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ARTICLE

Visible Light-Induced Transformation of Aldehydes to Esters, Carboxylic Anhydrides and Amides

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A transition metal- and organophotocatalyst free synthesis of esters, carboxylic anhydrides and amides from aldehydes induced by visible-light is reported. The proposed methodology can be carried out by the use of sunlight or artificial visible light as blue led. The methodology has a very broad applicability and the desired products are obtained in very satisfactory yields.

Introduction

Esters are one of the most meaning functional groups in organic chemistry and are contained in various natural products, polymers, pharmaceuticals and synthetic intermediates.[1] Classically esters are prepared via nucleophilic substitutions of carboxylic acid derivatives with alcohols.

The oxidative esterification of aldehydes is an elegant approach to classical ester synthesis,[2] which avoids many drawbacks related to esterification of carboxylic acid derivatives, as two additional steps with consequent increase of by-products and reduction of yields.

One of the most challenging research themes in modern organic synthesis is the development of new methodologies induced by visible light.[3] Photosynthesis can be defined as the conversion of sunlight into chemical energy effectively employed to carry out chemical reaction, allowing the development of sustainable and efficient procedures. Recently organic transformations carried out in the absence of transition metal- and organophoto- catalysts have received increasing attention due to their economic, sustainability and mechanistically novel features.[4]

A photocatalyzed synthesis of esters from aldehydes was recently investigated.

In 2018 Pandey and co-worker have developed a cross-dehydrogenating coupling of aldehydes with R-OTBS ethers by visible –light photoredox catalysis. The reaction is carried out by the use of photoredox catalyst based on Iridium, an equimolecular quantity of CCl_3Br and an excess of R-OTBS ethers (Scheme 1, path a).[5]

In 2017 Wolf and co-worker have proposed a photooxidation of aldehydes to methyl esters catalysed by riboflavin tetraacetate (RFT) induced by blue light (Scheme1, path b).[6] The reaction proceeds on aromatic aldehydes in methanol, under acidic conditions, *via* an acetal intermediate, providing the corresponding methyl esters.

Jain and co-workers have reported an esterification of aromatic aldehydes to the corresponding methyl or ethyl esters using cobalt complex immobilized to nanoporous graphitic carbon nitride (Co@npg-C_3N_4) as a photocatalyst (Scheme 1, path c).[7] The reaction proceeds in the alcohol (methanol or ethanol) employed as both a solvent and a reactant. In 2014 Zhaorigetu and Zhu have proposed one of the first photocatalytic conversion of aromatic aldehydes to ethyl esters under visible light irradiation using supported gold nanoparticles (AuNPs) as a catalyst (Scheme 1, path d) and ethanol as a solvent.[8] The reactions proceeds via hemiacetal intermediate formation.

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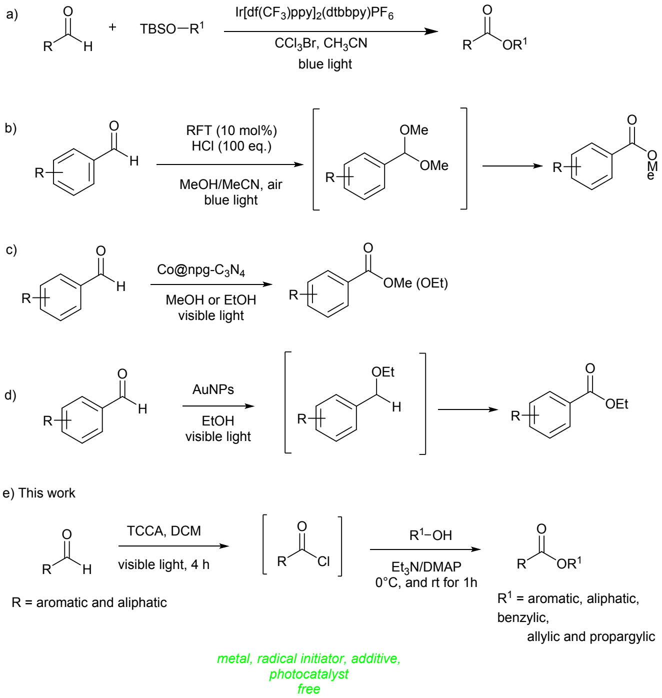


Scheme 1. Visible light induced transformation of aldehydes to esters

As far as we know, all the methodologies described provide only methyl or ethyl esters, work with more reactive aromatic aldehydes, and make use of alcohols (methanol and ethanol) as both solvents and reactants. The main restrictions of these procedures are the limited substrate scopes (related to the formation of a hemiacetal or an acetal as intermediates) and the unfavourable stoichiometric ratios of the reagents. Moreover the difficult preparation of transition metal-based catalysts immobilized on nanoporous materials or the synthesis of riboflavin tetraacetate[9] limits the accessibility of these methodologies.

