{quat}$), 142.4 (s, $C_{quat}$), 139.7 (s, $C_{quat}$), 139.4 (s, CH), 134.2 (s, $C_{quat}$), 130.3 (s, CH), 124.7 (s, CH), 118.8 (s, CH), 117.1 (s, CH), 116.4 (s, CH), 115.8 (s, CH), 88.0 (s, $C_{quat}$), 19.6 (s, $CH_3$). HRMS (APCI, $m/z$) calculated for $C_{13}H_{12}ONI$ [(M + H)$^+$]: 326.0036. Found: 326.0043. IR (neat, cm$^{-1}$) 3911, 3463, 3373, 3200, 3031, 2919, 2734, 2329, 2088, 1995, 1888, 1617, 1477, 1388, 1302, 1268, 1228, 1186, 1138, 1035, 926, 887, 815, 768, 741, 697, 662.

*2-(Trifluoromethyl)-10H-phenoxazine (**7**).* The title compound was synthesized according to the general procedure GP2 using **2** (1.24 g, 3.27 mmol), providing 655 mg (2.61 mmol, 80% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 1:9). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.50 (s, 1H), 6.89 (m, 1H), 6.76 (m, 2H), 6.63 (m, 3H), 6.46 (dd, $J$ = 7.7, 1.4 Hz, 1H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 145.8 (s, $C_{quat}$), 142.2 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 131.2 (s, $C_{quat}$), 124.6 (s, CH), 124.5 (q, $^2J_{CF}$ = 31.9 Hz, $C_{quat}$), 124.0 (q, $^1J_{CF}$ = 271.4 Hz, $C_{quat}$), 121.3 (s, CH), 117.5 (q, $^3J_{CF}$ = 4.2 Hz, CH), 115.4 (s, CH), 115.3 (s, CH), 113.6 (s, CH), 109.3 (q, $^3J_{CF}$ = 3.7 Hz, CH). $^{19}$F NMR (565 MH DMSO-$d_6$) $\delta$ (ppm) −61.22 (s, $CF_3$). HRMS (ESI, $m/z$) calculated for $C_{13}H_9ONF_3$ [(M + H)$^+$]: 252.0631. Found: 252.0624. IR (neat, cm$^{-1}$) 3399, 3088, 2665, 2323, 2191, 2086, 1936, 1883, 1716, 1590, 1502, 1454, 1319, 1253, 1230, 1195, 1157, 1101, 1066, 928, 867, 827 750, 696. Characterization data are in accordance with those from the literature.[18]

*2-(Bromo)-10H-phenoxazine (**8**).* The title compound was synthesized according to the general procedure GP2 using **3** (1.65 g, 4.23 mmol), providing 333 mg (1.27 mmol, 30% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 1:9). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.37 (s, 1H), 6.74 (ddd, J = 7.8, 6.4, 2.4 Hz, 1H), 6.69 (dd, $J$ = 8.4, 2.3 Hz, 1H), 6.60 (m, 2H), 6.55 (m, 2H), 6.45 (dd, $J$ = 7.7, 1.3 Hz, 1H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 142.5 (s, $C_{quat}$), 142.2 (s, $C_{quat}$), 134.2 (s, $C_{quat}$), 131.3 (s, $C_{quat}$), 124.2 (s, CH), 122.5 (s, CH), 121.0 (s, CH), 116.8 (s, CH), 115.3 (s, CH), 115.2 (s, CH), 115.1 (s, $C_{quat}$), 113.4 (s, CH). HRMS (ESI, $m/z$) calculated for $C_{12}H_9ONBr$ [(M + H)$^+$]: 261.9862. Found: 261.9857. IR (neat, cm$^{-1}$) 3369, 3041, 2863, 2734, 2060, 2543, 2472, 2325, 2195, 2161, 2082, 2033, 1988, 1925, 1848, 1786, 1715, 1628, 1582, 1483, 1447, 1373, 1288, 1233, 1192, 1121, 1071, 1032, 986, 950, 910, 829, 800, 740.

*10H-Phenoxazine-2-carbonitrile (**9**).* The title compound was synthesized according to the general procedure GP2 using **4** (1.44g, 4.28 mmol), providing 429 mg (2.06 mmol, 48% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 2:8). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 7.01 (dd, $J$ = 8.2, 2.0 Hz, 1H), 6.76 (td, $J$ = 7.4, 1.7 Hz, 1H), 6.71 (d, $J$ = 8.2 Hz, 1H), 6.68 (d, $J$ = 2.0 Hz, 1H), 6.62 (m, 2H), 6.47 (dd, $J$ = 7.7, 1.4 Hz, 1H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 146.8 (s, $C_{quat}$), 142.0 (s, $C_{quat}$), 133.6 (s, $C_{quat}$), 131.0 (s, $C_{quat}$), 125.6 (s, CH), 124.8 (s, CH), 121.2 (s, CH), 118.7 (s, $C_{quat}$), 116.0 (s, CH), 115.4 (s, CH), 115.2 (s, CH), 113.7 (s, CH), 106.2 (s, $C_{quat}$). HRMS (ESI, $m/z$) calculated for $C_{13}$ $H_8$ O $N_2$ Na [(M+Na)$^+$]: 231.0529. Found: 231.0525. IR (neat, cm$^{-1}$) 3829, 3350, 3035, 2970, 2896, 2761, 2623, 2577, 2428, 2288, 2216, 2124, 2053, 1851, 1748, 1630, 1579, 1491, 1450, 1382, 1307, 1242, 1212, 1186, 1126, 1095, 1028, 956, 909, 859, 835, 807, 728, 657. Characterization data are in accordance with those from the literature.[19]

*Methyl 10H-Phenoxazine-2-carboxylate (**10**).* The title compound was synthesized according to the general procedure GP2 using **5** (1.63 g, 4.41 mmol), providing 368 mg (1.53 mmol, 35% yield) of the product as a yellow solid after purification by flash chromatography (ethyl acetate/*n*-hexane 3:7). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.40 (s, 1H), 7.19 (dd, $J$ = 8.2, 2.0 Hz, 1H), 7.01 (d, $J$ = 2.0 Hz, 1H), 6.76 (t, $J$ = 7.5, 1.7 Hz, 1H), 6.62 (m, 3H), 6.44 (dd, $J$ = 7.7, 1.5 Hz, 1H), 3.78 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 165.5 (s, $C_{quat}$), 146.9 (s, $C_{quat}$), 142.2 (s, $C_{quat}$), 132.6 (s, $C_{quat}$), 131.6 (s, $C_{quat}$), 125.2 (s, $C_{quat}$), 124.6 (s, CH), 122.4 (s, CH), 120.7 (s, CH), 115.3 (s, CH), 115.1 (s, CH), 113.4 (s, CH), 113.4 (s, CH), 51.9 (s, $CH_3$). HRMS (ESI, $m/z$) calculated for $C_{14}$ $H_{12}$ $O_3$ N [(M + H)$^+$]: 242.0812. Found: 242.0813. IR (neat, cm$^{-1}$) 3785, 3701, 3577, 3365, 3188, 3030, 2989, 2943, 2901, 2843, 2645, 2322, 2213, 2183, 2088, 2044, 1986, 1907, 1873, 1698, 1631, 1582, 1498, 1448, 1313, 1205, 1104, 1030, 992, 920, 875, 832, 738. Characterization data are in accordance with those from the literature.[20]

