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$SbCl_3$-HAP catalyzed aza-Michael addition of aliphatic amines to *α,β* -unsaturated carbonyl compounds and nitriles

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ABSTRACT

An efficient aza-Michael addition of aliphatic amines (primary and secondary) to a series of α,β-unsaturated carbonyl compounds and nitriles has been carried out using antimony (III) chloride supported over hydroxyapetite ($SbCl_3$-HAP) as an effective catalyst in acetonitrile to produce the corresponding β-amino derivatives in high yields. The method is simple, general and offers limited chemoselectivity, as aromatic amines were found to be unreactive.

Keywords: Aza-Michael addition, aliphatic amines, *α, β*-unsaturated carbonyl compounds, nitriles, $SbCl_3$-HAP.

INTRODUCTION

The aza-Michael addition is one of the widely used reactions for carbon-nitrogen bond formation in synthetic organic chemistry. Michael addition of various amines to *α,β*-unsaturated carbonyl compounds and nitriles provide the corresponding *β*-amino derivatives, which have attracted great attention for their use as important synthons for the synthesis of several nitrogen containing bioactive natural products [1], chiral auxiliaries [2], antibiotics [3] and a number of other drugs [4]. The development of novel synthetic methodologies for the preparation of these compounds is an attractive area of research in organic chemistry. A variety of methods are known in the literature for the synthesis of *β*-amino carbonyl compounds and nitriles. Among these, the most common route is the Michael addition of nitrogen nucleophiles to *α,β*- unsaturated compounds and nitriles in the presence of an acid or a base catalyst [5]. Generally, aza-Michael addition has been catalyzed by strong acids and bases, and some side reactions occurred. As a result, various Lewis acid catalysts have been reported to effect aza-Michael reaction and these include $Yb(OTf_3)$ [6], $PtCl_4{\cdot}5H_2O$ [7], $Cu(OTf)_2$ [8], $FeCl_3.6H_2O$ [9], $LiClO_4$ [10], $Bi(NO_3)$ [11], $InCl_3$ [12], $CeCl_3.7H_2O$ [13], MgO [14], ZnO [14], CAN [15], and $MnCl_2$ [16]. Despite their usefulness, most of these methods have one or more drawbacks such as the use of stoichiometric amount of Lewis acid catalyst, prolonged reaction time and drastic reaction conditions. Thus, the development of an efficient and green method for aza-Michael addition of aliphatic amines to *α,β*-unsaturated compounds and nitriles is highly desirable to overcome these limitations. Further, the use of reagents impregnated on inorganic supports offer various advantages such as simple work-up and product purification, enhanced or reduced reactivity of the functional groups in the substrates and manipulative simplicity. Use of heterogeneous catalysts for the organic transformation is rapidly growing over the homogeneous catalytic systems because of several advantages of the heterogeneous catalysts such as high stability, ease of handling, recovery and reuse, non-corrosive nature, long time persisting catalytic activity and environmentally friendliness. In continuation to our efforts [17] on the development of facile methods for organic

synthesis and to explore the usage of $SbCl_3$-HAP as a Lewis acid catalyst in organic reactions [18], we wished to employ $SbCl_3$-HAP for the synthesis of *β*-amino ketones and nitriles. In the present paper, we have used $SbCl_3$-HAP as an effective and eco-friendly catalyst for the conjugate addition of a variety of amines to different Michael acceptors (**Scheme 1**).

MATERIALS AND METHODS

All experiments were performed in an oven dried glass apparatus under nitrogen atmosphere. The progress of the reaction was monitored by thin layer chromatography (TLC) using silica gel pre-coated aluminium sheets (60 F254, Merck). The visualization of spots was effected by exposure to iodine vapours and 2,4-dinitrophenylhydrazine in ethanol containing few drops of conc. H_2SO_4 and 5% anisaldehyde solution in acidic ethanol. Column chromatography was performed on silica gel (100-200 mesh) and the compounds were eluted with graded solvent systems of petroleum ether and ethyl acetate. NMR (^{1}H and ^{13}C NMR) spectra were recorded on Brucker Ac-400 spectrophotometer at 400 MHz and 100 MHz respectively, with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in δ (ppm) downfield from TMS. J values are given in hertz (Hz). ESIMS spectra were recorded on Micro-Mass VG- 7070 H mass spectrometer. IR spectra on KBr were recorded on Perkin-Elmer FTIR spectrophotometer. Elemental analysis was performed on Leco CHNS-932 analyser.

