Asian Journal of Chemistry; Vol. 25, No. 18 (2013), 0000-0000

ASIAN JOURNAL OF CHEMISTRY

Synthesis of Novel 2,3-Disubstituted 1,4-Naphthoquinone Derivatives Containing Indole, Quinoline, Thiazole and Imidazole Moieties

MONIRAH A. AL-ALSHAIKH and SIHAM A. LAHSASNI*

Department of Chemistry, Faculty of Science, King Saud University, P.O. Box 22452, Riyadh 11495, Saudi Arabia

*Corresponding author: E-mail: slahsasni@ksu.edu.sa

(*Received*: ; *Accepted*:) AJC-0000

The present work describes one-pot multicomponent synthesis in which Michael addition-elimination reactions of the precursors 2-chloro-3-(2-arylhydrazinyl)naphthalene-1,4-dione, 2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[*f*]indole-3-carbonitrile and 2-amino-4-aryl-5,10-dioxo-5,10-dihydrobenzo[*g*]quinoline-3-carbonitrile with carbon disulphide, followed by intramolecular cyclization in the presence of pyridine or sulphuric acid or hydrazine have led to formation of the corresponding 3-arylamino-2-thioxo-2,3-dihydro-naphtho[2,3-*d*]thiazole-4,9-dione, 2-thioxo-2*H*-benzo[f]thiazolo[4,5-b]indole-5-10(3*H*,4*H*)-dione, 2-mercapto benzo[f]thiazolo[4,5-b]indole-5-10(1*H*,4*H*)-dione, 11-aryl-2-thioxo-2,3-dihydrotobenzo[g]thiazolo [4,5-b]quinoline-5,10-dione and 1-amino-11-aryl-2-mercapto-1*H*-benzo[g]imidazo[4,5-b] quinoline-5,10-dione. The synthesized compounds have been identified and their structures are in confirmation with various spectroscopic techniques including IR, ^{1}H NMR, ^{13}C NMR and mass spectra.

Key Words: 2,3-Dichloro1,4-naphthoquinone, Michael addition-elimination, Intramolecular cyclization.

INTRODUCTION

The chemistry of quinone annulated heterocycles is highly dependent on the substituents at the quinonic or the adjacent rings[1,2]. Among various classes of heterocyclic quinones, naphthofluroquinones have attracted extensive interest owing to their presence in natural products and their versatile pharmacological activities. In this regard, many naphthofluroquinones are identified as natural products exhibiting a broad spectrum of biological activity[3-6].

Furthermore, as a result of their redox properties, hetero-1,4-naphthoquinones have shown potent biological affinity towards viral[7], molluscidal[8], malarial[9], leishmanial[10], cancer[11], bacterial and fungal diseases[12,13].

Structure-activity relationship studies on heterocyclic quinonoid compounds revealed that ring number and the position of the nitrogen or sulfur atoms in the heterocyclic ring play important role in manipulating the physiological and biological activities[14-16] of these compounds.

Thus, in order to study the effect of different heterocyclic (*e.g.* indole, quinoline, thiazole and thione) quinonoid on the antibacterial and antifungal activities, we have carried out the synthesis, reactions and biological applications of a series of 2,3-disubstituted-1,4-naphthoquinone derivatives *via* utilization of 2,3-dichloro-1,4-naphthoquinone substrate in presence of the strong nucleophiles.

EXPERIMENTAL

All synthetic procedures were undertaken *via* Schlenk technique with dried solvents. Most reagents were purchased from Across, Sigma Aldrich and Merck. All synthesized compounds gave satisfactory elemental analysis for C, H and N. Flash chromatography was carried out using a glass column with silica gel (particle size 0.035-0.07 mm, pore diameter *ca.* 6 nm). Solvent systems were determined *via* initial TLC analysis (Merck, silica gel 60F254).

Melting points were determined using an electrothermal's IA9000 series digital capillary melting point apparatus and used without correction. IR spectra were obtained, as KBr discs, a 1000-Perkin Elmer FT-IR spectrophotometer. Spectroscopic data were recorded as follows: ^{1}H and ^{13}C NMR spectra were acquired on a JEOL ECP-600 NMR in $CDCl_3$ (or DMSO-d_6) using TMS as an internal standard. Chemical shifts are given in δ ppm. Mass spectra were collected using a direct inlet system (70 eV) with a VL detector (ES, 4000 V).

Synthesis of 2-chloro-3-(4-arylhydrazinyl)naphthalene-1,4-dione: A mixture of 2,3-dichloro-1,4-naphthoquinone **1** (0.4 g, 0.88 mmol) and aryl hydrazine **2a-d** (0.88 mmol) in ethanol (15 mL) was stirred in ice-bath for 1-4 h; the solid product was filtered off and washed with ethanol. Flash chromatography on silica gel using methanol/chloroform (1:4) as eluent gave 2-chloro-3-(2-arylhydrazinyl)-

naphthalene-1,4-dione (**3a-d**) as a solid crystals with different colours as shown below.

2-Chloro-3-(2-phenylhydrazinyl)naphthalene-1,4-dione (3a): Red needles, yield: (80 %); m.p. 191-193 ºC; IR (KBr, ν_{max}, cm^{-1}): 3376 and 3213 (NH),1659 and 1579 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm 3.65 (bs, 1H, NH), 7.33-7.46 (m, 3H, phenyl), 7.52-7.57 (m, 2H, Phenyl), 7.85-8.06 (m, 2H, C5-H and C8-H), 8.13-8.18 (m, 2H, C6-H and C7-H); 9.75 (bs, 1H, NH); ^{13}C NMR: 113.16, 113.84, 121.69, 122.65, 124.18, 125.95, 127.45, 128.53, 129.13, 137.9, 142.2, 156.2 (sp^2 carbons), 179.71 and 187.45(C=O); Mass (M^+): 298.05; anal. calcd. (%) for $C_{16}H_{11}N_2O_2Cl$: C, 64.41; H, 3.69; N,9.39. Found (%): C, 64.18; H, 3.68; N, 9.27; Beilstein test[17]: Cl positive.

2-Chloro-3-[4-(4-nitrophenyl)hydrazinyl]naphthalene-1,4-dione (3b): Yellow needles, yield: (65 %); m.p. 220-123 ºC; IR (KBr, ν_{max}, cm^{-1}): 3379 and 3214 (NH),1658 and 1586 (C= O of quinone) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ ppm 3.65 (bs, 1H, NH), 6.92-7.03 (m, 2H, nitrophenyl), 7.85-8.06 (m, 2H, C5-H and C8-H), 8.12-8.17 (m, 2H, C6-H and C7-H); 8.21-8.27 (m, 2H, nitrophenyl), 9.45 (bs, 1H, NH); ^{13}C NMR: 113.16, 113.84, 121.69, 122.65, 124.18, 124.61, 125.95, 127.45, 128.53, 129.13, 137.7, 148.2, 156.2 (sp^2 carbons), 179.61 and 187.42 (C=O); mass (M^+):343.81; anal. calcd. (%) for $C_{16}H_{10}N_3O_4Cl$: C, 55.84; H, 2.90; N, 12.24. Found (%): C, 55.53; H, 2.60; N, 12.07; Beilstein test[17]: Cl positive.

