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# Graphitic Carbon Nitride as Photocatalyst for the Direct Formylation of Anilines

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Dedicated to Professor Maurizio Prato on the occasion of his 70th birthday.

The use of graphitic carbon nitride (g-CN) for the photocatalytic radical formylation of anilines, which represents a more sustainable and attractive alternative to the currently used approaches, is reported herein. Our operationally simple method occurs under mild conditions, employing air as an oxidant. In particular, the chemistry is driven by the ability of g-CN to reach an electronically excited state upon visible-light

absorption, which has a suitable potential energy to trigger the formation of reactive  $\alpha$ -amino radical species from anilines. Mechanistic investigations also proved the key role of the g-CN to form reactive superoxide radicals from O<sub>2</sub> via single electron transfer. Importantly, this photocatalytic transformation provides a variety of functionalized formamides (15 examples, up to 89% yield).

## Introduction

The direct formylation of amino groups to yield formamide derivatives is a chemical transformation of fundamental importance. Formamides play crucial roles in many different research fields, including synthetic, industrial and natural product chemistry.<sup>[1,2]</sup> For instance, formamides are widely employed in organ preservation and are also used as synthetic building blocks for the production of fungicides and antibiotics.<sup>[3–5]</sup> Moreover, formylation reactions are routinely

performed in biochemistry for stabilizing ribonucleic acid (RNA) in gel electrophoresis, but they can also be found in the methanogenesis cycle and in prebiotic chemistry.<sup>[6–9]</sup> Their use in organic chemistry is also well documented, where they can act as (i) solvents, (ii) Lewis bases, (iii) reagents in the Leuckart and Vilsmeier–Haack reactions, thus having a significant role in the synthesis of formamidines and isocyanates.<sup>[10–17]</sup>

Given the ubiquity and extensive use of formamides, during the years, a large number of approaches have been reported for their synthesis. Classical methods usually require harsh reaction conditions, involving for example high reaction temperature, stoichiometric amounts of metals, and potentially explosive oxidants.<sup>[18–22]</sup> More recently, catalysis has emerged as a powerful tool to convert amines into formamide derivatives under mild operative conditions. For this purpose, Lewis acids, transition metal complexes and organic compounds have been reported as effective catalytic systems for this chemical reaction (Figure 1a).<sup>[23–29]</sup> However, these catalytic methods often require the use of external carbon sources (e.g. chloral, formaldehyde, or CO) which exhibit some toxicity for ecosystems and human beings.

A modern strategy for the direct formylation of amines, in particular *N*-alkyl substituted amines, is based on the oxidation of the nearest C(sp<sup>3</sup>)–H moiety (namely the  $\alpha$ -carbon) to the amino group (Figure 1b). Such an oxidative process often relies on stoichiometric quantities of metal oxidants.<sup>[30]</sup> Besides, many catalytic approaches, that employ molecular oxygen or H<sub>2</sub>O<sub>2</sub> as oxidants, have been developed. However, most of these strategies employ metal-based (Fe, Pd, Cu) homogeneous catalysts (Figure 1b), which are in some cases of high costs, require multiple synthetic steps for their ligands and are difficult to adapt to industrial applications.<sup>[31–36]</sup> In addition, recurring to pure oxygen or other strong oxidants (e.g., H<sub>2</sub>O<sub>2</sub>) should be discouraged in favor of air, which is a natural, easily available, economic and non-hazardous source of oxygen.<sup>[37]</sup>

