Synthesis of benzonaphtho[1,4]diazepine derivatives via the reaction of 2-aminoarylbenzimidamides with 2,3-dichloro-1,4-naphthoquinone

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A series of (*Z*)-13-(arylimino)-12,13-dihydro-5*H*-benzo[*e*]naphtho[2,3-*b*][1,4]diazepine-6,11-dione derivatives have been synthesised by one pot cyclisation in good yield *via* electron donor–acceptor complexes by reacting 2-aminoarylbenzimidamides with 2,3-dichloro-1,4-naphthoquinone. The high yield and simplified workup procedure in addition to the mild and neutral reaction conditions are the main advantages of this approach.

Keywords: aminobenzimidamides, naphthoquinone, CT-complexes, benzonaphthodiazepines

1,4-Naphthoquinone derivatives have stimulated enormous interest due to their biological activities. These compounds exhibited various pharmacological properties including molluscidal, antileishmanial, antiviral, antiallergic, anti-inflammatory, antimalarial, antibacterial, antifungal, and anti-proliferative activities.[1–5] The recent pharmacophore modelling approach applied to 2,3-disubstituted-1,4-naphthoquinone in human promyelocytic leukaemia HL-60 cell line have explained the pronounced cytotoxic activity of these derivatives.[6] In the present work, we found reaction of 2,3-disubstituted-1,4-naphthoquinone with amidine derivatives led to the formation of benzonaphtho-1,4-diazepine derivatives *via* charge-transfer (CT) complexes. The formation of electron donor–acceptor (EDA) or CT-complexes has long been recognised as an important phenomenon in many chemical processes.[7] This approach led us to synthesise several heterocyclic systems that could not be synthesised by usual methods.[8–12] Similar benzodiazepine derivatives are widely distributed in nature and they represent a class of heterocycles which possesses a wide range of biological applications. Many of them are widely used as antileukaemic, antiplatelet, anticonvulsant, antianxiety, sedative, antidepressive, hypnotic and neuroleptic agents.[13–15] Some heterocycles containing benzodiazepines moiety were found to have anti-inflammatory, antiviral, anti-HIV-1, antimicrobial and antitumour activities.[16–19] Other than their biological importance, benzodiazepines are valuable synthons for the preparation of fused ring compounds, such as triazolo, thiazolo, imidazo and pyrimidobenzodiazepines.[20–21] It has been noticed that introduction of an additional ring to the benzodiazepine core tends to exert influence in conferring novel biological activities in these molecules.[22–23] Although many methods for synthesising benzodiazepine ring systems have been reported, they continue to receive a great deal of attention.[24–25]

Results and discussion

In the course of our research and as a part of our program involving the synthesis of new heterocyclic compounds having potential biological interest, we have recently synthesised several quinazoline derivatives with expected biological activities using 2-aminoarylbenzimidamides as starting material. The starting materials were prepared in good yields by treatment of 2-aminobenzonitrile with aniline derivatives in the presence of aluminium chloride as a catalyst and they were all fully characterised (Scheme 1).[26]

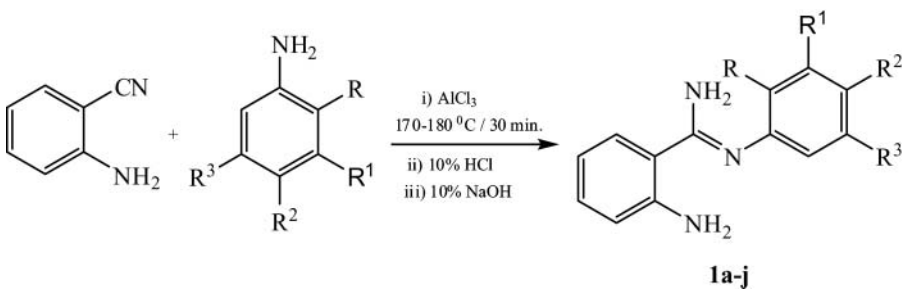
In the present study we are going to synthesise novel benzonaphtho[1,4]diazepine derivatives by mixing equimolar ratios of 2-aminoarylbenzimidamides (**1a–j**) with 2,3-dichloro-1,4-naphthoquinone (**2**) in dry ethyl acetate at room temperature. This approach led to the formation of the desired products **3a–j** in good yields by eliminating two HCl molecules as shown in Scheme 2.

