

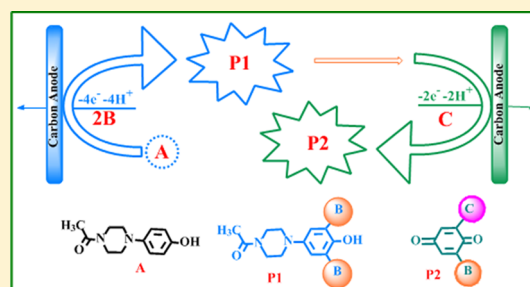
Electrochemical Synthesis Based on the Oxidation of 1-(4-(4-Hydroxyphenyl)piperazin-1-yl)ethanone in the Presence of Nucleophiles

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S Supporting Information

ABSTRACT: Electrochemical syntheses of new arylthiobenzazoles were carried out by electrochemical oxidation of 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone in the presence of 2-mercaptobenzothiazole and 2-mercaptobenzoxazole. Our voltammetric data indicate that electrochemically generated *p*-quinone imine participates in a Michael addition reaction with 2-SH-benzazoles leading to the disubstituted 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone. Also, a plausible mechanism for the oxidation of 1-(4-(3,5-bis(benzo[*d*]thiazol-2-ylthio)-4-hydroxyphenyl) in the presence of *p*-toluenesulfonic acid is presented. 1-(4-(3,5-Bis(benzo[*d*]thiazol-2-ylthio)-4-hydroxyphenyl) was converted into 2-(benzo[*d*]thiazol-2-ylthio)-6-tosylcyclohexa-2,5-diene-1,4-dione through a Michael-type addition of *p*-toluenesulfonic acid to anodically generated *p*-quinone imine, replacing 2-mercaptobenzothiazole and followed by hydrolysis.



Mercaptobenzazoles are known for their various biological activities such as antibacterial,¹ antiviral,² antiproliferative,³ and antifungal.⁴ Also, some therapeutic agents containing the 2-arylthiobenzothiazole moiety include inhibitors of cathepsin-D and a potent heat shock protein-90 inhibitors. These compounds also act as antimicrobial agents especially against *Piricularia oryzae* and *Xanthomonas oryzae*.⁵

On the other hand, phenylpiperazines are important pharmaceuticals that can be found in biologically active compounds across a number of different therapeutic areas,⁶ such as HIV protease inhibitor,⁷ antipsychotic agents,⁸ antifungal,⁹ and antitumor agents.¹⁰ For example ketoconazole has been used for oral treatment of systemic fungal infections.¹¹ Also, quinones are of considerable interest because many drugs such as doxorubicin in cancer chemotherapy contain quinones.¹² Some of them also exhibit antitumor and antimalarial activities,¹³ and many of them are also involved in enzyme inhibition and DNA cross-linking.¹⁴

According to these data, we think that synthesis of organic compounds with both structures of 2-mercaptobenzothiazole (2a) or 2-mercaptobenzoxazole (2b) and phenylpiperazine or quinone would be useful from the point of view of pharmaceutical properties. This idea prompted us to investigate electrochemical oxidation of 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone (1) in the presence of 2-SH-benzazoles (2a,b) as nucleophiles and present a one-pot electrochemical method for the synthesis of arylthiobenzazoles derivatives (compounds 7a,b) (Scheme 1). This reaction is carried out in a single step with high atom economy in ambient conditions and in an undivided cell using a carbon electrode. In this work, also, electrochemical oxidation of 1-(4-(3,5-bis(benzo[*d*]thiazol-2-

ylthio)-4-hydroxyphenyl) (7a) in the presence of *p*-toluenesulfonic acid (9) and synthesis of 2-(benzo[*d*]thiazol-2-ylthio)-6-tosylcyclohexa-2,5-diene-1,4-dione (13) have been investigated (Scheme 2).

