Tetrahedron xxx (2014) 1–9

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Magnetic $CuFe_2O_4$ nanoparticles: a retrievable catalyst for oxidative amidation of aldehydes with amine hydrochloride salts

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ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form 17 January 2014
Accepted 22 January 2014
Available online xxx

Keywords:
Aldehydes
Amidation
Amides
Amine salts
Magnetic nano-$CuFe_2O_4$

ABSTRACT

The application of magnetic $CuFe_2O_4$ nanoparticles for the oxidative amidation of aldehydes with amine hydrochloride salts is described. A wide range of amides have been synthesized in good to excellent yields under mild conditions. Chiral amide also synthesized from its corresponding chiral amine salt with retention of the stereochemistry. In particular, the performance of the magnetic separation of the catalyst was very efficient and an alternative to time, solvent and energy-consuming separation procedures. The catalytic activity of the catalyst remains unaltered after five consecutive cycles, making it environmentally benign and widely applicable due to its efficiency, ease of handling and cost effectiveness.

1. Introduction

The development of more direct catalytic approaches towards synthesis of chemical products represents one of the key efforts of achieving chemical sustainability.[1] On the other hand, the use of more benign catalysts and the simple separation of catalysts from reaction mixtures provide both economical and ecological benefits.[2] In the last few decades, global concern for environment protection boosted the development of cost effective eco-friendly catalytic processes. In this context, magnetic nanoparticles have emerged as a new generation of catalysts or catalyst supports owing to their large surface area, easy dispersion in several solvents and more remarkably, their efficient recovery from the reaction medium by magnetic separation.[3] The magnetic nanoparticles have been widely employed as novel magnetically recoverable catalysts in traditional metal catalyzed reactions,[4] organocatalysis and enzymatic catalysis.[5] They are valuable addition to sustainable methodologies as the demand for benign nanocatalysts and their applications in synthesis is on the rise.

Amide bond is one of the most important functional groups in contemporary chemistry. It plays a major role in the elaboration and composition of biological systems such as making up of peptide bonds in proteins. It is a versatile building block in synthetic organic chemistry and also exhibits a wide range of industrial applications and pharmacological interest (Fig. 1).[6] A comprehensive survey

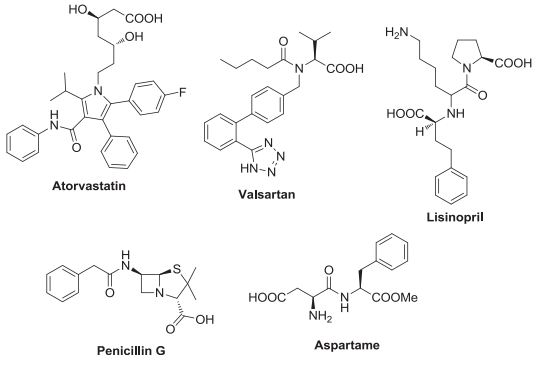

Fig. 1. Molecules containing an amide group.

revealed that the leading pharmaceutical companies Glaxo Smith-Kline, Astra Zeneca and Pfizer utilized amide bond formation in the synthesis of 66% of the drug molecules.[7] Recently, the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable identified amide formation as one of the most utilized and problematic synthesis in the pharmaceutical industry and has been labeled as a high priority research field.[8]

Traditionally, amides were prepared by the reaction of an amine with a carboxylic acid derivative (acyl halide or anhydride) or by using a coupling reagent.[9] However, these methods suffered from the lability of activated carboxylic acid derivatives, use of hazardous reagents, harsh conditions, tedious workup and generation of

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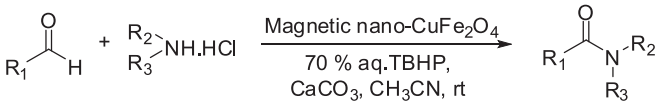
http://dx.doi.org/10.1016/j.tet.2014.01.051

wastes that not only reduce process efficiency but also pose environmental problems. To circumvent these problems, alternative strategies toward the synthesis of amides have been explored. These includes an azide based modified Staudinger reaction,[10] hydrative amide synthesis with alkynes,[11] thio-acid/ester ligation methods.[12] Due to the advanced properties, use of transition-metal catalysts has developed rapidly in organic synthesis, and was also employed to promote the formation of amides. For example, transition metal catalyzed amidations of nitriles,[13] aldehydes,[14] aldoximes,[15] alcohols,[16] alkenes,[17] alkynes,[18] and haloarenes[19] with amines have been reported. Although significant achievements were made, the high cost of transition metals and harsh reaction conditions restricted the large scale industrial application.

Among these the oxidative amidation of aldehydes with amine salts is an attractive method with practicality and potential industrial applications as both starting materials are readily available and less hazardous than those traditionally used. Recently, Li et al., reported an efficient and greener method for amide formation through the oxidative amidation of aldehydes with amine hydrochlorides using CuI–$AgIO_3$ as catalyst.[20] However, this protocol required a dual catalyst system and limited substrate scope. More recently, Chen group identified iron and copper salts as effective catalyst for the oxidative amidation of aldehydes with amine hydrochloride salts.[21]

Nanoparticles of spinel type $CuFe_2O_4$ have been recognized as magnetic material with catalytically active copper centers, which has resulted in a number of catalytic applications.[22] The characteristics of this catalyst, such as easy recovery of catalyst from the reaction mixture by using an external magnet, efficient recycling, and high stability make it very attractive for further applications. Recently, we have reported the preparation, characterization, and application of magnetic $CuFe_2O_4$ for the synthesis of tetrazoles, triazoles and aryl amines. In continuation of our research endeavors on the applications of magnetic nanocatalysts,[23] herein, we have exploited magnetic $CuFe_2O_4$ nanoparticles[22k] for the oxidative amidation of aldehydes with amine hydrochloride salts (Scheme 1).

