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Synthesis of fluorescent hydroxyl naphthalene-1,4-dione derivatives by a three-component reaction in water

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ABSTRACT

An efficient one-pot synthesis of fluorescent hydroxyl naphthalene-1,4-dione derivatives by a simple, atom-economical and three-component reaction of 2- hydroxynaphthalene-1,4-dione, aromatic aldehydes and heterocyclic or carbocyclic amines in the presence of a catalytic amount of $InCl_3$ in refluxing water is reported. The structures of the compounds were confirmed by IR, ^1H NMR, ^{13}C NMR, and elemental analysis. UV- visible absorption coefficient, maximum wavelength and fluorescence emission wavelength were measured in methanol. The products were fluorescent in solution emitting at green light (546–560 nm). The advantages of this procedure are mild reaction conditions, high yields of products, operational simplicity and easy work-up procedures. The workup of these very clean reactions involves only a filtration and simple washing step with EtOH.

1. Introduction

Multicomponent reactions (MCRs), in which multiple reactions are combined into the synthetic operation have been used extensively to form carbon-carbon bonds in synthetic chemistry [1]. Such reactions offer a wide range of possibilities for the efficient construction of highly complex molecules in a single procedural step, thus avoiding complicated purification operations and allowing savings of both solvents and reagents [2]. Designing of multi-component reactions in water is another attractive area in chemistry [3], because water is a cheap, safe and environmentally benign solvent. In this context, fluorescent heterocyclic compounds show interesting features that make them attractive for use in MCRs.

Fluorescent heterocyclic compounds are of interest in many disciplines such as emitters for electroluminescence devices [4], molecular probes for biochemical research [5], in traditional textile and polymer fields [6], fluorescent whitening agents [7] and photo conducting materials [8].

2-Hydroxy-1,4-naphthoquinone (HNQ; Lawsone) is the principal natural dye (1.0–1.4%) in the leaves of henna, Lawsonia inermis. Henna has been used for more than 4000 years not only as a hair dye, but also as a body paint and tattoo dye. Today, semi-permanent hair dyes containing Henna as well as its pure dye ingredient HNQ are widely used and have become increasingly popular due to their natural origin [9]. A series of related nahthoquinone pigments (streptocarpone, α-dunnione, dunniol and dunnione) from *Streptocapus dunnii* have been isolated and characterized [10]. Similarly, quinone derivatives were reported as fluorescence compounds [11]. On the other hand, molecules with the quinone structure constitute one of the most interesting classes of compounds in organic chemistry, due to their biological properties, their industrial applications and their potential as intermediates in the synthesis of heterocycles [12]. In 1946 Wendel [13] showed that certain 2-hydroxy-3-alkyl-naphthoquinones inhibited the growth of *P. Vivae* upon the influence on the respiratory and carbohydrate cycles in the parasite. Further studies proved that the toxicity of naphthoquinones to *Plasmodium* sp. is due to interaction with the mitochondrial respiratory chain [14]. The quinones are also associated with antitumor, molluscicidal, leischmanicidal, anti inflammatory, and antifungal activities [15]. Among the quinones the following should be pointed out: atovaquone (**I**) [16], a coenzyme Q analogue which inhibits selectively *P. Vivae* by affecting the mitochondrial electron transport; lapachol (**II**) [17], present in the heartwood of the lapacho tree, *Tabebuia avellanedae* Lorentz ex. Griseb. (Bignoniaceae), and other *Tabebuia* trees native to Central and South America (Fig. 1). Therefore, the development of simple

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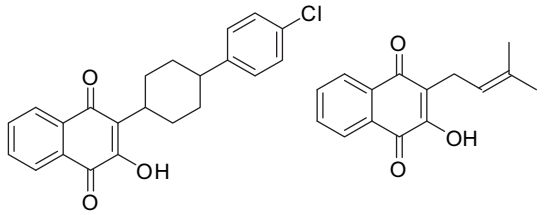


Fig. 1. Examples of antimalarial naphthoquinones.

synthetic methods for efficient preparation of the new quinone derivatives will be a beneficial and interesting challenge. Recently, the syntheses of quinones in water have been reported [18].

Considering the above reports, and as part of our program aimed at synthesis of heterocycles and new dyes containing nahthoquinone moiety [19], we are currently investigating the synthesis of hydroxyl naphthalene-1,4-dione derivatives via a facile, atom-economical, and three-component condensation reaction of 2-hydroxynaphthalene-1,4-dione **1**, aromatic aldehydes **2** and heterocyclic or carbocyclic amines **3** in the presence of a catalytic amount of $InCl_3$ in refluxing water (Fig. 2).

2. Experimental

2.1. General

Melting points were measured on an Elecrtothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Absorption spectra were recorded on an Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were recorded using PerkinElmer LS45 spectrofluorophotometer. The chemical used in this work were purchased from Fluka (Buchs, Switzerland) chemical company. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer.

