Indium(III) Halides as New and Highly Efficient Catalysts for *N-tert*-Butoxycarbonylation of Amines

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Abstract: Indium(III) bromide and chloride efficiently catalysed the *N-tert*-butoxycarbonylation of amines with $(Boc)_2O$ at room temperature and under solvent-free conditions. Various aromatic, heteroaromatic and aliphatic amines were converted to *N-tert*-butylcarbamates in excellent yields in short times. Chiral amines, esters of α-amino acids and β-amino alcohols afforded optically pure *N-t*-Boc derivatives in high yields. The reactions were chemoselective and no competitive side reactions such as isocyanate, urea, and *N*,*N*-di-*t*-Boc formation were observed. Chemoselective conversion to *N-tert*-butylcarbamates took place with amino alcohols without any formation of oxazolidinones.

Key words: indium(III) halides, *N-tert*-butylcarbamates, amines, chiral α-amino acid esters, di-*tert*-butyl dicarbonate, chemoselectivity, solvent-free, room temperature

The presence of amines in a wide range of biologically active compounds makes protection of amines an important and frequently needed exercise in synthetic organic/medicinal chemistry.[1] An easy process of protection of amines is through acylation[2] but the harsh reaction conditions[3] required to regenerate the parent amine from the acylated derivative is not suitable for a multifunctional substrate and a protecting group that is cleavable under mild conditions is required. The *N-tert*-butylcarbamates are stable towards a variety of experimental conditions, routinely adopted in synthesis, such as in the presence of nucleophiles but are easily deprotected to the parent amine under mild acidic conditions.[1a] Thus, the *N-tert*-butoxycarbonylation constitutes an efficient strategy for protection of amines during synthesis of multifunctional targets.[1–5] The various procedures of conversion of amines to *N-t*-Boc derivatives are reaction of an amine with (i) di-*tert*-butyl dicarbonate $[(Boc)_2O]$ in the presence of DMAP[6]/inorganic bases,[7] (ii) 4-dimethylamino-1-*tert*-butoxycarbonylpyridinium chloride[8]/tetrafluoroborate[9] in aqueous NaOH, (iii) 2-*tert*-butyloxycarbonyloxyimino-2-phenylacetonitrile in the presence of Et_3N in H_2O–dioxane,[10] (iv) *tert*-butyl-2-pyridyl carbonate in the presence of Et_3N in H_2O–DMF,[11] and (v) *tert*-butyl-1-chloroalkyl carbonates in the presence of K_2CO_3 in H_2O–THF.[12] These methodologies have various drawbacks such as requirement of long reaction times, special efforts for preparation of *tert*-butoxycarbonylation reagents,[8–12] and auxiliary substances (e.g., solvents and other reagents). The high toxicity of DMAP[13] is a serious concern on the view point of health hazard for use of DMAP and the *tert*-butoxycarbonylation reagents[8,9] derived from DMAP. Further, the maintenance of chemoselectivity is a major problem for the base-catalysed reactions as they are often associated with the formation of side products such as isocyanate,[6d,14] urea,[6d] and *N*,*N*-di-Boc derivatives.[6d,15] Recently, a few Lewis acid catalysed *N-t*-Boc formation have been reported that include the use of yttria-zirconia in MeCN,[16] $Zn(ClO_4)_2 \cdot 6H_2O$ in dichloromethane,[17] $ZrCl_4$ in MeCN,[18] and $LiClO_4$ in dichloromethane.[19] These procedures circumvented the problem associated with the side reactions such as isocyanate/urea/*N*,*N*-di-*t*-Boc formation. However, still they are not devoid of other drawbacks such as long reaction time, need to use solvent and hazardness (e.g., preparation of yttria-zirconia involved the use of sulfuric acid at 500 °C,[16] perchlorates are strong oxidisers and explosive in nature,[20] and $ZrCl_4$ is highly moisture sensitive, decomposes on storing and liberates corrosive HCl fumes) etc. Thus, the development of new synthetic methodology is in high demand.[21]

As the formation of isocyanate/urea/*N*,*N*-di-*t*-Boc was not observed in the Lewis acid catalysed reactions,[16–19,21] we focused on the 'electrophilic activation' strategy in the pursuit of development of a better method. We kept in mind the tight legislation on maintenance of greenness in synthetic processes that insists on prevention of waste and use of auxiliary substances (e.g. solvents, additional reagents).[22] To avoid the problems associated with the reported catalysts, we preferred to use In(III) halides as they are less susceptible to hydrolytic decomposition and do not pose environmental hazard due to apparent non-toxic nature which has qualified them for wide use in synthetic organic chemistry.[23] Herein we describe the catalytic efficiency of In(III) bromide and chloride for conversion of amines to *N-tert*-butylcarbamates.

