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'Claycop' catalyzed highly efficient and chemoselective aza-Michael addition under solvent free condition

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ABSTRACT

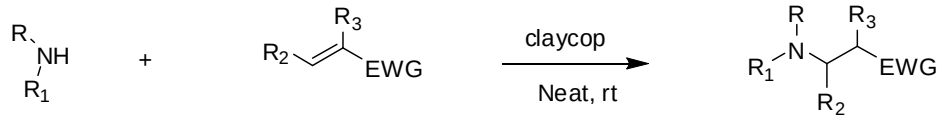
A chemoselective and highly efficient addition of amines to electron deficient alkenes is described in the presence of claycop in solvent free condition. The reaction is very rapid and exhibited higher yields in comparison with slurry reaction. Claycop can be readily recovered and reused after activation. This method is suitable for a variety of amines and alkenes. Solvent free condition and recyclability of supported catalyst makes procedure more environmental friendly.

Key words: 'claycop', aza-Michael addition, chemoselective, secondary amines.

INTRODUCTION

β-Amino ketones possess wide range of biological and pharmaceutical properties [1]. Some of the natural products and antibiotic analogues having β-amino ketones are used in cancer therapy [2]. In addition to this the chiral auxiliaries also contains β -amino ketones as core unit. Therefore, the search for efficient and simple method for the preparation of this unit is an area of continuous interest. A classical method based on Mannich reaction has been mainly utilized for the construction of β-amino carbonyl compounds [3]. However, it often requires harsh reaction conditions, allowing for a relatively narrow scope of substrates since it has to go through an iminium intermediate. Due to its drawbacks, aza-Michael reaction becomes promising alternative for the construction amino ketones. This reaction is usually carried out under acid or base catalysis. β-amino alcohols have been synthesized by the Lewis acid catalyzed addition of amines to *α,β*- ethylenic compounds. Lewis acidic catalysts such as transition metals $PdCl_2(MeCN)_2$ [4a], $FeCl_3{\cdot}6H_2O$ [4b], $Bi(OTf)_2$ [4c], $CeCl_3{\cdot}7H_2O$ [4d], SmI_2 [4e], $Cu(OTf)_2$ [4f], $Bi(NO_3)$ [4g], $Yb(OTf)_3$ [4h], $InCl_3$ [4i], $LiClO_4$ [4j] TMSCl [4k] have been shown to catalyze chemoselective addition of amines to *α,β*-ethylanic compounds. Boric acid has also been employed for aza-Michael addition in water [5]. In addition to this, heterogeneous catalysts like clay supported reagents have been reported for Michael addition [6]. Recently, Ceric Ammonium nitrate (CAN) [7a] and other reagents such as fluoride [7b], ionic liquid [7c-f], β-cyclodextrin [7g], sodium dodecylsulfate [7h] have been reported to catalyzed aza-Michael addition. However, the reported method for the synthesis of important new biologically active molecules often suffer from tedious work up, longer reaction time, narrow scope of substrate, substrate-selectivity for some catalysts and the involvement of some toxic solvents such as 1,2-dichloroethane or acetonitrile. To circumvent these problems associated with earlier methods, we envision choosing supported reagent which would provide efficient and operationally simple protocol. There is a growing interest in solid supported reagents because of distinct advantages like, simple reaction, easy separation of products and reaction selectivity. Solid supported reagents have been exploited extensively for the development of

environmental friendly reaction during past decades. Clay supported catalysts provide easy separation of the products from the reaction without tedious experimental workup and enable the efficient recovery of the catalysts [8]. The recyclability of these solid supports renders these processes into truly eco-friendly green protocols. Among the supported reagents, clay supported nitrates have been used for various organic transformations such as oxidizing, nitrating reagent and as catalyst which displayed the enhanced reactivity and selectivity, some of which were not readily accomplished in common organic solvents [9]. Although the preparation of copper nitrate supported on clay has been reported, the applications of claycop reagent for various organic transformations remain unexploited [10]. Our involvement in the area of solid supported regents in organic transformations [11], herein we wish to report the 'claycop' catalyzed efficient and chemoselective addition of amines on electron deficient alkenes in solvent free condition.