*2-(Methyl)-10H-phenoxazine (**11**).* The title compound was synthesized according to the general procedure GP2 using **6** (1.35 g, 4.15 mmol), providing 459 mg (2.33 mmol, 56% yield) of the product as a brown solid after purification by flash chromatography (ethyl acetate/*n*-hexane 1:9). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.09 (s, 1H), 6.70 (td, $J$ = 7.4, 1.7 Hz, 1H), 6.56 (dtd, $J$ = 15.0, 7.9, 1.6 Hz, 2H), 6.45 (m, 2H), 6.35 (m, 1H), 6.25 (d, $J$ = 2.0 Hz, 1H), 2.09 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 142.9 (s, $C_{quat}$), 140.6 (s, $C_{quat}$), 132.8 (s, $C_{quat}$), 132.4 (s, $C_{quat}$), 132.0 (s, $C_{quat}$), 123.7 (s, CH), 120.5 (s, CH), 120.2 (s, CH), 115.0 (s, CH), 114.7 (s, CH), 113.8 (s, CH), 113.3 (s, CH), 20.4 (s, $CH_3$). HRMS (ESI, $m/z$) calculated for $C_{13}H_{12}ON$ [(M + H)$^+$]: 198.0913. Found: 198.0908. IR (neat, cm$^{-1}$) 3876, 3372, 3035, 2912, 2858, 2726, 2616, 2393, 2082, 995, 1859, 1777, 1732, 1629, 1585, 1495, 1451, 1382, 1303, 1270, 1202, 1152, 1123, 1099, 1034, 922, 871, 834, 805, 785, 664.

*4-(tert-Butyl)-2-(10H-phenoxazin-10-yl)phenol (**12**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and 4-(*tert*- butyl)phenol (90 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a white solid (46 mg, 69%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.61 (bs, 1H), 7.36 (dd, $J$ = 2.5, 8.6 Hz, 1H), 7.18 (d, $J$ = 2.4 Hz, 1H), 7.03 (d, $J$ = 8.6 Hz, 1H), 6.68 (dd, $J$ = 1.9, 7.2 Hz, 1H), 6.65−6.59 (m, 4H), 5.81 (dd, $J$ = 2.0, 7.5 Hz, 2H), 1.26 (s, 9H). HRMS (ESI, $m/z$) calculated for $C_{22}H_{22}NO_2$ [(M + H)$^+$]: 332.1645. Found: 332.1641. Characterization data are in accordance with those from the literature.[8]

*Methyl-10-(5-(tert-Butyl)-2-hydroxyphenyl)-10H-phenoxazine-2-carboxylate (**13**).* The title compound was synthesized according to the general procedure GP3 using methyl 10*H*-phenoxazine-2-carboxylate **10** (48 mg, 0.2 mmol) and 4-(*tert*-butyl)phenol (90 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column


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chromatography (pentane/DCM 8:2), yielding the title compound as a yellow solid (59 mg, 76%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.42 (dt, $J$ = 2.4, 8.7 Hz, 2H), 7.24 (d, $J$ = 2.4 Hz, 1H), 7.10 (d, $J$ = 8.7 Hz, 1H), 6.76−6.66 (m, 5H), 6.00 (dd, $J$ = 1.3, 7.7 Hz, 1H), 5.58 (s, 1H), 3.74 (s, 3H), 1.31 (s, 9H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 166.5 (s, $C_{quat}$), 151.6 (s, $C_{quat}$), 148.4 (s, $C_{quat}$), 146.2 (s, $C_{quat}$), 143.8 (s, $C_{quat}$), 133.5 (s, $C_{quat}$), 132.9 (s, $C_{quat}$), 127.8 (s, CH), 126.9 (s, CH), 125.8 (s, $C_{quat}$), 124.7 (s, CH), 124.5 (s, CH), 123.5 (s, $C_{quat}$), 122.5 (s, CH), 116.9 (s, CH), 116.0 (s, CH), 115.6 (s, CH), 114.7 (s, CH), 113.9 (s, CH), 52.1 (s, $CH_3$), 34.6 (s, $C_{quat}$), 31.6 (s, $CH_3$). IR (neat, cm$^{-1}$) 3380, 3063, 2957, 2868, 2635, 2320, 2194, 2069, 1885, 1695, 1626, 1586, 1487, 1437, 1325, 1273, 1242, 1198, 1108, 1039, 998, 965, 885, 822, 742. HRMS (ESI, $m/z$) calculated for $C_{24}H_{23}O_4NNa$ ([M + Na]$^+$): 412.1519. Found: 412.1510.

*2-(2-Bromo-10H-phenoxazin-10-yl)-4-(tert-butyl)phenol (**14**).* The title compound was synthesized according to the general procedure GP3 using 2-(bromo)-10*H*-Phenoxazine **8** (66 mg, 0.25 mmol) and 4-(*tert*-butyl)phenol (113 mg, 0.75 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 1:1), yielding the title compound as a white solid (73 mg, 71%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.73 (s, 1H), 7.39 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.22 (d, $J$ = 2.4 Hz, 1H), 7.05 (d, $J$ = 8.6 Hz, 1H), 6.77 (dd, $J$ = 8.4, 2.3 Hz, 1H), 6.67 (m, 4H), 5.82 (m, 2H), 1.26 (s, 9H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 152.3 (s, $C_{quat}$), 143.7 (s, $C_{quat}$), 143.1 (s, $C_{quat}$), 142.8 (s, $C_{quat}$), 135.3 (s, $C_{quat}$), 132.7 (s, $C_{quat}$), 127.7 (s, CH), 127.2 (s, CH), 123.9 (s, CH), 123.1 (s, CH), 122.2 (s, $C_{quat}$), 121.6 (s, CH), 117.4 (s, CH), 116.7 (s, CH), 115.1 (s, CH), 114.9 (s, $C_{quat}$), 114.7 (s, CH), 113.0 (s, CH), 33.9 (s, $C_{quat}$), 31.3 (s, $CH_3$). IR (neat, cm$^{-1}$) 3823, 3467, 3054, 2962, 2870, 2611, 2286, 2060, 1971, 1829, 1753, 1679, 1624, 1588, 1483, 1418, 1363, 1321, 1270, 1206, 1181, 1133, 1039, 943, 917, 835, 792, 727. HRMS (ESI, $m/z$) calculated for $C_{22}H_{21}O_2NBr$ [(M + H)$^+$]: 410.0750. Found: 410.0743.

*10-(5-(tert-Butyl)-2-hydroxyphenyl)-10H-phenoxazine-2-carbonitrile (**15**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine-2-carbonitrile **9** (42 mg, 0.2 mmol), 4-(*tert*-butyl)phenol (90 mg, 0.6 mmol, 3 equiv), and $K_2HPO_4$ (35 mg, 0.2 mmol). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a yellow solid (70 mg, 98%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.46 (dd, $J$ = 2.2, 8.7 Hz, 1H), 7.20 (d, $J$ = 2.2 Hz, 1H), 7.11 (d, $J$ = 8.6 Hz, 1H), 7.00 (dd, $J$ = 1.5, 8.3 Hz, 1H), 6.78−6.68 (m, 4H), 6.16 (d, $J$ = 1.6 Hz, 1H), 6.00 (d, $J$ = 7.8 Hz, 1H), 5.41 (bs, 1H), 1.31 (s, 9H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 151.4 (s, $C_{quat}$), 148.2 (s, $C_{quat}$), 146.7 (s, $C_{quat}$), 143.5 (s, $C_{quat}$), 134.5 (s, $C_{quat}$), 132.3 (s, $C_{quat}$), 128.3 (s, CH), 127.2 (s, CH), 126.7 (s, CH), 124.8 (s, CH), 123.0 (s, CH), 122.8 (s, $C_{quat}$), 118.9 (s, $C_{quat}$), 117.2 (s, CH), 116.4 (s, CH), 116.3 (s, CH), 116.1 (s, CH), 114.0 (s, CH), 107.2 (s, $C_{quat}$), 34.6 (s, $C_{quat}$), 31.6 (s, $CH_3$). IR (neat, cm$^{-1}$) 3693, 3352, 3061, 2957, 2924, 2861, 2628, 2542, 2321, 2230, 2170, 2114, 2070, 1987, 1961, 1902, 1736, 1582, 1487, 1421, 1367, 1328, 1268, 1215, 1170, 1124, 1095, 1036, 989, 960, 921, 861, 820, 744, 672. HRMS (ESI, $m/z$) calculated for $C_{23}H_{20}O_2N_2Na$ [(M + Na)$^+$]: 379.1417. Found: 379.1411.