2-Chloro-3-(4-(4-chlorophenyl)hydrazinyl)naphthalene-1,4-dione(3c): Yellow needles, yield: (75 %); m.p. 205-207 ºC; IR (KBr, ν_{max}, cm^{-1}): 3381 and 3223 (NH),1657 and 1596 (C= O of quinone) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ ppm 3.55 (bs, 1H, NH), 6.62-6.72 (m, 2H, chlorophenyl), 7.61-7.67 (m, 2H, chlorophenyl), 7.85-7.06 (m, 2H, C5-H and C8-H), 8.12-8.17 (m, 2H, C6-H and C7-H); 9.55 (bs, 1H, NH); ^{13}C NMR: 113.16, 113.84, 121.69, 122.65, 124.18, 124.61, 125.95, 127.45, 128.53, 129.13, 136.8,140.2, 156.2 (sp^2 carbons), 179.61 and 187.42 (C=O); mass (M^+):333.41; anal. calcd. (%) for $C_{16}H_{10}N_2O_2Cl_2$: C, 57.65; H, 3.00; N, 8.40. Found (%): C, 57.23; H, 2.98; N, 8.07; Beilstein test[17]: Cl positive.

2-Chloro-3-(4-(4-methoxyphenyl)hydrazinyl)naphthalene-1,4-dione(3d): Greenish yellow needles, yield: (80 %); m.p. 198-202 ºC; IR (KBr, ν_{max}, cm^{-1}): 3481 and 3323 (NH), 1658 and 1593 (C= O of quinone) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ ppm 3.50 (bs, 1H, NH), 3.67 (s, 3H, OCH_3), 6.52-6.62 (m, 2H, methoxyphenyl), 6.91-7.07 (m, 2H, methoxyphenyl), 7.85-8.06 (m, 2H, C5-H and C8-H), 8.12-8.17 (m, 2H, C6-H and C7-H); 9.25 (bs, 1H, NH); ^{13}C NMR: 58 (CH_3), 113.16, 113.84, 118.53, 119.13, 121.69, 122.65, 124.18, 124.61, 125.95, 127.45, 134.8, 150.2, 156.2 (sp^2 carbons), 179.11 and 187.62 (C=O); Mass (M^+):329.55; anal. calcd. (%) for $C_{17}H_{13}N_2O_3Cl$: C, 61.90; H, 3.95; N, 8.49. Found (%): C, 61.79; H, 3.78; N, 8.38; Beilstein test[17]: Cl positive.

Synthesis of 3-arylamino-2-thioxo-2,3-dihydronaptho[2,3-d]thiazole-4,9-dione: A mixture of 2-chloro-3-(4-arylhydrazinyl)naphthalene-1,4-dione **3a-d** (0.01 mol) and carbon disulfide (0.05 mol) in pyridine (10 mL) was heated in oil-bath for 12-16 h. After cooling, ethanol was added and the precipitated solid was collected by filtration, purified *via* column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent to give 3-arylamino-2-thioxo-2,3-dihydro-naptho-[2,3-d]thiazole-4,9-dione **4a-d** as yellow powders.

3-Phenylamino-2-thioxo-2,3-dihydro-naptho[2,3-d]thiazole-4,9-dione (4a): Yellow powder, yield: (60 %); m.p. 230-233 ºC; IR (KBr, ν_{max}, cm^{-1}): 3423 (NH), 1656 and 1586 (C= O of quinone), 1190 (C=S of thiazole); ^{1}H NMR (DMSO-d_6): δ ppm 4.12 (bs, 1H, NH), 7.31-7.45 (m, 3H, phenyl), 7.52-7.57 (m, 2H, phenyl), 7.85-8.06 (m, 2H, C5-H and C8-H), 8.13-8.18 (m, 2H, C6-H and C7-H); ^{13}C NMR: 113.16, 113.84, 114.09, 122.65, 124.18, 125.95, 127.45, 128.53, 129.13, 137.9, 142.2, 166.2 (sp^2 carbons), 179.71 and 187.45(C=O), 190.12 (C=S); mass (M^+):338.47; anal. calcd. (%) for $C_{17}H_{10}N_2O_2S_2$: C, 60.27; H, 2.96; N, 8.27. Found (%): C, 60.08; H, 2.62; N, 7.99.

3-(4-Nitrophenyl)amino-2-thioxo-2,3-dihydronaptho[2,3-d]thiazole-4,9-dione (4b): Greenish yellow powder, yield: (55 %); m.p. 262-264 ºC; IR (KBr, ν_{max}, cm^{-1}): 3479 (NH),1658 and 1586 (C= O of quinone), 1196 (C=S of thiazole); ^{1}H NMR (DMSO-d_6): δ ppm: 4.65 (bs, 1H, NH), 6.92-7.03 (m, 2H, nitrophenyl), 7.85-8.06 (m, 2H, C5-H and C8-H), 8.12-8.17 (m, 2H, C6-H and C7-H); 8.21-8.27 (m, 2H, nitrophenyl), 9.45 (bs, 1H, NH); ^{13}C NMR: 113.16, 113.84, 114.18, 121.69, 122.65, 124.61, 125.95, 127.45, 128.53, 129.13, 137.7, 148.2, 166.32 (sp^2 carbons), 179.61 and 187.42 (C=O); 190.12 (C=S); mass (M^+): 383.44; anal. calcd. (%) for $C_{17}H_9N_3O_4S_2$: C, 53.20; H, 2.35; N, 10.97. Found (%): C, 52.98; H, 2.03; N, 10.63.

3-(4-Chlorophenyl)amino-2-thioxo-2,3-dihydronaptho[2,3-d]thiazole-4,9-dione (4c): Greenish yellow powder, yield: (57 %); m.p. 250-253 ºC; IR (KBr, ν_{max}, cm^{-1}): 3483 (NH), 1657 and 1596 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 6.62-6.72 (m, 2H, chlorophenyl), 7.61-7.67 (m, 2H, chlorophenyl), 7.85-7.06 (m, 2H, C5-H and C8-H), 8.12-8.17 (m, 2H, C6-H and C7-H); 9.55 (bs, 1H, NH); ^{13}C NMR: 113.16, 113.84, 114.18, 121.69, 122.65, 124.61, 125.95, 127.45, 128.53, 129.13, 136.8, 140.2, 166.2 (sp^2 carbons), 179.61 and 187.42 (C=O); 190.10 (C=S); mass (M^+):373.34; anal. calcd. (%) for $C_{17}H_9N_2O_2S_2Cl$: C, 54.70; H, 2.41; N, 7.50. Found (%): C, 54.45; H, 2.23; N, 7.29.