R= H/ alkyl; R_1= alkyl/ benzyl R_2= H,alkyl/Ph; R_3= H/ Me EWG =CO_2Me, CN, $COCH_2$alkyl, CONH2

Scheme 1: aza-Michael addition of amines to *α,β* -unsaturated compounds catalyses by claycop under solvent free conditions

MATERIALS AND METHODS

Experimental Part:-

All reactions were carried out without any special precautions in an atmosphere of air. Chemicals were purchased from *Fluka* and *S. D. Fine Chemicals*. TLC: precoated silica gel plates (*60 F_{254}*, 0.2 mm layer; *E. Merk*) ^{1}H-NMR Spectra: *Varian 200* or *Bruker 300* spectrometer; in $CDCl_3$; δ in ppm, *J* in Hz. Mass spectra: *VG Autospec*; in *m/z*.

General Procedure for the Preparation of claycop:

"Claycop" is prepared by adding 6 g of Montmorillonite K-10 clay to a solution of 4 g of copper(I1) nitrate trihydrate in 75 ml of acetone in a 250 ml round bottom flask. The resulting suspension is vigorously stirred at room temperature for 30 minutes. Then the suspension is placed in a rotary vacuum evaporator and the solvent is eliminated under reduced pressure. After 30 minutes, the dry solid crust adhering to the walls of the flask is flaked off with a spatula, and solvent evaporation is resumed for another 30 minutes, yielding about 10 g of "claycop", as a light blue free flowing powder which shows no loss of reactivity after standing in an open powder box for one month**.**

General Procedure for the aza-Michael reaction using claycop:

A mixture of amine (1 mmol), *α,β*-unsaturated ester (1.1 mmol) and 'claycop'(10 mol%) was stirred at room temperature for the stipulated time (see Table1). After completion of the reaction as indicated by TLC, the reaction mixture was diluted with DCM and filtered. The filtrate was concentrated under vacuum and the solution containing the product was passed through a flash chromatography column on silica gel to afford pure product.

All the products were prepared by following the same procedure and characterized by IR, Mass and ^{1}H NMR spectroscopy.

***Spectral data for new compounds are given below*:**

Methyl 3-(4-methylpiperidin-1-yl)propanoate **(13a)**:

Yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H), 2.82 (d, 2H, *J* = 11.33 Hz), 2.62 (t, 2H, *J* = 7.55 Hz), 2.45 (d, 2H, *J* = 6.80 Hz), 1.94 (td, 2H, *J* = 9.07, 2.27 Hz), 1.59 (td, 2H, *J* = 9.07, 2.27 Hz), 1.33 (m, 1H), 1.23 (qd, 2H, *J* = 9.07, 3.02 Hz), 0.92 (d, 3H, *J* = 6.04 Hz); IR (KBr): ν_{max} 2933, 2825, 1752, 1623, 1448, 1271, 1241, 1122, 1088, 686 cm^{-1}; MS (ESI): *m/z* 186 (M^+1). Anal. Calcd. for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56; O, 17.27. Found: C, 64.81; H, 10.38; N, 7.52; O, 17.29.

3-(4-Methylpiperidin-1-yl)propanenitrile **(13b)**:

Yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.85 (d, 2H, *J* = 10.75 Hz), 2.64 (t, 2H, *J* = 6.83 Hz), 2.44 (t, 2H, *J* = 6.83 Hz), 1.97 (td, 2H, *J* = 11.33, 3.02 Hz), 1.62 (td, 2H, , *J* = 11.33, 3.02 Hz), 1.34 (m, 1H), 1.24 (qd, 2H, *J* = 9.07,

3.02 Hz), 0.93 (d, 3H, *J* = 6.04 Hz); IR (KBr): ν_{max} 3379, 2851, 2812, 2243, 1412, 1324, 1201, 1028, 787, 625 cm^{-1}; MS (ESI) *m/z* 153 (M^+1). Anal. Calcd. for $C_9H_{16}N_2$: C, 71.01; H, 10.59; N, 18.40. Found: C, 71.04; H, 10.60; N, 18.41.

