Synthesis and Reactions of Some New Benzo[*a*]phenothiazine-3,4-dione Derivatives

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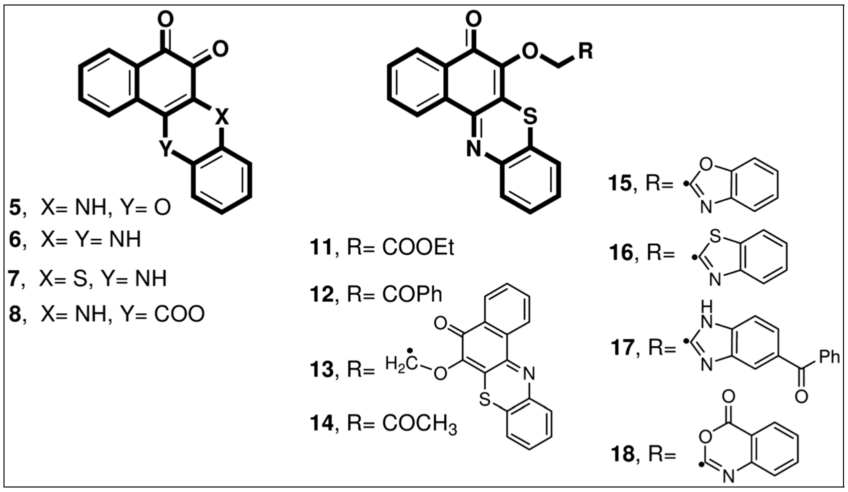

The reaction of 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (**4**) with substituted anilines furnished the corresponding benzo[fused]heterocyclic derivatives **5–8**. Furthermore, treatment of benzo[*a*]phenothiazine derivative **7** with halo compounds, namely, ethyl bromoacetate, phenacyl bromide, dibromoethane, or chloroacetone afforded ether derivatives **11–14**, respectively. Moreover, the reaction of **11** with *o*-substituted aniline gave the corresponding benzo[*a*]phenothiazin-5-one derivatives **15–17** and benzo[*d*][1,3]oxazin-4-one**18**, respectively. Finally, the chromenone derivative **19** was synthesized *via* the reaction of ester derivative **11** with salicyaldhyde in refluxing pyridine. The newly synthesized compounds were characterized by spectroscopic measurements (IR, ^{1}H NMR, ^{13}C NMR, and mass spectra).

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INTRODUCTION

Previously, aromatic bifunctionalized compounds and various benzoannulated five-, six- and seven-membered heterocycles were reported to posses promising biological activities [1, 2], in particular, phenoxazine [3, 4], phenazine [5, 6], phenothiazine [7, 8], and naphthoxazipine [9] derivatives. Therefore, number of methods has been developed for the preparation of these derivatives [10–13]. On the other hand, epoxy-1,4-naphthoquinone is an important intermediate in the synthesis of several biologically active compounds [14–17]. However, the reaction of bifunctionalized aromatic compounds with epoxy naphthoquinone has not been studied before. We report herein the scope and applicability of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**4**) as a unique precursor for the synthesis of some condensed heterocycles and their behavior toward different reagents in which a quinone ring is incorporated.

Control design for nonlinear systems has been developed in recent years leading to many different methods, including linearization [18], sliding mode control [19], and optimal state-space and H_∞ control [20]. A general theory of nonlinear systems in the frequency domain has been proposed by Banks [21]. Their method is based upon the extension of the Fourier transform of the input–output map into a Taylor series in an appropriate function space. Banks [22] and Sangelaji [23] have studied the stabilization of a general class of nonlinear systems by using the associated angular system and the method designs a controller, which stabilizes the system by converting the system to a spherical and a radial differential system. The stabilization of an inverted pendulum *via* the associated angular method has been studied by Sangelaji and Banks [24].

RESULTS AND DISCUSSION

Based on the chemistry of 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (**4**) [18–20], different benzo[*c*]phenoxazine, benzo[*a*]phenazine, and benzo[*a*]phenol-thiazine derivatives were synthesized as outlined in Schemes 1–4. It was reported that the reaction of 2,3-dichloronaphthoquinone with *o*-aminophenol [21–23] in pyridine afforded the 6*H*-benzo

[*b*]phenoxazine-6,11(12*H*)-dione (**1**). In addition, condensation of 2,3-dichloronaphthoquinone with aromatic thiols [21, 24, 25] or aromatic amines in NaN_3/DMF [26–27] afforded the linear heterocyclic quinones **2** and **3**, respectively (Fig. 1).