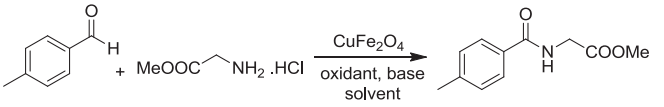


Scheme 1. Magnetically separable $CuFe_2O_4$ nanoparticles catalyzed oxidative amidation of aldehydes with amine hydrochloride salts.

2. Results and discussion

Initial experiments were performed between 4-methylbenzaldehyde and glycine methyl ester hydrochloride to determine the optimized reaction conditions and the results are summarized in Table 1. We first examined different oxidant sources and *tert*-butyl hydroperoxide (TBHP) was identified as the best-suited oxidant, while other oxidants were ineffective in giving the desired product (Table 1, entries 1–6). The effect of the bases was studied and $CaCO_3$ was found to be optimal, among other bases including Cs_2CO_3, Na_2CO_3, K_2CO_3, and $NaHCO_3$ (Table 1, entries 10–13). Screening of solvents was also carried out and it was found that acetonitrile was the best solvent among others solvents screened (Table 1, entries 14–20). Decreasing the reaction temperature from 80 °C to room temperature did not affect the reaction (Table 1, entry 6). The absence and low yield of product formation in control reactions (Table 1, entries 7–9) demonstrates the importance of catalyst, base, and oxidant for this transformation. Optimization of the reaction times showed that the reaction was completed within 10 h at room temperature as comparable yields obtained when the reaction was carried out for 24 h at the same temperature (Table 1, entries 6 and 21).

Table 1
Optimization of the reaction conditions[a]



Entry	Oxidant	Base	Solvent	Yield (%)[b]
1	H_2O_2	$CaCO_3$	CH_3CN	18
2	NaOCl	$CaCO_3$	CH_3CN	10
3	NaO_2Cl	$CaCO_3$	CH_3CN	15
4	$PhI(OAc)_2$	$CaCO_3$	CH_3CN	12
5	O_2 balloon	$CaCO_3$	CH_3CN	0
6	TBHP	$CaCO_3$	CH_3CN	86, 84[c]
7	—	$CaCO_3$	CH_3CN	0
8	TBHP	—	CH_3CN	14
9	TBHP	$CaCO_3$	CH_3CN	10[d]
10	TBHP	Cs_2CO_3	CH_3CN	15
11	TBHP	Na_2CO_3	CH_3CN	25
12	TBHP	K_2CO_3	CH_3CN	20
13	TBHP	$NaHCO_3$	CH_3CN	23
14	TBHP	$CaCO_3$	Toluene	28
15	TBHP	$CaCO_3$	*t*-BuOH	18
16	TBHP	$CaCO_3$	Dioxane	55
17	TBHP	$CaCO_3$	Water	15
18	TBHP	$CaCO_3$	THF	35
19	TBHP	$CaCO_3$	DMF	50
20	TBHP	$CaCO_3$	CH_3CN+H_2O (1:1)	38
21	TBHP	$CaCO_3$	CH_3CN	87[e]
22	TBHP	$CaCO_3$	CH_3CN	0[f], 55[g]

[a] Reaction conditions: 4-methylbenzaldehyde (1.0 mmol), glycine methyl ester HCl salt (1.2 mmol), base (1.1 mmol), oxidant (1.1 mmol), $CuFe_2O_4$ (10 mol %), solvent (2 mL), rt, under nitrogen atmosphere, 10 h.
[b] Isolated yields.
[c] Reaction was carried out at 80 °C.
[d] In the absence of catalyst.
[e] Reaction time was 24 h.
[f] Reaction with Fe_3O_4 nanoparticles (10 mol %) for 24 h.
[g] With 10 mol % CuO nanoparticles for 10 h.

The scope of the reaction was further probed under the established optimal reaction conditions. As depicted in Table 1, a wide range of aldehydes and primary amine hydrochloride salts were reacted to give secondary amides in good to excellent yields in 10 h. Benzaldehyde as well as benzaldehyde with electron-donating substituents at both *para* and *meta* positions reacted well and gave the corresponding products in 68–86% yield (Table 2, entries 1–5). Further, the reaction was extended to di- and tri-substituted aldehydes 3,5-dimethoxyaldehyde and 3,4,5-trimethoxyaldehyde that afforded the corresponding amides in 75 and 78% yield, respectively (Table 2, entries 6–7). Halogen substituted aldehydes, such as 3-fluoroaldehyde, 4-chloroaldehyde, 4-bromoaldehyde reacted smoothly and gave the desired products in 74–79% yield (Table 2, entries 8–10).

Electron withdrawing aldehydes, such as 4-cyanoaldehyde, 4-nitrobenzaldehyde, and 4-chloro-3-nitrobenzaldehyde reacted effectively to give the expected product in 60–78% yield (Table 2, entries 11–13). In addition, 2-naphthaldehyde and 4-phenyl substituted aldehyde reacted smoothly and gave the corresponding products in 72 and 70% yield, respectively (Table 2, entries 14 and 15). Hetero-aromatic and aliphatic aldehydes were reacted well and gave 70 and 68% yield of amide (Table 2, entries 16 and 17). The reaction between hindered aromatic aldehydes and glycine methyl ester hydrochloride also led to the corresponding amide formation in 72–75% yield (Table 2, entries 18–20).