Various aromatic, heteroaromatic, aliphatic, and heterocyclic amines were treated with $(Boc)_2O$ under solvent-free conditions at room temperature (~30–35 °C) in the presence $InBr_3$ (Method A) and $InCl_3$ (Method B). The *N-t*-Boc formation took place after two minutes to five hours and five minutes to ten hours (mostly 2 min to 2 h) in the presence of $InBr_3$ and $InCl_3$, respectively (Table 1). No competitive formation of isocyanate,[6d,14] urea,[6d] and *N*,*N*-di-Boc[6d,15] was observed (IR, GCMS). The aliphatic amines reacted at a faster rate compared to the aromatic amines. The catalysts were compatible with various func-

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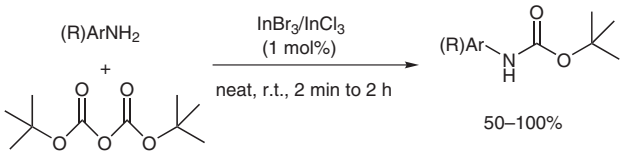
tional groups such as F, Cl, Br, OH, SH, OMe, OBn, and α,β-unsaturated carbonyl. Substrates with strong electron-withdrawing group(s) required longer time due to the decreased nucleophilicity of the nitrogen atom (Table 1, entries 13 and 14). Sterically hindered amine (Table 1, entry 6) afforded excellent yield. Substrates having OH/SH group (Table 1, entries 7 and 8) afforded the *N-t*-Boc derivative chemoselectively without O/S-*tert*-butyloxycarbonylation (IR).[6d,23] The chemoselectivity was further demonstrated by the reaction of amino acetaldehyde dimethyl acetal (Table 1, entry 26) that is sensitive to acids.

Table 1 InX_3-Catalysed Formation of *N-tert*-Butylcarbamates from Various Amines[a–c]



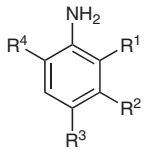
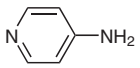
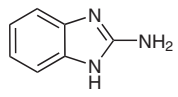
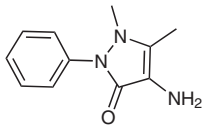
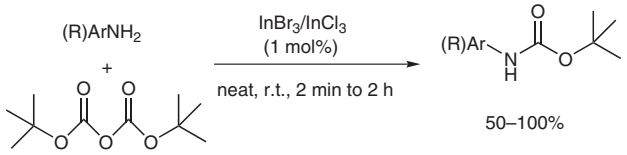
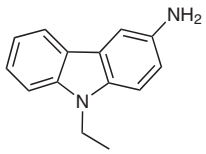
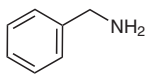
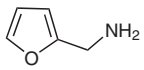
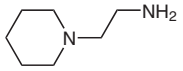
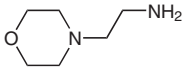
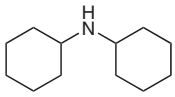
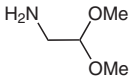
Entry	Amines	Time (min)[b]	Yield (%)[b,c]
			
