NJC

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Cite this: *New J. Chem.*, 2019, **43**, 18072

Pd/C-catalyzed synthesis of oxamates by oxidative cross double carbonylation of alcohols and tertiary amines through C–N bond cleavage†

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Received 10th August 2019,
Accepted 16th October 2019

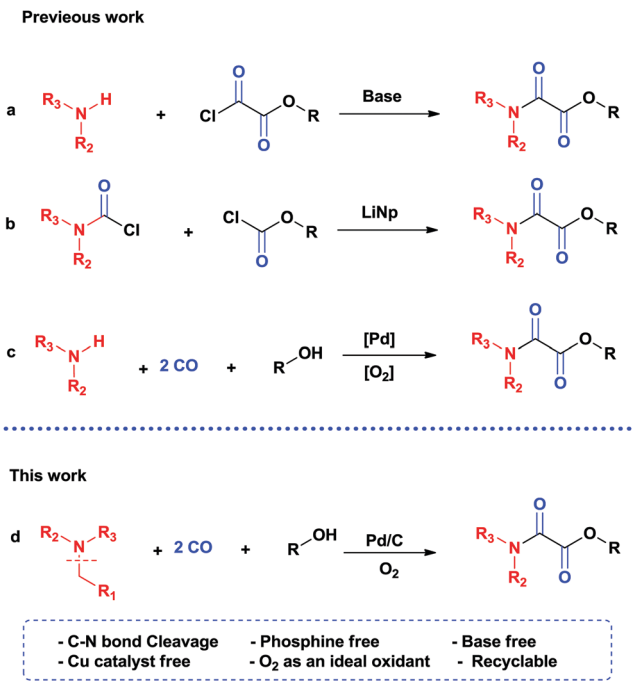
DOI: 10.1039/c9nj04156g

rsc.li/njc

An efficient synthesis of oxamates by Pd/C-catalyzed oxidative cross double carbonylation of alcohols and unactivated tertiary amines has been demonstrated. The *in situ* oxidative C–N bond cleavage of tertiary amines was achieved using molecular oxygen as an environmentally benign oxidant providing a user-friendly approach to the synthesis of oxamates. The developed protocol showed excellent activity towards the cyclic as well as aliphatic tertiary amines and long-chain alcohols. This developed protocol system is advantageous, as it is phosphine ligand free, base free, and copper-free and the Pd/C catalyst is easily recyclable. The Pd/C catalyst was recycled up to five consecutive cycles.

Introduction

Oxamates and their derivatives are significant building blocks in synthetic chemistry and their structural motifs have a widespread application in pharmaceuticals, natural products and agricultural chemicals (Scheme 1a).[1–6] They also play a crucial role in biologically active drugs, such as orally active antiallergic agents and an antimalarial agent.[7–10] The oxamates and their derivatives are also used as N- and O-functional ligands in organic transformations.[11–13] Recently, the synthesis of glycol derivatives has been demonstrated by the catalytic hydrogenation of oxamates.[14,15] Typically, those compounds are synthesized by the acylation of amines with diesters of oxalic acid or monoester of oxalyl chloride (Scheme 1b).[16–19] However, these methods are used stoichiometric reagents such as as phosgene and isocyanates, which are highly toxic and corrosive chemicals, and have serious effects on the environment as well as on human health. On the other hand, they need equimolar quantity of oxalyl chloride and alcohol and need a separate distillation assembly for the separation of the products from the reaction mixture. However, in the past two decades, several modifications have been made for the broadening of the area of carbonylation for the synthesis of oxamates and their derivatives. Recently, oxidative carbonylation has gained considerable attention from the economic point of view. Carbon monoxide (CO) is one of the most resourceful and cost-efficient C1-source that is easily available from natural gas, biomass and coal. The direct conversion of CO into the high value-added chemicals by catalytic processes becomes significant due to the fast decline of petroleum and coal resources.[20–23] Previous literature showed that there are several reports on oxidative carbonylation reactions, especially palladium-catalyzed carbonylative cross-coupling of primary/secondary amines with alcohols, for the synthesis of oxamates (Scheme 1c).[24–28]



Scheme 1 Comparison of previous protocol with current protocol.

