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Recent Advances in the Catalysis of Oxidative Esterification of Aldehydes

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Abstract: There is little research conducted on the recent advances in the catalysis of oxidative esterification of aldehydes. Ester groups are among the highly important and abundant functional groups in the field of chemistry and it can be found in bulk chemicals, fine chemicals, natural products, and polymers. We investigated both the metal-free and catalytic oxidative esterification of aldehydes. Alcohols, phenols, and primary and secondary aliphatic, benzylic, allylic, and propargylic acids were successfully used. This research mainly introduces the recent progress in this field of the formation of esters, based on the classification of the role of carboxylic acids in reactions.

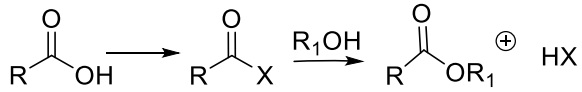
Keywords: Recent advances, Catalysis, Oxidative esterification, Aldehydes

1. INTRODUCTION

According to Otera and Nishikido (2010); Liu *et al*. (2011), ester groups are among the most important and prevalent functional groups in the study of chemistry, and they are present in a variety of natural products, synthetic materials, bulk chemicals, and fine chemicals. The functional group of esters is not only current in large quantities in natural products (Sumby et al., 2010) but is also necessary for many synthetic processes, according to a study by Heropoulos and Villalonga-Barber (Heropoulos and Villalonga-Barber, 2011). Benzyl esters, according to Dey and his coworkers, are practical functional groups that can be found in pharmaceutical and natural products. They are frequently used as protecting groups for a variety of functionalities, including carboxyl groups (Dey, Gadakh and Sudalai, 2015).

According to Valizadeh and Ahmadi (2012), esters are generally prepared by nucleophilic addition of an alcohol to activated carboxylic acid derivatives. These activated carboxylic acid derivatives include substances such as acid anhydrides and chlorides (Heropoulos & Villalonga-Barber, 2011).

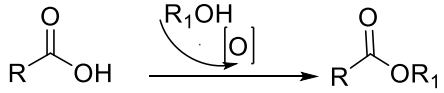
From the following reaction scheme, traditionally, esters are synthesized by the reaction of activated acid derivatives like acyl chlorides (Zhong et al., 2015), and anhydrides with alcohols (Gaspa et al., 2016) (Scheme 1, path A).



Scheme 1. Traditional route to esters: the coupling of activated acid derivatives with alcohols Gaspa, Porcheddu, & De Luca, (2016).

A carboxylic acid is stoichiometrically activated as an acyl halide, activated ester, or anhydride in the classic esterification techniques. This is followed by a nucleophilic substitution reaction with alcohols (Dey et al., 2015). The two-step processes examined by Mahmood and others, which include oxidation and C-O bond formation phases, were developed as alternatives to overcome these limitations (Gaspa et al., 2016). Direct oxidative esterification of aldehydes and alkanols is a theoretically and practically appealing method that has attracted increasing interest (Mahmood et al., 2017).

According to Gaspa, Porcheddu, and De Luca (2016), the direct transformation of aldehydes into esters and amides by means of one-pot oxidative processes has been highlighted as a valid and powerful alternative within the previous decade, as shown in the following scheme (Scheme 2).



Scheme 2. Oxidative esterification of aldehydes.

The direct conversion of aldehydes into esters is a valuable alternative, and to achieve this transformation, much effort has been devoted (Ekoue-Kovi & Wolf, 2008; Heropoulos & Villalonga-Barber, 2011).

According to Suzuki (2021), one of the most fundamental transformations in organic synthesis, esterification (the process of ester production), is frequently utilized in labs and enterprises (Gaspa, Porcheddu, & De Luca, 2016). Aldehydes are readily available as raw materials on an industrial scale (Suzuki & Yamamatsu, 2016), making esterification of aldehydes with alcohols an appealing approach for the production of esters (Suzuki et al., 2013).