1	$R^1 = R^2 = R^3 = R^4 = H$	5 (10)	~100 (95)
2	$R^1 = R^2 = R^4 = H$; $R^3 = OMe$	5 (10)	~100 (90)
3	$R^1 = R^3 = OMe$; $R^2 = R^4 = H$	30 (30)	~100 (70)
4	$R^1 = R^2 = R^4 = H$; $R^3 = Me$	10 (15)	~100 (93)
5	$R^1 = R^4 = Me$; $R^2 = R^3 = H$	30 (30)	~100 (86)
6	$R^1 = R^3 = R^4 = Me$; $R^2 = H$	30 (60)	~100 (90)
7	$R^1 = OH$; $R^2 = R^3 = R^4 = H$	60 (90)	70 (75)
8	$R^1 = R^2 = R^4 = H$; $R^3 = SH$	30 (60)	90 (80)
9	$R^1 = R^2 = R^4 = H$; $R^3 = OBn$	30 (90)	90 (90)
10	$R^1 = R^2 = R^4 = H$; $R^3 = F$	15 (30)	~100 (~100)
11	$R^1 = R^2 = R^4 = H$; $R^3 = Br$	30 (45)	~100 (87)
12	$R^1 = R^4 = H$; $R^2 = Me$; $R^3 = Br$	30 (60)	~100 (~100)
13	$R^1 = R^4 = H$; $R^2 = Cl$; $R^3 = F$	4 h (6 h)	90 (80)
14	$R^1 = R^2 = R^4 = H$; $R^3 = CN$	5 h (10 h)	50 (20)
15		30 (30)	95 (90)
16		60 (60)	80 (70)
17		60 (2 h)	90 (86)[d]

Table 1 InX_3-Catalysed Formation of *N-tert*-Butylcarbamates from Various Amines[a–c] (continued)



Entry	Amines	Time (min)[b]	Yield (%)[b,c]
18		15 (30)	92 (95)
19		2 (5)	~100 (~100)
20		15 (15)	~100 (~100)
21		5 (5)	~100 (95)
22		5 (5)	~100 (~100)
23		5 (5)	~100 (~100)
24		30 (60)	90 (86)
25		5 (5)	~100 (~100)
26		2 (5)	~100 (~100)

[a] The substrate was treated with $(Boc)_2O$ (1 equiv except for entry 17) in the presence of $InBr_3$ (1 mol%) under neat condition at r.t.
[b] The values in parenthesis correspond to $InCl_3$-catalysed reactions.
[c] Isolated yield of the corresponding *N-t*-Boc derivative.
[d] The reaction was carried out with 1.5 equiv of $(Boc)_2O$.

The reactions were monitored by TLC and IR spectra. However, the reactions could also be followed up visually. For aromatic amines (solid amines), a clear solution was obtained after addition of the amine to the magnetically stirred mixture of $(Boc)_2O$ and the catalyst. Immediately after that, commencement of slow effervescence took place and the formation of solid residue indicated the completion of the reaction (TLC). For reactions that took times longer than 30 minutes, the effervescence could not be noticed distinctly but the formation of solid mass indicated completion of the reaction (TLC). For aliphatic amines (liquid amines), an exothermic reaction took place immediately after the addition of the amine to the magnetically stirred mixture of $(Boc)_2O$ and the catalyst with vigorous effervescence. The cessation of effervescence indicated the completion of the reaction (TLC). The prod-

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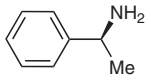
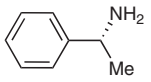
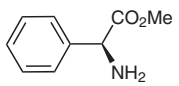
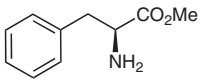
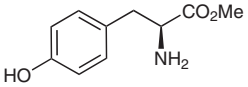
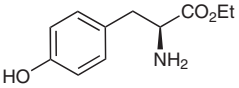
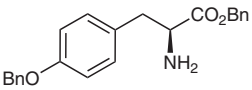
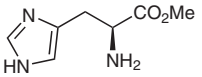
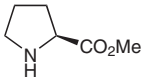
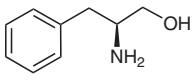
ucts obtained after the work-up were pure (spectral data) and purification was achieved by triturating with EtOAc–hexane, wherever required. For reaction with conversion of <80% (GC-MS), the product was purified by passing through a column of silica gel (60–120 mesh) and eluting with EtOAc–hexane.