General procedure for $SbCl_3$-HAP catalyzed synthesis of *β*-amino carbonyls and *β*-amino nitriles: $SbCl_3$-HAP (1.6 mol%, 0.310 g) was added to a mixture of an amine (1.0 mmol) and an *α,β*-unsaturated compound (1.0 mmol) in acetonitrile (5 mL) under N_2 atmosphere. The reaction mixture was stirred at 50 ^oC for about 1.5-10 hours till the completion of the reaction (TLC). Acetonitrile was distilled off under reduced pressure followed by dilution with diethylether (20 mL) and filteration to recover the catalyst. The combined organic layers were treated with brine, dried over Na_2SO_4 and concentrated in vacuum. The column chromatography was performed on silica gel (100-200 mesh) and the compounds were eluted with graded solvent systems of *n*-hexane-EtOAc to afford the pure products.

Spectral data of the products

3-(Benzylamino)propanenitrile (3a)

Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.2-7.0 (5H, m), 3.8 (2H, s), 2.8 (2H, m), 2.1 (1H, br s), 2.5 (2H, m); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 117, 138, 128, 127, 126, 54, 44, 21; **IR** (KBr) ν_{max}/cm^{-1}: 3340, 2980, 1460; **ESIMS** (*m/z*) = 161 $(M+H)^+$; *Anal Calcd.* for $C_{10}H_{12}N_2$: C, 74.97, H, 7.55, N, 17.48; Found: C, 75.22, H, 7.79, N, 17.98.

Ethyl 3-(benzylamino)propanoate (3b)

Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.2- 7.0 (5H, m), 4.1 (2H, q, *J* = 7.2 Hz), 3.6 (2H, s), 3.1-2.9 (2H, m), 2.7-2.6 (2H, t, *J* = 6.1 Hz), 2.1 (1H, br s), 1.2 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 172, 138, 128, 127, 126, 60, 55, 45, 14, 13; **IR** (KBr) ν_{max}/cm^{-1}: 3340, 2980, 1730; **ESIMS** (*m/z*) = 208 $(M+H)^+$; *Anal Calcd.* for $C_{12}H_{17}NO_2$: C, 69.54, H, 8.27, N, 6.76; Found: C, 69.88, H, 8.53, N, 7.02.

3-(Benzylamino)cyclohexanone (3c)

Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.3- 7.2 (5H, m), 3.8 (2H, s), 3.7-3.6 (1H, s), 2.8 (1H, m), 2.4-2.2 (5H, m), 2.1 (1H, br s), 1.7-1.6 (2H, m); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 212, 140, 138, 136, 54, 51, 47, 40, 32, 19; **IR** (KBr) ν_{max}/cm^{-1}: 3335, 2960, 1705; **ESIMS** (*m/z*) = 204 $(M+H)^+$; *Anal Calcd.* for $C_{13}H_{17}NO$: C, 76.81, H, 8.43, N, 6.89; Found: C, 76.99, H, 8.62, N, 7.04.

3-(Benzylamino)-2-methyl-5-(prop-1-en-2-yl)cyclohexanone (3d)

Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.4-7.2 (5H, m), 5.7-5.5 (2H, m), 3.8 (2H, s), 2.9 (1H, m), 2.7 (1H, m), 2.5-2.2 (6H, m), 2.1 (1H, br s), 1.3-1.1 (5H, m); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 212, 149, 140, 129, 127, 110, 59, 54, 38, 36, 21, 12; **IR** (KBr) ν_{max}/cm^{-1}: 3335, 2960, 1705; **ESIMS** (*m/z*) = 258 $(M+H)^+$; *Anal Calcd.* for $C_{17}H_{23}NO$: C, 79.33, H, 9.01, N, 5.44; Found: C, 79.66, H, 9.32, N, 5.78.

3-(Butylamino)propanenitrile (3e)

Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.9 (2H, t, *J* = 6.6 Hz), 2.6 (2H, t, *J* = 7.1 Hz), 2.5 (2H, t, *J* = 6.6 Hz), 2.1 (1H, br s), 1.7 -1.5 (2H, m), 1.3-1.1 (2H, m), 0.9 (3H, t, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 112, 52, 46, 34, 30, 21, 14; **IR** (KBr) ν_{max}/cm^{-1}: 3310, 2960, 1465; **ESIMS** (*m/z*) = 127 $(M+H)^+$; *Anal Calcd.* for $C_7H_{14}N_2$: C, 66.62, H, 11.18, N, 22.20; Found: C, 66.92, H, 11.34, N, 22.47.