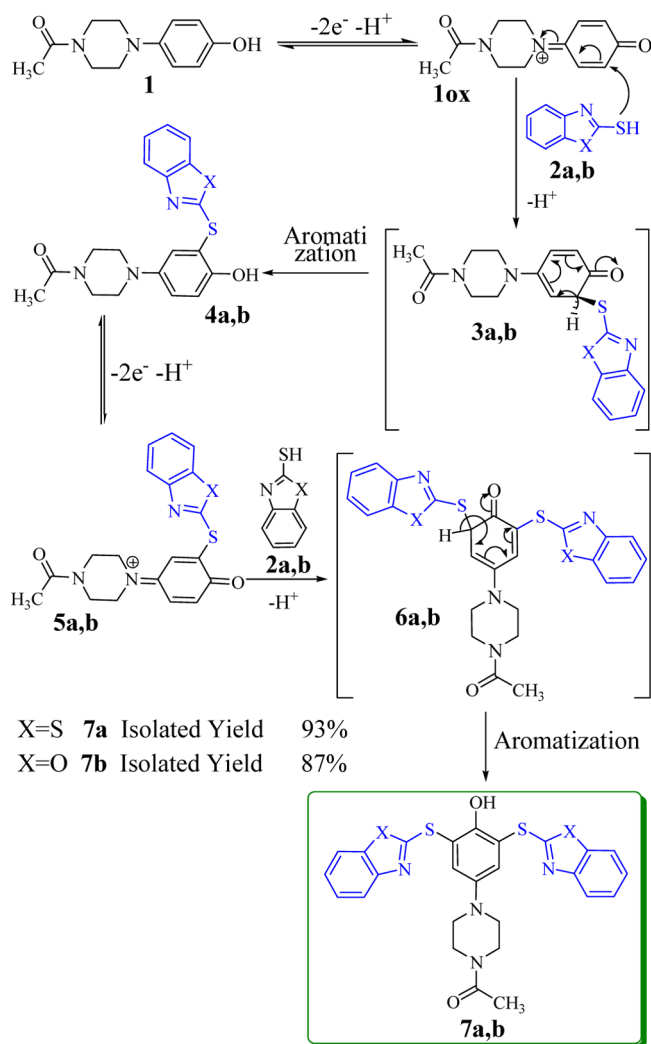
A cyclic voltammogram of 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone (1) in water (containing phosphate buffer, *c* = 0.2 M, pH = 2.0)/acetonitrile mixture (80/20 v/v) is shown in Figure 1, curve a. Under these conditions, the voltammogram shows one anodic (A₁) and two cathodic peaks (C₁ and C_s). Anodic and cathodic peaks A₁ and C₁ are counterparts and correspond to the transformation of 1 to *p*-quinone imine 1ox (Scheme 1) and vice versa within a quasi-reversible two-electron process.¹⁵ The peak current ratio (I_p^{C1}/I_p^{A1}) is dependent on pH and scan rate. It increases with decreasing pH and increasing scan rate. The cathodic peak C₁ disappears in basic solutions and/or in low potential sweep rates.¹⁵ The cathodic peak C_s (s = side reactions) has a different behavior. The current of this peak increases with increasing pH and its normalized current ($I_{pC_s}/v^{1/2}$) increases with decreasing scan rate. This peak is related to the occurrence of side reactions such as hydrolysis, hydroxylation and/or dimerization reaction, under the experimental conditions.^{15,16}

The oxidation of 1 in the presence of 2-mercaptobenzothiazole (2a) as a nucleophile was studied in some detail. Figure 1, curve b, shows the cyclic voltammogram obtained for 1 in the presence of 2a. Comparison of this voltammogram with the cyclic voltammogram of 1 in the absence of 2a shows that (a) the cathodic peak C₁ decreased intensively, (b) the anodic peak

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Scheme 1. Proposed Mechanism for the Electrochemical Oxidation of 1-(4-(4-Hydroxyphenyl)piperazin-1-yl)ethanone in the Presence of the 2-SH-benzazoles



A_1 increased slightly, and (c) a new anodic peak (A_2) appeared at more positive potentials. The occurrence of a chemical reaction after electron transfer process is supported by the decreasing of peak C_1 during the reverse scan, which could indicate that **1ox** formed at the surface of the electrode is consumed by a chemical reaction with **2a**. In Figure 1, curve d is the cyclic voltammogram of the isolated final product (**7a**). Comparison of this curve with curve b shows that peak A_2 is related to the electrooxidation of **7a**.