2.2. Typical procedure for the preparation of 2-hydroxy-naphthalene-1,4-diones *4* and *5*

A mixture of 2-hydroxynaphthalene-1,4-dione (1 mmol), amine (1 mmol), aldehyde (1 mmol), $InCl_3$ (20 mol%) was refluxed in water (5 mL) for appropriate time (Table 2 and 3). After completion of the reaction confirmed by TLC (eluent: EtOAc/n-hexane, 1:1), the reaction mixture was filtered and the precipitate washed with water (5 mL) and EtOH (5 mL) to afford the pure product **4** and **5**.

Due to very low solubility of the products **4a**, **4b**, **4e**, **4j**, **4k** and **4n** we cannot report the ^{13}C NMR data for these products.

2.2.1. 2-hydroxy-3-[phenyl(phenylamino)methyl]naphthalene-1,4-dione (*4a*)

Orange powder (yield 90%); mp 143–146 °C. IR (KBr) (ν_{max}/cm^{-1}): 3434 (OH), 3321 (NH), 1660 (CO), 1636(CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.98 (1H, s, CH), 7.25–8.07, (14H, m, H-Ar), 9.26 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 37.3, 113.4, 123.9, 125.9, 125.9, 126.4, 128.5, 129.6, 130.3, 132.6, 133.1, 133.5, 135.0, 138.1, 146.0, 156.8, 157.6, 181.8, 184. MS, *m*/*z*: 355 (M^+). Anal. Calcd for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94%. Found: C, 77.61; H, 4.73; N, 3.83%.

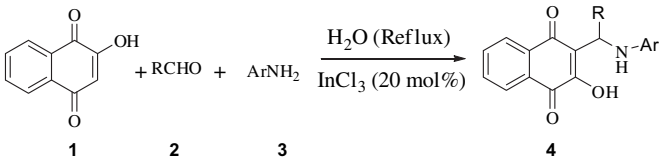


Fig. 2. Synthesis of hydroxyl naphthalene-1,4-diones **4**.

2.2.2. 2-hydroxy-3-[(phenylamino)(p-tolyl)methyl]naphthalene-1,4-dione (*4b*)

Orange Powder (yield 80%); mp 145–148 °C. IR (KBr) (ν_{max}/cm^{-1}): 3390 (OH), 3312 (NH), 1662 (CO), 1633 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.21 (3H, s, CH_3), 6.03 (1H, S, CH), 6.90–8.06, (13H, m, H-Ar), 9.09 (1H, s, OH). MS, *m*/*z*: 369 (M^+). Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79%. Found: C, 78.16; H, 5.10; N, 3.71%.

2.2.3. 2-Hydroxy-3-[(4-hydroxyphenyl)(phenylamino)methyl] naphthalene-1,4-dione (*4c*)

Yellow Powder (yield 86%); mp 185–190 °C. IR (KBr) (ν_{max}/cm^{-1}): 3423 (OH), 3221 (NH), 1630 (CO),1610 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.90, (1H, s, CH), 7.05-8.03, (13H, m, H-Ar), 9.26 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 37.8, 102.0, 124.1, 125.7, 126.4, 126.5, 128.0, 128.4, 130.2, 130.4, 130.8, 133.0, 133.1, 133.4, 135.3, 135.8, 146.8, 182.0, 182.8. MS, *m*/*z*: 371 (M^+). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77%. Found: C, 74.29; H, 4.66; N, 3.68%.

2.2.4. 2-Hydroxy-3-[(4-nitrophenyl)(phenylamino)methyl] naphthalene-1,4-dione (*4d*)

Orange Powder (yield 82%); mp 145–148 °C. IR (KBr) (ν_{max}/cm^{-1}): 3394 (OH), 3316 (NH), 1661 (CO), 1631 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.99 (1H, s, CH), 7.25-8.06, (13H, m, H-Ar), 9.25 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 37.8, 120.5, 122.7, 126.0, 126.1, 127.8, 128.3, 130.1, 130.3, 131.3, 132.6, 133, 135.1, 144.4, 156.9, 181.6, 183.8. MS, *m*/*z*: 400 (M^+). Anal. Calcd for $C_{23}H_{16}N_2O_5$: C, 69.00; H, 4.03; N, 7.00%. Found: C, 68.86; H, 4.09; N, 6.92%.

2.2.5. 2-Hydroxy-3-[phenyl(p-tolylamino)methyl]naphthalene-1,4-dione (*4e*)

Red Powder (yield 86%); mp 147–150 °C. IR (KBr) (ν_{max}/cm^{-1}): 3389 (OH), 3322 (NH), 1663 (CO), 1631 (CO).^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH_3), 6.03 (1H, s, CH), 7.10–8.06, (13H, m, H-Ar), 9.19 (1H, s, OH). MS, *m*/*z*: 369 (M^+). Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79%. Found: C, 77.91; H, 5.08; N, 3.64%.