Methyl 2-methyl-3-(4-methylpiperidin-1-yl)propanoate **(13f)**:
Yellow thick liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69 (s, 3H), 2.82 (d, 2H, *J* = 11.33 Hz), 2.57 (dd, 2H, *J* = 10.57, 8.03 Hz), 2.42 (m, 1H), 1.94 (td, 2H, *J* = 9.07, 2.27 Hz), 1.59 (td, 2H, *J* = 9.07, 2.27 Hz), 1.33 (m, 1H), 1.23 (qd, 2H, *J* = 9.07, 3.02 Hz), 1.18 (d, 3H, *J* = 6.80 Hz), 0.92 (d, 2H, *J* = 6.04 Hz); IR (KBr): ν_{max} 2943, 2820, 1759, 1568, 1448, 1277, 1244, 1122, 1088, 686 cm^{-1}; MS (ESI): *m/z* 200 (M^+1). Anal. Calcd. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03; O, 16.06. Found: C, 66.29; H, 10.62; N, 7.03; O, 16.06.

tert-Butyl 4-(3-methoxy-3-oxopropyl)piperazine-1-carboxylate **(14a)**:
Yellow solid; mp 98-101 ^oC; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.67 (s, 3H), 3.38 (t, 4H, *J* = 7.55 Hz), 2.66 (dd, 2H, *J* = 7.18, 2.46 Hz), 2.46 (dd, 2H, *J* = 7.18, 2.46 Hz), 2.38 (t, 4H, *J* = 7.55 Hz), 1.45 (s, 9H); IR (KBr): ν_{max} 2923, 2854, 1721, 1606, 1541, 1431, 1293, 1172, 1088, 760 cm^{-1}; MS (ESI) *m/z* 273(M^+1). Anal. Calcd. for $C_{13}H_{24}N_2O_4$: C, 57.33; H, 8.88; N, 10.29; O, 23.50. Found: C, 57.33; H, 8.88; N, 10.29; O, 23.50.

tert-Butyl 4-(2-cyanoethyl)piperazine-1-carboxylate **(14b)**:
Yellow solid, mp 103-105 ^oC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (t, 4H, *J* = 4.88 Hz), 2.69 (t, 2H, *J* = 6.83 Hz), 2.49 (t, 2H, *J* = 6.83 Hz), 2.44 (t, 4H, *J* = 4.88 Hz), 1.45 (s, 9H); IR (KBr): ν_{max} 2926, 2855, 2821, 1418, 1336, 1203, 1083, 806, 616 cm^{-1}; MS (ESI): *m/z* 240 (M^+1). Anal. Calcd. for $C_{12}H_{21}N_3O_2$: C, 60.23; H, 8.84; N, 17.56; O, 13.37. Found: C, 60.23; H, 8.84; N, 17.56; O, 13.37.

tert-Butyl 4-(3-methoxy-2-methyl-3-oxopropyl)piperazine-1-carboxylate **(14f)**:
Yellow solid, mp 101-103 ^oC; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.36 (t, 4H, *J* = 6.42 Hz), 2.63 (d, 2H, *J* = 7.18 Hz), 2.40 (m, 1H), 2.34 (t, 4H, *J* = 6.42 Hz), 1.43 (s, 9H), 1.13 (d, 3H, *J* = 4.72 Hz); IR (KBr): ν_{max} 2926, 2855, 1759, 1418, 1336, 1203, 1083, 806, 616 cm^{-1}; MS (ESI) *m/z* 287 (M^+1). Anal. Calcd. for $C_{14}H_{26}N_2O_4$: C, 58.72; H, 9.15; N, 9.78; O, 22.35. Found: C, 58.72; H, 9.15; N, 9.78; O, 22.35.

Methyl 3-(4-(4-chlorophenyl)-4-hydroxypiperidin-1-yl)propanoate **(15a)**:
Yellow solid, mp 145-147 ^oC; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.41 (d, 2H, *J* = 8.31 Hz), 7.28 (d, 2H, *J* = 8.49 Hz), 3.68 (s, 3H), 2.73 (m, 4H), 2.48 (m, 4H), 2.06 (t, 2H, *J* = 12.84 Hz), 1.66 (d, 2H, *J* = 13.60 Hz); IR (KBr): ν_{max} 3356, 2925, 2854, 1762, 1584, 1458, 1086, 959, 757, 709 cm^{-1}; MS (ESI) *m/z* 298 (M^+1). Anal. Calcd. for $C_{15}H_{20}ClNO_3$: C, 60.50; H, 6.77; Cl, 11.91; N, 4.70; O, 16.12. Found: C, 60.50; H, 6.77; Cl, 11.91; N, 4.70; O, 16.12.

