CONVENIENT AND SHORT WAYS TO SYNTHESIZE DIFFERENT ORGANIC COMPOUNDS BY USING GREEN CONDITIONS

Entesar A Hassan1*

*Corresponding Author: Entesar A Hassan entesar.abdelshafy@gmail.com

Green chemistry helps in reducing generation of hazardous substances during the manufacture and application of chemical products from this point of view several organic compounds such as xanthene derivatives, naphtalene derivatives, isoindole derivatives, isoquinoline derivatives and bis-adducts are prepared by using eco-friendly solvents such as water, eco-friendly conditions such as sunlight and eco-friendly catalysts such as chitosan.

**Keywords:** Green chemistry, ecofriendly, Chitosan, 1,3-cyclohexanedione, Maleic anhydride, p-benzoquionone.

INTRODUCTION

Green chemistry (Anastas and Warner, 1998; Anastas and Williamson, 1998; Anastas and Kirchhoff, 2002; Anastas et al., 2000; Anastas and Farris, 1994; Clark and Macquarrie, 2002; Matlack, 2001; Lancaster, 2002; Clark, 1995) plays an important role in avoiding hazard in the design of new chemicals (Schug et al., 2012). Also green chemistry contributes in elimination or replacement of the hazardous solvents with eco-friendly and safe solvents (Bharadwaj and Pashawar, 2012). Green chemistry represents challenges of the future in synthesis and the production of desired products (Ravichandran, 2010). According to these considerations belong to the green chemistry this work concentrate on the using of green solvents (Pal et al., 2013), green conditions (Li-Bin et al., 2006) and green catalysts (Abdou et al., 2008; Lee et al., 2009; Centi, 2003) in the synthesis of the various of organic compounds. During this work the synthesis of xanthenes (Takeshiba and Jiyoujima, 1981) is involved because these types of compounds are important in many fields such as agriculture. Also, they possess antibactericide activities (Poupilin, 1978), anti-inflammatory effects (Lambert et al., 1997), and have antiviral activities (Koeller et al., 2003). Recently, xanthenes used as clinical agents in treatment of cancer (Selvanayagam et al., 1996). Also xanthenes play an important role as a key-units in several natural products (Rohr and Mahrwald, 2009).

1 Chemistry Department, Faculty of Science, South Valley University, Qena 83523, Egypt.
RESULTS AND DISCUSSION

1,8-Dioxooctahydroxanthene derivatives 3a-d and 5 can be obtained in an eco-friendly way, and in satisfactory yields by stirring a three component mixture of 1,3-cyclohexanedione (Ammari et al., 2011; Lee and Kim, 2012; Rose, 1990; Sabakh, 2013; Xia and Zhang, 2012); Mosaddegh and Hassankhani, 2012; Wang et al., 2004; Martins et al., 2012) 1, CS$_2$ and $p$-chloroaniline 2a; 2-aminoypyridine 2b; sulphathiazole 2c; sulphdimidine 2d; w-cyanoacetophenone 4 in water at room temperature to furnish 9-(4-chlorophenylimino)-3,4,5,6,7,9-hexahydro-2$H$-xanthene-1,8-dione 3a; 9-(pyridin-2-ylimino)-3,4,5,6,7,9-hexahydro-2$H$-xanthene-1,8-dione 3b; $N$-(1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthen-9-yldiene)-4-(thi-azol-2-ylamino) benzene-sulfonamide 3c; 4-(4,6-dimethylpyrimidin-2-ylamino)-$N$-(1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthen-9-yldiene) benzene-sulfonamide 3d and 2-(1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthen-9-yldene)-3-oxo-3-phenylpropionitrile 5, respectively. The formation of these products is believed to be via the loss of two molecules of hydrogen sulfide and dehydration Scheme 1.  Also xanthene derivatives can be obtained via mixing 1,3-cyclohexanedione 1 with triethylorthoformate (Inavoshi et al., 1991) 6 in water as a solvent to gather 9-(2,6-dioxocyclohexyl)-3,4,5,6,7,9-hexahydro-2$H$-xanthene-1,8-dione 7. Here there are different green conditions were used to synthesize xanthene 7; where chitosan (Abdou et al., 2008; Lee et al., 2009) was added as a catalyst to the previous mixture, in this case the adduct 7 formed immediately. The same product 7 was obtained when the reaction mixture was heated under reflux for 20 min without addition of any catalyst. An actual trend to use a clean and cheap energy; that the use of the sun as a source of heat. It is found that xanthene 7 can also be obtained when the mixture of 1,3-cyclohexanedione 1 and triethylorthoformate 6 in water was left for about 8-10 h in the direct sunlight. These products are obtained in 65-91% yields and their structures were confirmed on the bases of their analysis and spectral data.