2.2.6. 2-Hydroxy-3-[(4-methoxyphenyl)(p-tolylamino)methyl] naphthalene-1,4-dione (*4f*)

Dark orange Powder (yield 85%); mp 144–147 °C. IR (KBr) (ν_{max}/cm^{-1}): 3452 (OH), 3324 (NH), 1665 (CO), 1631(CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH_3), 3.69 (3H, s, OCH_3), 6.03 (1H, s, CH), 7.22-8.06, (12H, m, H-Ar), 9.19 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.2, 37.3, 55.3, 113.4, 123.9, 125.9,125.9, 126.4, 128.5, 129.6, 130.3, 132.6, 133.1, 135.0, 138.1, 146, 156.8, 157.6, 181.8, 184.0. MS, *m*/*z*: 399 (M^+). Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51%. Found: C, 75.08; H, 5.20; N, 3.57%.

2.2.7. 2-Hydroxy-3-[p-tolyl(p-tolylamino)methyl]naphthalene-1,4-dione (*4g*)

Dark red Powder (yield 91%); mp 146–149 °C. IR (KBr) (ν_{max}/cm^{-1}): 3446 (OH), 3326 (NH), 1669 (CO), 1638 (CO). ^{1}H NMR

(300 MHz, DMSO-d_6): δ_H (ppm) 2.22 (3H, s, CH_3), 2.31 (3H,CH_3), 6.03 (1H, s, CH), 5.99-8.06, (12H, m, H-Ar), 9.19 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 19.3, 19.9, 101.9, 116.0, 121.7, 125.2, 125.7, 126.5, 130.5, 130.6, 130.8, 130.9, 132.9, 133.1, 134.0, 135.3, 137.7, 146.8, 182.0, 188.8. MS, *m*/*z*: 83 (M^+). Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65%. Found: C, 78.18; H, 5.43; N, 3.74%.

*2.2.8. 2-Hydroxy-3-[(4-hydroxyphenyl)(p-tolylamino)methyl] naphthalene-1,4-dione (**4h**)*

Dark red Powder (yield 85%); mp 149–152 °C. IR (KBr) (ν_{max}/cm^{-1}): 3440 (OH), 3315 (NH), 1660 (CO), 1633 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH3), 6.03 (1H, s, CH), 7.25–8.05, (12H, m, H-Ar), 9.19 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.0, 37.2, 102, 124, 125.7, 126.4, 126.5, 128.0, 128.4, 130.2, 130.8, 133, 133.1, 133.4, 135.1, 135.3, 135.8, 146.8, 182, 182.8. MS, *m*/*z*: 385 (M^+). Anal Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63%. Found: C, 74.71; H, 4.91; N, 3.54%.

*2.2.9. 2-Hydroxy-3-[(2-hydroxy-4-nitrophenyl)(p-tolylamino) methyl]naphthalene-1,4- dione (**4i**)*

Orange Powder (yield 78%); mp 141–144 °C. IR (KBr) (ν_{max}/cm^{-1}): 3434 (OH), 3320 (NH), 1682 (CO), 1673 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH_3), 5.93(1H, s, CH), 7.23–8.00, (11H, m, H-Ar), 9.10 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO- d_6): δ_C (ppm) 21.0, 37.7, 101.6, 112.8, 119, 121.7, 125, 126.1 127.5, 129, 130.1, 130.3, 130.7, 131.6, 133.0, 134.3, 135.1, 135.8, 146.2, 182.6, 182.8. MS, *m*/*z*: 414 (M^+). Anal. Calcd for $C_{24}H_{18}N_2O_6$: C, 66.97; H, 4.22; N, 6.51%. Found: Found: C, 66.90; H, 4.27; N, 6.45%.

*2.2.10. 2-[(4-Fluorophenyl)(p-tolylamino)methyl]- 3-hydroxynaphthalene-1,4-dione (**4j**)*

Orange Powder (yield 80%); mp 143–146 °C. IR (KBr) (ν_{max}/cm^{-1}): 3384 (OH), 3310 (NH), 1674 (CO), 1653 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH_3), 6.03 (1H, s, CH), 7.25–8.06, (12H, m, H-Ar), 9.20 (1H, s, OH). MS, *m*/*z*: 387 (M^+). Anal. Calcd for $C_{24}H_{18}FNO_3$: C, 74.41; H, 4.68; N, 3.62%. Found: C, 74.50; H, 4.59; N, 3.69%.

*2.2.11. 2-[(4-Bromophenyl)(p-tolylamino)methyl]- 3-hydroxynaphthalene-1,4-dione (**4k**)*

Orange Powder (yield 79%); mp 147–150 °C. IR (KBr) (ν_{max}/cm^{-1}): 3421 (OH), 3335 (NH), 1678 (CO), 1662 (CO). 1H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH_3), 6.00 (1H, s, CH), 7.23–8.07, (12H, m, H-Ar), 9.14 (1H, s, OH). MS, *m*/*z*: 449 (M^+), 447 (M^+). Anal. Calcd for $C_{24}H_{18}BrNO_3$: C, 64.30; H,4.05; N, 3.12%. Found: C, 64.41; H, 4.13; N, 3.04%.

