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An eco-sustainable green approach for the synthesis of propargylamines using LiOTf as a reusable catalyst under solvent-free condition

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Abstract. An efficient process has been developed for the synthesis of propargylamines *via* a three-component coupling reaction of aldehyde, secondary alicyclic amine and alkyne (A^3) under solvent-free condition using lithium triflate (LiOTf) as expeditious reusable catalyst. This one-pot transformation generates one C–C and one C–N bond, which presumably proceeds by lithium acetylide as well as formation of iminium ion *in situ* and then undergoes nucleophilic addition to the iminium ion to give the propargyl amine. The solvent-free condition, easy recovery of the catalyst, simple, user-friendly and quantitative yield in short time renders the protocol economic and reasonable.

Keywords. Lithium triflate (LiOTf); three-component coupling (A^3); propargylamine; C–H activation; solvent-free condition.

1. Introduction

Multicomponent reactions, especially those run under solvent-free conditions, have been attracted increasing research interest from chemists in recent years.[1a–c] Most of the organic reactions are conventionally carried out in solvent media. However, to minimize the environmental pollution caused by solvents, the chemists have been showing more concern for developing environment-friendly synthetic procedures. This initiative, aided with the recent development of new strategies in solid–solid reactions has prompted them to develop sufficiently valuable methodologies to achieve organic synthesis under solvent-free condition.[1d–f] Especially, multicomponent reactions that provide poly-functionalized heterocyclic scaffolds in single operation and in stereo-specific manner are of great importance in synthetic organic and medicinal chemistry.[2a–b] Metal-catalysed multi-component reactions (MCRs) are a classical synthetic tool to access complex molecules from simple precursors *via* a one-pot procedure, as they exhibit economical, practical and efficient ways for chemical synthesis and have become increasingly important in the organic synthetic research.[3a–c] Lithium triflate (LiOTf) has emerged as a highly efficient, mild, neutral Lewis acid and reusable catalyst for a variety of organic transformations such as aminolysis of oxiranes, glycosylation, dithioacetalization of carbonyl compounds, tetrahydropyranylation of alcohols/phenols and acetylation of alcohols as well as diacetylation of aldehydes have been reported.[4a–b] Elegant features like low toxicity, air/water compatibility, operational simplicity, and remarkable ability to suppress side reactions in acid sensitive substrates makes it valuable and advantageous catalyst in synthetic processes. Many LiOTf catalysed reactions such as carbon–carbon, carbon–heteroatom bond and heteroatom–heteroatom bond forming reactions have been described recently.[4c–e]

Three-component coupling of an aldehyde, alkyne, and amine (A^3-coupling) *via* activation of a terminal alkyne C–H bond by transition metal catalysts is a reaction of great interest in organic chemistry.[5a–b] The formed propargylamines are synthetically and biologically important because of a wide range of application such as optical devices, valuable building blocks for the synthesis of many different natural product synthesis, various nitrogen compounds such as pyrroles,[6a] β-lactams,[6b] pyrrolidines,[6c] and prized precursors for therapeutic drug molecules.[6d–k] Furthermore, they possess highly potent, irreversible, and selective inhibitory activity toward monoamine oxidase B (MAO B),[6g] while N-benzylpropargylamines show aldehyde dehydrogenase inhibitory activity.[6h] Very recently, a series of propargylamines such as rasagiline [N-propargyl-(1R)-aminoindan] have been employed as a selective

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irreversible monoamine oxidase (MAO)-B monotherapy in early Parkinson's disease or as an adjunct therapy in more advanced cases.[7a–b] Also they inhibit acetylcholinesterase (ChE) enzyme and are brain selective type A and B MAO inhibitors and have been shown to improve memory impairments in scopolamine treated rats. Its sisomer, TV-3326 and TV-3279 which is also a ChE (figure 1) has no MAO inhibitory activity but depicted similar action in scopolamine impairment test.[7c]