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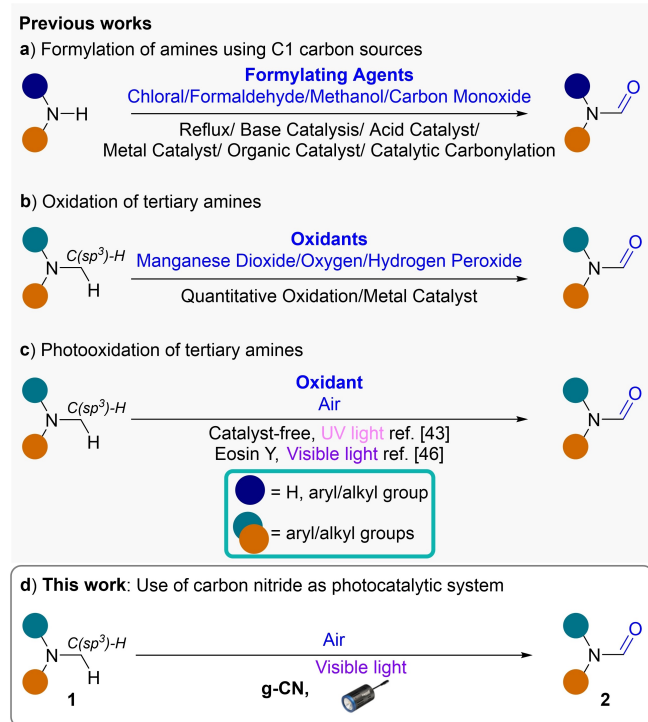
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**Figure 1.** Synthetic approaches for the formylation of amines: a) use of external formylating agents; b) direct oxidation of tertiary amines; c) photochemical oxidation of tertiary amines under UV light or using Eosin Y as homogeneous photocatalyst; d) synthetic protocol within this work, using g-CN as heterogeneous visible-light photocatalyst and air as oxidant.

Current industrial guidelines, that recommend the adoption of sustainable synthetic schemes in chemical production, have led to a widespread and topical interest in discovering novel photoinduced processes for the oxidation of amines.<sup>[38]</sup> Indeed, the exploitation of sunlight as source of energy to trigger organic transformations is today one of the most popular approaches in synthetic chemistry.<sup>[39–42]</sup> In this direction, in 2017, Yang et al. described a catalyst-free light induced methodology for the direct oxidation of *N*-alkyl-*N*-methylanilines with air (Figure 1c). Nevertheless, this method requires the exploitation of a high-energy ultraviolet (UV) light source (380–385 nm), which may be harmful to humans and represents only a small fraction of light emitted by the Sun.<sup>[43]</sup> In the same year, a visible-light approach for the direct formylation of a specific class of anilines, namely *N*-alkyl-*N*-(prop-2-yn-1-yl)anilines was developed. However, this photochemical method produces CO or CO<sub>2</sub> gases as undesired by-products.<sup>[44]</sup> In 2021, Zhou and co-workers have shown that violet light may be used to promote the cleavage of C(sp<sup>3</sup>)–C(sp<sup>3</sup>) bond, yielding a wide variety of aromatic formamides.<sup>[45]</sup>

Recently, Ghosh et al. reported a new method for the photo-driven oxidation of amines using Eosin Y as the active chromophore (Figure 1c).<sup>[46]</sup> However, homogeneous photocatalysts generally imply high catalyst loadings and are hard to recover and recycle. Thus, the general feeling is that the advance within this field hinges on the development of novel

metal-free heterogeneous photocatalytic systems capable of working in air under visible light irradiation.

Over the last decade, the family of carbon nitride (CN) materials, whose most frequently investigated form is the graphitic one (g-CN), has emerged as an appealing class of semiconductors, since they can effectively absorb visible light, owed to a bandgap approximately between 2.5 eV and 2.8 eV.<sup>[47–49]</sup> In addition, this photo-active material is composed of only abundant elements such as carbon, nitrogen, and small amounts of oxygen, and it can be prepared and tuned through facile and cost-effective methodologies.<sup>[50–52]</sup> Moreover, the successful applicability of CN to drive different classes of organic reactions<sup>[48,53–56]</sup> and energy-related processes (i.e. H<sub>2</sub> evolution)<sup>[52,57–60]</sup> demonstrates their high versatility.