The structures of the products **3a–j** were fully characterised and elucidated on the basis of spectral and analytical data. The detailed spectral data are given in the experimental section and only the salient features are discussed here.

Compounds **3a–j** exhibit in their ^{1}H NMR spectra broadened singlets around δ = 9.43–6.82 ppm, depending on the deuterated solvent, which is used and the nature of the substitutent in position 5, characterising the presence of NH. These NH groups absorbed in the IR spectrum at ν = 3327–3156 cm^{-1}. The IR spectra exhibited absorption peaks at ν = 1691–1668 cm^{-1} and ν = 1641–1603 cm^{-1} corresponding to (C=O) and (C=N), respectively. The carbon atoms of the carbonyl groups resonated in the ^{13}C NMR at 181.10–177.25 ppm, while the benzodiazepine carbon atom C-5 resonated in the ^{13}C NMR at 168.25–164.45 ppm. Moreover ^{13}C NMR spectra contain a signal around δ = 117.99–104.43 ppm assigned to the tertiary carbon C-11 in the benzodiazepine unit. Both mass spectra and elemental analyses confirm the molecular formulae of the products **3a–j**.

Conclusion

On the basis of the above experimental results, it is concluded that new heterocyclic 1,4-diazepine derivatives have been synthesised *via* an EDA complex. Here we report a simple



1a-j

Scheme 1 Synthesis of 2-aminoarylbenzimidamides **1a–j**.

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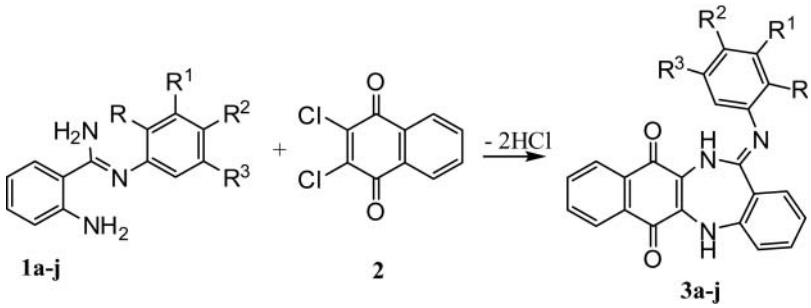

a) R = R¹ = R² = R³ = H
b) R = R³ = CH_3, R¹ = R² = H
c) R = R³ = Cl, R¹ = R² = H
d) R = R³ = H, R¹ = R² = Cl
e) R = R² = CH_3, R¹ = R³ = H
f) R = R¹ = R³ = H, R² = CH_3
g) R = R¹ = R³ = H, R² = OCH_3
h) R = R² = R³ = H, R¹ = OCH_3
i) R = R¹ = R³ = H, R² = Cl
j) R = R¹ = R³ = H, R² = Br

Scheme 2 Reaction of 2-aminoarylbenzimidamides (**1a–j**) with 2,3-dichloro-1,4-naphthoquinone (**2**).

and efficient one-pot synthesis of (*Z*)-13-(arylimino)-12,13-dihydro-5*H*-benzo[*e*]naphtho[2,3-*b*][1,4]diazepine-6,11-dione derivatives in good yield. In all cases, the two components of the reaction proceeded rapidly to afford the corresponding desired products. These products are expected to possess biological activities.

Experimental

All reagents were purchased from Alfa Aesar and Aldrich companies and were used without further purification. 2-Aminoarylbenzimidamide derivatives **1a–j** were prepared according to the literature.[26] The melting points were measured in capillary tubes without corrections using a Büchi 530 melting point apparatus. IR spectra were run using a Bruker Tensor 27 instrument. The mass spectra (EI, 70 eV) were performed using a Finnigan MAT 8430 spectrometer. The NMR spectra were recorded on a Bruker AM400 MHz spectrometer with TMS as internal standard; the coupling constants are given in Hz.

