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Solvent-free and room temperature visible light-induced C–H activation: CdS as a highly efficient photo-induced reusable nano-catalyst for the C–H functionalization cyclization of *t*-amines and C–C double and triple bonds†

Somayeh Firoozi, Mona Hosseini-Sarvari * and Mehdi Koohgard

Nano-sized CdS was successfully prepared, fully characterized and applied as a highly efficient reusable photocatalyst for the synthesis of pyrrolo[3,4-*c*]quinolone and pyrrolo[2,1-*a*]isoquinoline-8-carboxylate derivatives through a condensation reaction of *N*,*N*-dimethylanilines or alkyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetates with maleimides *via* a C–H activation approach under benign and eco-friendly conditions at room temperature without using any solvent and oxidant under visible light irradiation. Besides, the prepared photocatalyst has been successfully applied for the condensation reaction of *N*,*N*-dimethylanilines with alkyl but-2-ynedioates or phenyl acetylenes for the synthesis of novel 1,2-dihydroquinoline-3,4-dicarboxylate and aryl-1,2-dihydroquinoline derivatives for the first time. Using this method, all favourable products were obtained in good yields and relatively short reaction times under benign conditions with the application of visible light irradiation, a renewable energy source. The catalyst was easily recovered and reused several times without any loss of its activity.

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Introduction

It is noteworthy that C–H bonds are one of the least reactive bonds and their direct functionalization required pre-activation steps, such as halogenation and stoichiometric metalation of the starting materials. So, direct C–H bond functionalization has considerably attracted the interest of organic synthesis researchers over the past several years.[1] In particular, the direct functionalization at a C–H centre adjacent to a heteroatom (nitrogen, oxygen and/or sulfur) has been extensively studied.[2] In all cases, these synthetic routes involve a single electron transfer (SET) step and are highly restricted to the presence of both a catalyst and an oxidant. Though, in the case of some organic peroxides, coupling at the C–H centre has been achieved without any catalyst, the need for excess amounts of peroxides and the use of elevated temperatures are two crucial drawbacks that limit the practicability of these methods.[3] So, there still is a great demand for more practical and facile procedures and catalytic systems for C–H functionalization in organic synthesis.

Nowadays, synthesized molecules bearing amine based scaffolds have attracted the attention of pharmaceutical chemistry researchers because they can be applied as beneficial building blocks in pharmaceuticals and modern drug design approaches.[4] Among them, quinolones have attracted much attention because they show some important pharmaceutical activities including analgesic, antipsychotic, antibacterial, and antidepressant activities.[5]

Interestingly, pyrrolo[3,2-*c*]quinolines have been used for the treatment of Alzheimer's disease (Fig. 1 compound A)[6] and also, heterocyclic tetrahydroquinolines show potent antibacterial activity against a wide range of microorganisms (Fig. 1 compounds B–E).[7] In addition, these compounds have been frequently studied as antipsychotic, antidepressant, and analgesic agents (Fig. 1 compound F).[5]

Accordingly, introducing advanced practical pathways for the preparation of pyrrolo[3,2-*c*]quinolines will lead to the enhancement of pharmaceutical chemists' ability to synthesize structurally-diverse derivatives of these compounds. So, various non-photochemical[8–13] and photochemical[14–24] approaches have previously been reported for the synthesis of pyrrolo[3,4-*c*]quinolones (Scheme 1).

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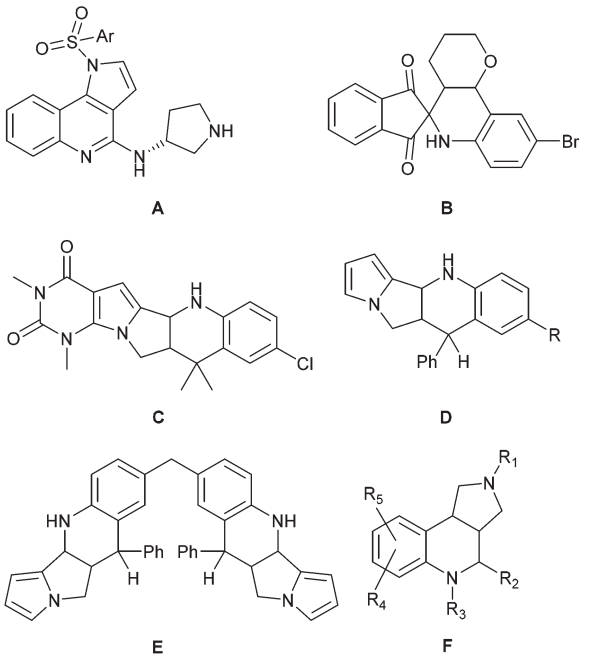
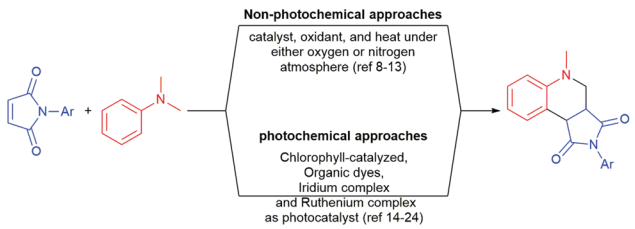


Fig. 1 The chemical structures of some biologically active pyrroloquinolones.