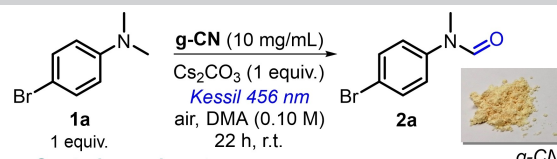
Hence, we developed a novel CN-based photocatalytic approach for the conversion of *N,N*-dialkyl anilines **1** into the corresponding *N*-formylated compounds **2** (Figure 1d). Noteworthy, the experiments were performed in air under visible-light irradiation, thus complying with modern sustainability philosophy for chemical synthesis. Finally, the heterogeneous nature of g-CN facilitates the recovery and reuse of the photocatalysts, overcoming the classical limitations of homogeneous catalysis, and therefore being of higher appeal for future translation to industrial scale.

## Results and Discussion

We tested the feasibility of our design plan by focusing on the formylation reaction of 4-bromo-*N,N*-dimethylaniline **1a** in air (Table 1). Specifically, a preliminary experiment was conducted in *N,N*-dimethylacetamide (DMA) using Cs<sub>2</sub>CO<sub>3</sub> as base, g-CN as photocatalyst and under irradiation by a Kessil lamp at 456 nm (entry 1, Table 1). At such a wavelength, photons are capable of promoting electrons from the valence band (VB) to the conduction band (CB) of the g-CN (see Supporting Information, Figure S1). Interestingly, under these operative conditions, the desired product **2a** was formed in moderate chemical yield (48%) with good selectivity (73%).

Additionally, a series of control experiments was carried out to elucidate the nature of this chemical process (entries 2–5, Table 1). The formation of product **2a** was not observed either in the absence of g-CN or in the dark (entries 2–3, Table 1), confirming that the reaction is driven by the photocatalytic activity of g-CN. Similarly, a complete inhibition of the reactivity was observed in the absence of the base (Cs<sub>2</sub>CO<sub>3</sub>) as well as when performing the reaction under argon atmosphere (entries 4–5, Table 1). In addition, both the yield and selectivity of the photocatalytic process were monitored over time (entries 6–8, Table 1). First, we observed that the yield of **2a** and the selectivity of the reaction progressively increased over time up to 22 h, but these values dropped when performing the experiment over a prolonged reaction time (such as 30 h).

After these preliminary insights on the proposed photocatalytic reaction, we tuned the settings to enhance the reactivity (Table 2).

**Table 1.** Preliminary studies and control experiments on the photocatalytic formylation reaction of **1a**.


Entry <sup>a</sup>	Variation	Yield% <sup>b</sup>	Selectivity% <sup>b</sup>
1	none	48%	73%
2	no g-CN	0%	0%
3	in the dark	0%	0%
4	no Cs <sub>2</sub> CO <sub>3</sub>	0%	0%
5	inert atmosphere <sup>c</sup>	0%	0%
6	reaction time: 4 h	18%	64%
7	reaction time: 16 h	32%	64%
8	reaction time: 30 h	36%	59%

[a] Reactions performed on a 0.1 mmol scale. [b] Yield and selectivity were determined through <sup>1</sup>H NMR analysis of the crude reaction using 1,3,5-trimethoxybenzene as internal standard. [c] Reaction vessel degassed by freeze-pump-thaw cycles (three times) and subsequently filled with argon. DMA: *N,N*-dimethylacetamide.