2. LITERATURE REVIEW

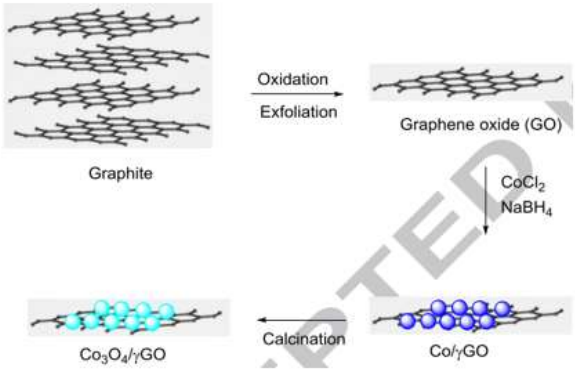
2.1 Catalytic Oxidative Esterification of Aldehydes

Metal Catalyzed Esterification of Aldehydes

According to Gaspa, Porcheddu, and De Luca, (2016), the direct catalytic conversion of aldehydes to esters has drawn significant interest in recent study. Many metal-based catalysts for the oxidative esterification of aldehydes have been reported in the literature in this area. The oxidation reaction process is a crucial step in the production of organic compounds. According to Shi et al. (2012), the development of late transition-metal catalyzed oxidations, which are essential for the synthesis of organic compounds, has occurred over the past few decades. Key examples of these metals are gold, copper, rhodium, iridium, palladium, and copper.

According to recent studies (conducted over the last ten years), there have been considerable improvements in transition-metal catalyzed oxidation reactions using molecular oxygen as the only oxidant, especially for copper and palladium (Shi et al., 2012).

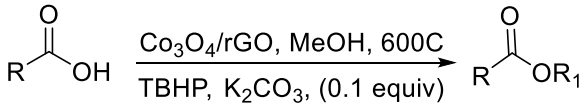
According to Panwar and others, processes catalyzed by heterogeneous catalysts have a number of benefits since the product is less likely to be contaminated and the catalyst is recovered and recycled effectively (Panwar et al., 2015). Aldehydes are converted to methyl esters in a single pot using Co_3O_4 nanoparticles supported on reduced graphene oxide (Co_3O_4/rGO). As indicated in Scheme 3 below, the Co_3O_4/rGO catalyst was created by chemically reducing grapheme oxide (GO) and $CoCl_2$ simultaneously (Gaspa et al., 2016).



Scheme 3. Schematic preparation of Co_3O_4/γGO

Oxidative Esterification of Aldehydes Catalyzed by Co_3O_4/rGO

Numerous aldehydes, both aliphatic and aromatic, were able to esterify methanol in good yields by using TBHP as the reaction's oxidant in the presence of catalytic amounts of K_2CO_3 as base sources, as shown in Scheme 4 below.



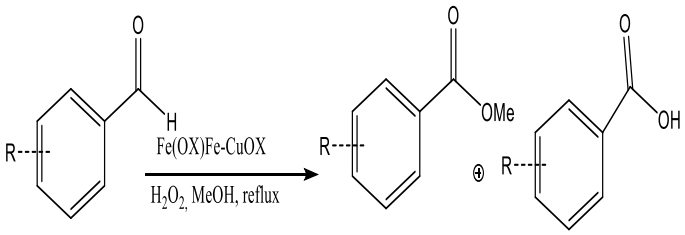
R= aryl, alkayl

Scheme 4. Oxidative esterification of aldehydes catalysed by Co_3O_4/rGO

When we contrasted our method with existing processes that use heterogeneous catalysts like alumina supported palladium catalyst (Norrby & Lloyd-Jones, 2010). This approach has many benefits, including the use of a cheap metal and the ease with which the catalyst may be easily separated from the reaction mixture using an external magnet.

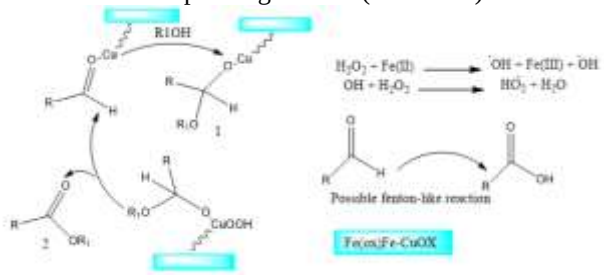
Oxidative Esterification of Aldehydes Catalyzed by Fe (Ox)Fe-CuOx

Parihar and coworkers have recently reported another instance of metal-catalyzed oxidative esterification of aldehydes. In combination with an excess of hydrogen peroxide as an oxidant and methanol as a solvent, they have disclosed an oxidative esterification of aromatic aldehydes, mediated by orthorhombic iron (oxalate) capped Fe-Cu oxide [Fe(ox)Fe-CuOx] (Scheme 5). This process enables a moderate to fair yield of methyl esters from the aldehydes. A trace amount of acid was occasionally found because some aldehydes were being overoxidized. The process for making the catalyst seems straightforward, efficient, and cost-efficient (Gaspa et al., 2015).