*2.2.12. 2-[(2,4-Dichlorophenyl)(p-tolylamino)methyl]- 3-hydroxynaphthalene-1,4-dione (**4l**)*

Red Powder (yield 89%); mp 144–147 °C. IR (KBr) (ν_{max}/cm^{-1}): 3380 (OH), 3314 (NH), 1658 (CO), 1650 (CO).^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.31 (3H, s, CH_3), 6.03 (1H, s, CH), 7.02–8.06, (11H, m, H-Ar), 9.10 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.1, 37.3, 124.1, 125.7, 126.1, 126.5, 130.1, 130.3, 130.8, 132.3, 133.6, , 135.1, 135.1, 135.3, 135.8, , 146.7, 181.9, 182.9, 182. MS, *m*/*z*: 437 (M^+). Anal. Calcd for $C_{24}H_{17}Cl_2NO_3$: C, 65.77; H, 3.91; N, 3.20%. Found: C, 65.62; H, 3.84; N, 3.13%.

*2.2.13. 2-[(2-Chlorophenyl)(p-tolylamino)methyl]- 3-hydroxynaphthalene-1,4-dione (**4m**)*

Red Powder (yield 89%); mp 149–152 °C. IR (KBr) (ν_{max}/cm^{-1}): 3383 (OH), 3324, (NH),1665 (CO), 1644 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.30 (3H, s, CH_3), 6.01 (1H, s, CH), 7.26–8.16, (12H, m, H-Ar), 9.20 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.0, 37.7, 101, 124.1, 125.7, 125.9, 126.4, 126.5, 129.5, 130.2, 130.3, 130.8, 132.7, 133.0, 135.1, 135.5, 135.8, 146.8, 182.0, 182.8. MS, *m*/*z*: 403 (M^+). Anal. Calcd for $C_{24}H_{18}ClNO_3$: C, 71.38; H, 4.49; N, 3.47%. Found: C, 71.27; H, 4.56; N, 3.40%.

*2.2.14. 2-hydroxy-3-[(3-nitrophenyl)(p-tolylamino)methyl] naphthalene-1,4-dione (**4n**)*

Red Powder (yield 90%); mp 144–147 °C. IR (KBr) (ν_{max}/cm^{-1}): 3388 (OH), 3289, (NH),1668 (CO), 1643(CO).1H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.30 (3H, s, CH_3), 5.97 (1H, s, CH), 6.58–7.93, (12H, m, H-Ar), 9.14 (1H, s, OH). MS, *m*/*z*: 414 (M^+).Anal. Calcd for $C_{24}H_{18}N_2O_5$: C, 69.56; H, 4.38; N, 6.76%. Found: C, 69.43; H, 4.29; N, 6.66%.

*2.2.15. 2-[(4-Fluorophenylamino)(phenyl)methyl]- 3-hydroxynaphthalene-1,4-dione (**4o**)*

Dark red Powder (yield 85%); mp 150–153 °C. IR (KBr) (ν_{max}/cm^{-1}): 3431 (OH), 3328 (NH), 1669 (CO), 1646 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.98 (1H, s, CH), 7.25-8.06, (13H, m, H-Ar), 9.25 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 37.3, 102, 124.1, 125.7, 126.4,126.5, 128.0, 128.4, 130.2, 130.4, 130.8, 133, 133.1, 133.4, 135.1, 135.3, 135.8, 146.8, 182.0, 182.8. MS, *m*/*z*: 373 (M^+). Anal. Calcd for $C_{23}H_{16}FNO_3$: C, 73.99; H, 4.32; N, 3.75%. Found: C, 73.90; H, 4.26; N, 3.68%.

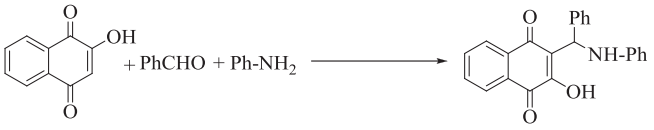
*2.2.16. 2-[(4-Fluorophenylamino)(p-tolyl)methyl]- 3-hydroxynaphthalene-1,4-dione (**4p**)*

Orange Powder (yield 78%); mp 149–152 °C. IR (KBr) (ν_{max}/cm^{-1}): 3426 (OH), 3315 (NH), 1680 (CO), 1643 (CO). ^{1}H NMR (300 MHz, DMSO-d6): δ_H (ppm) 2.20 (3H, s, CH_3), 6.06 (1H, s, CH), 6.09–8.06, (12H, m, H-Ar), 9.25 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.0, 38.0, 110.8, 114.9, 121.1, 123.4, 126.0, 126.4, 128.9, 130.3, 132.6, 133.5, 135.1, 142.8, 156.7, 159.3, 181.6, 183.9. MS, *m*/*z*: 387 (M^+). Anal. Calcd for $C_{24}H_{18}FNO_3$: C, 74.41; H, 4.68; N, 3.62%. Found: C, 74.33; H, 4.58; N, 3.51%.