Ethyl 3-(butylamino)propanoate (3f)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 4.1 (2H, q, *J* = 7.5 Hz), 2.9 (2H, t, *J* = 7.2 Hz), 2.8 (2H, t, *J* = 6.8 Hz), 2.6-2.5 (2H, m), 2.1 (1H, br s), 1.4-1.2 (4H, m), 1.0 (3H, t, *J* = 7.5 Hz), 0.9 (3H, t, *J* = 7.5 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 172, 60, 49, 45, 36, 34, 21, 14, 13; **IR** (KBr) ν_{max}/cm^{-1}: 3410, 2960, 1730; **ESIMS** (*m/z*) = 174 $(M+H)^+$; *Anal Calcd*. for $C_9H_{19}NO_2$: C, 62.39, H, 11.05, N, 8.08; Found: C, 62.68, H, 11.26, N, 8.43.

3-(Butylamino)cyclohexanone (3g)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 3.6 (1H, m), 3.0 (1H, m), 2.5 - 2.3 (4H, m), 2.2 – 2.1 (5H, m), 1.7-1.6 (4H, m), 0.9 (3H, t, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 208, 51, 50, 47, 43, 39, 35, 22, 21, 14; **IR** (KBr) ν_{max}/cm^{-1}: 3340, 2970, 1700; **ESIMS** (*m/z*) = 170 $(M+H)^+$; *Anal Calcd*. for $C_{10}H_{19}NO$: C, 70.96, H, 11.31, N, 8.28; Found: C, 70.64, H, 11.02, N, 8.59.

3-(Isopropylamino)propanenitrile (3h)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 2.8 (2H, t, *J* = 6.5 Hz), 2.7 (1H, m), 2.4 (2H, t, *J* = 6.5 Hz), 2.1 (1H, br s), 1.0 (6H, d, *J* = 6.2 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 119, 53, 42, 24, 19; **IR** (KBr) ν_{max}/cm^{-1}: 3340, 2960, 1450; **ESIMS** (*m/z*) = 113 $(M+H)^+$; *Anal Calcd.* for $C_6H_{12}N_2$: C, 64.24, H, 10.78, N, 24.97; Found: C, 64.56, H, 10.98, N, 25.21.

Ethyl 3-(isopropylamino)propanoate (3i)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 4.1 (2H, q, *J* = 7.2 Hz), 2.9- 2.8 (1H, m), 2.7 (2H, t, *J* = 6.3 Hz), 2.5 (2H, t, *J* = 6.3 Hz), 2.1 (1H, br s), 1.2 (3H, t, *J* = 7.2 Hz), 1.0 (6H, d, *J* = 6.1 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 174, 60, 36, 48, 42, 24, 14; **IR** (KBr) ν_{max}/cm^{-1}: 3345, 2960, 1740; **ESIMS** (*m/z*) = 160 $(M+H)^+$; *Anal Calcd*. for $C_8H_{17}NO_2$: C, 60.35, H, 10.76, N, 8.80; Found: C, 60.56, H, 10.94, N, 9.06.

3-((1-Phenylethyl)amino)propanenitrile (3j)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.4 - 7.2 (5H, m), 3.6 (1H, q, *J* = 7.5 Hz), 2.8 (2H, m), 2.7 (2H, m), 1.3 (3H, d, *J* = 6.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 138, 128, 127, 126, 118, 53, 42, 24, 21; **IR** (KBr) ν_{max}/cm^{-1}: 3320, 2245, 1490; **ESIMS** (*m/z*) = 175 $(M+H)^+$; *Anal Calcd.* for $C_{11}H_{14}N_2$: C, 75.82, H, 8.10, N, 16.08; Found: C, 76.03, H, 8.22, N, 16.26.