Scheme 5. Oxidative esterification of aldehydes catalyzed by Fe(ox)Fe-CuOx

The suggested reaction mechanism states that an aldehyde and alcohol combine in the presence of a [Fe(ox)Fe-CuOx] nanomaterial to create a hemiacetal 1, which is subsequently oxidized by the peroxide complex of Cu (II) to produce the corresponding ester 2. (Scheme 6).

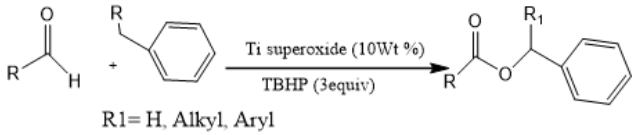


Scheme 6. Possible reaction mechanism of Fe(ox)Fe-CuOx catalyzed esterification

Ti Superoxide Catalyzed Esterification of Aldehydes with Alkyl Arenes

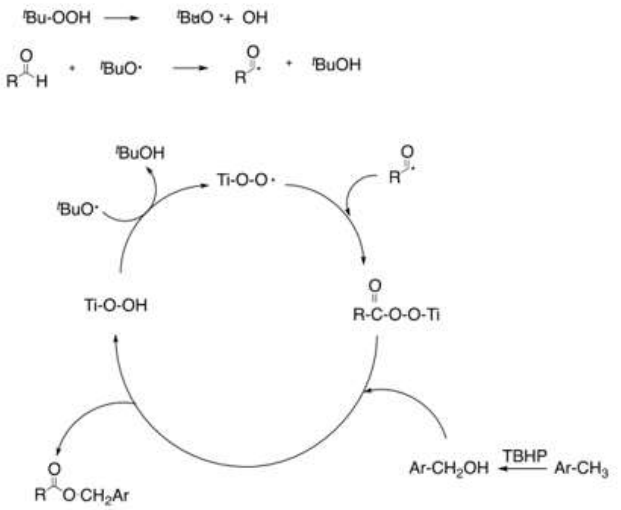
According to Gaspa et al. (2016), there is an alternative to conventional practices (Sudalai et al., 2015). They discussed the direct conversion of both aliphatic and aromatic aldehydes into carboxylic esters that was catalyzed by Ti-superoxide and involved either C-H activation of alkylarenes or the use of alcohols. Notably, alkyl aromatics are efficient in this process despite rarely being used in oxidative esterification due to the low reactivity of SP3 C-H

bonds. Alkyl arenes (or alcohols) are used as both reagents and solvents in this process, which also uses a large amount of TBHP as an oxidant and titanium superoxide as a catalyst (Scheme 7). The catalyst can be easily recovered by straightforward filtration and utilized again and again as the reaction continues under truly heterogeneous catalytic conditions.



Scheme 7. Ti superoxide catalyzed esterification of aldehydes with alkyl arenes.

With regards to the reaction mechanism, a plausible catalytic cycle was proposed (Scheme 8) by the same authors.

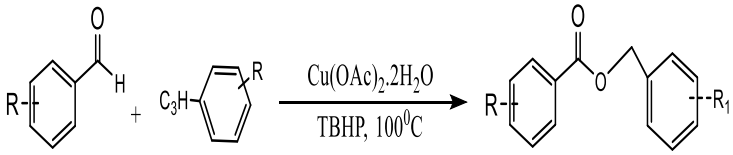


Scheme 8. Proposed mechanism for Ti superoxide catalyzed esterification of aldehydes with alkyl arenes

Tert-Butylperoxy radical, formed by thermal decomposition of TBHP generates, in the presence of aldehyde, an acyl radical. The titanium superoxide radical ion and the acyl radical subsequently combine to create the Ti peroxo specie. The matching ester is produced when alcohol interacts nucleophilically with the Ti peroxo species (Gaspa et al., 2016).