*4-(tert-Butyl)-2-(2-(trifluoromethyl)-10H-phenoxazin-10-yl)-phenol (**16**).* The title compound was synthesized according to the general procedure GP3 using 2-(trifluoromethyl)-10*H*-phenoxazine **7** (126 mg, 0.5 mmol) and 4-(*tert*-butyl)phenol (225 mg, 1.5 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 1:1), yielding the title compound as a white solid (180 mg, 90%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.76 (s, 1H), 7.39 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.26 (d, $J$ = 2.4 Hz, 1H), 7.06 (d, $J$ = 8.6 Hz, 1H), 6.96 (m, 1H), 6.84 (d, $J$ = 8.2 Hz, 1H), 6.70 (m, 3H), 5.95 (d, $J$ = 2.1 Hz, 1H), 5.84 (m, 1H), 1.25 (s, 9H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 152.3 (s, $C_{quat}$), 146.5 (s, $C_{quat}$), 143.8 (s, $C_{quat}$), 142.9 (s, $C_{quat}$), 134.5 (s, $C_{quat}$), 132.6 (s, $C_{quat}$), 127.7 (s, CH), 127.2 (s, CH), 124.3 (s, CH), 124.2 (q, $^2J_{CF}$ = 31.8 Hz, $C_{quat}$) 123.9 (q, $^1J_{CF}$ = 271.5 Hz, $C_{quat}$), 122.1 (s, $C_{quat}$), 121.7 (s, CH), 118.2 (q, $^3J_{CF}$ = 4.1 Hz, CH), 117.4 (s, CH), 115.5 (s, CH), 115.2 (s, CH), 113.1 (s, CH), 108.5 (q, $^3J_{CF}$ = 3.8 Hz, CH), 33.9 (s, $C_{quat}$), 31.2 (s, $CH_3$). IR (neat, cm$^{-1}$) 3482, 3060, 2963, 2872, 2625, 2321, 2202, 2149, 2075, 2030, 1986, 1945, 1889, 1844, 1728, 1593, 1495, 1437, 1348, 1327, 1274, 1252, 1201, 1169, 1110, 1073, 1040, 959, 923, 863, 814, 745, 690. HRMS (ESI, $m/z$) calculated for $C_{23}H_{21}O_2NF_3$ [(M + H)$^+$]: 400.1519. Found: 400.1511.

*4-(tert-Butyl)-2-(2-methyl-10H-phenoxazin-10-yl)phenol (**17**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and 4-(*tert*-butyl)phenol (90 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a white solid (63 mg, 91%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.59 (bs, 1H), 7.36 (dd, $J$ = 2.4, 8.5 Hz, 1H), 7.17 (d, $J$ = 2.5 Hz, 1H), 7.03 (d, $J$ = 8.6 Hz, 1H), 6.66 (dd, $J$ = 2.8, 6.7 Hz, 1H), 6.63−6.60 (m, 2H), 6.57 (d, $J$ = 7.9 Hz, 1H), 6.42 (d, $J$ = 8.1 Hz, 1H), 5.78 (dd, $J$ = 2.3, 7.1 Hz, 1H), 5.63 (d, $J$ = 1.4 Hz, 1H), 1.96 (s, 3H), 1.26 (s, 9H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 151.9 (s, $C_{quat}$), 145.9 (s, $C_{quat}$), 144.6 (s, $C_{quat}$), 142.2 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 133.2 (s, $C_{quat}$), 132.9 (s, $C_{quat}$), 127.4 (s, CH), 127.1 (s, CH), 124.3 (s, $C_{quat}$), 123.7 (s, CH), 122.6 (s, CH), 122.3 (s, CH), 116.3 (s, CH), 115.8 (s, CH), 115.6 (s, CH), 114.4 (s, CH), 113.8 (s, CH), 34.5 (s, $C_{quat}$), 31.6 (s, *t*Bu), 21.0 (s, $CH_3$). IR (neat, cm$^{-1}$) 3862, 3430, 3042, 2957, 2867, 2700, 2541, 2468, 2391, 2301, 2210, 2171, 2101, 2060, 2027, 1991, 1928, 1859, 1753, 1709, 1589, 1492, 1420, 1326, 1270, 1216, 1167, 1041, 1013, 958, 920, 890, 857, 826, 803, 742, 675. HRMS (ESI, $m/z$) calculated for $C_{23}H_{24}O_2N$ [(M + H)$^+$]: 346.1802. Found: 346.1810.

*1-(4-Hydroxy-3-(2-methyl-10H-phenoxazin-10-yl)phenyl)-ethan-1-one (**18**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (82 mg, 0.6 mmol). The crude product was purified by flash column chromatography (DCM/MeOH 98:2), yielding the title compound as an orange oil (25 mg, 38%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.04 (dd, $J$ = 2.1, 8.6 Hz, 1H), 7.94 (d, $J$ = 2.1 Hz, 1H), 7.25 (d, $J$ = 8.6 Hz, 1H), 6.75 (m, 2H), 6.66 (m, 2H), 6.55 (d, $J$ = 7.9 Hz, 2H), 5.96 (d, $J$ = 7.7 Hz, 1H), 5.77 (d, $J$ = 1.3 Hz, 1H), 2.54 (s, 3H), 2.05 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 196.1 (s, $C_{quat}$), 159.2 (s, $C_{quat}$), 144.5 (s, $C_{quat}$), 142.2 (s, $C_{quat}$), 133.6 (s, $C_{quat}$), 132.8 (s, $C_{quat}$), 132.5 (s, $C_{quat}$), 132.3 (s, $C_{quat}$), 132.1 (s, CH), 131.2 (s, CH), 125.8 (s, $C_{quat}$), 123.7 (s, CH), 123.2 (s, CH), 122.9 (s, CH), 117.1 (s, CH), 116.1 (s, CH), 115.9 (s, CH), 114.5 (s, CH), 113.9 (s, CH), 26.5 (s, $CH_3$), 21.0 (s, $CH_3$). IR (neat, cm$^{-1}$) 3817, 3750, 3652, 3405, 3339, 3190, 3060, 2923, 2854, 2651, 2543, 2507, 2443, 2320, 2170, 2112, 2063, 2015, 1959, 1921, 1872, 1662, 1601, 1489, 1428, 1329, 1270, 1202, 1104, 1068, 1040, 991, 916, 808, 744, 670. HRMS (ESI, $m/z$) calculated for $C_{21}H_{18}O_3N$ [(M + H)$^+$]: 332.1281. Found: 332.1275.