When the oxidative amidation reaction was applied to L-valine methyl ester, the reaction proceeded smoothly in 86% (ee=98%) yield with the retention of configuration (Table 2, entry 23). Good activity of the catalyst for the synthesis of secondary amides from primary amine salts inspired us, to explore its catalytic activity for the synthesis of tertiary amides, yielding the desired amides in

Please cite this article in press as: Suresh Kumar, A.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.01.051

Table 2
Magnetically separable $CuFe_2O_4$-catalyzed synthesis of secondary amides from aldehydes and primary amine hydrochloride salts[a]

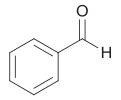
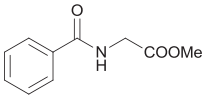
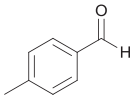
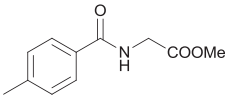
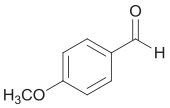
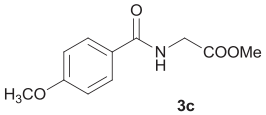
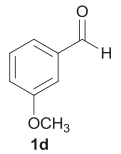
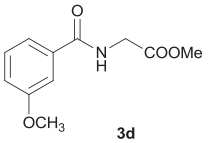
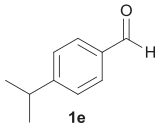
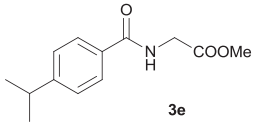
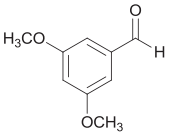
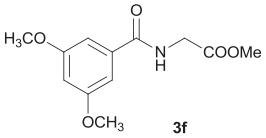
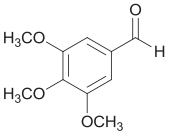
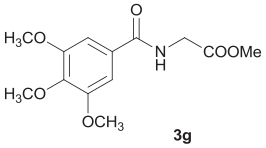
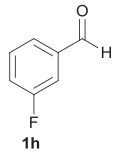
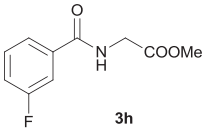
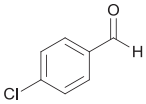
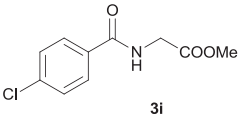
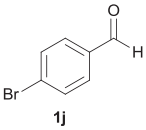
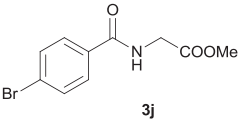
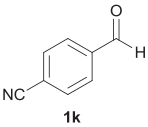
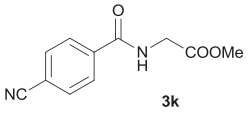
Entry	Aldehyde	Amine salt	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	82
2	 **1b**	**2a**	 **3b**	86
3	 **1c**	**2a**	 **3c**	68
4	 **1d**	**2a**	 **3d**	72
5	 **1e**	**2a**	 **3e**	80
6	 **1f**	**2a**	 **3f**	75
7	 **1g**	**2a**	 **3g**	78
8	 **1h**	**2a**	 **3h**	74
9	 **1i**	**2a**	 **3i**	76
10	 **1j**	**2a**	 **3j**	79
11	 **1k**	**2a**	 **3k**	60

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Table 2 (*continued*)

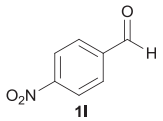
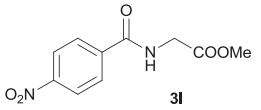
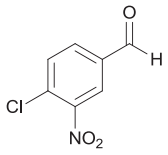
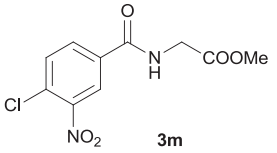
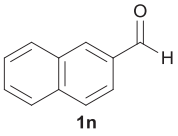
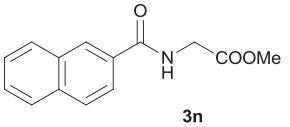
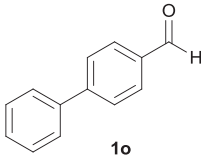
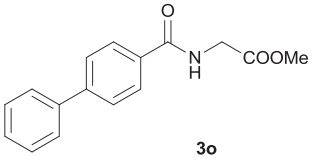
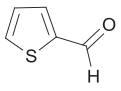
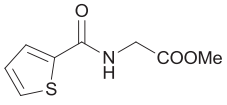
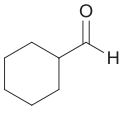
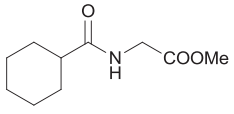
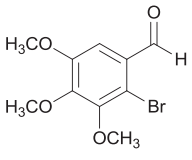
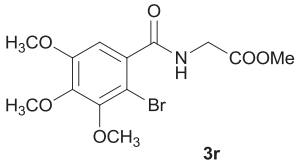
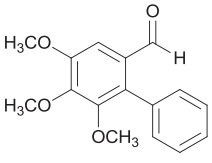
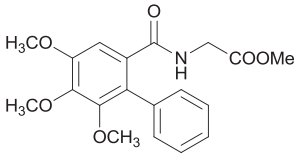
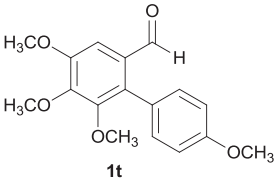
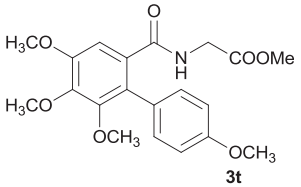
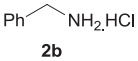
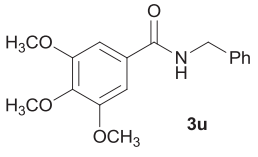
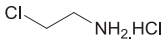
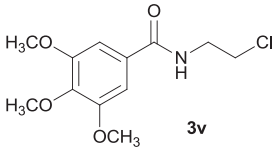
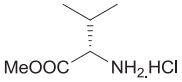
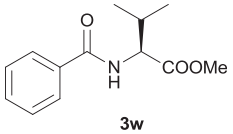
Entry	Aldehyde	Amine salt	Product	Yield (%)[b]
12	 **1l**	**2a**	 **3l**	78
13	 **1m**	**2a**	 **3m**	72
14	 **1n**	**2a**	 **3n**	72
15	 **1o**	**2a**	 **3o**	70
16	 **1p**	**2a**	 **3p**	70
17	 **1q**	**2a**	 **3q**	68
18	 **1r**	**2a**	 **3r**	75
19	 **1s**	**2a**	 **3s**	72
20	 **1t**	**2a**	 **3t**	74
21	**1g**	 **2b**	 **3u**	78, 75[c]