The purpose of this work is to synthesize these linear naphthoquinones using 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone involving a novel heterocyclization procedure in high yield. But unexpectedly, the data of the synthesized compounds were not compatible with the reported data of these known linear heterocyclic quinones. In view of this purpose and with the spectral data of the formed products, the products were seemed to be the angular heterocyclic quinones (Scheme 1).

Condensation of **4** with *o*-substituted-aniline derivatives namely; *o*-aminophenol, *o*-phenylenediamines, *o*-aminothiophenol, and *o*-aminobenzoic acid in ethanol afforded the corresponding benzo[*c*]phenoxazinedione, benzophenazinedione, benzo[*a*]phenothiazinedione, and naphtho[4,3-*b*][1,4]oxazepine-1,2,6(9*H*)-trione derivatives **5–8**, respectively. The proposed mechanism for the formation of these angular compounds involves nucleophillic attack at C_3 with the opening of the epoxide ring yielded the expected intermediate **9**. Subsequent oxidation and cyclization formed the fully aromatized angular compounds **5–8** (Scheme 2).

The enole tautomer is expected to be more stable than the keto one. This was revealed from the results of *ab initio*/3-21G molecular orbital calculations that were carried out, *in vacuo*, individually on the two tautomers. Results from Table 1 showed that the total energy of the enol form has lower value than that of the keto form (more negative by about 6.0 Kcal/mole, which is an indication for relative stability). Moreover, the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is higher in case of the enol form than in the keto form (indication for relative stability). The calculated molecular dipole moment is lower in case of the enol form than in the keto form (4.159 and 9.469 D, respectively).

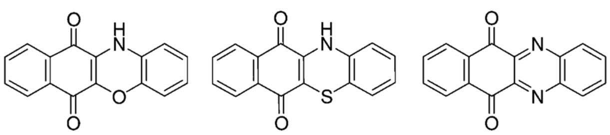


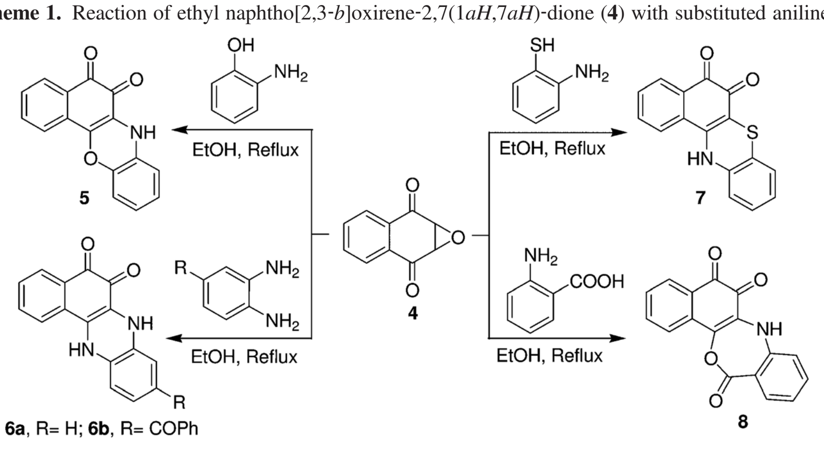
Figure 1. Linear heterocyclic quinones **1–3**.

As thiols are more reactive nucleophile than amines [28], it should be expected that *o*-aminothiophenol would attack the epoxide ring through thiol function leading to **7** as final product. The thiazinone **7** can exist in two tautomeric forms **7a** and **7b**, and it appears to be identical with the thiazinone derived previously from *o*-aminothiophenol with 3-chloro-1,2-naphthoquinone, 3-chloro-2-hydroxy-1,4-naphthoquinone, or 2-hydroxy-1,4-naphthoquinone [29]. Thus, it was found that the reaction of α-haloketones and dibromoethane with **7** favored the enol form rather than NH to give the more stable 1,4-quinone derivatives **11–14** (Fig. 2).

The evidence for this postulate was developed from the IR spectrum of **11** which showed stretching absorption bands at 3284 and 1617 cm^{-1} due to (NH) and (CO) groups, respectively. Moreover, the ^{13}C NMR spectrum of **11** revealed the presence of signals at 13.96 (CH_3), 60.55 (COOCH_2), and 68.042 (OCH_2); this suggested the presence of C-O bond rather than C-N bond. Furthermore, the ^1H NMR spectrum showed absence of singlet signal at δ 9.6 ppm due to NH proton. The mass spectrum showed the molecular ion peak at *m/z* 365 (M^+, 33.7).