The suggested mechanism for the formation of these adducts 3a-d may follow the one illustrated below.

While the formation of xanthene 7 may pass through the following mechanism.

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**Scheme 1**

![Scheme 1](image-url)

- condition a: $H_2O$, chitosan, immediately
- condition b: $H_2O$, sunlight, 8-10 hrs
- condition c: $H_2O$, reflux, 20 min.

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This article can be downloaded from [http://www.ijerst.com/currenttissue.php](http://www.ijerst.com/currenttissue.php)
Because water (Li et al., 2006) is safe, eco-friendly, cheap compared with other solvents and non-toxic, actual trends to use water as solvent are achieved in this work. The synthesis of 3-(2,6-dioxocyclohexyl)-4-oxo-4,5,6,7-tetrahydro-3aH-isooindole-1-carboxylic acid 8; 1-(2,6-dioxocyclohexyl)-4-hydroxy-8-oxo-3,5,6,7,8,8a-hexahydroisoquinoline-3-carboxylic acid 9 and 8-hydroxy-1-(2-hydroxy-6-oxocyclohex-1-enyl)-3-oxo-3,5,6,7-tetrahydronaphthalene-2-carbonitrile 12 were performed via a one-pot reaction mixture; thus a mixture of 1,3-cyclohexanedione 1, CS₂ and glycine 2e; dl-serine 2f; cyanoacetone 11 in water was stirring at room temperature for 2 h. While on treatment of 1,3-cyclohexanedione 1 with CS₂ and 3-amino-1,2,4-triazole 2g the bis-adduct (Li et al., 2006) 10 was obtained. Also the bis-compounds (14a-d) can be obtained in excellent yields (93-98% yields) via the reaction of 1,3-cyclohexanedione with the aromatic aldehydes 13a-d in water by using different green conditions Scheme 2.

The suitable mechanism suggested for the formation of the adduct 8 may be as the following:

A one-pot component reaction; maleic anhydride 15, CS₂ and p-chloroaniline 2a; 2-amino-pyridine 2b; sulphathiazole 2c; sulphdimidine 2d; glycine 2e; dl-serine 2f; 3-amino-1,2,4-triazole 2g and by using ethanol as a solvent the bis-adducts 16a-g were obtained (Scheme 3).
Scheme 2

Scheme 3

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When \( p \)-benzoquinone 17 reacts with \( \text{CS}_2 \) and aromatic amines such as \( p \)-chloroaniline 2a or heterocyclic amines such as 2-aminopyridine 2b or 3-amino1,2,4-triazol 2g in ethanol and by stirring at room temperature it was found that the reaction pass through reaction of two moles of \( p \)-benzoquinone 17 with a one mole of these amines and different products (18-20) were obtained. Also the same notes repeated during the reaction of \( p \)-benzoquinone 17 with glycine 2e and/or sulfa drugs 2c,d in the presence of \( \text{CS}_2 \) and water as a solvent, where the adducts 21 and 22a,b were obtained.
The in vitro studies for the most active compounds, showed high activities for the derivatives 3c, 22a, 22b, 19, 16c, 8, 3d and 21 (93-100%) inhibition of growth of Bacillus sub. at concentration 1000 ppm. The in vitro activities of the other compounds ranged from 62-92% at the same concentrations of 1000 ppm.

CONCLUSION
In conclusion the author tried to synthesize different organic substances via using simple, economic and safe ways. The prepared organic substances were found to have an effect on microorganisms such as Bacillus subtilis.