*Methyl-10-(5-bromo-2-hydroxyphenyl)-10H-phenoxazine-2-carboxylate (**19**).* The title compound was synthesized according to the general procedure GP3 using Methyl 10*H*-phenoxazine-2-carboxylate **10** (48 mg, 0.2 mmol) and 4-bromophenol (104 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 9:1), yielding the title compound as a brown solid (34 mg, 41%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.52 (dd, $J$ = 1.8, 8.7 Hz, 1H), 7.44 (d, $J$ = 8.3 Hz, 1H), 7.41 (d, $J$ = 1.5 Hz, 1H), 7.09 (d, $J$ = 8.8 Hz, 1H), 6.79−6.69 (m, 3H), 6.64 (s, 1H), 6.01 (d, $J$ = 7.7 Hz, 1H), 5.92 (bs, 1H), 3.77 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 166.4 (s, $C_{quat}$), 154.0 (s, $C_{quat}$), 148.2 (s, $C_{quat}$), 143.6 (s, $C_{quat}$), 134.1 (s, CH), 133.2 (s, CH), 132.7 (s, $C_{quat}$), 132.2 (s, $C_{quat}$), 126.1 (s, $C_{quat}$), 125.9 (s, $C_{quat}$), 125.3 (s, CH), 124.5 (s, CH), 123.2 (s, CH), 119.1 (s, CH), 116.2 (s, CH), 115.9 (s, CH), 114.8 (s, CH), 114.2 (s, CH), 113.6 (s, $C_{quat}$), 52.2 (s, $CH_3$). IR (neat, cm$^{-1}$) 3745, 3336, 3063, 2923, 2854, 2632, 2319, 2173, 2030, 2010, 1956, 1888, 1769, 1697, 1623, 1578, 1484, 1435, 1292,1 242, 1203, 1111, 1041, 992, 943, 881, 856, 820, 710, 681. HRMS (ESI, $m/z$) calculated for $C_{20}H_{15}O_4NBr$ [(M + H)$^+$]: 412.0179. Found: 412.0180.



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*4-Bromo-2-(2-bromo-10H-phenoxazin-10-yl)phenol (**20**).* The title compound was synthesized according to the general procedure GP3 using 2-bromo-10*H*-phenoxazine **8** (52 mg, 0.2 mmol) and 4-bromophenol (104 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 8:2), yielding the title compound as a white solid (42 mg, 48%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.52 (dd, $J$ = 2.4, 8.9 Hz, 1H), 7.41 (d, $J$ = 2.4 Hz, 1H), 7.09 (d, $J$ = 8.8 Hz, 1H), 6.86 (dd, $J$ = 2.3, 8.5 Hz, 1H), 6.76 (m, 2H), 6.71 (m, 1H), 6.62 (d, $J$ = 8.5 Hz, 1H), 6.10 (d, $J$ = 2.2 Hz, 1H), 6.01 (dd, $J$ = 1.3, 8.0 Hz, 1H), 5.73 (s, 1H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 153.8 (s, $C_{quat}$), 144.0 (s, $C_{quat}$), 143.5 (s, $C_{quat}$), 134.2 (s, CH), 134.1 (s, $C_{quat}$), 133.2 (s, CH), 131.9 (s, $C_{quat}$), 125.9 (s, $C_{quat}$), 125.6 (s, CH), 124.2 (s, CH), 123.4 (s, CH), 119.0 (s, CH), 117.5 (s, CH), 116.6 (s, CH), 116.2 (s, CH), 116.1 (s, $C_{quat}$), 114.1 (s, CH), 113.6 (s, $C_{quat}$). IR (neat, cm$^{-1}$) 3450, 3060, 2923, 2308, 2062, 1763, 1701, 1586, 1478, 1412, 1318, 1268, 1195, 1156, 1126, 1075, 1039, 945, 884, 808, 738. HRMS (ESI, $m/z$) calculated for $C_{18}H_{12}O_2NBr_2$ [(M + H)$^+$]: 431.9229. Found: 431.9233.

*4-Bromo-2-(2-(trifluoromethyl)-10H-phenoxazin-10-yl)phenol (**21**).* The title compound was synthesized according to the general procedure GP3 using 2-(trifluoromethyl)-10*H*-phenoxazine **7** (126 mg, 0.5 mmol) and 4-bromophenol (260 mg, 1.5 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a white solid (152 mg, 72%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.37 (s, 1H), 7.60 (d, $J$ = 2.5 Hz, 1H), 7.57 (dd, $J$ = 8.8, 2.5 Hz, 1H), 7.11 (d, $J$ = 8.8 Hz, 1H), 7.01 (dd, $J$ = 8.2, 2.2, 0.9 Hz, 1H), 6.88 (d, $J$ = 0.9 Hz, 1H), 6.76 (m, 1H), 6.71 (m, 2H), 5.94 (d, $J$ = 2.1 Hz, 1H), 5.88 (m, 1H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 154.8 (s, $C_{quat}$), 146.4 (s, $C_{quat}$), 142.7 (s, $C_{quat}$), 134.0 (s, CH), 133.9 (s, $C_{quat}$), 133.7 (s, CH), 132.2 (s, $C_{quat}$), 124.4 (s, CH), 124.2 (q, $^2J_{CF}$ = 32.2 Hz, $C_{quat}$), 123.8 (q, $^1J_{CF}$ = 272 Hz, $C_{quat}$), 122.1 (s, CH), 120.0 (s, CH), 118.7 (q, $^3J_{CF}$ = 4.0 Hz, CH), 115.7 (s, CH), 115.4 (s, CH), 113.1 (s, CH), 110.6 (s, $C_{quat}$), 108.4 (q, $^3J_{CF}$ = 4.0 Hz, CH). $^{19}$F NMR (565 MHz, DMSO-$d_6$) $\delta$ (ppm) −61.17 (s, $CF_3$). IR (neat, cm$^{-1}$) 3455, 3065, 2321, 2203, 2171, 2141, 2032, 2000, 1946, 1878, 1735, 1627, 1587, 1489, 1435, 1348, 1318, 1278, 1255, 1165, 1120, 1071, 1041, 962, 865, 818, 740, 677. HRMS (ESI, $m/z$) calculated for $C_{19}H_{12}O_2NBrF_3$ [(M + H)$^+$]: 421.9998. Found: 421.9988.

*4-Bromo-2-(2-methyl-10H-phenoxazin-10-yl)phenol (**22**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and 4-bromophenol (104 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 7:3), yielding the title compound as an orange solid (55 mg, 74%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.19 (s, 1H), 7.52 (dd, $J$ = 2.5, 8.8 Hz, 1H), 7.47 (d, $J$ = 2.5 Hz, 1H), 7.09 (d, $J$ = 8.8 Hz, 1H), 6.68 (m, 1H), 6.64 (m, 2H), 6.59 (d, $J$ = 8.0 Hz, 1H), 6.46 (d, $J$ = 8.1 Hz, 1H), 5.83 (m, 1H), 5.66 (d, $J$ = 1.4 Hz, 1H), 1.99 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 155.0 (s, $C_{quat}$), 143.3 (s, $C_{quat}$), 141.1 (s, $C_{quat}$), 134.3 (s, CH), 133.0 (s, CH), 132.9 (s, $C_{quat}$), 132.6 (s, $C_{quat}$), 132.5 (s, $C_{quat}$), 125.5 (s, $C_{quat}$),123.5 (s, CH), 121.4 (s, CH), 121.2 (s, CH), 119.8 (s, CH), 115.0 (s, CH), 114.9 (s, CH), 113.2 (s, CH), 112.8 (s, CH), 110.4 (s, $C_{quat}$), 20.5 (s, $CH_3$). IR (neat, cm$^{-1}$) 3394, 3059, 2922, 2860, 2610, 2320, 2176, 2068, 2027, 1875, 1699, 1623, 1585, 1483, 1421, 1324, 1269, 1219, 1181, 1126, 1070, 1038, 971, 939, 886, 848, 809, 737, 656. HRMS (ESI, $m/z$) calculated for $C_{19}H_{14}O_2NBr$ [(M)$^+$•]: 367.0202. Found: 367.0203.