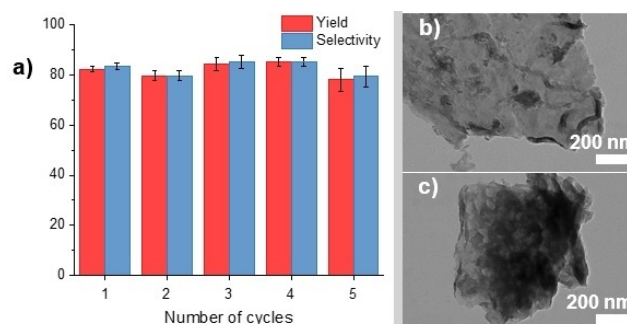
Screening of the solvents (entries 1–5, Table 2) indicated that while the use of acetonitrile (MeCN), toluene and ethyl acetate (EtOAc) resulted in poor reactivity (entries 2–4, Table 2), the reaction performed in *N,N*-dimethylformamide (DMF) provided product **2a** in good chemical yield (44%). Hence, we decided to move forward optimizing the transformation using DMF as reaction medium and examining different organic and inorganic bases (entries 6–9, Table 2), namely 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and 1,1,3,3-tetramethylguanidine (TMG). In particular, TMG turned out to be the best one for the studied reaction (entry 9, Table 2), without any significant difference due to the amount of base added (entries 9–11, Table 2). In addition, we investigated the effect of the light source on the reactivity (entries 12–14, Table 2). To this end, different irradiation wavelengths (427 nm, 440 nm and 525 nm) were employed. In agreement with what already stated, we observed that the green lamp (525 nm) did provide the final product in low chemical yield (<5%). Indeed, green photons are not sufficiently energetic to overcome semiconductor's band gap. On the other hand, the purple lamps (427 and 440 nm) resulted in the highest productivity levels (above 80% yield). Therefore, subsequent experiments were carried out with the Kessil lamp at 440 nm, since it emits less energetic photons compared to the one at 427 nm.

Noteworthy, the catalyst was found to be stable under the reaction conditions (entry 14, Table 2) and recyclable over five

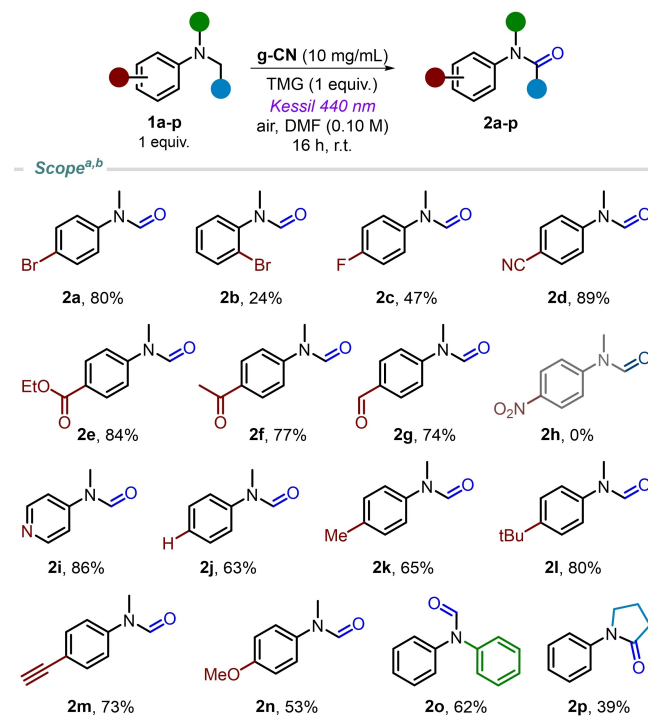
independent cycles with only little deviations from the initial efficiency and without evident structural modifications (see Figure 2 and Supporting Information, Figure S3).

Then, we evaluated the generality of the photocatalytic reaction with respect to the aniline derivatives **1a–p** (Scheme 1).

In particular, the use of 2-bromo-*N,N*-dimethylaniline (**1b**) provided the corresponding product **2b** in low chemical yield (20%), probably due to its increased steric hindrance that could hamper the oxidative reaction on the amino moiety. Interestingly, a variety of electron-withdrawing substituents at the *para*-position including fluoride, cyano, ester, ketone and aldehyde moieties (**1c–g**), were well tolerated under the reaction conditions and the desired products (**2c–g**) were

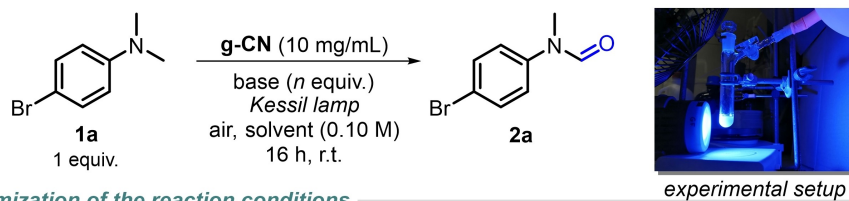


**Figure 2.** Investigation into catalyst's recyclability by means of yield and selectivity trends (a) and TEM images (20k magnification) of the g-CN before use (b) and after the 5th cycle (c).