Experimental Instruments
The following instruments have been used in this experimental work.

1. Mass spectra: were obtained on a GCMC-QP 1000 EX mass Spectrometer with ionization potential of 70 ev.

2. I. R. Spectra: were determined with Shimadzu IR 408 Infrared Spectrophotometer using KBr wafer technique.

3. 1H-NMR: carried out on Varian EM 390 (200 MHz) using TMS as internal standard and chemical shifts are expressed as (d).

4. Melting points: all m. p.s. are uncorrected and were determined on Kofler melting point apparatus.

General Procedures for the Synthesis of (3a-d and 5).
A mixture of 1,3-cyclohexanedione (0.01 mol), compounds (2a-d) or (4) (0.01 mol) and CS₂ (0.01 mol) in water (50 mL) as solvent was stirred for 2 h at room temperature. The reaction mixture was left a side to settle and concentrate. The solid products, so formed, were recrystallized from the suitable solvents.

9-(4-Chlorophenylimino)-3,4,5,6,7,9-hexahydro-2H-xanthene-1, 8-dione (3a).
Orange crystals from ethanol, yield 91%; m.p. 190°C; Anal. Calcd. for C₁₉H₁₆ClNO₃ (341.79) calcd: C, 66.77; H, 4.72; N, 4.10. Found: C, 66.75; H, 4.69; N, 3.92; IR (KBr) υ (cm⁻¹), 1650 (CO); 1H-NMR (DMSO): δ = 1.8-2.7 (m, 12H, Ar-CH₃); 7.1, 7.2 (2d, 4H, Ar-H); MS: m/z (%) 341 (M⁺, 13), 98 (91), 77 (100), 76 (83).
9-(Pyridin-2-ylimino)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (3b).

White crystals from ethanol, yield 65%; m.p. 250°C; Anal. Calcd. for C_{16}H_{16}N_{2}O_{3} (308.33) calcd: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.24; H, 5.19; N, 9.12; IR (KBr) ν (cm<sup>-1</sup>), 1625 (CO); <sup>1</sup>H-NMR (DMSO): δ = 1.7-2.8 (m, 12H, 6CH<sub>2</sub>); 7.2-7.7 (m, 5H, Ar-H); MS: m/z (%) 358 (M+, 17), 357 (38), 257 (47), 83 (100).

General Procedures for the Synthesis of (7).

To a mixture of 1,3-cyclohexanedione (0.01 mol), and triethylorthoformate 6 (0.01 mol) in water (50 mL) as solvent was added 0.5 g of chitosan and at room temperature the product formed immediately as soon as addition of chitosan. The reaction mixture was filtered off and the product was collected and recrystallized from ethanol. The same product can be obtained without addition of chitosan but by heating the previous mixture under reflux for 20 min. or when it is left in direct sunlight for 8-10 h.

N-(1,8-Dioxo-1,2,3,4,5,6,7,8-octahydroxanthen-9-ylidene)-4-[(thiazol-2-ylamino)benzenesulfonamide (3c).

Shining buff crystals from ethanol, yield 88% m.p. 170°C; Anal. Calcd. for C_{22}H_{19}N_{4}O_{5}S (469.53) calcd: C, 56.28; H, 4.08; N, 8.95; S, 13.66. Found: C, 56.27; H, 4.11; N, 8.97; S, 13.63; IR (KBr) ν (cm<sup>-1</sup>), 1670 (CO), 3200 (NH); <sup>1</sup>H-NMR (DMSO): δ = 1.9-2.7 (m, 12H, 6CH<sub>2</sub>); 5.4 (s, 1H, NH); 5.6, 5.7 (m, 2H, thiazolyl-H); 6.9-7.1 (m, 4H, Ar-H); MS: m/z (%) 468 (M<sup>+</sup>, 28), 368 (53), 149 (100), 71 (100).

4-(4,6-Dimethylpyrimidin-2-ylamino)-N-(1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthen-9-ylidene)benzenesulfonamide (3d).