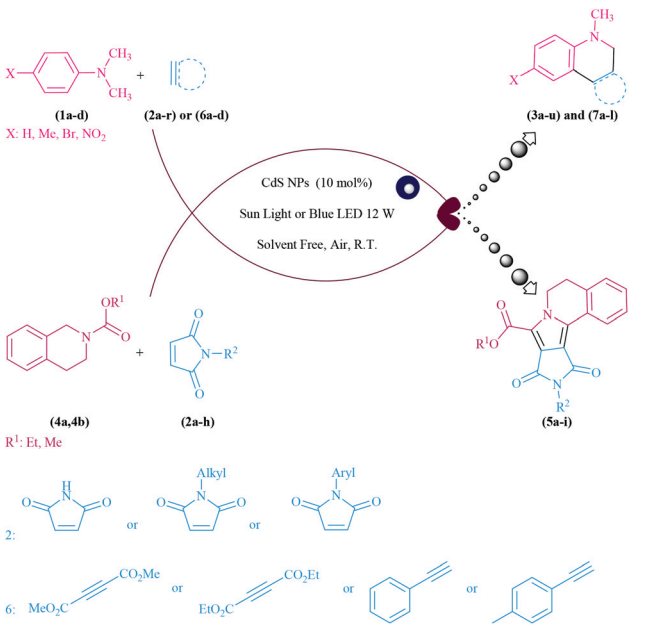


Scheme 1 The synthesis of pyrrolo[3,4-*c*]quinolone derivatives from maleimides and *N*,*N*-dimethylanilines in previous reports.

Non-photochemical approaches are restricted to the presence of a catalyst and an oxidant at the same time and high temperatures under either an oxygen or nitrogen atmosphere.[8–13] However, photochemical approaches use organic colours as photocatalysts[14–16] in which the challenges created by the homogeneity of catalyst and environmental contamination are unavoidable. Recently, chlorophyll-catalysed pathways have also been reported.[17] Furthermore, toxic and expensive metal complexes such as iridium[18] and ruthenium[19] for these kinds of C–H activations were applied.[20] So, introducing more benign and recoverable catalysts with lower toxicity to avoid environmental pollution is of great interest.

Heterogeneous photocatalytic reactions using semiconductors or other irradiated solids are noteworthy catalytic approaches. In recent decades, noticeable researches on semiconductor nanoparticles have been done.[25] Having unique mechanical and optical attributes compared with bulky counterparts, chalcogenide semiconductor nanostructures such as PbS, CdS, ZnS, PbSe, and CdSe have found wide applications.[26] Among them, CdS nanoparticles (CdS NPs) are glamorous semiconductors that are frequently used as a heterogeneous photocatalyst. In addition, they have charming applications in photo-devices and logic circuits and also, they have been notably applied in the transmutation solar energy to chemical energy and solar fuels.[27] These particles are efficient, practical, and cost effective candidates for changing solar energy to chemical energy, and are granted *a place in the sun* for supplying a reliable long-term solution with potential to address the environmental and energy issues.[28–32] It is usually supposed that CdS NPs effectively absorb solar light because of a suitable band gap and high surface area leading to more photon absorption on their surfaces, which make them useful as versatile photocatalysts in the treatment of organic wastes from water.[33–39]

In continuation of our recent research on the introduction of efficient photocatalysts for the synthesis of pyrrolo[3,4-*c*]quinolones[40] and in order to improve the simplicity and catalyst efficiency and to develop a more eco-friendly procedure, we herein report the synthesis and characterization of nano-sized CdS as a heterogeneous reusable and highly efficient photocatalyst for the synthesis of pyrrolo[3,4-*c*]quinolones (**3a–u**), pyrrolo[2,1-*a*]isoquinoline-8-carboxylates (**5a–i**), 1,2-dihydroquinoline-3,4-dicarboxylates (**7a–f**) and aryl-1,2-dihydroquinolines (**7g–k**) *via* a photo-induced C–H activation approach through the reaction between *N*,*N*-dimethylanilines (**1a–d**) or alkyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetates (**4a,4b**) with



Scheme 2 The photo-induced C–H functionalization for the synthesis of pyrrolo[3,4-*c*]quinolones, pyrrolo[2,1-*a*]isoquinoline-8-carboxylates, 1,2-dihydroquinoline-3,4-dicarboxylates and aryl-1,2-dihydroquinolines in the presence of CdS NPs as a highly efficient heterogeneous reusable photocatalyst.

maleimide, *N*-aryl and *N*-alkyl maleimides (**2a–r**) or a condensation reaction between *N*,*N*-dimethylanilines (**1a–c**) and alkyl but-2-ynedioates (**6a**, **6b**) and phenyl acetylenes (**6c**, **6d**) at room temperature under irradiation with sunlight or a blue LED lamp without the use of any solvent and oxidant (Scheme 2). It is worth mentioning that, nevertheless, there is no report on the condensation of *N*,*N*-dimethylanilines and triple bonds *via* a C–H activation approach. This strategy is attractive and novel for the synthesis of 1,2-dihydroquinoline-3,4-dicarboxylates and aryl-1,2-dihydroquinolines as new categories of quinolines. Moreover, according to a literature survey there is no report based on using solvent-free conditions for the synthesis of organic compounds in the presence of photocatalysts as visible light-induced catalysts.

Experimental

All required chemicals were obtained from Fluka and Merck companies and were used without any extra purification. A FT-IR spectrometer model Shimadzu FT-IR 8300 was applied to FT-IR measurement using KBr pellets. The X-ray diffraction (XRD) of all samples was performed using a Bruker AXS D8-advance X-ray diffractometer using CuKα radiation (λ = 1.54178 Å). The morphology of catalyst was determined using Leica Imaging Systems, Cambridge, England model s360, version V03.03. Scanning electron microscopy (SEM) was performed using a HITACHI S-4160. A Bruker advanced DPX-250 spectrometer was applied to obtain NMR spectra in $CDCl_3$ operating for ^{13}C at 62.9 MHz and for ^{1}H at 250 MHz. The product yield was measured using a GC model Shimadzu GC 14B.