*2-(2-Bromo-10H-phenoxazin-10-yl)-4-(methylthio)phenol (**23**).* The title compound was synthesized according to the general procedure GP3 using 2-(bromo)-10*H*-Phenoxazine **8** (66 mg, 0.25 mmol) and 4-(methylthio)-phenol (105 mg, 0.75 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a red solid (75 mg, 75%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.00 (s, 1H), 7.33 (dd, $J$ = 8.7, 2.4 Hz, 1H), 7.23 (d, $J$ = 2.4 Hz, 1H), 7.10 (d, $J$ = 8.6 Hz, 1H), 6.79 (dd, $J$ = 8.5, 2.3 Hz, 1H), 6.68 (m, 4H), 5.85 (dd, $J$ = 6.0, 3.1 Hz, 2H), 2.44 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 153.0 (s, $C_{quat}$), 143.0 (s, $C_{quat}$), 142.8 (s, $C_{quat}$), 134.9 (s, $C_{quat}$), 132.4 (s, $C_{quat}$), 130.0 (s, CH), 129.9 (s, CH), 128.8 (s, $C_{quat}$), 123.9 (s, CH), 123.7 (s, $C_{quat}$), 123.3 (s, CH), 121.8 (s, CH), 118.7 (s, CH), 116.8 (s, CH), 115.2 (s, CH), 114.9 (s, $C_{quat}$), 114.7 (s, CH), 113.1 (s, CH), 16.3 (s, $CH_3$). IR (neat, cm$^{-1}$) 3450, 3059, 2921, 2853, 2698, 2159, 2059, 1884, 1760, 1623, 1548, 1478, 1411, 1318, 1267, 1195, 1156, 1125, 1077, 1039, 947, 844, 802, 741, 689. HRMS (APCI, $m/z$) calculated for $C_{19}H_{15}O_2NBrS$ [(M + H)$^+$]: 400.0001. Found: 399.9997.

*10-(2-Hydroxy-5-(methylthio)phenyl)-10H-phenoxazine-2-carbonitrile (**24**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine-2-carbonitrile **9** (42 mg, 0.2 mmol), 4-(methylthio)phenol (84 mg, 0.6 mmol, 3 equiv), and $K_2HPO_4$ (35 mg, 0.2 mmol). The crude product was purified by flash column chromatography (pentane/DCM 1:9), yielding the title compound as a yellow solid (27 mg, 39%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.38 (dd, $J$ = 2.0, 8.8 Hz, 1H), 7.16 (d, $J$ = 2.0 Hz, 1H), 7.14 (d, $J$ = 8.7 Hz, 1H), 7.01 (dd, $J$ = 1.6, 8.3 Hz, 1H), 6.78−6.69 (m, 4H), 6.18 (d, $J$ = 1.5 Hz, 1H), 6.03 (d, $J$ = 7.8 Hz, 1H), 5.61 (bs, 1H), 2.48 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 152.2 (s, $C_{quat}$), 148.1 (s, $C_{quat}$), 143.4 (s, $C_{quat}$), 134.1 (s, $C_{quat}$), 132.2 (s, $C_{quat}$), 131.9 (s, $C_{quat}$), 131.0 (s, CH), 129.3 (s, CH), 127.4 (s, CH), 124.8 (s, CH), 124.2 (s, $C_{quat}$), 123.3 (s, CH), 118.7 (s, $C_{quat}$), 118.4 (s, CH), 116.6 (s, CH), 116.4 (s, CH), 116.2 (s, CH), 114.1 (s, CH), 107.2 (s, $C_{quat}$), 17.5 (s, $CH_3$). IR (neat, cm$^{-1}$) 3747, 3329, 3067, 2921, 2854, 2629, 2481, 2290, 2229, 2167, 2074, 2043, 2002, 1957, 1870, 1757, 1624, 1579, 1484, 1421, 1327, 1269, 1215, 1166, 1125, 1037, 954, 860, 815, 744, 662. HRMS (ESI, $m/z$) calculated for $C_{20}H_{15}O_2N_2S$ [(MH)$^+$]: 347.0850. Found: 347.0849.

*2-(2-Methyl-10H-phenoxazin-10-yl)-4-(methylthio)phenol (**25**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and 4-(methylthio)phenol (84 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a white solid (54 mg, 81%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.85 (s, 1H), 7.30 (dd, $J$ = 2.3, 8.6 Hz, 1H), 7.16 (d, $J$ = 2.2 Hz, 1H), 7.08 (d, $J$ = 8.6 Hz, 1H), 6.67 (m, 1H), 6.63 (m, 2H), 6.58 (d, $J$ = 8.0 Hz, 1H), 6.44 (d, $J$ = 7.9 Hz, 1H), 5.82 (m, 1H), 5.66 (s, 1H), 2.43 (s, 3H), 1.98 (3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 152.8 (s, $C_{quat}$), 144.4 (s, $C_{quat}$), 142.1 (s, $C_{quat}$), 133.5 (s, $C_{quat}$), 132.9 (s, $C_{quat}$),132.4 (s, $C_{quat}$), 131.1 (s, $C_{quat}$), 130.4 (s, CH), 129.7 (s, CH), 125.8 (s, $C_{quat}$), 123.6 (s, CH), 122.8 (s, CH), 122.5 (s, CH), 117.6 (s, CH), 115.9 (s, CH), 115.7 (s, CH), 114.5 (s, CH), 113.9 (s, CH), 20.8 (s, $CH_3$), 17.3 (s, $CH_3$). IR (neat, cm$^{-1}$) 3867, 3456, 3056, 2920, 2857, 2692, 2531, 2347, 2213, 2176, 2063, 2033, 1987, 1953, 1925, 1712, 1626, 1583, 1486, 1325, 1268, 1216, 1161, 1131, 1040, 975, 951, 924, 881, 854, 804, 742, 704, 663. HRMS (ESI, $m/z$) calculated for $C_{20}H_{17}O_2NS$ [(M$^+$•)]: 335.0975. Found: 335.0974.

*4-Methoxy-2-(2-(trifluoromethyl)-10H-phenoxazin-10-yl)-phenol (**26**).* The title compound was synthesized according to the general procedure GP3 using 2-(trifluoromethyl)-10*H*-phenoxazine **7** (63 mg, 0.25 mmol) and 4-methoxyphenol (93 mg, 0.75 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a white solid (59 mg, 63%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.50 (s, 1H), 7.07 (d, $J$ = 9.0 Hz, 1H), 6.99 (m, 2H), 6.90 (d, $J$ = 3.1 Hz, 1H), 6.86 (d, $J$ = 8.2 Hz, 1H), 6.74 (m, 1H), 6.69 (hept, $J$ = 5.4 Hz, 2H), 5.98 (d, $J$ = 2.2 Hz, 1H), 5.89 (m, 1H), 3.70 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 153.4 (s, $C_{quat}$), 148.6 (s, $C_{quat}$), 146.4 (s, $C_{quat}$), 142.8 (s, $C_{quat}$), 134.3 (s, $C_{quat}$), 132.5 (s, $C_{quat}$), 124.3 (s, CH), 124.2 (q, $^2J_{CF}$ = 31.7 Hz, $C_{quat}$), 123.9 (q, $^1J_{CF}$ = 272 Hz, $C_{quat}$), 122.8 (s, $C_{quat}$), 121.8 (s, CH), 118.6 (s, CH), 118.4 (q, $^3J_{CF}$ = 3.7 Hz, CH), 116.8 (s, CH), 115.5 (s, CH), 115.5 (s, CH), 115.3 (s, CH), 113.2 (s, CH), 108.5 (q, $^3J_{CF}$ = 3.7 Hz, CH), 55.6 (s, CH). $^{19}$F NMR (565 MHz, DMSO-$d_6$) $\delta$ (ppm) −61.20. IR (neat, cm$^{-1}$) 3727, 3480, 3066, 2923, 2845, 2624, 2323, 2193, 2165, 2140, 2052, 2007, 1976, 1863, 1743, 1614, 1497, 1436, 1348, 1314, 1274, 1249, 1200, 1164, 1110, 1070, 1035, 956, 917, 867, 811, 741, 671. HRMS (ESI, $m/z$) calculated for $C_{20}H_{15}O_3NF_3$ [(M + H)$^+$]: 374.0999. Found: 374.0992.