3-(4-Methoxyphenyl)amino-2-thioxo-2,3-dihydronaptho[2,3-d]thiazole-4,9-dione (4d): Greenish yellow powder, yield: (68 %); m.p. 239-242 ºC; IR (KBr, ν_{max}, cm^{-1}): 3483 (NH), 1657 and 1596 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 3.67 (s, 3H,OCH_3), 6.52-6.62 (m, 2H, methoxyphenyl), 6.91-7.07 (m, 2H, methoxyphenyl), 7.85-8.06 (m, 2H, C5-H and C8-H), 8.12-8.17 (m, 2H, C6-H and C7-H); 9.25 (bs, 1H, NH); ^{13}C NMR: 58 (CH_3), 113.16, 113.84, 114.18, 118.53, 119.13, 121.69, 122.65, 124.61, 125.95, 127.45, 134.8, 150.2, 166.2 (sp^2 carbons), 179.11 and 187.62 (C=O), 190.10 (C=S); mass (M^+): 369.49; anal. calcd. (%) for $C_{18}H_{12}N_2O_3S_2$: C, 58.54; H, 3.25; N, 7.58. Found (%): C, 58.38; H, 3.06; N, 7.32.

Synthesis of 2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indole-3-carbonitrile (5): A mixture of 2,3-dichloro-1,4-naphthoquinone **1** (0.8 mmol) and malonitrile (0.8 mmol) in absolute ethanol was heated under reflux for 5 h in the presence of ammonium acetate (4 mmol). The reaction mixture was then cooled, filtered off, then washed with absolute ethanol and air dried. Recrystallization from chloroform afforded

2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indole-3-carbonitrile **(5)** as a violet powder. Violet powder, yield: (85 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3270 (NH), 3155 and 3033 (NH_2), 2169 (CN), 1672 and 1595 (C= O of quinone) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ ppm: 2.49 (bs, NH_2), 6.52 (bs, NH), 7-7.20 (m, 1H, C5-H), 7.64-7.76 (m, 2H, C6-H and C7-H); 7.89-7.91 (m, 1H, C8-H); ^{13}C NMR: 113.16 (CN),121.40, 125.34, 126.27, 131.43, 131.85, 132.83, 134.26, 144.35 (sp^2 carbons), 171.97 and 182.645 (C=O); mass (M^+): 237.39; anal. calcd. (%) for $C_{13}H_7N_3O_2$: C, 65.82; H, 2.95; N, 17.72. Found (%): C, 65.68; H, 2.64; N, 17.58.

Synthesis of potassium 3-cyano-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indol-2-ylcarbamodithioate (6): A mixture of compound **5** (0.4 mmol) and carbon disulphide (0.44 mmol) together with potassium hydroxide (0.4 mmol) in absolute ethanol was stirred for 24 h at room temperature. Dry ether was then added and the precipitated solid was collected by filtration, thereby obtaining the corresponding potassium 3-cyano-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indol-2-yl-carbamodithioate (**6**).

Synthesis of 2-thioxo-2*H*-benzo[f]thiazolo[4,5-b]indole-5-10(3*H*,4*H*)-dione (7): An aqueous solution of potassium 3-cyano-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indol-2-yldithiocarbazate **6** (0.04 mmol) was added dropwise with constant stirring to concentrated sulphuric acid (98 %, 15 mL) and the reaction mixture was stirred for 24 h. The mixture was cautiously added to crushed ice, stirred for 1 h, refrigerated for 2 h and the precipitated solid was filtered off and purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to give a green solid of the title compound 2-thioxo-2*H*-benzo[f]thiazolo[4,5-b]indole-5-10(3*H*,4*H*)-dione (**7**). Green powder, yield: (60 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3428 (NH), 1656 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.43 (bs, NH), 7-7.20 (m, 1H, C6-H), 7.64-7.76 (m, 2H, C7-H and C8-H); 7.89-7.91 (m, 1H, C9-H), 9.85 (bs, 1H, NH); ^{13}C NMR: 121.40, 125.34, 126.27, 131.43, 131.85, 132.83, 134.26, 164.35 (sp^2 carbons), 171.97 and 182.645 (C=O), 184.52 (C=S); mass (M^+): 286.56; anal. calcd. (%) for $C_{13}H_6N_2O_2S_2$: C, 54.54; H, 2.09; N, 9.79. Found (%): C, 54.28; H, 1.98; N, 9.54.

Synthesis of 2-mercaptobenzo[f]thiazolo[4,5-b]indole-5-10(1*H*,4*H*)-dione (8): A mixture of compound **5** (0.04 mmol) and 98 % hydrazine hydrate (10 mL) was heated under reflux for 3 h. After cooling, water was added and the mixture was neutralized with 10 % hydrochloric acid. The separated crude product was then filtered off and purified *via* column chromatography using methanol/chloroform (1:4) as eluent to yield compound **8** in 25 %. Gray powder, yield: (55 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3328 (NH), 3155 and 3033 (NH_2), 2560 (SH), 1656 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.43 (bs, NH), 6.66 (bs, 2H, NH_2), 7-7.20 (m, 1H, C6-H), 7.64-7.76 (m, 2H, C7-H and C8-H); 7.89-7.91 (m, 1H, C9-H), 12.05 (s, 1H, SH); ^{13}C NMR: 121.40, 125.34, 126.27, 131.43, 131.85, 132.83, 134.26, 164.35 (sp^2 carbons), 171.97 and 182.645 (C=O); mass (M^+): 284.81; anal. calcd. (%) for $C_{13}H_8N_4O_2S$: C, 54.93; H, 2.82; N, 19.72. Found (%): C, 54.75; H, 2.56; N, 19.53.

2-Arylidenemalononitrile (9a-d): All these compounds were prepared as reported[23-25].

Synthesis of 2-amino-4-aryl-5,10-dioxo-5,10-dihydrobenzo[g]quinoline-3-carbonitrile: A mixture of 2,3-dichloro-1,4-naphthoquinone (0.3 mmol) 1, 2-arylidenemalononitrile **9a-d** (0.3 mmol) and ammonium acetate (1.2 mmol) in ethanol (15 mL) was heated under reflux for 4-7 h. The solid product was filtered, washed with ethanol, dried and recrystallized from chloroform to yield compounds **10a-d** as violet powders.