General procedure for the synthesis of CdS NPs

In a typical procedure, in a 500 mL round bottom flask, *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide (CTAB) (0.4 g) and sodium sulfide hexahydrate ($Na_2S{\cdot}6H_2O$) (0.93 g, 5 mmol) were dissolved in deionized water (300 mL). Then, cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$) (100 mL, 0.045 M) was added dropwise and the obtained solution was stirred for 1 h at room temperature. After this time, the resulting mixture was stirred at reflux temperature for 36 h. Finally, the resultant yellow precipitates were collected by centrifugation at 4000 rpm for 5 min, washed with deionized water and ethanol (100 mL, 3 times) and dried at 50 °C for 24 h.

General procedure for the synthesis of pyrrolo[3,4-*c*] quinolones and pyrrolo[2,1-*a*]isoquinoline-8-carboxylates

An open test tube equipped with a magnetic stir bar was charged with CdS NPs (0.01 mmol, 0.014 g). Then, maleimide (1.0 mmol) and *N*,*N*-dimethylaniline or alkyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate derivatives (1.5 mmol) were added. The open test tube was placed under sunlight or a blue LED and the mixture was stirred at room temperature for 12–36 h under solvent-free conditions. The reaction improvement was checked by thin layer chromatography (TLC). After the completion of the reaction, ethanol (2 ml) was added to the reaction mixture and insoluble CdS NPs were completely separated by centrifugation, washed with ethanol (1 mL, 3 times), dried under reduced pressure and reused. In order to obtain pure products, the solvent (ethanol) was evaporated under reduced pressure and the obtained crude products were purified by column chromatography to afford pure pyrrolo[3,4-*c*]quinolone products. When both thereactants are solid, for instance in the synthesis of **3q**, acetonitrile (3 mL) as a solvent was used instead of solvent-free conditions.

General procedure for the synthesis of 1,2-dihydroquinoline-3,4-dicarboxylates and aryl-1,2-dihydroquinolines

An open test tube equipped with a magnetic stir bar was charged with CdS NPs (0.01 mmol, 0.014 g). Then, *N*,*N*-dimethylaniline (1.5 mmol) and alkyl but-2-ynedioate or phenyl acetylene (1.0 mmol) derivatives were added. The open test tube was placed under sunlight or a blue LED and the mixture was stirred at room temperature for 24–36 h under solvent-free conditions. The reaction improvement was checked by thin layer chromatography (TLC). After the completion of the reaction, ethanol (2 ml) was added to the reaction mixture and insoluble CdS NPs were completely separated by centrifugation, washed with ethanol (1 mL, 3 times), dried under reduced pressure and reused. In order to obtain pure products, the solvent (ethanol) was evaporated under reduced pressure and the obtained raw products were purified by column chromatography to afford pure 1,2-dihydroquinoline-3,4-dicarboxylate products.

Results and discussion

At first, the CdS NPs were synthesized using a facile thermal approach and were fully characterized by XRD, FT-IR, SEM, and TEM as well as solid UV analysis. The crystalline structure of CdS NPs was investigated by XRD. The obtained XRD patterns are shown in Fig. 2 and compared with the published data (JCPDS 10-454). Reflections are observed at 2θ = 26.3, 30.5, 44.7 and 51.9 belonging to the (111), (200), (220) and (311) crystallographic planes, respectively. The average crystal-

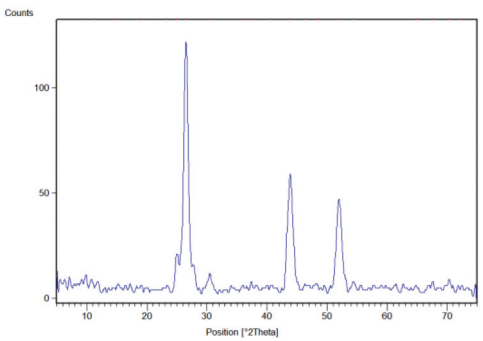


Fig. 2 The XRD patterns of freshly synthesized CdS NPs.

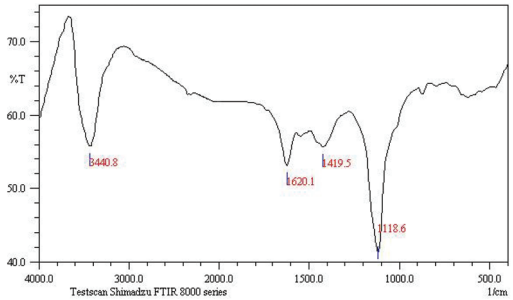


Fig. 3 FT-IR spectra of CdS.

line nanoparticle size of CdS was calculated using the Scherrer equation and is equal to 7 nm (Fig. 2).

The FT-IR spectra of CdS NPs show absorption in regions 3440.8, 1620.1, 1419.5, and 1118.6 cm^{-1} (Fig. 3).

The SEM image of freshly synthesized CdS NPs is shown in Fig. 4. The nanoparticles of CdS with a diameter around 20–30 nm can be observed. These particles have a spherical morphology.

The TEM image of the synthesized CdS NPs is shown in Fig. 5. Spherical particles could be clearly seen for the CdS NPs, and the range of size is approximately between 6 and 8 nm measuring from TEM which confirms the data from XRD analysis.

To determine the optical properties of the synthesized CdS NPs, UV-visible absorption measurements were accomplished and the obtained graph is shown in Fig. 5. Clearly, the CdS NPs could be excited in the presence of visible light. The CdS NPs show the photo-absorption from UV light to visible light, and the wavelength of the absorption edge is about 400–480 nm, which could explain its visible-light induced photo-catalytic activity (Fig. 6).

Fig. 7 shows the photoluminescence spectra of the synthesized CdS nanoparticles at an excitation wavelength of 420 nm. It is seen that maximum emissions appear at a wavelength of 624 nm with the excitation wavelength at 420 nm.