*2.2.17. 2-[(4-Fluorophenylamino)(4-nitrophenyl)methyl]- 3-hydroxynaphthalene-1,4- dione (**4q**)*

Orange Powder (yield 81%); mp 149–152 °C. IR (KBr) (ν_{max}/cm^{-1}): 3446 (OH), 3315 (NH), 1680 (CO), 1643 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.90 (1H, s, CH), 7.20–8.06, (12H,

Table 1
Model reaction, conditions, and yield.[a]

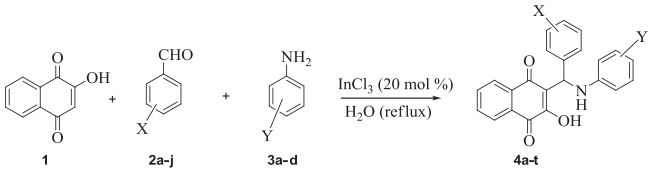


1 2a 3a 4a

Entry	Conditions	Catalyst	Time (h)	Yield (%)
1	H_2O (reflux)	$InCl_3$ (10mol %)	6	67
2	H_2O (reflux)	$InCl_3$ (20 mol %)	6	90
3	H_2O (reflux)	$InCl_3$ (25 mol %)	6	91
4	H_2O/r.t	$InCl_3$ (20 mol %)	6	45
5	H_2O (reflux)	None	10	Trace
6	H_2O (reflux)	LiCl (20 mol %)	6	53
7	H_2O (reflux)	$LiClO_4$ (20 mol %)	6	61
8	H_2O (reflux)	$ZnCl_2$ (20 mol %)	6	43
9	H_2O (reflux)	*p*-TSA (20 mol %)	6	73
10	EtOH (reflux)	$InCl_3$ (20 mol %)	10	78
11	MeCN (reflux)	$InCl_3$ (20 mol %)	10	<40
12	$PhCH_3$ (reflux)	$InCl_3$ (20 mol %)	10	<40

[a] 2-hydroxynaphthalene-1,4-dione (1 mmol), benzaldehyde (1 mmol) and aniline (1 mmol).

Table 2
2-Hydroxy (aryl(arylamino) methyl)naphthalene-1,4-diones **4**.



Product **4**	X	Y	Time (h)	Yield (%)
a	H	H	6	90
b	4-Me	H	6.5	80
c	4-OH	H	6	86
d	4-NO_2	H	5	82
e	H	4-Me	7	86
f	4-OMe	4-Me	5.5	85
g	4-Me	4-Me	6.5	91
h	4-OH	4-Me	7	85
i	4-NO_2	4-Me	6	78
j	4-F	4-Me	7	80
k	4-Br	4-Me	7	79
l	2,4-diCl	4-Me	7.5	89
m	2-Cl	4-Me	5.5	89
n	3-NO_2	4-Me	5	90
o	H	4-F	7	85
p	4-Me	4-F	6.5	78
q	4-NO_2	4-F	5	81
r	H	2-Cl, 4-NO_2	6.5	80
s	Me	2-Cl, 4-NO_2	6	79
t	4-NO_2	2-Cl, 4-NO_2	7	78

m, H-Ar), 9.20 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 37.3, 101.9, 116.0, 121.7, 125.2, 125,7, 126.5, 130.5, 130.6, 130.8, 130.9, 132.9, 133.1, 134.0, 135.3, 136.0, 137.7, 146.8, 182.0, 182.8. MS, *m*/*z*: 418 (M^+).Anal. Calcd for $C_{23}H_{15}FN_2O_5$: C, 66.03; H, 3.61; N, 6.70%. Found: C, 66.17; H, 3.67; N, 6.62%.

*2.2.18. 2-[(2-Chloro-4-nitrophenylamino)(phenyl)methyl]-3-hydroxynaphthalene-1,4-dione (**4r**)*

Orange Powder (yield 80%); mp 153–156 °C. IR (KBr) (ν_{max}/cm^{-1}): 3428 (OH), 3315 (NH), 1683 (CO), 1636 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.09 (1H, s, CH), 7.20–8.08, (12H, m, H-Ar), 9.22 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 38.1, 111.8, 114.1, 121.1, 123.4, 126.1, 126.4, 128.1, 130.3, 132.6, 133.1, 135.1, 142.8, 156.1, 159.1, 181.6, 183.9. MS, *m*/*z*: 434 (M^+).Anal. Calcd for $C_{23}H_{15}ClN_2O_5$: C, 63.53; H, 3.48; N, 6.44%. Found: C, 63.45; H, 3.57; N, 6.51%.

*2.2.19. 2-[(2-Chloro-4-nitrophenylamino)(p-tolyl)methyl]-3-hydroxynaphthalene-1,4- dione (**4s**)*

Orange Powder (yield 79%); mp 145–148 °C. IR (KBr) (ν_{max}/cm^{-1}): 3435 (OH), 3321 (NH), 1685 (CO), 1645 (CO). 1H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.19 (3H, s, CH_3), 6.04(1H, s, CH), 7.19–8.01, (11H, m, H-Ar), 9.15 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO- d_6): δ_C (ppm) 20.2, 38.7, 101.0, 104.9, 114.1, 123.7, 125.8, 126.4, 126.5, 129.8, 130.2, 130.3, 131.0, 132.3, 133.0, 133.1, 135.5, 135.8, 149.8, 182.0, 182.8. MS, *m*/*z*: 448 (M^+). Anal. Calcd for

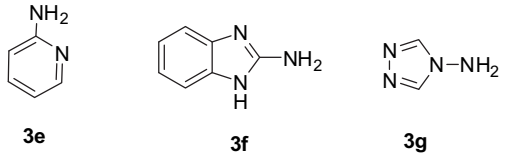
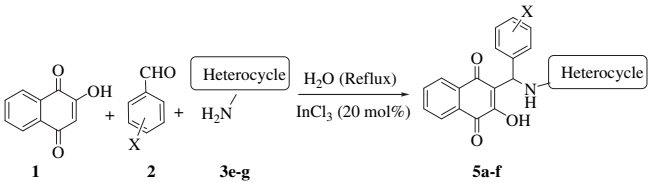


Fig. 3. Diversity heterocyclic amines **3e**–**g**.

