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CuI-NPs catalyzed mechanochemical-assisted *N*-Boc protection of organic amines

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A simple, solvent-free, faster and mechanochemical approach for the *N*-*tert*-butoxycarbonylation of amines catalyzed by copper iodide nanoparticles as a recyclable catalyst is described. The advantages of this method are simplicity, shorter reaction time (5–15 min), a cost-effective catalyst, and excellent product isolation (82-92%). *N*-Boc protection of various structurally diverse aliphatic, aromatic, and heterocyclic amines have been carried out with $(Boc)_2O$ with 10 mol% catalyst under pestle mortar grinding under solvent-free conditions. The catalyst possesses distinct advantages, ease of handling as well as removal, cleaner reactions, high activity, and environmentally benign. The final product has been characterised by various spectroscopic techniques.

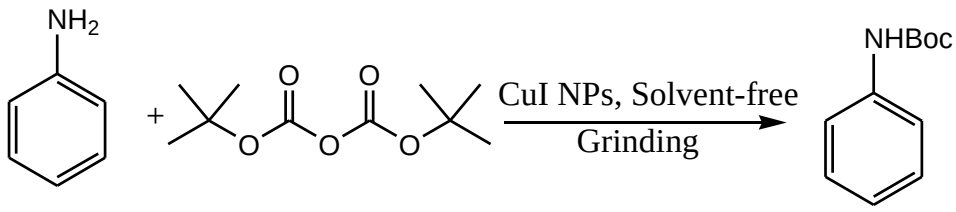
Keywords: Amine protection, CuI-NPs, nanocatalysis, mechanochemical, *N*-Boc protected amine

An important part of the organic synthesis is the development and implementation of functional group protection protocols to organic molecules. It has become challenging to develop protecting group strategies for the commonly present functional groups in organic synthesis[1] such as amines, carboxylic acids and thiols. The selection of the protecting group is that, the group is temporarily blocked and reached the target molecule, and it may be removed with a mild condition without affecting the final product. Synthetic organic or medicinal chemistry does required protection and deprotection of amino groups in an orthogonal synthesis of biologically active molecules in multi-step protocol[2]. The development of a mild and simple synthetic method for the protection of the amine group is still challenging due to the sensitivity of the chirality and required simple synthetic protocol development. The extensively employed protecting group is *tert*-butyloxy carbonyl, due to its ease of formation[3], stability under basic condition and ease of deprotection using mild acidic condition[4], and have been used for the directed lithiation of aromatic rings[5] and preparation of unsymmetrical ureas[6]. However, aryl amines are particularly difficult to protect with the Boc group because of the reduced nucleophilicity of the nitrogen atom when compared to primary or secondary aliphatic amines. Therefore, the synthetic protocol for them often requires Curtius rearrangement of aryl azides followed by trapping with *tert*-butyl alcohol[7]. There are various conventional base mediated strategies are available for the N-Boc protection of amines in the literature such as DMAP[8], aq.NaOH[9], Pyridine and NaHMDS[10], $La(NO_3)_3$-$6H_2O$[11], $Cu(BF_4)_2$-$9H_2O$[12], K_2CO_3[13], 2-*tert*-butyloxy carbonyl oxyimine-2-phenylacetonitrile in the presence of NEt_3[14]. On the other hand methods using a Lewis acid catalyzed to perform Boc protection are also been reported in the literature such as $MgBr_2$-OEt_2[15], $LiClO_4$[16], $Zn(ClO_4)_2$-$6H_2O$[17], $HClO_4$-SiO_2[18], Cu-NPs[19], $ZrCl_4$[20], $ZnCl_2$[21], Montmorillonite-K_{10}[22], Poly(*n*-Vinylimidazole)[23]. However, the base catalyzed reaction often lead to the formation of undesirable side product such as isocyanates[24], ureas[25] and N, N-di-Boc derivatives[26]. In recent years, copper and copper iodide nanoparticles[27] have extensively considered interest because of their unusual properties and potential applications in diverse fields. The application of copper iodide nanoparticles were employed as an active catalyst in many reactions including carbon heteroatom coupling[28], synthesis of phenols, anilines and thiophenols[29], synthesis of 1, 4-dihydropyridines[30], alkyne-azide cycloadditions[31], Mannich reaction[32], aza-Michael reactions[33] and hydroxylation of