3-(4-(4-Chlorophenyl)-4-hydroxypiperidin-1-yl)propanenitrile **(15b)**:
Yellow solid, mp 163-165 ^oC; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.40 (d, 2H, *J* = 9.07 Hz), 7.29 (d, 2H, *J* = 8.31 Hz), 2.75 (t, 4H, *J* = 6.80 Hz), 2.53 (m, 4H), 2.07 (td, 2H, *J* = 12.84, 4.53 Hz), 1.69 (d, 2H, *J* = 12.09 Hz); IR (KBr): ν_{max} 2924, 2854, 2221, 1456, 1260, 1108, 1021, 842, 546 cm^{-1}; MS (ESI) *m/z* 265 (M^+1). Anal. Calcd. for $C_{14}H_{17}ClN_2O$: C, 63.51; H, 6.47; Cl, 13.39; N, 10.58; O, 6.04. Found: C, 63.51; H, 6.47; Cl, 13.39; N, 10.58; O, 6.04.

Methyl 3-(4-(4-chlorophenyl)-4-hydroxypiperidin-1-yl)-2-methylpropanoate **(15f)**:
Yellow solid, mp 152-153 ^oC; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.41 (d, 2H, *J* = 8.31 Hz), 7.27 (d, 2H, *J* = 8.31 Hz), 3.70 (s, 3H), 2.85 (m, 4H), 2.56 (dd, 2H, *J* = 12.09, 10.56 Hz), 2.42 (m, 1H), 2.15 (m, 2H), 1.67 (d, 2H, *J* = 14.35 Hz), 1.18 (d, 3H, *J* = 6.80 Hz); IR (KBr): ν_{max} 2923, 2853, 1759, 1492, 1440, 1308, 1196, 1049, 959, 843, 718, 539 cm^{-1}; MS (ESI) *m/z* 312 (M^+1). Anal. Calcd. for $C_{16}H_{22}ClNO_3$: C, 61.63; H, 7.11; Cl, 11.37; N, 4.49; O, 15.39. Found: C, 61.63; H, 7.11; Cl, 11.37; N, 4.49; O, 15.39.

tert-Butyl 4-(3-methoxy-3-oxopropyl)-1,4-diazepane-1-carboxylate **(18a)**:
Yellow solid, mp 112-114 ^oC; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.47 (m, 2H), 3.41 (t, 2H, , *J* = 5.67 Hz), 2.84 (m, 2H), 2.66 (m, 4H), 2.46 (t, 2H, *J* = 6.42 Hz), 1.82 (m, 2H), 1.45 (s, 9H); IR (KBr): ν_{max} 2928, 2843, 1762, 1459, 1263, 1112, 830 cm^{-1}; MS (ESI) *m/z* 287 (M^+1). Anal. Calcd. for $C_{14}H_{26}N_2O_4$: C, 58.72; H, 9.15; N, 9.78; O, 22.35. Found: C, 58.72; H, 9.15; N, 9.78; O, 22.35.

tert-Butyl 4-(2-cyanoethyl)-1,4-diazepane-1-carboxylate **(18b)**:
Yellow solid, mp 121-123 ^{o}C; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.45 (m, 2H), 3.39 (t, 2H, *J* = 5.67 Hz), 2.83 (m, 2H), 2.65 (m, 4H), 2.42 (t, 2H, *J* = 6.82 Hz), 1.79 (m, 2H), 1.44 (s, 9H); IR (KBr): ν_{max} 2924, 2853, 2221, 1755, 1535, 1458, 1247, 1089, 955, 759 cm^{-1}; MS (ESI) *m/z* 254 (M^+1). Anal. Calcd. for $C_{13}H_{23}N_3O_2$: C, 61.63; H, 9.15; N, 16.59; O, 12.63. Found: C, 61.63; H, 9.15; N, 16.59; O, 12.63.

tert-Butyl 4-(3-methoxy-2-methyl-3-oxopropyl)-1,4-diazepane-1-carboxylate (**18f**):
Yellow solid, mp 117-119 ^{o}C; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.67 (s, 3H), 3.45 (m, 2H), 3.41 (t, 2H, , *J* = 5.67 Hz), 2.84 (m, 1H), 2.66 (m, 4H), 2.44 (t, 2H, *J* = 6.82 Hz), 1.81 (m, 2H), 1.45 (s, 9H), 1.13 (d, 3H, *J* = 6.80 Hz); IR (KBr): ν_{max} 2931, 2853, 1758, 1492, 1440, 1308, 1196, 1049, 959, 843, 539 cm^{-1}; MS (ESI) *m/z* 301 (M^+1). Anal. Calcd. for $C_{15}H_{28}N_2O_4$: C, 59.97; H, 9.40; N, 9.33; O, 21.30. Found: C, 59.97; H, 9.40; N, 9.33; O, 21.30.