Due to our interest in the synthesis of esters[10] and anhydrides[11] via acyl chloride formation by the use of trichloroisocyanuric acid (TCCA), we have looked for an alternative a more general visible light induced synthesis of esters from both aliphatic and aromatic aldehydes.

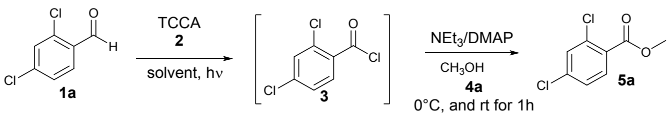
The selected reagents have several advantages. Aldehydes are readily accessible, inexpensive and commercially available compounds. Trichloroisocyanuric acid is a safe, easy-to-handle, shelf-stable solid commonly used as a swimming pool and public places disinfectant and as a preservative in fruits and vegetables.[12] Besides the reagents chosen, the use visible light and ,in particular of sunlight as an activator,[13] was shown to be a cheap and ecological way to improve the value of the procedure. Solar energy is a promising tool as the green energy source because it is a reliable, renewable and inexhaustible source of energy.[14]

In addition, the majority of photochemical reactions need of catalysts of heavy or rare metals, as ruthenium and iridium, or of organic photocatalysts so a photoreaction, that arises without any catalyst, represents a great aim.

Results and discussion

We started our investigation by treating 2,4-dichlorobenzaldehyde (Table 1, 1a, 1.1 mmol) with TCCA (Table 1, **2**, 1.1 mmol) in dichloromethane (1mL) and exposed under sunlight irradiation. The reaction was monitored by TLC until the disappearance of the aldehyde, and after 4 hours, the corresponding benzoyl chloride (Table 1, **3**) was quantitatively formed. This reaction mixture, containing the acyl chloride generated in situ, was treated with methanol (Table 1, **4a**, 1 mmoL) and NEt_3 in the presence of a catalytic amount of DMAP (2 mmol/10 mol%) and after 1 h at room temperature the desired ester was formed in 98% yield (Table 1, **5a**, entry 1). In order to optimize the stoichiometric ratio of the reactants, the reduction of the amount of TCCA **2** was investigated. The same reaction was carried out employing 0.55 mmol (Table 1, **2**, entry 2) and 0.37 mmol (Table 1, **2**, entry 3) of TCCA and the ester was obtained in 97% yield. All reagents were so used in an optimal stoichiometric ratio in a concentration of 1.1 M, leading to a more economical and sustainable method. Often photochemical reactions are not clean, and even photochemical reactions are carried out at a low concentration (< 0.01 M) in order to reduce the secondary photoreactions and, in general, to minimize the product distribution.[15] For these reasons, a reaction that occurs by means of sunlight or visible light and at a high concentration (> 1 M) is an ideal gunpoint. After the optimised stoichiometric ratio of the reactants was established, a screening of solvents was carried out; cyclopentyl methyl ether (Table 1, entry 4), tetrahydrofuran (Table 1, entry 6) and acetonitrile (Table 1, entry 7), were tested, but no 2,4-dichlorobenzoyl chloride **3** formation was detected. Using dichloroethane (Table 1, entry 5), as a solvent the ester **5a** was obtained in trace amounts. In order to extend applicability of the methodology was explored the use of artificial lighting. The reaction was carried out respectively for 8 hours under blue led irradiation and by using of a solar simulator for 4 hours and the methyl 2,4-dichlorobenzoate **5a** was obtained respectively in 75% (Table 1, entry 8), and 98% (Table 1, entry 9) yield. The same reaction was carried out respectively in dark and in the absence of TCCA, but no reaction was observed (Table 1, entries 10-11).