phenol[34]. In an effort to develop a simple and eco-friendly catalyst for the protection of Boc group to aromatic and aliphatic amines, here we attempted CuI-NPs as a catalytic promoter under mechanochemical approach under solvent-free condition.

Results and Discussion

In recent years, the use of heterogeneous catalyst showed importance because of its easy recovery and recyclability, which lead to clean product formation. Previously researchers demonstrated the reaction of aryl amines with di-*tert*-butyl dicarbonate $(Boc)_2O$ requires the use of a base with extended reaction time and elevated temperature. The Boc-protection reaction under basic conditions may lead to the formation of side products like racemization. Addition to these side products, the pungent smell, high toxicity, large excess amount requirement and non-recyclability of these reagents make the method restricted to use in current sustainable development chemistry. On the other hand, Lewis acids and ionic liquid (IL)[35] have also been applied as a catalytic promoter for the Boc-protection reaction. The major problem associated with these reagents is the usage of special equipment, longer reaction times and lack of recyclability. Recently, metal nanoparticles have drawn much attention due to the advantages offered by these semi-heterogeneous catalysts. The replacement of expensive catalyst with inexpensive copper (I) salt as a catalyst would be allowed for economic benefits and low toxicity issues. The characteristics of heterogeneous catalysis and those of homogeneous catalysis (relatively low catalyst loadings and good selectivity) were combined in nanoparticle catalyst. In addition, because of their large surface area, metal nanoparticles usually showed high reactivity under mild conditions. Thus, transition metal nanoparticles have been used widely as catalysts for organic transformations. The nanomaterial enhance catalytic activity opens the potential to replace expensive catalysts with lower amounts of inexpensive nanomaterial catalysts. Among various NPs, Cu-NPs have been received much interest because of their unusual properties of potential diverse applications. CuI-NPs have also been used as an active catalyst in many reactions including carbon heteroatom coupling, synthesis of phenols, anilines, and thiophenols, synthesis of 1,4-dihydropyridines, alkyne-azide cycloadditions, the Mannich reaction, aza-Michael reactions and hydroxylation of phenol[28-34]. In this work, our group is attempted to employ CuI-NPs as a catalytic promoter for the protection of Boc group on less nucleophilic sites as well as a rich nucleophilic centre of amine groups by the simple mechanochemical approach with solvent-free condition. For the present work synthesized CuI-NPs using reported protocol and was characterized by FT-IR and XRD techniques. The obtained spectral results are in accordance with literature reported[36]. Initially, we have targeted aniline and substituted aniline as a substrate for the N-Boc protection reaction with $(Boc)_2O$ in the presence of different mole percentage of CuI-NPs under solvent-free conditions by the ground method (Scheme I). To check the loading of CuI-NPs minimal requirement for the reaction, we have selected aniline as a substrate. Taken 1 equivalent of aniline and 1.2 eq of $(Boc)_2O$ with three different mol percentage of catalyst in a different reaction with a loading of catalyst from 10 mol%, 20 mol% and 30 mol% respectively yielded 89% (Table I, entry 7), 88% (Table I, entry 6), and 89% of N-Boc protected product (Table I, entry 7). This observation of reaction revealed that any increase in the catalytic loading from 10mol% to 30mol% did not increase the product yield. We also checked the above reaction using lesser quantity (5 mol%) of CuI-NPs and observed N-Boc product in lower yield. Hence, the minimal loading of CuI-NPs mol % for the reaction used is 10 mol% CuI-NPs. Before fixing the catalyst loadings, we have checked compatibility of CuI-NPs for N-Boc protection of amines with organic solvents. The screened solvent effects for the N-Boc protection are CH_2Cl_2, CH_3CN and EtOH (Table I) at room temperature stirring method. The solvent assisted