Initially, in 1987, Murahashi and co-workers revealed oxamate synthesis by the carbonylative coupling of secondary amines with

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9nj04156g

alcohols using homogeneous palladium complexes and excess base.[26] Further, they reported the synthesis of cyclic as well as simple oxamates using a modified Pd–Cu catalyst with molecular oxygen as an effective oxidant. However, they required high CO pressure (80 kg cm^{-2}) and also trimethoxymethane as a dehydrating agent with triethylamine as a base.[27] Subsequently, Alper and co-workers established a method for the synthesis of oxamates using D-TBP (Di-*tert*-butyl Peroxide) as an oxidant in 1987.[28] However, they have faced several drawbacks including the use of a hazardous oxidant, high pressure of CO, high catalyst and ligand loading, and use of co-catalyst and base. This methodology produces a lot of side products, which leads to the decrease in the atom economy. Our group also reported the synthesis of oxamates using Pd/C and ionic liquid immobilized Pd as heterogeneous catalysts without the need of a co-catalyst under base-free conditions.[24,25] The cleavage of the highly stable C–N bond of tertiary amine is a challenging task.[29–39]

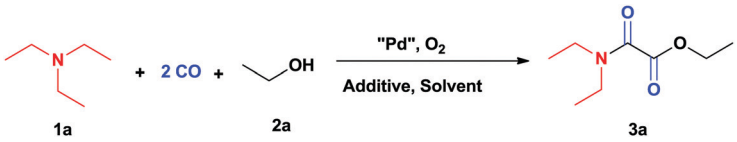
To the best of our knowledge, the synthesis of oxamates through the oxidative double carbonylation of tertiary amine with alcohol is not yet reported. This is due to the fact that the breaking of strong C–N bond of the highly stable tertiary amine and oxidative double carbonylation between the two nucleophiles are still a challenge. However, this method is routinely used in the laboratory due to its inherent features including not requiring an equimolar quantity of the reactants, not requiring the Lewis acid, low catalyst loading and wide substrate scope. However, a comprehensive literature survey reveals that there is no report on the synthesis of oxamates by the carbonylative cross-coupling of tertiary amines with alcohols.

Herein, we report an efficient synthesis of oxamates through the oxidative cross double carbonylation of cyclic as well as aliphatic tertiary amines with alcohols using Pd/C as a heterogeneous recyclable catalyst and their carbon support provides a reasonable surface area and also showed redeposition ability.[40] Reactions were progressed without the use of the phosphine ligand co-catalyst and base using O_2 as an oxidant. Generally, phosphines are not recommended under oxidative conditions because if they dissociate, they are prone to oxidation forming phosphine oxides and thus deactivating the catalyst. The catalyst was easily separable and could be recycled up to five runs.