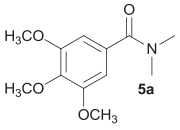
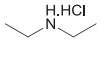
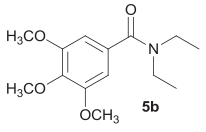
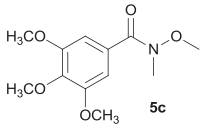
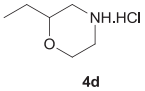
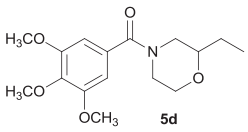
Table 2 (*continued*)

Entry	Aldehyde	Amine salt	Product	Yield (%)[b]
22	**1g**	 **2b**	 **3v**	82
23	**1a**	 **2b**	 **3w**	86

[a] Reaction conditions: aldehyde (1.0 mmol), primary amine HCl salt (1.2 mmol), $CaCO_3$ (1.1 mmol), TBHP (1.1 mmol), $CuFe_2O_4$ (10 mol %), CH_3CN (2 mL), rt, under nitrogen atmosphere, 10 h.
[b] Isolated yields.
[c] Reaction was carried out by in situ HCl salt formation.

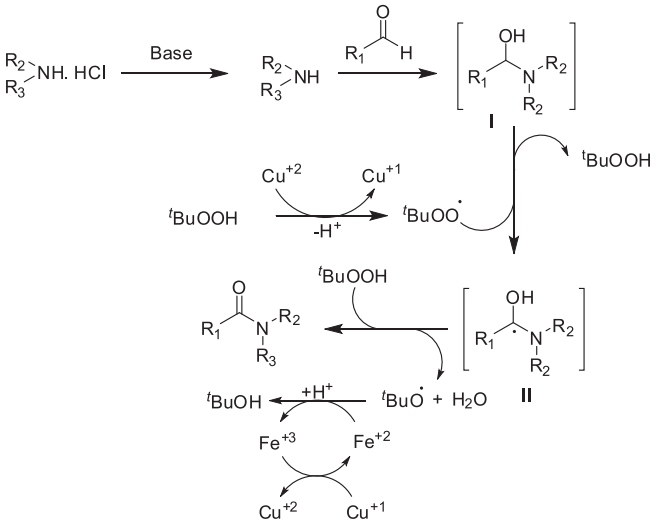
69–73% yield (Table 3, entries 1–4). We investigated the reaction between 3,4,5-trimethoxybenzaldehyde and benzyl amine and observed no formation of the corresponding product. Generally it is known that amines undergo *N*-oxidative decomposition or imine formation in the presence of TBHP.[24] Hence, the use of amine salts is crucial for this oxidative amidation, as it is less prone to oxidation by TBHP.[24] The use of insoluble base $CaCO_3$ further slows down the formation of the amine and thus minimizes the undesired amine oxidation reactions. Further, when the reaction was carried out via in situ generated HCl salt of benzyl amine[21] the corresponding amide was obtained in yields comparable to that obtained with commercially available amine salt (Table 2, entry 21). So, all the reactions were carried out with commercially available amine salts only.

Table 3
Magnetically separable $CuFe_2O_4$-catalyzed synthesis of tertiary amides from secondary amine hydrochloride salts and 3,4,5-trimethoxybenzaldehyde[a]

Entry	Amine salt	Product	Yield (%)[b]
1	 **4a**	 **5a**	73
2	 **4b**	 **5b**	71
3	 **4c**	 **5c**	69
4	 **4d**	 **5d**	70

[a] Reaction conditions: 3,4,5-trimethoxybenzaldehyde (1.0 mmol), secondary amine hydrochloride salt (1.2 mmol), $CaCO_3$ (1.1 mmol), TBHP (1.1 mmol), $CuFe_2O_4$ (10 mol %), CH_3CN (2 mL), rt, under nitrogen atmosphere, 10 h.
[b] Isolated yields.

To understand the role of iron in the present catalytic system, we carried out two independent reactions with 10 mol % of nano Fe_3O_4 and nano CuO catalysts under the optimized reaction conditions. As can be seen in Table 1, no yield was observed with nano Fe_3O_4, whereas nano CuO (entry 22) afforded 55% of the desired product; clearly indicating that Cu is the active catalytic center in this reaction. An increase in yield (Table 1, entry 6) with $CuFe_2O_4$ nanoparticles shows that iron plays a constructive role, possibly in the reoxidation of copper during the catalytic cycle. On the basis of these results, together with literature reports,[20,21,25] we propose a plausible mechanism as shown in Scheme 2. Initially, in the presence of $CaCO_3$, the amine salt is converted to free amine that then reacts with the aldehyde and forms hemi-aminal intermediate (I). Cu^{+2} metal center catalysis the heterolytic cleavage of TBHP to *tert*-butyl peroxide radical and a proton.[25a] The *tert*-butyl peroxide radical abstracts a proton from hemi-aminal (I) to give radical intermediate (II). This intermediate (II), further undergoes oxidation to form an amide in the presence of $CuFe_2O_4$ catalyst via a free-radical mechanism. The free-radical nature of the reaction is confirmed by the addition of 1 equiv of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), which completely inhibited the formation of the amide product.



Scheme 2. Plausible mechanism for the $CuFe_2O_4$-catalyzed oxidative amidation of aldehydes with amine salts.

After establishing the activity and versatility of the $CuFe_2O_4$ catalyst for oxidative amidation of aldehydes, its recyclability was subsequently tested by recycling and reuse of the catalyst in the reaction between 4-methylbenzaldehyde and glycine methyl ester hydrochloride under the optimized reaction conditions. For this,

after completion of the reaction, the catalyst was separated by simple decantation using an external magnet, washed with ethyl acetate, dried under at 50 °C under vacuum to remove residual solvents and subjected to the next cycle. The $CuFe_2O_4$ catalyst could be reused up to five cycles without any significant loss of catalytic activity (Fig. 2). Atomic absorption spectroscopy (AAS) was employed to determine the copper content of $CuFe_2O_4$ nanoparticles, and it was found to be 27.30%. The leaching of the metal after the third cycle was determined by AAS and was found to be negligible (0.042%).