Scheme I — N-*tert*-butyloxycarbonylation of primary amines using copper iodide nanoparticles

Table I — Optimization of catalyst amount/solvent effect/method for the synthesis of *tert*-butyl phenylcarbamate **1a**

Entry	Catalyst (mol%)	Conditions	Time	Yield[a] (%)
1	50	CH_2Cl_2, RT	2 h	77
2	25	CH_2Cl_2, RT	2.5 h	76
3	25	CH_3CN, RT	1h	64
4	10	EtOH, RT	1 h	66
5	10	CH_2Cl_2, RT	1 h	72
6	10	Neat, RT	25min	81
7	10	Neat, grinding	5 min	89
8	20	Neat, grinding	5 min	88
9	30	Neat, grinding	5 min	89

[a]Yields refer to the isolated yields.

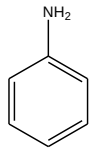
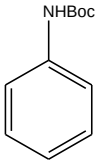
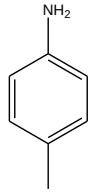
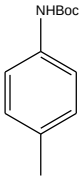
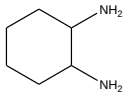
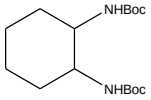
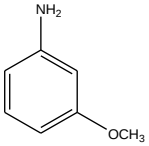
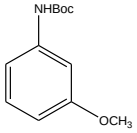
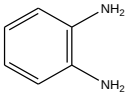
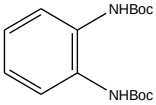
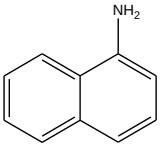
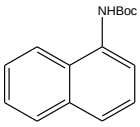
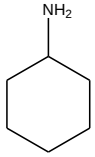
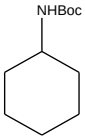
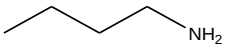
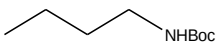
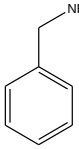
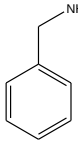
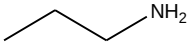
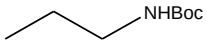
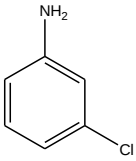
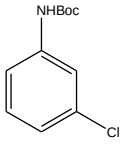
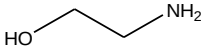
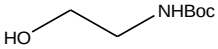
reaction revealed that, the reaction in the presence of dichloromethane showed better efficacy towards the N-Boc protection, which is observed in 2hrs with 50mol% of catalyst (Table I, entry 1). We also optimized the reaction condition by changing the catalyst loadings from 50mol% to 10mol% (Table I, entry 1-7), among which neat condition in 10 mol% of the catalyst loading showed the efficient conversion of aniline to Boc-aniline product yielded 81%. Later to reduce the reaction time and to avoid usage of the organic solvent and make synthetic protocol completely eco-friendly, we performed the reaction using pestle and mortar in a solvent-free method (Table I, entry 7). Surprisingly, we noticed the conversion of aniline to Boc-aniline within 5min of duration with the separation of product in a better yield. Further, we also extended this method to secondary amine (Table II, entry 13) and to amino acid (Table II, entry 14) protection and found satisfactorily results. With this optimized process (Table I, entry 7), the efficacy of CuI-NPs was evaluated using various substituted amines with $(Boc)_2O$ under solvent-free benign conditions (Table II). In order to show the merit of this present method, we compared different methods available for the N-Boc preparation of aniline as a model reaction from reported method to present method in Table III. It is clearly revealed that the results obtained from the N-Boc protection of aniline by present method is showed added advantages over other reported methods. The present method overcomes the various disadvantages accompanied with the previous methods for the N-Boc protection of amines like heating, reflux conditions, usage of expensive catalyst, involving environmentally hazardous solvents, long reaction times, tedious workup and usage of the column chromatography.