Ethyl 2-((3-oxocyclohexyl)amino)acetate (3k)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 4.2 (2H, q, *J* = 7.2 Hz), 3.7 (1H, m), 3.4 (2H, s), 2.9 (1H, m), 2.5-2.3 (4H, m), 2.2-2.1 (5H, m), 1.7-1.6 (4H, m), 0.9 (3H, t, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 211, 169, 63, 55, 49, 46, 41, 30, 19, 14; **IR** (KBr) ν_{max}/cm^{-1}: 3340, 2950, 1620; **ESIMS** (*m/z*) = 200 $(M+H)^+$; *Anal Calcd*. for $C_{10}H_{17}NO_3$: C, 60.28, H, 8.60, N, 7.03; Found: C, 60.62, H, 8.94, N, 7.36.

Ethyl 2-((2-cyanoethyl)amino)acetate (3l)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 4.2 (2H, q *J* = 7.2 Hz), 3.8 (2H, s), 2.6 (2H, t, *J* = 6.9 Hz), 2.5 (2H, t, J = 6.8 Hz), 1.1 (3H, t. *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 171, 117, 63, 50, 47, 19, 14; **IR** (KBr) ν_{max}/cm^{-1}: 3250, 1620, 1450; **ESIMS** (*m/z*) = 157 $(M+H)^+$; *Anal Calcd.* for $C_7H_{12}N_2O_2$: C, 53.83, H, 7.74, N, 17.94; Found: C, 54.15, H, 8.06, N, 18.29.

3-(Piperidin-1-yl)propanenitrile (3m)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 2.8 (2H, t, *J* = 6.7 Hz), 2.7-2.5 (6H, m), 1.3-1.1 (6H, m); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 118, 52, 49, 26, 25, 18; **IR** (KBr) ν_{max}/cm^{-1}: 2930, 1430; **ESIMS** (*m/z*) = 139 $(M+H)^+$; *Anal Calcd*. for $C_8H_{14}N_2$: C, 69.52, H, 10.21, N, 20.27; Found: C, 69.84, H, 10.52, N, 20.63.

Ethyl 3-(piperidin-1-yl)propanoate (3n)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 4.1 (2H, q, *J* = 7.2 Hz), 2.9 (2H, t, *J* = 6.7 Hz), 2.7-2.5 (6H, m), 1.4-1.2 (6H, m) 1.1 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 172, 60, 52, 49, 33, 26, 25, 14; **IR** (KBr) ν_{max}/cm^{-1}: 2950, 1730; **ESIMS** (*m/z*) = 186 $(M+H)^+$; *Anal Calcd.* for $C_{10}H_{19}NO_2$: C, 64.83, H, 10.34, N, 7.56; Found: C, 64.47, H, 10.69, N, 7.88.

3-Morpholinopropanenitrile (3o)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 3.7 (4H, t, *J* = 4.5 Hz), 2.8 (2H, t, *J* = 6.9 Hz), 2.6 (2H, t, *J* = 6.8 Hz), 2.5 (4H, t, *J* = 4.5 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 118, 72, 56, 49, 18; **IR** (KBr) ν_{max}/cm^{-1}: 2850, 1440; **ESIMS** (*m/z*) = 141 $(M+H)^+$; *Anal Calcd.* for $C_7H_{12}N_2O$: C, 59.98, H, 8.63, N, 19.98; Found: C, 60.19, H, 8.98, N, 20.29.

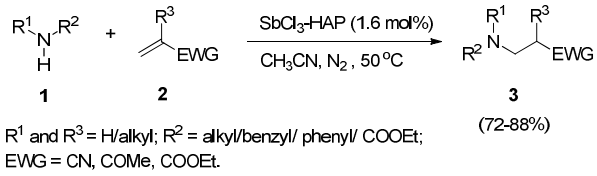
Ethyl 3-morpholinopropanoate (3p)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 4.1 (2H, q, *J* = 7.2 Hz), 3.8 (4H, t, *J* = 4.5 Hz), 2.9 (2H, t, *J* = 6.9 Hz), 2.7 (2H, t, *J* = 6.8 Hz), 2.5 (4H, t, *J* = 4.5 Hz), 1.2 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 172, 72, 60, 57, 49, 34, 14; **IR** (KBr) ν_{max}/cm^{-1}: 2030, 1730; **ESIMS** (*m/z*) = 188 $(M+H)^+$; *Anal Calcd.* for $C_9H_{17}NO_3$: C, 57.73, H, 9.15, N, 7.48; Found: C, 57.99, H, 9.47, N, 7.82.