Copper Catalyzed Oxidative Esterification of Aldehydes with Alkyl Benzenes

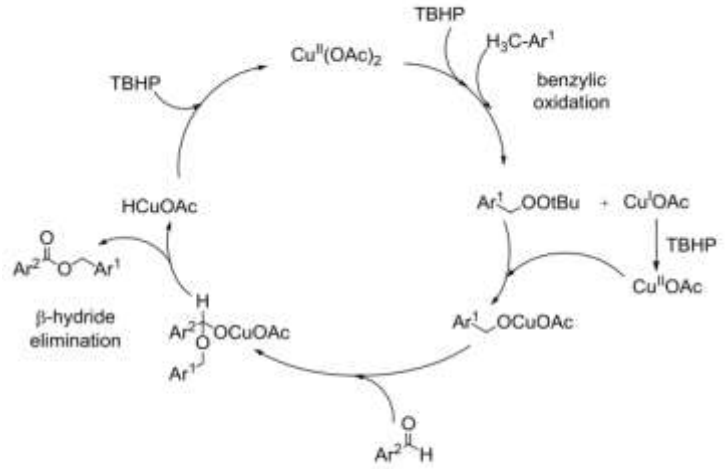
Aromatic aldehydes and alkylbenzenes were successfully used as coupling partners in a cross dehydrogenative coupling (CDC) to prepare benzylic esters (Rout et al., 2012). Alkylbenzene's sp3 C-H bond is activated via a benzylic reaction utilizing the catalyst Cu (OAc)2 and the oxidant TBHP (Scheme 9). Notably, this approach allows the direct esterification of readily accessible and reasonably priced feedstocks, notably nonactivated alkylbenzenes.



R= H, Ph, OMe, Cl, NO_2; R1= H, CH_3, Cl

Scheme 9. Copper catalyzed oxidative esterification of aldehydes with alkylbenzenes.

Aldehyde and the in-situ produced alcohol (from alkylbenzene) are thought to couple through a hemiacetal intermediate to cause this reaction. After a -hydride elimination, the hemiacetal is then changed into the appropriate ester (Scheme 10).



Scheme 10. Proposed mechanism of copper catalysed oxidative esterification of aldehydes with alkylbenzenes.

Copper Catalyzed Oxidative Esterification of Aldehydes to Esters of Tertiary Alcohols

Wei and colleagues recently reported an oxidative esterification of mostly aromatic aldehydes with dialkyl peroxides in the presence of the -imine ligand L to produce esters of tertiary alcohols (Scheme 11). Due to the bulkiness of tertiary alcohols, it is exceedingly challenging to accomplish the synthesis of tertiary esters through the direct esterification of aldehydes. The dialkyl peroxides function as an oxidant and a precursor of tertiary alcohol (Zhu & Wei, 2013).

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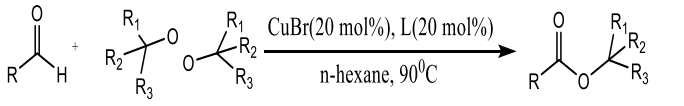
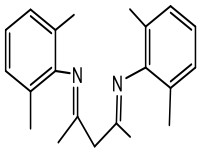


R= Alkyl, Aryl, Hetroaryl

R1, R2, R3 = Me, Ph

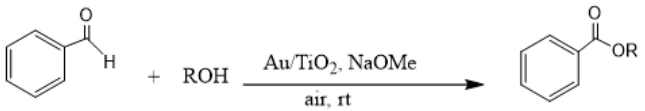


L

Scheme 11. Copper catalyzed oxidative esterification of aldehydes to esters of tertiary alcohols

Ti Superoxide Catalyzed Esterification of Aldehydes with Alkyl Arenes

Christensen and associates presented a green approach to esterify benzaldehyde and acrolein to esters. The reaction is carried out at room temperature and in the presence of a base, and it is catalyzed by supported gold on titanium dioxide (1 wt percent Au/TiO2) (Scheme 12). It is noteworthy that the reaction can be carried out in an open flask with air as the oxidizing agent.