After successfully preparing CdS NPs, their application as a heterogeneous photocatalyst was pursued in the synthesis of pyrrolo[3,4-*c*]quinolone derivatives. The condensation reaction between *N*-phenylmaleimide (**2a**) and *N*,*N*-dimethylaniline (**1a**) was chosen as a model reaction for the synthesis of 5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (**3a**). Various reaction conditions were optimized and the best results were obtained with 10 mol% of CdS NPs without any solvent under sunlight or blue light irradiation and air at room temperature. According to Tables 1 and 2 various solvents, catalyst quantities, different wavelengths of irradiation produced from distinct resources and different atmospheres were tested. A batch of solvents including H_2O,

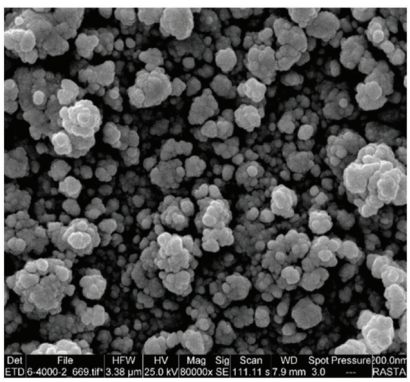


Fig. 4 SEM images of CdS.

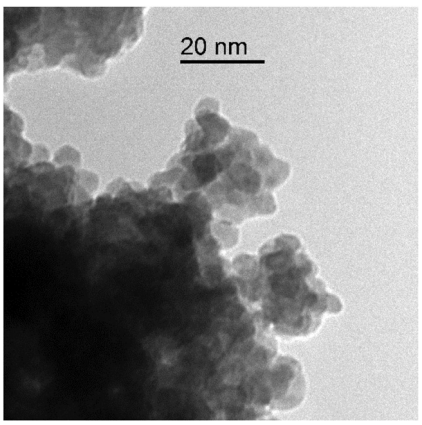


Fig. 5 TEM images of CdS.

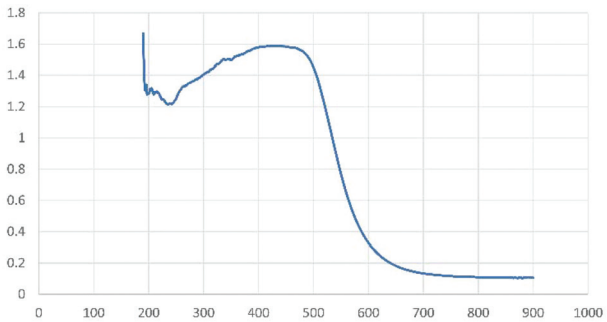


Fig. 6 The UV-visible absorption graph of freshly synthesized CdS NPs.

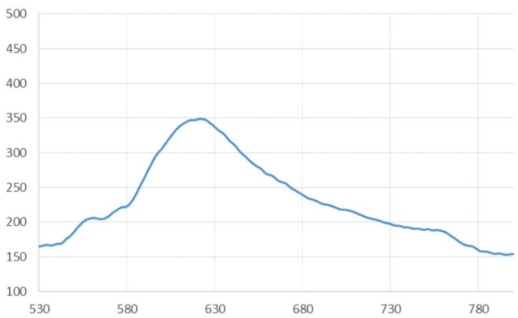
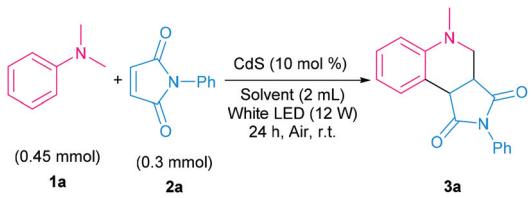


Fig. 7 The photoluminescence spectra of freshly synthesized CdS NPs.

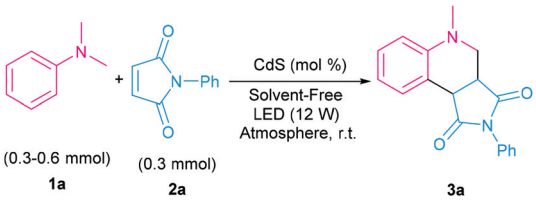
Table 1 The effect of various solvents and different quantities of *N*,*N*-dimethylaniline as a precursor in the synthesis of 5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione



Entry	Solvent	Yield (%)
1	H_2O	50[a]
2	EtOH	84[a]
3	CH_3CN	91[a]
4	EtOAc	67[a]
5	Acetone	74[a]
6	CH_2Cl_2	18[a]
7	$CHCl_3$	23[a]
8	THF	47[a]
9	DMSO	89[a]
10	DMF	77[a]
11	Solvent-free	88[b]
12	Solvent-free	91[c]
13	Solvent-free	95[a]
14	Solvent-free	95[d]

The condensation reaction of *N*,*N*-dimethylaniline (1–2 eq.), *N*-phenylmaleimide (0.3 mmol), CdS as nano photocatalyst (10 mol%) and solvent (2 mL) under irradiation with a white LED 12 W lamp for 24 h at room temperature in air. [a] *N*,*N*-Dimethylaniline 1.5 eq. (0.45 mmol). [b] *N*,*N*-Dimethylaniline 1 eq. (0.3 mmol). [c] *N*,*N*-Dimethylaniline 1.2 eq. (0.36 mmol). [d] *N*,*N*-Dimethylaniline 2 eq. (0.6 mmol).