Table 1. Screening of Reaction Conditions



Entry	**1a** (mmol)	TCCA (mmol)$^{)}$	Solvent	Yield [%]$^{a)}$
1$^{b)}$	1.1	1.1	DCM	98%
2$^{b)}$	1.1	0.55	DCM	97%
3$^{b)}$	1.1	0.37	DCM	97%
4$^{b)}$	1.1	0.37	CPME	-
5$^{b)}$	1.1	0.37	DCE	trace
6$^{b)}$	1.1	0.37	THF	-
7$^{b)}$	1.1	0.37	CH_3CN	-
8$^{c)}$	1.1	0.37	DCM	75%
9$^{d)}$	1.1	0.37	DCM	98%
10$^{e)}$	1.1	0.37	DCM	-
11)$^{b)}$	1.1	-	DCM	-

$^{a)}$ Isolated yields. $^{b)}$ Reaction conditions: 2,4-dichlorobenzaldehyde **1a** was reacted with TCCA **2** in solvent (1 mL), under sun light irradiation for 4 hours. Then methanol (1 mmol) and NEt_3/DMAP (2 mmol, 10% mol) were added at 0 °C, and after 1 hour at room temperature, the desired ester **5a** was obtained. $^{c)}$ Using blue LED as light source. $^{d)}$ Using solar simulator as light source. $^{e)}$ Reaction in dark.

With the optimized conditions (Table 2, entry 9) in hand the reaction scope was investigated by the use of a solar simulator and by blue led and sunlight (Figure 1, **5a**, **5j**, **5n**, **5o**, **5q**).

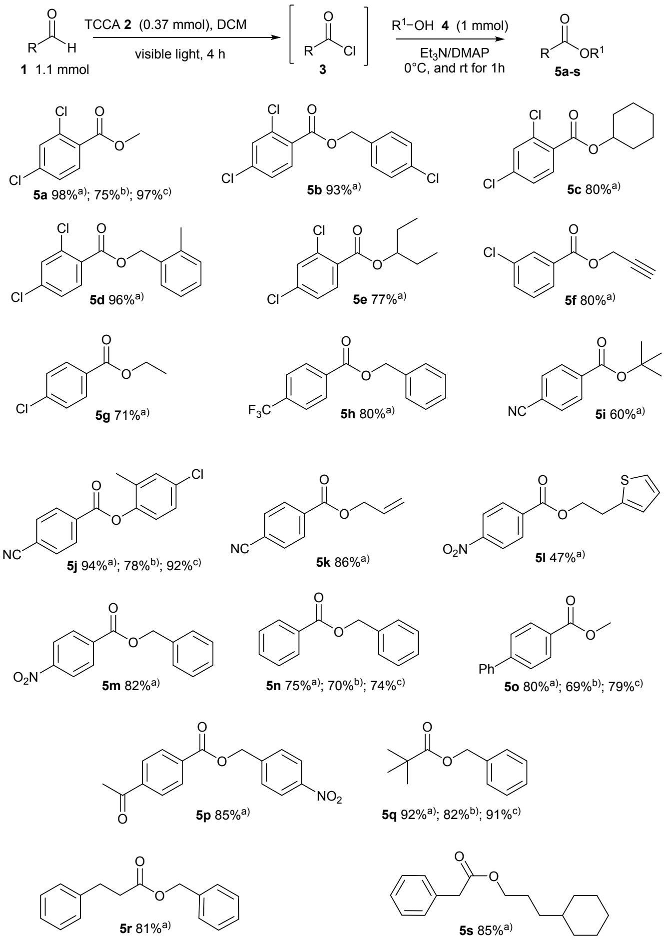


Figure 1. Reaction scope. $^{a)}$ solar simulator; $^{b)}$ blue LED; $^{c)}$ sun light

An array of aldehydes and alcohols was tested, both aromatic and aliphatic. Regarding the aromatic aldehydes, in general, the ester products were obtained in very good yields. Differently functional groups on aromatic aldehydes as NO_2 (Figure 1, **5l**, **5m**), CF_3 (Figure 1, **5h**), CN (Figure 1, **5i**, **5j**), halides (Figure 1, **5a**, **5b**, **5c**, **5d**, **5e**, **5f**, **5g**), carbonyl (Figure 1, **5p**), and phenyl (Figure 1, **5o**) have proven to be suitable for delivering the corresponding esters.[16] Aliphatic aldehydes, which typically cannot survive under strong oxidative conditions, were converted to the desired esters in high yields (Figure 1, **5q**, **5r**, **5s**). Even very sterically hindered pivalaldehyde reacted well (Figure 1, **5q**).