It was reported that benzo[*a*]phenothiazine has a number of physicochemical [30] and biochemical studies [31, 32], and they present interesting spectroscopic [33–34] and photophysical [35, 36] properties. In view of these observations, compound **7** was used as a building block for the synthesis of other derivatives [37]. Subsequent alkylation of **7** with α-haloketones, namely, ethyl bromoacetate, chloroacetone, and phenacyl bromide in boiling acetone in the presence of K_2CO_3 afforded the corresponding alkylated benzo[a] phenothiazine-3-one derivatives **11–14**, respectively, in high yields. On a similar manner, reaction of **7** with 1,2-dibromoethane in acetone and potassium carbonate afforded

Scheme 1. Reaction of ethyl naphtho[2,3-*b*]oxirene-2,7(1*aH*,7*aH*)-dione (**4**) with substituted anilines.



Scheme 2. Mechanism of formation of benzo[*c*]phenoxazinedione, benzophenazinediones, benzo[*a*]phenothiazinedione, and naphtho[4,3-*b*][1,4] oxazepine-1,2,6(9*H*)-trione derivatives **5**–**8**.

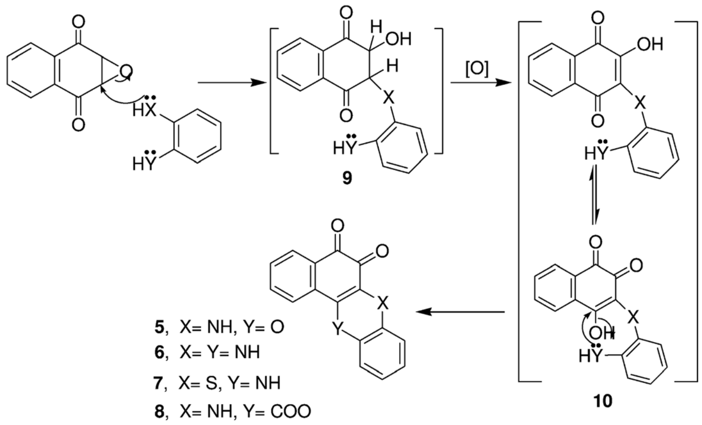


Table 1

Quantum mechanical data obtained from PM3 semiempirical MO and *ab initio* (3-21G) calculations of the configurations of **7a** and **7b**.

Method	Binding energy (Kcal/mol)	Δ*E* (LUMO–HOMO)	Dipole moment (D)
7a			
PM3	−3482.66	6.6534 Kcal/mol	6.513
Ab initio (3-21G)	−756947.595	−7.5259 − (0.6941) = 6.8318 eV	7.946
7b			
PM3	−3480.125	6.9691 Kcal/mol	2.882
Ab initio (3-21G)	−756953.6	−7.9829 − (0.7053) = 7.2776 eV	4.159

the corresponding benzo[a]phenothiazine derivative **13** in 92% yield (Scheme 3).

In addition, the structures of compounds **12–14** were established on the basis of elemental analyses and spectral data. The IR spectrum of compounds **12–14** revealed the absence of (NH) group. The ^{1}H NMR spectrum of **12** revealed singlet signal at δ 6.0 ppm due to methylene protons, while for compound **14** singlet signals appeared at δ 2.1 and 5.1 ppm for CH_3 and CH_2 protons, respectively. The ^{1}H NMR spectrum of **13** showed signal at 4.6 ppm (dd, 4H, $2CH_2$). The mass spectra of **12–14** showed the molecular ion peaks at *m*/*z* 397 (M^+, 13%), 584 (M^+, 6.9%), and 336 (M^+ + 1, 3.7%), respectively.