Further, we noticed that the structure effect of electron withdrawing and electron donating substituents on aromatic ring influenced on Boc-group protection. In the case of electron donating group on aniline, reaction underwent faster (Entry 4 and 5, Table II) compare to electron withdrawing group (Entry 11, Table II), but the final product isolated in both substituent groups reasonably gave the good yield. The catalytic pathway and selectivity of Boc protection of primary amines with CuI-NPs are unknown to us. However, it is expected that the strongly polarized and active surface of CuI-NPs first perform the N-H insertion on the catalytic surface of the CuI-NPs (Scheme II). The reactive CuI-N bond immediately inserted on one of the carbonyl group of the $(Boc)_2O$ and subsequent release of the N-Boc protected product with a side product of *tert*-butanol and the generation of CuI-NPs complete catalytic cycle. The selectivity of this catalyst for the protection of N-Boc may be explained due to the highly polarized surface of the CuI-NPs. We also examined commercially available copper iodide (CuI) sample for the reaction directly, the reaction showed lesser N-Boc product formation under solvent-free condition. The progress and amount of product formation has been found to unsatisfactory, due to the lack of polarized reactive surface, which are the important properties of CuI-NPs.

Recycling and reusing of the catalyst

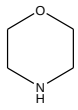
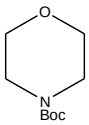
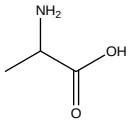
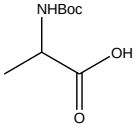
We also examined the most advantages of heterogeneous catalyst is to recycle and reuse again for the catalytic reaction. To reuse the first cycle catalyst after completion of the reaction, the reaction mixture was centrifuged and CuI-nanoparticles were separated. The separated nanoparticles were washed

Table II — CuI-NPs catalyzed Boc-protection of amines and physical data

Entry	Substrate	Product	m.p. (ºC)		Time (min)	Yield[a] (%)
			Found	Reported		
1			132-134	132 (Ref 44)	5	89
2			83-84	84-85 (Ref 44)	8	83
3			167-169	167-169 (Ref 45)	7	90[b]
4			Yellow oil	Yellow oil (Ref 44)	6	86
5			105-107	104-106 (Ref 45)	6	88[b]
6			99-101	95-97 (Ref 44)	10	89
7			66-68	65-67 (Ref 45)	15	88
8			Oil	Oil (Ref 46)	11	89
9			55-57	55-57 (Ref 45)	10	85
10			32-34	30-32 (Ref 47)	9	87
11			67-70	68-71 (Ref 44)	7	89
12			Oil	Oil (Ref 45)	8	89

(*Contd*.)

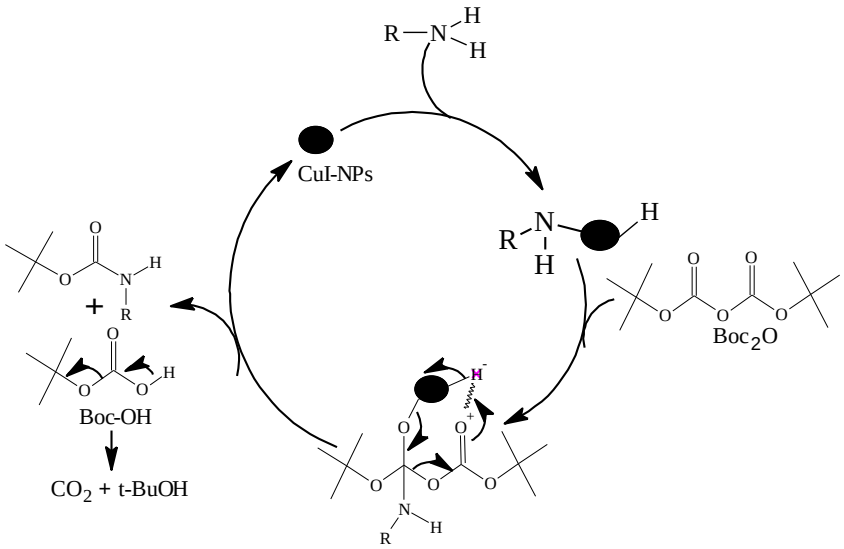
Table II — CuI-NPs catalyzed Boc-protection of amines and physical data (*Contd*.)