Table 2 The optimization of the model reaction based on diverse amounts of photocatalyst, wavelengths of light, and atmosphere (gas)



Entry	CdS amount (mol %)	Light	Atmosphere	Yield (%)
1	Catalyst free	White	Air	—
2	5	White	Air	75
3	10	White	Air	95[a]
4	15	White	Air	95
5	20	White	Air	96
6	25	White	Air	95
7	10	Dark	Air	—
8	10	Blue	Air	96[b]
9	10	Green	Air	33
10	10	Red	Air	24
11	10	White	O_2	96[a,c]
12	10	Blue	O_2	95[b,c]
13	10	White	Ar	—[d]
14	10	Blue	Ar	—[d]
15	10	Sun	Air	96[e]

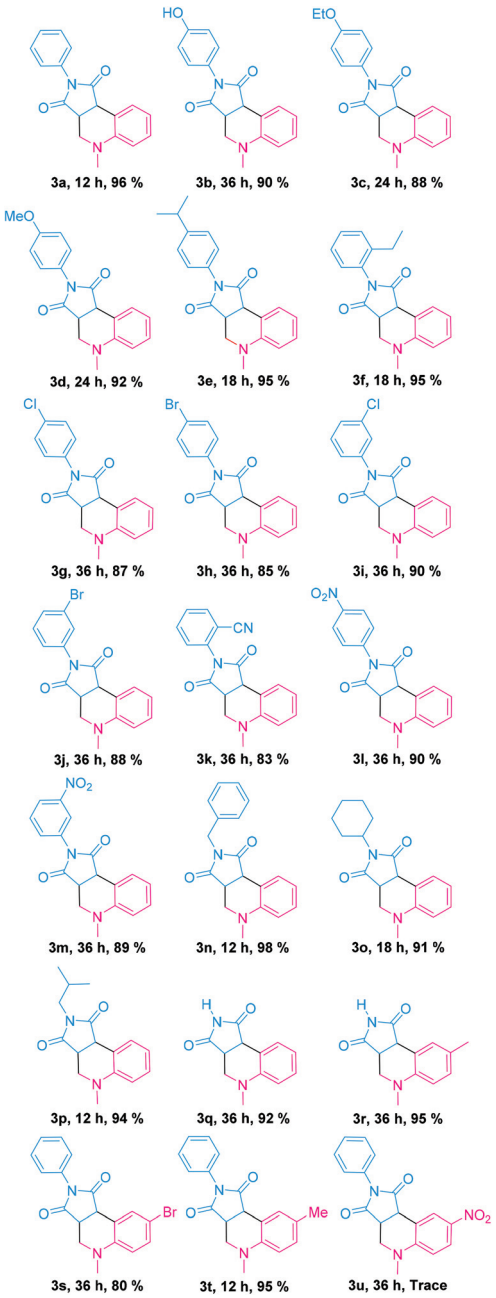
The condensation reaction of *N*-phenylmaleimide (0.3 mmol), *N*,*N*-dimethylaniline (0.45 mmol) and different amounts of CdS as a nano photocatalyst (mol %) under different LED 12 W lamps and solvent-free conditions for 24 h at room temperature in air. [a] The completion time of reaction is 18 h. [b] The completion time of reaction is 12 h. [c] Oxygen balloon. [d] Argon balloon. [e] The completion time of reaction is 8 h.

EtOH, CH_3CN, EtOAc, acetone, $CHCl_3$, CH_2Cl_2, THF, DMF and DMSO in the presence of CdS NPs and under white light and solvent-free conditions were tested. As can be seen in Table 1, the best results have been obtained under solvent-free conditions.

After finding the solvent-free conditions, diverse amounts of catalyst were tested. The efficiency of reaction in the presence of less than 10 mol% of CdS was negligible (Table 2, entry 2) and amounts more than 10 mol% of CdS showed no increase in the yield of desired product or reduction in the reaction time (Table 2, entries 4–6). The reaction was not proceeded without CdS NPs as a photocatalyst (Table 2, entry 1). Effects of light irradiation and different atmospheres were also studied and it was observed that the reaction did not progress in the absence of light (Table 2, entry 7). This phenomenon shows that CdS photocatalyst gets excited by light radiation. The yield of the reaction was decreased and the reaction time was increased with the red and green lights, while the same yield and reaction time was found for white (Table 2, entries 3 and 11) and blue (Table 2, entries 8 and 12) lights. However, the reaction time reduced from 18 h to 12 h with blue light irradiation. On the other hand, the reaction time decreased to 8 h with sunlight irradiation (Table 2, entry 15). The same data were obtained for the oxygen and air atmosphere but there was no noticeable result under an argon atmosphere. So, the air atmosphere was selected as the best condition.

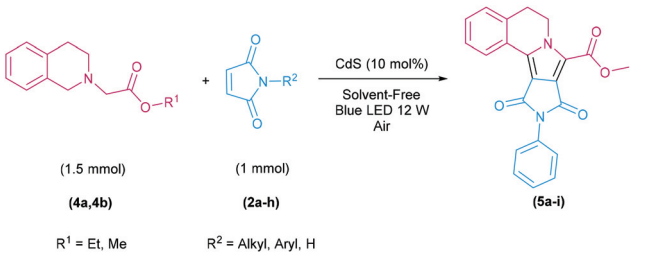
Next, in order to find the generality, different pyrrolo[3,4-*c*]quinolone derivatives were synthesized under the optimized conditions (Table 3). Both electron releasing groups (ERG) (Table 3, products **3b–j**) and electron withdrawing groups (EWG) (Table 3, products **3k–m**) at *ortho*, *meta* and *para* positions on the aromatic ring in *N*-aryl maleimides as the precursor showed no impressive distinction in reaction yields. It is supposed that due to being away from the reaction site, aromatic rings have no effect on the reaction outcome. *N*-Aryl maleimides and also *N*-alkyl maleimides (Table 3, products **3n–p**) yielded the corresponding products in excellent yields. There are somehow different results for *N*,*N*-dimethylaniline compared with *N*-aryl maleimide. In this case, electron donating and electron withdrawing groups such as Br, CH_3 and NO_2, have different effects on the reaction. An increment in the yield and a reduction in the reaction time were observed with electron donating groups at aromatic ring of amines. It may come from the stability of the cation radical related to the presence of electron donating groups that can accelerate the radical creation process (Table 3, products **3r**, **3s**, **3t**). These substitutions can also increase the electron releasing capability of the amines. With NO_2 substitution on *N*,*N*-di-methylaniline, the reaction was not progressed (Table 3, product **3u**). It may be due to the high electron withdrawing effect of NO_2 substituent causes an inhibition of amine to place its electrons in the hole and evanescence cation radicals.