2-Amino-5,10-dioxo-4-phenyl-5,10-dihydrobenzo[g]-quinoline-3-carbonitrile (10a): Yield: (86 %); m. p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3250 and 3138 (NH_2), 2171 (CN), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 5.51 (bs, 2H, NH_2), 7.09-7.18 (m, 1H, phenyl), 7.27-7.35 (m, 2H, phenyl), 7.46-7.52 (m, 2H, phenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H); ^{13}C NMR: 112.40 (CN), 93.6, 120.59, 124.53, 125.45, 128.4, 130.64, 131.03, 132.04, 133.45, 143.60, 153, 156.3, 164.60 (sp^2 carbons), 171.17 and 181.85 (C=O); Mass (M^+): 325.35; anal. calcd. (%) for $C_{20}H_{11}N_3O_2$: C, 73.84; H, 3.38; N, 12.92. Found (%): C, 73.55; H, 3.18; N, 12.73.

2-Amino-5,10-dioxo-4-(4-nitrophenyl)-5,10-dihydrobenzo-[g]quinoline-3-carbonitrile (10b): Yield: (80 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3245 and 3123 (NH_2), 2168 (CN), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 5.51 (bs, 2H, NH_2), 7.56-7.60 (m, 2H, nitrophenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H), 8.27-8.35 (m, 2H, nitrophenyl); ^{13}C NMR: 112.40 (CN), 93.6, 120.59, 124.53, 125.45, 128.4, 130.64, 131.03, 132.04, 140.45, 148.4, 153.0, 156.3, 164.60 (sp^2carbons), 171.17 and 181.85 (C=O); mass (M^+): 370.25; anal. calcd. (%) for $C_{20}H_{10}N_4O_4$: C, 64.86; H, 2.70; N, 20.74. Found (%): C, 64.52; H, 2.47; N, 20.51.

2-Amino-5,10-dioxo-4-(4-chlorophenyl)-5,10-dihydrobenzo[g]quinoline-3-carbonitrile (10c): Yield: (84 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3255 and 3133 (NH_2), 2170 (CN), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 5.51 (bs, 2H, NH_2), 7.29-7.35 (m, 2H, chlorophenyl), 7.53-7.58 (m, 2H, chlorophenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H); ^{13}C NMR: 112.40 (CN), 93.6, 120.59, 124.53, 125.45, 128.4, 130.64, 131.03, 132.04, 134.4, 136.65, 153.0, 156.3, 164.60 (sp^2 carbons), 171.17 and 181.85 (C=O); mass (M^+): 359.85; anal. calcd. (%) for $C_{20}H_{10}N_3O_2Cl$: C, 66.85; H, 2.78; N, 11.70. Found (%): C, 66.65; H, 2.43; N, 11.47.

2-Amino-5,10-dioxo-4-(4-methoxyphenyl)-5,10-dihydrobenzo[g]quinoline-3-carbonitrile (10d): Yield: (87 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3233 and 3123 (NH_2), 2170 (CN), 1676 and 1586 (C=O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 3.63 (s, 3H, CH_3), 5.51 (bs, 2H, NH_2), 7.09-7.15 (m, 2H, methoxyphenyl), 7.43-7.48 (m, 2H, methoxyphenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H); ^{13}C NMR: 56.8 (CH_3), 112.40 (CN), 93.6, 114.4, 120.59, 124.53, 125.45, 130.64, 130.95, 131.03, 132.04, 153.0, 156.3, 160.14, 164.60 (sp^2 carbons), 171.17 and 181.85 (C=O); mass (M^+): 355.85; anal. calcd. (%) for $C_{21}H_{13}N_3O_3$: C, 70.98; H, 3.66; N, 11.83. Found (%): C, 70.75; H, 3.48; N, 11.59.

Synthesis of potassium 4-aryl-3-cyano-5,10-dioxo-5,10-dihydrobenzo[g]quinolin-2-ylcarbamodithiate (11a-d): A mixture of compound **10a-d** (0.4 mmol) and carbon disulphide

(0.44 mmol) together with potassium hydroxide (0.4 mmol) in absolute ethanol was stirred for 24 h at room temperature. Dry diethyl ether was then added and the precipitated solid was collected by filtration to give the corresponding potassium 4-aryl-3-cyano-5,10-dioxo-5,10-dihydrobenzo[*g*] quinolin-2-ylcarbamodithiate **11a-d**.

Synthesis of 11-aryl-2-thioxo-2,3-dihydrotobenzo[g] thiazolo[4,5-b]quinoline-5,10-dione: A solution of potassium 4-aryl-3-cyano-5,10-dioxo-5,10-dihydrobenzo[*g*]quinolin-2-ylcarbamodithiate **(11a-d)** (0.04 mmol) was added dropwise to a conc. sulphuric acid (15 mL, 98 %) and then stirred for 24 h. The mixture was cautiously added to crushed ice, stirred for 1 h, refrigerated for 2 h and the separated precipitate was filtered off and purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to afford 11-aryl-2-thioxo-2,3-dihydrotobenzo[*g*]thiazolo[4,5-b]quinoline-5,10-dione.

11-Phenyl-2-thioxo-2,3-dihydrotobenzo[g]thiazolo-[4,5-b]quinoline-5,10-dione (12a): Green powder, yield: (55 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3350 (NH), 1676 and 1586 (C=O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.49 (bs, H, NH), 7.09-7.18 (m, 1H, phenyl), 7.27-7.35 (m, 2H, phenyl), 7.46-7.52 (m, 2H, phenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H); ^{13}C NMR: 119.40, 120.59, 124.53, 125.45, 128.4, 130.64, 131.03, 132.04, 133.45, 143.60, 148.7, 150.6, 161.60 (sp^2 carbons), 171.17 and 181.85 (C=O), 185.41 (C=S); mass (M^+): 374.40; anal. calcd. (%) for $C_{20}H_{10}N_2O_2S_2$: C, 64.17; H, 2.67; N, 7.48. Found (%): C, 63.94; H, 2.38; N, 7.27.

11-(4-Nitrophenyl)-2-thioxo-2,3-dihydrotobenzo[g]-thiazolo[4,5-b]quinoline-5,10-dione (12b): Green powder, yield: (50 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3345 (NH), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.49 (bs, H, NH), 7.56-7.60 (m, 2H, nitrophenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H), 8.27-8.35 (m, 2H, nitrophenyl); ^{13}C NMR: , 124.53, 125.45, 126.09, 128.4, 130.64, 131.03, 132.04, 134.23, 140.45, 142.3, 144.0, 148.4, 161.60 (sp^2 carbons), 171.17 and 181.85 (C=O), 185.41 (C=S); mass (M^+): 419.40; anal. calcd. (%) for $C_{20}H_9N_3O_4S_2$: C, 57.28; H, 2.14; N, 10.02. found: C, 57.04; H, 1.95; N, 9.84.