3-Morpholinocyclohexanone (3q)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 3.7 (4H, t, *J* = 4.6 Hz), 3.4-3.3 (1H, m), 2.6-2.5 (1H, m), 2.4 (4H, t, *J* = 4.6 Hz), 2.3-2.2 (3H, m), 2.1-2.0 (2H, m), 1.7-1.6 (2H, m); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 209, 68, 65, 52, 42, 41, 29, 19; **IR** (KBr) ν_{max}/cm^{-1}: 2030, 1520; **ESIMS** (*m/z*) = 184 $(M+H)^+$; *Anal Calcd.* for $C_{10}H_{17}NO_2$: C, 65.54, H, 9.35, N, 7.64; Found: C, 65.89, H, 9.68, N, 7.97.

2-Methyl-3-morpholino-5-(prop-1-en-2-yl)cyclohexanone (3r)
Oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.4 - 7.2 (5H, m), 5.7-5.5 (2H, m), 3.9 (2H, s), 3.7 (2H, t, *J* = 4.5 Hz), 3.0-2.9 (1H, m), 2.8-2.7 (1H, m), 2.5 (4H, t, J = 4.5 Hz), 2.3-2.1 (6H, m), 1.3-1.1 (5H, m); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 212, 148, 111, 80, 69, 54, 51, 47, 38, 36, 24, 13; **IR** (KBr) ν_{max}/cm^{-1}: 2950, 1520; **ESIMS** (*m/z*) = 238 $(M+H)^+$; *Anal Calcd.* for $C_{14}H_{23}NO_2$: C, 70.85, H, 9.77, N, 5.90. Found: C, 71.18, H, 10.02, N, 6.24.

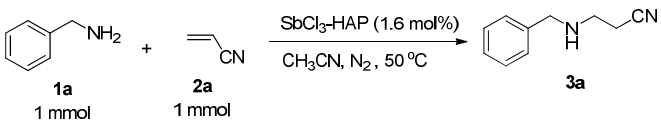
RESULTS AND DISCUSSION

We herein report an efficient and simple method for the synthesis of *β*-amino ketones and nitriles by the aza-Michael addition of primary and secondary aliphatic amines to *α,β*-unsaturated carbonyl compounds and nitriles in the presence of a non-toxic, inexpensive $SbCl_3$-HAP catalyst in acetonitrile at 50 °C under N_2 atmosphere (**Scheme 1**). In view of our earlier reported work [18] on the usage of $SbCl_3$-HAP as an efficient catalyst for organic synthesis, we found that $SbCl_3$-HAP could catalyze the addition of a primary and secondary aliphatic amines to electron deficient *α,β*-unsaturated carbonyl compounds and nitriles to produce the corresponding *β*-amino derivatives in excellent yields. The best result was achieved by carrying out the reaction with 1.6 mol% $SbCl_3$-HAP in acetonitrile.



Scheme 1: Aza-Michael addition reaction

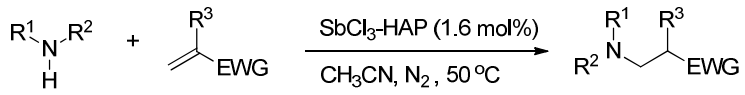
For optimization of the reaction conditions, a mixture of benzyl amine **1a** (1.0 mmol), acrylonitrile **2a** (1.0 mmol) and $SbCl_3$-HAP (1.6 mol%, 0.310 g) was stirred in acetonitrile (5 mL) in an oven dried round bottom flask at 50 °C under N_2 atmosphere as shown in **Scheme 2**. After 1.5 hours of reaction run, the formation of a new compound was noticed on TLC which was isolated in 88% yield by column chromatography over silica gel (100-200 mesh using *n*-hexane:EtOAc (*v:v* = 8:2) as eluent. The isolated compound was found to be 3-(butylamino)propanenitrile **3a** as revealed by comparison of its physical and spectroscopic data with the literature data [10].