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*10-(6-Hydroxy-2,3,4-trimethylphenyl)-10H-phenoxazine-2-carbonitrile (**27**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine-2-carbonitrile **9** (41 mg, 0.2 mmol) and 3,4,5-trimethylphenol (82 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a white solid (41 mg, 60%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 6.97 (dd, $J$ = 1.9, 8.3 Hz, 1H), 6.83 (s, 1H), 6.72−6.5 (m, 4H), 6.08 (d, $J$ = 1.9 Hz, 1H), 5.95 (d, $J$ = 7.8 Hz, 1H), 2.34 (s, $CH_3$), 2.18 (s, 3H), 2.09 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 151.1 (s, $C_{quat}$), 148.1 (s, $C_{quat}$), 143.3 (s, $C_{quat}$), 139.7 (s, $C_{quat}$), 136.4 (s, $C_{quat}$), 133.9 (s, $C_{quat}$), 131.5 (s, $C_{quat}$), 129.5 (s, $C_{quat}$), 127.1 (s, CH), 124.9 (s, CH), 122.9 (s, CH), 119.3 (s, $C_{quat}$), 118.9 (s, $C_{quat}$), 116.4 (s, CH), 116.1 (s, CH), 115.8 (s, CH), 115.8 (s, CH), 113.5 (s, CH), 107.3 (s, $C_{quat}$), 21.1 (s, $CH_3$), 15.7 (s, $CH_3$), 15.0 (s, $CH_3$). IR (neat, cm$^{-1}$) 3498, 2922, 2624, 2215, 2166, 2069, 2010, 1979, 1917, 1846, 1742, 1624, 1581, 1486, 1424, 1329, 1294, 1270, 1235, 1197, 1165, 1101, 1039, 981, 919, 855, 812, 742. HRMS (ESI, $m/z$) calculated for $C_{22}H_{18}O_2N_2Na$ [(M + H)$^+$]: 365.1261. Found: 365.1257.

*3,4,5-Trimethyl-2-(2-methyl-10H-phenoxazin-10-yl)phenol (**28**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and 3,4,5-trimethylphenol (82 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a white solid (57 mg, 86%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.26 (s, 1H), 6.73 (s, 1H), 6.63 (m, 1H), 6.58 (m, 2H), 6.55 (d, $J$ = 8.0 Hz, 1H), 6.39 (dd, $J$ = 1.1, 7.8 Hz, 1H), 5.67 (m, 1H), 5.54 (d, $J$ = 1.7 Hz, 1H), 2.24 (s, 3H), 2.10 (s, CH3), 2.02 (s, $CH_3$), 1.95 (s, $CH_3$). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 151.6 (s, $C_{quat}$), 144.3 (s, $C_{quat}$), 142.0 (s, $C_{quat}$), 138.8 (s, $C_{quat}$), 136.8 (s, $C_{quat}$), 133.6 (s, $C_{quat}$), 132.5 (s, $C_{quat}$), 132.0 (s, $C_{quat}$), 128.8 (s, $C_{quat}$), 123.7 (s, CH), 122.5 (s, CH), 122.2 (s, CH), 120.65 (s, $C_{quat}$), 115.8 (s, CH), 115.6 (s, CH), 115.1 (s, CH), 113.8 (s, CH), 113.2 (s, CH), 21.1 (s, $CH_3$), 21.0 (s, $CH_3$), 15.6 (s, $CH_3$), 15.1 (s, $CH_3$). IR (neat, cm$^{-1}$) 3458, 2922, 2861, 2613, 2217, 2070, 2016, 1954, 1875, 1735, 1627, 1587, 1485, 1422, 1327, 1295, 1269, 1199, 1169, 1085, 1039, 1005, 970, 911, 861, 804, 743, 685. HRMS (ESI, $m/z$) calculated for $C_{22}H_{21}O_2NNa$ [(M + H)$^+$]: 354.1465. Found: 354.1470.

*10-(2-Hydroxy-5-methylphenyl)-10H-phenoxazine-2-carbonitrile (**29**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine-2-carbonitrile **9** (42 mg, 0.2 mmol) and *p*-cresol (65 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 1:9), yielding the title compound as a yellow solid (50 mg, 79%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.23 (dd, $J$ = 1.7, 8.4 Hz, 1H), 7.07 (d, $J$ = 8.4 Hz, 1H), 7.01 (d, $J$ = 1.6 Hz, 1H), 6.98 (dd, $J$ = 1.9, 8.3 Hz, 1H), 6.75−6.67 (m, 4H), 6.18 (d, $J$ = 1.8 Hz, 1H), 6.02 (dd, $J$ = 1.2, 7.8 Hz, 1H), 5.52 (s, 1H), 2.34 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 151.7 (s, $C_{quat}$), 148.1 (s, $C_{quat}$), 143.4 (s, $C_{quat}$), 134.5 (s, $C_{quat}$), 132.8 (s, $C_{quat}$), 132.2 (s, $C_{quat}$), 132.0 (s, CH), 130.2 (s, CH), 127.2 (s, CH), 124.7 (s, CH), 123.3 (s, $C_{quat}$), 123.0 (s, CH), 118.9 (s, $C_{quat}$), 117.5 (s, CH), 116.5 (s, CH), 116.4 (s, CH), 116.1 (s, CH), 114.1 (s, CH), 107.1 (s, $C_{quat}$), 20.7 (s, $CH_3$). IR (neat, cm$^{-1}$) 3346, 3060, 2922, 2858, 2628, 2466, 2320, 2229, 2160, 2091, 2045, 1997, 1957, 1710, 1624, 1580, 1484, 1421, 1326, 1268, 1230, 1177, 1130, 1102, 1039, 986, 960, 920, 860, 815, 740. HRMS (ESI, $m/z$) calculated for $C_{20}H_{14}O_2N_2Na$ [(M + H)$^+$]: 337.0942. Found: 337.0948.

*4-Methyl-2-(2-methyl-10H-phenoxazin-10-yl)phenol (**30**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and *p*-cresol (65 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a white solid (47 mg, 77%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.54 (bs, 1H), 7.14 (dd, $J$ = 2.0, 8.4 Hz, 1H), 7.02 (d, $J$ = 1.6 Hz, 1H), 7.00 (d, $J$ = 8.3 Hz, 1H), 6.65 (m, 1H), 6.60 (m, 2H), 6.57 (d, $J$ = 7.9 Hz, 1H), 6.42 (dd, $J$ = 1.1, 8.2 Hz, 1H), 5.80 (m, 1H), 5.64 (d, $J$ = 1.5 Hz, 1H), 2.26 (s, 3H), 1.97 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 152.2 (s, $C_{quat}$), 144.5 (s, $C_{quat}$), 142.1 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 132.1 (s, $C_{quat}$), 131.2 (s, CH), 130.5 (s, CH), 125.0 (s, $C_{quat}$), 123.6 (s, CH), 122.6 (s, CH), 122.4 (s, CH), 116.6 (s, CH), 115.8 (s, CH), 115.6 (s, CH), 114.6 (s, CH), 114.0 (s, CH), 21.0 (s, $CH_3$), 20.7 (s, $CH_3$). IR (neat, cm$^{-1}$) 3870, 3446, 3036, 2922, 2860, 2679, 2470, 2298, 2208, 2167, 2066, 2024, 1992, 1959, 1929, 1846, 1704, 1623, 1588, 1489, 1322, 1270, 1231, 1160, 1205, 1130, 1040, 1010, 957, 922, 858, 803, 738. HRMS (ESI, $m/z$) calculated for $C_{20}H_{17}O_2N$ [(M)$^+$•]: 303.1254. Found: 303.1254.