Table 3
Heterocyclic 2-hydroxy naphthalene-1,4-diones **5**.



Product **5**	X	Compound **3**	Time (h)	Yield (%)
a	H	**3e**	5	81
b	4-NO_2	**3e**	4	80
c	H	**3f**	5	83
d	4-NO_2	**3f**	6	80
e	H	**3g**	5.5	82
f	4-OH	**3g**	6	78

$C_{24}H_{17}ClN_2O_5$: C, 64.22; H, 3.82; N, 6.24%. Found: C, 64.33; H, 3.77; N, 6.31%.

*2.2.20. 2-[(2-chloro-4-nitrophenylamino)(4-nitrophenyl)methyl]-3-hydroxynaphthalene-1,4-dione (**4t**)*

Orange Powder (yield 78%); mp 143–146 °C. IR (KBr) (ν_{max}/cm^{-1}): 3389 (OH), 3320 (NH), 1680 (CO), 1647 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.04 (1H, s, CH), 7.24–8.09, (11H, m, H-Ar), 9.19 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 38.0, 112.8, 113.1, 122.1, 124.4, 125.1, 126.7, 128.4, 132.3, 133.6, 134.1, 135.1, 141.8, 156.4,159.8, 181.3, 183.6. MS, *m*/*z*: 479 (M^+). Anal. Calcd for $C_{23}H_{14}ClN_3O_7$: C, 57.57; H, 2.94; N, 8.76%. Found: C, 57.43; H, 2.85; N, 8.65%.

*2.2.21. 2-Hydroxy-3-[phenyl(pyridin-2-ylamino)methyl] naphthalene-1,4-dione (**5a**)*

Orange Powder (yield 81%); mp 145–148 °C. IR (KBr) (ν_{max}/cm^{-1}): 3435 (OH), 3328 (NH), 1676 (CO), 1653(CO). 1H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.55 (1H, s, CH), 6.57–7.97, (14H, m, H-Ar, NH), 9.78 (1H, s, OH). MS, *m*/*z*: 356 (M^+). Anal. Calcd for $C_{22}H_{16}N_2O_3$: $C_{22}H_{16}N_2O_3$: C, 74.15; H, 4.53; N, 7.86%. Found: C, 74.03; H, 4.46; N, 7.78%.

Due to very low solubility of the products **5a**, **5b**, **5e** and **5f**, we cannot report the ^{13}C NMR data for these products.

*2.2.22. 2-Hydroxy-3-[(4-nitrophenyl)(pyridin-2-ylamino)methyl] naphthalene-1,4-dione (**5b**)*

Orange Powder (yield 80%); mp 148–151 °C. IR (KBr) (ν_{max}/cm^{-1}): 3387 (OH), 3325 (NH), 1678 (CO), 1665 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.50 (1H, s, CH), 6.64–8.09, (13H, m, H-Ar, NH), 9.81 (1H, s, OH). MS, *m*/*z*: 401 (M^+). Anal. Calcd for $C_{22}H_{15}N_3O_5$: C, 65.83; H, 3.77; N, 10.47%. Found: C, 65.74; H, 3.85; N, 10.34%.

*2.2.23. 2-[(1H-benzo[d]imidazol-2-ylamino)(phenyl)methyl]-3-hydroxynaphthalene-1,4- dione (**5c**)*

Orange Powder (yield 83%); mp 151–155 °C. IR (KBr) (ν_{max}/cm^{-1}): 3438 (OH), 3335 (NH), 3329 (NH), 1680 (CO), 1665 (CO). ^{1}H

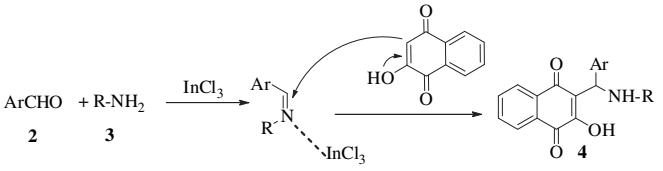


Fig. 4. Possible mechanism for the formation of products **4**.

Table 4
Photophysical data for absorption (abs) and fluorescence (flu) of selected products in methanol.