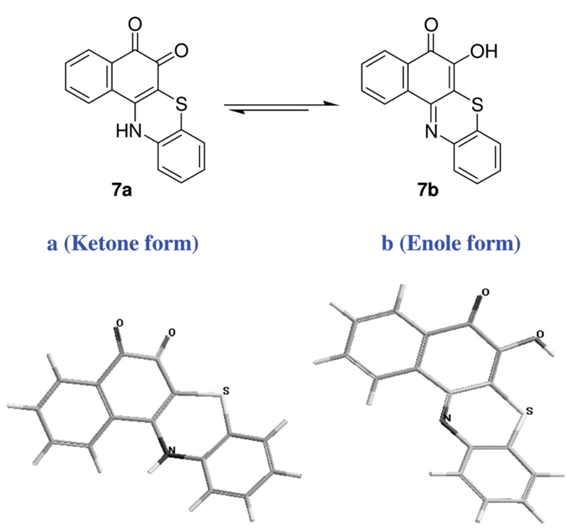
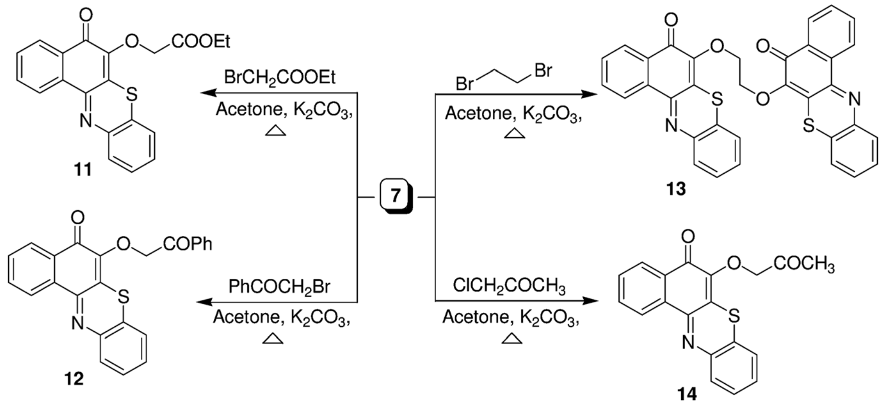


Figure 2. The enole-keto tautomers of the configurations **7a,b**.

The ethyl ester **11** served as a good precursor for the synthesis of heterocycles attached to the benzonaphthoquinone moiety. For compounds **15–19**, the ethyl ester derivative was fused with *o*-aminophenol or *o*-aminothiophenol in the presence of potassium carbonate to give the desired products benzoxazole derivative **15** and benzothiazol derivative **16**, respectively, in 40–50% yield. Compound **15** was also prepared from the reaction of the ethyl ester **11** and *o*-aminophenol in boiling toluene in the presence of potassium carbonate. Indication of the structures **15** and **16** are based on the elemental analyses and spectral data. The IR and ^{1}H NMR spectra of compounds **15** and **16** revealed the disappearance of ester group.

Under the same conditions, cyclocondensation of the ethyl ester **11** with the *o*-phenylenediamine derivative gave the corresponding benzimidazol derivative **17** in 58% yield. The IR spectrum showed bands at 3438 (NH) and 1633, 1589 (2C=O). The ^{1}H NMR spectrum of **17** revealed the disappearance of signals corresponding to ester protons and revealed singlet signals at δ 5.082 and 5.2 ppm for

Scheme 3. Reaction of **7** with different halogenated compounds.



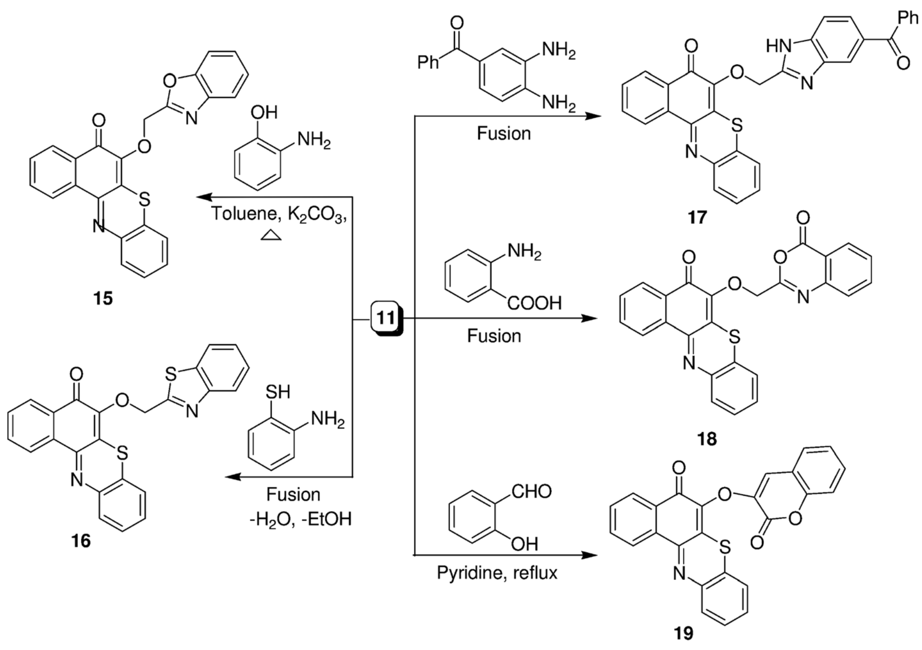
CH_2 and NH protons, respectively. In addition, the mass spectrum showed the molecular ion peak at 513 (M^+, 18). Also, the benzoxazinone derivative **18** was synthesized by the fusion of **11** with anthranilic acid. The IR spectrum of **18** showed bands at 1700 (C═O, cyclic ester), 1666, 1623 (2C═O), and 1587 cm^{-1} (C═N), while the ^1H NMR spectrum revealed singlet signal at δ 6.1 ppm due to methylene protons.

