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An efficient synthesis of naphtha[1,2-*e*]oxazinone and 14-substituted-14*H*-dibenzo[*a,j*]xanthene derivatives promoted by zinc oxide nanoparticle under thermal and solvent-free conditions

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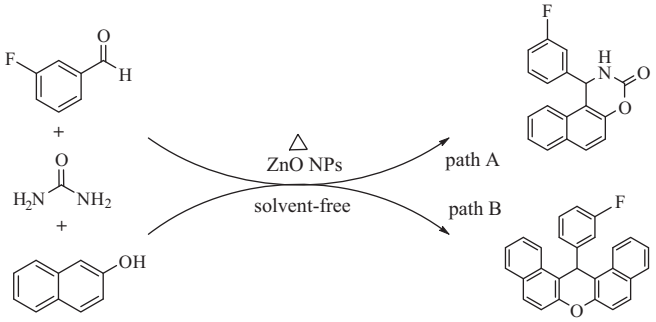
ABSTRACT

A general synthetic route to the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one and 14-substituted-14*H*-dibenzo[*a,j*]xanthenes derivatives has been developed using ZnO-NPs under thermal and solvent-free conditions. The union of 2-naphthol, aldehyde, urea enabling the synthesis of naphtho[1,2-*e*][1,3]oxazinone and 2-naphthol, aldehyde gave dibenzo[*a,j*]xanthenes in excellent yields. This method provides several advantages like simple work-up, environmentally benign, and shorter reaction times along with high yields.

Oxazinone, benzoxazinone, and their derivatives are an important class of heterocyclic compounds. In recent years oxazinones core containing heterocyclic derivatives have received considerable attention, due to its biological activities.[1,2] Naphthalene condensed oxazinone derivatives have a broad spectrum of antibacterial properties[3] and the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one which involves a three-component condensation reaction of 2-naphthol, arylaldehyde, and urea in one-pot (Scheme 1, Path A). These compounds have also been used as a precursor in the synthesis of chiral amino phosphine ligands for asymmetric catalysis.[4] Due to the pharmacological importance, several protocols have been developed over a period of time. The conventional method includes condensation of phenols, formaldehyde, and amines through Mannich reaction,[5] additionally they have also been synthesized by the reaction of amino alkylnaphthols with phosgene[6] and reaction with carbonyl di-imidazole.[7] However, these methods have some drawbacks like prolonged reaction time, lack of easy availability/preparation of starting materials, and hazardous reaction conditions. To overcome these drawbacks, several methods are reported in the literature utilizing acidic and basic catalysts[8] each of these methods has their own advantages but also suffer from some bottlenecks, such as modest yields and tedious work-up procedure. Therefore, these drawbacks prompted us to examine a new catalyst for the environmentally benign synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one.

Nano-chemistry is an up growing research area due to their unique properties.[9] The usage of nanomaterials such as heterogeneous catalyst has gained significant role in organic synthesis due to simple work-up procedure, environmentally benign nature, reusability, low cost, and ease of isolation. Zinc oxide nanoparticles (ZnO-NPs) are heterogeneous catalysts and widely used in cosmetics, paints, and fibers. It can also play a role of Lewis acid in various



Path A: **aldehyde** + **urea** + **2-naphthol** sequence addition

Path B: **aldehyde**, **urea**, **2-naphthol** rando maddition

Scheme 1. General synthetic approach of naphtha[1,2-*e*]oxazinone.

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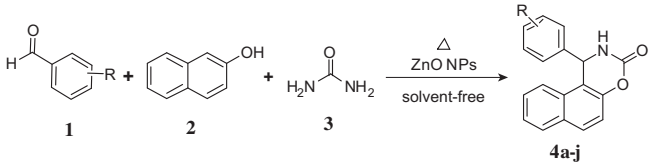
organic transformations.[10] Recently, Prasad et al. have reported the crystalline sizes of ZnO-NPs prepared by the calcination of xerogel at 500 °C, 900 °C, 1000 °C, 1100 °C, which were characterized by TEM, XRD, N_2 BET.[11] They have also studied the photocatalytic decontamination of sulfur mustered (CWA) on the surface of zinc oxide nanoparticles. Inspired by the above catalytic activity of ZnO-NPs, we examined the ZnO-NPs as a heterogeneous catalyst in the synthesis of naphtha[1,2-*e*]oxazinone and dibenzoxanthenes derivative.