**Scheme 1.** Scope for the photocatalytic formylation reaction. [a] Reactions performed on a 0.1 mmol scale. [b] The values here are expressed as isolated yields. DMF: *N,N*-dimethylformamide, TMG: 1,1,3,3-tetramethylguanidine.

Table 2. Optimization of the experimental conditions.



## - Optimization of the reaction conditions

Entry <sup>a</sup>	Solvent	Base (equiv.)	Kessil lamp	Yield% <sup>b</sup>	Selectivity% <sup>b</sup>
1	DMA	Cs <sub>2</sub> CO <sub>3</sub> (1 equiv.)	456 nm	32%	64%
2	MeCN	Cs <sub>2</sub> CO <sub>3</sub> (1 equiv.)	456 nm	0%	0%
3	Toluene	Cs <sub>2</sub> CO <sub>3</sub> (1 equiv.)	456 nm	9%	24%
4	EtOAc	Cs <sub>2</sub> CO <sub>3</sub> (1 equiv.)	456 nm	14%	28%
5	DMF	Cs <sub>2</sub> CO <sub>3</sub> (1 equiv.)	456 nm	44%	72%
6	DMF	K <sub>2</sub> CO <sub>3</sub> (1 equiv.)	456 nm	73%	78%
7	DMF	NaHCO <sub>3</sub> (1 equiv.)	456 nm	46%	46%
8	DMF	DBU (1 equiv.)	456 nm	72%	72%
9	DMF	TMG (1 equiv.)	456 nm	75%	78%
10	DMF	TMG (1.5 equiv.)	456 nm	75%	80%
11	DMF	TMG (2 equiv.)	456 nm	75%	78%
12	DMF	TMG (1 equiv.)	525 nm	4%	40%
13	DMF	TMG (1 equiv.)	427 nm	83%	84%
<b>14</b>	<b>DMF</b>	<b>TMG (1 equiv.)</b>	<b>440 nm</b>	<b>82%</b>	<b>84%</b>

[a] Reactions performed on a 0.1 mmol scale. [b] Yield and selectivity were determined through <sup>1</sup>H NMR analysis of the crude reaction using 1,3,5-trimethoxybenzene as internal standard. DMA: *N,N*-dimethylacetamide, MeCN: acetonitrile, DMF: *N,N*-dimethylformamide, EtOAc: ethyl acetate, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, TMG: 1,1,3,3-tetramethylguanidine.

isolated from moderate to good yield (up to 89%). Surprisingly, our attempts to react 4-nitro-*N,N*-dimethylaniline (**1h**) were not successful. Indeed, the formation of a number of by-products (such as 4-nitro-*N*-methylaniline) was observed when using **1h** as starting material. Interestingly, *N,N*-dimethylaminopyridine (**1i**) was a suitable substrate, and the resulting adduct **2i** was isolated in good yield (86%). Besides, the use of simple *N,N*-dimethylaniline (**1j**) led to the formation of product **2j** in good yield (63%). Interestingly, the presence of weak electron-donating alkyl groups on the arene ring of **1** was also tolerated and compounds **2k–m** were isolated in good yields (up to 80%). Conversely, we observed a decrease in reactivity (53% yield) when employing a substrate bearing an electron-donating methoxy moiety (**1n**). The photocatalytic method was also useful to directly functionalize *N*-methyl-diphenylamine (**1o**), affording the corresponding product (**2o**) in 62% yield,

and *N*-phenylpyrrolidine (**1p**) to produce the corresponding 2-pyrrolidinone (**2p**) in moderate yield (39%).