*Reactions of 2-aminoarylbenzimidamides (**1a–j**) with 2,3-dichloro-1,4-napthoquinone (**2**);general procedures*

To a magnetically stirred solution of **2** (57 mg, 0.25 mmol) in dry ethyl acetate (15 mL) was added a solution of **1a–j** (0.25 mmol) in dry ethyl acetate (15 mL) and the mixture was allowed to react at room temperature for 5–9 h (as monitored by TLC). The reaction mixture was concentrated by rotatory evaporation to a volume of 15 mL and then stored in a refrigerator for 3 h. The precipitate obtained was filtered, washed several times with ethyl acetate and dried to afford compounds **3a–j** in (43–59%) yield.

(Z)-13-(Phenylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b][1,4]diazepine-6,11-dione (**3a**): Red powder (39 mg, 43%), m.p. 204–206 °C; this product is insoluble in the following available deuterated solvents: $CDCl_3$, CD_3OD, d_6-DMSO, d_6-acetone. Thus we could not measure either ^{1}H NMR or ^{13}C NMR spectra; IR (KBr): ν_{max} = 3157, 1672, 1609, 1554 cm^{-1}; MS (EI): *m/z* (%) = 365 (M^+, 100), 336 (20), 308 (12), 273 (6), 261 (40), 236 (70), 205 (12), 180 (10), 151 (4), 143 (8), 118 (10), 104 (20), 93 (16), 77 (40), 65 (4), 51 (10); $C_{23}H_{15}N_3O_2$ (365.39): Calcd: C, 75.60; H, 4.14; N, 11.50. Found: C, 75.37; H, 4.11; N, 11.33%.

(Z)-13-(2,5-Dimethylphenylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b][1,4]diazepine-6,11-dione (**3b**), Red powder, (58 mg, 59%), m.p. 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.11 (m, 2 H, H-15,16), 7.76–7.72 (m, 2 H, H-14,17), 7.32–7.27 (m, 1 H, H-6), 7.23 (s, 1 H, NH), 7.20–7.16 (m, 1 H, H-8), 7.06 (d, 1 H, *J* = 7.67 Hz, H-24), 6.99–6.95 (dd, 1 H, *J* = 1.69, 7.71 Hz, H-23), 6.90 (d, 1 H, *J* = 1.67 Hz, H-21), 6.82 (s, 1 H, NH), 6.71–6.63 (m, 2 H, H-7,9), 2.22 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.74 (C-12), 176.02 (C-19), 168.22 (C-5), 150.86 (C-20), 143.52 (C-10), 136.41 (C-22), 134.66 (2 CH, C-15,16), 133.95 (C-2), 132.63 (C-3), 132.29 (CH, C-24), 131.50 (CH, C-8), 131.07 (C-13,18), 130.90 (CH, C-6), 128.50 (CH, C-23), 127.80 (2 CH, C-14,17), 124.13 (C-25), 117.49 (CH, C-21), 116.90 (CH, C-7), 115.14 (CH, C-9), 105.91 (C-11), 20.76 (CH_3), 17.43 (CH_3) ppm; IR (KBr): ν_{max} = 3156, 1679, 1612, 1586, 1558 cm^{-1}; MS (EI): *m/z* (%) = 393 (M^+, 46), 286 (14), 279 (16), 264 [M^+- (2,5-diMePh) 100], 247 (12), 221 (8), 159 (6), 143 (10), 118 (18), 91 (10), 77 (14), 51 (6); $C_{23}H_{15}N_3O_2$ (393.45): Calcd: C, 76.32; H, 4.87; N, 10.68. Found: C, 76.10; H, 4.84; N, 10.56%.