In continuation of our studies on the synthesis of various bioactive compounds[12] herein, we report an efficient, facile, and convenient procedure for the synthesis of naphtha[1,2-*e*]oxazinone derivatives employed by the union of 2-naphthol, aldehyde, and urea in the presence of catalytic amount of ZnO-NPs as an environmentally benign and heterogeneous catalyst under thermal and solvent-free conditions.

Initially we investigated the catalytic activity of ZnO-NPs for the synthesis of naphtha[1,2-*e*]oxazinone derivatives. A set of control experiments on 3-fluoro benzaldehyde, 2-naphthol, and urea were carried out under solvent-free conditions. The utility of ZnO bulk in the synthesis of naphtha[1,2-*e*]oxazinone shows that its efficiency which is lower than ZnO-NPs. From the above observations, it was revealed that the sequential addition of reactants had played a significant role in the synthesis of target molecule. Any alternation in the sequential addition or random addition of reactants led to the formation of the new product (Scheme 1).

By the random addition of the 3-fluoro benzaldehyde, 2-naphthol, urea, and ZnO-NPs (Scheme 1, Path B), we observed xanthene derivative (Table 2, entry 6) as a major product and there was no formation of naphthoxazinone derivative. The sequential addition of reactants like 3-fluoro benzaldehyde, urea, and catalyst followed by 2-naphthol played a crucial role and influenced toward the course of desired naphthoxazinone (Table 1, entry 4) product which was observed as a major product (Scheme 1, Path A). The formation of xanthene derivative as a major product in random addition might be due to the highly reactive nature of benzaldehyde with 2-naphthol than urea. ZnO-NPs (0.3 equiv) was efficiently accelerated by the reaction of arylbenzaldehyde (1.0 equiv), 2-naphthol (1.0 equiv) and urea (2.0 equiv) toward the formation of desired product under thermal and solvent-free conditions.[22a] Further, we extended the optimized reaction conditions to various aldehydes and all the results are appended in Table 1.

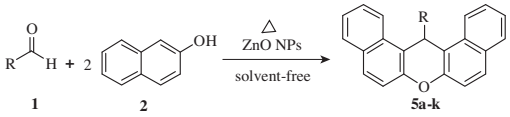
Table 1
Synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one (**4a**–**j**) using ZnO-NPs[a]



Entry	Aldehyde (R)	Product	Time (min)	Yield[b] (%)	M.P.[ref]
1	4-CH_3-C_6H_5	**4a**	90	85	164–166[8a]
2	4-OCH_3-C_6H_5	**4b**	90	82	188–190[8a]
3	4-F-C_6H_5	**4c**	60	92	198–200[8a]
4	3-F-C_6H_5	**4d**	50	92	218–220
5	4-Cl-C_6H_5	**4e**	60	90	210–212[8a]
6	3-Cl-C_6H_5	**4f**	60	88	194–196[8c]
7	4-OC_2H_5-C_6H_5	**4g**	80	80	216–218
8	4-CF_3-C_6H_5	**4h**	50	94	234–236
9	4-OCF_3-C_6H_5	**4i**	45	90	168–170
10	4-$(CH_3)_3C$-C_6H_5	**4j**	120	76	180–182[8b]

[a] Reaction condition: **1** (1.0 equiv), **2** (1.0 equiv), **3** (2.0 equiv) and ZnO-NPs (0.3 equiv).
[b] Isolated yield.

Table 2
ZnO-NPs catalyzed synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes derivatives (**5a**–**k**)[a]



Entry	Aldehyde (R)	Product	Time (min)	Yield[b] (%)	M.P.[ref]
1	4-OCH_3 -C_6H_5	**5a**	60	82	202–204[21a]
2	4-OC_2H_5 -C_6H_5	**5b**	60	88	172–174
3	4-Cl-C_6H_5	**5c**	40	92	288–290[21a]
4	3-Cl-C_6H_5	**5d**	60	90	210–212[21c]
5	4-F -C_6H_5	**5e**	50	85	240–242[21a]
6	3-F -C_6H_5	**5f**	45	90	258–260[21d]
7	4-C_2H_5-C_6H_5	**5g**	70	88	186–188
8	3-C_5H_4N-	**5h**	60	85	202–204[21b]
9	$(CH_3)_2CH$-	**5i**	80	86	156–158[21a]
10	C_6H_5	**5j**	60	80	182–184[21a]
11	4-NO_2-C_6H_5	**5k**	55	86	310–312[21a]

[a] Reaction conditions: **1** (1.0 equiv), **2** (2.0 equiv) and ZnO-NPs (0.3 equiv).
[b] Isolated yields.

