

Facile *N*-*tert*-butoxycarbonylation of amines using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as a mild and efficient catalyst under solvent-free conditions^{☆,☆☆}

N. Suryakiran, P. Prabhakar, T. Srikanth Reddy, K. Rajesh and Y. Venkateswarlu*

Natural Products Laboratory, Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 3 August 2006; revised 6 September 2006; accepted 15 September 2006

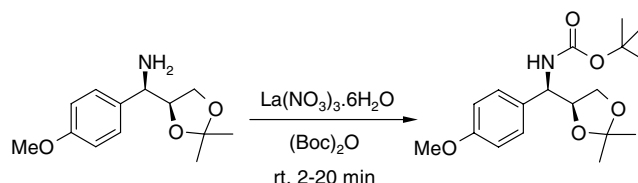
Available online 4 October 2006

Abstract—Facile *N*-*tert*-butoxycarbonylation of amines is described by the treatment of various primary, secondary, benzylic and aryl amines with di-*tert*-butyl dicarbonate in the presence of catalytic amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under solvent-free conditions at room temperature to afford *N*-*tert*-butylcarbamates in excellent yields.

© 2006 Elsevier Ltd. All rights reserved.

Functional group protection/deprotection strategies are central to target molecule synthesis. The protection of amines is one of the most fundamental and useful transformations in organic synthesis, especially in peptide synthesis.¹ Among the protecting groups for amines, *N*-*tert*-butoxycarbonylation² is used frequently, because *N*-*tert*-butylcarbamates are stable in the presence of a wide range of nucleophiles under alkaline conditions and are very labile under mild acidic conditions liberating the parent amine.^{1a} Although, various base mediated methods are available for the preparation of *N*-*tert*-butylcarbamates using di-*tert*-butyl dicarbonate,^{3–11} there are only a few reports on the Lewis acid catalyzed reactions such as, ‘Yttria–Zirconia’ which needs long reaction times 3–48 h¹² and, very recently, ZrCl_4 , copper(II) tetrafluoroborate, InBr_3 and $\text{HClO}_4\text{--SiO}_2$ (Scheme 1).¹³

In the course of our on-going search for chemoselective reagents, our group has identified $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as a mild and efficient catalyst for the chemoselective tetrahydropyranylation of primary alcohols,¹⁴ chemoselective deprotection of acetonides,¹⁵ synthesis of quinazolinones¹⁶ and the mild and efficient acetylation



Scheme 1.

of alcohols, phenols and amines with acetic anhydride.¹⁷ It has been observed that substrates containing other acid labile functional groups such as acetonides, TBDMS ethers, isopropylidene protected diols and *N*-*tert*-butylcarbamates were intact in the presence of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Further, we report here that $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is a mild and efficient catalyst for *N*-*tert*-butoxycarbonylation of amines using di-*tert*-butyl dicarbonate under solvent-free conditions.

The reaction of aniline (1 mmol) with di-*tert*-butyl dicarbonate (1.2 mmol) using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mol %) at room temperature rapidly gave the corresponding *N*-*tert*-butylcarbamate in a 100% yield (Table 1, entry 1). This success encouraged us to extend the generality of the reaction. In order to establish the scope of the catalytic activity of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, we carried out the reaction of various primary, secondary, benzylic and aryl amines (Table 1) with di-*tert*-butyl dicarbonate, which gave the corresponding *N*-*tert*-butylcarbamates in excellent yields. Furthermore, it was observed that when the

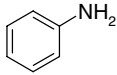
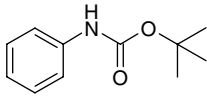
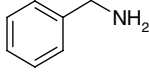
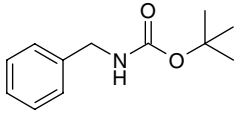
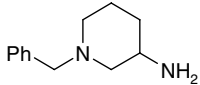
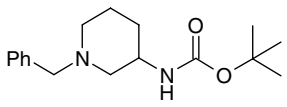
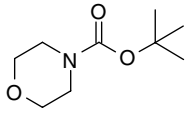
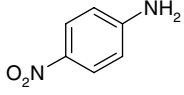
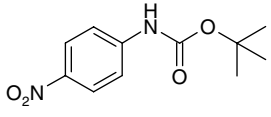
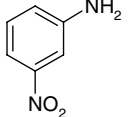
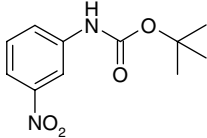
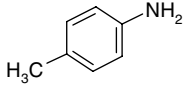
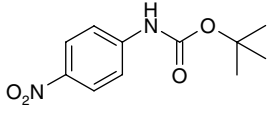
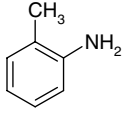
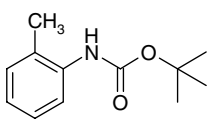
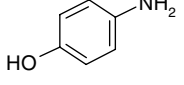
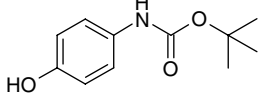
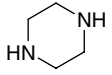
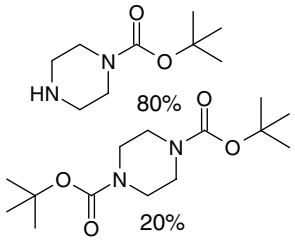
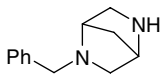
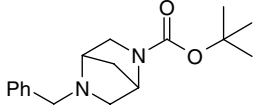
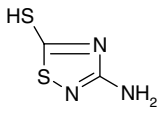
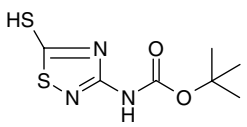
Keywords: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Amines; *N*-*tert*-Butoxycarbonylation; Solvent-free conditions.

[☆] Reactions using lanthanum(III) nitrate hexahydrate paper 5.

^{☆☆} ICT Communication No. 060904.

* Corresponding author. Tel.: +91 40 27193167; fax: +91 40 27160512; e-mail: luchem@iict.res.in

Table 1. *N*-*tert*-Butoxycarbonylation of amines in the presence of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under solvent-free conditions

Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)
1			2	100
2			2	98
3			3	95
4			2	100
5			3	95
6			3	98
7			3	98
8			2	100
9			3	98
10		 80% 20%	3	98
11			3	98
12				

Download English Version:

<https://daneshyari.com/en/article/5288309>

Download Persian Version:

<https://daneshyari.com/article/5288309>

[Daneshyari.com](https://daneshyari.com)