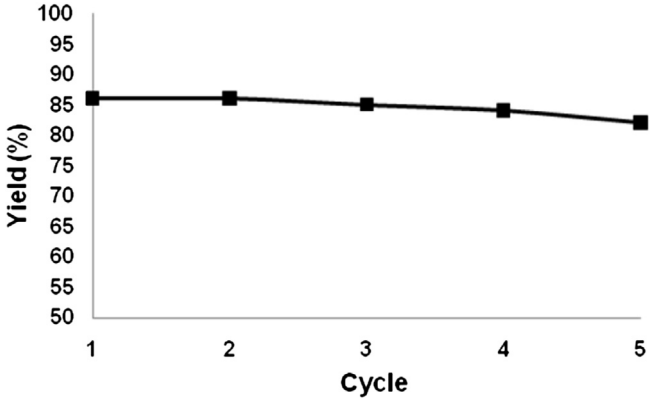


Fig. 2. Recyclability and reusability of magnetic nano-$CuFe_2O_4$ catalyst.

3. Conclusion

In conclusion, we have developed a simple and efficient protocol for the oxidative amidation of aldehydes with amine hydrochloride salts using magnetically separable $CuFe_2O_4$ nanoparticles. This catalyst has been used for the synthesis of both secondary and tertiary amides in good to excellent yields. Furthermore, this method was applied in the oxidative amidation of chiral amine salt in which the stereochemistry was retained in the resulting amide product. Easy magnetic separation of the catalyst eliminates the requirement of catalyst filtration after completion of the reaction, which is an additional green attribute of this protocol.

4. Experimental section

4.1. General remarks

All chemicals were purchased from Sigma–Aldrich and S.D Fine Chemicals, Pvt. Ltd. India and used as received. ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F_{254} plates. The IR spectra of all compounds were recorded on a Perkin–Elmer, Spectrum GX FTIR spectrometer. The IR values are reported in reciprocal centimeters (cm^{-1}). The ^1H, ^{13}C NMR spectra were recorded on a Bruker-Avance 300 MHz Spectrometer. Chemical shifts (δ) are reported in parts per million, using TMS (δ=0) as an internal standard in $CDCl_3$. ESI mass spectra were recorded on a Finnigan LCQ Advantagemax spectrometer. High-resolution mass spectra (HRMS) were recorded on QSTAR XL Hybrid MS/MS mass spectrometer. All products reported showed ^1H NMR and ^{13}C NMR spectra in agreement with the assigned structures. The purity of compounds was determined by HRMS and all tested compounds yielded data consistent with a purity of at least 95% compared with the theoretical values.

4.2. General procedure for the oxidative amidation of aldehydes with amine hydrochloride salts

To a mixture of primary amine hydrochloride salt (1.2 mmol), $CuFe_2O_4$ (10 mol %) and $CaCO_3$ (1.1 mmol) in acetonitrile (2 mL) were added aldehyde (1 mmol) and TBHP (70 wt % in H_2O, 1.1 mmol) under nitrogen atmosphere, at room temperature. The reaction vessel was capped and allowed to stir at room temperature for 10 h. The catalyst was separated with an external magnet after completion of the reaction. The volatiles were removed under reduced pressure, and the crude product was purified by column chromatography on silica.

*4.2.1. Methyl 2-benzamidoacetate (**3a**).*[21] Colorless oil. IR (Neat): 3339, 3064, 2954, 1749, 1649, 1538, 1490, 1439, 1371, 1313, 1213, 1183, 1078, 1006, 975, 719, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 4.25 (d, 2H, J=5.0 Hz), 6.79 (br s, 1H), 7.40–7.47 (m, 2H), 7.49–7.54 (m, 1H), 7.76–7.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.4, 52.1, 126.9, 128.2, 131.5, 133.3, 167.7, 170.3. ESI-MS (m/z): 194 $[M+H]^+$.

*4.2.2. Methyl 2-(4-methylbenzamido)acetate (**3b**).*[21] White solid. Mp 93–95 °C. IR (KBr): 3272, 3076, 2925, 1751, 1625, 1545, 1472, 1324, 1209, 1111, 989, 841, 763, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.80 (s, 3H), 4.25 (d, 2H, J=5.2 Hz), 6.69 (br s, 1H), 7.42 (d, 2H, J=8.3 Hz), 7.72 (d, 2H, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 41.6, 52.4, 127.0, 129.2, 130.7, 142.2, 167.3, 170.0. ESI-MS (m/z): 230 $[M+Na]^+$.

*4.2.3. Methyl 2-(4-methoxybenzamido)acetate (**3c**).*[21] White solid. Mp 100–102 °C. IR (KBr): 3270, 2925, 1749, 1642, 1545, 1438, 1328, 1265, 1177, 1024, 975, 849, 772, 675 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 3.85 (s, 3H), 4.23 (d, 2H, J=5.0 Hz), 6.73 (br s, 1H), 6.92 (d, 2H, J=8.8 Hz), 7.78 (d, 2H, J=8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.2, 55.2, 113.6, 125.7, 128.8, 162.2, 167.0, 170.6. ESI-MS (m/z): 224 $[M+H]^+$.

*4.2.4. Methyl 2-(3-methoxybenzamido)acetate (**3d**).* Colorless oil. IR (Neat): 3336, 3073, 2953, 1749, 1649, 1538, 1486, 1437, 1370, 1312, 1211, 1147, 1041, 1013, 979, 756, 688 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.84 (s, 3H), 4.24 (d, 2H, J=5.1 Hz), 6.76 (br s, 1H), 7.02–7.09 (s, 1H), 7.32–7.36 (m, 2H), 7.37–7.40 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.1, 55.1, 112.2, 117.7, 118.8, 129.3, 134.8, 159.5, 167.4, 170.3. ESI-MS (m/z): 224 $[M+H]^+$. HRMS (ESI, 70 eV): calcd $C_{11}H_{14}O_4N$=224.09173, found: 224.09041.