Xanthenes have active oxygen atom and they are widely used as a leuco-dye[13] in laser technologies[14] and in fluorescent materials for the visualization of bio-molecule[15] cascades due to their useful spectroscopic properties. Xanthenes have also received significant attention from organic chemists essentially because of the wide range of their pharmaceutical properties.[16–18] Also these compounds have been utilized as antagonists for the paralyzing action of zoxazolamine[19] and in photodynamic therapy.[20] In recent years, several attempts have been made for the synthesis of xanthenes derivatives to increase the yield.[21]

In order to demonstrate the catalytic activity of this ZnO-NPs, the same procedure was extended for one-pot synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes class of compounds by using 2-naphthol and aldehyde under the same reaction conditions[22b] and all the results are depicted in Table 2. We observed that ZnO-NPs promoted the reaction of 2-naphthol as well as 2-naphthol and urea smoothly with aryl aldehyde bearing electron-releasing or electron-withdrawing substituents.

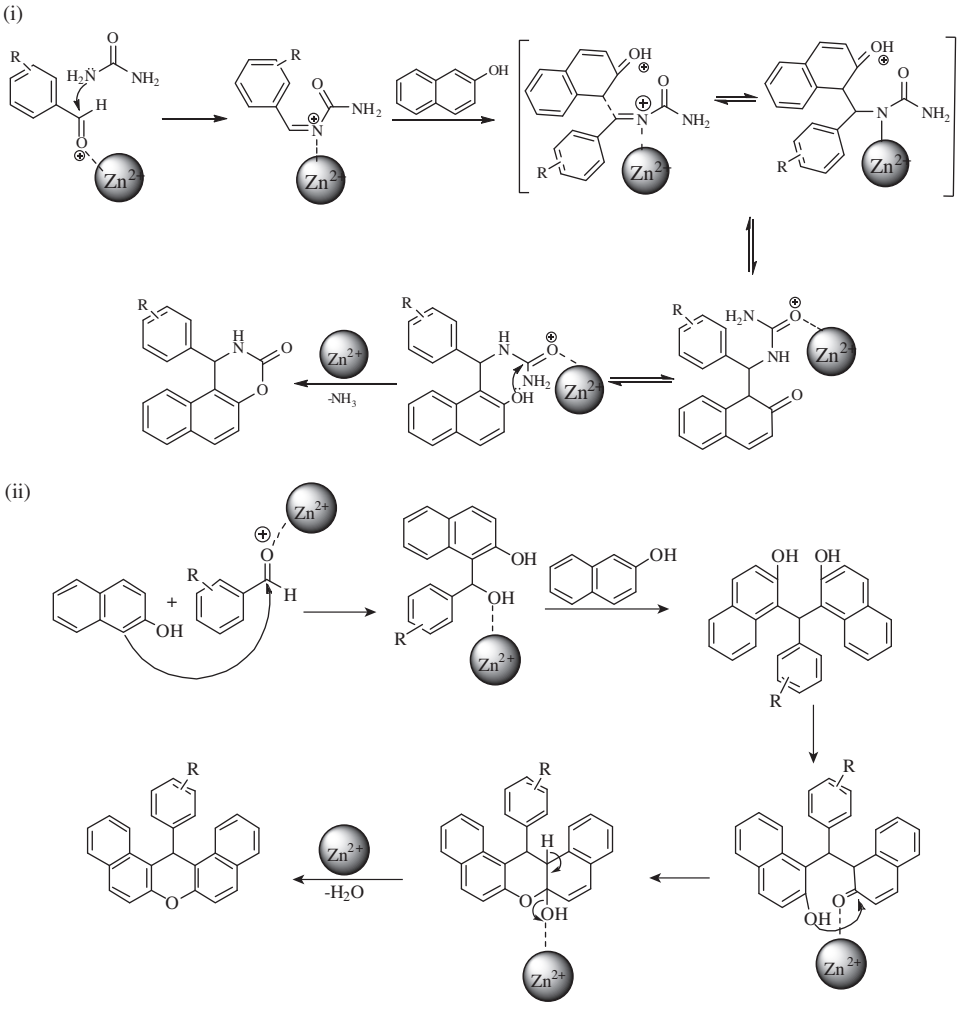
From the green chemistry point of view, efficient recovery and reuse of the catalyst are highly desirable, thus the recovery and reusability of ZnO-NPs were investigated. After the reaction was completed, ethylacetate was added until the solid crude product was dissolved. Then, ZnO-NPs as the catalysts were isolated from the mixture of reaction by simple filtration and reused again after washing with ethylacetate. The reusability of ZnO-NPs was examined efficiently (without any activation) by using 3-fluoro benzaldehyde as a model substrate. The recovered ZnO-NPs were reused directly for four consecutive cycles and all the results are tabulated in Table 3.