Results and discussion

We begin the optimization reaction with triethylamine and ethanol for the synthesis of oxamates as a model reaction. For this purpose, here we have used triethylamine **1a** (1 mmol) as an *in situ* aminal source and ethyl alcohol **2a** (10 mL) as a solvent as well as nucleophile with 10 mol% Pd/C catalyst, and KI as an additive under the atmospheric pressure of $CO:O_2$ (5 : 1 atm, 6 bar) at 100 °C for 24 h, which afforded only 18% yield of the desired oxidative cross double carbonylative product **3a**. Given the unsatisfactory yield, we optimized the reaction conditions to enhance the yield of the oxamate product. Next, we moved the attention towards the study on the effects of various solvents on the model reaction. Conversely, at first, we optimized several non-polar as well as polar solvents along with alcohols (Table 1). The influence of 10 mL (3 : 7) mixture of EtOH : toluene, EtOH : THF, EtOH : 1,4-dioxane and EtOH : MeCN was studied, which provided 12%, 20%, 25% and 60% yields of the oxamate, respectively (Table 1, entries 2–5). However, acetonitrile is a polar aprotic solvent, which is necessary for such types of reactions. Polarity is required for the activation of the C–N bond and protic solvents affect the catalyst performance. We found that the mixture solvent EtOH : MeCN with a ratio of 3 : 7 (mL) was highly effective compared to other solvents. To ensure a higher yield, we further changed the EtOH : MeCN solvent ratio such as 2 : 8 and 1 : 9 (10 mL) to obtain 81% and 95% yields of the oxamate **3a**, respectively (Table 1, entries 6 and 7). It is notable that the combination of EtOH : MeCN (1 : 9) is the best solvent and afforded 95% yield of the corresponding oxamate (Table 1, entry 7). Next, we investigated the influence of catalysts and catalyst loading, and the results are explained in Table 1. It was found that 10% Pd/C catalyst was a highly efficient catalyst compared to homogeneous $PdCl_2$ and $PdCl_2(PPh_3)_2$ complexes (Table 1, entries 8 and 9). Then, the effect of loading of the Pd/C catalyst was studied ranging from 3 to 10 mol% (Table 1, entries 10 and 11). The phosphine-free 10 mol% Pd/C provided an excellent yield of **3a**. The additive plays an essential role in the oxidative carbonylation reaction; in this regard, we further investigated the effect of various additives on the model reaction. When we used NaI as an additive, it was observed that 83% yield of **3a** was obtained, while TBAI provided 91% yield (Table 1, entries 12 and 13). Next, to confirm the influence of the additive in this transformation, we carried out the reaction without an additive and failed to get the desired oxamate product (Table 1, entry 14). Next, we moved our attention towards the effect of temperature and time on the model reaction. When we increased the reaction temperature from 100 °C to 120 °C, no significant changes were observed in the yield of **3a** (Table 1 entries 16 and 17). However, when we decreased the temperature to 80 °C, only 62% yield of the product was obtained. Next, in the time study, it was observed that on decreasing the reaction time from 24 to 20 h, the yield of the products also decreased to 77% (Table 1 entry 18). Hence, temperature and time study outcomes revealed that a temperature of 100 °C and duration of 24 h were required for the completion of the reaction. Next, we performed the same reaction without an oxidant; unfortunately, the reaction did not proceed (Table 1, entry 19). Hence, we conclude that the additives and the oxidants played a crucial role in this transformation. Under 5 : 1 (6 bar) ratio of $CO:O_2$ pressure, the reaction proceeded well toward the expected product. So finally, the efficiently optimized reaction parameters are as follows: **1a** (1 mmol), **2a** (1 mL), Pd/C (10 mol%), EtOH : MeCN (1 : 9), $CO:O_2$ (1 : 5 atm) at 100 °C for 24 h. With the optimized reaction condition in hand, next, we explore whether the current protocol could be applicable for the synthesis of a range of oxamate derivatives (Table 2). Here, we have used Pd/C as a heterogeneous, recyclable catalyst along with KI as an additive using molecular oxygen as an environmentally benign oxidant. Initially, we used triethylamine, tripropylamine and tri-*n*-butyl amines that underwent double carbonylation with ethyl alcohol to provide corresponding oxamates **3a**, **3b** and **3c**,

Table 1 Optimization reaction parameters for oxamate synthesis[a,b]



Entry	Solvent	Solvent ratio	[Pd] (10 mol%)	Additive	Temp. (°C)	Time (h)	Yield[b] (%)
Effect of solvent							
1	EtOH	10 mL	10% Pd/C	KI	100	24	18
2	EtOH : Toluene	3 : 7	10% Pd/C	KI	100	24	12
3	EtOH : THF	3 : 7	10% Pd/C	KI	100	24	20
4	EtOH : dioxane	3 : 7	10% Pd/C	KI	100	24	25
5	EtOH : MeCN	3 : 7	10% Pd/C	KI	100	24	60
6	EtOH : MeCN	2 : 8	10% Pd/C	KI	100	24	81
7	EtOH : MeCN	1 : 9	10% Pd/C	KI	100	24	95
Effect of catalyst and catalyst loading							
8	EtOH : MeCN	1 : 9	$PdCl_2$	KI	100	24	68
9	EtOH : MeCN	1 : 9	$PdCl_2(PPh_3)_2$	KI	100	24	70
10[c]	EtOH : MeCN	1 : 9	10% Pd/C	KI	100	24	88
11[d]	EtOH : MeCN	1 : 9	10% Pd/C	KI	100	24	93
Effect of additive							
12	EtOH : MeCN	1 : 9	10% Pd/C	NaI	100	24	83
13	EtOH : MeCN	1 : 9	10% Pd/C	TBAI	100	24	91
14	EtOH : MeCN	1 : 9	10% Pd/C	—	100	24	—
Effect of temperature and time							
15	EtOH : MeCN	1 : 9	10% Pd/C	KI	80	24	62
16	EtOH : MeCN	1 : 9	10% Pd/C	KI	110	24	95
17	EtOH : MeCN	1 : 9	10% Pd/C	KI	120	24	95
18	EtOH : MeCN	1 : 9	10% Pd/C	KI	100	20	77
19[e]	EtOH : MeCN	1 : 9	10% Pd/C	KI	100	24	—

[a] Reaction condition: **1a** (1 mmol), **2a** (1 mL), solvent (9 mL), additive (0.5 mmol), $CO : O_2$ (5 : 1 atm). [b] Yield of the product determined by GC, GC-MS. [c] 5 mol% Pd/C. [d] 8 mol% Pd/C. [e] In the absence of O_2.