Table 3 The synthesis of pyrrolo[3,4-*c*]quinolone derivatives



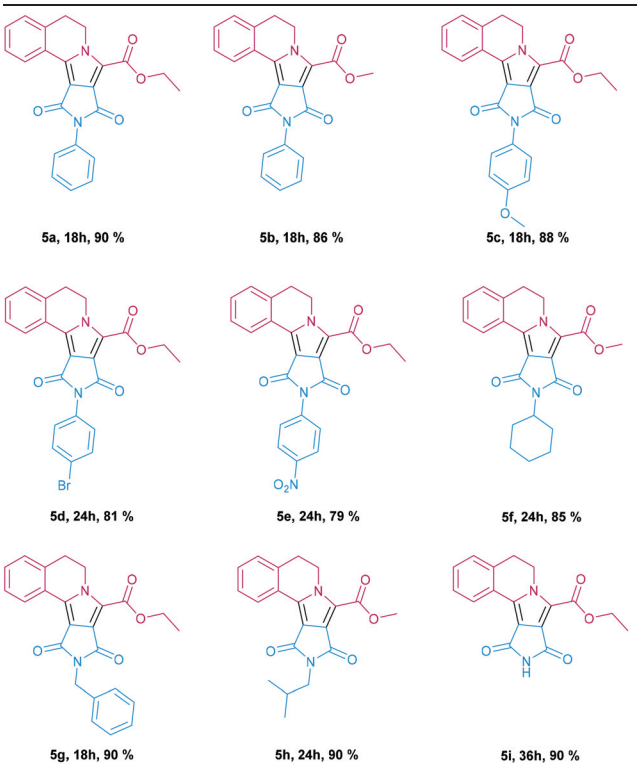
Reaction conditions: *N*,*N*-Dimethylaniline (1.5 mmol), maleimide derivatives (1.0 mmol), and CdS nanoparticles (10 mol%) under irradiation with a blue LED 12 W lamp and solvent-free conditions at room temperature in air.

Furthermore, the scope of this reaction was explored with an oxidation-[3 + 2] cycloaddition-aromatization reaction for the synthesis of aryl-1,2-dihydroquinolines. In order to appraise this proposed implication, initially a reaction between ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate (**4a**) and *N*-phenylmaleimide (**2a**) in the presence of CdS as a photocatalyst was selected as a model reaction and various reaction conditions were optimized (see the ESI† for details). Based on the obtained results, the best reaction conditions for the synthesis of pyrrolo[2,1-*a*]isoquinoline-8-carboxylate are highly similar to the optimized reaction conditions for the synthesis of pyrrolo[3,4-*c*]quinolones. The best reaction conditions were obtained with CdS (10 mol%) as a photocatalyst under sunlight or blue LED lamp irradiation without any solvent and oxidant at room temperature and under air. The generality of this reaction was established using various alkyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetates and maleimides and the corresponding products were yielded in excellent amounts (Scheme 3 and Table 4).



Scheme 3 The photo-induced C–H functionalization for the synthesis of pyrrolo[2,1-*a*]isoquinoline-8-carboxylates in the presence of CdS NPs.

Table 4 The synthesis of pyrrolo[2,1-*a*]isoquinoline-8-carboxylate derivatives

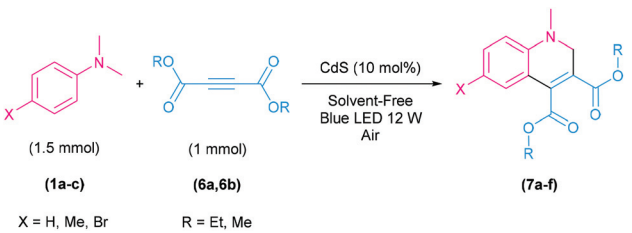


Reaction conditions: Alkyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetates (1.5 mmol), maleimide derivatives (1.0 mmol), and CdS nanoparticles (10 mol%) under irradiation with a blue LED 12 W lamp and solvent-free conditions at room temperature in air.

These interesting results encouraged us to establish the condensation of *N*,*N*-dimethylanilines and the triple C–C bond as an attractive and new strategy for the synthesis of novel aryl-1,2-dihydroquinolines. For this purpose, the optimized reaction conditions for the synthesis of pyrrolo[3,4-*c*]quinolones and pyrrolo[2,1-*a*]isoquinoline-8-carboxylates have been applied and some new 1,2-dihydroquinoline-3,4-dicarboxylate derivatives (**7a–f**) were successfully synthesized with the reaction of *N*,*N*-dimethylanilines (**1a–c**) and alkyl but-2-ynedioates (**6a,b**) (Scheme 4 and Table 5).