The mildness of the protocol was demonstrated by the conversion of chiral amines (Table 2, entries 1 and 2), esters of α-amino acids (Table 2, entries 3–9), and amino alcohol (Table 2, entry 10) to the optically pure *N*-*t*-Boc derivatives (determined by optical rotation)[24] in excellent yields. Phenylalaninol (Table 2, entry 10) gave the *N*-*t*-Boc derivative without formation of oxazolidinone.[6d,25]

The advantages of $InBr_3$ and $InCl_3$ over the reported Lewis acid catalysts were evident from the following representative examples. The *N*-*t*-Boc derivative of 2,4,6-trimethylaniline was obtained in ~100 and 90% yields after 30 and 60 minutes in the presence of 1 mol% of $InBr_3$ and $InCl_3$, respectively, under solvent-free conditions. The corresponding product was formed in 94% yield after 48 hours in the presence of $Zn(ClO_4)_2$ (5 mol%) in dichloromethane.[17] The $LiClO_4$ (20 mol%)-catalysed reaction of morpholine afforded the *N*-*tert*-butylcarbamate in 86% yield after five hours in dichloromethane[18] and the use of yttria-zirconia (20% by weight) in MeCN afforded 85% yield after four hours.[16] Compared to these, quantitative yields were obtained after five minutes under solvent-free conditions in the presence of 1 mol% of $InBr_3$ and $InCl_3$. The *N*-*t*-Boc derivative of (*S*)-phenylalanine methyl ester was obtained in 90% yield after five hours in acetonitrile in the presence of yttria-zirconia (20% by weight).[16] However, 93% and 90% yields were obtained with (*S*)-phenylalanine methyl ester under solvent-free conditions after 15 minutes and 30 minutes by using 1 mol% of $InBr_3$ and $InCl_3$, respectively. The use of $LiClO_4$ (20 mol%) provided 88% yield of the *N*-*t*-Boc derivative of (*S*)-phenylglycine methyl ester after five hours in dichloromethane[18] compared to 91% and 82% yields obtained after 15 minutes and 30 minutes in the presence of 1 mol% of $InBr_3$ and $InCl_3$, respectively, under solvent-free conditions. Recently, it has been reported that *N*-*t*-Boc 4- and 2-phenylbutyl amines were obtained in 57% and 58% yields, respectively, following a one-pot Curtius rearrangement after 16–24 hours.[24] The *N*-*t*-Boc derivative of structurally similar benzylamine (Table 1, entry 19) and α-methylbenzylamine (Table 2, entries 1 and 2) were synthesised in quantitative yields after 2–5 minutes under the present methodologies.

Table 2 InX_3-Catalysed Formation of *N*-*tert*-Butylcarbamates of Chiral Amines, Esters of Amino Acids, Amino Alcohols[a–c]

Entry	Amines	Time (min)[b]	Yield (%)[b,c]
1		2 (5)	~100 (~100)
2		2 (5)	~100 (~100)
3		15 (30)	91 (82)
4		15 (30)	93 (90)
5		30 (30)	80 (70)
6		30 (30)	90 (80)
7		30 (60)	90 (~100)
8		30 (30)	92 (90)
9		15 (30)	90 (87)
10		15 (15)	90 (80)

[a] The substrate was treated with $(Boc)_2O$ (1 equiv) in the presence of $InBr_3$ (1 mol%) under neat condition at r.t.
[b] The values in parenthesis correspond to $InCl_3$-catalysed reactions.
[c] Isolated yield of the corresponding *N*-*t*-Boc derivative.

In summary, we have discovered In(III) bromide and chloride as new and highly efficient catalysts for *N*-*tert*-butoxycarbonylation of amines. The advantages such as the (i) use of commercially available, cheap and apparently non-toxic catalyst, (ii) solvent-free[26] and room temperature reaction conditions, (iii) short reaction times, (iv) high yields, and (iv) ease of product isolation/purification offered by the present methodology fulfill the triple requirements of green chemical reactions.[27]

Indium bromide, indium chloride and $(Boc)_2O$ were purchased from Aldrich India. Silica gel was procured from Spectrochem Pvt. Ltd. India. All commercial reagents and solvents were used without further purification unless otherwise specified. NMR spectra were recorded on a Bruker Avance DPX 300 MHz NMR spectrometer using TMS as an internal standard. Mass spectra were obtained using a GCMS-QP 5000 (Shimadzu) [for EI] and LCMS-Finnigan MAT LCQ [for APCI] mass spectrometers. The IR spectra were recorded either as KBr pellets (for solids) or neat (for liquids) on a Nicolet Impact 410 FTIR spectrometer. Elemental analysis was carried out on an Elementar Vario EL.