Entry	Substrate	Product	m.p. (ºC)		Time (min)	Yield[a] (%)
			Found	Reported		
13			Oil	–	9	88
14			Oil	–	10	87

[a] Yields refer to the isolated yields.
[b] The reaction was carried out using 2 equiv of $(Boc)_2O$.

Table III — Comparison of the literature reported methods with present approach

Entry	Catalyst	Conditions	Time	Yield (%)	Ref. No.
1	Yttria-zirconia	CH_3CN, RT	14 h	90	37
2	β-Cyclodextrine	H_2O, RT	2.5 h	75	38
3	Saccharin sulfonic acid	*n*-Hexane, reflux	1 h	97	39
4	Sulfonic-acid-functionalized silica	CH_2Cl_2, RT	45 min	83	40
5	Iodine	Neat, reflux	30 min	95	41
6	RiH	Neat, RT	10 min	95	42
7	Thioglycolic acid	EtOH, RT	8 min	95	43
8	CuI-NPs	Neat, grinding	5 min	92	This work



Scheme II — Plausible CuI-NPs catalyzed mechanistic pathway of *N*-Boc protection of amines

three times with ethyl acetate and three times with water and then dried overnight in a temperature-controlled oven at 80 °C. The recovered catalyst was reused further for the two cycles of N-Boc protection and the results of the percentage of yield isolated are graphically shown in Figure 1.

Characterization of Catalyst: CuI nanoparticles

The FT-IR spectra and XRD pattern of the synthesized CuI nanoparticles were shown in Figure 2 and Figure 3 respectively and are very much comparable with the data reported in literature[27].

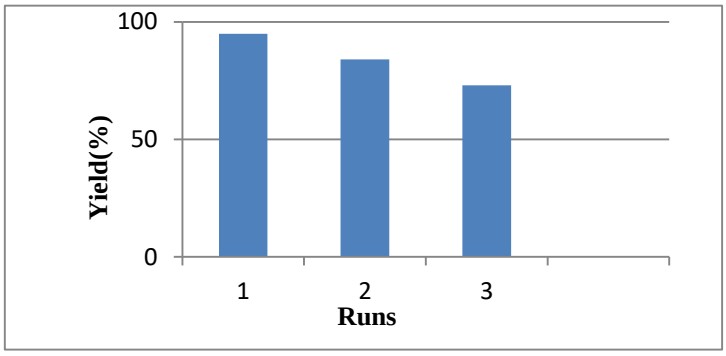


Figure 1 — Recycled catalytic efficacy of CuI-NPs for N-Boc protection of amine **1a**