Curve c in Figure 1 shows the irreversible oxidation of **2a**.¹⁷ Wittstock and co-workers reported that the main product in oxidation of 2-mercaptobenzoxazole is bis(benzoxazolyl) disulfide.¹⁸

Controlled-potential coulometry was performed in a cell containing 0.25 mmol of **1** and 0.50 mmol of **2a**. Cyclic voltammetric analysis was carried out during the coulometry. It is shown that, proportional to the advancement of coulometry, the anodic peak A_1 decreases. This peak disappears when the charge consumption becomes $4e^-$ per molecule of **1**. Coulometry, cyclic voltammetry and spectroscopic data of the final product obtained from exhaustive oxidation of **1** in the presence of **2a**, allow us to propose the following mechanism

for the electrooxidation of **1** in the presence of **2a** and **2b** (Scheme 1).

The oxidation of **7a** is more difficult than the oxidation of **1** by virtue of the presence of electron-withdrawing 2-mercaptobenzothiazole groups on **7a**. Therefore, the oxidation of **7a** was prevented during the reaction because of the presence of the electron-withdrawing group as well as by the insolubility of it in the water/acetonitrile (45/15 v/v) solution. According to our results, the anodic peak A_2 pertains to the oxidation of **7a** to related *p*-quinone-imine **8a** (Scheme 2). Obviously, the cathodic peak C_2 corresponds to the reduction of **8a** to **7a**.

The oxidation of **7a** in the presence of *p*-toluenesulfonic acid (**9**) (Scheme 2) as a nucleophile was studied in next step. Figure 2, curve b, shows the cyclic voltammogram obtained for **7a** in the presence of **9**. Comparison of this voltammogram with cyclic voltammogram of **7a** in the absence of **9** (curve a), shows that; a) the cathodic peaks C_2 and C_5 decreased and b) a new anodic peak (A_3) appeared at more positive potentials. The peak current ratio ($I_p^{A_2}/I_p^{A_3}$) is related to the scan rate and increases with increasing it. The occurrence of a chemical reaction after electron transfer process is supported by the decreasing of peak C_2 during the reverse scan, which could indicate that *p*-quinone-imine **8a** (Scheme 2) formed at the surface of the electrode is consumed by a chemical reaction with **9**.

Comparison of voltammograms b and c reveals that the peak A_3 corresponds to the oxidation of toluenesulfonic acid **9** linked covalently to **7a**.

Controlled-potential coulometry was performed in a cell containing 0.22 mmol of **7a** and 0.22 mmol of **9** at 0.60 versus Ag/AgCl. Cyclic voltammetric analysis was carried out during the coulometry shows when peak A_2 disappears, the charge consumption becomes more than $2e^-$ per molecule of **7a**.

The cyclic voltammetry results accompanied by the molecular mass of 430 ($M + 3H$) of final product allow us to propose an EC_1C_2 mechanism for the electrochemical oxidation of **7a** in the presence **9** (Scheme 2). "E" represents an electron transfer at the electrode surface, and "C" represents a homogeneous chemical reaction (C_1 = addition-elimination and C_2 = hydrolysis). In this mechanism, the key step in the formation of *p*-benzoquinone **12** is replacement of an strong nucleophile (*p*-toluenesulfonic acid) with a weak nucleophile (2-mercaptobenzothiazole) after generation Michael acceptor. The unexpected number of transferred electrons was explained by the oxidation of separated mercaptobenzothiazole (**2a**) from **7a** and formation of bis(mercaptobenzothiazolyl) disulfide.¹⁸

The possibility of the direct synthesis of **12** was also examined by the stirring of a solution containing **7a** and **9** (in water/acetonitrile (50/50) v/v, pH = 2.0) (without oxidation). However, our results did not show any evidence of synthesis of **12**.

In a recent published paper,¹⁵ we have shown that the *p*-quinone-imine derived from oxidation of **1** participates in Michael type addition reaction with **9** as a nucleophile and via an EC mechanism converts to the 1-(4-(4-hydroxy-3-tosylphenyl)piperazin-1-yl)ethanone (**13**) (Scheme 3). In the second strategy for electrochemical synthesis of **12**, we examined the synthesis of **12** via electrochemical synthesis of **13** in the first step¹⁵ and electrooxidation of **13** in the presence of **2a** in the second step (Scheme 3). Figure 3 curve a, shows the cyclic voltammograms obtained for **13** (synthesized according to ref 15). The voltammogram exhibits one anodic

Scheme 2. Proposed Mechanism for the Electrochemical Oxidation of 1-(4-(3,5-Bis(benzo[d]thiazol-2-ylthio)-4-hydroxyphenyl)piperazin-1-yl)ethanone in the Presence of *p*-Toluenesulfonic Acid