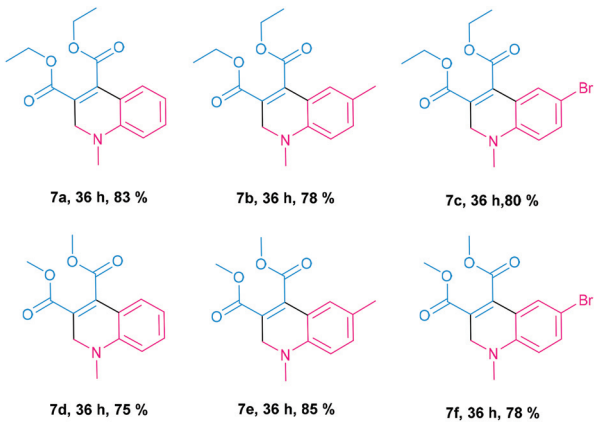
Phenyl acetylenes (**6c**, **6d**) have been applied instead of alkyl but-2-ynedioates (**6a**, **6b**) and all desired products (**7g–l**) were successfully obtained in the presence of CdS as a photocatalyst by irradiating with sunlight or a blue LED lamp without any solvent at room temperature and under air for the first time (Scheme 5) and the obtained results are summarized in Table 6.

The recyclability of CdS catalyst as a heterogeneous nano-photocatalyst showed an acceptable photo-catalytic activity of CdS, and it can be used repeatedly with no significant reduction in the reaction yield (Fig. 8).

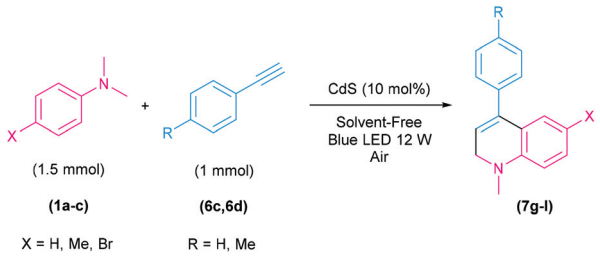


Scheme 4 The photo-induced C–H functionalization for the synthesis of 1,2-dihydroquinoline-3,4-dicarboxylates in the presence of CdS NPs.

Table 5 The synthesis of 1,2-dihydroquinoline-3,4-dicarboxylate derivatives

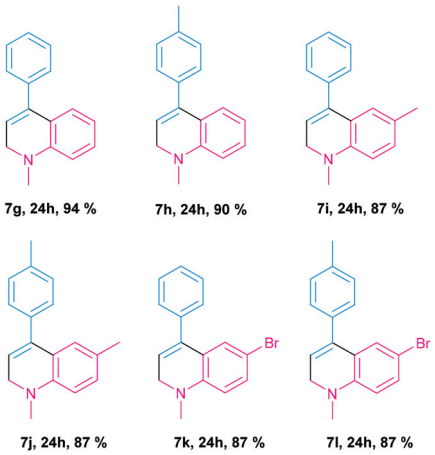


Reaction conditions: *N*,*N*-Dimethylaniline (1.5 mmol), but-2-ynedioate derivatives (1.0 mmol), and CdS NPs (10 mol%) under irradiation with a blue LED 12 W lamp and solvent-free conditions at room temperature in air.



Scheme 5 The photo-induced C–H functionalization for the synthesis of aryl-1,2-dihydroquinolines in the presence of CdS NPs.

Table 6 The synthesis of aryl-1,2-dihydroquinoline derivatives



Reaction conditions: *N*,*N*-Dimethylaniline (1.5 mmol), phenyl acetylene derivatives (1.0 mmol), and CdS NPs (10 mol%) under irradiation with a blue LED 12 W lamp and solvent-free conditions at room temperature in air.

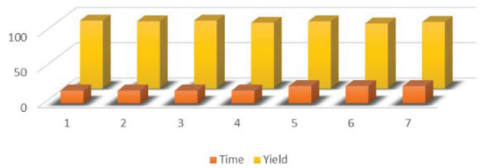
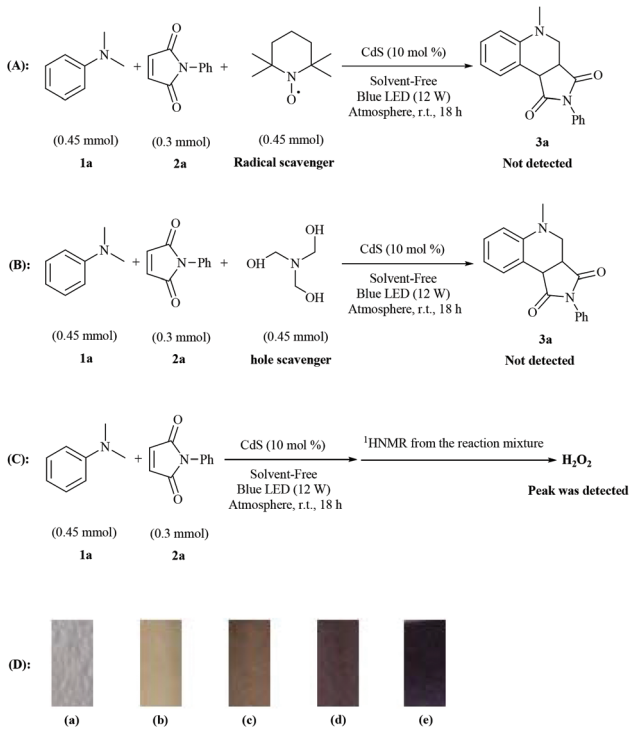
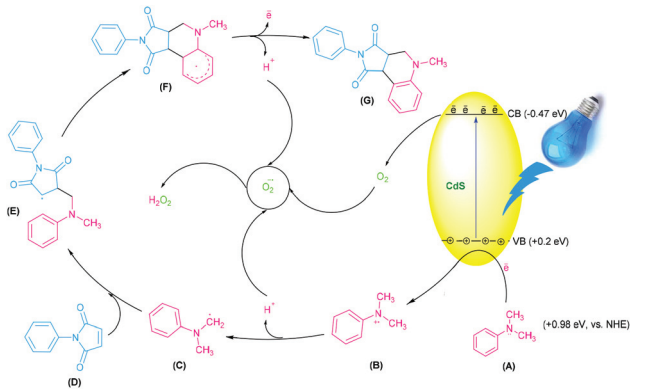


Fig. 8 The reusability of the catalyst for a series of seven consecutive runs of the reaction of *N*-phenylmaleimide (0.3 mmol), *N*,*N*-dimethylaniline (0.45 mmol) and CdS as a nano-photocatalyst (10 mol%) under LED 12 W lamp irradiation and solvent-free conditions at room temperature.