RESULTS AND DISCUSSION

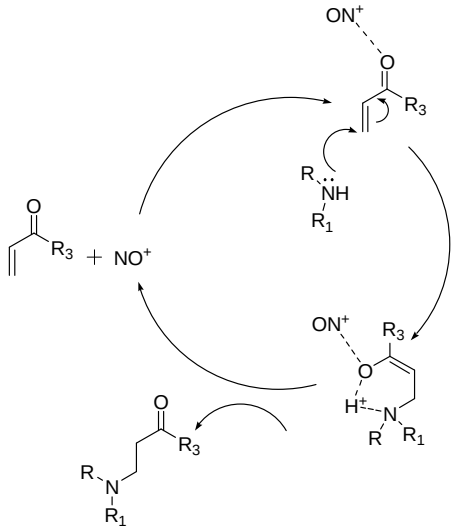
Thus to optimise the reaction conditions, we have examined the reaction of piperidine with methyl acrylate in the presence of 'claycop' in different solvents such as toluene, chloroform and dichloromethane. It was found that reaction proceeded well in DCM and completed in 1 hrs (78% yield). However, the other solvent showed less conversion even after longer reaction time (12 hrs). As some of the reactions are effective in solid phase [8], we have attempted the same reaction in solvent free condition, simply by mixing amine and methyl acrylate in presences of 'claycop'. To our delight, the reaction was completed within 5 minutes and after filtration the desired aza-Michael product was isolated in high yield (89 %). The used claycop was washed thoroughly with acetone and dried at 100 ^{0}C. Further it was used for four cycles without any substantial lose in activity. After performing numerous experiments, we have established that desired reaction proceeds by the addition of 1.5 equiv of claycop. Further, the aza-Michael addition reaction was examined with different supported reagents like $Fe(NO_3)_3$-clay (clayfen), NH_4NO_3-clay (clayan), $ZrOCl_2.8H_2O$ on K10 clay, Triflic acid supported on silica gel (TfOH–SiO_2), 1- in identical condition which gave moderate yield of expected product (Table 1).

Table 1
aza-Michael reaction between morpholine and methyl acrylate using different supported catalysts and ionic liquids under solvent free conditions[a].

Entry	Supported catalyst	Time(min)	Yield(%)[b]
1	$Fe(NO_3)_3$-clay (clayfen)	45	71
2	$Cu(NO_3)_2$-clay (claycop)	3	93[c]
3	NH_4NO_3-clay (clayan)	45	62
4	K 10 clay	120	--
5	$ZrOCl_2.8H_2O$ on K10 clay	40	65
6	triflic acid supported on silica gel (TfOH–SiO_2)	60	57
7	1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6)	45	72
8	1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF_4)	45	68

[a] Reaction conditions: Amines(1 mmol), α,β-unsaturated compounds (1.1 mmol), supported catalyst/ionic liquid (10 mol%), rt, neat.
[b] Isolated yields.
[c] Best results was observed.

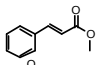
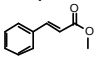
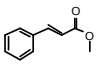
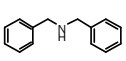
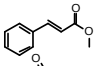
We reasoned that the emanated nitronium (NO_2^+) and nitrosonium (NO^+) ions generated from 'claycop' enabled an insitu activation of α,β-unsaturated ketone/nitriles [12]. This soft nitrosonium ion interact with π-electron system of α,β-unsaturated ketone/nitriles under orbital control as explained by Klopman [13]. The intermediate reacted with amine and subsequent elimination of NO^+ takes place which results in the more stable aza-Michael addition product (1,4-addition product) (Scheme 2).



Scheme2: Plausible Mechanism

The scope of this reaction was explored in optimized conditions for a variety of secondary amines and electron deficient alkenes. In general, electron deficient alkenes like, acrylonitrile and methyl acrylate reacted spontaneously while methyl substituted alkenes (Table 2, entry 12, 30, 45, 48) reacted comparatively slowly. Further investigation revealed that the presence of oxygen either in ring or exocyclic, accelerate the reaction. For example morpholine (Table 2, entry 37, 38) and 4-(4-chloropheny)-4-hydroxy piperidine reacted with alkenes (Table 2, entry 34, 35, 36) very efficiently and resulted into high yield of product (Table 2).