Knoevenagel reaction of active methylene esters with *o*-hydroxyaldehydes was reported as facile synthesis condensed α-pyranones and coumarines [38]. Thus, the ester **11** underwent cyclocondensation with salicylaldehyde in refluxing pyridine to afford the corresponding coumarine derivative **19** in 88% yield. Compound **19** was established in the bases of elemental analysis and spectral data. The ^1H NMR spectrum of **19** revealed the absence of methylene and ester protons (Scheme 4).

EXPERIMENTAL

All melting points are recorded on Gallenkamp electric melting point apparatus and are uncorrected. The IR spectra υ′ (cm^{-1}) (KBr) were recorded on a Perkin Elmer Infrared Spectrophotometer Model 157 at Faculty of Science, Mansoura University. The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer using the indicated solvents using TMS as an internal reference (Faculty of Science, Cairo University, Egypt). The mass spectra (EI) were recorded on 70 eV with Kratos MS equipment at the Microanalytical Center (Faculty of Science, Cairo University, Egypt). Elemental analyses (C, H, and N) were carried out at the Microanalytical Center of Cairo University (Giza, Egypt).

Scheme 4. Reaction of ethyl 2-(5-oxo-5*H*-benzo[*a*]phenothiazin-6-yloxy)acetate (**11**) with 1,2-substituted benzene derivatives.



2,3-Dihydro-2,3-epoxy-1,4-naphthoquinone (**4**) was prepared according to the previously reported methods [22, 25].

Reaction of 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (4) with substituted-aniline derivatives: General procedure. A mixture of 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (**4**) (1.7 g, 10 mmol) and substituted aniline derivatives, namely, *o*-aminophenol (1.1 g, 10 mmol), *o*-phenylenediamine (1 g, 10 mmol), 3,4-diaminobenzophenone (2.1 g, 10 mmol), *o*-aminothiophenol (1.2 g, 10 mmol), or *o*-aminobenzoic acid (1.4 g, 10 mmol) in ethanol (15 mL) was refluxed for 30 min up to 1 h. The reaction mixture was left to cool. The separated solid was filtered off, dried, and recrystallized from ethanol to afford compounds **5–8**, respectively.

5H-Benzo[c]phenoxazine-5,6(7H)-dione (5). Deep blue crystals, Yield, 95%, mp: 150°C; IR (KBr): v_{max}, cm^{-1}: 3307 (NH), 1648, 1614 (C=O); ^1H NMR (DMSO): δ 6.6–7.9 (m, 8H, Ar-H), 9.6 (s, 1H, NH); MS: *m/z* (%) = 265 (M^+ + 2, 3.3), 213 (24.7), 104 (42.0), 78 (46), 44 (100.0). Anal. Calcd for $C_{16}H_9NO_3$ (263.25): C, 73.00; H, 3.45; N, 5.32%. Found: C, 73.12; H, 3.51; N, 5.38%.

Benzo[a]phenazine-5,6(7H,12H)-dione (6a). Deep blue crystals, Yield, 90%, mp: 257°C, IR (KBr): v_{max}, cm^{-1}: 3367 (2NH), 1648 (2C=O); ^1H NMR (DMSO): δ 7.5–9.5 (m, 8H, Ar-H), 10.1 (s, 1H, NH), 11.0 (s, 1H, NH); MS: *m/z* (%) = 265 (M^+ + 3, 100.0), 234 (26.8), 205 (23.0). Anal. Calcd for $C_{16}H_{10}N_2O_2$ (262.26): C, 73.27; H, 3.84; N, 10.68%. Found: C, 73.31; H, 3.88; N, 10.72%.