The array of alcohols used didn't shows any impediment. Benzylic alcohols (Figure 1, **5b**, **5d**, **5h**, **5m**, **5n**, **5p**, **5q**, **5r**) are known to readily oxidize to the corresponding aldehydes however these by-products were not be detected. Allylic and propargylic alcohols were successfully employed in this procedure (Figure 1, **5f**, **5k**). Primary alcohols such as methanol (Figure 1, **5a**, **5o**), 2-(thiophen-2-yl)ethanol (Figure 1, **5l**) and 3-cyclohexyl-1-ol (Figure 1, **5s**) were demonstrated to be good substrates for the synthesis of esters. Notably, more sterically hindered secondary alcohols, such as pental-3-ol and cyclohexyl alcohol were successfully employed (Figure 1, **5c**, **5e**).

Carboxylic anhydrides are important precursors for amides and esters and have been largely applied in peptide synthesis.[16] Classical carboxylic anhydrides preparations make use of toxic reagents. Due to the anhydrides instability, mild and sustainable syntheses are a crucial aim. [18]

In this context and in order to broaden the applicability of the present methodology, carboxylic acids were used in place of alcohols and it was possible to synthesize both aromatic and aliphatic carboxylic anhydrides (Figure 2). Benzaldehyde (Figure 2, **1a**, 1.1 mmol) was treated with TCCA (Figure 2, **2**, 0.37 mmol) in 1 mL of DCM and exposed to a solar simulator and after 4 hours the corresponding benzoyl chloride (Figure 2, **3**) was quantitatively formed. To this reaction mixture were added benzoic acid (Figure 2, **6a**, 1 mmol) and NEt_3 (2 mmol) and after 1 h at room temperature the desired carboxylic anhydrides was formed in 80% yield (Figure 2, **7a**). The same reaction was carried out under blue led or sunlight irradiation, giving comparable results, as reported in Figure 2, **7a**.

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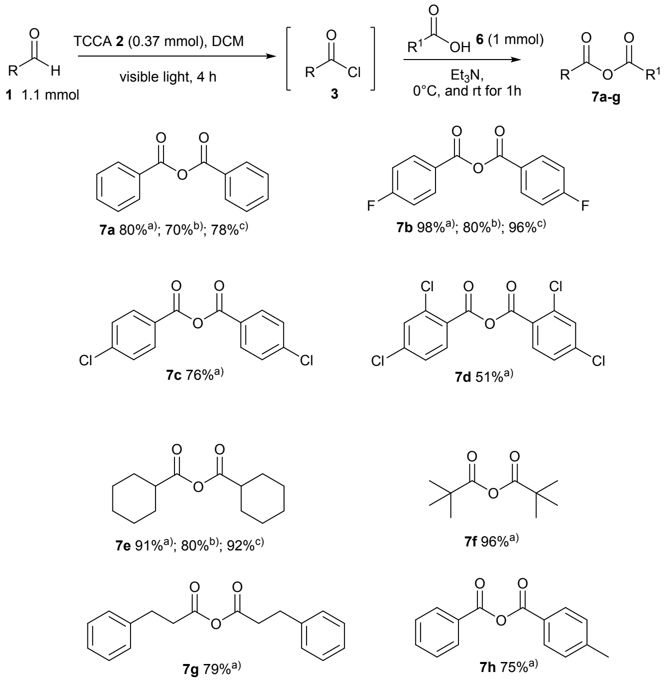

Figure 2. Carboxylic anhydrides reaction scope. a) solar simulator; b) blue LED; c) sun light

The scope of the reaction was investigated and as shown in Figure 2, both aromatic (Figure 2, **7a**, **7b**, **7c**, **7d**) and aliphatic carboxylic anhydrides (Figure 2, **7e**, **7f**, **7g**) were obtained in good yield. The methodology was tested for the synthesis of mixed anhydrides and the compound **7h** was obtained in very satisfactory yield.