respectively, in excellent yields (Table 2, entries 1–3). Cyclic tertiary amines such as *N*-ethyl piperidine, *N*-methyl piperidine and *N*-ethyl morpholine also smoothly underwent cross double carbonylation with alcohols to provide an excellent yield of oxamate derivatives (Table 2, entries 5, 6 and 11–13). Here we observed that in the symmetrical tertiary amine, the cleavage of one of the C–N bond did not depend on the length of the alkyl chain. Next, we investigated that the unsymmetrical tertiary amine could undergo carbonylative coupling under the optimized reaction conditions. Remarkably, we observed that in unsymmetrical amines, the cleavage of the C–N bond is at the less substituted side and it gets carbonylatively coupled with alcohols, leading to oxamates (Table 2, entries 4 and 10).

Next, we focused our attention on the reactions using different alcohols. Then, triethylamine, tripropylamine and tributylamine showed successful cross carbonylation with methanol to furnish products with excellent yields (Table 2, entries 7–9). For further exploration of the substrate scope, next, we carried out the reaction between triethylamine and propanol under the optimized reaction condition, which provided 90% yield of the respective product (Table 2, entry 14). Encouraged with the abovementioned results, next, we used aromatic tertiary amines as a substrate with ethanol. Unfortunately, the reaction proceeded to 0% yield of the respective oxamates. This result indicates that aromatic amines are not suitable for the reaction (Table 2, entries 15–17).

Reaction mechanism

The mechanism of the Pd/C-catalyzed synthesis of oxamates by the oxidative carbonylation reaction was proposed according to the previous reports, as shown in Scheme 2. We proposed two reaction pathways for the cleavage of an inert tertiary amine. In path A, the lone pair electron of nitrogen of the tertiary amine directly coordinates with Pd(0) to give a Pd-iminium intermediate,[36,41,42] which on hydrolysis affords a secondary amine and an aldehyde as a byproduct.[27,36,37,43] In path B, the reaction between iodine and tertiary amine gives ammonium iodide as an intermediate.[36,44,45] Next, HI could be eliminated from ammonium iodide to obtain iminium iodide. Further, iminium iodide gets hydrolyzed to afford an aldehyde and a secondary amine.

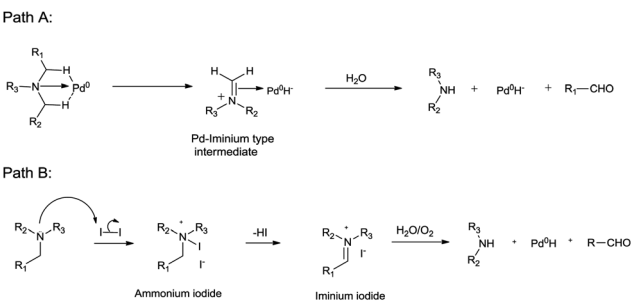
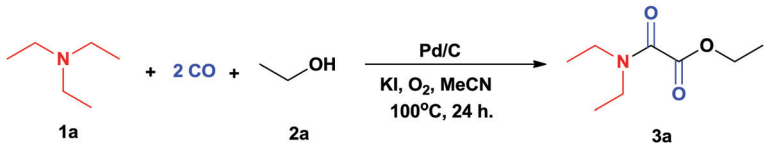


Table 2 Pd/C-catalyzed oxidative double carbonylation of tertiary amines and alcohols[a]