(Z)-13-(2,5-Dichlorophenylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b][1,4]diazepine-6,11-dione (**3c**): Red powder, (50 mg, 46%), m.p. = 186–187 °C; ^{1}H NMR (400 NHz, CD_3OD): δ = 8.05–8.01 (m, 2 H, H-15,16), 7.83–7.77 (dd, 1 H, *J* = 1.07, 7.75 Hz, H-23), 7.74–7.67 (m, 3 H, H-6,14,17), 7.63 (d, 1 H, *J* = 7.78 Hz, H-24), 7.58 (d, 1 H, *J* = 1.03 Hz, H-21), 7.49 (s, 1 H, NH), 7.42–7.37 (m, 2 H, H-7,8), 7.32 (s, 1 H, NH), 7.27–7.23 (m, 1 H, H-9); ^{13}C NMR (100 NHz, CD_3OD): δ = 181.10 (C-12), 178.06 (C-19), 166.12 (C-5), 151.07 (C-20), 149.63, (C-10), 139.33 (C-2), 136.32 (C-3), 134.88 (CH, C-15), 134.77 (CH, C-16), 134.13 (CH, C-24), 132.09 (C-22), 131.04 (CH, C-8), 130.58 (2 CH, C-14,17), 129.98 (C-13,18), 127.14 (CH, C-23), 126.08 (CH, C-21), 125.96 (CH, C-6), 125.20 (C-25), 124.33 (CH, C-7), 122.43 (CH, C-9), 114.21 (C-11); IR (KBr): ν_{max} = 3218, 1691, 1632, 1545, 1507 cm^{-1}; MS (EI): *m/z* (%) = 437 (M^{+4}, 4), 435 (M^{+2}, 28), 433 (M^+, 46), 399 (M^+- Cl, 32), 364 (M^+- 2Cl, 10), 289 (12), 261 (4), 234 (8), 205 (8), 190 (12), 152 (10), 129 (22), 107 (12), 78 (26), 65 (8), 41 (14); $C_{23}H_{13}Cl_2N_3O_2$ (434.28): Calcd: C, 63.61; H, 3.02; N, 9.68. Found: C, 63.38; H, 2.97; N, 9.51%.

(Z)-13-(3,4-Dichlorophenylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b][1,4]diazepine-6,11-dione (**3d**): Red powder, (53 mg, 49%), m.p. = 200–203 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.22 (s, 1 H, NH), 8.12–8.07 (m, 2 H, H-15,16), 7.86–7.78 (m, 3 H, H-6,14,17), 7.65 (d, 2 H, *J* = 8.31 Hz, H-21,22), 7.54 (d, 1 H, *J* = 1.18 Hz, H-25), 7.42–7.37 (m, 2 H, H-7,8), 7.35 (s, 1 H, NH), 7.29–7.25 (m, 1 H, H-9); ^{13}C NMR (100 NHz, d_6-DMSO): δ = 181.07 (C-12), 178.16 (C-19), 166.21 (C-5), 151.10 (C-20), 149.73, (C-10), 139.57 (C-2), 136.32 (C-3), 134.88 (CH, C-15), 134.77 (CH, C-16), 134.02 (C-23), 132.09 (CH, C-22), 131.26 (CH, C-8), 131.04 (C-24), 130.58 (2 CH, C-14,17), 129.98 (C-13,18), 127.60 (CH, C-6), 126.28 (CH, C-21), 125.96 (CH, C-25), 124.33 (CH, C-7), 122.43 (CH, C-9), 113.87 (C-11); IR (KBr): ν_{max} = 3188, 1677, 1624, 1559, 1512 cm^{-1}; MS (EI): *m/z* (%) = 437 (M^{+4}, 10), 435 (M^{+2}, 62), 433 (M^+, 100), 399 (M^+- Cl, 10), 364 (M^+- 2Cl, 8), 289 (8), 261 (12), 234 (18), 205 (12), 190 (4), 152 (10), 129 (22), 107 (12), 78 (26), 65 (8), 41 (14); $C_{23}H_{13}Cl_2N_3O_2$ (434.28): Calcd: C, 63.61; H, 3.02; N, 9.68. Found: C, 63.38; H, 2.98; N, 9.54%.