Product	log ϵ	$\lambda_{abs,max}$/nm	$\lambda_{flu,max}$/nm	Stock's shift
4a	3.44	462	560	98
4b	3.40	514	559	45
4c	3.39	471	558	87
4d	3.58	476	558	82
4e	3.45	477	557	80
4g	3.50	473	556	83
4i	3.58	444	550	106
4j	3.55	469	549	80
4l	3.47	477	548	71
4n	3.42	476	548	72
4o	4.45	473	547	74
4q	3.55	469	547	78
4r	3.46	476	547	71
4t	3.46	478	546	68
5a	3.49	440	548	108
5c	3.76	418	558	140
5f	3.41	449	555	106

NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.91 (1H, s, CH), 6.56–8.06, (14H, m, H-Ar, NH), 9.09 (1H, s, OH), ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 35.5, 101.2, 111,4, 113.5, 123.8, 126.4, 127.3, 127.9, 128.2, 128.6, 129.0, 130.0, 130.3, 135.7, 136.9, 138.5, 140.3, 141.7, 178.9, 181.0. MS, *m*/*z*: 395 (M^+). Anal. Calcd for $C_{24}H_{17}N_3O_3$: C, 72.90; H, 4.33; N, 10.63%. Found: C, 72.79; H, 4.40; N, 10.72%.

*2.2.24. 2-[(1H-benzo[d]imidazol-2-ylamino)(4-nitrophenyl) methyl]-3-hydroxynaphthalene-1,4-dione (**5d**)*

Orange Powder (yield 80%); mp 150–153 °C. IR (KBr) (ν_{max}/cm^{-1}): 3440 (OH), 3337 (NH), 3331 (NH), 1685 (CO), 1673 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.21 (1H, s, CH), 6.26–8.71, (13H, m, H-Ar, NH), 9.05 (1H, s, OH). 13C NMR (75 MHz, DMSO-d6): δ_C (ppm) 34.7, 110.4, 123.8, 126.5, 127.4, 128.0, 128.2, 128.6, 130.0, 130.4, 131.4, 132.2, 132.6, 133.8, 135.6, 138.5, 139.5, 142.2, 149.7, 178.9, 181.0. MS, *m*/*z*: 440 (M^+). Anal. Calcd for $C_{24}H_{16}N_4O_5$: C, 65.45; H, 3.66; N, 12.72%. Found: C, 65.32; H, 3.57; N, 12.64%.

*2.2.25. 2-[(4H-1,2,4-triazol-4-ylamino)(phenyl)methy]-3-hydroxynaphthalene-1,4-dione (**5e**)*

Orange Powder (yield 82%); mp 145–148 °C. IR (KBr) (ν_{max}/cm^{-1}): 3338 (OH), 3333 (NH), 1681 (CO), 1675 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.26 (1H, s, CH), 6.55–8.02, (11H, m, H-Ar, NH), 9.15 (1H, s, OH). MS, *m*/*z*: 346 (M^+). Anal. Calcd for $C_{19}H_{14}N_4O_3$: C, 65.89; H, 4.07; N, 16.18%. Found: C, 65.75; H, 4.16; N, 16.09%.

*2.2.26. 2-[(4H-1,2,4-triazol-4-ylamino)(4-hydroxyphenyl)methyl]-3-hydroxynaphthalene-1,4-dione (**5f**)*

Orange Powder (yield 78%); mp 161–163 °C. IR (KBr) (ν_{max}/cm^{-1}): 3342 (OH), 3323 (NH), 1683 (CO), 1671 (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.99 (1H, S, CH), 7.25–8.06 (11H, m, H-Ar, NH), 9.90 (1H, s, OH), MS, *m*/*z*: 362 (M^+). Anal. Calcd for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.89; N, 15.46%. Found: C, 62.90; H, 3.82; N, 15.74%.

3. Results and discussion

The choice of an appropriate reaction media is of crucial importance for successful synthesis. Initially, the three-component reaction of 2-hydroxynaphthalene-1,4-dione **1**, benzaldehyde **2a** and aniline **3a** as a simple model substrate was investigated to establish the feasibility of the strategy and optimize the reaction conditions (Table 1). Different solvents and catalysts were screened in the model reaction. As could be seen in Table 1, the best result was obtained with a 20 mol% of $InCl_3$ as the catalyst in refluxing water and the desired product, 2-hydroxy-(phenyl(phenylamino) methyl)naphthalene-1,4- dione **4a,** is obtained in good yield (Entry 2). Using lower amount of catalyst resulted in lower yields, while higher amount of catalyst did not affected reaction times and yields (Table 1). When this reaction was carried out without any catalyst, TLC and ^{1}H NMR spectra of the reaction mixture showed a combination of starting materials and numerous products, the yield of the expected product was very poor (Table 1, entry 5).

After optimizing the reaction conditions, a variety of aromatic aldehydes and amines were employed under similar circumstances to evaluate the substrate scope of this reaction. The results are shown in Table 2. As anticipated from our original results, these reactions proceeded very cleanly at refluxing water and no undesirable side reactions were observed.

The aromatic aldehydes carrying both electron-withdrawing and electron-releasing substituents were also converted to their corresponding 2-hydroxy naphthalene-1,4- diones derivatives in good yields. It is noteworthy that the reactions of halosubstituted benzaldehydes proceeded with the expected mechanism and exhibit good yields (Table 2).