## Mechanistic Considerations

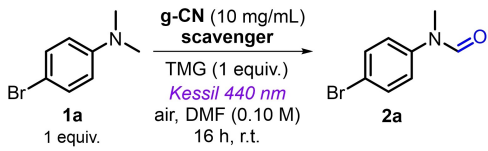
Our initial explorations, detailed in Table 1, indicated that the photo-induced activity of g-CN was essential for reactivity. Charge separation as consequence of light-induced promotion of electrons from the VB to the CB is hypothesized to be the first step of the catalytic cycle.<sup>[47,54]</sup> This is corroborated by the control experiments in absence of light (entry 3, Table 1). Moreover, oxidation from direct excitation of the starting material has to be cut out since none of the chemicals used absorbs the selected wavelength (see Supporting Information, Figure S2), differently from other observations found in literature.<sup>[43]</sup>



To get an outline about which kind of intermediates could be involved into the oxidation pathways, we performed a series of experiments in presence of inhibitors/scavengers,<sup>[61,62]</sup> as shown in Table 3.

As pointed out in Table 3, we found that the presence of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), a typical radical scavenger, decreased the reactivity (entry 1, Table 3). However, a complete inhibition was observed with CuCl<sub>2</sub> and benzoquinone (entries 2 and 3, Table 3), which respectively hamper the single electron transfer (SET) events and quickly react with superoxide radicals. On the contrary, the addition of the hydroxyl radical quenchers as *tert*-butanol (entry 4, Table 3) mildly affected the reactivity. The presence of NaN<sub>3</sub> as singlet oxygen scavenger led to the formation of **2a** in lower yield (entry 5, Table 3), suggesting a minor contribution also from <sup>1</sup>O<sub>2</sub>. Lower reactivity levels were also observed using KI (quencher of photogenerated holes), as depicted in entry 6 of Table 3.

**Table 3.** Screening of the effect from different scavengers.



Entry <sup>a</sup>	Scavenger	Quenched species/events	Yield% <sup>b</sup>
1	TEMPO (0.5 equiv.)	radicals	51%
2	CuCl <sub>2</sub> (1 equiv.)	SET	0%
3	BQ (1 equiv.)	O <sub>2</sub> <sup>•-</sup>	0%
4	<i>t</i> BuOH (1 equiv.)	HO <sup>•</sup>	78%
5	NaN <sub>3</sub> (2 equiv.)	<sup>1</sup> O <sub>2</sub>	50%
6	KI (1 equiv.)	h <sup>+</sup>	22%

[a] Reactions performed on a 0.1 mmol scale. [b] Yield and selectivity were determined through <sup>1</sup>H NMR analysis of the crude reaction using 1,3,5-trimethoxybenzene as internal standard. TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, BQ: benzoquinone, *t*BuOH: *tert*-butanol, SET: single electron transfer.

Therefore, in line with previous reports<sup>[63]</sup> and with recent findings from Galushchinskiy et al.,<sup>[64]</sup> we proposed that the excited photocatalyst may react with **1** through a proton-coupled electron transfer (PCET) process. As shown in Figure 3, photo-holes may be quenched by SET from the anilines (**1**), thus producing a radical-cation intermediate (**Ia**). This intermediate may be deprotonated under basic condition delivering an  $\alpha$ -amino radical (**Ila**). This carbon centered radical can then react with O<sub>2</sub><sup>•-</sup> (**Ib**), obtained through the reduction of molecular oxygen via photo-induced SET process from the CB, eventually forming the final product **2**.