9-Benzoylbenzo[a]phenazine-5,6(7H,12H)-dione (6b). Yellow crystals, Yield, 86%, mp: >300°C, IR (KBr): v_{max}, cm^{-1}: 3415, 3390 (2NH), 1650, 1598 (3C=O); ^1H NMR (DMSO): δ 7.6–8.6 (m, 12H, Ar-H), 9.2 (s, 2H, 2NH); MS: *m/z* (%) = 366 (M^+, 2), 234 (5.6), 212 (99.0), 135 (100.0). Anal. Calcd for $C_{23}H_{14}N_2O_3$ (366.37): C, 75.40; H, 3.85; N, 7.65%. Found: C, 75.37; H, 3.81; N, 7.69%

5H-Benzo[a]phenothiazine-5,6(12H)-dione (7). Deep violet crystals, Yield, 96%, mp: 286°C (lit. [32], 270–272), IR (KBr): v_{max}, cm^{-1}: 3284 (NH), 1617, 1596 (2CO). ^1H NMR (DMSO): δ 7.4–8.83 (m, 8H, Ar-H), 11.2 ppm (s, 1H, NH); MS: *m/z* (%) = 280 (M^+ + 1, 100.0), 264 (66.6), 105 (50.8), 63 (73.0). Anal. Calcd for $C_{16}H_9NO_2S$ (279.31): C, 68.80; H, 3.25; N, 5.01%. Found: C, 68.87; H, 3.32; N, 5.08%.

Benzo[e]naphtho[1,2-b][1,4]oxazepine-5,6,12(7H)-trione (8). Deep blue crystals, Yield, 88%, mp: 250°C, IR (KBr): v_{max}, cm^{-1}: 3334 (NH), 1683, 1637 (3C=O); ^1H NMR (DMSO): δ 6.6–7.9 (m, 8H, Ar-H), 9.6 (s, 1H, NH); ^{13}C NMR (DMSO): δ 186.7, 181.4, 164.3, 155.2, 148.7, 134.7, 134.3, 134.2, 133.1, 131.6, 129.5, 129.0, 128.6, 128.5, 122.3, 120.1, 118.9, 109.7; MS: *m/z* (%) = 292 (M^+ + 1, 100.0), 227 (15), 235 (50), 159 (65), 156 (88), 91 (15). Anal. Calcd for $C_{17}H_9NO_4$ (291.26): C, 74.18; H, 3.30; N, 5.09%. Found: C, 74.23; H, 3.36; N, 5.14%.

Reaction of benzo[*a*]phenothiazine derivative 7 with halo compounds: General procedure. A mixture of **7** (1.4 g, 5 mmol) and halo compounds, namely, ethyl bromoacetate (0.84 g 5 mmol), phenacylbromide (1 g, 2.8 mmol) dibromoethane (0.47 g, 2.5 mmol), or chloroacetone (0.53 g, 2.8 mmol) in acetone (20 mL) in the presence of potassium carbonate (0.39 g) was refluxed on water bath for the appropriate time (2–5 h). The reaction mixture was left to cool and the formed precipitate was collected by filtration, washed with cold water, dried *in vacuo* and crystallized from the appropriate solvent to afford compounds **11–14**, respectively.

Ethyl 2-(5-oxo-5H-benzo[a]phenothiazin-6-yloxy)acetate (11). Reaction time 3 h, red needles, Yield, 91%; mp: 169–170° C, crystallization from ethanol, IR (KBr): v_{max}, cm^{-1}: 2939 (CH, aliphatic), 1617 (C=O), 1751 (C=O, ester), 1214 (C-O, stretch); ^1H NMR (DMSO): δ 1.2 (t, 3H, $CH_2\mathit{CH_3}$), 4.1 (q, 2H, $\mathit{CH_2}CH_3$), 5.1 (s, 2H, N-CH_2), 7.5-8.8 (m, 8H, Ar-H). ^{13}C NMR (DMSO): δ 13.96 (CH_3), 60.5 (COO$\mathit{CH_3}$), 68.04 (OCH_2), 124.9, 125.1, 125.4, 125.7, 126.5, 128.04, 129.3, 131.5, 131.6, 132.7, 165.07, 168.47, 173.3, 174; MS: *m/z* (%) = 365 (M^+, 33.7), 292 (62.0), 322 (13.6), 250 (100.0), 278 (19.0). Anal. Calcd for $C_{20}H_{15}NO_4S$ (365.40): C, 65.74; H, 4.14; N, 3.83%. Found: C, 65.85; H, 4.20; N, 3.88%.