*4.2.5. Methyl 2-(4-isopropylbenzamido)acetate (**3e**).* White solid. Mp 60–62 °C. IR (KBr): 3265, 3029, 2962, 1758, 1642, 1542, 1458, 1370, 1207, 1181, 1012, 982, 861, 710, 681 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 3H), 1.27 (s, 3H), 2.95 (sep, 1H, J=6.8 Hz), 3.80 (s, 3H), 4.25 (d, 2H, J=5.0 Hz), 6.70 (br s, 1H), 7.29 (d, 2H, J=8.3 Hz), 7.75 (d, 2H, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.5, 33.9, 41.5, 52.1, 126.4, 127.1, 130.9, 152.8, 167.5, 170.5. ESI-MS (m/z): 236 $[M+H]^+$. HRMS (ESI, 70 eV): calcd $C_{13}H_{18}O_3N$=236.12812, found: 236.12791.

*4.2.6. Methyl 2-(3,5-dimethoxybenzamido)acetate (**3f**).* Pale yellow solid. Mp 98–100 °C. IR (KBr): 3439, 3011, 2924, 1732, 1659, 1592, 1453, 1347, 1201, 1154, 1067, 1014, 968, 842, 763, 675 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 3.83 (s, 6H), 4.24 (d, 2H, J=5.2 Hz), 6.59 (t, 1H, J=2.2 Hz), 6.65 (br s, 1H), 6.93 (d, 2H, J=2.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.1, 55.2, 103.7, 104.8, 135.5, 160.6, 167.4, 170.3. ESI-MS (m/z): 254 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{12}H_{16}O_5N$=254.10230, found: 254.10101.

*4.2.7. Methyl 2-(3,4,5-trimethoxybenzamido)acetate (**3g**).* White solid. Mp 109–111 °C. IR (KBr): 3286, 2947, 1751, 1638, 1585, 1464,

1345, 1211, 1128, 1078, 990, 846, 769, 664 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.88 (s, 3H), 3.89 (s, 6H), 4.23 (d, 2H, J=5.1 Hz), 6.75 (br s, 1H), 7.04 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.4, 52.1, 55.8, 60.5, 104.2, 128.5, 140.5, 152.7, 167.1, 170.5. ESI-MS (m/z): 284 $[M+H]^+$. HRMS (ESI, 70 eV): calcd $C_{13}H_{18}O_6N$=284.11286, found: 284.11220.

*4.2.8. Methyl 2-(3-fluorobenzamido)acetate (**3h**).* Colorless oil. IR (Neat): 3343, 3074, 2955, 1750, 1653, 1541, 1483, 1440, 1371, 1221, 1136, 1078, 1015, 981, 756, 680 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.25 (d, 2H, J=4.9 Hz), 6.70 (br s, 1H), 7.18–7.24 (m, 1H), 7.39–7.46 (m, 1H), 7.51–7.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.3, 114.3 (d, J=22.7 Hz), 118.6 (d, J=2.7 Hz), 122.5, 130.9 (d, J=7.2 Hz), 135.5 (d, J=6.3 Hz), 162.4 (d, J=247.0 Hz), 166.5, 170.3. ESI-MS (m/z): 234 $[M+Na]^+$. HRMS (ESI, 70 eV): calcd for $C_{10}H_{10}O_3NFNa$=234.05369, found: 234.05292.

*4.2.9. Methyl 2-(4-chlorobenzamido)acetate (**3i**).*[21] White solid. Mp 121–123 °C. IR (KBr): 3277, 3088, 2924, 1750, 1648, 1552, 1437, 1365, 1172, 1091, 1008, 978, 847, 794, 666, 554 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 4.22 (d, 2H, J=5.0 Hz), 6.95 (br s, 1H), 7.39 (d, 2H, J=8.4 Hz), 7.55 (d, 2H, J=8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.3, 128.4, 128.6, 131.7, 137.9, 166.5, 170.4. ESI-MS (m/z): 228 $[M+H]^+$.

*4.2.10. Methyl 2-(4-bromobenzamido)acetate (**3j**).*[21] White solid. Mp 108–110 °C. IR (KBr): 3267, 3090, 2945, 1750, 1646, 1558, 1482, 1435, 1368, 1331, 1208, 1168, 1066, 1010, 978, 761, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.23 (d, 2H, J=5.1 Hz), 6.76 (br s, 1H), 7.57 (d, 2H, J=8.6 Hz), 7.68 (d, 2H, J=8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.6, 52.4, 126.5, 128.6, 131.7, 132.2, 166.5, 170.4. ESI-MS (m/z): 271 $[M+H]^+$.

*4.2.11. Methyl 2-(4-cyanobenzamido)acetate (**3k**).*[21] White solid. Mp 159–161 °C. IR (KBr): 3284, 3093, 2953, 2233, 1745, 1654, 1552, 1435, 1370, 1214, 1075, 1012, 970, 863, 770, 699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 4.26 (d, 2H, J=5.0 Hz), 6.83 (br s, 1H), 7.75 (d, 2H, J=8.3 Hz), 7.92 (d, 2H, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 52.3, 115.3, 117.8, 127.7, 132.4, 137.4, 165.6, 170.1. ESI-MS (m/z): 219 $[M+H]^+$.

*4.2.12. Methyl 2-(4-nitrobenzamido)acetate (**3l**).* Pale yellow solid. Mp 148–151 °C. IR (KBr): 3304, 3105, 2935, 1744, 1658, 1551, 1491, 1351, 1214, 1196, 1010, 966, 729, 684 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 4.28 (d, 2H, J=5.0 Hz), 6.84 (br s, 1H), 7.99 (d, 2H, J=8.8 Hz), 8.31 (d, 2H, J=8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.8, 52.6, 123.8, 128.3, 139.1, 149.1, 165.4, 170.1. ESI-MS (m/z): 239 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{10}H_{11}O_5N_2$=239.06625, found: 239.06723.