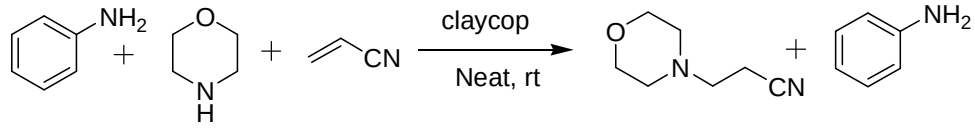
Table 2: aza-Michael Additon of amines to α,β-unsaturated compounds catalyses by claycop under solvent free conditions[a]

Entry	Amine	Acceptor	Product	Time(min)	Yield(%)[b]
1.	 1	a 	**1a**	8	85
2.		b 	**1b**	7	86
3.		c 	**1c**	10	72
4.		d 	**1d**	10	69
5.		e 	**1e**	13	78
6.	 2	a 	**2a**	7	67[c]
7.		b 	**2b**	7	90
8.		c 	**2c**	9	81
9.	 3	a 	**3a**	15	68
10.	 4	a 	**4a**	11	82
11.		b 	**4b**	9	76
12.		f 	**4f**	15	82
13.	 5	g 	**5g**	12	89
14.		e 	**5e**	15	81
15.	 6	a 	**6a**	20	74[c]
16.		b 	**6b**	22	79
17.		c 	**6c**	23	67
18.		e 	**6e**	29	72
19.	 7	a 	**7a**	25	82
20.	 8	a 	**8a**	30	76[c]
21.	 9	a 	**9a**	35	73
22.	 10	a 	**10a**	5	94
23.		b 	**10b**	4	93
24.		e 	**10e**	9	89
25.	 11	a 	**11a**	5	90
26.		b 	**11b**	4	92

Entry	Amine	Acceptor	Product	Time(min)	Yield(%)[b]
27.	 12	a 	**12a**	6	87[c]
28.		a	**13a**	5	85
29.	13	b	**13b**	6	91
30.		f	**13f**	11	86
31.		a	**14a**	4	95
32.	14	b	**14b**	3.5	92
33.		f	**14f**	9	81
34.		a	**15a**	3	90
35.	15	b	**15b**	3	94
36.		f	**15f**	9	83
37.	16	a	**16a**	3	93
38.		b	**16b**	3	95
39.		e	**16e**	11	85
40.		f	**16f**	8	86
41.		g	**16g**	15	72
42.	17	a	**17a**	4	89
43.		b	**17b**	5	92
44.		e	**17e**	15	72
45.		f	**17f**	11	82
46.		g	**17g**	17	83
47.		a	**18a**	7	85
48.	18	f	**18f**	14	76
49.		b	**18b**	8	94
50.	19	a	**19a**	5	81

[a] Reaction conditions:Amines(1mmol), unsaturated compounds(1.1mmol), clay copp(10mol%), room temperature.
[b] Isolated yields.
[c] Traces of bis product was observed.

Similarly, the reaction of piperidine and N-Boc piperazine (Table 2, entry 27, 31, 32, 33) underwent smoothly with methyl acrylate, acrylonitrile and methyl methacrylate to give aza-Michael product in good yield. As expected, the reaction of piperazine and alkenes resulted in to mixture of monosubstituted and disubstituted products (Table 2, entry 27). In addition to this, the present method was also found suitable for open chain aliphatic secondary amines. Thus, diisopropyl amine and dibenzyl amine also reacted in identical condition to afford the corresponding product in moderate yield. However, the aromatic amines failed to react in optimised conditions (Scheme 3).



Scheme 3: aza-Michael addition for aromatic amines

An independent experiment was carried out to show the chemoselectivity of reaction. When a mixture of aniline, morpholine and acrylonitrile were subjected to standard reaction condition, only morpholine addition product was observed whereas aniline remained unreacted. We believe that the present protocol is a useful alternative over conventional methods for the same transformations, since our method can save time and solvent for reaction.

CONCLUSION

In summery, we have developed a highly efficient, rapid and chemoselective protocol for aza-Michael addition of amines to electron deficient alkenes. The low cost and easy availability of the reagent, simple work up only by filtration and high yield makes this procedure an attractive alternative. The solvent free condition and reusability of catalyst are the additional features of the procedure. Thus these facts may contribute to the green chemistry.

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