White powder from ethanol, yield 86% m.p. 196°C; Anal. Calcd. for C_{25}H_{24}N_{4}O_{5}S (492.55) calcd: C, 60.99; H, 4.91; N, 11.37; S, 6.91. Found: C, 60.99; H, 4.89; N, 11.28; S, 6.55; IR (KBr) ν (cm<sup>-1</sup>), 1670 (CO), 3190 (NH); <sup>1</sup>H-NMR (DMSO): δ = 1.7-2.9 (m, 12H, 6CH<sub>2</sub>); 3.8 (s, 6H, 2CH<sub>3</sub>); 5.5 (s, 1H, NH); 5.7 (s, 1H, pyrimidinyl-H); 6.9-7.1 (m, 4H, Ar-H); MS: m/z (%) 492 (M<sup>+</sup>, 15), 385 (17), 107 (100), 91 (83).

2-(1,8-Dioxo-1,2,3,4,5,6,7,8-octahydroxanthen-9-ylidene)-3-oxo-3-phenylpropionitrile (5).

White powder from ethanol, yield 76% m.p. 106°C; Anal. Calcd. for C_{22}H_{17}NO_{4} (359.37) calcd: C, 73.53; H, 4.77; N, 3.90. Found: C, 73.61; H, 4.78; N, 3.83; IR (KBr) ν (cm<sup>-1</sup>), 2205 (CN), 1670, 1655 (CO); <sup>1</sup>H-NMR (DMSO): δ = 1.9-2.8 (m, 12H, 6CH<sub>2</sub>); 7.2-7.7 (m, 5H, Ar-H); MS: m/z (%) 358 (M<sup>+</sup>, 17), 357 (38), 257(47), 83 (100).

General Procedures for the Synthesis of (8,9,10 and 12).

A mixture of 1,3-cyclohexanedione (0.01 mol), compounds (2e-g) or (11) (0.01 mol) and CS<sub>2</sub> (0.01 mol) in water (50 mL) as solvent was added 0.5 g of chitosan and at room temperature the product formed immediately as soon as addition of chitosan. The reaction mixture was filtered off and the product was collected and recrystallized from ethanol. The same product can be obtained without addition of chitosan but by heating the previous mixture under reflux for 20 min. or when it is left in direct sunlight for 8-10 h.

3-(2,6-Dioxocyclohexyl)-4-oxo-4,5,6,7-tetrahydro-3aH-isooindole-1-carboxylic acid (8).

White crystals from ethanol, yield 80% m.p. 230°C; Anal. Calcd. for C_{15}H_{15}NO_{5} (289.28) calcd:
C, 62.28; H, 5.23; N, 4.84. Found: C, 62.17; H, 5.26; N, 4.91; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3440, (OH); 1720, 1645 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 1.9-2.4 (m, 12H, 6CH\(_2\)); 3.7 (s, 1H); 4.7 (s, 1H); 7.8 (s, 1H, OH); MS: \( m/z \) (%) 288 (M\(^+\), 30), 96 (100), 96(82), 95 (92).

1-(2,6-Dioxocyclohexyl)-4-hydroxy-8-oxo-3,5,6,7,8,8a-hexahydroisoquinoline-3-carboxylic acid (9)

White crystals from ethanol, yield 83% m.p. 240°C; Anal. Calcd. for C\(_{16}\)H\(_{17}\)NO\(_6\) (319.31) calcd: C, 60.18; H, 5.37; N, 4.39. Found: C, 60.07; H, 5.37; N, 4.28; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3500 (OH); 1690, 1645 (CO); 1H-NMR (DMSO): \( \delta \) = 1.9-2.4 (m, 12H, 6CH\(_2\)); 3.7 (s, 1H); 4.7 (s, 1H); 7.8 (s, 1H, OH); MS \( m/z \) (%) 318 (M\(^+\), 3), 169 (1), 75 (64), 74 (100).

2,2'-(1,2,4-Triazol-3-ylimino)bis(1-hydroxycyclohex-1-en-3-one) (10)

Dark yellow crystals from ethanol, yield 67% m.p. 270°C; Anal. Calcd. for C\(_{15}\)H\(_{16}\)N\(_4\)O\(_4\) (316.31) calcd: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.88; H, 5.11; N, 17.54; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3450 (OH), 1645 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 1.9-2.5 (m, 12H, 6CH\(_2\)); 5.7 (s, 1H) 6.4 (s, 1H), 8.3 (s, 2H, 2OH); MS \( m/z \) (%) 312 (M\(^+\), 3), 293 (62), 128 (100), 82 (13).