*4.2.13. Methyl 2-(4-chloro-3-nitrobenzamido)acetate (**3m**).* Pale yellow solid. Mp 125–127 °C. IR (KBr): 3327, 3084, 2925, 2111, 1740, 1642, 1546, 1478, 1404, 1364, 1223, 1113, 1042, 970, 843, 743, 641 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 4.25 (d, 2H, J=5.1 Hz), 7.10 (br s, 1H), 7.46 (d, 1H, J=8.3 Hz), 7.97 (dd, 1H, J=2.0 Hz, 8.3 Hz), 8.33 (d, 1H, J=2.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 52.6, 124.3, 130.4, 131.4, 132.2, 133.2, 147.7, 164.2, 170.2. ESI-MS (m/z): 295 $[M+Na]^+$. HRMS (ESI, 70 eV): calcd for $C_{10}H_9O_5N_2ClNa$=295.00922, found: 295.00885.

*4.2.14. Methyl 2-(2-naphthamido)acetate (**3n**).* White solid. Mp 94–96 °C. IR (KBr): 3318, 3046, 2925, 1746, 1643, 1543, 1435, 1363, 1211, 1068, 961, 898, 786, 648 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.32 (d, 2H, J=5.3 Hz), 6.85 (br s, 1H), 7.42–7.47 (m, 1H), 7.50–7.57 (m, 2H), 7.65–7.68 (m, 1H), 7.84–7.88 (m, 1H), 7.92 (d, 1H, J=8.2 Hz), 8.36 (d, 1H, J=8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.8, 124.5, 125.1, 125.2, 126.2, 127.0, 128.1, 129.9, 130.7, 133.3, 133.4, 169.6. 170.2. ESI-MS (m/z): 244 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{14}H_{14}O_3N$=244.09682, found: 244.09517.

*4.2.15. Methyl 2-(biphenyl-4-ylcarboxamido)acetate (**3o**).* White solid. Mp 118–120 °C. IR (KBr): 3327, 2949, 1766, 1647, 1537, 1441, 1379, 1210, 1006, 973, 852, 748, 688 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 4.27 (d, 2H, J=4.9 Hz), 6.89 (br s, 1H), 7.38 (t, 1H, J=7.1 Hz), 7.42–7.48 (m, 2H), 7.57–7.66 (m, 4H), 7.88 (d, 2H, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.2, 126.9, 127.5, 127.8, 128.7, 130.3, 132.0, 139.6, 144.3, 167.8, 170.5. ESI-MS (m/z): 292 $[M+Na]^+$. HRMS (ESI, 70 eV): calcd for $C_{16}H_{15}O_3NNa$=292.09441, found: 292.09332.

*4.2.16. Methyl 2-(thiophene-2-carboxamido)acetate (**3p**).* White solid. Mp 94–96 °C. IR (KBr): 3093, 2925, 2854, 1726, 1644, 1539, 1440, 1370, 1226, 1160, 1081, 978, 857, 728 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 4.22 (d, 2H, J=5.3 Hz), 6.76 (br s, 1H), 7.04–7.10 (m, 1H), 7.46–7.52 (m, 1H), 7.56–7.59 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.3, 52.1, 127.5, 128.5, 130.3, 137.8, 162.1, 170.3. ESI-MS (m/z): 222 $[M+Na]^+$. HRMS (ESI, 70 eV): calcd for $C_8H_9O_3NNaS$=222.01954, found: 222.01820.

*4.2.17. Methyl 2-(cyclohexanecarboxamido)acetate (**3q**).*[21] White solid. Mp 102–104 °C. IR (KBr): 3283, 3077, 2930, 2853, 1762, 1642, 1595, 1442, 1367, 1242, 1206, 1180, 1010, 915, 845, 719, 685 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.25–1.52 (m, 5H), 1.73–1.95 (m, 5H), 2.09–2.23 (m, 1H), 3.76 (s, 3H), 4.04 (d, 2H, J=5.0 Hz), 6.01 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.4, 25.5, 29.3, 40.9, 44.9, 52.1, 170.5, 176.3. ESI-MS (m/z): 200 $[M+H]^+$.

*4.2.18. Methyl 2-(2-bromo-3,4,5-trimethoxybenzamido)acetate (**3r**).* White solid. Mp 115–117 °C. IR (KBr): 3255, 3075, 2932, 1730, 1644, 1545, 1483, 1387, 1239, 1105, 1006, 936, 834, 754, 699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 3.88 (s, 3H), 3.90 (s, 3H), 3.91 (s, 3H), 4.27 (d, 2H, J=5.0 Hz), 6.75 (br s, 1H), 7.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 52.4, 52.6, 61.0 (2C), 106.4, 108.8, 131.9, 144.8, 151.0, 152.8, 167.0, 169.9. ESI-MS (m/z): 362 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{13}H_{17}O_6NBr$=362.02338, found: 362.02104.

*4.2.19. Methyl 2-(4,5,6-trimethoxy-biphenyl-2-ylcarboxamido)acetate (**3s**).* Pale yellow solid. Mp 122–124 °C. IR (KBr): 3230, 3054, 2936, 1755, 1640, 1567, 1480, 1437, 1368, 1200, 1142, 1092, 1005, 933, 852, 709 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 3H), 3.65 (s, 3H), 3.84 (d, 2H, J=4.9 Hz), 3.94 (s, 3H), 3.95 (s, 3H), 5.66 (br s, 1H), 7.20 (s, 1H), 7.32–7.38 (m, 3H), 7.41–7.45 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 52.2, 126.9, 127.5, 127.8, 128.7, 130.3, 132.0, 139.6, 144.3, 167.8, 170.5. ESI-MS (m/z): 360 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{19}H_{22}O_6N$=360.14416, found: 360.14485.

*4.2.20. Methyl 2-(4,4′,5,6-tetramethoxy-biphenyl-2-ylcarboxamido) acetate (**3t**).* Pale yellow solid. Mp 127–129 °C. IR (KBr): 3241, 3075, 2927, 1747, 1643, 1565, 1485, 1400, 1347, 1210, 1179, 1094, 1027, 993, 846, 739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.576 (s, 3H), 3.66 (s, 3H), 3.85 (s, 3H), 3.88 (d, 2H, J=5.0 Hz), 3.92 (s, 3H), 3.94 (s, 3H), 5.74 (br s, 1H), 6.99 (d, 2H, J=8.3 Hz), 7.18 (s, 1H), 7.27 (d, 2H, J=8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 52.1, 55.1, 56.0, 60.8, 60.9, 108.2, 113.9, 126.9, 127.4, 130.1, 131.0, 144.3, 151.3, 152.6, 159.1, 168.3, 169.5. ESI-MS (m/z): 390 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{20}H_{24}O_7N$=390.15473, found: 390.15568.