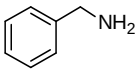
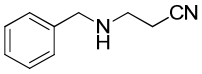
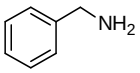
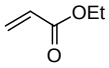
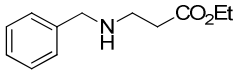
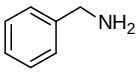
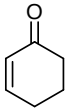
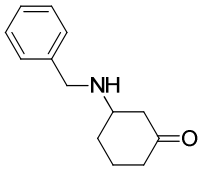
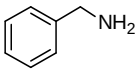
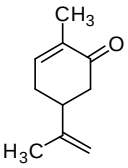
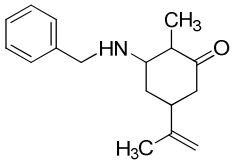
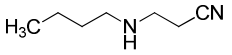
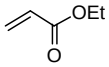
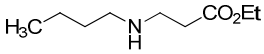
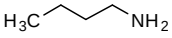
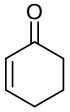
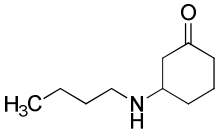
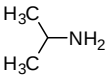
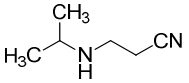
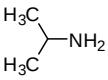
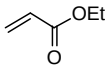
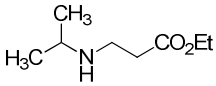
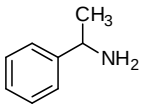
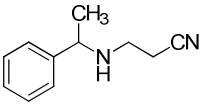
Scheme 2: $SbCl_3$-HAP catalyzed synthesis of 3-butylaminopropionitrile 3a

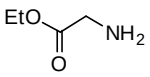
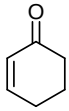
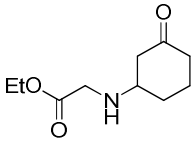
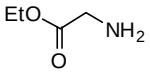
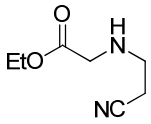
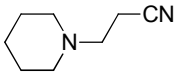
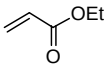
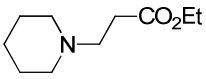
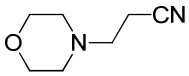
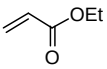
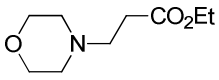
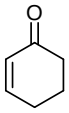
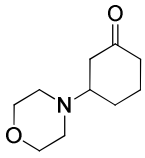
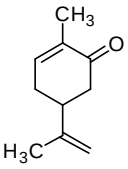
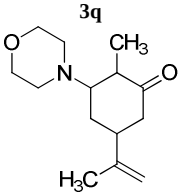
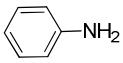
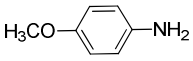
Using the optimized reaction conditions, several structurally varied amines were coupled with a wide range of α,*β*-unsaturated carbonyls and nitriles and the results are summarized in Table 1.

Table 1: $SbCl_3$-HAP catalyzed aza-Michael addition of *α,β*-unsaturated carbonyls and nitriles with primary and secondary amines[a]



1 **2** **3**

Entry	Amine (1)	Unsaturated compound (2)	Product (3)	Time (hrs)	Yield (%)[b]
1			 **3a**	1.5	88
2			 **3b**	3.5	85
3			 **3c**	4.0	82
4			 **3d**	5.0	70
5			 **3e**	1.5	88
6			 **3f**	3.5	87
7			 **3g**	4.0	88
8			 **3h**	1.5	87
9			 **3i**	3.5	85
10			 **3j**	1.5	88

11			 **3k**	**10**	**72**
12			 **3l**	**7**	**70**
13			 **3m**	**6**	**88**
14			 **3n**	**8**	**87**
15			 **3o**	**6**	**86**
16			 **3p**	**8**	**87**
17			 **3q**	**10**	**83**
18			 **3r**	**12**	**85**
19			-	**10**	**NR**
20			-	**10**	**NR**

[a] *Reaction condition: amine (1.0 mmol), α,β-unsaturated compound (1.0 mmol) and $SbCl_3$-HAP (1.6 mol%, 0.310 g), acetonitrile (5 mL), 50 °C, N_2 atmosphere;*
[b] *Yield obtained after column chromatography purification;*
NR = No reaction.

CONCLUSION

In summary, a simple, efficient aza-Michael addition of aliphatic amines (primary and secondary) to a series of *α,β*-unsaturated carbonyl compounds and nitriles using $SbCl_3$-HAP catalyst to produce the corresponding β-amino derivatives has been achieved. Operational simplicity, mild and eco-friendly reaction conditions, high yields and use of inexpensive, non-toxic, easily available catalyst are the main advantages of this method.

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