11-(4-Chlorophenyl)-2-thioxo-2,3-dihydrotobenzo-[g]thiazolo[4,5-b]quinoline-5,10-dione (12c): Green powder, yield: (56 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3455 (NH), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.49 (bs, H, NH), 7.29-7.35 (m, 2H, chlorophenyl), 7.53-7.58 (m, 2H, chlorophenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H); ^{13}C NMR: 124.53, 125.45, 127.59, 128.4, 130.64, 131.03, 132.04, 134.4, 135.02, 136.65, 140.13, 148.4, 161.60 (sp^2 carbons), 171.17 and 181.85 (C=O) 185.41 (C=S); mass (M^+): 408.80; anal. calcd. (%) for $C_{20}H_9ClN_2O_2S_2$: C, 58.88; H, 2.20; N, 6.86. Found (%): C, 58.52; H, 1.98; N, 6.55.

11-(4-Methoxyphenyl)-2-thioxo-2,3-dihydrotobenzo [g]thiazolo[4,5-b]quinoline-5,10-dione (12d): Green powder, yield: (51 %); m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3433 and 3343 (NH_2), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 3.63 (s, 3H, OCH_3), 4.49 (bs, H, NH), 7.09-7.15 (m, 2H, methoxyphenyl), 7.43-7.48 (m, 2H, methoxyphenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H); ^{13}C NMR: 56.8 (CH_3), 112.40 (CN), 93.6, 114.4, 124.53, 125.45, 127.59, 130.64, 130.95, 131.03, 132.04, 143.0, 146.3, 148.4, 161.60 (sp^2 carbons), 171.17 and 181.85 (C=O) 185.41 (C=S); Mass (M^+): 404.26; anal. calcd. (%) for $C_{21}H_{12}N_2O_3S_2$: C, 62.37; H, 2.97; N, 6.93. Found (%): C, 62.14; H, 2.69; N, 6.71.

Synthesis of 1-amino-11-aryl-2-mercapto-1*H*-benzo[g]-imidazo[4,5-b]quinoline-5,10-dione (13a-d): A mixture of compound **11a-d** (0.04 mmol) and hydrazine hydrate (10 mL, 98 %) was heated under reflux for 3 h. After cooling, water was added and the mixture was neutralized with 10 % hydrochloric acid. The separated crude product was then filtered off and purified by column chromatography using methanol/chloroform (1:4) as eluent to yield compounds **13a-d.**

1-Amino-2-mercapto-11-phenyl-1*H*-benzo[g]imidazo-[4,5-b]quinoline-5,10-dione (13a): Gray powder, yield: (46 %); m.p. >300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3320 and 3310 (NH_2), 2550 (SH), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.49 (bs, 2H, NH_2), 7.09-7.18 (m, 1H, phenyl), 7.27-7.35 (m, 2H, phenyl), 7.46-7.52 (m, 2H, phenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H), 12.05 (s, 1H, SH); ^{13}C NMR: 120.59, 122.40, 124.53, 125.45, 128.4, 130.64, 131.03, 132.04, 133.45, 136.01, 138.7, 143.60, 148.7, 152.6, 153.60 (sp^2 carbons), 171.17 and 181.85 (C=O); Mass (M^+): 372.65; anal. calcd. (%) for $C_{20}H_{12}N_4O_2S$: C, 64.51; H, 3.22; N, 15.05. Found (%): C, 64.22; H, 3.03; N, 14.89.

1-Amino-2-mercapto-11-(4-nitrophenyl)-1*H*-benzo[g]-imidazo[4,5-b]quinoline-5,10-dione (13b): Gray powder, yield: (43 %); m.p. >300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3350 and 3310 (NH_2), 2552 (SH), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.49 (bs, 2H, NH_2), 7.56-7.60 (m, 2H, nitrophenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H), 8.27-8.35 (m, 2H, nitrophenyl), 12.05 (s, 1H, SH); ^{13}C NMR: 120.59, 122.40, 124.53, 125.45, 126.6, 128.4, 130.64, 131.03, 132.04, 136.60, 145.45, 148.7, 152.0, 153.60 (sp^2 carbons), 171.17 and 181.85 (C=O); Mass (M^+): 417.56; anal. calcd. (%) for $C_{20}H_{11}N_5O_4S$: C, 57.55; H, 2.63; N, 16.78. Found (%): C, 57.21; H, 2.63; N, 16.55.

1-Amino-2-mercapto-11-(4-chlorophenyl)-1*H*-benzo-[g]imidazo[4,5-b]quinoline-5,10-dione (13c): Gray powder, yield: (48 %); m.p. >300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3455 and 3437 (NH_2), 2549 (SH), 1676 and 1586 (C=O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 4.49 (bs, 2H, NH_2), 7.29-7.35 (m, 2H, chlorophenyl), 7.53-7.58 (m, 2H, chlorophenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H), 12.05 (s, 1H, SH); ^{13}C NMR: 122.40, 124.53, 125.45, 128.4, 129.69, 130.64, 131.03, 132.04, 134.4, 136.65, 137.0, 148.7, 152.0, 153.60 (sp^2 carbons), 171.17 and 181.85 (C=O); Mass (M^+): 406.81; anal. calcd. (%) for $C_{20}H_{11}N_4O_2SCl$: C, 59.11; H, 2.71; N, 13.79. Found (%): C, 58.92; H, 2.54; N, 13.51.

1-Amino-2-mercapto-11-(4-methoxyphenyl)-1*H*-benzo[g]imidazo[4,5-b]quinoline-5,10-dione (13d): Gray powder, yield: (48 %); m.p. >300 ºC; IR (KBr, ν_{max}, cm^{-1}): 3433 and 3393 (NH_2), 2553 (SH), 1676 and 1586 (C= O of quinone); ^{1}H NMR (DMSO-d_6): δ ppm: 3.63 (s, 3H, CH_3), 4.49 (bs, 2H, NH_2), 7.09-7.15 (m, 2H, methoxyphenyl), 7.43-

7.48 (m, 2H, methoxyphenyl), 7.62-7.67 (m, 1H, C6-H), 7.72-7.77 (m, 1H, C9-H); 7.87-7.91 (m, 2H, C7-H and C8-H), 12.05 (s, 1H, SH); ^{13}C NMR: 56.8 (CH_3), 114.4, 124.53, 125.45, 129.19, 130.64, 130.95, 131.03, 132.04, 153.0, 148.7, 152.0, 153.60, 160.14 (sp^2 carbons), 171.17 and 181.85 (C=O); Mass (M^+): 402.23; anal. calcd. (%) for $C_{21}H_{14}N_4O_3S$: C, 62.68; H, 3.48; N, 13.93. Found (%): C, 62.47; H, 3.26; N, 13.65.

RESULTS AND DISCUSSION

It is clearly established that 2,3-dichloro-1,4-naphthoquinone **1** reacts with nucleophiles and, depending on their strength, it may undergo substitution of one or both chlorine atoms[21]. Based on the reactivity of **1**, we have studied its reaction with different phenyl hydrazine, malononitrile, arylmalononitrile and carbon disulphide *via* undertaking of nucleophilic substitution and Michael addition-elimination reactions.