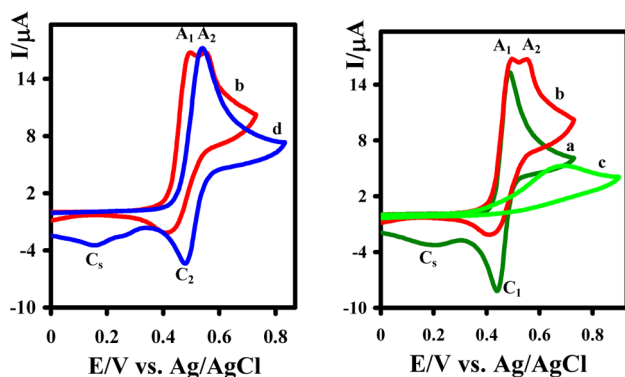
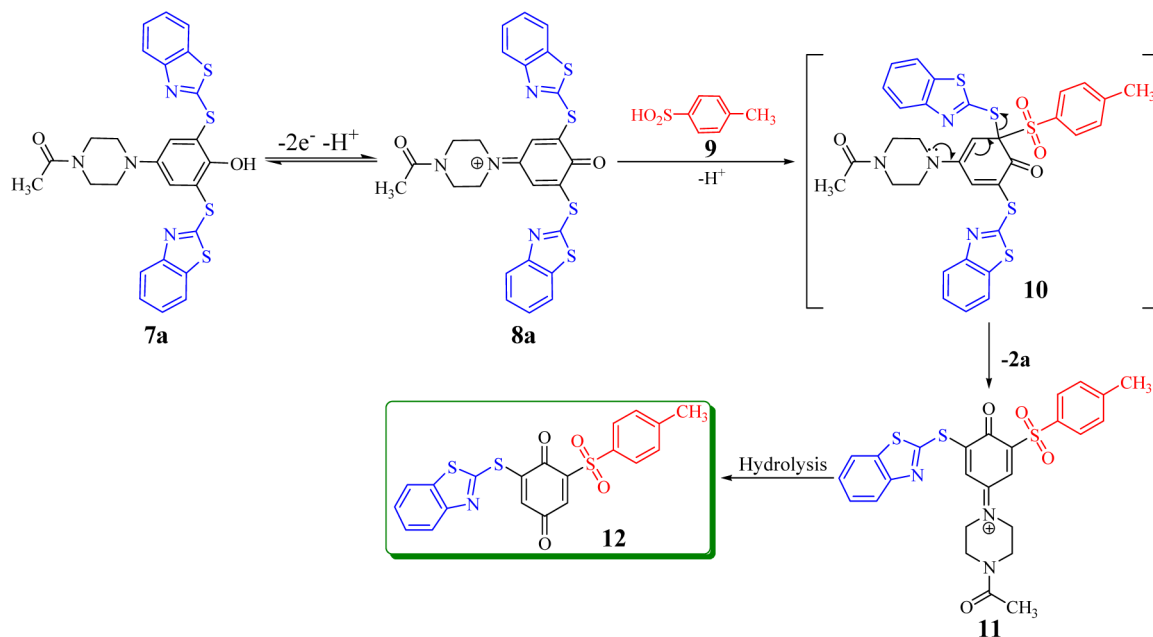


Figure 1. Cyclic voltammograms of (a) 1.0 mM 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone (**1**); (b) 1.0 mM **1** in the presence of 1.0 mM 2-mercaptobenzothiazole (**2a**); (c) 1.0 mM **2a** in the absence of **1**; (d) 1.0 mM of the final product (**7a**) at a glassy carbon electrode in water (phosphate buffer, $c = 0.2$ M, $\text{pH} = 2.0$)/acetonitrile (80/20) solution. Scan rate 100 mV s^{-1} . $t = 25 \pm 1$ °C.