8-Hydroxy-1-(2-hydroxy-6-oxocyclohex-1-enyl)-3-oxo-3,5,6,7-tetrahydronaphthalene-2-carbonitrile (12)

Shining buff powder from ethanol/water, yield 74% m.p. up 300°C; Anal. Calcd. for C\(_{17}\)H\(_{15}\)NO\(_4\) (297.31) calcd: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.81; H, 5.12; N, 4.72; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3500 (OH), 1655 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 1.5-2.5 (m, 12H, 6CH\(_2\)); 6.1 (s, 1H), 7.2 (s, 1H, OH), 7.6 (s, 1H, OH); MS \( m/z \) (%) 297 (M\(^+\), 6), 263 (62), 128 (100), 111 (85).

### General Procedures for the Synthesis of (14a-d)

To a mixture of 1,3-cyclohexanediene (0.01 mol), and compounds (13a-d) (0.01 mol) in water (50 ml) as solvent was added 0.5 g of chitosan and at room temperature, the products formed immediately as soon as addition of chitosan. The reaction mixture was filtered off and the products were collected and recrystallized from the appropriate solvents. The same products can be obtained without addition of chitosan but when the previous mixture is heated under reflux for 30 min. or when it is left in the direct sunlight for 6 h.

2, 2'-(Phenylmethyl)bis(1-hydroxycyclohex-1-en-3-one) (14a)

White crystals from ethanol, yield 95% m.p. 203°C; Anal. Calcd. for C\(_{19}\)H\(_{20}\)O\(_4\) (312.36) calcd: C, 73.06; H, 6.45. Found: C, 72.79; H, 6.50; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3350 (OH), 1720 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 1.85-2.4 (m, 12H, 6CH\(_2\)); 4.2 (s, 1H) 6.5, 6.6 (2s, 2H, 2OH), 7.2 (m 5H, Ar-H); MS \( m/z \) (%) 312 (M\(^+\), 3), 293 (50), 217 (100), 105 (20).

2, 2'-(4-Chlorophenylmethyl)bis(1-hydroxycyclohex-1-en-3-one) (14b)

White crystals from ethanol, yield 96% m.p. 214°C; Anal. Calcd. for C\(_{19}\)H\(_{19}\)O\(_4\)Cl (346.81) calcd: C, 65.80; H, 5.52; Cl, 10.22. Found: C, 65.49; H, 5.30; Cl, 9.94; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3450 (OH), 1725 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 1.9-2.4 (m, 12H, 6CH\(_2\)); 5.3 (s, 1H) 6.8 (s, 2H, 2OH) 7.2 (m 4H, Ar-H); MS \( m/z \) (%) 346 (M\(^+\), Cl\(^{35}\), 17), 348 (M\(^+\), Cl\(^{37}\), 7), 328 (45), 199 (100).

2, 2'-(4-Methoxyphenylmethyl)bis(1-hydroxycyclohex-1-en-3-one) (14c)

White crystals from benzene, yield 95% m.p. 180°C; Anal. Calcd. for C\(_{20}\)H\(_{22}\)O\(_5\)Cl (342.39) calcd: C, 70.16; H, 6.48. Found: C, 65.04; H, 6.51; IR (KBr) \( \nu \) (cm\(^{-1}\)) : 3450 (OH), 1725 (CO); \(^1\)H-NMR
2,2'-[(4-Hydroxy-3-methoxyphenylmethyl)bis(1-hydroxycyclohex-1-en-3-one) (14d)

White crystals from ethanol, yield 98% m.p. 190 °C; Anal. Calcd. for C_{20}H_{22}O_{6} (358.39) calcd: C, 67.03; H, 6.19; Found: C, 65.15; H, 6.12; IR (KBr) \nu (cm^{-1}), 3475 (OH), 1725 (CO); 1H-NMR (DMSO): \delta = 1.9-2.7 (m, 12H, 6CH_{2}); 3.9 (s, 3H, CH_{3}); 4.7 (s, 1H); 6.3-6.7 (m, 3H, Ar-H); 7.05, 7.06 (2s, 2H, 2OH); MS m/z (%) 358 (M+, 23), 229 (100) 199 (79), 145 (55).