Recently some examples of visible-light photocatalyzed synthesis of amides were reported. [5,13b,19]

In relation to the current interest in the development of catalyst-free visible-light mediated procedures, and to broaden the applicability of the present methodology, an array of amines was employed in place of carboxylic acids. This made it possible to synthesize both aromatic and aliphatic amides (Figure 3). Benzaldehyde (Figure 3, **1a**, 1.1 mmol) was treated with TCCA (Figure 3, **2**, 0.37 mmol) in 1 mL of DCM and exposed to a solar simulator and after 4 hours the corresponding benzyl chloride (Figure 3, **3**) was quantitatively formed. To this reaction mixture were added dibenzylamine (Figure 3, **8a**, 1 mmol) and NEt$_3$ (1.2 mmol) and after 1 h at room temperature the desired amide was formed in 78% yield (Figure 3, **9a**). The same reaction was carried out under blue led or sunlight irradiation, giving comparable results, as reported in Figure 3, **9a** and **9g**.

The scope of the reaction was investigated and as shown in Figure 3, both aromatic (Figure 3, **9a**, **9b**, **9c, 9d, 9e, 9f**) and aliphatic aldehydes (Figure 3, **9g**, **9h**) were reacted with primary and secondary amines providing the corresponding amides in good yield.

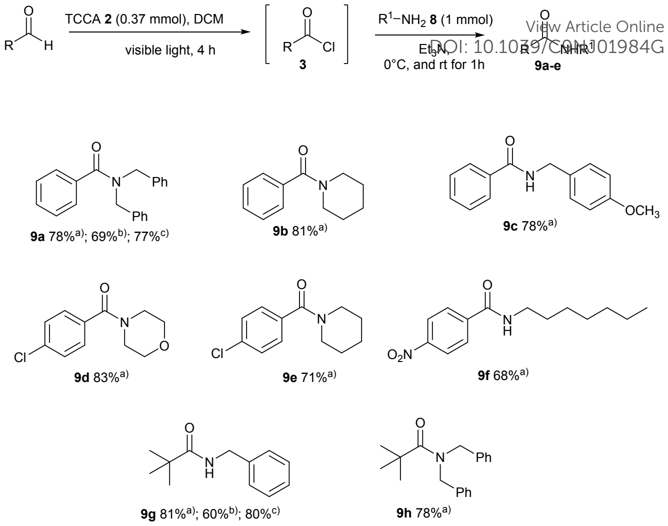

Figure 3. Amide reaction scope. a) solar simulator; b) blue LED; c) sun light

Two plausible pathways of mechanism for the formation of acyl chlorides from aldehydes with TCCA is given in Scheme 2 The process is supposed be a radical mechanism. It initiates from a visible-light-assisted homolytic cleavage of *N*-Cl bond in TCCA to form the amidyl radical[20, 12b] **A** and the radical chlorine atom **B**. In the first pathway (Scheme 2, path 1) the *N*-centered radical **A** then abstracts a hydrogen atom at the carbonyl to form the acyl radical **C**. The intermediary acyl radical **C** and chlorine radical react together to form the acyl chloride **D**.[21] These key steps are repeated until the formation of cyanuric acid **E** allowing the complete reaction of all chlorine atoms. In alternative another plausible pathway is proposed (Scheme 2, path 2). The reaction is initiated by a homolytic cleavage of the *N*-Cl bond of trichloroisocyanuric acid to generate the radical chlorine atom **B** and the nitrogen-centered radical **A**. The reaction propagates *via* abstraction of aldehydes' hydrogen by **A** to generate the intermediate **C**. Quenching of the acyl radical by chloride transfer generates the acyl chloride **D**. The reaction continues until the halogen source has been consumed.

The reaction was tested in the dark with all of different aldehydes, but no acyl chloride formation was never observed.