Due to importance of propargylamines in organic synthesis and lack of efficient and convenient methods for their synthesis, there is an imperative need to develop competent synthetic procedure that would be a useful protocol for the synthesis of this important precursor. As a consequence, many efforts have been devoted towards these valuable structures. In this context, many Lewis acid catalysts of transition metals reported earlier, such as $Zn(OAc)_2$, $FeCl_3$, CuI, $Si(CH_2)_3SO_3CuCl$, $ZnOTiO_2$ (nano powder), AgI, $AuBr_3$, Au-HS/SO_3H-PMO (Et) in various toxic organic solvents such as acetonitrile, DMF, toluene, and DCM under an inert atmosphere have been employed.[8a–i] The use of recyclable catalysts under solvent-free condition in organic transformations have become an interesting area of research in the field of green chemistry.[9a–b] Keeping in view the limitations associated with reported methods, there is a high demand for the improved synthesis of propargylamines *via* the activation of a terminal alkyne C–H bond using transition metal-catalyst. As an extension of our contributions in the field of environmentally friendly Lewis acid mediated one-pot synthesis,[10a–d] we studied for the development of highly efficient protocol for this three-component coupling of aldehydes, secondary amines, and alkynes (A^3-coupling) in terms of cost effectiveness, reduce in reaction time with better yields.

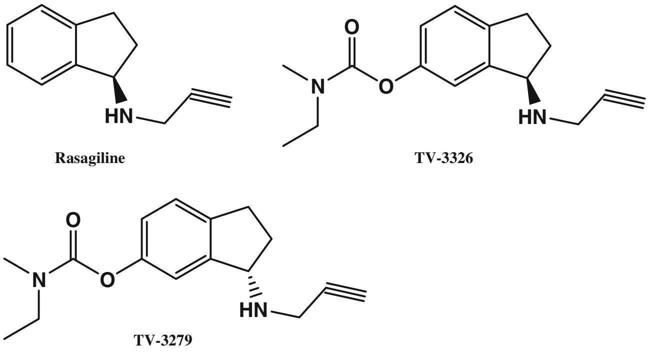


Figure 1. Propargylamine inhibitors of monoamine oxidase (MAO)-B.

To the best of our knowledge, there is no report available in the literature on the use of LiOTf as reusable catalyst in the synthesis of propargylamine using secondary amine, aldehyde and acetylene under solvent-free conditions. The main focus of our study was to develop a solvent-free reaction for the enhancement of reaction rate with a cleaner conversion, leading to an economical protocol for this one-pot three component (A^3) system. In this paper, we wish to disclose the development of a new, mild and truly efficient one-pot three component (A^3) synthesis of propargylamines using alicyclic amines, aldehyde and alkynes in the presence of LiOTf as reusable catalyst in air under solvent-free condition (scheme 1).

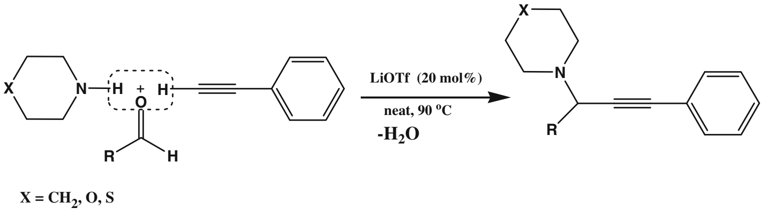
2. Experimental

2.1 *Typical procedure for the A^3 coupling reaction*

A mixture of benzaldehyde 106 mg (1 mmol), piperidine 85 mg (1 mmol), phenylacetylene 132 mg (1.3 mmol) and LiOTf 31 mg (20 mol%) was taken in a round-bottom flask and stirred at 90°C temperature. After completion of the reaction (monitored by TLC), the mixture was allowed to cool at room temperature and the reaction was subsequently quenched with water (25 mL) followed by the extraction with ethyl acetate (20 mL). The organic layer was separated, washed with saturated $NaHCO_3$ (20 mL) and water (15 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the crude product, which was chromatographed on silica gel to afford the pure product. The ^{1}H and ^{13}C NMR data of the known compounds are in good agreement with those in the literature. All new compounds were completely characterized by their analytical and spectral data. Spectroscopic data for new compounds are given and scan files provided as supporting information.