1a 2a 3a

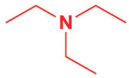
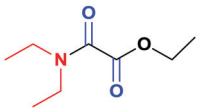
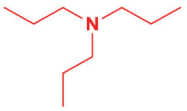
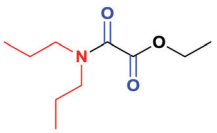
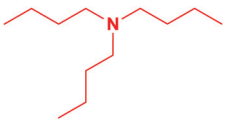
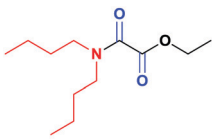
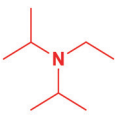
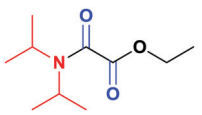
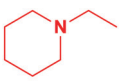
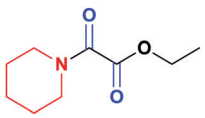
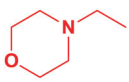
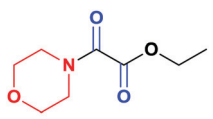
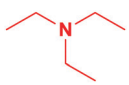
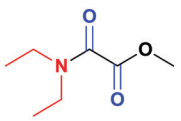
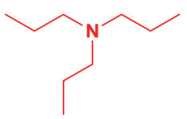
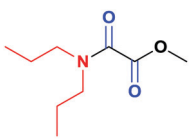
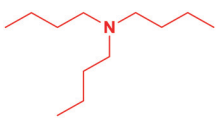
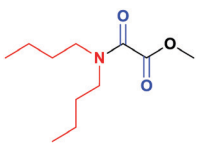
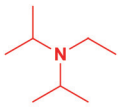
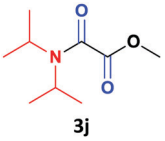
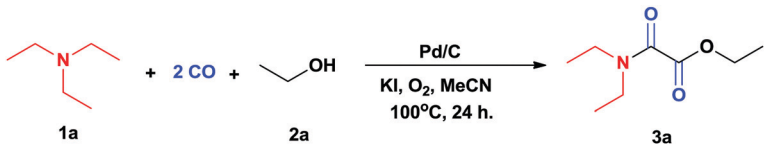
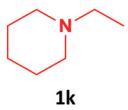
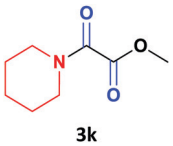
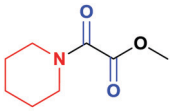
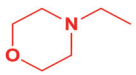
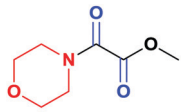
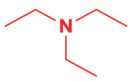
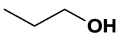
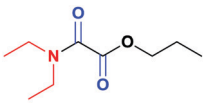
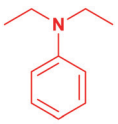
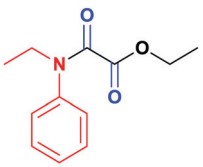
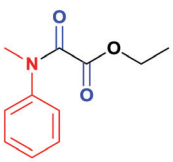
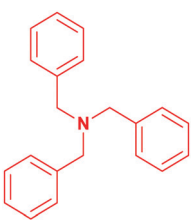
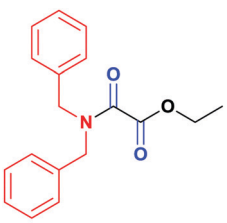
Entry	3° Amine	Alcohol	Product	Yield[b] (%)
1	 1a	 2a	 3a	93
2	 1b	2a	 3b	89
3	 1c	2a	 3c	87
4	 1d	2a	 3d	69
5	 1e	2a	 3e	81
6	 1f	2a	 3f	78
7	 1g	 2b	 3g	93
8	 1h	2b	 3h	91
9	 1i	2b	 3i	76
10	 1j	2b	 3j	70

Table 2 (*continued*)

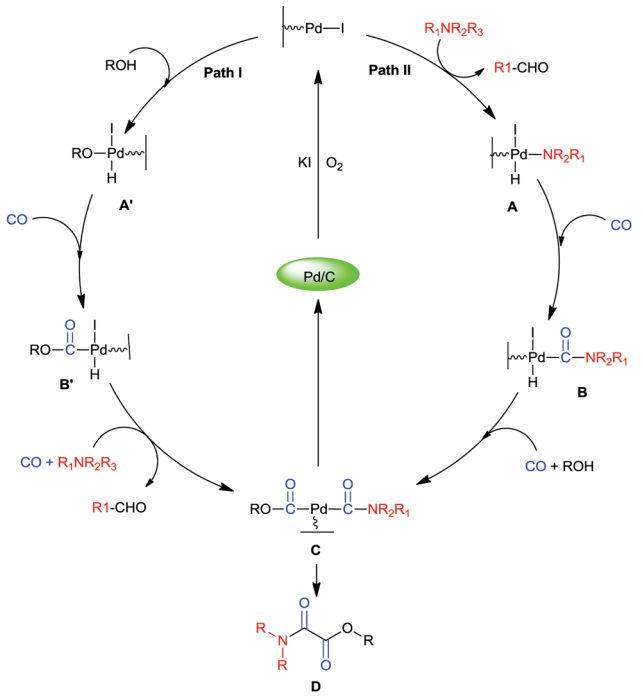


1a 2a 3a

Entry	3° Amine	Alcohol	Product	Yield[b] (%)
11	 1k	2b	 3k	84
12	 1l	2b	 3l	76
13	 1m	2b	 3m	75
14	 1n	 2c	 3n	88
15	 1os	 2a	 3o	NR
16	 1p	2a	 3p	NR
17	 1q	2a	 3q	NR

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mL), MeCN (9 mL), KI (0.5 mmol), CO/O_2 (5 : 1 atm), 100 °C, 24 h. [b] Isolated yield of the product, NR = no reaction.