6-(2-Oxo-2-phenylethoxy)-5H-benzo[a]phenothiazin-5-one (12). Reaction time 5 h, purple crystals, Yield, 95 %, mp: 211° C, crystallization from ethanol, IR (KBr): v_{max}, cm^{-1}: 2923 (CH, aliphatic), 1672, 1660 (2C=O), 1625 (C=N), 1192 (C-O, stretch). ^1H NMR (DMSO): δ 6.0 (s, 2H, N-CH_2), 7.4–8.9 (m, 13H, Ar-H); MS: *m/z* (%) = 397 (M^+, 13), 292 (62), 278(12.2), 250(88), 190(17), 105(100). Anal. Calcd for $C_{24}H_{15}NO_3S$ (397.45): C, 72.53; H, 3.80; N, 3.52%. Found: C, 72.59; H, 3.84; N, 3.57%.

6,6′-(Ethane-1,2-diylbis(oxy))bis(5H-benzo[a]phenothiazin-5-one) (13). Reaction time 3 h, green crystals, Yield, 92%, mp: 242°C, crystallization from acetone, IR (KBr): v_{max}, cm^{-1}: 2923 (CH, aliphatic), 1631, 1610 (2C=O), 1585 (C=N), 1231 (C-O, stretch). ^1H NMR (DMSO): δ 4.6 (t, 4H, 2CH_2), 7–8.5 (m, 16H, Ar-H); ^{13}C NMR (DMSO): δ 178.3, 177.9, 166.3, 165.1, 159.2, 158.8, 147.8, 147.0, 137.2, 136.0, 135.3, 135.0, 132.6, 132.4, 131.8, 131.3, 131.0, 130.8, 130.7, 130.1, 129.7, 129.6, 128.1, 127.6, 127.3, 124.3, 124.2, 123.0, 122.8, 110.9, 109.6, 67.9, 67.1, 66.0. MS: *m/z* (%) = 584 (M^+, 6.9), 292 (3.2), 379(100), 146(19.5), 121(36). Anal. Calcd for $C_{34}H_{20}N_2O_4S_2$ (584.66): C, 69.85; H, 3.45; N, 4.79%. Found: C, 69.93; H, 3.52; N, 4.84%.

6-(2-Oxopropoxy)-5H-benzo[a]phenothiazin-5-one (14). Reaction time 2 h, deep violet crystals, Yield, 62%, mp: 191°C, crystallization from acetonitrile, IR (KBr): v_{max}, cm^{-1}: 2919 (CH, aliphatic), 1772, 1610 (2C=O), 1590 (C=N), 1217 (C-O, stretch). ^1H NMR (DMSO): δ 2.1 (s, 3H, CH_3), 5.1 (s, 2H, CH_2), 7.5–8.8 (m, 8H, Ar-H). MS: *m/z* (%) = 336 (M^+ + 1, 3.7), 292 (44.9), 278 (4.6), 263(13.4), 250 (100), 190 (33.1). Anal. Calcd. for $C_{19}H_{13}NO_3S$ (335.38): C, 68.04; H, 3.91; N, 4.18%. Found: C, 68.08; H, 3.97; N, 4.23%.

Reaction of 11 with *o*-substituted anilines: General procedure. A mixture of ester **11** (1.07 g, 3 mmol) and *o*-substituted aniline derivatives, namely, *o*-aminophenol (0.33 g, 3 mmol), *o*-aminothiophenol (0.38 g, 3 mmol), 3-benzoyl-1,2-phenylenediamine (0.34 g, 3 mmol), or anthranilic acid (0.41 g, 3 mmol) was fused at 150 and 170°C in case of reaction with 3-benzoyl-1,2-phenylenediamine in oil bath for the appropriate reaction time. The fused solid was left to cool then the formed solid product was collected and recrystallized from ethanol to afford benzo[*a*]phenothiazinone derivatives **15**–**17** and benzo[*d*][1,3]oxazinone derivative **18**, respectively.