*4-Methyl-2-(2-(trifluoromethyl)-10H-phenoxazin-10-yl)-phenol (**31**).* The title compound was synthesized according to the general procedure GP3 using 2-(trifluoromethyl)-10*H*-phenoxazine **7** (63 mg, 0.25 mmol) and *p*-cresol (81 mg, 0.75 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a yellow solid (72 mg, 81%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.74 (s, 1H), 7.19 (dd, $J$ = 8.3, 2.2 Hz, 1H), 7.09 (d, $J$ = 2.2 Hz, 1H), 7.03 (d, $J$ = 8.3 Hz, 1H), 6.97 (m, 1H), 6.85 (d, $J$ = 8.2 Hz, 1H), 6.73 (m, 1H), 6.68 (hept, $J$ = 5.1 Hz, 2H), 5.95 (d, $J$ = 2.1 Hz, 1H), 5.85 (m, 1H), 2.26 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 152.5 (s, $C_{quat}$), 146.5 (s, $C_{quat}$), 142.8 (s, $C_{quat}$), 134.4 (s, $C_{quat}$), 132.7 (s, $C_{quat}$), 131.3 (s, CH), 131.1 (s, CH), 130.1 (s, $C_{quat}$), 124.3 (s, CH), 124.2 (q, $^2J_{CF}$ = 34.4 Hz, $C_{quat}$), 123.9 (q, $^1J_{CF}$ = 272 Hz, $C_{quat}$), 122.4 (s, $C_{quat}$), 121.7 (s, CH), 118.3 (q, $^3J_{CF}$ = 3.9 Hz, CH) 117.8 (s, CH), 115.5 (s, CH), 115.3 (s, CH), 113.2 (s, CH), 108.5 (q, $^3J_{CF}$ = 3.7 Hz, CH), 19.9 (s, CH). $^{19}$F NMR (565 MHz, DMSO-$d_6$) $\delta$ (ppm) −61.20. IR (neat, cm$^{-1}$) 3468, 3035, 2928, 2625, 2162, 2039, 1981, 1863, 1718, 1597, 1495, 1435, 1347, 1321, 1270, 1236, 1201, 1160, 1110, 1070, 1042, 958, 917, 860, 814, 738, 671. HRMS (ESI, $m/z$) calculated for $C_{20}H_{15}O_2NF_3$ [(M + H)$^+$]: 358.1049. Found: 358.1042.

*5-(Dimethylamino)-2-(2-methyl-10H-phenoxazin-10-yl)phenol (**32**).* The title compound was synthesized according to the general procedure GP3 using 2-methyl-10*H*-phenoxazine **11** (39 mg, 0.2 mmol) and 3-(dimethylamino)phenol (82 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (pentane/DCM 6:4), yielding the title compound as a violet solid (10 mg, 15%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.05 (d, $J$ = 8.6 Hz, 1H), 6.70 (m, 2H), 6.65 (d, $J$ = 7.7 Hz, 1H), 6.62 (d, $J$ = 8.5 Hz, 1H), 6.49 (d, $J$ = 7.8 Hz, 1H), 6.46 (s, 1H), 6.44 (d, $J$ = 8.9 Hz, 1H), 6.08 (d, $J$ = 7.8 Hz, 1H), 5.91 (s, 1H), 5.57 (s, 1H), 3.03 (s, 6H), 2.06 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ (ppm) 154.9 (s, $C_{quat}$), 152.1 (s, $C_{quat}$), 144.6 (s, $C_{quat}$), 142.3 (s, $C_{quat}$), 134.0 (s, $C_{quat}$), 133.6 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 130.6 (s, CH), 123.6 (s, CH), 122.3 (s, CH), 122.1 (s, CH), 115.6 (s, CH), 115.4 (s, CH), 114.6 (s, CH), 114.0 (s, CH), 113.7 (s, $C_{quat}$), 106.8 (s, CH), 99.4 (s, CH), 40.6 (s, $CH_3$), 21.0 (s, $CH_3$). IR (neat, cm$^{-1}$) 3881, 3393, 3056, 2922, 2855, 2791, 2611, 2318, 2190, 2071, 1981, 1872, 1721, 1609, 1585, 1483, 1326, 1266, 1208, 1150, 1093, 1040, 992, 920, 887, 840, 801, 740. HRMS (ESI, $m/z$) calculated for $C_{21}H_{21}O_2N_2$ [(M + H)$^+$]: 333.1598. Found: 333.1592.

*N-(2-Hydroxy-5-phenylphenyl)-10H-phenoxazine (**33**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and 4-phenylphenol (102 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a white solid (56 mg, 80%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.03 (s, 1H), 7.68 (dd, $J$ = 8.5, 2.3 Hz, 1H), 7.62 (d, $J$ = 7.4 Hz, 2H), 7.55 (d, $J$ = 2.3 Hz, 1H), 7.38 (t, $J$ = 7.7 Hz, 2H), 7.27 (t, $J$ = 7.3 Hz, 1H), 7.19 (d, $J$ = 8.5 Hz, 1H), 6.70−6.67 (m, 2H), 6.64−6.59 (m, 4H), 5.92−5.87 (m, 2H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ 154.8 (s, $C_{quat}$), 143.4 (s, $C_{quat}$), 138.9 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 132.9 (s, $C_{quat}$), 129.6 (s, CH), 128.9 (s, CH), 128.2 (s, CH), 126.8 (s, CH), 126.0 (s, CH), 124.2 (s, $C_{quat}$), 123.7 (s, CH), 121.0 (s, CH), 118.4 (s, CH), 115.0 (s, CH), 112.8 (s, CH). IR (neat, cm$^{-1}$) 3853, 3409, 3033, 2656, 2322, 2193, 2076, 1993, 1873, 1749, 1590, 1484, 1411, 1330, 1270, 1158, 1127, 1040, 953, 917, 888, 841,731, 695, 657. HRMS (ESI, $m/z$) calculated for $C_{24}H_{17}O_2NNa$ [(M + Na)$^+$]: 374.1152. Found: 374.1144.


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*Methyl 4-Hydroxy-3-(10H-phenoxazin-10-yl)benzoate (**34**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and methyl 4-hydroxybenzoate (91 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 1:1), yielding the title compound as a white solid (23 mg, 35%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 10.89 (s, 1H), 7.96 (dd, $J$ = 8.6, 2.2 Hz, 1H), 7.80 (d, $J$ = 2.2 Hz, 1H), 7.20 (d, $J$ = 8.6 Hz, 1H), 6.70−6.69 (m, 2H), 6.65−6.61 (m, 4H), 5.81−5.80 (m, 2H), 3.78 (s, 3H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 165.3 (s, $C_{quat}$), 160.1 (s, $C_{quat}$), 143.3 (s, $C_{quat}$), 133.7 (s, CH), 133.0 (s, $C_{quat}$), 131.8 (s, CH), 124.0 (s, $C_{quat}$), 123.7 (s, CH), 122.3 (s, $C_{quat}$), 121.4 (s, CH), 118.1 (s, CH), 115.2 (s, CH), 112.7(s, CH), 51.9 (s, CH). IR (neat, cm$^{-1}$) 3846, 3408, 3063, 2951, 2851, 2655, 2320, 2183, 1994, 1882, 1709, 1613, 1586, 1485, 1439, 1328, 1270, 1207, 1771, 1120, 1085, 1043, 990, 937, 843, 806, 768, 733, 661. HRMS (ESI, $m/z$) calculated for $C_{20}H_{16}O_4N$ [(M + H)$^+$]: 334.1074. Found: 334.1067.