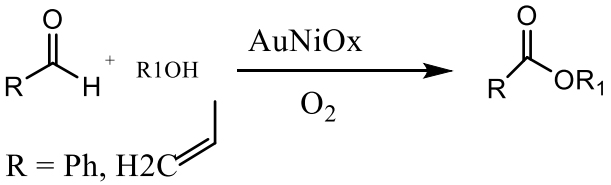


R = CH_3, CH_2CH_3, $(CH_2)_2CH_3$, $(CH_2)_3CH_3$, $CH_2(C_6H_5)$

Scheme 12. Ti superoxide catalyzed esterification of aldehydes with alkyl arenes.

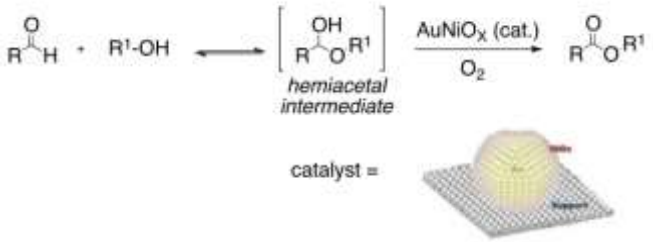
Auniox Catalyzed Oxidative Esterification of Benzaldehyde and Methacrolein

Afterwards another oxidative esterification of activated aldehydes with alcohols and AuNiOx as a catalyst was reported (Suzuki et al., 2013). The procedure appears environmentally benign because it makes use of molecular oxygen as the terminal oxidant, giving water as the only side product. The methodology works well with activated aldehydes such as benzaldehyde and methacrolein, which is extremely unstable (Scheme 13).



Scheme 13. AuNiOx catalyzed oxidative esterification of benzaldehyde and methacrolein

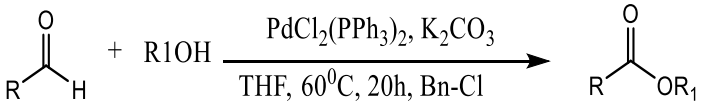
The supposed reaction pathway consists of the condensation between the aldehyde and alcohol, which results in the formation of a hemiacetal intermediate. Then the hemiacetal undergoes oxidative dehydrogenation to give the corresponding ester (Scheme 14). The AuNiOx nanoparticle was supposed to have a core−shell structure with Au nanoparticle at the core and its surface covered by highly oxidized NiOx. NiO exists in a highly oxidized state in the AuNiOx catalyst due to heterometallic bonding interactions with Au (ligand effect).



Scheme 14. Proposed mechanism for AuNiOx catalyzed oxidative esterification of aldehydes

Palladium Catalyzed Oxidative Esterification of Aldehydes

Lei and coworkers have proposed an oxidative esterification of aldehydes catalyzed by $[PdCl_2(PPh_3)_2]$ which makes use of benzyl chloride as an oxidant (Scheme 15). The methodology works well with both aliphatic and aromatic aldehydes and gives good results with benzylic and aliphatic alcohols (Gao et al., 2017).



R= Alkyl, Aryl

R1= Alkyl, Benzyl

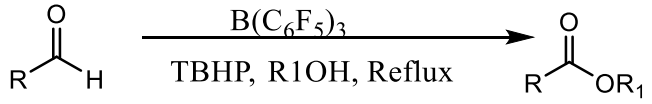
Scheme 15. Palladium catalyzed oxidative esterification of aldehydes.

2.2 Metal free Esterification of Aldehydes

The metal catalyzed procedures described below have a drawback related to the catalyst cost which represent an impractical aspect for large-scale use. For this reason an interesting alternative approach to the esterification of aldehydes are the metal free procedures (Gaspa et al., 2016).

Tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ was recently proposed as a non–toxic, air-stable, and thermal-abiding Lewis acid able to catalyze oxidative esterification of a number of aldehydes in the presence of an excess of TBHP as an oxidant and alcohols as both as solvents and reagents (Scheme 16) (Guggilapu et al., 2015).

The methodology has a good compatibility with a wide range of differently substituted either aliphatic or aromatic aldehydes, but works only with few alcohols such as methanol, ethanol, n- propanol and n-butanol.