On the basis of the above observations and the literature reports, a plausible reaction pathway for the formation of naphthoxazinone

Table 3
Recyclability of the catalyst for the synthesis of **4d**[a]

Entry	Cycle	Time (min)	Yield[b] (%)
1	Cycle 1	50	92
2	Cycle 2	60	87
3	Cycle 3	75	78
4	Cycle 4	90	68

[a] Reaction conditions: 2-naphthol (1.0 equiv), 3-fluoro benzaldehyde (1.0 equiv), urea (2.0 equiv) and ZnO-NPs (0.3 equiv).
[b] Isolated yields.



Scheme 2. Proposed mechanism for naphthoxazinone (i) and dibenzoxanthene (ii).

is depicted in Scheme 2. (i) The interaction of aryl aldehyde with the catalyst surface generated the more electrophilic carbon center followed by the nucleophilic attack of urea to give reactive acylimine intermediate. The resulting acylimine intermediate undergoes a cyclization with 2-naphthol affording the corresponding desired naphtha[1,2-e]oxazinone followed by the elimination of ammonia. (ii) The more electrophilic carbon center generated by catalytic surface was attacked by the nucleophilic 2-naphthol. Aryl- or alkylmethane bisnaphthol was formed by the attack of 2-naphthol in second step. Elimination of water molecule take place from bisnaphthol to form final desired product 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes.

In summary, we have described a simple, efficient, and environmentally benign one-pot procedure for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one and 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes derivatives by using catalytic amount of ZnO-NPs under thermal and solvent-free conditions. Salient features of this method are mild reaction conditions, environmental compatibility, ease of isolation of product, and excellent reusability of the catalyst. ZnO-NPs make the reaction inexpensive and the procedure an attractive alternative to the existing methodologies for the synthesis naphthoxazinone and 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes derivatives. The present procedure gave the products in good to excellent yields at reduced reaction time, which might be due to the increased reactivity of the reactants on high surface area of ZnO-nanoparticles.