(Z)-13-(2,4-Dimethylphenylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b][1,4]diazepine-6,11-dione (**3e**): Red powder, (54 mg, 55%), m.p. = 214–217 °C; ^{1}H NMR (400 NHz, CD_3OD): δ = 8.06–8.01 (m, 2 H, H-15,16), 7.66–7.55 (m, 3 H, H-6,14,17), 7.41–7.34 (m, 1 H, H-8), 7.30 (s, 1 H, NH), 7.27 (d, 1 H, *J* = 1.27 Hz, H-24), 7.22–7.17 (dd, 1 H, *J* = 1.24, 7.89 Hz, H-22), 7.06 (d, 1 H, *J* = 7.84 Hz, H-21), 6.93–6.88 (m, 1 H, H-7), 6.74 (s, 1 H, NH), 6.63–6.59 (m, 1 H, H-9), 2.24 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3) ppm; ^{13}C NMR (100 NHz, CD_3OD): δ = 180.02 (C-12), 177.60 (C-19), 167.11 (C-5), 151.04 (C-20), 143.55 (C-10), 135.87 (C-2), 134.63 (2 CH, C-15,16), 133.91 (C-3), 132.56 (C-13), 132.42 (CH, C-24), 131.57 (CH, C-8), 131.21 (C-18), 130.69 (C-25), 128.81 (C-23), 127.83 (2 CH, C-14,17), 125.95 (CH, C-22), 124.31 (CH, C-6), 117.49 (CH, C-21), 116.90 (CH, C-7), 115.14 (CH, C-9), 105.87 (C-11), 20.77 (CH_3), 17.48 (CH_3) ppm; IR

(KBr): ν_{max} = 3175, 1643, 1603, 1525 cm^{-1}; MS (EI): *m/z* (%) = 394 (M^{+1}, 20), 393 (M^+, 100), 378 (M^+- CH_3, 22), 362 (10), 309 (4), 279 (6), 264 [M^+- (2,5-diMePh), 84], 247 (12), 221 (8), 159 (6), 143 (10), 118 (18), 91 (10), 77 (14), 51 (6); $C_{25}H_{19}N_3O_2$ (393.45): Calcd: C, 76.32; H, 4.87; N, 10.68. Found: C, 76.13; H, 4.88; N, 10.50%.

(Z)-13-(p-Tolylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b] [1,4]diazepine-6,11-dione (**3f**): Red powder, (55 mg, 58%), m.p. = 201–202 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.17 (s, 1 H, NH), 8.08–8.04 (m, 1 H, H-15), 7.87–7.76 (m, 4 H, H-6,14,16,17), 7.69–7.63 (m, 1 H, H-8), 7.59 (d, 2 H, *J* = 8.38 Hz, H-22,24), 7.51–7.48 (dd, 1 H, *J* = 0.87, 8.27 Hz, H-7), 7.36 (d, 2 H, *J* = 8.36 Hz, H-21,25), 7.31 (s, 1 H, NH), 7.29 (d, 1 H, *J* = 1.07 Hz, H-9), 2.38 (s, 3 H, CH_3) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 179.27 (C-12), 177.96 (C-19), 166.55 (C-5), 150.03 (C-20), 149.73, (C-10), 139.57 (C-23), 136.32 (C-2), 134.88 (CH, C-15), 134.77 (CH, C-16), 134.02 (CH, C-8), 132.09 (C-3), 131.04 (CH, C-6), 130.58 (2 CH, C-22,24), 129.98 (C-13), 127.60 (2 CH, C-21,25), 126.28 (CH, C-14), 125.96 (CH, C-17), 124.33 (CH, C-7), 122.43 (CH, C-9), 117.99 (C-11), 20.77 (CH_3) ppm; IR (KBr): ν_{max} = 3182, 1676, 1641, 1596, 1508 cm^{-1}; MS (EI): *m/z* (%) = 379 (M^+, 100), 364 (M^+–CH_3, 20), 350 (16), 322 (6), 307 (4), 277 (18), 261 (36), 234 (8), 205 (8), 190 (10), 152 (6), 129 (8), 107 (20), 77 (16), 65 (8), 43 (14); $C_{24}H_{17}N_3O_2$ (379.42): Calcd: C, 75.97; H, 4.52; N, 11.08. Found: C, 75.81; H, 4.50; N, 10.89%.