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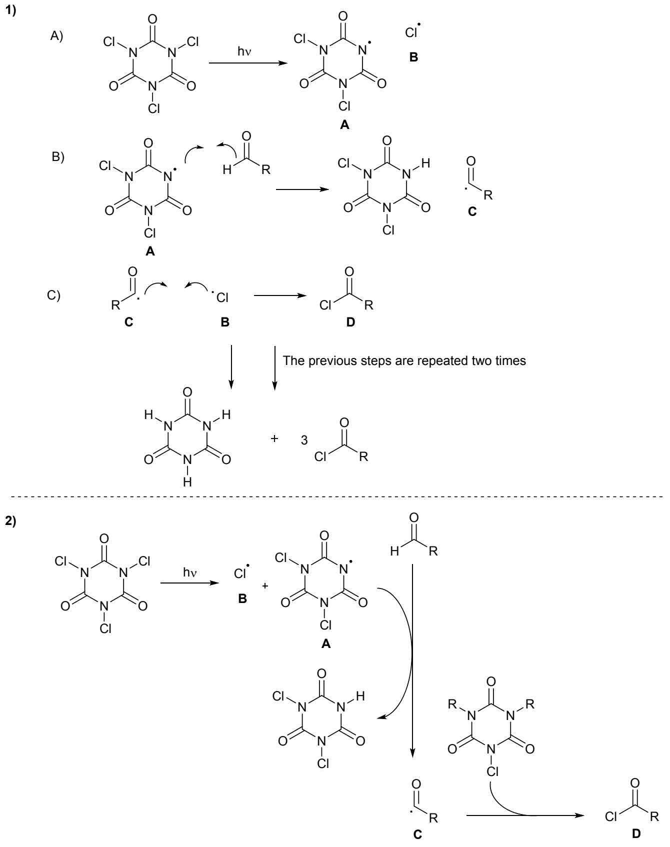

Scheme 2. Two proposed mechanism pathways for the acyl chloride formation

Quantum yield measurement were performed to afford insight into the effective reaction mechanism,[22] and the result furnishes the evidence that the reaction proceeds through a light-initiated chain propagation mechanism.[20d, 21d, 23] The measured quantum yield corresponds to 3 equivalents of product formed per absorbed proton (φ = 3), thus showing that this reaction proceeds through a chain propagation mechanism.

Conclusions

In conclusion a novel photocatalyst free methodology for transformation of aldehydes into acyl chlorides induced by visible light was reported. The acyl chlorides can be then converted into esters, carboxylic anhydrides or amides. The methodology has shown a big versatility and applicability on both aliphatic and aromatic aldehydes. The stoichiometric ratio of the reactants is optimal and the use of visible light as source of energy is very appealing from an ecological point of view. A key advantage of this process is that avoids the use of any expensive and toxic transition metals-based catalysts and of any organic-based photocatalysts. The reaction can be driven using different visible light source, such as a blue led, a solar simulator and, more importantly, the sun. The procedure is operationally simple and the starting reagents as well as the visible light sources are inexpensive and readily available.

Conflicts of interest

There are no conflicts to declare.

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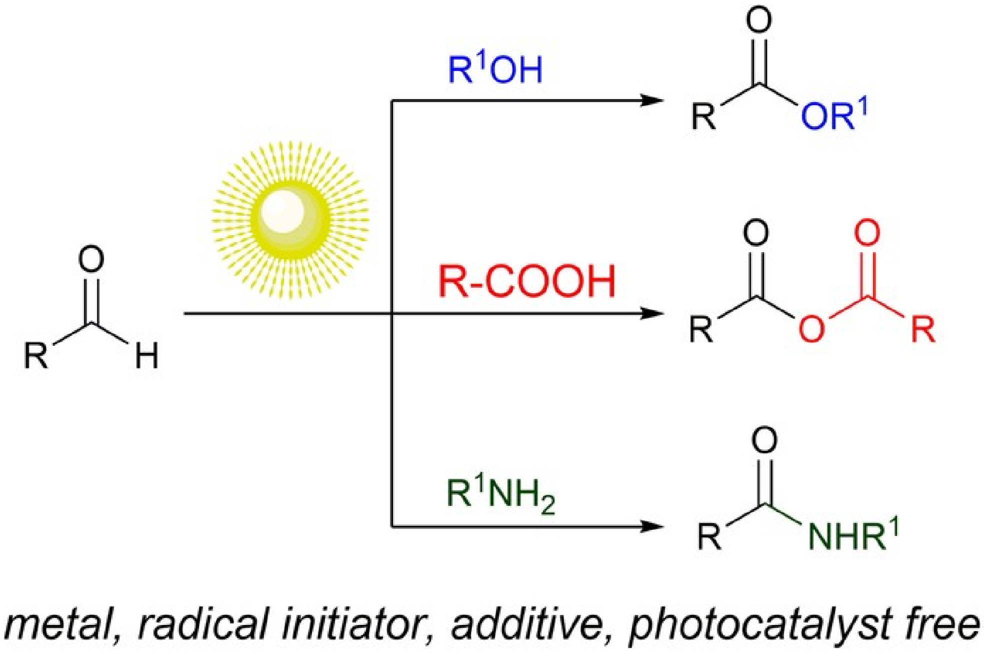

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