The SET event between the excited g-CN and **1** was found to be thermodynamically favored according to cyclovoltammetry measurements. For example, the anilines **1a**, **1d**, **1j** and **1k** show adequate redox potentials in similar environments (see Supporting Information, Figure S5) that match the position of g-CN VB (1.83 eV, according to previous literature reports).<sup>[48]</sup> According to the impedance data summarized by Nyquist plots of Figure S4 (see Supporting Information), a slightly decrease of impedance values was observed between the dark and light acquisition for each probe molecule investigated; this is mainly evident in the low frequency range ( $\leq 10$  Hz), accounting for a change in diffusional phenomena occurring at the electrode surface. The high-level complexity of the electrochemical system did not allow us to discriminate differences in the high frequency range for a useful discussion of charge-transfer phenomena.

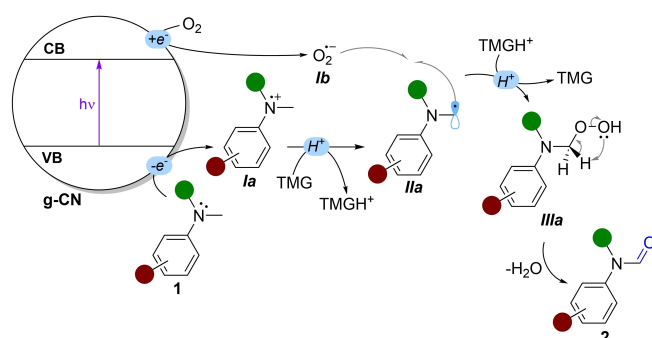
## Conclusions

We have developed an efficient radical methodology for the direct formylation of anilines **1**. We found that the reaction was driven by the photocatalytic activity of g-CN under visible-light irradiation ( $\lambda = 440$  nm). Products **2** were isolated from good to high overall isolated yields (up to 89% yield) employing mild operative conditions and air as oxidant. Importantly, the photocatalyst exhibits excellent stability under the reaction conditions and is recyclable for at least five independent cycles. Hence, our research offers an effective and elegant approach for the preparation of formamide derivatives, which may be attractive for industrial purposes.

## Experimental Section

**Material synthesis:** g-CN was prepared according to a previously reported protocol.<sup>[48]</sup> Briefly, 5 g of melamine were heated to 550 °C for 5 h and the resulting polymer was milled in a mortar before further use.

**General procedure for the synthesis of **2**:** A 10 mL Schlenk tube was charged with the aniline **1** (0.1 mmol), TMG (1 equiv, 12.5  $\mu$ L), g-CN (10 mg) and DMF (1 mL). A balloon filled with air was connected to the Schlenk tube to ensure an abundant reservoir of air. The reaction vessel was then placed at 1.5 cm from a Kessil lamp ( $\lambda = 440$  nm) and kept at around 30 °C by means of a fan.



**Figure 3.** Proposed reaction mechanism which drives the photocatalytic formylation of anilines.

After stirring for 16 h, the reaction crude was filtrated on a Celite plug to remove the catalyst powder and purified by column chromatography (see Supporting Information for specific details).

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[65–73]</sup>

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** aniline · carbon nitrides · formylation reactions · heterogeneous catalysis · photooxidation

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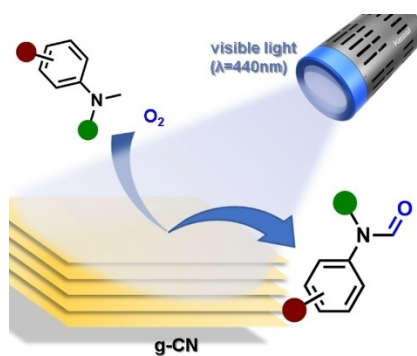
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## RESEARCH ARTICLE

**A new metal-free photocatalytic approach** for the direct conversion of *N,N*-difunctionalized anilines into formamides derivatives (up to 89% yield) under mild operative conditions is described herein. In this reaction, graphitic carbon nitride (g-CN) acts as a robust and fully recyclable visible-light photocatalyst that was easily recovered and reused up to five times without any significant drop in yield.



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1 – 8

**Graphitic Carbon Nitride as Photocatalyst for the Direct Formylation of Anilines**