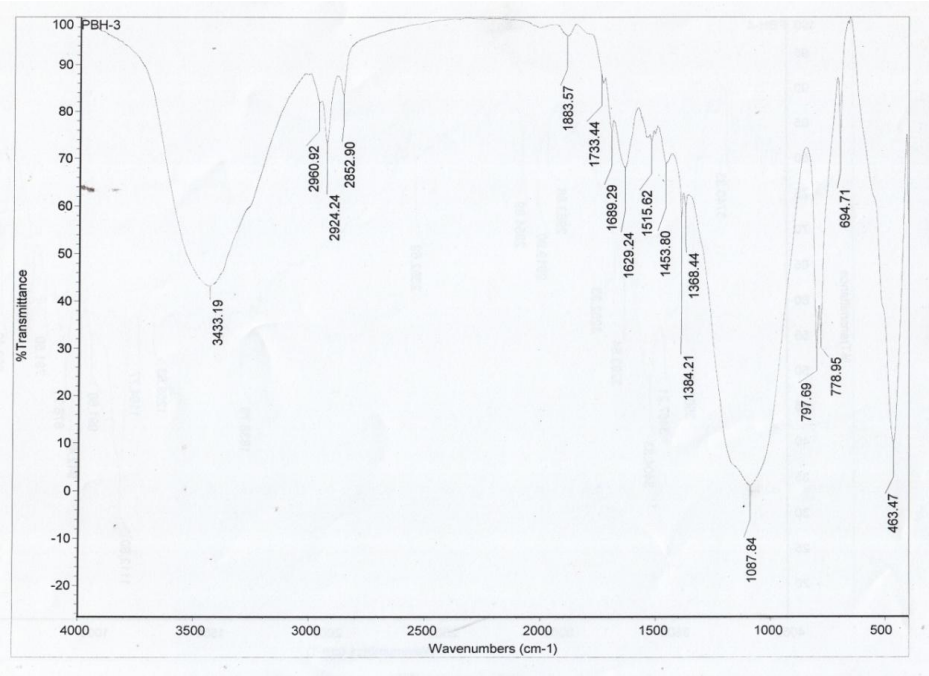


Figure 2 — FT-IR spectrum of CuI nanoparticles

FT-IR Analysis (Figure 2)

In order to characterize the catalyst (CuI-NPs), we have shown the FT-IR spectrum of CuI-NPs in Figure 2. It is found that the peaks observed at C=O, C-N and C-H stretching vibrations from DMF locate at 1689, 1453 and 1087 cm^{-1}, respectively. Due to the contribution of the two possible resonating structures of an amide, the bond order of the carbonyl C=O bond is reduced, while that of the carbon-nitrogen bond is increased. The stretching frequency of 3433cm^{-1} contributes to the O-H bond. This shows that the alkyl group is present in the system, due to the presence of ethanol or water.

XRD Analysis (Figure 3)

The XRD pattern of CuI nanoparticles was shown in Figure 3. All reflection peaks in Figure 3 can be readily indexed to pure cubic phase of CuI with F-43m space group (JCDPS No. 77-2391). The crystallite size diameter (D) of the CuI nanoparticles has been calculated by Debye–Scherrer equation (D = Kk/bcosh), where FWHM (full-width at half-maximum or half-width) is in radian and h is the position of the maximum of diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and k is the X-ray wavelength (1.5406 A ˚ for Cu Ka). Crystallite size of CuI has been found to be 55 nm.