When 2,3-dichloro-1,4-naphthoquinone **1** was stirred with aryl hydrazine **2a-d** (1 equiv.) in ethanol using ice-bath, mono substituted products; 2-chloro-3-(2-arylhydrazinyl)naphthalene-1,4-dione **3a-d** were obtained in a good yield. The reaction of compounds **3a-d** with carbon disulphide in dry pyridine was refluxed for 12-16 h to yield 3-arylamino-2-thioxo-2,3-dihydro-naphtho[2,3-*d*]thiazole-4,9-dione **4a-d** (**Scheme-I**). The latter products were synthesized according to a known method[22] with minor modification.

The spectroscopic analysis using IR, NMR and MS conformed the structure of compounds **4a-d**. For instance, IR spectra of compound **4a** revealed the presence of vibration bands for NH at 3300 and 3250 cm^{-1}, carbonyl groups at 1672 and 1596 cm^{-1}, as well as thione group at 1190 cm^{-1}. Moreover, ^{13}C NMR spectrum for compound **4a**, showed the signals of both C=O groups at δ 171 and 181 ppm, while that for C=S appeared at δ 184 ppm.

We also conducted a reaction of 2,3-dichloronaphthoquinone **1** with malonitrile or arylmalononitrile in the presence of ammonium acetate. The generated precursor is then used for the preparation of naphthoquinones containing indole, quinoline, thiazole and imidazole fragments.

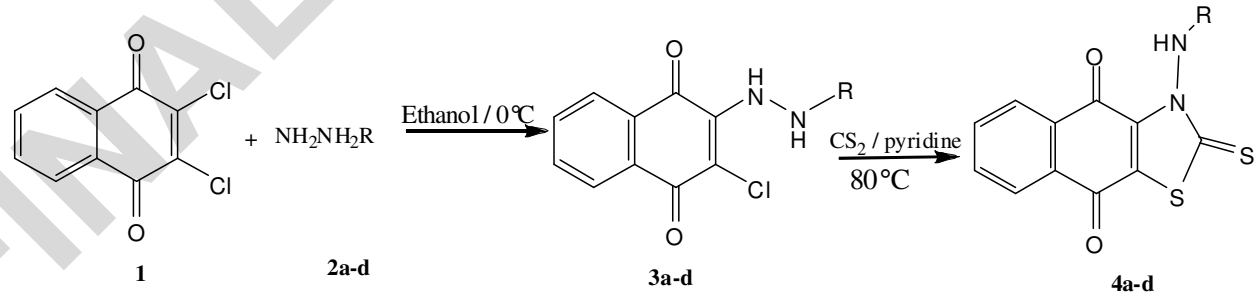
In this context, reaction of naphthoquinone **1** with malonitrile and ammonium acetate in ethanol afforded 2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[*f*]indole-3-carbonitrile **5** (**Scheme-II**). The method used for the synthesis of compound **5** is shown in **Scheme-II**. Furthermore, we have adopted one-pot multicomponent reactions for 2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indole-3-carbonitrile synthesis. The outcome of this synthetic approach is significant when noting that Chung-KyuRyu *et al.*[23] have prepared the structurally and conceptually related 2-amino-1-alkyl and aryl-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indole-3-carbonitriles in two steps.

The Hantzsch-type reaction, performed in this study, furnished 2-amino-3-cyano-4,9-dihydro-1*H*-benzo[f]indole-4,9-dione in very good yields, in spite of the number of steps involved. This reaction was carried out under metal-free conditions and in the presence of ammonium acetate, a soft Bronsted acid, which served as a reactant and a catalyst as well. The catalytic role of ammonium acetate in this reaction is evident by noting that the reaction did not take place when ammonia is used instead of the ammonium acetate.

We have also synthesized 2-Amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indole-3-carbonitrile **5** by nucleophilic substitution of both Cl using Michael addition-elimination reactions, in the presence of activated methylene group and ammonia solution.

Description of the method employed for the synthesis of potassium 3-cyano-4,9-dioxo-4,9-dihydro-1*H*-benzo[*f*]indol-2-ylcarbamodithioate **6** is depicted in **Scheme-II**. The synthesis was performed following the method developed by El-Emam *et al.*[24], where the reaction of 2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indole-3-carbonitrile **5** is allowed to react with carbon disulphide in ethanolic potassium hydroxide solution. The resultant product is identified as potassium 3-cyano-4,9-dioxo-4,9-dihydro-1*H*-benzo[*f*]indol-2-ylcarbamodithioate **6**. Additionally, the cyanide group in **6** was hydrolyzed by concentrated sulphuric acid to the corresponding carboxylic acid (COOH) group. Nucleophilic substitution of the COOH group by SH yielded the new target compound 2-thioxo-2*H*-benzo[f]thiazolo[4,5-b]indole-5-10(3*H*,4*H*)-dione **7**. Compound **7** was also prepared by intramolecular cyclization of compound **6** in the presence conc. H_2SO_4, by adopting the same procedure reported as in literature[24,25] followed by purification by column chromatography to produce a green solid in 60 % yield.