In the presence of an oxidant and an additive, the species of Pd(0) gets converted into Pd(II), then oxidative addition of amines and alcohols followed by carbonylation forms species such as amoylpalladium (**A**) and alkoxy (**A′**) complex, respectively (Path I and Path II). Next, the co-ordination of CO to (**A**) or (**A′**) complex and the consequent nucleophilic attack of amine or alcohol give the alkoxycarbonylcarbamoylpalladium complex (**C**).[27,28,39,46,47] Finally reductive elimination of complex (C) to obtained oxamate (D) and recovered palladium is used for next cycle.



Scheme 2 Tentative reaction mechanism for the cross double carbonylation of tertiary amines and alcohols.

Experimental

Recyclability study of Pd/C

Next, we investigated the recyclability of the Pd/C catalyst in oxidative double carbonylation using triethylamine and ethanol as substrates under the pressure of $CO:O_2$ (5 : 1 atm) at 100 °C (Fig. 1).

After the completion of the reaction, the catalyst was separated and washed first with distilled water and then with methanol for the removal of trace impurities and was dried in an oven. For the next run, we charged the reactor with the starting material with the same catalyst. It was shown that the catalyst could be reused up to five consecutive runs with a marginal loss in its catalytic activity.

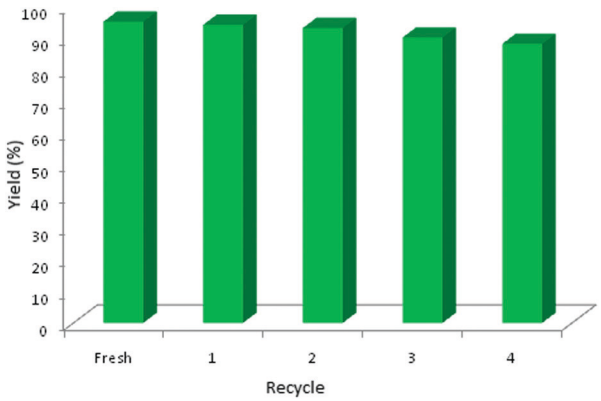


Fig. 1 Recyclability study of Pd/C.

General

The Pd/C was commercially purchased from Sigma-Aldrich. Products were monitored using TLC and GC-MS techniques and purified by column chromatography on silica (100–200 mesh). The ^1H and ^{13}C NMR spectra were recorded on 400, 500 MHz and 101, 126 MHz spectrometers, respectively, in $CDCl_3$. The products were confirmed by GC, GC-MS, and NMR spectroscopy with those of reported data.

General experimental procedure for oxamate

We took tertiary amine (1 mmol), alcohol (1 mL) and 10 mol% Pd/C as a catalyst in a 100 mL stainless steel autoclave. Then, 9 mL of acetonitrile was added as a solvent and the autoclave was closed tightly and pressurized with oxygen (1 atm) and CO (5 atm) at 100 °C for 24 h. The mixture was stirred with a mechanical stirrer with 450 rpm. After the completion of the reaction, the autoclave cooled down at room temperature and the remaining pressure was removed carefully. The reactor vessel was opened and the catalyst was separated using a centrifuge tube. Then, the residue was concentrated by a rotary evaporator. Finally, the crude product was purified by column chromatography and the separated product was confirmed by GC, GC-MS and NMR techniques.

Conclusions

In summary, we have developed a process for the synthesis of oxamate and their derivatives by oxidative *N*-dealkylation/double carbonylation of highly stable tertiary amines with alcohols. This transformation has been attained by using molecular oxygen as an environmentally benign oxidant. This is the first report where the synthesis of a wide range of oxamates *via* sp^3 C–N bond cleavage of a variety of aliphatic and cyclic tertiary amines as a secondary amine resource has been achieved. Additionally, the advantages of the developed protocol include the use of simple and easily available starting materials, low pressure of CO/O_2, not requiring external ligand and Cu-catalyst-free reaction conditions. The catalyst was easily separable and could be recycled up to five consecutive runs with a marginal loss of yield of the product.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Y. A. Kolekar gratefully acknowledges the University Grants Commission (UGC), New Delhi, India, for the award of Junior Research Fellowship (JRF).

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