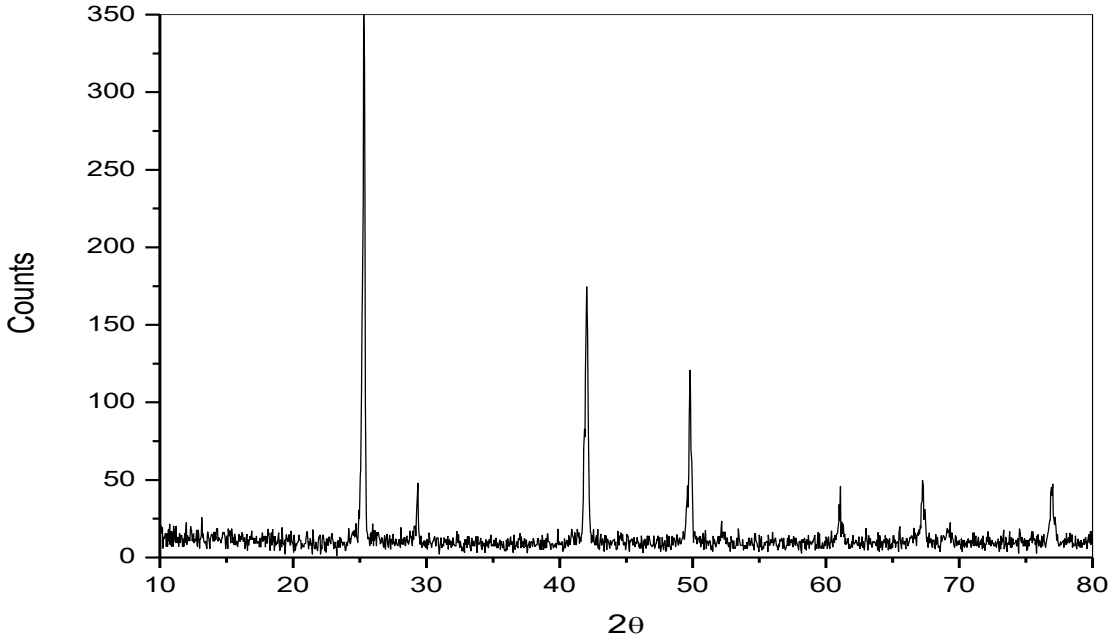


Figure 3 — XRD spectrum of CuI nanoparticles

In continuation of our effort to develop green and efficient catalytic approaches to biologically potent molecule synthesis by employing numerous bio/agro-waste sourced catalysts are reported by our team[48-54].

Material and methods

Melting points were determined in open capillaries and are uncorrected. Laboratory grade chemicals were purchased from S D Fine-Chem Limited and used as received without further purification. IR spectra were recorded in KBr disks on a Shimadzu FT-IR with a scan range 400 to 4000 cm^{-1}. Powder X-ray diffraction measurements were performed by employing Panalytical X'Pert Pro diffractometer and scans were taken with a 2θ and with an increment of 0.03° ranging from 10° to 90° using Cu $K\alpha_c$ radiation source generated at 45 kV and 40 mA, ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz and 75 MHz respectively using TMS as an internal standard. The progress of the reaction monitored by TLC, yields refer to isolated pure products.

Experimental Section

Preparation of CuI-NPs catalyst

The reported protocol[36] was adopted for the synthesis of CuI-NPs. Briefly, copper iodide (0.1 g, 0.5 mmol) in 5 mL of acetonitrile taken in a 50mL conical flask and dissolved mixture under ultrasonic irradiation, slowly added 10 mL of DMF and continued sonication to afford a yellowish solution. The reaction mixture was heated to 30°C to remove acetonitrile after removal added 10 ml of water drop wise under mechanical stirring. The cloudy green precipitate formed was centrifuged and washed with ethanol several times to afford pure CuI-nanoparticles, which was characterized by FT-IR (Figure 2) and XRD (Figure 3) which was in accordance with the literature[27].

General experimental procedure for N-Boc protection of amines

A mixture of amine (1.0 mmol) and copper iodide nanoparticles (10 mol %, 0.02g) ground together using pestle and mortar followed by the addition of $(Boc)_2O$ (1.2 eq) and continued ground for the appropriate time until total disappearance of amine spot observed in the TLC. After completion of the reaction, the viscous residue diluted with ethyl acetate (10 mL), separated catalyst by centrifugation (3000 rpm), and washed with ethyl acetate (5 mL). The combined filtrate given water wash (2×5 mL) followed by brine wash (5mL) and organic layer was dried using anhyd. Na_2SO_4. The solvent was removed using rotary evaporator, dried under vacuum, and the crude product was recrystallized using methanol. The physical data were found to be identical to the reported literature (Table II).