2.2 *4-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl) thiomorpholine (table 3, entry 11)*

Pale yellow solid, Mp. 56–58°C, Yield 92%, FT-IR (cm^{-1}): 684, 748, 818, 950, 1011, 1088, 1214, 1276, 1310, 1401, 1445, 1486, 1593, 1658, 2824, 2908, 3057. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$(d, $J = 8.0$ Hz, 2H), 7.51–7.49 (m, 2H), 7.31–7.29 (m, 5H), 4.73 (s, 1H), 2.86–2.79 (m, 4H), 2.67–2.62 (m, 4H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 143.1$, 131.7, 131.0, 129.6, 128.4, 128.3, 128.2, 122.6, 88.8, 84.2, 62.0, 51.7, 28.2. HRMS: m/z calculated: 327.0871, found: 327.0851.



Scheme 1. Lithium trifluoromethanesulphonate catalysed three component synthesis of propargylamines.

2.3 *1-(1-(2, 3-Dihydrobenzo[b][1,4]dioxin-7-yl)-3-phenylprop-2-ynyl)piperidine (table 3, entry 14)*

Brown solid, Mp. 58–60°C, Yield 89%, FT-IR (cm^{-1}): 690, 755, 780, 860, 909, 1000, 1088, 1066, 1113, 1253, 1285, 1453, 1503, 1590, 2820, 2853, 2926, 3055. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.47 (m, 2H), 7.30–7.25 (m, 3H), 7.16 (s, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.8 Hz, 1H), 4.67 (s, 1H), 4.20 (s, 4H), 2.54 (unresolved dt, 4H), 1.59–1.55 (m, 4H), 1.42–1.39 (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 143.1, 131.7, 131.0, 128.2, 122.9, 121.4, 117.3, 116.8, 88.1, 85.2, 67.0, 64.2, 61.3, 49.7, 14.1. HRMS: m/z calculated: 323.4235, found: 327.1730.

2.4 *4-(1-(2,3-Dihydrobenzo[b][1,4]dioxin-7-yl)-3-phenylprop-2-ynyl)morpholine (table 3, entry 15)*

Pale yellow solid, Mp. 63–65°C, Yield 94%, FT-IR (cm^{-1}): 697, 762, 823, 885, 903, 988, 1066, 1092, 1112, 1199, 1251, 1381, 1424, 1456, 1501, 1588, 1663, 2360, 2749, 2808, 2851, 2928, 3052. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 2H), 7.29–7.28 (m, 3H), 7.15 (d, J = 1.8 Hz, 1H), 7.08 (dd, J_1 = 1.8 Hz, J_2 = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 4.66 (s, 1H), 4.19 (s, 4H), 3.74–3.69 (m, 4H), 2.64–2.54 (m, 4H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 143.1, 131.7, 131.0, 128.3, 122.9, 121.4, 117.3, 116.8, 88.1, 85.1, 67.0, 64.2, 61.3, 49.7, 14.1. HRMS: m/z calculated: 335.3963, found: 335.1519.

2.5 *4-(1-(2,3-Dihydrobenzo[b][1,4]dioxin-7-yl)-3-phenylprop-2-ynyl)thiomorpholine (table 3, entry 16)*

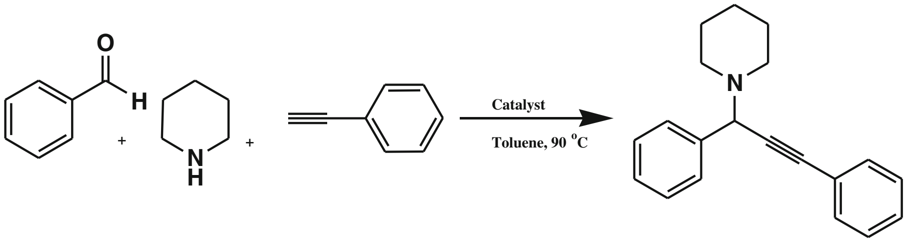
Pale yellow solid, Mp. 120–122°C, Yield 92%, FT-IR (cm^{-1}): 700, 763, 827, 888, 953, 1065, 1140, 1200, 1253, 1283, 1424, 1452, 1501, 1584, 2830, 2873, 2918, 2952. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 2H), 7.31 (t, J = 3.3 Hz, 3H), 7.15 (d, J = 1.8 Hz, 1H), 7.08 (dd, J_1 = 1.8 Hz, J_2 = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 4.70 (s, 1H), 4.23 (s, 4H), 2.90–2.81 (m, 4H), 2.73–2.62 (m, 4H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 143.2, 131.8, 131.2, 128.3, 123.0, 121.4, 117.3, 116.9, 88.3, 85.1, 64.4, 62.2, 51.7, 28.3. HRMS: m/z calculated: 351.1350, found: 351.1296.