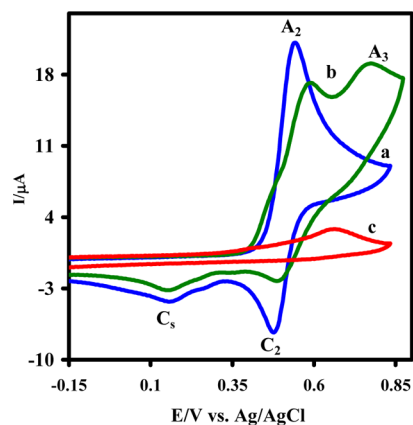


Figure 2. Cyclic voltammograms of (a) 1.0 mM **7a**; (b) 1.0 mM **7a** in the presence of 1.0 mM *p*-toluenesulfonic acid; (c) 1.0 mM *p*-toluenesulfonic acid. Scan rate 150 mV s^{-1} , at a glassy carbon electrode in water (phosphate buffer, $c = 0.2$ M, $\text{pH} = 2.0$)/acetonitrile (50/50 v/v). $t = 25 \pm 1$ °C.

peak (A_4) in the positive-direction scan and two cathodic peaks (C_4 and C_5) in the negative-direction scan. Anodic and cathodic peaks A_4 and C_4 are counterpart and are correspond to the transformation of **13** to its corresponding *p*-quinone-imine **13ox** (Scheme 3) and vice versa.^{15,16}

The oxidation of **13** in the presence of **2a** as a nucleophile was studied in some detail. We expected that **13** via an *EC* mechanism convert to compound **14** (Scheme 3). Figure 3, curve b, shows the cyclic voltammogram obtained for **13** in the presence of **2a**. The voltammogram clearly exhibits an increase in anodic peak A_4 . This is unexpected result for an *EC* mechanism. For an *EC* reaction, the flux of **13** is not changed very much, so that any index of that flux, such as the limiting current is only slightly perturbed. On the other hand, the limiting current for a catalytic reaction (*EC'*) (a reaction mechanism in which the sequence involves a catalytic reaction of the product after the electron transfer) will be increased

because **13** is continuously replenished by the chemical reaction (Scheme 3).¹⁹

Controlled-potential coulometry was performed in a cell containing 0.2 mmol of **13** and 0.2 mmol of **2a**. The continual increase of n_{app} (charge consumed) up to $8e^-$ under these conditions confirms catalytic oxidation of **2a** by **13ox**. Since, this reaction (*EC'*) competes with substitution reaction (*EC*), in this strategy we could not synthesize successfully compound **12** in a good yield and purity.

In the third strategy for electrochemical synthesis of disubstituted-*p*-benzoquinone **12**, we examined a one-pot process for the synthesis of **12** via electrochemical oxidation of **1** in the presence of both **2a** and **9**. In this strategy, electrochemical synthesis of **12** was also unsuccessful. Because of the higher nucleophilicity of **9**, the generation of *p*-quinone-imine (**10ox**) is first followed by a Michael addition of **9** on **10ox**, producing the 1-(4-(4-hydroxy-3-tosylphenyl)piperazin-1-yl)-

Scheme 3. Proposed Mechanism for the Electrochemical Oxidation of 1-(4-(4-Hydroxy-3-tosylphenyl)piperazin-1-yl)ethanone in the Presence of 2-Mercaptobenzothiazole