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22. *Typical experimental procedure*:
(a) A 25 ml round bottom flask was charged with benzaldehyde (1.0 equiv), urea (2.0 equiv) and catalytic amount of ZnO-NPs (0.3 equiv). The reactants are finely powdered and mixed together and allowed to stir for 30 min at room temperature. The 2-naphthol (1.0 equiv) was added to the above mixture and the resulting reaction mixture was heated at 150 °C (oil bath) with constant stirring till the reaction was complete. After completion of reaction as indicated on TLC, the reaction mixture was cooled to room temperature and the crude reaction mixture was dissolved in ethylacetate and the catalyst was separated out by simple filtration. The reaction mixture in ethylacetate was washed with water and excess of solvent was removed under reduced pressure. The solid mass was washed with cold diethylether (20 ml × 2) and dried. The pure product was obtained in 76–94% yield. (b) A mixture of aldehyde (1.0 equiv) and 2-naphthol (2.0 equiv) was charged in a round bottom flask. A catalytic amount of ZnO-NPs (0.3 equiv) was added and the reaction was heated at 120 °C (oil bath) with constant stirring under solvent-free condition for certain period of time as required. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature. The reaction mixture was dissolved in ethylacetate and the catalyst was separated out by simple filtration. Excess of solvent was removed under reduced pressure and the crude product was recrystallized with ethanol to afford the pure product in 80–92% yield. The spectral data for some selected compounds are given below.
1-(3-Fluorophenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one ***4d***: mp 218–220, IR (ν_{Max}): 794, 929, 1184, 1226, 1397, 1487, 1756, 2966, 3132, 3216. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.932 (s, 1H), 6.082 (s, 1H), 6.965 (m, 2H), 7.119 (m, 1H), 7.337–7.359 (m, 2H), 7.427–7.451 (m, 2H), 7.519 (s, 1H), 7.880–7.903 (m, 2H). ^{13}C NMR (DMSO-d_6) δ = 53.170, 113.410, 113.860, 114.077, 114.738, 114.945, 116.837, 122.833, 122.858, 122.983, 125.119, 127.450, 128.846, 130.430, 131.105, 145.427, 147.557, 149.204, 160.954, 163.388. ESI-MS: *m/z* = 294.671 [M+1].
1-(4-Ethoxyphenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one ***4g***: mp 216–218, IR (ν_{Max}): 812, 921, 1178, 1223, 1400, 1513, 1722, 2977, 3128, 3240. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.363 (t, *J* = 7.2 Hz, 3H), 3.926 (q, *J* = 7.2 Hz, 2H), 6.025 (s, 1H), 6.644 (s, 1H), 6.780–6.802 (m, 2H), 7.146–7.175 (m, 2H), 7.257–7.853 (m, 6H). ^{13}C NMR ($CDCl_3$) δ = 14.721, 55.393, 63.438, 112.910, 115.130, 117.051, 122.955, 125.132, 127.366, 128.236, 128.742, 129.394, 130.376, 131.001, 133.862, 147.522, 150.625, 159.011. ESI-MS: *m/z* = 320.216 [M+1].
1-(4-(Trifluoromethyl)phenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one 4h: mp 234–236, IR (ν_{Max}): 814, 1068, 1120, 1325, 1516, 1727, 1760, 3151, 3234. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.154 (s, 1H), 6.798 (s, 1H), 7.343–7.912 (m, 10H). ^{13}C NMR ($CDCl_3$) δ = 55.279, 111.717, 117.043, 122.346, 122.471, 125.051, 125.439, 126.394, 126.430, 126.467, 127.458, 127.750, 128.973, 129.083, 130.663, 131.007, 131.032, 145.247, 147.717, 150.474. ESI-MS: *m/z* = 344.08 [M+1].
1-(4-(Trifluoromethoxy)phenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one 4i: mp 168–170, IR (ν_{Max}): 816, 923, 1175, 1224, 1262, 1512, 1739, 2968, 3140, 3226. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.117 (s, 1H), 6.865 (s, 1H), 7.139–7.160 (m, 2H), 7.259–7.515 (m, 6H), 7.846–7.898 (m, 2H). ^{13}C NMR ($CDCl_3$) δ = 54.945, 112.154, 117.051, 119.072, 121.656, 122.645, 125.413, 127.699, 128.608, 128.946, 129.202, 130.876, 131.074, 140.196, 147.702, 149.179, 149.192, 150.765. ESI-MS: *m/z* = 360.481 [M+1].
14-(4-Ethoxyphenyl)-14H-dibenzo[a,j]xanthenes ***5b***: mp 172–174 °C, IR (ν_{Max}): 2976, 2905, 1591, 1510, 1397, 1244, 1044, 806. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.255 (t, *J* = 6.8 Hz, 3H), 3.808 (q, *J* = 6.8 Hz, 2H), 6.418 (s, 1H), 6.645 (d, *J* = 8.8 Hz, 2H), 7.404–7.367 (m, 4H), 7.465 (d, *J* = 8.8 Hz, 2H), 7.558–7.534 (m, 2H), 7.812–7.745 (m, 4H), 8.372 (d, 2H). ^{13}C NMR ($CDCl_3$) δ = 14.643, 37.025, 63.034, 114.266, 117.479, 117.880, 122.650, 124.084, 126.609, 128.593, 128.676, 129.047, 130.987, 131.358, 137.111, 148.562, 157.167.
14-(4-Ethylphenyl)-14H-dibenzo[a,j]xanthenes ***5g***: mp 186–188 °C, IR (ν_{Max}): 2961, 2927, 1592, 1513, 1399, 1244, 961, 806. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.045 (t, *J* = 7.6 Hz, 3H), 2.411 (q, *J* = 7.6 Hz, 2H), 6.428 (s, 1H), 6.947 (d, *J* = 8.0 Hz, 2H), 7.350–7.390 (m, 4H), 7.411 (d, *J* = 8.0 Hz, 2H), 7.439–7.561 (m, 2H), 7.793–7.730 (m, 4H), 8.381 (d, 2H). ^{13}C NMR ($CDCl_3$) δ = 15.021, 28.136, 37.532, 117.468, 117.908, 122.679, 124.086, 126.622, 127.845, 128.027, 128.630, 128.671, 130.993, 131.421, 141.986, 142.216, 148.656.