Spectral data of some representative compounds

***tert*-Butyl phenylcarbamate, 1a**

IR (KBr): 1689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.54(s, 9H), 6.5 (bs, 1H), 7.02-7.07 (m, ^1H), 7.27-7.39(m, 4H); ^{13}C NMR ($CDCl_3$): δ 28.3, 80.4, 118.5, 122.9, 128.9, 138.3, 152.7.

***tert*-Butyl (4-methylphenyl) carbamate, 1b**

^1H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 9H, Boc), 2.30 (s, 3H, Me), 6.57 (br s, 1H, NH), 7.09 (d, *J* = 7.6 Hz, 1H, ArCH), 7.25 (d *J* = 7.6 Hz, 2H, Ar CH); ^{13}C NMR ($CDCl_3$): δ 20.7, 28.4, 80.2, 118.7, 129.4, 132.5, 135.8, 153.0.

di-*tert*-Butyl cyclohexyl-1, 2-diylbiscarbamate, 1c

IR (KBr): 3390, 2988, 1686, 1610, 1289, 1260, 1182, 993, 855 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.55 (s, 9H), 1.79 (qin, *J* = 7.2, 7.6 Hz, 2H), 2.61 (dd, *J* = 7.6 and 8.0, 2H), 3.21 (d, *J* = 6.0 Hz, 2H), 7.24 (dd, *J* = 5.6 and 7.6 Hz, 3H), 7.36 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 29.5, 32.8, 33.6, 40.7, 124.9, 127.4, 128.8, 142.6, 157.1.

***tert*-Butyl (3-methoxyphenyl) carbamate, 1d**

IR (KBr): 3320, 2990, 2920, 1690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 9H), 3.92 (s, 3H), 6.5 (dd, *J* = 8.0 and 8.4 Hz, 1H), 6.61 (br s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 9.21 (dd, *J* = 8.0 and 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 28.4, 55.3, 80.5, 104.1, 108.9, 110.7,129.7, 139.7, 152.7, 160.3.

di-*tert*-Butyl benzene-1, 2-diylbiscarbamate, 1e

^1H NMR (300 MHz, $CDCl_3$): δ 1.49 (s, 18H, Boc), 6.72 (br s, 2H, NH), 7.12 (m, 2H, Ar CH), 7.50 (m, 2H, ArCH); ^{13}C NMR ($CDCl_3$): δ 28.3, 80.7, 124.1, 125.2, 130.2, 153.9.

***tert*-Butyl naphthalen-1-ylcarbamate, 1f**

^1H NMR (300 MHz, $CDCl_3$): δ 1.57 (s, 9H, Boc), 6.89 (br s, 1H, NH), 7.42-7.55 (m, 3H, Ar CH), 7.63 (d *J* = 8.4 Hz, 1H, Ar CH), 7.80-7. 95 (m, 3H, Ar CH); ^{13}C NMR ($CDCl_3$): δ 28.4, 80.7, 118.7, 120.5, 124.5, 125.8, 126.0, 126.5, 128.7, 132.9, 134.0, 153.5.

***tert*-Butyl cyclohexylcarbamate, 1g**

IR (CCl_4): 3365, 2975, 2931, 1529, 1168 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.04-1.18 (m, 3H), 1.25-1.33 (m, 2H), 1.42 (s, 9H), 1.58- 1.72(m, 3H), 1.92-1.95 (m, 2H), 3.46 (bs, 1H), 4.47 (bs, 1H).

Conclusion

In summary, the present study demonstrated a simple, faster, solvent-free, mechanochemical approach of *N*-*tert*-butoxycarbonylation of amines catalyzed by copper iodide nanoparticles at room temperature. The method is compatible with variety of substituted, aromatic, aliphatic, amino acids containing amine group is targeted for the Boc-protection resulted in a good to excellent yield isolation. The advantages of the present protocols are shorter reaction time, easier work up and greener method.

Conflict of interest

The author(s) confirm that this article content has no conflict of interest.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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