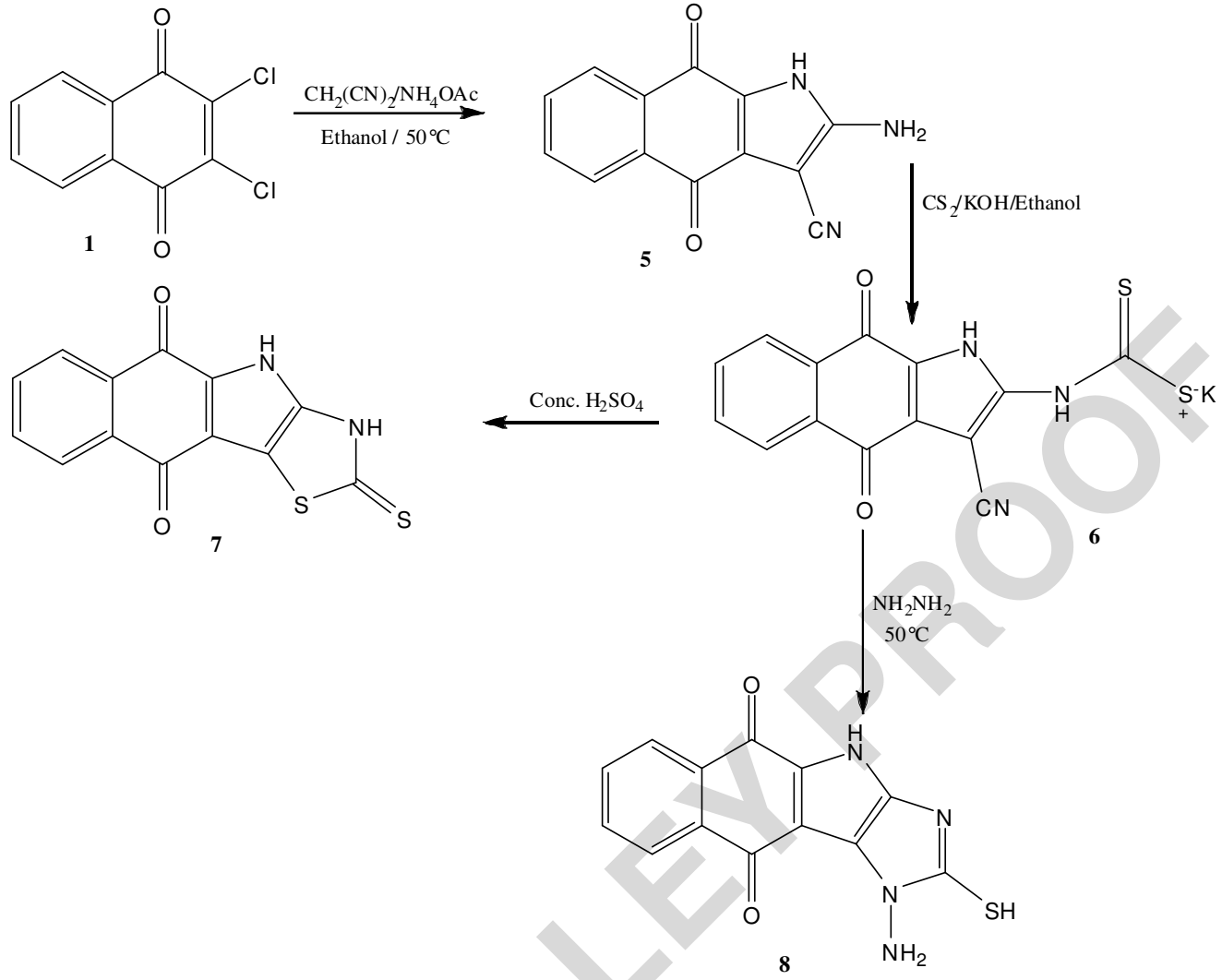
Spectral characterization of compound **7** *via* IR, ^{1}H NMR and ^{13}C NMR confirmed its existence in the thione form. Careful inspection of the IR spectra of this compound showed the



1 **2a-d** **3a-d** **4a-d**

(a) R= C_6H_5
(b) R= 4-$NO_2C_6H_4$
(c) R= 4-ClC_6H_4
(d) R= 4-$CH_3OC_6H_4$

Scheme-I



Scheme-II

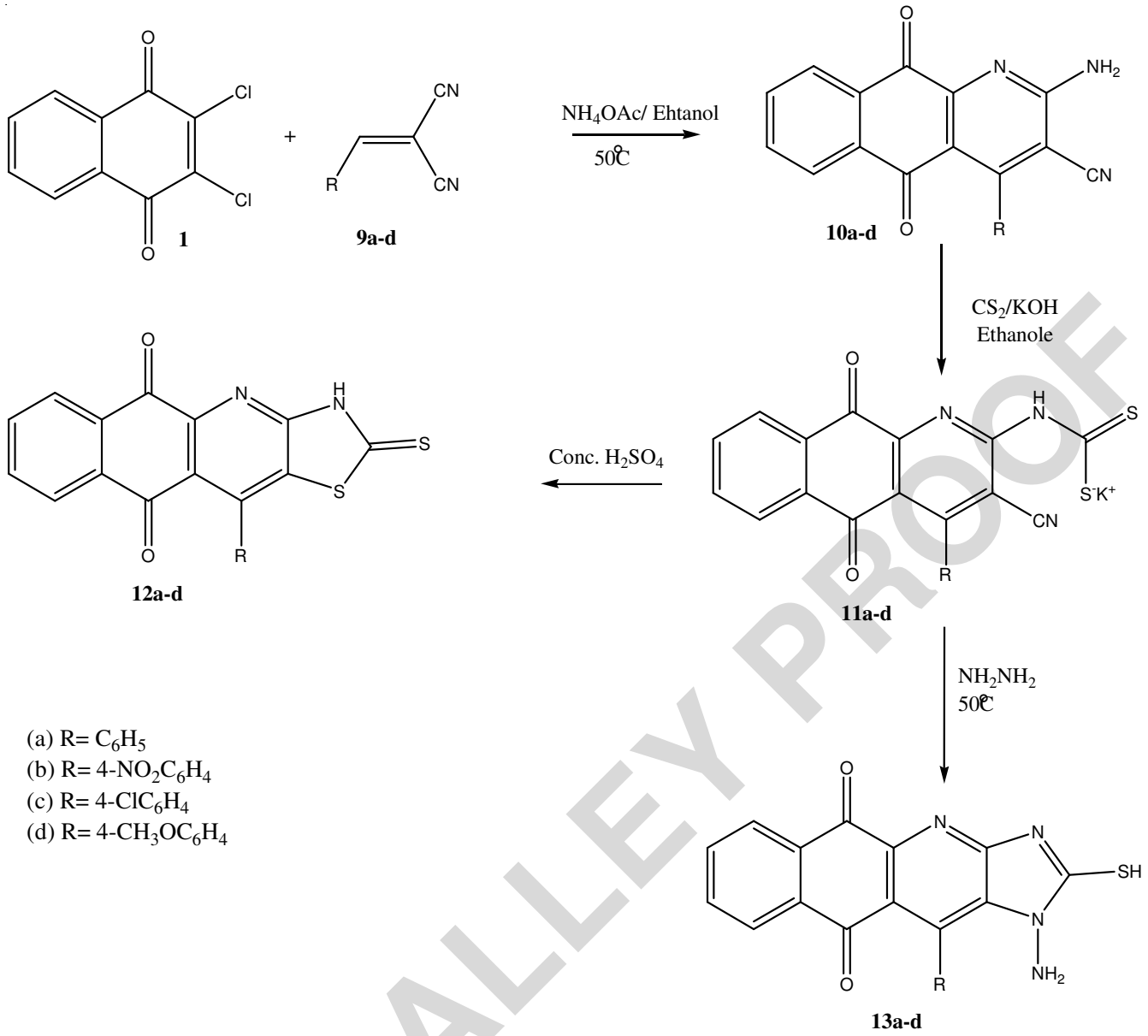
absence of cyanide peak and the presence of the common characteristic absorption peaks at 3428 cm^{-1} for (NH), as well as 1656 and 1586 cm^{-1} for (C=O of quinone). The ^1H NMR spectrum displayed the nitrogen proton as singlet at δ4.43 (1H) and the aromatic protons as different multiples from δ 7 to 7.91 ppm. In addition, the ^{13}C NMR spectrum showed the sp^2 carbons at δ 121.40, 125.34, 126.27, 131.43, 131.85, 132.83, 134.26 and 164.35, the C=O at δ 171.97 and 182.645 and the C=S at δ 184.52 ppm.