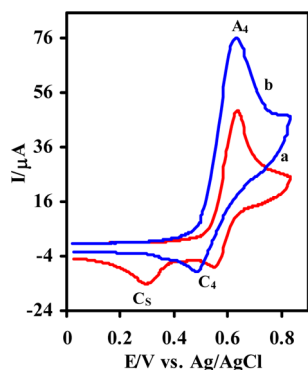
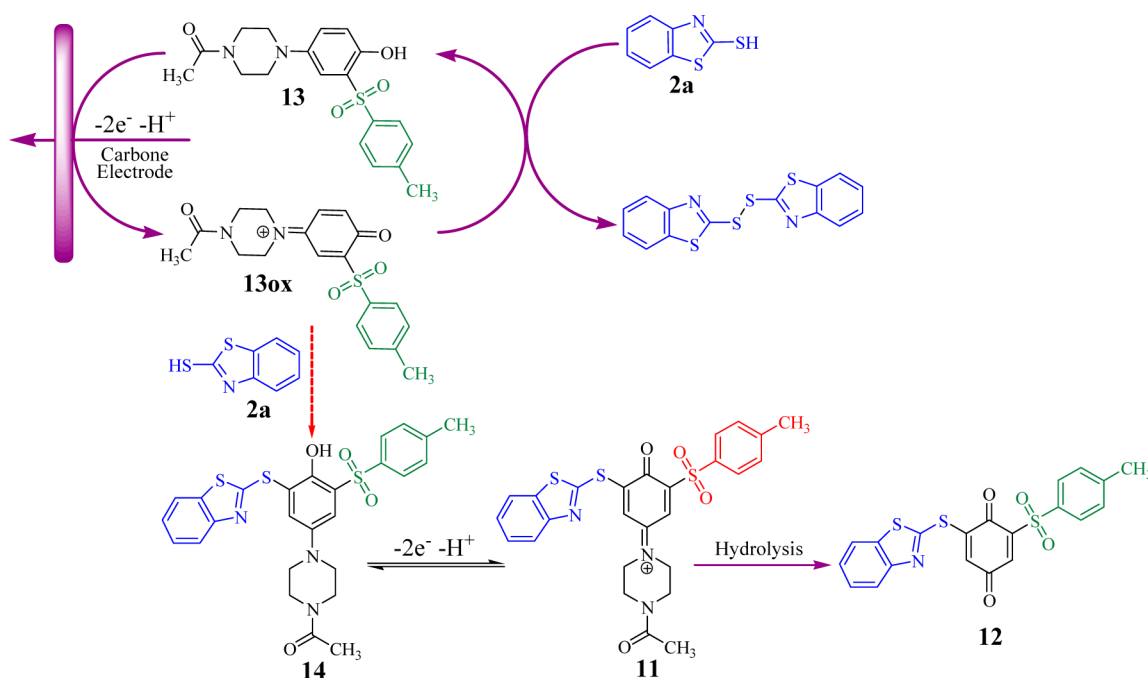


Figure 3. Cyclic voltammograms of (a) 1.0 mM 1-(4-(4-hydroxy-3-tosylphenyl)piperazin-1-yl)ethanone (13) and (b) 1.0 mM 13 in the presence of 1.0 mM 2-mercaptobenzothiazole. Scan rate 700 mV s⁻¹. Other conditions are the same as same as Figure 2.

ethanone (13) as the major product.¹⁵ As described in second strategy, the competition of catalytic reaction with substitution reaction causes that in this strategy we could not produce successfully compound 12 in a good yield and purity.

Finally, the results of this work show that 1 is oxidized to their respective *p*-quinone-imine. The formed *p*-quinone-imine is attacked by 2-*SH*-benzazoles to form disubstituted 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone (7a,b) as the final products. The reaction mechanism for anodic oxidation of 1 in the presence of 2a,b is presented in Scheme 1. This method provides a one-pot procedure in ambient conditions with high atom economy for the synthesis of compounds 7a,b. Also, for the synthesis of 1 with two different substituent groups, electrochemical oxidation of 7a has been performed in the presence of *p*-toluenesulfonic acid. Our results show that oxidized form of 7a is attacked by *p*-toluenesulfonic acid to form 2-(benzo[*d*]thiazol-2-ylthio)-6-tosylcyclohexa-2,5-diene-1,4-dione (12) as a final product. In addition, in this work we examined two other strategies for the synthesis of 12. In these

strategies, because of the competition of catalytic reaction with substitution reaction, we could not produce successfully compound 12 in a good yield and purity.

EXPERIMENTAL SECTION

Apparatus and Reagents. Reaction equipment was described in a previous paper.²⁰ 1-(4-(4-Hydroxyphenyl)piperazin-1-yl)ethanone, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, phosphoric acid, acetic acid, and other solvents were obtained from commercial sources. These chemicals were used without further purification. 1-(4-(4-Hydroxy-3-tosylphenyl)piperazin-1-yl)ethanone (13) was synthesized according to a previously reported procedure.¹⁵

Electroorganic Synthesis of 7a,b and 12. A solution of phosphate buffer (60 mL; *c* = 0.2 M, pH = 2.0) in water/acetonitrile (45/15 v/v) solution, containing 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone (1) (0.25 mmol) and 2-*SH*-benzazoles (2a,b) (0.5 mmol), was electrolyzed in an undivided cell at 0.50 V vs SCE. The electrolysis was terminated when the current decreased by more than 95%. At the end of the electrolysis, the precipitated solid was collected by filtration and washed with water. The isolated yields of 7a,b are reported in Scheme 1. For electrochemical synthesis of 12, a solution of phosphate buffer (ca. 60 mL; *c* = 0.2 M, pH = 2.0) in water/acetonitrile (50/50 v/v) solution, containing 7a (0.22 mmol) and 9 (0.22 mmol), was electrolyzed in an undivided cell at 0.60 V vs SCE. The electrolysis was terminated when the current decreased by more than 95%. At the end of the electrolysis, the precipitated solid was collected by filtration and washed with water.