3. Results and discussion

Initially, to find out the suitable catalyst for this A^3 coupling, the optimization of various reaction parameters like different metal Lewis acid catalysts, temperature, and solvent was carried out (tables 1 and 2, respectively). In search of highly effective catalyst, we initially performed a reaction in the absence of catalyst in toluene at 90°C (table 1, entry 1). It was observed that no product was formed in the absence of catalyst even after 12 h. From this study, we concluded that a catalytic system is mandatory for this A^3 coupling. To ensure the reusability of catalyst, a Cu–Sn nano alloy (200 mesh, 100 mg) was employed as a catalyst which unfortunately resulted in poor yield even after a long reaction time. It is important to mention that when we increased amount of Cu–Sn catalyst 200, 300 and 400 mg respectively, the results indicated that 400 mg Cu–Sn alloy was providing higher isolated yields in shorter times as compare to 100 mg of Cu–Sn (table 1, entry 5). We further experimented with different metal Lewis acid catalysts such as zinc triflate, lithium triflate, magnesium triflate and $BF_3 \cdot SiO_2$, $Cu(OTf)_2.SiO_2$, $Zn(OTf)_2.SiO_2$ catalyst (table 1), and found that among all screened catalysts, lithium triflate gave the best yield in least reaction time (table 1, entry 10).

Optimization of LiOTf as best catalyst for this reaction (table 1, entry 10), was followed by solvent optimization for enhancing yields, we also tested different solvents such as EtOH, CH_3CN, water, PEG and [BMIM]Cl as polar solvent at 90°C. Among the various solvents tested, toluene was found to give the best result in which the reaction proceeded smoothly giving the maximum yield in minimum time. It is noteworthy here that when water was used as a solvent, very low yield was obtained even after a prolonged reaction time

Table 1. Optimization of the catalyst.[a]



Entry	Catalyst (10 mol%)	Time (h)	Yield[b]
1	–	12	No product
2	Cu–Sn (200 mesh, 100 mg)	12	54
3	Cu–Sn (200 mesh, 200 mg)	8	63
4	Cu–Sn (200 mesh, 300 mg)	8	70
5	Cu–Sn (200 mesh, 400 mg)	8	73
6	$Cu(OTf)_2.SiO_2$	12	67
7	$Zn(OTf)_2.SiO_2$	12	52
8	$BF_3{\cdot}SiO_2$	08	37
9	Zinc triflate	12	70
10	LiOTf	06	78
11	Magnesium triflate	12	63
12	LiOTf (20 mol%)	5	84
13	LiOTf (30 mol%)	5	84

[a]All reactions were run with benzaldehyde (1 mmol), piperidine (1 mmol), phenylacetylene (1.3 mmol) and catalyst (10 mol%) in 1 ml of toluene at 90°C in air; [b]Isolated yields

(table 2, entry 4). Moreover, when we used [BMIM]Cl as polar medium, no product formation was noticed even after 12 h of reaction time (table 2, entry 6). It is important to report that when the reaction was performed under solvent-free conditions, reaction was completed in shorter time with increased in yield (89%), probably due to high concentration of reactants under neat condition (table 2, entry 7). Consequently, the optimum 20 mol% loading of the LiOTf provided the maximum yield in minimum time (table 2, entry 7), but loading of higher amount of catalyst neither increased the yield nor reduced the reaction time

Table 2. Optimization of the reaction conditions with different solvents.[a]