(Z)-13-(4-Methoxyphenylimino)-12,13-dihydro-5H-benzo[e] naphtho[2,3-b] [1,4]diazepine-6,11-dione (**3g**): Brown solid, (49 mg, 50%), m.p. = 251–253 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.01 (s, 1 H, NH), 8.11–8.05 (m, 2 H, H-15,16), 7.95–7.87 (m, 2 H, H-14,17), 7.76–7.69 (m, 2 H, H-6,8), 7.59 (d, 2 H, *J* = 8.29 Hz, H-21,25), 7.45 (d, 2 H, *J* = 8.33 Hz, H-22,24), 7.41–7.36 (dd, 1 H, *J* = 0.87, 8.27 Hz, H-7), 7.30 (s, 1 H, NH), 7.24–7.19 (m, 1 H, H-9), 3.78 (s, 3 H, OCH_3) ppm; IR (KBr): ν_{max} = 3238, 1668, 1621, 1579, 1511 cm^{-1}; MS (EI): *m/z* (%) = 395 (M^+, 100), 364 (M^+- OCH_3, 60), 350 (4), 320 (8), 307 (4), 277 (18), 261 (10), 234 (12), 205 (22), 190 (10), 152 (6), 129 (18), 107 (22), 77 (6), 65 (18), 43 (4); $C_{24}H_{17}N_3O_3$ (395.42): Calcd: C, 72.90; H, 4.33; N, 10.63. Found: C, 72.71; H, 4.28; N, 10.47%.

(Z)-13-(3-Methoxyphenylimino)-12,13-dihydro-5H-benzo[e] naphtho[2,3-b] [1,4]diazepine-6,11-dione (**3h**): Brown solid, (46 mg, 47%), m.p. = 111–112 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.01 (s, 1 H, NH), 8.11–8.05 (m, 2 H, H-15,16), 7.95–7.87 (m, 2 H, H-14,17), 7.45–7.39 (m, 3 H, H-6,8,22), 7.37–7.33 (m, 1 H, H-23), 7.31–7.26 (m, 1 H, H-25), 7.24–7.20 (m, 1 H, H-7), 7.18 (s, 1 H, NH), 6.81–6.76 (m, 1 H, H-9), 6.72–6.69 (m, 1 H, H-21), 3.87 (s, 3 H, OCH_3) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 180.12 (C-12), 177.49 (C-19), 165.37 (C-5), 151.10 (C-24), 149.73, (C-20), 139.57 (C-10), 136.32 (C-2), 134.88 (CH, C-15), 134.77 (CH, C-16), 134.02 (CH, C-22), 132.09 (C-3), 131.04 (CH, C-8), 130.58 (2 CH, C-14,17), 129.98 (C-13,18), 127.60 (2 CH, C-6,7), 126.28 (CH, C-9), 125.96 (CH, C-21), 124.33 (CH, C-25), 122.43 (CH, C-23), 104.43 (C-11), 55.27 (OCH_3) ppm; IR (KBr): ν_{max} = 3278, 1687, 1624, 1596, 1508 cm^{-1}; MS (EI): *m/z* (%) = 395 (M^+, 100), 364 (M^+- OCH_3, 32), 350 (16), 320 (12), 307 (14), 277 (8), 261 (30), 234 (28), 205 (22), 190 (4), 152 (16), 129 (12), 107 (12), 77 (16), 65 (8), 43 (14); $C_{24}H_{17}N_3O_3$ (395.42): Calcd: C, 72.90; H, 4.33; N, 10.63. Found: C, 72.66; H, 4.34; N, 10.45%.