*4.2.21. N-Benzyl-3,4,5-trimethoxybenzamide (**3u**).* White solid. Mp 120–122 °C. IR (KBr): 3303, 2925, 2853, 1730, 1626, 1581, 1498, 1458, 1331, 1235, 1127, 1077, 989, 840, 751, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 6H), 3.86 (s, 3H), 4.61 (d, 2H, J=5.6 Hz),

6.67 (br s, 1H), 7.04 (s, 2H), 7.27–7.37 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 43.6, 55.7, 60.4, 104.3, 126.9, 127.3, 128.2, 129.3, 138.2, 140.3, 152.7, 166.9. ESI-MS (m/z): 302 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{17}H_{20}O_4N$=302.13868, found: 302.13927.

*4.2.22. N-(2-Chloroethyl)-3,4,5-trimethoxybenzamide (**3v**).* Pale yellow solid. Mp 116–118 °C. IR (KBr): 3301, 2925, 2854, 1715, 1632, 1584, 1462, 1336, 1235, 1129, 992, 850, 767, 653 cm^{-1}. ^{1}H NMR (300 MHz, CDCl3): δ 3.73–3.77 (m, 2H), 3.78–3.81 (m, 2H), 3.89 (s, 3H), 3.91 (s, 6H), 6.65 (br s, 1H), 7.02 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 43.7, 56.2, 60.8, 104.4, 129.3, 140.9, 153.0, 167.3. ESI-MS (m/z): 296 $[M+Na]^+$. HRMS (ESI, 70 eV): calcd for $C_{12}H_{16}O_4N$-ClNa=296.06556, found: 296.06556.

*4.2.23. (S)-Methyl-2-benzamido-3-methylbutanoate (**3w**).*[21] White solid. Mp 114–116 °C. IR (KBr): 3347, 2967, 2872, 1739, 1641, 1521, 1489, 1360, 1203, 1150, 994, 894, 733 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, 6H, J=6.9 Hz), 2.15–2.39 (m, 1H), 3.78 (s, 3H), 4.79 (dd, 1H, J=4.9 Hz, 8.6 Hz), 6.67 (d, 1H, J=7.7 Hz), 7.35–7.61 (m, 3H), 7.67–7.95 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8, 18.8, 31.4, 52.0, 57.3, 126.9, 128.4, 131.5, 133.9, 176.9, 172.5. ESI-MS (m/z): 236 $[M+H]^+$. $[\alpha]_D^{25}$ +42.3 (c 1, $CHCl_3$) [lit.[21] $[\alpha]_D^{24}$ +43.0 (c 1, $CHCl_3$)]. ee=98%.

*4.2.24. 3,4,5-Trimethoxy-N,N-dimethylbenzamide (**5a**).*[26] Light yellow oil. IR (neat): 2931, 1721, 1632, 1585, 1494, 1411, 1327, 1237, 1168, 1127, 1005, 970, 862, 766 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (br s, 3H), 3.11 (br s, 3H), 3.86 (s, 3H), 3.87 (s, 6H), 6.65 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.3, 39.6, 56.1, 60.8, 104.3, 131.5, 138.9, 153.1, 171.3. ESI-MS (m/z): 240 $[M+H]^+$.

*4.2.25. N,N-Diethyl-3,4,5-trimethoxybenzamide (**5b**).*[26] Light yellow oil. IR (neat): 2933, 1724, 1630, 1584, 1461, 1413, 1332, 1236, 1163, 1127, 1007, 927, 819, 765 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (br s, 6H), 3.41 (br d, 4H), 3.86 (s, 3H), 3.87 (s, 6H), 6.60 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.8, 14.2, 39.3, 43.2, 56.1, 60.8, 103.5, 132.5, 138.6, 153.1, 170.9. ESI-MS (m/z): 268 $[M+H]^+$.

*4.2.26. N-3,4,5-Tetramethoxy-N-methylbenzamide (**5c**).* Colorless oil. IR (neat): 2926, 2854, 1762, 1639, 1582, 1460, 1414, 1374, 1238, 1126, 1003, 938, 858, 747 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (s, 3H), 3.60 (s, 3H), 3.89 (s, 9H), 6.98 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.9, 56.1, 60.8, 61.0, 105.8, 128.9, 140.0, 152.6, 169.2. ESI-MS (m/z): 256 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{12}H_{18}O_5N$=256.11850, found: 256.11727.

*4.2.27. (2-Ethylmorpholino)(3,4,5-trimethoxyphenyl)methanone (**5d**).* Colorless oil. IR (neat): 2926, 2853, 1723, 1633, 1583, 1462, 1419, 1328, 1232, 1127, 1103, 966, 862, 764 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91–1.03 (m, 3H), 1.55 (br s, 3H), 1.82 (br s, 2H), 3.45 (br d, 4H), 3.86 (s, 3H), 3.87 (s, 6H), 6.62 (s, 2H). 13C NMR (75 MHz, $CDCl_3$): δ 9.4, 26.0, 46.6, 47.8, 56.1, 60.7, 66.4, 77.2, 104.2, 130.6, 139.1, 153.2, 169.9. ESI-MS (m/z): 310 $[M+H]^+$. HRMS (ESI, 70 eV): calcd for $C_{16}H_{24}O_5N$=310.16545, found: 310.16401.

Acknowledgements

A.S.K. and B.T.R. thank University Grant Commission (UGC), New Delhi for the award of Senior and Junior Research Fellowship (SRF-JRF), respectively.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.01.051.

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Please cite this article in press as: Suresh Kumar, A.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.01.051