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A mild and efficient acetylation of alcohols, phenols and amines with acetic anhydride using $La(NO_3)_3{\cdot}6H_2O$ as a catalyst under solvent-free conditions☆,☆☆

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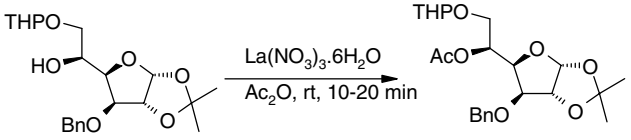
Abstract—A wide variety of alcohols, phenols and amines are efficiently and selectively converted into the corresponding acetates by treatment with acetic anhydride in the presence of catalytic amounts of $La(NO_3)_3{\cdot}6H_2O$ under solvent-free conditions at room temperature. The method is compatible with acid sensitive hydroxyl protecting groups such as TBDMS, THP, OBz, OBn, Boc and some isopropylidenes and offers excellent yields of the mono acetates of 1,3-, 1,4- and 1,5-diols.

Functional group protection strategies are central to target molecule synthesis. The protection of alcohols, phenols and amines are fundamental and useful transformations in organic synthesis. Among the many protecting groups for hydroxyls, phenols and amines, acetate is used with high frequency. Although, numerous methods are available for the preparation of acetates using acetic acid and a protic acid, acetic anhydride and pyridine are the most commonly used reagents.[1] 4-(Dimethylamino)pyridine (DMAP) and 4-pyrrolidinopyridine (PPY) catalyze the acetylation of alcohols.[2] Further, other catalysts such as $TaCl_5$,[3] TMSOTf,[4] $Sc(OTf)_3$,[5] Bu_3P,[6] $CoCl_2$,[7] montmorillonite K-10 and KSF,[8] TMSCl,[9] $Sn(OTf)_2$, $Cu(OTf)_2$ and $In(OTf)_3$[10–12] have been used for the acetylation of alcohols. However, most of these reported methods suffer from one or more disadvantages like long reaction times, harsh reaction conditions, the occurrence of side reactions, toxic reagents, poor yields of the desired products and intolerance of other functional groups. Here, we report a mild and efficient method for the acetylation of alcohols, phenols and amines using acetic anhydride in the presence of $La(NO_3)_3{\cdot}6H_2O$ (Scheme 1).

In the course of our ongoing search for chemoselective reagents, we identified $La(NO_3)_3{\cdot}6H_2O$ as a mild and efficient catalyst for the chemoselective tetrahydropyranylation of primary alcohols,[13] the chemoselective deprotection of acetonides[14] and for the synthesis of quinazolinones.[15] In continuation of these studies, we found that $La(NO_3)_3{\cdot}6H_2O$ is an efficient and mild acidic catalyst for the acetylation of alcohols with Ac_2O under solvent-free conditions. In order to establish the catalytic activity of $La(NO_3)_3{\cdot}6H_2O$, we carried out the acetylation of glucose diacetonide (1 mmol) with acetic anhydride (1.2 mmol) using $La(NO_3)_3{\cdot}6H_2O$ (5 mol %) at room temperature which gave the corresponding acetate in 96% yield (Table 1, entry 1). Encouraged by the success of this reaction, various primary, secondary, benzylic and allylic alcohols and phenols (Table 1) and amines (Table 2) were subjected



Scheme 1.

Keywords: Lanthanum(III) nitrate hexahydrate; Alcohols; Phenols; Amines; Acetylation; Solvent-free conditions.

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☆☆ Reactions using lanthanum(III) nitrate hexahydrate paper 4.

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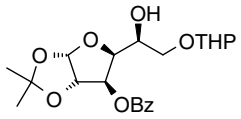
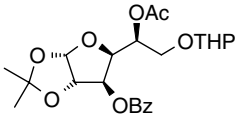
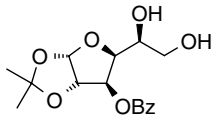
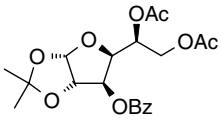
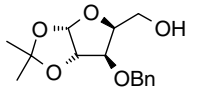
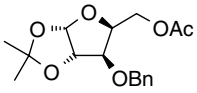
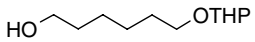
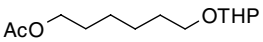
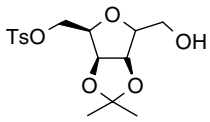
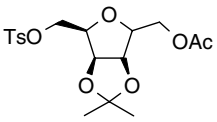
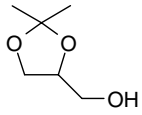
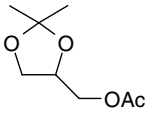
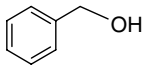
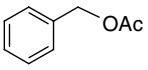
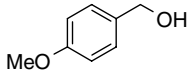
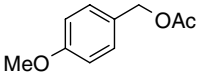
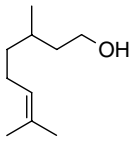
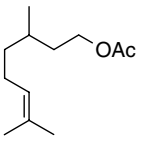
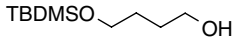
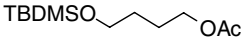
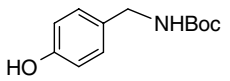
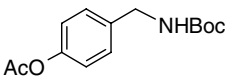
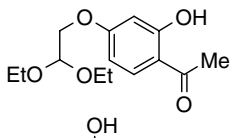
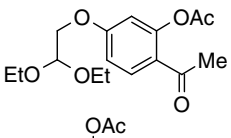
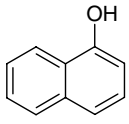
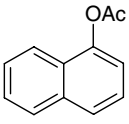
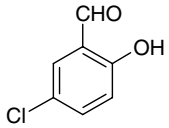
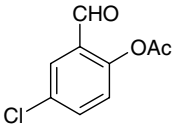
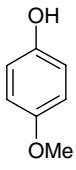
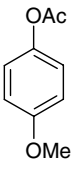
Table 1. Acetylation of alcohols and phenols in the presence of lanthanum(III) nitrate hexahydrate

Entry	Substrate	Product[a]	Time (min)	Yield[b] (%)
1			15	96
2			15	95
3			15	96
4			15	98
5			10	96
6			15	94
7			18	93
8			18	95
9			10	95
10			15	96
11			20	98
12			20	95
13			15	96
14			15	95
15			15	96