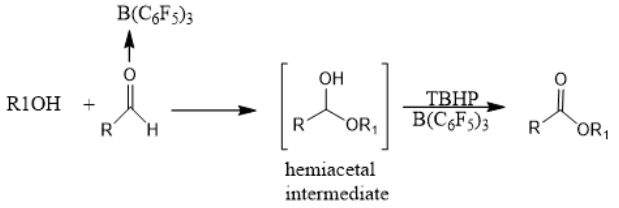


R= Aryl, Alkyl

R1= CH_3, CH_2CH_3, $(CH_2)_2CH_3$, $(CH_2)_3CH_3$

Scheme 16. $B(C_6F_5)_3$ catalyzed esterification of aldehydes.

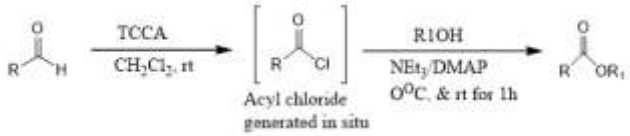
The reaction may proceed through the hemiacetal intermediate formation with the assistance of $B(C_6F_5)_3$, followed by TBHP oxidation to generate the corresponding ester (Scheme 17).



Scheme 17. A plausible reaction mechanism for $B(C_6F_5)_3$ catalyzed esterification of aldehydes

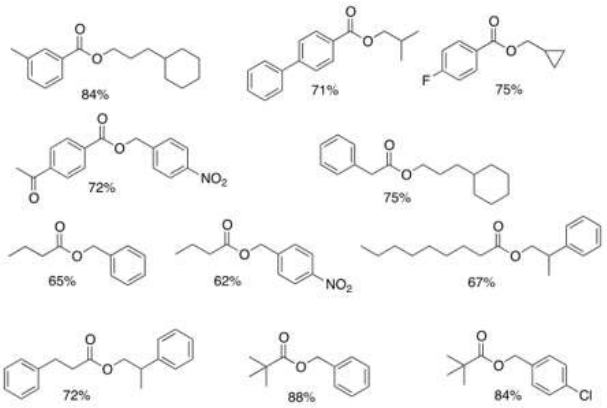
Our team created a novel effective protocol for the oxidative esterification of aldehydes with the intention of creating a more universal technique that would be suited for converting both aromatic and aliphatic aldehydes to esters (Gaspa et al., 2015). To get over the steric issues associated with the hemiacetal production, a plan was developed to find an alternative technique. We used a novel and effective technology to convert aldehydes into acyl chlorides, which were then reacted with alcohols.

When trichloroisocyanuric acid (TCCA) is used to convert aldehydes in situ into the appropriate acyl chlorides because of their interest in employing it as an oxidant and chlorinating reagent, the matching esters were then produced by reacting the acyl chlorides with the respective alcohols (Scheme 18). (Gaspa et al., 2016).



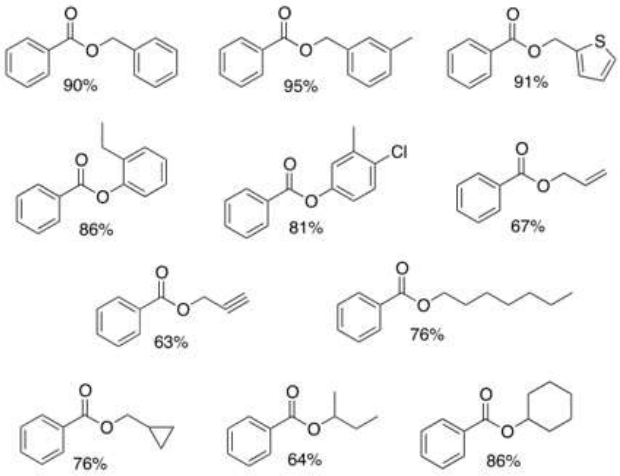
Scheme 18. Metal-free oxidative esterification of aldehydes using TCCA.

As demonstrated below, the method was used to make esters directly from activated and inactive aldehydes with a variety of alcohols.



These compounds depicted from the above scheme are selected results for metal-free oxidative esterification of aldehydes using TCCA.

Primary and secondary aliphatic, benzylic, allylic, and propargylic alcohols and phenols were successfully employed as shown in the following (Gaspa et al., 2016).



The above compounds showed the selected results for metal-free oxidative esterification of benzaldehyde and alcohols using TCCA.

The procedure appears to be highly universal and selective, uses green reagents and moderate reaction conditions, and has an optimum stoichiometric molar ratio of reactants (Gaspa et al., 2016).

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