Entry	Solvent	LiOTf (20 mol%)	Temp. (°C)/time (h)	Yield[b]
1	Toluene	–	90/5	84
2	Acetonitrile	–	90/12	80
3	Ethanol	–	90/12	25
4	Water	–	100/24	<10
5	PEG	–	100/24	56
6	[BMIM]Cl	–	100/12	No product
7	Neat	–	90/45 min	89
8	Neat	30 mol%	90/1	90
9	Neat	40 mol%	90/1	90
10	Neat	05 mol%	90/2	72
11	Neat	IInd cycle	90/1	86
12	Neat	IIIrd cycle	90/1	78
13	Neat	IVth cycle	90/1	72

[a]Phenylacetylene:piperidine:benzaldehyde (1.3:1:1).
[b]Isolated yields

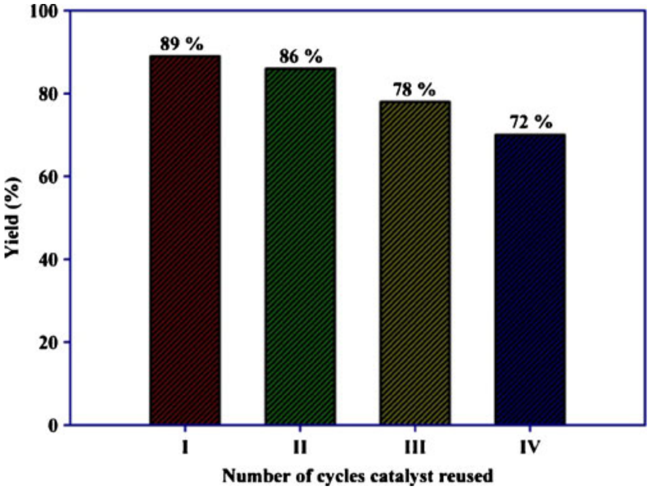


Figure 2. The reuse of LiOTf in the synthesis of compound **5**.

(table 2, entry 8 and 9), however the yield decreased by using the lower amount of LiOTf (table 2, 10).

We were also interested to study the reusability of the LiOTf catalyst for at least three more cycles. Accordingly, after the first run with 89% yield, the catalyst was recovered from aqueous layer of first washing of the work-up. After evaporation of water under reduced pressure, the resulting solid residue was precipitated out in acetonitire to give the corresponding pure LiOTf (95% catalyst was recovered). The recovered LiOTf was dried at 90–100°C for 12 h and tested up to three more reaction cycles. Recycling and reuse of the catalyst showed minimal decreases in yields (table 2, entries 11, 12 and 13), thus proving the catalyst's reusability. Figure 2 shows the variation of yield of 1-(1,3-diphenylprop-2-ynyl)piperidine (table 2, entries 10, 11, 12 and 13) with the number of times the LiOTf were recycled and reused. We have determined that 20 mol% LiOTf is the optimum catalytic amount under solvent-free condition for this system. Once the effective catalytic amount of catalyst was proven, general applicability and efficiency of developed protocol were investigated using aldehydes with different functional groups, various secondary amine and alkynes for the synthesis of different propargylamines under solvent-free condition (table 3).

Among all screened secondary amines, in which alicyclic amines like morpholine and thiomorpholine gave better yield in short time (table 3). The only exception was the reaction with 4-nitrobenzaldehyde, in this case very low yield was obtained after long reaction time due to strong electron withdrawing substituents (table 3, entry 12). In addition, 3-hydroxy benzaldehyde also showed comparably good yields (table 3, entry 13). It is important to note that aliphatic aldehyde also showed high reactivity with good yield in short reaction time

Table 3. Synthesis of different propargylamines under solvent-free condition.[a]