General Procedures for the Synthesis of (16a-g)

A mixture of maleic anhydride (0.01 mol), compounds (2a-g) (0.01 mol) and CS\textsubscript{2} (0.01 mol) in ethanol (50 mL) as solvent was stirred for 2 h at room temperature. The reaction mixture was left a side to settle and concentrate. The solid products so formed, were collected and crystallized from the suitable solvents.

1-\{[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino\}-4-chlorobenzene (16a)

Lightening luminous crystals from ethanol, yield 86% m.p. 210 °C; Anal. Calcd. for C_{15}H_{6}ClNO_{6} (331.66) calcd: C, 54.32; H, 1.82; Cl, 10.69; N, 4.22; Found: C, 54.51; H, 1.90; Cl, 10.22; N, 4.03; IR (KBr) \nu (cm^{-1}), 1810 (CO); 1H-NMR (DMSO): \delta = 6.0 (s, 2H, 2CH), 7.2, 7.3 (2d, 4H, Ar-H); MS m/z (%) 330 (M+, 3), 225 (100) 129 (99), 127 (98).

2-\{[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino\}pyridine (16b)

White crystals from ethanol, yield 86% m.p. 220 °C; Anal. Calcd. for C_{14}H_{6}N_{2}O_{6} (298.21) calcd: C, 56.39; H, 2.03; N, 9.39. Found: C, 56.42; H, 2.03; N, 9.27; IR (KBr) \nu (cm^{-1}), 1790 (CO); 1H-NMR (DMSO): \delta = 6.0 (s, 2H, 2CH), 6.9 (m, 4H, pyridinyl-H); MS m/z (%) 298 (M+, 57), 206 (28) 97 (94), 78 (100).

4-\{[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino\}-N-thiazol-2-ylbenzenesulfonamide (16c)

White crystals from ethanol, yield 90% m.p. 190 °C; Anal. Calcd. for C_{18}H_{9}N_{3}O_{8}S_{2} (459.41) calcd: C, 47.06; H, 1.97; N, 9.15; S, 13.96. Found: C, 47.06; H, 1.94; N, 9.12; S, 14.02; IR (KBr) \nu (cm^{-1}), 3200 (NH), 1795 (CO); 1H-NMR (DMSO): \delta = 5.4 (s, 1H, NH), 6.1 (s, 2H, 2CH), 6.5, 6.7 (2d, 2H, thiazolyl-H), 7.2-7.6 (m, 4H, Ar-H); MS m/z (%) 459 (M+, 7), 191 (90) 108 (60), 92 (100).

4-\{[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino\}-N-(4,6-dimethylpyrimidin-2-yl)benzenesulfonamide (16d)

White crystals from ethanol, yield 78% m.p. 205°C; Anal. Calcd. for C_{21}H_{14}N_{4}O_{8}S (482.42) calcd: C, 52.28; H, 2.93; N, 11.61; S, 6.65. Found: C, 52.22; H, 2.88; N, 11.76; S, 6.64; IR (KBr) \nu (cm^{-1}), 3120 (NH), 1800 (CO); 1H-NMR (DMSO): \delta = 4.6 (s, 6H, 2CH_{3}), 5.4 (s, 1H, NH), 5.9 (s, 2H, 2CH), 7.1-7.8 (m, 5H, primidinyl-H, Ar-H); MS m/z (%) 482 (M+, 16), 122 (100), 107 (73), 97 (81).