To propose a feasible mechanism for the synthesis of the title compounds in the presence of CdS NPs some additional studies were performed. Therefore, for the synthesis of 5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (**3a**), according to the optimized conditions, the reaction between *N*,*N*-dimethylaniline and *N*-phenylmaleimide was carried out in the presence of radical and hole scavengers to show the radical pathway of the reaction (Scheme 6).



Scheme 6 The mechanism studies: the condensation reaction of *N*-phenylmaleimide (0.3 mmol) and *N*,*N*-dimethylaniline (0.45 mmol) in the presence of CdS NPs (10 mol%) under irradiation of a blue LED 12 W lamp and solvent-free conditions for 24 h at room temperature under air. (A) In the presence of TEMPO (0.45 mmol) as a radical scavenger. (B) In the presence of triethanolamine (0.45 mmol) as a filler of holes. (C) ^{1}H NMR from the reaction mixture (solubilized in $CDCl_3$ as a NMR solvent) and the detected H_2O_2 peak. (D) The starch paper study of the presence of H_2O_2 during the expedition of the reaction: [a] the starch test paper, [b] the starch test paper after being in the reaction mixture (solubilized in EtOH (2 mL)), [c] the starch test paper after being in a mixture of H_2O_2 (30% w/w, 0.1 mL) and EtOH (2 mL), [d] the starch test paper after being in a mixture of H_2O_2 (30% w/w, 0.3 mL) and EtOH (2 mL), [e] the starch test paper after being in a mixture of H_2O_2 (30% w/w, 1 mL) and EtOH (2 mL).



Scheme 7 The proposed mechanism for the synthesis of 5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (**3a**) *via* a C–H activation approach in the presence of CdS NPs as a heterogeneous photocatalyst.

As shown in Scheme 6, in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical scavenger (Scheme 6A) and triethanolamine (TEA) as a filler of the holes (Scheme 6B) the target molecule (**3a**) was not formed. These results confirmed that the reaction is likely to involve a radical process. On the other hand, to confirm the formation of H_2O_2 during the reaction, the ^{1}H NMR spectrum was obtained from the reaction mixture (Scheme 6C).

The H_2O_2 representative peak was detected in the ^{1}H NMR spectrum at δ = 9.63 ppm (in $CDCl_3$ as a NMR solvent). In addition, starch test paper was applied to determine the presence of peroxides (H_2O_2) during the reaction (Scheme 6D). The color of the starch test paper changed from white to pale yellow that confirms the presence of H_2O_2 in the reaction mixture.

Our proposed mechanism is illustrated in Scheme 7. Firstly, electrons will be excited from the valence band to the conduction band by the incidence of photons to CdS NPs. Therefore, a hole is created in the valence band and an electron in the conduction band is absorbed by oxygen. Then, a *N*,*N*-dimethylaniline radical cation (B) can be created by electron transfer from *N*,*N*-dimethylaniline (A) to the holes. Then, the radical (C) forms *via* losing a proton from the *N*,*N*-dimethylaniline radical cation (B). In the next step, this radical (C) attacks the maleimide double bond (D) and the intermediate E will be produced. The attack on the π bond of the benzene ring leads to intra-cyclization (F) and finally, the corresponding product (G) can be obtained by losing an electron and proton to set up aromaticity.

Finally, the existence of cadmium in the final products was checked with the ICP-OES method. For this purpose, the model reaction of *N*,*N*-dimethylaniline (**1a**) and *N*-phenylmaleimide (**2a**) was conducted under the optimized conditions and after the purification of the final products (**3a**), the isolated products were dissolved in HNO_3. The ICP-OES analysis result showed that Cd is not present in the analysed sample.

Conclusion

In summary, nano-sized CdS was prepared as a heterogeneous photocatalyst. The actual structure of the prepared photocatalyst was investigated with XRD, IR, SEM, TEM and solid UV-visible spectroscopy techniques. The synthesized catalyst was then successfully applied for the synthesis of a wide spectrum of quinolone derivatives to enhance their ecofriendly aspects. In this method, *N*,*N*-dimethylanilines and/or alkyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetates were successfully condensed with maleimides and triple C–C bonds *via* a C–H activation approach in the presence of CdS NPs as a photo-induced catalyst under visible light irradiation at room temperature without any solvent. The method takes advantage of the visible-light photoredox catalytic cycle to generate pyrrolo[3,4-*c*]quinolones and novel 1,2-dihydroquinoline-3,4-dicarboxyl-

ates under very mild reaction conditions (room temperature, visible-light irradiation under air) with physical and chemical stability, recoverability and reusability of applied photocatalyst, high yields of products, avoidance of the toxic waste production, ease of product isolation, application of a highly efficient and renewable energy source, and finally good agreement with some aspects of green chemistry. To the best of our knowledge, this is the first report on the synthesis of 1,2-dihydroquinoline-3,4-dicarboxylate and condensation of *N*,*N*-dimethylaniline and phenyl acetylenes for the synthesis of aryl-1,2-dihydroquinolines through a photo-induced C–H activation approach.

Conflicts of interest

There are no conflicts to declare.

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