*N-(2-Hydroxy-5-trifluoromethoxyphenyl)-10H-phenothiazine (**35**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and 4-(trifluoromethoxy)phenol (107 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 7:3), yielding the title compound as a white solid (32 mg, 45%). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.32 (s, 1H), 7.42−7.37 (m, 2H), 7.21−7.17 (m, 1H), 6.72−6.64 (m, 6H), 5.86−5.80 (m, 2H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 155.2 (s, $C_{quat}$), 143.7 (s, $C_{quat}$), 141.5 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 125.6 (s, CH), 124.7 (s, $C_{quat}$), 124.1 (s, CH), 124.0 (s, CH), 121.8 (s, CH), 120.6 (q, $J$ = 255.2 Hz, $C_{quat}$), 119.0 (s, CH), 115.6 (s, CH), 113.1(s, CH). $^{19}$F NMR (282 MHz, DMSO-$d_6$) $\delta$ (ppm) −57.49. IR (neat, cm$^{-1}$) 3422, 3059, 2926, 2188, 1878, 1755, 1594, 1488, 1330, 1257, 1210, 1159, 1042, 989, 917, 889, 861, 824, 781, 660. HRMS (ESI, $m/z$) calculated for $C_{19}H_{13}O_3NF_3$ [(M + H)$^+$]: 360.0842. Found: 360.0834.

*1-(10H-Phenoxazine-10-yl)naphthalen-2-ol (**36**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and 2-naphthol (86 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a pinkish white solid (55 mg, 85%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.24 (s, 1H), 7.97 (d, $J$ = 9.0 Hz, 1H), 7.94 (d, $J$ = 8.1 Hz, 1H), 7.71 (d, $J$ = 8.4 Hz, 1H), 7.44−7.42 (m, 1H), 7.39 (d, $J$ = 9.0 Hz, 1H), 7.36−7.34 (m, 1H), 6.73 (dd, $J$ = 7.9, 1.4 Hz, 2H), 6.62−6.59 (m, 2H), 6.53−6.51 (m, 2H), 5.61 (dd, $J$ = 8.0, 1.3 Hz, 2H). $^{13}$C{$^1$H} NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 154.0 (s, $C_{quat}$), 144.0 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 132.17 (s, $C_{quat}$), 130.9 (s, CH), 129.6 (s, CH), 129.2 (s, CH), 128.0 (s, CH), 124.1 (s, CH), 123.9 (s, CH), 121.5 (s, CH), 119.9 (s, CH), 115.5 (s, CH), 114.9 (s, $C_{quat}$), 113.0 (s, CH). IR (neat, cm$^{-1}$) 3815, 3414, 3060, 2924, 2320, 2196, 1989, 1912, 1752, 1623, 1597, 1483, 1392, 1326, 1270, 1187, 1135, 1067, 1041, 967, 916, 864, 819, 776, 732, 663. HRMS (ESI, $m/z$) calculated for $C_{22}H_{15}O_2NNa$ [(M + Na)$^+$]: 348.0995. Found: 348.0989. For the scale-up experiment, 10H-phenoxazine (370 mg, 2 mmol), 2-naphthol (860 mg, 6 mmol, 3 equiv), and $K_2CO_3$ (280 mg, 2 mmol, 1 equiv) were dissolved in ODCB (6 mL) in a closed 20 mL vial. $O_2$ was bubbled through the solution for about 5 min. The reaction mixture was stirred for 3 h at 130 °C. The crude product is purified directly by column chromatography (*n*-hexane/DCM 6:4), yielding the title compound as a pinkish white solid (455 mg, 70%).

*10-(6-Hydroxy-2,3,4-trimethoxyphenyl)-10H-phenoxazine (**37**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and 3,4,5-trimethoxylphenol (110 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 1:1), yielding the title compound as a white solid (60 mg, 82%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.63 (s, 1H), 6.68−6.59 (m, 6H), 6.49 (s, 1H), 5.88 (dd, $J$ = 7.1, 1.4 Hz, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H). $^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) $\delta$ (ppm) 153.9 (s, $C_{quat}$), 152.0 (s, $C_{quat}$), 151.8 (s, $C_{quat}$), 143.4 (s, $C_{quat}$), 135.1 (s, $C_{quat}$), 133.4 (s, $C_{quat}$), 123.5 (s, CH), 120.8 (s, CH), 114.8 (s, CH), 112.7 (s, CH), 109.2 (s, $C_{quat}$), 96.2 (s, CH), 60.7 (60.73) (s, CH), 60.7 (60.68) (s, CH), 55.6 (s, CH). IR (neat, cm$^{-1}$) 3424, 3061, 2939, 2849, 2611, 2323, 2167, 2040, 1978, 1868, 1742, 1593, 1483, 1381, 1329, 1294, 1268, 1237, 1191, 1117, 1047, 997, 951, 920, 831, 738. HRMS (ESI, $m/z$) calculated for $C_{21}H_{20}O_5N$ [(M + H)$^+$]: 366.1336. Found: 366.1327.

*10-(2-Phenyl-1H-indol-3-yl)-10H-phenoxazine (**38**).* The title compound was synthesized according to the general procedure GP3 using 10*H*-phenoxazine (37 mg, 0.2 mmol) and 2-phenylindole (116 mg, 0.6 mmol, 3 equiv). The crude product was purified by flash column chromatography (*n*-hexane/DCM 7:3), yielding the title compound as a white solid (65 mg, 87%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 11.92 (s, 1H), 7.85 (d, $J$ = 7.5 Hz, 2H), 7.55 (d, $J$ = 8.1 Hz, 1H), 7.46 (t, $J$ = 7.8 Hz, 2H), 7.33 (t, $J$ = 7.4 Hz, 1H), 7.27−7.20 (m, 2H), 7.01 (t, $J$ = 7.4 Hz, 1H), 6.77 (dd, $J$ = 7.8, 1.5 Hz, 2H), 6.67−6.63 (m, 2H), 6.60−6.55 (m, 2H), 5.96 (dd, $J$ = 7.9, 1.6 Hz, 2H). $^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) $\delta$ (ppm) 143.6 (s, $C_{quat}$), 135.7 (s, $C_{quat}$), 134.7 (s, $C_{quat}$), 133.1 (s, $C_{quat}$), 130.5 (s, $C_{quat}$), 129.1 (s, CH), 128.3 (s, CH), 126.0 (s, CH), 124.0 (s, $C_{quat}$), 123.9 (s, CH), 122.7 (s, CH), 121.5 (s, CH), 120.0 (s, CH), 117.6 (s, CH), 115.3 (s, CH), 113.3 (s, CH), 112.3 (s, CH), 109.1 (s, $C_{quat}$). IR (neat, cm$^{-1}$) 3747, 3388, 3059, 2923, 2855, 2603, 2323, 2088, 1996, 1923, 1881, 1754, 1678, 1590, 1479, 1374, 1322, 1264, 1190, 1150, 1119, 1042, 1007, 963, 918, 857, 736, 690. HRMS (ESI, $m/z$) calculated for $C_{26}H_{18}ON_2Na$ [(M + Na)$^+$]: 397.1311. Found: 397.1302.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c02827.

Copies of spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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