[[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino]acetic acid (16e)

White crystals from ethanol/water, yield 81% m.p. 200 °C; Anal. Calcd. for C_{11}H_{5}NO_{8} (279.16) calcd: C, 47.33; H, 1.81; N, 5.02. Found: C, 47.33; H, 1.81; N, 4.99; IR (KBr) \nu (cm^{-1}), 3490 (OH), 1780, 1625 (CO); 1H-NMR (DMSO): \delta = 3.2 (s, 2H, CH_{2}), 6.0 (s, 2H, 2CH), 8.1 (br, 1H, OH); MS m/z (%) 279 (M+, 5), 267 (49) 127 (58), 95 (100).

2-\{[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino\}-3-hydroxypropionic acid (16f)

White crystals from ethanol, yield 87% m.p. 212
9°C; Anal. Calcd. for C_{12}H_{7}NO_{9} (309.19) calcd: C, 46.62; H, 2.28; N, 4.53. Found: C, 46.62; H, 2.33; N, 4.52; IR (KBr) \( \nu \) (cm\(^{-1} \)) 3480 (OH), 1790, 1705 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 1.5 (s, 1H, OH), 2.9 (t, 1H, CH), 3.2 (d, 2H, CH\(_2\)), 6.1 (s, 2H, 2CH) 8.0 (br, 1H, COOH); MS \( m/z \) (%) 309 (M\(^+\), 40), 307 (70) 149 (100), 71 (60).  

3-\{[Bis-(2,5-dioxo-2,5-dihydrofuran-3-yl)methylene]amino\}-1, 2,4-triazol (16g)  
Brown crystals from ethanol, yield 66% m.p. 265°C; Anal. Calcd. for C\(_{11}\)H\(_4\)N\(_4\)O\(_6\) (288.17) calcd: C, 45.85; H, 1.40; N, 19.44. Found: C, 45.85; H, 1.44; N, 19.51; IR (KBr) \( \nu \) (cm\(^{-1} \)), 1795 (CO); \(^1\)H-NMR (DMSO): \( \delta \) = 6.1 (s, 2H, 2CH), 6.3 (s, 1H, triazolyl-H); MS \( m/z \) (%) 288 (M\(^+\), 20), 270 (1) 99 (15), 72 (100).

General Procedures for the Synthesis of (18-20)  
A mixture of \( p \)-benzoquinone (0.01 mol), compounds (2a, 2b, 2e and 2g) (0.01 mol) and CS\(_2\) (0.01 mol) in ethanol (50 mL) as solvent was stirred for 2 h at room temperature. The reaction mixture was left a side to settle and to concentrate. The solid products so formed, were recrystallized from the suitable solvents.

2-(2-Chloro-8-hydroxyphenanthridin-6-yl)benzene-1,4-diol (18)  
Dark brown powder from ethanol/water, yield 89% m.p. up 300°C; Anal. Calcd. for C\(_{19}\)H\(_{12}\)ClNO\(_3\) (337.76) calcd: C, 67.56; H, 3.58; Cl, 10.50; N, 4.15; Found: C, 67.56; H, 3.45; Cl, 10.55; N, 4.09; IR (KBr) \( \nu \) (cm\(^{-1} \)), 3340 (OH); \(^1\)H-NMR (DMSO): \( \delta \) = 1.1 (s, 3H, 3OH), 6.5-6.8 (m, 9H, Ar-H), 8.4 (s, 1H, OH); MS \( m/z \) (%) 337 (M\(^+\), 12), 339 (M\(^+\), Cl\(^{35}\), 53), 263 (100), 180 (98).

2-(8-Hydroxybenzo[c][1,8]naphthyridin-6-yl)benzene-1,4-diol (19)  
Dark brown powder from ethanol/water, yield 71% m.p. 278 °C; Anal. Calcd. for C\(_{18}\)H\(_{12}\)N\(_2\)O\(_3\) (304.30) calcd: C, 71.05; H, 3.97; N, 9.21. Found: C, 71.07; H, 3.97; N, 9.23; IR (KBr) \( \nu \) (cm\(^{-1} \)), 3420 (OH); \(^1\)H-NMR (DMSO): \( \delta \) = 1.1 (s, 3H, OH), 6.7-7.5 (m, 9H, Ar-H, pyridyl-H); MS \( m/z \) (%) 303 (M\(^+\), 68), 250 (77), 221 (100), 186 (92).