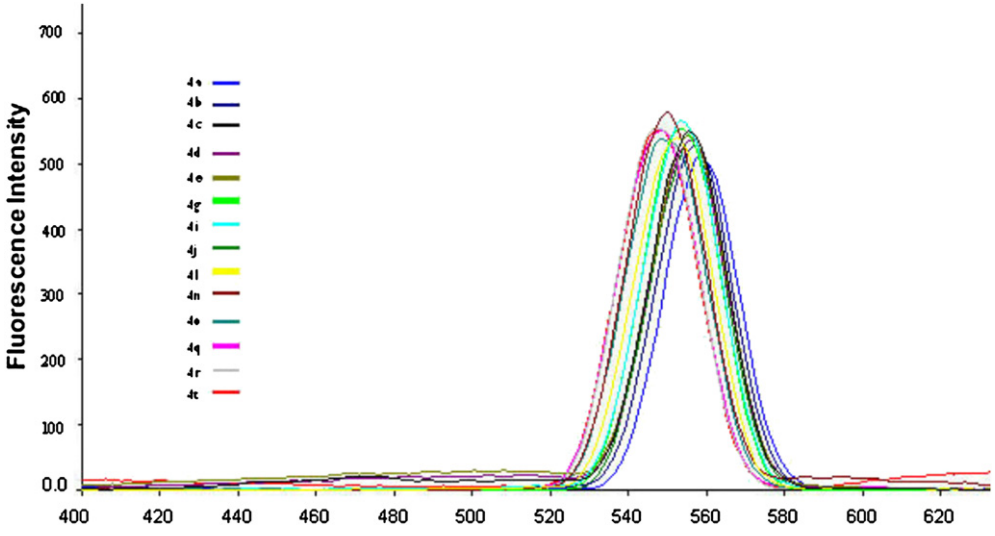


Fig. 5. The emission spectra of selected compounds **4** (5×10^{-5} M in CH_3OH).

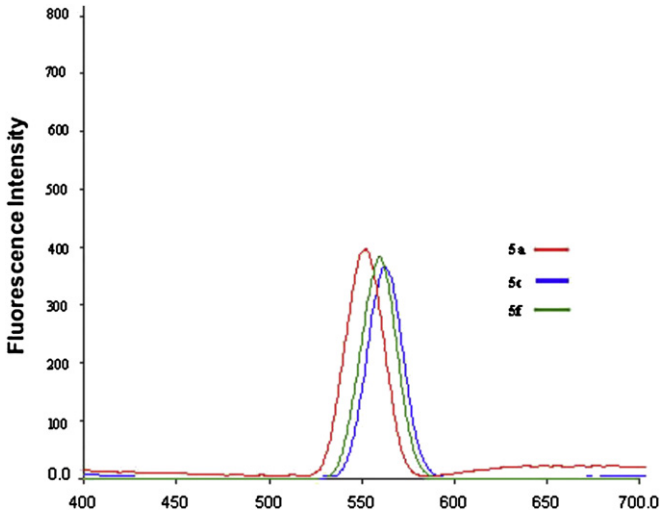


Fig. 6. The emission spectra of selected compounds **5** (5×10^{-5} M in CH_3OH).

The reaction proceeds under mild conditions and is compatible with a wide range of functional groups. Two substituents in the products can be varied independently of each other. Therefore, given the large number of available aldehydes and amines, the present method should be applicable to synthesis of libraries with high diversity.

Due to the biological importance of polyfunctionalized heterocyclic compounds, we used heterocyclic amines: 2-amino pyridine **3e**, 2-amino-benzimidazole **3f** and amino triazole **3g** in the reaction (Fig. 3). This made it possible to synthesize a series of hydroxyl naphthalene-1,4-diones containing pyridine, benzimidazole or triazole moiety **5a**–**h** (Table 3).

We have not established an exact mechanism for the formation of hydroxy naphthalene-1,4-diones **4**, however, a reasonable possibility is shown in (Fig. 4).

The work-up of these very clean reactions involves only a filtration and simple washing step with EtOH. Using this simple purification protocol the desired products are obtained in high purity. Compounds **4** and **5** are stable solids whose structures were established by IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Electronic absorption and fluorescence spectra of 5×10^{-5} M solutions of selected products **4** and **5** in methanol were measured and the results are shown in Table 4. All selected compounds showed strong absorptions, with maximum wavelengths in the range of 418–514 nm. Figs. 5 and 6 show the emission spectra of selected products. From Figs. 5 and 6, it can be observed that the products are fluorescent in solution. The λ_{flu} changed slightly and were located at green light (546–560 nm). The λ_{flu} are presented in Table 4.

4. Conclusion

In conclusion, an efficient, clean, atom-economical, and simple method for the preparation of hydroxy naphthalene-1,4-dione library using a wide diversity of substituents in aldehydes and amines in a three-component reaction in the presence of $InCl_3$ in water is reported. Prominent among the advantages of this method are operational simplicity, good yields and easy work-up procedures employed.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2010.09.004.

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