(Z)-13-(4-Chlorophenylimino)-12,13-dihydro-5H-benzo[e]naphtho[2,3-b] [1,4]diazepine-6,11-dione (**3i**): Red powder, (51 mg, 51%), m.p. = 215–217 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.43 (s, 1 H, NH), 8.12–8.07 (m, 1 H, H-15), 7.77–7.73 (m, 1 H, H-16), 7.70–7.67 (m, 2 H, H-14,17), 7.64 (d, 2 H, *J* = 8.38 Hz, H-22,24), 7.55–7.52 (dd, 1 H, *J* = 1.02, 8.32 Hz, H-6), 7.35 (d, 2 H, *J* = 8.36 Hz, H-21,25), 7.33 (s, 1 H, NH), 7.27–7.23 (m, 1 H, H-8), 6.91–6.87 (m, 1 H, H-7), 6.77–6.71 (m, 1 H, H-9) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 180.12 (C-12), 178.59 (C-19), 166.25 (C-5), 150.78 (C-20), 149.67 (C-10), 139.57 (C-23), 136.79 (C-2), 135.25 (CH, C-15), 134.88 (CH, C-16), 134.77 (CH, C-8), 134.02 (C-3), 132.80 (CH, C-6), 131.69 (2 CH, C-22,24), 131.37 (C-13), 130.95 (CH, C-21), 129.98 (CH, C-25), 127.57 (CH, C-14), 126.20 (CH, C-17), 125.96 (CH, C-7), 124.33 (C-18), 123.17 (CH, C-9), 117.99 (C-11) ppm; IR (KBr): ν_{max} = 3183, 1673, 1642, 1589, 1504 cm^{-1}; MS (EI): *m/z* (%) = 401 (M^{+2}, 44), 399 (M^+, 100), 370 (16), 364 (M^+- Cl, 24), 354 (6), 336 (4), 297 (8), 273 (10), 261 (44), 234 (10), 205 (10), 178 (8), 151 (8), 111 (12), 105 (16), 97 (10), 77 (18), 43 (12); $C_{23}H_{14}ClN_3O_2$ (399.84): Calcd: C, 69.09; H, 3.53; Cl, 8.87; N, 10.51. Found: C, 68.87; H, 3.48; Cl, 8.64; N, 10.32%.

(Z)-13-(4-Bromophenylimino)-12,13-dihydro-5H-benzo[e] naphtho[2,3-b] [1,4]diazepine-6,11-dione (**3j**): Red powder, (60 mg, 54%), m.p. = 179–181 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 8.09–8.01 (m, 1 H, H-15), 7.79–7.76 (m, 1 H, H-16), 7.70–7.67 (m, 2 H, H-14,17), 7.65 (d, 2 H, *J* = 8.73 Hz, H-22,24), 7.58 (s, 1 H, NH), 7.35 (d, 2 H, *J* = 8.72 Hz, H-21,25), 7.32 (s, 1 H, NH), 7.28–7.23 (m, 2 H, H-6,8), 6.83 (d, 1 H, *J* = 8.28 Hz, H-7), 6.72–6.67 (m, 1 H, H-9) ppm; ^{13}C NMR (100 MHz, CD_3OD): δ = 180.49 (C-12), 177.26 (C-19), 165.67 (C-5), 151.64 (C-20), 150.70 (C-10), 148.25, (C-2), 139.18 (C-3), 136.86 (C-13), 136.22 (CH, C-15), 135.71 (CH, C-16), 134.89 (2 CH, C-22,24), 134.53 (2 CH, C-14,17), 132.52 (C-18), 131.23 (CH, C-8), 130.43 (CH, C-6), 128.45 (2 CH, C-21,25), 127.71 (C-23), 123.47 (CH, C-7), 118.11 (CH, C-9), 114.47 (C-11) ppm; IR (KBr): ν_{max} = 3327, 1678, 1608, 1586, 1554 cm^{-1}; MS (EI): *m/z* (%) = 445 (M^{+2}, 98), 443 (M^+, 100), 414 (16), 400 (8), 364 (M^+- Br, 40), 336 (8), 307 (4), 289 (12), 261 (54), 234 (10), 205 (12), 171 (20), 133 (10), 129 (10), 104 (18), 76 (20), 65 (12); $C_{23}H_{14}BrN_3O_2$ (444.29): Calcd: C, 62.18; H, 3.18; N, 9.46. Found: C, 61.97; H, 3.14; N, 9.29%.

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