2-(7-Hydroxy-[1,2,4]triazolo[1,5-a]quinazolin-5-yl)benzene-1,4-diol (20)  
Black powder from ethanol/water, yield 71% m.p. up 300 °C; Anal. Calcd. for C\(_{15}\)H\(_{10}\)N\(_4\)O\(_3\) (294.26) calcd: C, 63.22; H, 3.43; N, 19.04. Found: C, 63.22; H, 3.43; N, 19.04; IR (KBr) \( \nu \) (cm\(^{-1} \)): 3500 (OH); \(^1\)H-NMR (DMSO): \( \delta \) = 1.1 (s, 3H, OH), 6.5-6.8 (m, 6H, Ar-H), 8.0 (s, 1H, triazolyl-H); MS \( m/z \) (%) 294 (M\(^+\), 15), 279 (98), 113 (167), 71 (100).

General Procedures for Synthesis of (21 and 22a,b)  
A mixture of \( p \)-benzoquinone (0.01 mol), compounds (2c,d,e) (0.01 mol) and CS\(_2\) (0.01 mol) in water (50 mL) as solvent was stirred for 2 hrs at room temperature. The reaction mixture was left a side to settle and to concentrate. The solid products so formed were collected and recrystallized from the suitable solvents.

3-(2,5-Dihydroxyphenyl)-5-hydroxy-1H isoindole-1-carboxylic acid (21)  
Dark brown powder from ethanol/water, yield 78% m.p. up 300 °C; Anal. Calcd. for C\(_{15}\)H\(_{10}\)ClNO\(_5\) (285.25) calcd: C, 63.16; H, 3.89; N, 4.91. Found: C, 63.22; H, 3.87; N, 4.90; IR (KBr) \( \nu \) (cm\(^{-1} \)), 3470 (OH); \(^1\)H-NMR (DMSO): \( \delta \) = 1.1 (s, 3H, OH), 3.1 (s, 1H), 6.7 (m, 6H, Ar-H), 8.4 (s, 1H, OH); MS \( m/z \) (%) 284 (M\(^+\), 10), 250 (1), 83 (4), 75 (100).

6-(2,5-Dihydroxyphenyl)-8-hydroxy phenanthridine-2-sulfonic acid thiazol-2-ylamide (22a)  
Dark brown powder from ethanol/water, yield 66% m.p. 293°C; Anal. Calcd. For C\(_{22}\)H\(_{15}\)N\(_3\)O\(_5\)S\(_2\).
(465.50) calcd: C, 56.76; H, 3.25; N, 9.03; S, 13.78. FOUND: C, 63.63; H, 3.37; N, 9.01; S, 13.81; IR (KBr) $\nu$ (cm$^{-1}$), 3470 (OH), 3210 (NH); $^1$H-NMR (DMSO): $\delta$ = 1.1 (s, 3H, OH), 5.4 (s, 1H, NH), 6.7-7.5 (m, 8H, Ar-H, thiazolyl-H), 8.1 (m, 3H, Ar-H); MS m/z (%) 468 (M+, 25), 257 (92), 97 (100), 83 (93).

6-(2,5-Dihydroxyphenyl)-8-hydroxyphenanthridine-2-sulfonic acid (4,6-dimethylpyrimidin-2-yl) amide (22b)

Dark brown powder from ethanol/water, yield 72% m.p. up 300°C; Anal. Calcd. For C$_{25}$H$_{20}$N$_4$O$_5$S (488.52) calcd: C, 61.47; H, 4.13; N, 11.47; S, 6.56. Found: C, 61.47; H, 4.15; N, 11.47; S, 6.46; IR (KBr) $\nu$ (cm$^{-1}$), 3500 (OH), 3150 NH; $^1$H-NMR (DMSO): $\delta$ = 1.1 (s, 3H, OH), 3.1 (s, 3H, 2CH$_3$), 5.4 (s, 1H, NH), 6.7-7.5 (m, 7H, Ar-H, pyrimidinyl-H), 7.9 (m, 3H, Ar-H); MS m/z (%) 489 (M+, 100), 250 (91), 129(62), 93 (82).

REFERENCES