N-*tert*-Butylcarbamates; *tert*-Butyl Phenylcarbamate; Typical Procedures

Method A: Aniline (0.235 g, 2.5 mmol) was added to a magnetically stirred mixture of $(Boc)_2O$ (0.545 g, 2.5 mmol, 1 equiv) and $InBr_3$ (9.0 mg, 0.025 mmol, 1 mol%) at r.t. (30–35 °C). The mixture was stirred at r.t. until completion of the reaction (5 min, TLC, IR, GC-MS). The mixture was diluted with EtOAc (25 mL), and the organic layer was washed with H_2O (2 × 10 mL), dried (Na_2SO_4) and concentrated under reduced pressure to afford *tert*-butyl phenylcarbam-

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ate (Table 1, entry 1); yield: 0.485 g (~100%); white solid; mp 132–133 °C.

IR (KBr): 3314, 2985, 1689, 1598, 1531, 1245, 1150 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 9 H), 6.55 (br s, 1 H), 6.99–7.04 (m, 1 H), 7.24–7.36 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3, 80.4, 118.5, 123, 128.9, 138.3, 152.7.

MS (ESI): *m*/*z* = 193 (M^+).

Method B: The reactions with $InCl_3$ were carried out in the same way as those using $InBr_3$.

The remaining reactions were carried out following these general procedures (Method A and Method B). The physical data (mp, IR, NMR and MS) of known compounds were found to be identical with those of authentic samples. Unknown compounds were characterised by spectral (IR, NMR and MS) and elemental analyses.

The physical data of new compounds are provided below.

(4-Benzyloxyphenyl)carbamic Acid *tert*-Butyl Ester (Table 1, Entry 9)
Off-white solid; mp 114–115 °C.

IR (KBr): 3428, 3294, 2986, 1696, 1590, 1527, 1450, 1326, 1228, 1152, 1055, 750 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 9 H), 5.03 (s, 2 H), 6.32 (s, 1 H), 6.90 (d, *J* = 8.82 Hz, 2 H), 7.24–7.43 (m, 7 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.93, 70.87, 80.80, 115.81, 121.07, 128.03, 128.48, 129.11, 132.25, 137.62, 153.73, 155.36.

MS (EI): *m*/*z* = 299 (M^+).

Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 71.99; H, 7.14; N, 4.71.

(9-Ethyl-9*H*-carbazol-3-yl)carbamic Acid *tert*-Butyl Ester (Table 1, Entry 18)
Yellow solid; mp 161–162 °C.

IR (KBr): 3165, 2960, 1726, 1608, 1526, 1332, 1255, 1158, 1045, 999, 820 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 6.82 Hz, 3 H), 1.54 (s, 9 H), 4.21 (q, *J* = 6.98 Hz, 2 H), 6.65 (br s, 1 H), 7.12–7.43 (m, 5 H), 7.99–8.13 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.35, 29.02, 38.10, 80.69, 109.02, 112.08, 119.10, 121.22, 123.31, 123.67, 126.27, 130.68, 137.23, 140.96, 154.14.

MS (EI): *m*/*z* = 310 (M^+).

Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.51; H, 7.15; N, 8.96.

(2-Morpholin-4-yl-ethyl)carbamic Acid *tert*-Butyl Ester (Table 1, Entry 22)
Yellow oil.

IR (neat): 2974, 2875, 1695, 1407, 1255, 1266, 1128 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9 H), 2.17–2.45 (m, 6 H), 3.69–3.70 (m, 2 H), 4.11–4.13 (m, 4 H), 4.97 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.94, 37.31, 53.89, 58.15, 67.42, 79.80, 156.47.

MS (EI): *m*/*z* = 230 (M^+).

Anal. Calcd for $C_{11}H_{22}N_2O_3$: C, 57.37; H, 9.63; N, 12.16. Found: C, 57.14; H, 9.75; N, 12.04.

Dicyclohexylcarbamic Acid *tert*-Butyl Ester (Table 1, Entry 24)
Colourless solid, mp 58–59 °C.

IR (KBr): 2970, 2934, 2853, 1678, 1435, 1367, 1295, 1240, 1157 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.04–1.77 (m, 31 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.49, 26.22, 28.50, 31.21, 54.69, 78.84, 155.32.

MS (APCI): *m*/*z* = 181 (M^+ – 100).

Anal. Calcd for $C_{17}H_{31}NO_2$: C, 72.55; H, 11.10; N, 4.98. Found: C, 72.45; H, 10.95; N, 4.95.

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