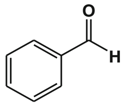
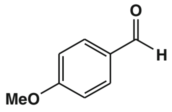
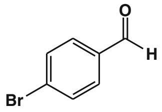
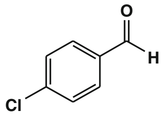
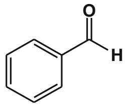
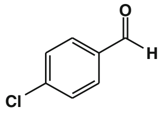
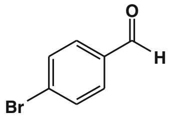
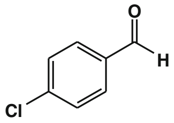
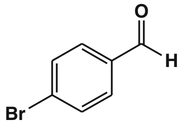
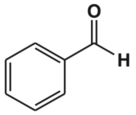
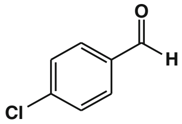
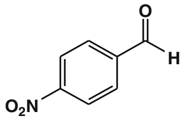
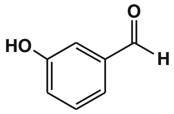
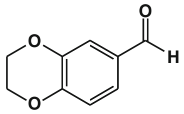
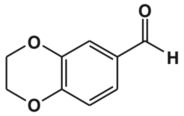
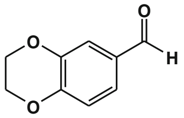
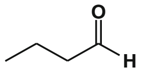
Entry	R	X	Time (min)	Yield[b]
1		N-CH_3	65	84
2		N-CH_3	70	82
3		N-CH_3	45	83
4		N-CH_3	30	86
5		CH_2	60	89
6		CH_2	40	91

Table 3. (*continued*).

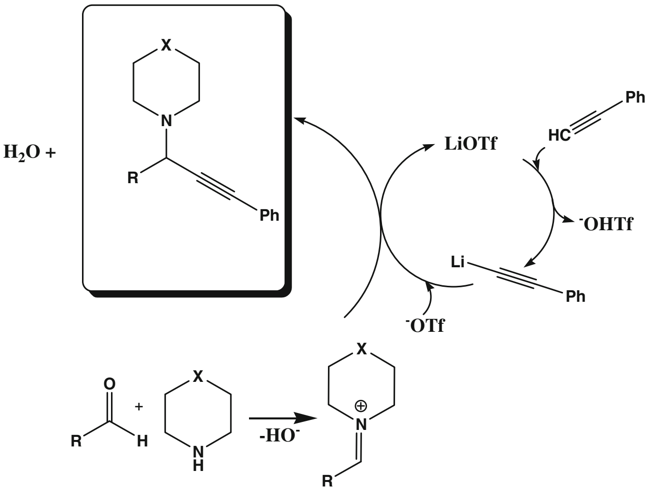
Entry	R	X	Time (min)	Yield[b]
7		CH_2	50	87
8		O	25	93
9		O	25	88
10		S	40	86
11		S	30	92
12		CH_2	180	58
13		CH_2	70	79
14		CH_2	40	90
15		O	30	94
16		S	50	92
17		S	45	91

[a] Reaction condition: aldehyde (1 mmol), alicyclic amine (1 mmol), phenylacetylene (1.3 mmol) and catalyst (20 mol%) at 90°C under neat condition in air

[b] Isolated yields

(table 3, entry 17). From the study of different screened aldehydes and secondary amines, it is concluded that not only electronic effect of aldehyde substituent affect the rate and yield of reaction but also the nature of secondary amine matters for this A^3 coupling.

On the basis of previously well-documented results,[8a–c] it is postulated that the A^3 coupling reaction proceeds by terminal alkyne C–H bond activation. The LiOTf activate the C–H bond of alkyne give the lithium acetylide as well as formation of iminium ion from



Scheme 2. Posulated mechanism for the synthesis of propargylamine using LiOTf catalyst.

an aldehyde and secondary amine *in situ*. The lithium acetylide intermediate reacts with the iminium ion to give the corresponding propargylamine and releases the LiOTf catalyst for further reaction. A postulated mechanism is shown in scheme 2.

4. Conclusion

In conclusion, we have developed an efficient, simple and economic protocol for the three-component (A^3) reaction of terminal alkynes, alicyclic amines, and aldehydes under solvent-free condition using LiOTf as expeditious and reusable catalyst. The main advantages of this method lie in the usage of LiOTf catalyst under solvent-free condition, which include shorter reaction time, simple work-up and enhanced yield.

Supporting Information

For supporting information (figures S1–S8), see www.ias.ac.in/chemsci website.

Acknowledgement

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