On the other hand, when potassium 3-cyano-4,9-dioxo-4,9-dihydro-1*H*-benzo[f]indol-2-ylcarbamodithioate **6** was heated with hydrazine hydrate, it gave rise to 1-amino-2-mercaptobenzo[f]imidazo[4,5-*b*]indole-5-10(1*H*,4*H*)-dione **8** as the major product.

The structure of compound **8** was predicted on the basis of its IR, ^1H NMR, ^{13}C NMR and mass spectral data. The IR spectra of this compound showed the characteristic absorption bands for (NH) at 3328 cm^{-1}, NH_2 at 3155 and 3033 cm^{-1}, SH at 2560 cm^{-1}, as well as quinone C= O at 1656 and 1586 cm^{-1}. Moreover, the ^1H NMR spectra of the compound revealed the presence of the nitrogen protons as two singlet at δ 4.43 and 6.66 and the aromatic carbons as a different multiples from δ 7 to 7.91, while the SH proton appears as a singlet at δ 12.05 ppm. The ^{13}C NMR spectra for compound **8** gave evidence for the aryl and diazole carbon atoms at δ 121.40, 125.34, 126.27, 131.43, 131.85, 132.83, 134.26 and 164.35 along with the C=O peaks at δ 171.97 and 182.64 ppm.

One-pot multicomponent reactions have been also adopted for the synthesis of the 2-amino-4-aryl-5,10-dioxo-5,10-dihydrobenzo[*g*]quinoline-3-carbonitrile **10a-d,** following the reflux method for a mixture 2-arylidenemalononitrile **9a-d** and 2,3-dichloro-1,4-naphthoquinone **1** in the presence of ammonium acetate (**Scheme-III**). The structures of synthesized compounds **10a-d** were confirmed on the basis of their spectroscopic results.

After structural characterizations the compounds **10a-d** were allowed to react at room temperature with carbon disulphide in the presence of potassium hydroxide in ethanol, to generate the corresponding potassium 4-aryl-3-cyano-5,10-dioxo-5,10-dihydrobenzo[*g*]quinolin-2-yl-carbamodithiate **11a-d** compounds. Importantly, cyclization of the resultant products (**11a-d**) by using concentrated sulphuric acid, at room temperature yielded the new products 11-aryl-2-thioxo-2,3-dihydrotobenzo[g]thiazolo[4,5-b]quinoline-5,10-dione **12a-d** as illustrated in **Scheme-III**. Formation of compounds **12a-d** is probably occurs by acid hydrolysis of the CN group in the



Scheme-III

precursors potassium 4-aryl-3-cyano-5,10-dioxo-5,10-dihydrobenzo[*g*]quinolin-2-ylcarbamodithiate**11a-d** to yield the carboxylic acid (COOH) derivatives. The final products (**12a-d**) were accomplished by nucleophilic substitution of SH on the COOH group followed by intramolecular cyclization.

Careful analysis of the spectral data obtained for compounds **12a-d** disclosed their existences as thione forms. For instance the IR spectra of the compound **12a** showed the presence of the characteristic absorption bands at 3350 cm^{-1} (NH), 1656 and 1586 cm^{-1} (C=O of quinone). The ^{1}H NMR spectrum showed the nitrogen proton as singlet at δ 4.49 (1H) and the aromatic protons as different multiples from δ 7.09 to 7.91 ppm. The ^{13}C NMR spectrum attested for the presence of the sp^2 carbons at δ 119.40, 120.59, 124.53, 125.45, 128.4, 130.64, 131.03, 132.04, 133.45, 143.60, 148.7, 150.6, 161.60 ppm, the two C=O at δ 171.17 and 181.85 ppm and the C=S at δ 185.41 ppm.

Moreover, potassium 4-aryl-3-cyano-5,10-dioxo-5,10-dihydrobenzo[g]quinolin-2-ylcarbamodithiate compounds **11a-d** were heated with hydrazine hydrate, very good yields of 1-amino-11-aryl-2-mercapto-1*H*-benzo[g]imidazo[4,5-b]quinoline-5,10-dione derivatives (**13a-d**) were obtained. Similarly, the proposed mechanism for formation of compounds **13a-d** involves initially nucleophilic substitution of S by NH_2 followed by another nucleophilic substitution of CN by NH.

Consistent with other derivatives, spectral data obtained for compounds **13a-d** confirmed their existence in the thiol form. This is clearly evidenced *via* IR data of the parent compound **13a**, which revealed the presence of the vibration bands of NH_2 at 3320 and 3310 cm^{-1}, along with a carbonyl group at 1676 and 1586 cm^{-1}. Additionally, the ^{1}H NMR results are consistent with the presence of nitrogen protons as a singlet at δ 4.49 (bs, 2H, NH_2) and the aromatic protons as different multiples from δ 7.09 to 7.91, whereas, the SH proton appeared as a singlet at δ 12.05 ppm. The^{13}C NMR data also lend additional support concerning identification of **13a** structure. The obtained spectrum showed the presence of the aryl and the diazole carbons at δ 120.59, 122.40, 124.53, 125.45, 128.4,

130.64, 131.03, 132.04, 133.45, 136.01, 138.7, 143.60, 148.7, 152.6, respectively, together with a 153.60 ppm peak for sp^2 carbons the characteristic peaks for C=O are detected at 171.17 and 181.85 ppm.

Conclusion

In the present work, we reported one-pot multicomponent synthesis of 2-amino-4,9-dioxo-4,9-dihydro-1*H*-benzo-[f]indole-3-carbonitrile **5** and 2-amino-4-aryl-5,10-dioxo-5,10-dihydrobenzo[g]quinoline-3-carbonitrile (**10a-d**). We have also demonstrated the feasibility of the the Mickael addition-elimination reaction of compounds **3a-d**, **5** and **10a-d** with carbone disulphide in presence of pyridine or conc. H_2SO_4 or hydrazine hydrate gives respectively the compounds 3-arylamino-2-thioxo-2,3-dihydro-naphto[2,3-d]thiazole-4,9-dione (**4a-d**), 2-thioxo-2*H*-benzo[f]thiazolo[4,5-b]indole-5-10(3*H*,4*H*)-dione (**7**), 2-Mercaptobenzo[f]thiazolo[4,5-b]indole-5-10(1*H*,4*H*)-dione (**8**), 11-aryl-2-thioxo-2,3-dihydro-tobenzo[g]thiazolo[4,5-*b*]quinoline-5,10-dione (**12a-d**) and 1-amino-11-aryl-2-mercapto-1*H*-benzo[*g*]imidazo[4,5-*b*]quinoline-5,10-dione **13a-d**. Structural elucidation of the target compounds was fully demonstrated by various spectral data.

The biological activities concerning the antibacterial and antifungal of all products prepared in this work are under investigations.

ACKNOWLEDGEMENTS

The authors extended their sincere appreciation to the Deanship of Scientific at King Saud University for its funding of this research through the Research Group Project No. RGP-VPP-222.

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