6-(Benzo[d]oxazol-2-ylmethoxy)-5H-benzo[a]phenothiazin-5-one (15). Reaction time 1 h, violet crystals, Yield, 40%, mp: 234°C, IR (KBr): v_{max}, cm^{-1}: 2923 (CH, aliphatic), 1616 (C=O), 1594, 1560 (2C=N); ^1H NMR (DMSO): δ 6.3 (s, 2H, OCH_2), 7.0–8.0 (m, 12H, Ar-H); MS: *m/z* (%) = 410 (M^+, 21.2), 291 (28.0), 278 (26.0), 118 (13.7), 77 (100.0). Anal. Calcd for $C_{24}H_{14}N_2O_3S$ (410.44): C, 70.23; H, 3.44; N, 6.83%. Found: C, 70.18; H, 3.41; N, 6.78%.

6-(Benzo[d]thiazol-2-ylmethoxy)-5H-benzo[a]phenothiazin-5-one (16). Reaction time 1 h, deep violet crystals, Yield, 50%, mp: 218°C, IR (KBr): ν_{max}, cm^{-1}: 1616 (C=O), 1592, 1560 (C=N); ^{1}H NMR (DMSO): δ 5.2 (s, 2H, OCH_2), 7.4–8.0 (m, 12H, Ar-H); MS: *m/z* (%) = 426 (M^+, 5.9), 368 (100), 336 (15.4), 292 (12), 162 (52.4). Anal. Calcd for $C_{24}H_{14}N_2O_2S_2$ (426.51): C, 67.58; H, 3.31; N, 6.57%. Found: C, 67.63; H, 3.37; N, 6.61%.

6-((5-Benzoyl-1H-benzo[d]imidazol-2-yl)methoxy)-5H-benzo[a]phenothiazin-5-one (17). Reaction time 2 h, deep red crystals; 58% yield; mp 156°C; IR (KBr): ν_{max}, cm^{-1}: 3438 (NH), 1722, 1689, 1633 (3C=O), 1523 (C=N); ^{1}H NMR (DMSO): δ 5.0 (s, 2H, CH_2), 5.2 (s, 1H, NH), 7.4–8.2 (m, 17H, Ar-H); MS: *m/z* (%) = 513 (M^+, 18), 408 (20), 278 (65), 235 (33), 116 (46), 105 (80). Anal. Calcd for $C_{31}H_{19}N_3O_3S$ (513.57): C, 72.50; H, 3.73; N, 8.18%. Found: C, 72.56; H, 3.81; N, 8.24%.

2-((5-Oxo-5H-benzo[a]phenothiazin-6-yloxy)methyl)-4H-benzo[d][1,3]oxazin-4-one (18). Reaction time 2 h, reddish brown crystals; 66%; mp 240°C; IR (KBr): ν_{max}, cm^{-1}: 1700 (C=O, cyclic ester), 1666, 1623 (2C=O), 1587 (C=N); ^{1}H NMR (DMSO): δ 6.1 (s, 2H, CH_2), 7.7–8.0 (m, 12H, Ar-H); MS: *m/z* (%) = 438 (M^+, 39.0), 292 (100.0), 279 (34.0), 250 (60.1), 145 (29.0). Anal. Calcd for $C_{25}H_{14}N_2O_4S$ (438.45): C, 68.48; H, 3.22; N, 6.39%. Found: C, 68.54; H, 3.28; N, 6.46%.

Synthesis of 6-(2-oxo-2*H*-chromen-3-yloxy)-5*H*-benzo[*a*]phenothiazin-5-one (19). Equimolar amounts of the acetate ester **11** (1.07 g, 3 mmol) and salicylaldehyde (0.43 g, 3.5 mmol) in pyridine (15 mL) was refluxed for 15 h. The separated solid obtained during the course of the reaction, was filtered while hot, dried and then recrystallized from acetone to give **19**. Reddish brown crystals, Yield, 88%, mp: >300°C; IR (KBr): ν_{max}, cm^{-1}: 1690 (C=O, cyclic ester), 1664 (C=O), 1610 (C=N); ^{1}H NMR (DMSO): δ, 7.1–8.05 (m, 13H, Ar-H); MS: *m/z* (%) = 424 (M^+ + 1, 39.0), 262 (100.0), 145 (25.0), 108 (44.1). Anal. Calcd for $C_{25}H_{13}NO_4S$ (423.44): C, 70.91; H, 3.09; N, 3.31%. Found: C, 70.96; H, 3.15; N, 3.38%.

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