1-(4-(3,5-Bis(benzo[*d*]thiazol-2-ylthio)-4-hydroxyphenyl)piperazin-1-yl)ethanone (C₂₆H₂₂N₄O₂S₄) (7a). Mp: 96–98 °C dec. ¹H NMR (400 MHz CDCl₃): δ = 2.16 (s, 3H, methyl), 3.16 (t, 4H, aliphatic), 3.67 (t, 2H, aliphatic), 3.82 (t, 2H, aliphatic), 7.35 (m, 2H, aromatic), 7.44 (m, 4H, aromatic), 7.73 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 9.51 (broad, 1H, OH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 21.4, 41.2, 46.1, 50.1, 50.3, 111.7, 119.8, 121.0, 121.5, 122.1, 124.9, 126.5, 127.1, 135.5, 145.5, 152.9, 153.2, 167.4, 169.1. IR_(KBr): 726.4, 756.3, 1006.1, 1080.1, 1155.9, 1235.0, 1425.4, 1455.7, 1620.2, 3424.3 cm⁻¹. MS: *m/z* (relative intensity) = 550 [M]⁺ (1.6), 538 (2.4), 524 (3.2), 440 (39.7), 423 (3.2), 385 (31.7), 368 (40.5), 323 (19.8), 313 (34.1), 300 (100), 242 (89.7). Anal. Calcd for

C₂₆H₂₂N₄O₂S₄: C, 56.70; H, 4.03; N, 10.17; S, 23.29. Found: C, 56.41; H, 4.02; N, 9.94; S, 23.38.

1-(4-(3,5-Bis(benzo[d]oxazol-2-ylthio)-4-hydroxyphenyl)-piperazin-1-yl)ethanone (C₂₆H₂₂N₄O₄S₂) (**7b**). Mp: 113–115 °C dec. ¹H NMR (400 MHz CDCl₃): δ = 2.16 (s, 3H, methyl), 3.11 (t, 2H, aliphatic), 3.17 (t, 2H, aliphatic), 3.63 (t, 2H, aliphatic), 3.78 (t, 2H, aliphatic), 7.31 (m, 4H, aromatic), 7.37 (s, 3H, aromatic), 7.47 (m, 2H, aromatic), 7.56 (m, 2H, aromatic), 9.12 (broad, 1H, OH). ¹³C NMR (100 MHz, CDCl₃): δ = 21.4, 41.3, 46.1, 50.0, 50.3, 110.1, 110.3, 117.5, 118.9, 123.7, 124.0, 124.8, 124.8, 126.5, 141.2, 151.7, 152.0, 162.9, 169.3. IR_(KBr): 3424.1, 2908.8, 2822.7, 1624.0, 1571.6, 1496.1, 1472.0, 1452.4, 1363.5, 1320.1, 1281.9, 1164.8, 1132.5, 1001.7, 981.3, 927.4, 849.6, 805.8, 744.4, 623.9, 594.6, 422.7 cm⁻¹. MS: m/z (relative intensity) = 518 [M]⁺•• (5.5), 484 (4.7), 397 (3.9), 367 (35.4), 324 (13.4), 297 (23.6), 259 (37.8), 242 (40.2), 226 (34.6), 175 (44.1), 151 (99.2), 91 (100). Anal. Calcd for C₂₆H₂₂N₄O₄S₂: C, 60.21; H, 4.28; N, 10.80; S, 12.34. Found: C, 60.51; H, 4.22; N, 10.39; S, 12.09.

2-(Benzo[d]thiazol-2-ylthio)-6-tosylcyclohexa-2,5-diene-1,4-dione (C₂₀H₁₃NO₄S₃) (**12**). Mp > 120 °C dec. MS: m/z (relative intensity) = 430 [M + 3]⁺•• (24), 402 (17.5), 338 (23.4), 284 (21), 171 (100), 128 (15.8), 95 (25.2).

■ ASSOCIATED CONTENT

● Supporting Information

FT-IR, ¹H, ¹³C NMR, and NOESY spectra for compounds **7a** and **7b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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